Società Chimica Italiana
Divisione di Chimica
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CONGRESSO ABC

XX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali

ISCHIA, 28 settembre - 1 ottobre 2023

Società Chimica Italiana
Divisione di Chimica
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XX Congresso Nazionale della Divisione di Chimica dell’Ambiente e dei Beni Culturali

LIBRO DEGLI ABSTRACT

Ischia, 28 Settembre – 01 Ottobre 2023

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Il XX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei Beni Culturali si tiene nel periodo 28 Settembre – 1 Ottobre 2023 presso l'Isola d'Ischia (NA) ed è organizzato dalle Università campane: Università degli Studi di Salerno, Università degli Studi di Napoli "Federico II", Università della Campania "Luigi Vanvitelli" ed Università degli Studi di Napoli "Parthenope".

Il congresso raccoglie le diverse anime interne alla divisione, con un numero significativo di contributi sia orali (88) che poster (53) incentrati su argomenti propri sia della chimica dell'ambiente che dei beni culturali, tra i quali: contabilità ambientale, nuovi materiale per la depurazione di acque e suoli, nuovi materiali per il restauro e la conservazione dei beni culturali, metodogie innovative e sostenibili per il consolidamento ed il restauro dei beni culturali, studio della dispersione e degli effetti dei contaminanti emergenti, nuovi approcci per la diagnostica per i beni culturali, nanomaterali. La numerosità e la varietà dei contributi sono un indice significativo dell'impegno della divisione nell'affrontare problematiche ed argomenti di ampio interesse scentifico ed applicativo nell'ambito delle criticità ambientali e nell'ambito della salvaguardia e tutela del patrimonio storico artistico.

Il congresso ospita, inoltre, il Corso di Aggiornamento dell'Ordine Regionale dei Chimici e dei Fisici della Campania dal titolo "Dal Rifiuto all'End-of-Waste: il recupero come reale spinta all'economia circolare" (8 relazioni) e diversi contibuti orali e poster degli sponsor del congresso stesso (5 comunicazioni orali e 3 poster) a testimonienza delle connessioni tra la divisione e gli altri stakeholders del settore. Vanno, inoltre, ringraziati per il supporto economico: Metrohm S.r.l.; cleprin-chimica italiana; Prometeon, SRA-Instruments; Sense Square; Università Cà Foscari di Venezia; Istemi.

Sono, inoltre, conferite le medaglie: Medaglia Meadows & Feller - Fabrizio Passarini (Università di Bologna); Medaglia Mario Molina - Luca Ciacci (Università di Bologna); Medaglia Raffaella Rossi Manaresi - Enrico Greco (Università di Trieste) ed i premi per le tesi di laurea/dottorato: Cardito Alice (Università degli Studi di Salerno); Punis Riccardo (Università degli Studi di Padova); Gatti Lucrezia (Università di Bologna); Fenti Angelo (Università degli Studi della Campania Luigi Vanvitelli.

Il comitato scientifico ed il comitato organizzatore si augurano che il XX Congresso Nazionale della Divisione di Chimica dell'Ambiente e dei beni culturali sia un'occasione di conoscenza per tutti i partecipanti nonché un'occasione di scambio di idee per lo sviluppo di nuove proposte di ricerca ed il consolidamento di quelle già in essere. La piacevolezza dell'isola d'Ischia, luogo scelto per il congresso, sarà lo sfondo ideale per il raggiungimento di questi obiettivi.

Auguriamo dunque un buon congresso a tutti i partecipanti.

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Relazioni su Invito

ENVIRONMENTAL CHEMISTRY: ADVANCES AND CHALLENGES TOWARDS A POLLUTION FREE SOCIETY

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Environmental global change and its consequences on humans and ecosystems are dominating the actual public and political debate. Understanding the chemistry of the environment and the underpinned concern about the impact of anthropogenic activity are the general mission of environmental chemists. The presentation will move from the results of the recent international ICCE 2023 Conference to identify major advances and challenges paving the future development of environmental chemistry. It is anticipated that it will be crucial to maintain the focus and further develop the capability to, among others:

- studying kinetics and mechanisms of pollutants of concern (i.e., pharmaceuticals, pesticides, plasticizers, PFASs, etc.) and their (bio)degradation products under natural and engineered conditions
- processing rich sets of data from human biomonitoring for discovering health-impairing exposures and advancing in the analytical screening to decipher the problematic nature of persistent contaminants in material recycling
- providing guidance towards more accurate prevention measures (e.g. Safe-by-Design approach) that protect against exposure to (emerging) environmental contaminants and their substitutes in new materials and products
- assessing and managing the water-energy-food-ecosystem nexus under a changing climate
- specifically targeting different chemical vs nano forms of the materials with different hazards.

In addition, the Strategic Approach to International Chemicals Management (SAICM), a UN framework aiming at a sound management of chemicals and waste (SMCW), complements the Chemical Conventions (e.g. Stockholm, Minamata, etc.) and the EU Chemicals Strategy for Sustainability (CSS, October 2020) that is part of the EU's zero pollution ambition, a key commitment of the European Green Deal. The objectives and targets of the new SMCW mandate, expected to be adopted by the end of 2023, are partially linked to specific Sustainable Development Goals (SDG) of the Agenda 2030 and require to identify appropriate indicators to measure progress of sustainable chemistry at the international level.

Finally, considering that chemical pollution is now seen as one of the three main global crises in addition to climate change and biodiversity loss, a global science-policy panel on chemicals, waste and pollution prevention, similar to the Intergovernmental Panel on Climate Change (IPCC) and Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES), will be soon (2024/2025) established.

Environmental chemists are strongly encouraged to take an active role in these new or renewed international panels to appreciate what are their implications for scientific research, for regulatory risk assessment, and for science communication about chemicals, health, and the environment.

IS02

PREVENT THE COLOR CHANGES IN PAINTINGS: A MULTI-MATERIAL, MULTI-TECHNIQUE AND MULTI-SCALE APPROACH

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1. Introduction

The understanding of color changes of painting surfaces is one of the grand challenges in the field of heritage science. Darkening or fading often occur along with flaking, crumbling, and chalking of the paint, with serious risks for the long-term conservation of the artwork.

For several inorganic pigments, the color degradation is the result of redox reactions. The process leads to the formation of alteration products that are usually present as superficial layers and/or aggregates of limited sizes (below 80 µm) within the stratigraphy of the paint, thus complicating its overall study.

Over the last two decades, the research on pigments' alteration has benefitted from the exploitation of synchrotron radiation (SR)-based µ-XRF, XANES and µ-XRD techniques (in point analysis and mapping/imaging mode), due to their capabilities to provide spatially resolved elemental speciation and structural information down to the (sub)micrometre scale length. [1] Complementary knowledge into the molecular properties of the newly formed compounds were instead obtained by integrating SR-based X-ray methods with macro-scale non-invasive measurements (from the IR to the X-ray range) by portable devices. The latter investigations, performed *in situ* directly on paintings, have opened the possibility to visualize and map areas where paint components at major risk of degradation are present or alterations are currently in development. [2]

2. Results and Discussion

This paper reviews the most recent application of non-destructive/non-invasive X-ray methods (employing SR and traditional sources) combined with UV-visible and vibrational spectroscopies to study the alteration processes of the following class of pigments in paint matrixes: the discoloration of orpiment (As_2S_3) and realgar (As_4S_4) used by Medieval artists; the darkening of chrome yellows ($PbCrO_4/PbCr_{1-x}S_xO_4$) in paintings by Vincent van Gogh; the fading of cadmium yellows ($CdS/Cd_{1-x}Zn_xS$) and cadmium reds ($CdS_{1-x}Se_x$) in artworks by Edvard Munch and Jackson Pollock. [3-6]

SR-based X-ray data [acquired at ESRF (Grenoble, FR) and PETRA III-DESY (Hamburg, DE)] and conventional vibrational and UV-visible spectroscopy results obtained from the analysis of artificially aged paint mock-ups (under controlled conditions of light and humidity), historical artworks and related paint micro-samples will be presented and discussed.

Notably, the outcomes of these studies have permitted to provide first evidences about the following aspects: 1) the mechanism responsible of the color change (i.e., a redox reaction in all the selected pigments); 2) the internal parameters (i.e., composition and crystalline structure of the pigment; nature of the binding medium) and the main external factors (i.e., light and/or humidity) prompting the overall degradation paths.

Moreover, the findings arising from the integrated research of paint mock-ups and historical paintings, including the *Sunflowers* by Vincent Van Gogh (Van Gogh Museum, Amsterdam, NL) and *The Scream (ca. 1910)* by Edvard Munch (MUNCH Museum, Oslo, NO), are helping museums and conservators to define the safest illumination and microclimatic conditions in their Collections.

3. Conclusions

The multi-material, multi-technique and multi-scale approach here proposed have permitted: 1) to define the key-parameters that govern the overall alteration of painted surfaces for a selection of pigments; 2) to identify the markers of degradation risk important to predict their chemical alteration; 3) to devise monitoring strategies and draw conservation guidelines for a sustainable preservation of artworks.

The research also opens new perspectives for the development of digital tools for the virtual reconstruction of original colors and the prediction of their change overtime.

References

[1] M. Cotte et al., *Comptes Rendus Physique*, 19, **2018**, 575-588.
[2] F. Vanmeert et al., *Angewandte Chemie International Edition*, 57, **2018**, 7418-7422.
[3] L. Monico et al., *Journal of Analytical Atomic Spectrometry*, 37, **2022**, 114-129.
[4] L. Monico et al., in: *Van Gogh's Sunflowers Illuminated - Art meets Science,* Eds: Van Gogh Museum, M. van Bommel, E. Hendriks, M. Vellekoop, M. Geldof, Amsterdam University Press (Amsterdam), **2019**, pp. 125-157.
[5] L. Monico, et al. *Science Advances*, 6, **2020**, eaay3514.
[6] L. Monico et al. *The European Physical Journal Plus*, 137, **2022**, 311.

IS03

CHEMICAL INDUSTRY AND LIFE CYCLE ASSESSMENT

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1. Introduction

Chemical industry represents one of the sectors with major consumptions in Europe. An energy demand of 2,159 PJ was accounted for 2021, corresponding to 21% of the whole industrial sector request [1]. The same amount is also confirmed at global level [2]. Oil and gas represent the main feedstocks [3], either for the material and energy [2] production confirming its lower grade of renewability. However, starting from 90's, the adoption of the green chemistry principles [4] allowed to increase the environmental sensitivity and several goals were achieved: -54% on greenhouse gases emissions, -33% on waste production and -50% of the polluted water discharged [5]. Green and environmental chemistry are those disciplines that encourage the minimization of waste, avoiding unnecessary derivatization and designing for degradation; the utilization of renewable sources, in replacement of the more consolidated; the development of safe reactions, by also designing safer chemicals; the online control of processes, for pollution and accidents prevention.

2. Results and Discussion

Green and environmental chemistry need some tools to address the environmental and social feasibility of a reaction under study. Among these, Life Cycle Assessment (LCA) is an analytical branch of the "Life Cycle Thinking" approach, which can provide important information about the consequences of anthropic activities from a systemic point of view. It is aimed at quantifying environmental impacts starting from the collection of many inventory data; thus, similarly to any other scientific analytical methodologies, data quality requirements should address many features, like precision, completeness, representativeness, consistency, reproducibility, uncertainty. LCA is a standardized approach (ISO 14040-14044) and worldwide recognized by the sector as one of the key methods [6]. In these years, LCA was applied to several reactions briefly described below. The production of acrylonitrile to identify the most suitable reagent between propylene and propane. The synthesis of acrolein from glycerol to compare the usage of rapeseed oil vs beef tallow as starting materials. The production of bio-butadiene to counterpose the single-step pathway with the two-steps route. The sildenafil citrate synthesis to underline the benefits from the application of the green chemistry principles from the fist preparation up to the commercialization of an active pharmaceutical ingredient. The recovery of glycidol from a reaction waste streams of the Epicerol® process. The preparation of acetonitrile from bio-ethanol, combining LCA with process simulation. The synthesis of 100% bio-PET, one of the major commodities worldwide. The bio-based routes to maleic anhydride at pilot scale, for selecting the best building block (furfural or butanol). The methyl methacrylate production, to evaluate the potentialities of substituting formaldehyde with its production in situ. And, finally, the Guerbet reaction for the preparation of bio-based butanol from second generation alcohol.

3. Conclusions

Life Cycle Assessment can integrate, from a systemic standpoint, data concerning the environmental effects of chemical substances monitored by the classical approach of environmental analytical chemistry. A LCA is always recommended when the chemical sector is under study. Reactions can be studied at laboratory scale as well as at pilot and industrial level to select the best precursors, evaluate different catalytic systems and compare several conditions. These achievements were obtained thanks to a strict cooperation with many colleagues, undergraduate and PhD students to whom I should express my greatest appreciation.

IS03

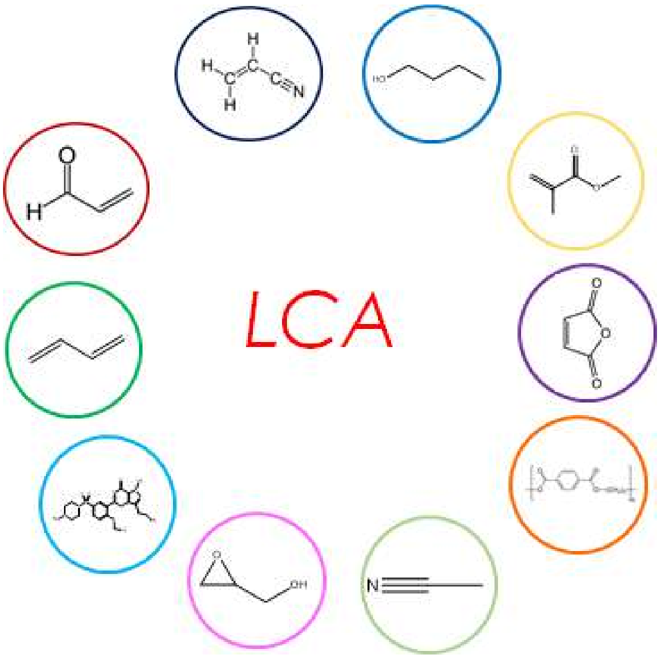

Figure 1: Life Cycle Assessment of different chemical products

References

[1] eurostat 2023, "Final energy consumption in industry - detailed statistics".
[2] IEA (International Energy Agency) 2023, https://www.iea.org/fuels-and-technologies/chemicals.
[3] IEA (International Energy Agency), https://www.iea.org/reports/chemicals.
[4] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, 1998.
[5] Cefic (the European Chemical Industry Council) 2023 https://cefic.org/a-pillar-of-the-european-economy/facts-and-figures-of-the-european-chemical-industry/environmental-performance/.
[6] *Green Chem., 2018, 20, 1929-1961.*

THE THERMAL RESOURCES OF THE ISLAND OF ISCHIA

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1. Introduction

Ischia island is the emerged top of a large volcanic complex rising more than 1000 m above the sea floor at the north-western corner of the Naples Gulf. It is an active volcanic field that covers an area of about 46 km^2 and it is morphologically dominated by the Mt. Epomeo (787 m a.s.l.), located in its central part. Volcanic activity in the last 55.000 years has been subdivided into three periods: the first period (55.000-33.000 years) started with the eruption of the Mt. Epomeo Green Tuff and the subsequent caldera formation. The second period lasted from 28 to 18 ka and the third period began about 10 ka and lasted up 1302 A.D., with the Arso eruption.

Ischia has long been known for being the site of intense and widespread hydrothermal circulation, with surface thermal manifestations including hot springs with outlet temperatures up to 90 °C. There is evidence that surface discharges are fed by a chemically complex hydrothermal system, consisting of different superimposed (150 to 1000 m depth range) reservoirs recharged by meteoric and marine water in various proportions, and in which heat and mass budgets are probably sustained by degassing of a deep magmatic body. Ischia southwestern sector is one of the areas where hydrothermal circulation is most evident, with measured temperatures of spring waters up to boiling and of bottom-well temperatures up to ∼200 °C at 1100 m depth [1,2].

2. Results and Discussion

The classification of waters is a difficult work on which several authors have expressed themselves. The most complete and recognized classification is that of Marotta and Sica 1929-1933, which divides mineral waters according to chemical characteristics and temperature. In fact they can be distinguished:
- Salty water, if there is a prevalence of chloride anion;
- Sulphurous waters, if there is a prevalence of sulfhydryl anion;
- Ferrugineous-arsenical waters,
- Bicarbonate waters, if there is a prevalence of bicarbonate anion.
- Sulphate waters, if the sulphate anion prevails;

Waters are also classified according to their temperature registered at the source:
- Cold waters, whose temperature does not exceed 20 °C;
- Hypothermal waters, whose temperature is between 20 °C and 30 °C;
- Omeothermal waters, whose temperature is between 30 °C and 40 °C;
- Hyperthermal waters, whose temperature is higher than 40 °C [3].

The Ischia hydrothermal system appears particularly complex, given the interaction between fluids having different origins; meteoric, marine and deep geothermals. The mixing of the three components in various proportions explains the composition of the various types of thermal fluids present on the island. The phenomenon of marine intrusion is present mainly along the coasts of Casamicciola and Ischia Porto, north of the island, and those of Serrara Fontana and Barano, to the south. There upwelling of magmatic gases, mainly CO_2 and H_2S, affects several areas of the island corresponding to the presence of tectonic discontinuities.

Based on the temperatures observed, most of the waters of Ischia fall within the field of mesothermal (between 35 and 50 °C) and hyperthermal (> 50 °C), a little less are the establishments with hypothermal waters (between 20 and 35 °C).

Based on the chemical characteristics it is possible to divide the waters of the island of Ischia into four hydrogeochemical faces which are:
- chlorinated waters alkaline,

- calcium bicarbonate waters,
- alkaline bicarbonate waters,
- alkaline sulphate waters.

Such chemical composition is strongly influenced by the cooperation of three different factors:-

- rainfall,
- marine intrusion,
- lift of magmatic fluids from fractures in the Earth.

The thermal waters of the island of Ischia are used in therapy above all in the form of external practices (baths, mud treatments, inhalation treatments, gynecological applications).

Salty waters and the like, in their use for inhalation treatments and gynecological treatments, first of all take into account the phenomena of permeabilization of the mucosa induced by them.

The general meaning is that of an anti-inflammatory activity in the sense of supporting and promoting anti-inflammatory reactions and effects.

Of the bicarbonate and sulphate waters, the local effects on the organic surfaces in contact with the outside mainly concern the respiratory system. The tracheo-bronchial secretion is affected by the bicarbonate anions with mucolytic effects as well as the acid respiratory environment associated with subchronic and chronic inflammation is mitigated. Not negligible is also the relaxing action on the tracheo-bronchial smooth muscle by sulphate radicals when they are present [1,2,4].

3. Conclusions

On the island of Ischia there are four hydrogeochemical facies of chlorinated waters alkaline, calcium bicarbonate waters, alkaline bicarbonate waters, waters alkaline sulphate. There chemical and physical composition of the thermal waters of the island of Ischia is influenced by the cooperation of three factors: rainfall, marine intrusion, and ascent of magmatic fluids from fractures in the Earth. The phenomenon of marine intrusion is present mainly along the coasts of Casamicciola and Ischia Porto, north of the island, and those of Serrara Fontana and Barano, to the south. There upwelling of magmatic gases, mainly CO_2 and H_2S, affects several areas of the island corresponding to the presence of tectonic discontinuities. The presence of many thermal springs has allowed the island to use these waters for various therapeutic purposes.

Representation of the hydrothermal basins of Ischia and the corresponding water classes [1].

References

1. Sbrana A., Taccaceli R. M., Carta Geologica della Regione Campania (1989). Foglio 464, 2011. Celico P., Prospezioni idrogeologiche. Liguori Ed., 1986.
2. Di Napoli *et.al.*, A model for Ischia hydrothermal system: Evidence from the chemistry of thermal groundwaters (2009). Journal of Volcanology and geothermal Research, 186:133-159.
3. Marotta D., Sica C., Composizione e classificazione delle acque minerali italiane. Ann. Chim. Appl., Vol. 23, 1933.
4. Molin P., *et al.*, Structural, seismic, and hydrothermal features at the border of an active intermittent resurgent block: Ischia Island (Italy) (2003). Journal of Volcanology and Geothermal Research, 121:65-81.

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SP01

ADSORBABLE ORGANIC FLUORINE (AOF) – A SUM PARAMETER FOR NON-TARGETED SCREENING OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFASS) IN WATERS

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1. Introduction

The prevalence of per- and polyfluorinated alkyl substances (PFASs) and other perfluorinated compounds (PFCs) that persist and accumulate in the environment (as well as in our own bodies) is becoming an increasing concern to international health authorities. They are a challenge to monitor individually and quantify in low concentrations, even in drinking water. The full scope of organofluorine compounds that are potentially detrimental to the environment is largely unknown, and therefore TOF is a good indicator.

Combustion IC can not only determine TF and TOF, but also AOF and EOF (extractable organic fluorine) in waters and solids, respectively. Beside PFASs, AOF and EOF also include non-PFASs that still have similar properties (Figure 2), as well as pesticides and other fluorinated compounds that are not included when using more targeted analysis methods. Measurement of the sum parameter of AOF in water samples as an initial screening step is simpler, faster, and more robust than targeted methods, giving laboratories an overview of the actual amount of fluorinated compounds present in samples which can be followed by targeted analyses of individual PFASs if indicated by higher concentrations of AOF.

2. Results and Discussion

Measuring AOF via CIC follows the sample preparation according to DIN EN ISO 9562 beginning with adsorption of the non-acidified liquid sample on a stationary phase (activated carbon), generally with a packed column or cartridge. To ensure complete adsoption, at least two consecutive packed columns or cartridges are used. The activated carbon becomes enriched with organofluorine compounds after a specified amount of sample is introduced (100 mL) and is then washed with sodium nitrate (NaNO3) to remove the sample matrix and any inorganic fluoride in order to achieve the most accurate results. The rinsed AOF-enriched carbon is transferred to ceramic sample boats and then is inserted into the combustion module at 1050 °C for pyrohydrolytic combustion in an oxygen/argon gas stream. This stream is passed through an absorption solution which captures the fluorine as fluoride (F-) and is then transferred, injected, and analyzed with IC using an anion exchange separation column (Figure 5). The AOF-CIC method can determine F^- in a range of 1–100 µg/L, with a limit of detection (LOD) of 0.5 µg/L F- (determined according to DIN 32645).

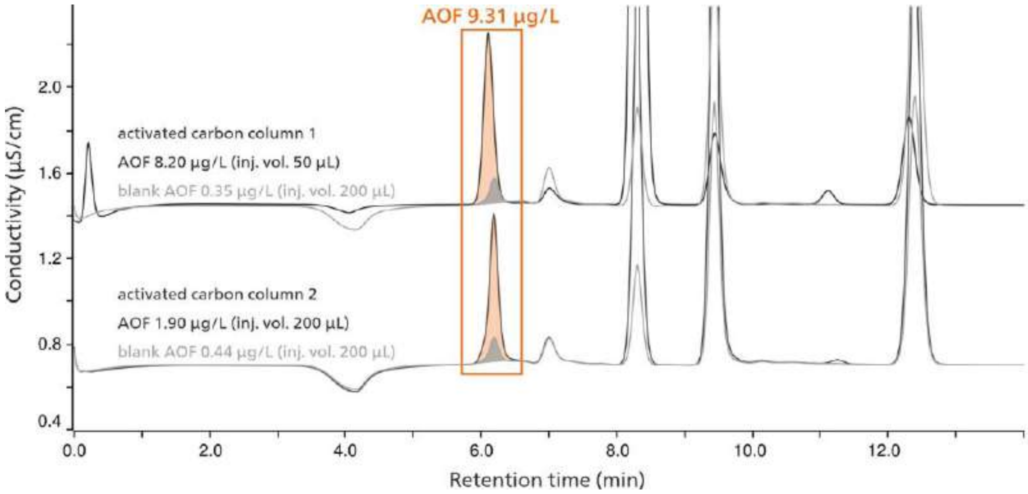
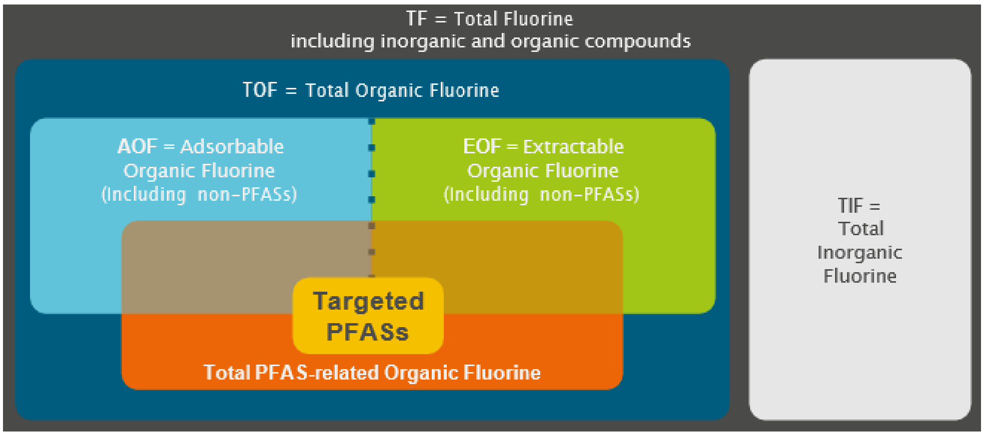


Figure 1 - . AOF determination in a wastewater sample. A volume of 100 mL sample (not acidified) was adsorbed on two consecutive activated carbon cartridges (disposable tube for AOF determination, flow rate: 3 mL/min) and treated with a neutral $NaNO_3$ rinsing solution (0.01 mol/L). The rinsed activated carbon enriched with organic fluorine was subsequently combusted and analyzed using Metrohm CIC (Metrosep A Supp 5 - 250/4.0 column, column temperature: 55 °C, eluent: 2.8 mmol/L Na_2CO_3, sequential suppression). The total AOF concentration of the wastewater sample was determined as sum of the individual AOF contents of the two adsorption cartridges (in orange) from which the AOF method blank (in grey) was substracted.

With such a setup, low levels of organofluorine compounds including PFASs, isomers, precursors, metabolites, pharmaceuticals, pesticides, and other related substances can be quickly measured. Higher values of the sum parameter AOF measured with CIC can be used as a trigger for laboratories to check samples with a more in-depth targeted analysis method for specific PFASs. The complementary approach of measuring AOF as a non-targeted screening method for PFASs alongside targeted methods like LC-MS/MS helps researchers to better monitor the actual amount of fluorinated substances in water, and in the environment in general.

3. Conclusions

Measurement of AOF with CIC as a non-targeted screening method for PFASs in waters can be faster and easier and is a more robust alternative to the determination of individual substances with the more costly and complex methods. The advantage of measuring AOF as an estimate for PFASs over the indirect TOF analysis lies in its higher accuracy and sensitivity due to preconcentration and direct determination. The AOF sum parameter is more comprehensive to estimate the overall impact of organofluorine substances in water samples. It is a good indicator to initiate detailed targeted analyses if values are high. This can be especially helpful to determine whether water treatment processes have been effective enough in municipal water facilities and wastewater treatment plants to sufficiently remove harmful fluorinated substances.



General overview of the relationships and overlaps from total fluorine (measured by CIC) to targeted PFASs (measured by LC-MS/MS or GC-MS/MS)

References

[1] U.S. Environmental Protection Agency. PFAS Master List of PFAS Substances (Version 2) https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster (accessed 2021-11-05).
[2] Secretariat of the Stockholm Convention (SSC). Stockholm Convention on Persistent Organic Pollutants (POPs); Châtelaine, Switzerland, 2020; p 79.
[3] Buck, R. C.; Franklin, J.; Berger, U.; et al. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. Integr. Environ. Assess. Manag. 2011, 7 (4), 513–541. DOI:10.1002/ieam.258.

SUSTAINABLE STRATEGIES FOR MINIMIZING ENVIRONMENTAL IMPACT: PROMETEON TYRE GROUP'S JOURNEY

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1. Introduction

The industrial revolution, its technological innovations and consequently population growth, pushed our society at the current stage in which the satisfaction goods and services demand is reached, at this point, by overexploiting the natural resources, and on the other hand, increasing the environmental pressure to a threshold in which ecosystems are collapsing and the risk of losing important services deriving from them is always more tangible.

In this context, tyres makers, and more in general all the industrial sector, need to become aware of their impact on the society and the environment and therefore implement strategies to minimize it.

2. Results and Discussion

Under these circumstances, well known by Prometeon, the Company, since the year 2017, is monitoring, managing, and compensating its impact by including Sustainability as a core pillar of its business strategy. The Sustainability strategy in Prometeon consists of the four following main pillars:

- **Governance and Business Ethics**: is the Sustainable Management Model adopted by the Company, it consists in the set of Policies and Procedures that guide how the Company act with the internal and the external actors;
- **Social Dimension**: is the governance dedicated to the Internal Community (Compensation & Benefits policies, International Mobility, Training & Development, Welfare, Industrial Relations). Occupational Health, Safety & Hygiene. Within this dimension are present also all the actions that contribute to the External Community such as donations and all the initiatives aimed to increase external community welfare;
- **Environmental Dimension**: consists in all the investment done to assess, monitor and reduce the Group environmental footprint. The company track its performances monitoring the following five KPIs: Energy Consumption, Water withdrawal & consumption, Green Gas emissions, Waste recovery Management, Solvents and Nox/Sox;
- **Economic Dimension**: distribution of added value is detailed along with the management and performance relating to customers and suppliers and the investments done to continuously upgrade the product portfolio of Prometeon.

Moreover, in order to minimize and ultimately eliminate the negative effects of tires on the environment, Prometeon Tyre Group has focused its research and development efforts on the "3R" concept, Recycle, Reduce and Rethink & Reinvent. The objective is to achieve a complete transition to sustainable materials, aiming for 100% usage throughout the production process. This will be accomplished by reducing the consumption of raw materials and optimizing manufacturing processes, recycling used materials and incorporating them into new tires, and exploring new renewable materials and formulations. By embracing the "3R" approach, the tire quality will be improved, resulting in enhanced product lifespan and retreadability, thereby reducing the demand for new tires.

3. Conclusions

Prometeon Tyre Group recognizes its impact on society and the environment and implements strategies to minimize it. The Company has actively addressed sustainability since 2017, incorporating it as a core pillar of its business strategy. This includes governance, social initiatives, environmental investments, and economic considerations. By embracing the "3R" concept, Prometeon aims to transition to sustainable materials, reduce raw material consumption, optimize processes, recycle materials, and enhance tire quality, leading to a decreased demand for new tires.

Prometeon Tyre Group Sustainability

References

https://www.prometeon.com/OU/en_US/sustainability

IN SITU DIAGNOSTIC ANALYSES OF THE *FRESCO* PAINTINGS OF SAN PIETRO A CORTE COMPLEX (SALERNO, CAMPANIA, ITALY) AND ASSESSMENT OF ENVIRONMENTAL EFFECTS ON THEIR STATE OF CONSERVATION

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1. Introduction

Since 2008, Istemi has been active in the field of diagnostics of Cultural Heritage. The activities include the application of several diagnostics methods, from structural investigations, to geological and geophysical surveys, monitoring services, as well as chemical and physical materials characterization. Particular attention is paid to non-destructive methods, in order to point out the importance of knowledge, preservation, and conservation of Cultural Heritage, from a completely non-invasive point of view.

In the present work, combined non-invasive and non-destructive *in situ* analyses have been used forthe diagnostic investigation of the hypogeum artworks of the San Pietro a Corte complex, located inSalerno, Campania, Italy. The main aim of the work has been the characterization of the *fresco* paintings, relatively to the identification of pigments and the substrates, as well as the evaluation of environmental effects, as air quality, humidity, temperature, and distribution of soluble salts on the degradation processes and the state of conservation of the *frescoes* materials.

2. Results and Discussion

Preliminary non-invasive investigations have been performed through thermographic and igrometric surveys, in order to evaluate the humidity distribution along the hypogeum surfaces, together with the verification of any discontinuities and detachments in correspondence of the artworks surfaces. Moreover, by means of non-invasive analytical techniques such as handled X-Ray Fluorescence (XRF) spectrometer, and Infrared Reflectography (IR-R), characterization of pigments and substrateshas been carried out, in order to define chemical and morphological features of the artworks surface, how the surrounding environment interacts with the materials, and how it influences their state of conservation.

The preliminary in situ results have shown the use of natural mineral pigments such as ochres and earths, for both frescoes analyzed. The analyses of the substrates have revealed a support made of plaster layer characterized by lime-based binder. Moreover, the presence of a high amount of sulfates has been detected, in different concentration, probably related to a possible degradation processes of the materials, and strongly affecting their state of conservation

3. Conclusions

The overall results confirm that the employment of a multi-analytical characterization approach, involving non-invasive and non-destructive in situ investigations, provides important information allowing conservators and restorers to better understand the artworks features, from a scientific and conservative point of view.

Through the expertise of Istemi team, together with important partnerships and collaborations as Universities and Research Centers, Istemi promotes and discloses the knowledge on the Cultural Heritage materials analyses, becoming an important aspect to be deepened, in order to define, plan, and carry out the best restoration and valorization strategies.

One of the fresco paintings investigated from the hypogeum of the San Pietro a Corte: "Teoria di Santi".

References

- Istemi s.r.l. website: https://www.istemi.it/
- Caliano, E., Messuti, N., Napoli, C. The diagnostic of cultural heritage: active and historical research discipline and guardianship. The case of the "Cenacolo" by Ghirlandaio of the Badia of Passignano in Florence. In: ART'17 - 12th International Conference on non-destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage - Associazione Italiana Prove Non Distruttive (AIPND), Milano (2017).
- Fiorillo R. Salerno medievale e l'area della curtis longobarda, Opulenta Salernum. Una città tra mito e storia, Gangemi Roma (2020), 57-68.
- Ricciardi, M., Pironti, C., Motta, O. *et al.* Investigations on historical monuments' deterioration through chemical and isotopic analyses: an Italian case study. Environ Sci Pollut Res 29, 29409–29418 (2022). https://doi.org/10.1007/s11356-021-15103-x
- Zicarelli, M.A.; La Russa, M.F.; Alberghina, M.F. *et al.* A Multianalytical Investigation to Preserve Wall Paintings: A Case Study in a Hypogeum Environment. Materials 16, 1380 (2023). https://doi.org/10.3390/ma16041380.

BIO-SUSTAINABLE AND LOW-ENVIRONMENTAL IMPACT FORMULATIONS FOR AUTOMATIC CLEANING SYSTEMS

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1. Introduction

This presentation deals with the development of bio-sustainable formulations from Cleprin S.r.L, an Italian industry specialized in cleaning products for the industrial and professional sectors. The plant has an operational capacity of more than 200 tons per day and has obtained the certifications ISO 9001 – 14001 – 45001 – B-Corp. With a keen interest in environmental issues, the industry started a research project with the University of Salerno to optimize the production of a green sequestering agent that can replace EDTA. The sequestering agent chosen is tetrasodium imminodisuccinate (IDS) that can be prepared by reacting maleic anhydride with ammonia and sodium hydroxide. The ideal formulation containing IDS is supposed to be suitable for hard water (hardness higher than 40°F) and biodegradable. The project is divided into three steps. Initially the most suitable raw materials and their relative concentrations have been selected to produce IDS based on scientific articles and patents. Then the conditions of production and the technological process have been studied to improve the characteristics of the product and recover the unreacted reagents. The second step has included stability tests and chemical/physical analysis to certify the final formulation. In the last step the unreacted reagents have been reconverted in high value products for the agricultural and automotive sector to improve the production cycle and reduce the environmental impact.

2. Results and Discussion

Several conditions of synthesis have been tested. The reaction occurs according to the following stoiochiometry:

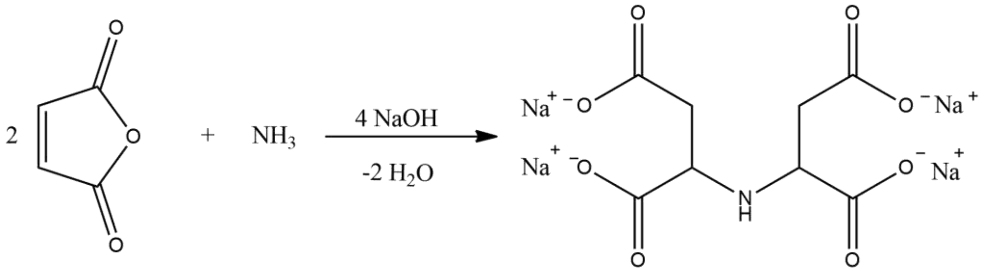

Figure 1. Reaction scheme for the synthesis of sodium imminodisuccinate.

The reaction can lead to five products: imminodisuccinate (reported in Figure 1), aspartate, malate, fumarate, and maleate. The reaction was performed at a temperature of 100-120°C and at different reaction times (above 6 hours). Ammonia was also replaced with ammonium carbonate and ammonium bicarbonate that are solid and easier to manipulate compared to liquid ammonia.

IDS was successfully obtained in all the conditions tested. The yield of IDS compared to the other subproducts depends on the experimental conditions used like the reaction temperature (usually above the melting point of maleic anhydride), the time and the order of addition of the reactants.

The products obtained have been characterized with NMR, FT-IR and TGA to estimate the amount of the various subproducts and the inorganic residue. NMR analysis confirmed the IDS formation with typical signals at 2.88 e 3.89 ppm (^{1}H-NMR) and at 34.8, 36.4, 57.9, 58.6, 173.8 e 177.6 ppm for the ^{13}C-NMR.

After the optimization of the synthesis, three formulations suitable for dishwasher have been prepared, and biodegradability was evaluated in all the cases after neutralization of the pH (the biochemical oxygen demand was measured with the respirometric method and compared with the chemical oxygen demand). Of the three formulations, the less biodegradable is the one containing also polyacrylates and phosphonates as chelating agents, the more biodegradable contains gluconate and IDS. All the three formulations prepared with different concentrations of IDS have been used in domestic dishwashers with optimal results.

Subsequently, a method for removing the unreacted ammonia from IDS was developed. On a lab scale a round-bottom flask containing IDS with the unreacted ammonia and sodium hydroxide was heated at 120°C and connected with nitrogen gas to let ammonia evaporate and be captured in a trap with hydrochloric acid. The ammonia recovered was analyzed with UV spectroscopy.

The ammonia neutralized was considered for applications such as additive in ad-blue, fertilizer in agriculture or in other formulations.

3. Conclusions

Tetrasodium salt of IDS can be a valid alternative to EDTA as chelating agent with a reduced environmental impact. The subproducts like malate, maleate, fumarate and aspartate do not influence the properties of the final product and don’t need to be removed. The unreacted ammonia can be troublesome especially in alkaline conditions like those required in dishwasher formulations. The IDS sodium salt can be produced from maleic anhydride, ammonia and soda and the unreacted ammonia can be recovered and reused for other cleaning products. The synthesis performed directly in the industry allows to reduce the costs and the environmental waste.

References

Pinto, I.S.S.; Neto, I.F.F.; Soares, H.M.V.M. Biodegradable Chelating Agents for Industrial, Domestic, and Agricultural Applications—A Review. Environ. Sci. Pollut. Res. 2014, 21, 11893–11906.

Asemave, K. Greener Chelators for Recovery of Metals and Other Applications. Organic & Medicinal Chem IJ. 2018, 6 (4), 555694.

Folliero, V.; Ricciardi, M.; Dell’Annunziata, F.; Pironti, C.; Galdiero, M.; Franci, G.; Motta, O.; Proto, A. Deployment of a Novel Organic Acid Compound Disinfectant against Common Foodborne Pathogens. Toxics. 2022, 10, 768.

THE PROTECTION OF ARCHAEOLOGICAL AND ENVIRONMENTAL HERITAGE THROUGH THE USE OF NEW MONITORING TECHNOLOGIES: THE CASE OF THE ECO-ARCHAEOLOGICAL PARK OF PONTECAGNANO

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1. Introduction

The Eco-archaeological Park of Pontecagnano, located in the Campania region of Italy, is a unique and valuable cultural and environmental resource. The park is home to important archaeological sites dating back to the Roman and pre-Roman periods, as well as a diverse range of flora and fauna. However, like many other cultural and natural heritage sites around the world, the park faces significant threats from pollution and other environmental pressures [1].

In order to protect and preserve the park's archaeological and environmental heritage, a joint monitoring project has been launched by Legambiente, Sense Square, and the Department of Chemistry and Biology at the University of Salerno. The project aims to use new monitoring technologies to track air pollution levels in real time and assess the impact of pollutants on the park's archaeological structures. The collaboration between these organizations reflects a growing recognition of the importance of using advanced technologies to protect and preserve cultural and natural heritage sites for future generations.

The use of new monitoring technologies, such as those offered by Sense Square, will provide precise and up-to-date data on air quality in the park. Sense Square is a company that provides advanced monitoring technologies for air quality and pollution. Their cutting-edge sensors and data analysis tools allow for precise and real-time monitoring of air quality, including the levels of particulate matter, gases, and other pollutants. This data, combined with the specific analyses conducted by the Department of Chemistry and Biology, will help researchers to evaluate the impact that pollutants have on the archaeological structures within the park. This information will be useful in developing effective strategies for mitigating the effects of pollution on the park's cultural and natural resources [2].

The joint monitoring project is an important step towards ensuring the long-term protection and preservation of the Eco-archaeological Park of Pontecagnano. By utilizing modern technologies and interdisciplinary collaboration, this project represents a model for safeguarding cultural and natural heritage sites around the world.

2. Results and Discussion

The joint monitoring study of air quality within the Eco-archaeological Park of Pontecagnano lasted for 7 months. During the monitoring period, the observed levels of pollutants were found to be moderately high, with PM10 and PM2.5 particulate matter exceeding legal limits on several occasions. In particular, the levels of fine particulate matter (PM2.5) were found to be particularly high in some areas of the park.

Moreover, during the analysis of the archaeological structures, there was a high degree of darkening of the surfaces. From the analysis conducted, it appears that this phenomenon is connected to the high concentrations of fine particulate matter in the air. In particular, the extremely high presence of PM2.5 particulate matter seems to be correlated with the darkening of the surfaces.

The results of our study indicate that the Eco-archaeological Park of Pontecagnano is subject to high levels of air pollution, with PM2.5 particulate matter exceeding legal limits in several areas of the park. Additionally, the darkening of the archaeological surfaces seems to be connected to the high concentrations of fine particulate matter in the air.

These results are concerning as air pollution can irreversibly damage archaeological structures and compromise their long-term preservation. However, the collaboration between Legambiente, Sense Square, and the Department of Chemistry and Biology at the University of Salerno has demonstrated that the use of advanced monitoring technologies can be an effective tool in protecting cultural and environmental heritage.

Based on the results of our study, it is recommended that measures be taken to reduce air pollution within the park. In particular, it would be important to reduce emissions of fine particulate matter from vehicular traffic and industrial activities in the surrounding area.

Moreover, it is suggested that air quality monitoring within the park be continued to evaluate the effectiveness of the measures taken and to verify any improvements. Finally, it is hoped that the collaboration between Legambiente, Sense Square, and the Department of Chemistry and Biology at the University of Salerno can continue in the future to ensure the protection and preservation of the cultural and environmental heritage of the Eco-archaeological Park of Pontecagnano.

3. Conclusions

In conclusion, the joint monitoring study of air quality within the Eco-archaeological Park of Pontecagnano has highlighted the need for measures to reduce air pollution in the park. The observed levels of pollutants were moderately high, with particulate matter exceeding legal limits on several occasions. The darkening of the archaeological surfaces seems to be connected to the high concentrations of fine particulate matter in the air.

By continuing to monitor air quality within the park and implementing measures to reduce pollution, we can ensure the long-term preservation of the park's valuable archaeological and environmental resources.

Overall, our findings underscore the importance of interdisciplinary collaboration and the use of advanced technologies in safeguarding cultural and natural heritage sites around the world.

References

[1] D. Sofia, N. Lotrecchiano, A. Giuliano, D. Barletta, M. Poletto, “Optimization of Number and Location of Sampling Points of an Air Quality Monitoring Network in an Urban Contest”, Chemical Engineering Transactions. vol.74, May 2019, pp. 277–282. https://doi.org/10.3303/CET1974047.

[2] N. Lotrecchiano, L. Montano, I.M. Bonapace, T. Giancarlo, P. Trucillo, D. Sofia, “Comparison Process of Blood Heavy Metals Absorption Linked to Measured Air Quality Data in Areas with High and Low Environmental Impact”, Processes, vol.10, No.7, July 2022, pp. 1409. https://doi.org/10.3390/pr10071409.

Comunicazioni orali

OP1

CROSS-LIFE: POLY(VINYL ACETATE-CO-CROTONIC ACID) FROM BIO-BASED SYNTHESIS - PRELIMINARY LCA RESULTS

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1. Introduction

The treatment of industrial and urban wastewater is fundamental to ensuring public health and environmental protection, but it may generate huge amounts of sludge which has to be properly disposed of. Sludge treatment is usually a costly operation that includes several management options, namely landfilling, incineration, composting, anaerobic digestion, and direct usage on land. However, the relatively high content of organic material makes wastewater treatment sludge (WWTS) a potential source for bio-based chemicals and materials that can replace their fossil-based equivalents and meet with the circular economy principles.

To this aim, the EU-funded project "CROSS-LIFE" (G.A. 101074164) explores the upcycling of the carbon contained in WWTS to the production of bio-based crotonic acid (CA), which is employed in the copolymerization with vinyl acetate to poly(vinyl acetate-co-crotonic acid). Herein, preliminary life cycle assessment (LCA) is applied to estimate the potential for greenhouse gas emissions reduction achievable by replacing fossil-based CA with the WWTS-to-CA route. [1]

2. Results and Discussion

"Cradle-to-gate" system boundaries were set to cover the main life cycle phases from raw material extraction to the production of 1 kg CA, which is set as the functional unit. Life cycle inventories were developed for fossil-based and bio-based CA, respectively. More in detail, fossil-based CA has been modelled using data gathered from the existing relevant literature, which provided the dataset of material and energy inputs and outputs by process, from oil extraction to acetaldehyde production and further processing to purified CA [2,3]. For bio-based CA, the biological–thermochemical process has been developed based on the modelling of the system material and energy inputs and outputs for each process stage at the semi-pilot scale: (i) hydrothermal carbonization (HTC) pre-treatment of WWTS, (ii) anaerobic digestion of the entire pre-treated WWTS under thermophilic conditions; (iii) solid/liquid separation of the mixture through a filter press to get a volatile fatty acids (VFAs) enriched solution; (iv) aerobic fermentation of the VFA stream to produce polyhydroxybutyrate (PHB) as intracellular granules; (v) drying of the microbial biomass enriched in PHB, followed by its thermolytic distillation to give bio-based CA.

The preliminary LCA results demonstrate demonstrates a GHG emission reduction from 13.9 kg CO_2eq per kg CA to 7.75 kgCO_2eq per kg CA in favor of the replacement of fossil sources with the WWTS upcycling route here proposed. The main contribution to such carbon emission reduction is due to much lower steam inputs to the depolymerization of PHB through thermolytic distillation than those required for fossil-based CA. For bio-based CA, the most contributing stage to carbon emissions is HTC due to intensive thermal energy requirements. In contrast, anaerobic fermentation is given a credit for the recovery of energy during the combustion in a combined heat and power plant of the biogas produced.

It is worth noting that the WWTS-to-CA process provides the supplemental function of dewatering the sludge input thanks to the application of HTC: during HTC, 40–60% of WWTS is converted into a carbon-densified product (hydrochar) containing most of the suspended solids in the sludge coming out of the HTC reactor. For this reason, it can be filtered at high pressure, getting an effective dehydration result impossible to achieve without HTC, ultimately reducing the amount of waste to be disposed of (i.e., the dry matter increases from 4% wt in the sludge in input to about 40–60% wt in the sludge in output). To include this further benefit into our preliminary assessment, we have expanded the system boundaries to include and compare the main end-of-life (EoL) scenarios for managing WWTS and normalized the results to a reference flow of 1 tonne of dry sludge ($t_{dry\_\_WWTS}$). Based on a review of 35 LCA studies [4], the carbon footprint of the most common WWTS management strategies including direct land application, incineration, and composting has been quantified at 1.3 ± 1.7, 0.42 ± 0.52, and 0.028 ± 0.12 t CO_2 per t_{dry_WWTS}, respectively.

These estimates will be used as a quantitative basis for further refinement of the avoided impacts related to (i) the production of CA from fossil sources, (ii) the dewatering of digestate, and (iii) the transport of a higher quantity of treated sludge to the final disposal site.

3. Conclusions

Despite preliminary, these results highlight a significant potential for carbon savings achievable by a bio-based production process of CA, which will be ultimately embedded into the environmental profile of its derived copolymer poly(vinylacetate-co-crotonic acid).

The copolymers constituted from fossil-based or bio-based CA have the same composition and thermal properties, independently of the origin and the purity of the starting CA monomer, suggesting their equivalency for the investigated application.

References

[1] A. Jorea et al. RSC Sustain., 2023, https://doi.org/10.1039/D3SU00052D.
[2] Research Laboratory for IDEA, Research Institute of Science for Safety and Sustainability and National Institute of Advanced Industrial Science and Technology, LCI Database IDEA Version 2.
[3] G. Wernet et al. Int. J. Life Cycle Assess., 2016, 21, 1218–1230, https://doi.org/10.1007/s11367-016-1087-8.
[4] H. Yoshida et al., Waste Manage. Res., 2013, 31, 1083–1101, tps://doi.org/10.1177/0734242X13504.

LIFE CYCLE ASSESSMENT OF WET WIPES BY MEANS OF CHROMATOGRAPHIC AND MASS SPECTROMETRIC TECHNIQUES

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1. Introduction

The intensive everyday usage of plastic materials causes the release of a large amount of microplastics in all environmental compartments. Recently, biobased and biodegradable polymers have been looked at as a potential alternative to conventional plastics in terms of environmental impact[1–2]. However, biodegradation is a complex process influenced by many factors, requiring the development of reliable analytical methods to assess the lifecycle of bioplastic materials and to monitor their degradation once in the environment[3].

Commercial wet wipes are disposable nonwoven materials pre-moistened with a specifically formulated solution or emulsion[4]. According to the recent "flushability" policy in the UK, echoed in the Implementing Regulation (EU) 2020/2151, wet wipes can be differentiated into non-flushable and flushable, depending on their chemical composition and suggested disposal practices[4]. Non-flushable wipes must be disposed of with the solid waste, while flushable ones are claimed suitable to be disposed of through the toilet and are designed to disintegrate into small pieces once in the sewage systems. Unfortunately, the environmental risks associated to such practice are far from being fully assessed and deserve specific attention.

2. Results and Discussion

In this work, different samples of commercial wet wipes from the UK market were investigated: (a) flushable with the UK certification, (b) flushable with no UK certification, (c) biodegradable but not flushable, (d) not biodegradable and not flushable. Each wet wipe was subjected to morphological analysis by scanning electron microscopy (SEM), and chemical analysis by evolved gas analysis-mass spectrometry (EGA-MS), and double-shot pyrolysis-gas chromatography-mass spectrometry (DSPy-GC-MS). EGA-MS and DSPy-GC-MS (T^1 = 300 °C, T^2 = 600 °C) enabled the determination of fiber composition whether the tissues were composed of one or two different materials. Many additives reported in the product labels such as humectants (e.g. glycerin, 2-phenoxyethanol) and preservatives (e.g. benzoic acid) were also detected. As expected, the method confirmed the presence of synthetic fibers in the conventional samples only, whereas all the other wipes resulted to be composed of cellulosic fibers. Even though analytical pyrolysis techniques failed to discriminate between natural and regenerated cellulosic fibers, SEM analysis detected the presence of both natural and regenerated cellulose in all flushable certified samples, and only regenerated fibers in all the other non-conventional wipes.

Subsequently, non-flushable (composed of a mixture of cellulose and polyethylene terephthalate, PET) and flushable (composed of cellulose) wet wipes were subjected to two different types of artificial degradation.

A set of samples was sonicated in deionized water to simulate the mechanical degradation occurring in sewage waters, while a second set of samples was soaked in deionized water and exposed to UV-Vis radiation in an ageing chamber to simulate an outdoor photodegradation. At the end of each ageing cycle, the tissue was squeezed, and the water was filtered on quartz filters to collect the released microfibers (diameter of the filter 37 mm). The residual tissues were analyzed by SEM and DSPy-GC-MS, while the filters were pyrolyzed at 600 °C. Subsamples of the water in which the wipes were immersed during the treatments were analyzed by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) to detect soluble organic leachates (organic compounds).

The Py-GC-MS analysis of the filters confirmed the presence of higher levels of microfibers in samples aged longer and highlighted an effect of the ageing conditions. In particular, significant amounts of cellulose microfibers were detected in the filters obtained for the artificially aged non-flushable wipes. DSPy-GC-MS of the leftover tissues highlighted a decrease of the peaks related to additives (e.g. glycerin, 2-phenoxyethanol, benzoic acid) with ageing time in the first shot (Figure 1). As for the second shot, an increase of cellulose pyrolysis products (e.g. levoglucosan) was observed for the flushable certified wipes, whereas no significant changes were detected for the non-flushable wipes. The above was confirmed by HPLC-MS/MS data of the leachates.

3. Conclusions

Both flushable and non-flushable wet wipes generated significant amount of microfibers when subjected to simulated mechanical and photo-induced ageing. Cellulose fibers underwent extended fragmentation, releasing the greatest amount of microfibers during the experiments compared to synthetic fibers. The experiments also highlighted the importance of the leaching of additives and chemicals such as glycerin, 2-phenoxyethanol and benzoic acid, whose release into water is pivotal in assessing the environmental risk of flushable wet wipes. Thus, the evaluation of the environmental impact of flushable wet wipes shall not be limited to the assessment of the composition of the fiber support and should take care of the variety of possible formulations.

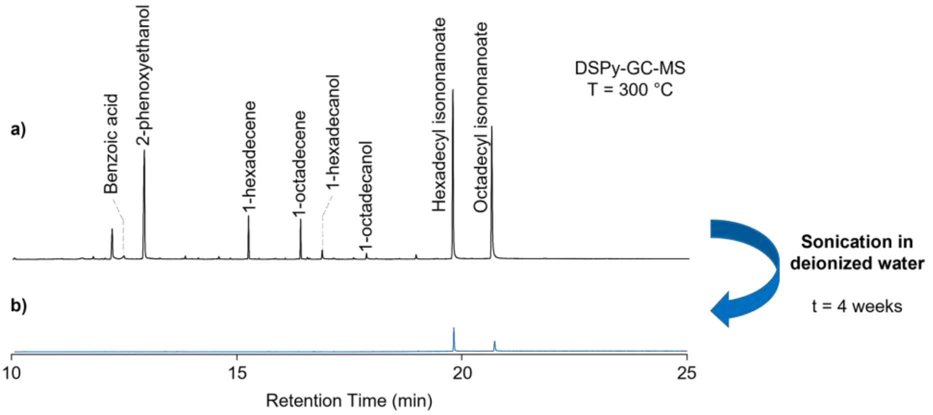

Figure 1. First shot pyrograms of flushable certified wipes before (a) and after (b) sonication.

References

[1] R.A. Gross, B. Kalra, Biodegradable polymers for the environment, Science, 297, 803-807 (2002).
[2] L. Manfra et al., Biodegradable polymers: A real opportunity to solve marine plastic pollution?, J. Hazard. Mater., 416, 237-280 (2012).
[3] SAPEA, Biodegradability of plastics in the open environment (2020).
[4] T. Harter et al., Reduced dispersibility of flushable wet wipes after wet storage, Sci. Rep., 11, 1–9 (2021).

OP3

WOOD-BASED BUILDING MATERIALS SUSTAINABILITY ASSESSMENT VIA EMERGY EVALUATION AND LIFE CYCLE ASSESSMENT: INSIGHTS FROM COMPLEMENTARY METHODS

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1. Introduction

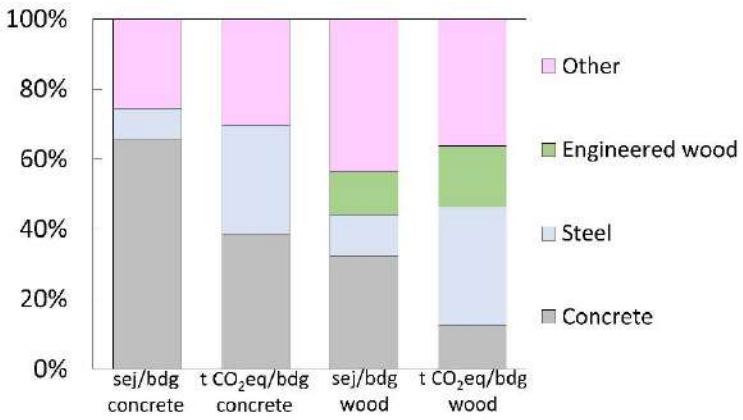
One fifth of the global greenhouse gas emission is linked with building sector (Cabeza et al., 2022). Traditional materials such as concrete and steel are emission intensive (Davis et al., 2018). Alternative materials such as engineered wood (e.g., Cross Laminated Timber) could partly replace them while acting as carbon storage after absorbing CO_2 from the atmosphere. This provides engineered wood a comparative advantage in terms of sustainability. Assessments to quantify this advantage must encompass the whole manufacturing process of engineered wood. However, since such materials cannot replace concrete and steel *ex aequo*, comparisons must be conducted in functional terms, considering the application in a building. Life Cycle Assessment (LCA) is a standardized and widespread method to evaluate the environmental impact of products throughout their whole life cycle. However, LCA considers inputs form the technosphere only, neglecting the biosphere role in providing natural resources such as wood. Emergy evaluation fills this gap by capturing inputs of any sort. Our work shows the complementarity of the two approaches attempting to fill the gap left by a stand-alone LCA application.

2. Results and Discussion

Cross Laminated Timber (CLT) is used as reference for engineered wood. The manufacture of 1 m^3 of CLT through LCA is linked with 150 kg CO_2eq. Most of it derives from the energy used for both the harvesting and the engineering processes (41%), while the remaining part consists of materials that are consumed during the same phases. Energy and consumable materials belong to the technospere. There is no impact attributed to the provision of wood (in forest) nor to human labor input. These do not belong to the technosphere but to the biosphere and, as such, are neglected by LCA. The same analysis conducted via Emergy evaluation (EME), quantifies in $6.03 \cdot 10^{14}$ sej the effort of nature and technosphere to manufacture 1 m^3 of CLT. Opposite to LCA, EME highlights the outstanding role that the biosphere plays in the provision of engineered wood indicating that almost half of the overall emergy (45%) required is linked to forest growth. Moreover, the second largest contribution in terms of emergy is human labor (25%), which LCA fails to capture too. Inputs from the technosphere such as energy consumption (13%) and materials other than wood, such as glue (17%) are less relevant considering all the inputs. Such results are used as input for the estimation of the environmental sustainability of the partial replacement of concrete and steel with engineered wood in a residential building composed of one 5 story block and one 4 story block. Replacing concrete and steel resulted in a reduction of (-3%) in terms of GHG emission (- 36 t CO_2eq). Instead, EME shows that such replacement resulted in a much larger reduction of (-42%) in terms of emergy (- $4.49 \cdot 10^{18}$ sej). The results from the two approaches are significantly different due to the different system boundaries that intrinsically underpin the respective methodologies. LCA does not reflect the role that ecosystems play in contributing to the provision of material to human activities and the technosphere while EME provides information on the natural ecosystems' effort to provide resources. The greater environmental advantage that results from EME is due to its ability to capture the renewability of all the inputs required for a process, feature that is not available in LCA. Nevertheless, LCA provides punctual and accurate estimates in terms of multiple impact categories. This suggests that while analyzing goods that are predominantly based on non-renewable materials such as concrete and steel LCA could provide information comprehensive enough for sustainability assessment, it would overlook the fundamental role played by renewable materials such as wood.

3. Conclusions

We showed that wood-based buildings are much more sustainable compared to concrete-based buildings from an EME perspective, while the sustainability gain is only marginal from an LCA point of view. We conclude that since renewable resources will have to be the basis for the transition to a sustainable development and that buildings will play a major role in this transition, the sustainability assessment for buildings should shift from the current approach – uniquely based on LCA – to an integration between LCA and EME.



Brakedown of the results for the construction of a residential building from both EME and LCA

References

Cabeza, L. F. et al. (2022). Buildings. In P. R. Shukla et al. (Eds.), In IPCC, 2022: *Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. https://doi.org/10.1017/9781009157926.011

Davis, S. J. et al. (2018). Net-zero emissions energy systems. Science, 360(6396). https://doi.org/10.1126/science.aas9793

OP4

TOWARDS A SIMPLIFIED LCA FOR AGRIFOOD PRODUCTS: EVIDENCE FROM AGRITECH NATIONAL PROJECT

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1. Introduction

LCA is recognized as one of the widest used tools for environmental impact assessment of goods, especially for those of agri-food sector. LCA simplified approaches have been recently proposed to support enterprises and optimize both the big data-demand and time-consuming process while maintaining the methodological rigor and the results reliability (Arzoumanidis, 2017).

In this work, a simplified LCA dedicated to wine production is first set up and then calibrated using a robust sample of around forty wines. This sample is quite heterogenous and representative, being formed by different: i) types of wines (red, white, sparkling), ii) company size (small, medium and large), iii) cultivation practices (conventional, organic). All the LCA analyses are realized with the same functional unit, system boundaries, assumption, software (SimaPro) and database (Ecoinvent). Therefore all wine environmental profiles elaborated are perfectly comparable. The simplified LCA approach proposed is aimed to the identification of the lowest number of relevant inputs (hotspot), directly supplied as primary data, able to describe the results with the highest representativity.

2. Results and Discussion

For a sample of eight representative wines, high detailed LCA profiles, from cradle to gate, has been elaborated, including inventories and impact assessment, in order to produce two different LCA matrixes: the first we call "product *vs* impacts" (i.e. the main relevant impacts has been assessed for each wine analyzed) while the second "impact *vs* products" (i.e. all wines, disaggregated by inputs, are compared within the same impact category). The considered impact categories are climate change, acidification, eutrophication potential, acidification potential, ozone layer depletion potential. The cross-matrix analysis has identified 5 main hotspot (chemicals and fertilizers, diesel, energy consumption, glass and paper for packaging), able to document a very representative portion of the total impacts (> 95%). When Water Footprint, measured as Water Scarcity, is also included the number of hotspot grows by one unit including the input "water direct consumption". The hotspot identified are representative of all the three main phases in which the system is organized i.e. agricultural phase, winery and packaging.

Once set up, the approach has been validated, using a sample of about 30 wines performing the LCA with just the six hotspots. The environmental impact profile of each wine is completed by including the rest of the inputs accounted for as secondary data. Results show an estimated error of around 10-15% with respect to the true value. The largest error is found for the category "red wine" and "sparkling wine". This suggest performing a cluster analysis and organizing the model according also to other critical issues i.e. cultivation practices or winery procedure.

3. Conclusions

The preliminary results of the simplified experimental LCA approach focused on the wine industry are quite comforting and push us to deepen the topic, both using a statistically even more significant sample and adapting it to other agricultural production chains. The main advantage of using a simplified approach like the one proposed lies above all in giving the enterprises an easy to use, flexible and smart tool so that they can monitor the improvements made in the company and translate them into avoided impacts.

References

Arzoumanidis I., Salomone R., Petti L., Mondello G., Raggi A., 2017. Is there a simplified LCA tool suitable for the agri-food industry? An assessment of selected tools. Journal of Cleaner Production 149, 406-425.

ENVIRONMENTAL IMPACT ASSESSMENT AND OPTIMIZATION OF CHEMICALS FOR CERAMIC PRODUCTION PROCESSES

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1. Introduction

In the EU manufacturing context, the ceramic industry is one of the sectors most aware of environmental sustainability [1]. Various initiatives have been undertaken over the years at the level of this production sector and recently a dynamic environmental impact assessment system has been developed in order to meet the environmental monitoring needs of a ceramic tile manufacturer [2]. However, the lack of qualitative consistency between primary (manufacturing) and secondary (sourcing, distribution, installation and use) data significantly influences the final results of the environmental assessment. The implementation of the circular economy paradigm at the micro level is also hindered by the lack of upstream and downstream information in the supply chain [3]. The IESMAN project intends to fill the gap in the environmental performance of a chemical company that supplies raw materials for ceramic production. The Life Cycle Assessment (LCA) methodology has been applied on the entire chemical factory in order to define all the environmental impacts and based on the most impactful product category, a more sustainable material was developed using the Mixture Design approach from Design of Experiments (DoE) method.

2. Results and Discussion

The manufacturing of the chemical industry is particularly intricate and differentiated when compared to other industries due to the multiplicity of raw materials and production lines. The LCA analysis, performed according to UNI EN ISO 14040–14044 regulations, has been developed on a system consisting of pigments, compounds, glazes and inks for the decoration of ceramic tiles and slabs. In particular, the following 13 production lines have been defined for the LCA study: flamings, frits, grits, spherical grits, inks, raw materials, colouring oxides, body colouring oxides, dry powders, flakes, atomised glazes, compound glazes and liquid glazes. The functional unit for the LCA analysis of the entire factory is the annual production of chemicals, being equal to 41408.098 t. Once the collection of primary data of the 13 production lines and the related 316 raw materials has been completed, the inventory analysis was modeled in SimaPro 9.3.0.2 and with Ecoinvent 3.8.1 database for the background processes. The results of the environmental LCA analysis of the entire production show a total damage of 25581.5 Pt and the production line that cause the highest damage is the compound glazes for 36.11% followed by grits, inks and mixing colour oxides for 14.34%, 14.21% and 12.18% respectively (Figure 1). In particular, in the production line of compound glazes, 88.79% of the damage is due to the raw material production process mainly by the use of frits (41.33%), nepheline syenite (15.68%), barium carbonate (9.21%), zirconium silicate (8.18%) and zirconium oxide (6.97%). Therefore, in the IESMAN project, a frit-free glaze formulation obtained using secondary raw materials (SRM) has been experimentally developed by applying statistical techniques without affecting the quality of conventional ceramic products. In particular, the traditional industrial glaze formulation was modified with alternative raw materials by replacing frit with recycled borosilicate glass and recycled soda-lime glass, quartz with chamotte, and kaolin with metakaolin, respectively. A systematic experimental approach based on Mixture Design by DoE was adopted in order to study mixtures with varying replacement levels of selected (based on the preliminary screening) alternative raw materials. A total of 20 mixtures were chosen for the detailed study. Specimens of each mixture were prepared at laboratory and industrial conditions to eliminate any variations in kiln firing conditions. The measured responses or output factors selected based on the industrial interest from different glaze formulations were: (i) cleanability after interaction with methylene blue dye, (ii) coefficient of linear thermal expansion, (iii) colour difference between the standard and modified glazes, and (iv) softening temperature. The results allowed to select three optimized formulations further characterized using TG- DTA thermal analysis and the best glaze formulation was derived. The obtained frit-free glaze composition with secondary raw material represents a more sustainable and energy-efficient solution for the ceramic manufacturing industries.

3. Conclusions

The value creation toward a circular value chain, has drastically changed requiring a substantial effort by industries to reinvent processes, products and business models in a sustainable perspective. In the IESMAN project, tracking the environmental sustainability of chemicals supplied to ceramics manufacturers demonstrates that the most impactful product category are compound glazes and in particular the contained frits. Consequently, using a statistical approach, a new glaze formulation has been obtained to ensure a reduction in environmental loads.

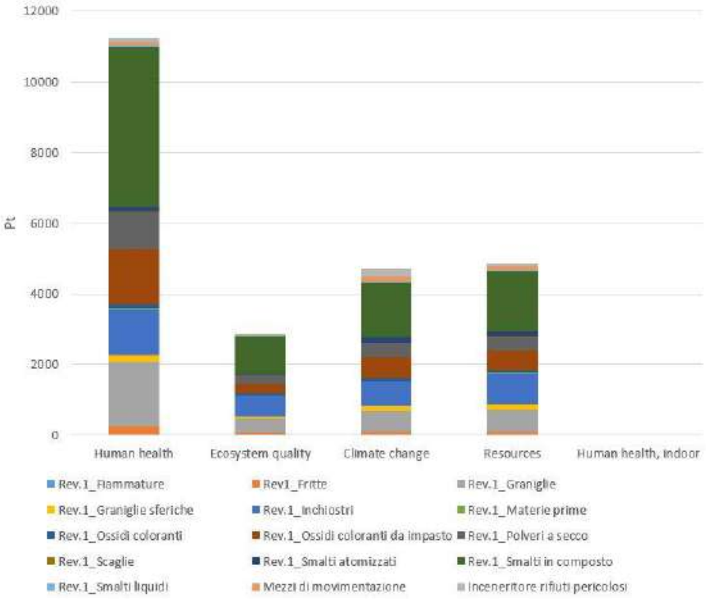

Figure 1. LCA results of the entire chemical production

References

[1] Gabaldón-Estevan, D.; Criado, E.; Monfort, E. The green factor in European manufacturing: A case study of the Spanish ceramic tile industry. J. Clean. Prod. 2014, 70, 242–250.

[2] Ferrari A.M., Volpi L., Settembre Blundo D., García-Muina F.E. Dynamic life cycle assessment (LCA) integrating life cycle inventory (LCI) and Enterprise resource planning (ERP) in an industry 4.0 environment. J. Clean. Prod. 2021, 286, 125-314.

[3] Fernández-Miguel A., Riccardi M.P., Veglio V., García-Muiña F.E., Fernández del Hoyo A.P., Settembre-Blundo D. 2022. "Disruption in Resource-Intensive Supply Chains: Reshoring and Nearshoring as Strategies to Enable Them to Become More Resilient and Sustainable," Sustainability, 2022, 14(17), 1-13.

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LIFE CYCLE SAFETY AND SUSTAINABILITY ASSESSMENT OF INNOVATIVE SOLUTIONS FOR ART RESTORATION

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1. Introduction

The management of cultural heritage requires continuous conservation and restoration efforts, which can be harmful to human health, especially for operators and curators, and at the same time impactful to the environment. To promote a sustainable approach to heritage restoration, attention should be paid to the impact assessment of all phases of a restoration project: from the environmental impacts generated by the production of the chemicals and devices used for restoration to the management of the waste resulting from such activities. Coping with these issues, GREENART (GREen ENdeavor in Art ResToration) project, part of the HORIZON Europe programme, proposes new solutions based on green and sustainable materials and methods, to preserve, conserve and restore CH. The innovative solutions proposed in GREENART are: i) protective coatings; ii) foams and packaging materials; iii) consolidants; iv) gels and cleaning fluids; v) green tech sensors. As part of the project, a Life Cycle Safety and Sustainability Assessment is planned to provide step-by-step guidance to product developers during the early design phase, facilitating the development of sustainable and innovative solutions.

2. Results and Discussion

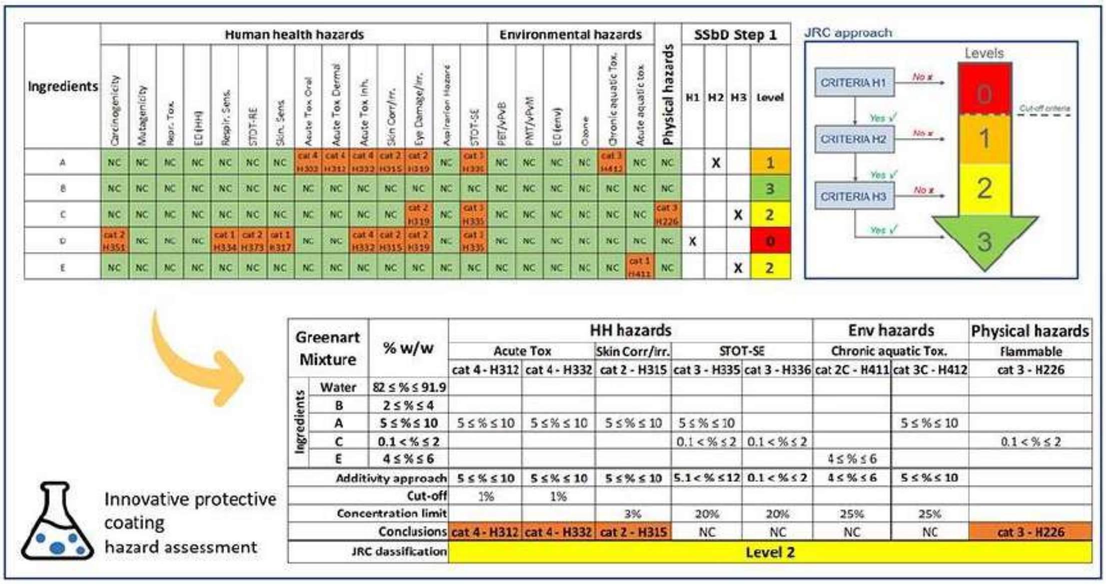
The sustainability framework implementing the Safe by Design (SbD) concept developed in the H2020 NANORESTART project was used as starting point (Semenzin et al., 2019). The "Safe and Sustainable by Design" (SSbD) approach consist in the identification of potential human or environmental impacts of a new material or product, with the objective of modifying its design to avoid undesired properties while keeping their functionalities. As a first step a state-of-the-art assessment in the safe and sustainable by design field with a specific focus on innovative chemicals was performed. The main current reference in the European landscape is the "Safe and Sustainable by Design chemicals and materials" framework by the Joint Research Center (JRC) (Caldeira et al., 2022). This JRC report, published in 2022, proposes a hierarchical stepwise approach in which safety aspects are considered, followed by environmental, social and economic sustainability aspects. This tiered approach also refers to information requirements since data availability is limited at the first stage of the research process. The framework foresees the assessment of the entire life cycle of a chemical or material, including the design phase and considering among others its functionality and end use. The first step of the JRC framework, which involves a hazard assessment of the chemicals, has been used as a guideline for the safety assessment that has to be performed on GREENART chemical solutions.

This first evaluation is performed according REACH and CLP regulations, which represent the actual European regulatory baseline, to look at the intrinsic properties of the chemical or material in order to understand its hazard profile before further assessing the safety during use. Three main criteria have been defined by the JRC SSbD framework, based on intrinsic hazard properties, which relate to: H1) most harmful substances; H2) substances of concern; H3) other hazard classes. The chemicals that fail the H1 criterion should be prioritised for a substitution or re-designed; they could be kept only if their uses are essential for society. The data collection focused on the innovative and most promising ingredients of cleaning fluids, coating and consolidants. Moreover, conventional products that should be replaced by innovative ones, developed within GREENART project, was assessed. Besides the list of ingredients also safety data sheets and the percentage of each ingredient in the formulation have been collected. The formulations proposed have been checked by screening hazard assessment. In this step health, environmental and physical hazards were assessed by applying the EU CLP self-classification for mixtures.

3. Conclusions

Based on the outcomes of this initial phase, the developers of the product have the option to modify the original formulation in order to minimize any potential risks, or they can choose to eliminate it altogether if altering the composition would adversely affect its technical effectiveness and functionality.

After that safety aspects will be assessed taking into account production/processing phase and the final application phase. In the final step Life Cycle Assessment (LCA) and Life Cycle Cost (LCC) methodologies will be used to estimate environmental and economic impacts of the most innovative solutions along the entire life cycle.



Ingredients	Human health hazards														Environmental hazards						Physical hazards	SSbD Step 1			
	Carcinogenicity	Mutagenicity	Repr. Tox.	ED (HH)	Respir. Sens.	STOT-RE	Skin. Sens	Acute Tox Oral	Acute Tox Dermal	Acute Tox Inh.	Skin Corr/Irr.	Eye Damage/Irr.	Aspiration Hazard	STOT-SE	PBT/vPvB	PMT/vPvM	ED (env)	Ozone	Chronic aquatic Tox.	Acute aquatic tox		H1	H2	H3	Level
A	NC	NC	NC	NC	NC	NC	NC	cat 4 H302	cat 4 H312	cat 4 H332	cat 2 H315	cat 2 H319	NC	cat 3 H335	NC	NC	NC	NC	cat 3 H412	NC	NC		X		1
B	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC				3
C	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	cat 2 H319	NC	cat 3 H335	NC	NC	NC	NC	NC	NC	cat 3 H226			X	2
D	cat 2 H351	NC	NC	NC	cat 1 H334	cat 2 H373	cat 1 H317	NC	NC	cat 4 H332	cat 2 H315	cat 2 H319	NC	cat 3 H335	NC	NC	NC	NC	NC	NC	NC	X			0
E	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	cat 1 H411	NC			X	2

Greenart Mixture		% w/w	HH hazards					Env hazards		Physical hazards
			Acute Tox		Skin Corr/Irr.	STOT-SE		Chronic aquatic Tox.		Flammable
			cat 4 - H312	cat 4 - H332	cat 2 - H315	cat 3 - H335	cat 3 - H336	cat 2C - H411	cat 3C - H412	cat 3 - H226
Ingredients	Water	82 ≤ % ≤ 91.9								
	B	2 ≤ % ≤ 4								
	A	5 ≤ % ≤ 10	5 ≤ % ≤ 10	5 ≤ % ≤ 10	5 ≤ % ≤ 10	5 ≤ % ≤ 10			5 ≤ % ≤ 10	
	C	0.1 < % ≤ 2				0.1 < % ≤ 2	0.1 < % ≤ 2			0.1 < % ≤ 2
	E	4 ≤ % ≤ 6						4 ≤ % ≤ 6		
Additivity approach			5 ≤ % ≤ 10	5 ≤ % ≤ 10	5 ≤ % ≤ 10	5.1 < % ≤ 12	0.1 < % ≤ 2	4 ≤ % ≤ 6	5 ≤ % ≤ 10	
Cut-off			1%	1%						
Concentration limit					3%	20%	20%	25%	25%	
Conclusions			cat 4 - H312	cat 4 - H332	cat 2 - H315	NC	NC	NC	NC	cat 3 - H226
JRC classification			Level 2							

Results of step 1: Innovative protective coating hazard assessment of an example formulation

References

Caldeira, Farcal, R., Moretti, C., Mancini, L., Rauscher, H., Rasmussen, K., Riego, J., & Sala, S. (2022). *Safe and Sustainable chemicals by design chemicals and materials. Framework for the definition of criteria and evaluation procedure for chemicals and materials.* (Issue March). https://doi.org/10.2760/487955

Semenzin, E., Giubilato, E., Badetti, E., Picone, M., Volpi Ghirardini, A., Hristozov, D., Brunelli, A., & Marcomini, A. (2019). Guiding the development of sustainable nano-enabled products for the conservation of works of art: proposal for a framework implementing the Safe by Design concept. *Environmental Science and Pollution Research*, *26*(25), 26146–26158. https://doi.org/10.1007/s11356-019-05819-2

https://cordis.europa.eu/project/id/101060941

LIFE CYCLE ASSESSMENT (LCA) OF A LAB SCALE BIO-FUEL CELL FED WITH WASTE BIOMASS: CAN IT BE AN ALTERNATIVE TO TRADITIONAL TREATMENT SCENARIOS?

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1. Introduction

Turning waste into a valuable resource is globally mainstreamed by approaches and legislations including the circular economy and several SDG goals (Kaza et al, 2018). However, effective implementation of virtuous waste management strategies often requires innovative and versatile technologies and proven environmental preference over traditional waste treatment and disposal routes. In particular, biowaste is a material stream under investigation because of its potential source for added-value chemicals and renewable energy.

A team from the University of Bologna has developed a biofuel cell technology to serve as a treatment for discarded biomass originated from agriculture. This cell aims to valorize biomass by producing electricity and soil conditioner. A patent application has been filed for this technology (Setti and Maggiore, 2022).

In this study, the life cycle assessment (LCA) is applied to estimate the environmental performance of the bio-fuel cell developed, with emphasis to understand which stages of the process are the most impactful to the environment and where prioritizing efforts should be dedicated to achieving sustainability improvements.

2. Results and Discussion

The analysis of environmental impacts consists of the compilation of the life cycle inventory (LCI), in collaboration with the developing teams, and then the assessment of impacts (LCIA). In this study at this last stage, two methods were chosen: CED is focused on energy consumption; and ReCiPe, which considers impacts on human health, resources and ecosystems.

In addition to assessing the lab-scale impacts of the cell, various considerations were made from an eco-design perspective.

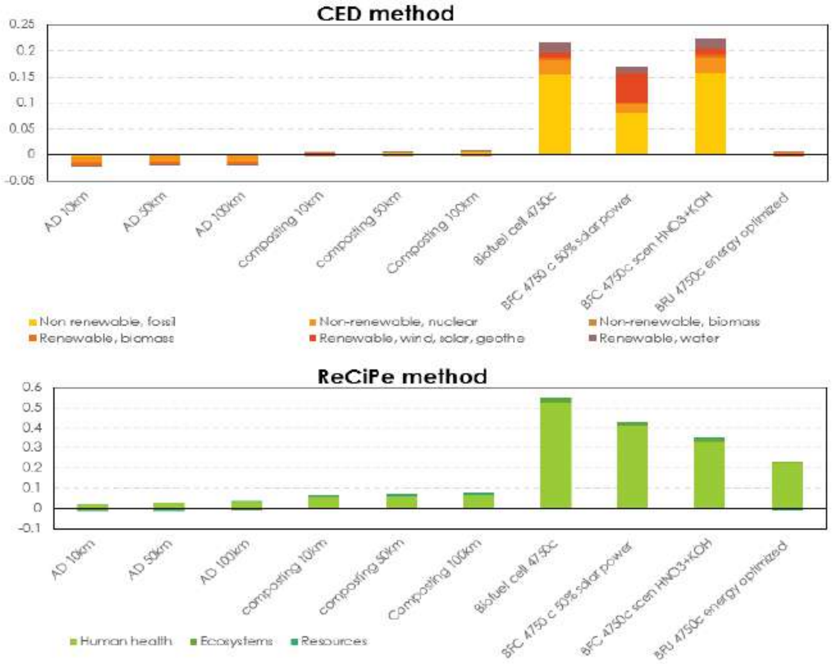
One aspect that has been investigated is how much the impact of cell production weighs on the total and after how many uses it can be significantly reduced. The results showed that the impacts related to the production of the cell (i.e., infrastructure) are negligible if it is used about 400 times, at least. During subsequent analysis, the average lifetime of a fuel cell was considered, thus 4750 cycles (Hua et al., 2020).

After that, the focus was on which aspects were most impactful on the environment during cell use. It was observed that the greatest impact is due to energy consumption and the usage of phosphoric acid and other chemicals. The study, therefore, focused on how these two aspects can be optimized. It was noted that the total impact of the chemicals can be decreased significantly if they are expected to be recovered as fertilizer, and total recovery of the elements P, N and K in a soil conditioner was therefore assumed.

To look for a less impactful alternative to the reagents I already tested in the laboratory, alternative scenarios were created to test different combinations of acids and bases. Nitric acid and potassium hydroxide were used instead of phosphoric acid and sodium hydroxide. The use of KOH use seems promising because it adds potassium to the nutrient output.

Because of the large portion of impacts due to energy consumption, scenarios based on renewable sources have been also explored. The renewable resource investigated the most is photovoltaic energy because it is the one most easily applicable to the sector for which this cell was designed, which is the agricultural sector. The benefit in environmental terms (ReCiPe method) turns out to be 48 % if the energy comes totally from solar power. A further model was also created to check the benefits of heat recovery during the hydrolysis reaction and other energy consumption optimization. Impacts decrease by 56% for the ReCiPe method and 98% for the CED method.

Finally, all these scenarios were compared with traditional treatments for biomass waste, such as composting and anaerobic digestion. Since the use of the cell does not involve transportation, while in traditional methods often it must be taken into account, scenarios with plants 10, 50 and 100 km away have been considered. The results indicate that the optimized cell can be comparable with composting for the CED method, while for the ReCiPe method, where the impacts of chemicals weigh more, the traditional scenarios are still significantly less impactful.



Comparison of the impacts of anaerobic digestion (AD) and composting with various biofuel cell use scenarios.

3. Conclusions

From the results of this study, it can be said that this technology is promising and can be competitive as long as energy consumption is minimized, and nutrients used in the reagents are recovered. Impacts related to reagents can be slightly reduced by changing them, and energy consumption can be reduced if heat is recovered, and the required energy is obtained from renewable sources.

However, all these observations must be accompanied by knowledge of the limitations of this study and possible future developments. First, the scale of the process, which is the laboratory scale with model molecules, should be considered. Part of the limitations come from the data; in fact, some are primary data, while other come from personal estimations.

Reference

Hua, Z, Zheng, Z, Péra, MC, Gao, F, 2020. ‘Remaining useful life prediction of PEMFC systems based on the multi-input echo state network’, Applied Energy, 265(114791).

Kaza, S, Yao, L, Bhada-Tata, P, Van Woerden, F, 2018. ‘What a Waste 2.0 -Snapshot of Solid Waste Management to 2050. Urban Development Series, World Bank Group, Washington DC.

Setti L. and Maggiore I, 2022. “Cella a biocombustibile abiotica” – “Abiotic biofuel cell”: Italian patent pending n°102022000024867 by Università Di Bologna.

OP8

VOCS EMISSION BY GASOLINE SERVICE STATIONS IN RESIDENTIAL AREAS: EVALUATION OF THE IMPACT ON AMBIENT AIR QUALITY

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1. Introduction

VOCs concentration at gasoline service stations located in residential areas may adversely affect air quality and may pose health risk and odour annoyance to population living nearby. VOCs emission from service stations is mainly determined by gasoline evaporation following refuelling operations (fuel transfer from bulk storage tanks to oil tank trucks or dispensing from the service station to individual vehicles) and/or by leaks from underground or vehicular tanks used for gasoline storage [1]. Therefore, depending on the daily number of refuelling operations and the efficiency of the conveying system of gasoline vapours coming from storage tanks, the gasoline service stations may cause air impairment and both short- and long-term adverse effects on human health. To date, a limited number of investigations have been carried out worldwide to evaluate the extent of the impact the gasoline service stations determine on their surroundings [1-3]. The present study is contextualized in this research field and is addressed to fill the existing knowledge gap and to raise awareness among stakeholders on the need of safeguarding public health in exposed residential areas.

2. Results and Discussion

With the purpose to assess the impact of VOC emissions coming from a gasoline service station on the air quality of the nearby residential area, an experimental design comprising two monitoring campaigns, contextually carried out over 2 months, was developed. One monitoring campaign was based on the high temporal and spatial resolution monitoring of TVOCs concentration by means of photo-ionization detector units (*Corvus IAQ monitor, Ion Science*) deployed in the area surrounding the gas station, addressed at the identification of emissive sources and short-term emissive events; the other one was focused on VOCs chemical characterization of ambient air at both outdoor and indoor receptor sites i.e., 3 outdoor sites located at different distance from the gas station and 1 indoor site representing a private dwelling opposite the gas station, performing passive air sampling onto suitable adsorbent (*Radiello*®, *Maugeri*) on a 3-days scale followed by TD-GC/MS analysis.

The analysis of the collected real-time TVOCs concentration data highlighted the occurrence, over the entire duration of the monitoring campaign, of peak concentrations ranging from 1.0 to 2.0 ppm (short-term events) at 3 on 4 of the investigated outdoor receptor sites, due to their closer proximity to the gas station. Moreover, the comparative evaluation of temporal trends of TVOCs concentration registered at both outdoor and indoor sites revealed that the data were highly correlated, supporting the hypothesis that a common source (e.g., the gas station) impaired air quality in terms of VOCs both outdoors and indoors. The daily temporal variation in TVOCs concentration appears also to be repeatable over the weekdays with peak concentrations occurring during selected daytime hours (8:00-11:00 a.m., 1:00-5:00 p.m.), when the transfer operation of the fuel into the storage tanks of the gas station occurred and/or a greater affluence of customers was registered. Finally, with specific regard to the outcomes of the chemical characterization, the highest concentration of BTEX (Benzene: 4.1 $\mu g/m^3$; Toluene: 6.2 $\mu g/m^3$, Ethylbenzene: 1.6 $\mu g/m^3$, Xylenes: 2.7 $\mu g/m^3$) were found in correspondence of the outdoor sites closest to the gas station even considering that the sites further away from it were instead very close to high traffic roads, therefore likely to be highly impacted by the traffic source. This outcome was further confirmed by the diagnostic ratio T/B, whose values at the receptor sites close to the gas station revealed to be, over the monitoring campaign, systematically lower than those calculated at a greater distance demonstrating in this way the existence of a point source of Benzene in the investigated area.

3. Conclusions

The outcomes of the present study, obtained through the application of an integrated methodological approach based on the simultaneous chemical characterization and the real-time monitoring of VOCs, add further evidence on the impact determined by a point emissive source like a gasoline service station on the ambient air quality in the surrounding residential area. The vicinity of the gas station to private dwellings can definitively pose a health risk for the exposed population due to the inhalation exposure to target pollutants as aromatic hydrocarbons (Benzene).

References

[1] Zeng L. et al., 2022. *Species profiles, in-situ photochemistry and health risk of volatile organic compounds in the gasoline service station in China*. Science of the Total Environment 842, 156813.
[2] Vitale S. et al., 2015. *Filling station short-range impact on the surrounding area: A novel methodology for environmental monitoring based on the shadows study*. Environmental Technology & Innovation 4, 210-217.
[3] Terrés I.M.M. et al., 2010. *Assessing the impact of petrol stations on their immediate surroundings*. Journal of Enviromental Management 91 (12), 2754-2762.

OP9

CHARACTERIZATION OF MULTI-COMPOSITE NANOMATERIALS FOR SUPPORTING SAFE & SUSTAINABLE BY DESIGN STRATEGIES

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1. Introduction

In recent decades, the development of new technologies has significantly increased the use of engineered nanomaterials in consumer products. Among the most recent materials we find multicomponent nanomaterials (MCNMs), characterized by the integration of two or more nanometer-sized components in a single system, which can give the final product additional innovative properties compared to those with a single component. However, despite the numerous benefits associated with the use of MCNMs, concern is growing about their potential risk to human health and the environment. This concern is related both to their nanometric size and to the complexity of estimating the degradation rates and toxicity of a multi-composite system. Therefore, investigating the interactions between MCNMs and the surrounding media, e.g. dissolution, aggregation/disaggregation and surface ligand adsorption, are of great importance for supporting the risk and safety assessment of these materials, as such changes can affect their toxicity[1].

2. Results and Discussion

This work is framed within the EU funded H2020 SUNSHINE Project and aims to support Safe and Sustainable by Design (S&SbD) strategies for mortars incorporating advanced multi-component nanomaterials to the photocatalytic NO_x decontamination. Colloidal stability, surface charge and ion release of both single and MCNMs dispersed in different media relevant for (eco)toxicological testing were investigated, as well as the release of ions from mortars. From the combination of different analytical techniques, such as dynamic and electrophoretic light scattering (DLS and ELS), centrifugal separation analysis, Raman spectroscopy, infrared spectroscopy (IR), transmission and scanning electron microscopy (TEM and SEM) and inductively coupled plasma mass spectrometry (ICP-MS), a comprehensive characterization of MCNMs have been performed. The obtained results allowed to estimate the qualitative and quantitative stability of the tested dispersions over time, and to gather further significant information for a better correlation with the results from (eco)toxicity studies.

3. Conclusions

The approach presented here will greatly support the development and implementation of environmental risk assessment and management methodologies for MCNMs, within S&SbD strategies.

References

[1]Abdolahpur Monikh, F., et al. (2022) ‘"Advanced materials" and the challenges on the horizon for testing their (eco)toxicity and assessing their hazard’, Environmental Science: Advances 2(2), pp. 162-170, doi: 10.1186/s12989-022-00487-6.

OP10

SAFE BY DESIGN SYNTHESIS OF 2D MATERIALS

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1. Introduction

2D-materials become an outstanding technological field in recent years due to their promising physical, electrical, chemical, and optical properties. The starting point of this research line is probably due to the first synthesis of graphene in 2004 by Gejm and Novosëlov.[1] Since the first discovery of graphene, more and more 2D materials have been synthesized, such as C_3N_4 and MXenes. The favorable functional properties of these materials must be governed for obtaining specific characteristics suitable in many industrial sectors. However, a proper structure-function relationship for these new materials still lacks.

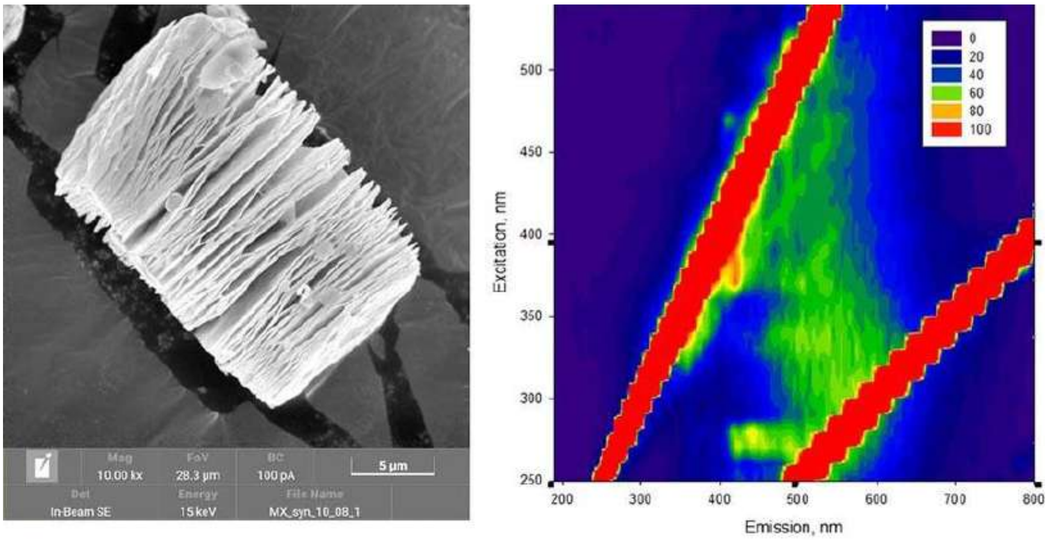
2. Results and Discussion

The synthesis of 2D materials with controlled morphology is having an increasingly prominent role in materials science, because the variation of the synthesis parameters allows optimizing the functional properties of the materials themselves. Not all the synthesis parameters can be modified as desired and the influence that each parameter has on the final characteristics of the product is different.[2] At the beginning, a proper definition of the chemical, structural and morphological characteristics that can drive the functional properties at nanoscale and molecular level can be scouted by an extensive literature search. In order to recognize the most significant parameters, a Design of Experiment (DoE) screening approach can be applied to the selected parameters to explain experimental variability. Starting from the synthesis conditions for the specific materials obtained through the screening DoE, series of morphology controlled 2D-materials can be synthetized and characterized with different analytical methods such as electron microscopy (SEM, TEM), electrochemistry (CV, OCP, LSV, EIS), UV-Vis and IR Spectroscopy, Dynamic Light Scattering (DLS), X-Ray diffraction (XRD), etc.[3] Of course, even functional properties can be tested. For example, by using Microtox bioassay which uses the bioluminescent Vibrio Fischeri bacteria as probe and through other more specific techniques such as enzyme inhibition tests. Moreover, the catalytic properties towards the abatement of recalcitrant pollutants in air and water and H_2 production through hydrogen evolution reaction (HER) can be assessed.

Finally, materials' characteristics can be collected and evaluated using Principal Component Analysis (PCA) and data fusion approaches. These chemometric techniques should allow us to establish the relationship between the synthesis parameters and the materials' characteristics. These relationships can be exploited to develop a DoE optimization model for the Safe and Sustainable-by-Design (SSbD) synthesis of specific 2D-materials with the use also of regression models (such as Multiple Linear Regression) and Machine Learning approach for the evaluation of the collected data. Further, this methodology allow us to create a model able to predict the functional properties of a specific 2D material starting from the synthesis parameters and vice versa.[2]

3. Conclusions

In conclusion, the use of this combined approach (DoE for synthesis, characterization and Chemometric Analysis) is a valuable method for the safe-by-design synthesis of several kind of materials for large-scale application in catalysis, energy harvesting, biomedical and environmental applications, etc. Of course, this approach is not only related to the material synthesis but can be expanded to any kind of molecules/material, with relevant saving of solvents, energy and times.



SEM micrograph of one of the synthesized MXene (left) and fluorescence matrix analysis on graphene oxide material (right).

References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov; Electric Field Effect in Atomically Thin Carbon Films; Science, Vol. 306, Issue 5696, pp. 666-669, 2004

2. F. Pellegrino, R. Isopescu, L. Pellutiè, F. Sordello, A. M. Rossi, E. Ortel, G. Martra, V.-D. Hodoroaba, V. Maurino; Machine learning approach for elucidating and predicting the role of synthesis parameters on the shape and size of TiO_2 nanoparticles; Scientific Reports, 10: 18910, 2020

3. M. Minella, M. Demontis, M. Sarro, F. Sordello, P. Calza, C. Minero; Photochemical stability and reactivity of graphene oxide; J Mater Sci, 50:2399–2409, 2015

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OP11

THE SYNERGY OF INDOOR AIR QUALITY ASSESSMENT AND ARTWORK MATERIALS CHARACTERISATION: THE SANTUARIO DELLA BEATA VERGINE IN SARONNO AS A CASE STUDY

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1. Introduction

Time and environmental conditions are among the main factors related to the degradation of artwork and historical buildings. It is, well-known that artistic materials exposed to light, humidity, variation in temperature, and pollution undergo chemical physical characteristics changing and, as a consequence, are subject to various kinds of corruption processes. Therefore, the study of degradation mechanisms and possible strategies for their prevention has become of main importance in the field of cultural heritage.

In this research, several microclimatic parameters, the presence of particulate matter and/or pollutants such as nitrogen dioxide and BTEX, were monitored to assess the indoor and outdoor characteristics of the Santuario della Beata Vergine dei Miracoli in Saronno (VA). In addition, in-situ measurements for the characterisation of pigments, binders, and products of degradation on several works of art in the sanctuary were taken. Special attention was paid to Bernardino Luini's frescoes' colour palette, with the main aims of establishing the state of conservation of the paintings and taking part in the possible authentication of the fresco located outside the church.

2. Results and Discussion

The microclimates surrounding the beautiful frescoes cycle by the master of the Renaissance Bernardino Luini and the valuable wooden sculptures representing the Deposition and the Last Supper were monitored during different periods of the year, including important religious events like Easter Week. Several dataloggers for temperature, relative humidity, and illuminance detection and an optical particle counter (OPC) for particulate matter (PM) continuous evaluation were placed around the area of interest. Moreover, some diffusive, passive samplers to determine the mean concentration of NO_2 and BTEX were also used. As part of the research, the outdoor parameters were also monitored and a comparison with the indoor values was made with the purpose of finding possible correlations.

The preliminary results of this part of the research indicate that, notwithstanding the indoor concentration of pollutants and changes in thermal and humidity parameters are on average lower with respect to the outdoor values, the microclimate inside the Sanctuary was often above the threshold outlined by the Italian legislation and technical standards [1].

Several non-invasive measurement campaigns were performed in the meantime, with the aim of identifying pigments, binders and possible products of degradation on the "Marriage of the Virgin" by Bernardino Luini (Figure 1), the "Adoration of the Christ Child" (which is located outside the church and is thought to be an original Bernardino Luini as well), and some of the wooden painted sculptures. This study was performed by means of totally-non-invasive spectroscopic and imaging complementary techniques such as Raman, FTIR, visible reflectance and XRF spectroscopies, hyperspectral imaging and colourimetry.

The resulting palettes of the two frescoes are both characterised by the presence of calcium carbonate (used both in white details and to lighten other colours), yellow ochre and Naples yellow, red ochre and/or umber, and Fe-based green. Nevertheless, some differences were also evidenced, especially with regard to the blue areas. Indeed, while smalt was used to paint Joseph's mantle in both works, Mary's mantle showed the presence of valuable lapis lazuli only in the "Marriage of the Virgin". Azurite, and traces of smalt were instead identified in the "Adoration of the Christ Child". Some products of degradation like gypsum and oxalates were detected here and there on both frescoes.

Furthermore, some in-situ XRF and visible reflectance analyses were carried out on the wooden sculptures placed in the two main chapels of the Sanctuary. Apart from the identification of cinnabar (HgS) as the main pigment for the red clothes of the characters, the occurrence of the phenomena of degradation was also observed. Still under study is the possible correlation of the detachment of some of the painted film with unsuitable air quality and microclimate of the environment.

The study of the possible correlation between environmental conditions/pollution and degradation on all the investigated objects is ongoing, and some modeling experiments are being performed to delve deeper into this issue.

3. Conclusions

This research highlights the importance of the synergic application of environmental monitoring and artistic material analysis in museum contexts.

Indeed, the monitoring of air quality allowed assessing the environmental conditions inside and outside the Sanctuary over time, even covering important liturgic events. On the other hand, the analyses performed on the frescoes and sculptures highlighted several products of degradation that are probably correlated with the environmental conditions.

The knowledge about the mechanisms behind the corruption of works of art is one the most challenging topics nowadays, and this makes this study a pioneer in interdisciplinary research for it is being performed in real conditions and over a long time, which is not so common to find in the literature.

Fig. 1: Bernardino Luini's Marriage of the Virgin (Santuario della Beata Vergine, Saronno (VA))

References

[1] Bergomi, A.; Comite, V.; Guglielmi, V.; Borelli, M.; Lombardi, C.A.; Bonomi, R.; Pironti, C.; Ricciardi, M.; Proto, A.; Mariani, C.; and Fermo P,. Preliminary Air Quality and Microclimatic Conditions Study in the Santuario della Beata Vergine dei Miracoli in Saronno (VA). Molecules 2023, 28, 1615. https://doi.org/10.3390/molecules28041615

OP12

INDOOR AIR QUALITY IN A NATURALLY VENTILATED CHURCH: EMISSION CHARACTERISTICS OF AIR POLLUTANTS FROM INCENSE BURNING

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1. Introduction

In recent years, indoor air quality (IAQ) has become a very important issue because in developed countries people tend to spend most of their time in indoor environments as home, workplace, school, etc. Moreover, many studies showed that indoor air is frequently more contaminated than outdoors one [1, 2]. In fact, in addition to outdoor pollutants penetrating through windows and doors, most of the indoor pollutants are emitted from indoor sources as building materials, furniture, cleaning and combustion processes: heating, cooking and incense burning. Indoor air pollution, resulting from specific indoor activities such as cooking or cigarettes smoking, has been deeply characterized [3, 4] in contrast to incense burning emissions. In a poorly ventilated area as the churches where large amounts of people gather in a relatively short time and incense is commonly burned, high concentrations of harmful chemical pollutants could affect IAQ. Therefore, this study aims to investigate the time profiles of pollutants concentrations in a church and basilica during the liturgical celebrations to estimate the emissions dynamic induced by incense burning and its potential health impacts.

2. Results and Discussion

This study represents a pilot project for the assessment of air quality inside churches and basilicas. An high-time resolved monitoring campaign was carried out in 2023 from January 20th to April 30th in a church (total volume of about 600 m$^{3)}$. More specifically, sensors and analyzers for high-time resolution monitoring of the main pollutants in both gaseous and particulate phase were installed on the altar of the church in a beeline with the first lines of pews. The size distribution of airborne particles with optical dimensions between 0.28 and 10 µm was continuously monitored by an optical particle counter (OPC - OPTacer, Fai Instruments srl); the real time concentrations of total polycyclic aromatic hydrocarbons (TPAHs) and total volatile organic compounds (TVOCs) were determined by a photoionization analyzer (PAS2000 - EcoChem Analytics) and a photoionization detector PID (NetPid, Labservice), respectively. An integrated system consisting of low-cost sensors for the real time measurements of PM, TVOCs, CO_2 and microclimatic parameters as temperature and humidity named NOSE (Beefrest srl) was also used. Finally, a microGC for the continuous measurement (every 15 minutes) of Benzene, Toluene, Xylenes and Ethylbenzene (Pyxis, Pollution srl) was included in the monitoring setup.

The preliminary results reported, for example, in Figure 1 for the period from March 20th to April 10th , when several liturgical celebrations linked to Lent and Easter took place in the investigated church, show that during the hours of greatest crowd of faithful (CO_2 concentration peaks) and in correspondence of incense use, significant increment of PM10 (maximum value: 203 mg/m^3), PM2.5 (maximum value: 171 mg/m^3), TVOCs (maximum value: 3.9 ppm) and Benzene (maximum value: 2.2 ppb) concentrations were registered. These peak concentrations were higher than the limit values established by law for the PM10 and Benzene outdoors concentrations (Legislative Decree 155/10). In fact, PM10 and PM2.5 concentration values registered during Easter celebrations resulted up to 6 times higher than the annual limit values and the Benzene peak concentration reached a value higher than 5 ug/m^3.

Moreover, in order to determine the concentration–time profiles of VOCs, TPAHs and particle during and after combustion events of different type of incense and to evaluate the potential health impacts in terms of peak concentration and exposure duration, specific monitoring activities have been carried out in an test chamber on the basis of a tailored experimental design. More specifically, inside the experimental room with dimensions of 2.53×3.15 m and a volume of 21.9 m^3, three different type of incense and two different kind of charcoal were burned in controlled conditions in the middle of the room at 1 m above floor level and three test runs were performed for every kind of incense. The high time-resolved concentrations of PM10, TPAHs and benzene registered in test chamber during the different experiments reached maximum values up to 250 mg/m^3, 800 ng/m^3 and 35 ppb, respectively. PM10 concentrations higher than 50 μg/m^3 (limit value for outdoor) were continuously registered for three hours at least before windows opening.

3. Conclusions

The high-time resolved monitoring campaign of indoor gaseous and particulate pollutants carried out in a church showed that the incense burning during the Lent and Easter celebrations produces significant concentrations of PM10, PM2.5 and VOCs as benzene deeply affecting indoor air quality. Finally, the chamber tests showed that some incenses determine an increase of the benzene concentration in the air just slightly above background levels whereas other ones determine a significant increase of benzene concentrations reaching values higher than 200 μg/m^3 in the test room. Anyway, these results highlighted the sure potential impact of incense burning during the liturgical celebrations on heath of priests and altar boys.

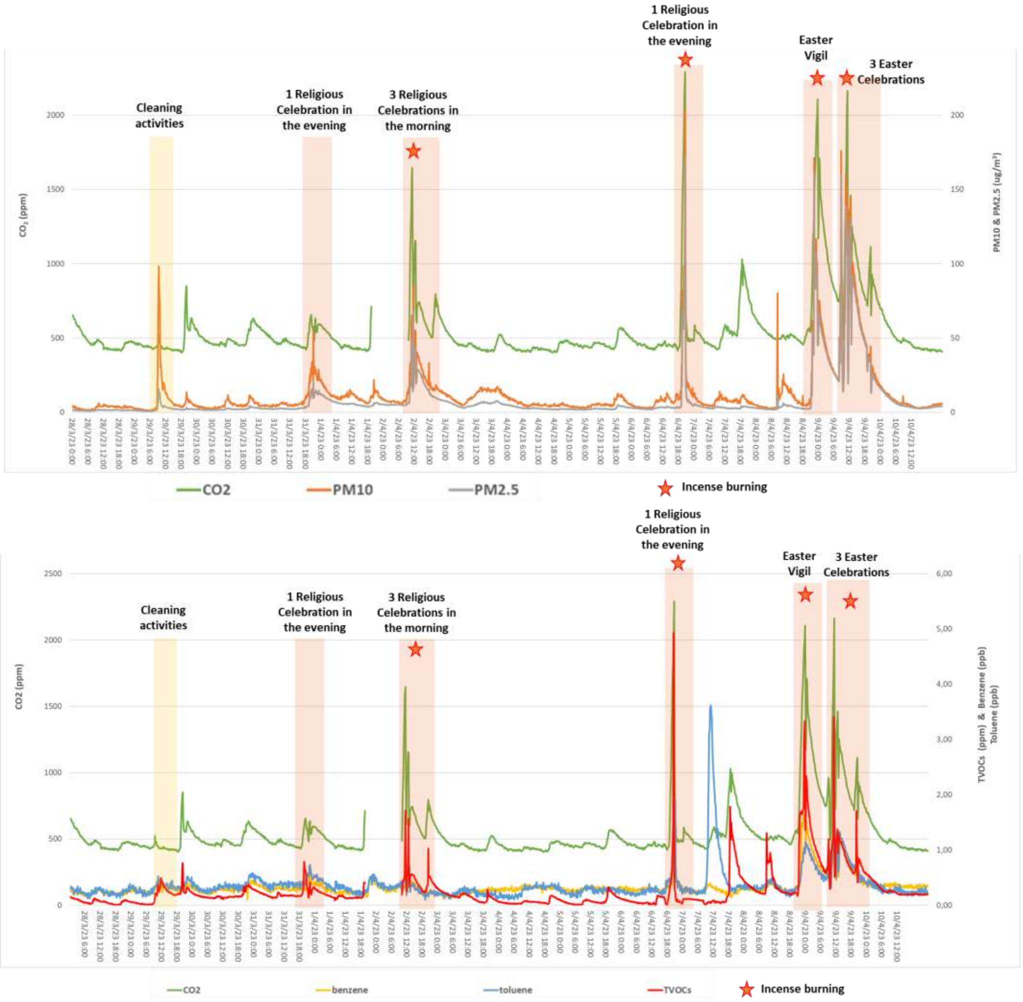

Figure 1: High time-resolved concentrations of PM10, PM2.5, PM1 (μg/m^3), CO_2 (ppm), TVOCs (ppm), Benzene(ppb) and Toluene (ppb)

References

[1] IARC, (2013). Outdoor air pollution a leading environmental cause of cancer deaths.
[2] M. Manigrasso et al., (2019). Science of the Total Environment, 653, 1192–1203.

OP13

STUDY OF PARTICULATE MATTER, WET AND DRY DEPOSITION IN A SUB URBAN SITE OF SOUTH ITALY

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1. Introduction

Atmospheric particulate matter has been identified as an important source of pollutants for environment, especially near urban area where anthropogenic activities (i.e. traffic, combustion, nearby industrial plants) can introduce different pollutants, influencing the composition of air (Querol et al., 2013). The main objective of this study was to investigate the influence of SARS-covid19 restrictions on PM10, PM2.5 and wet and dry deposition in an sub urban area.

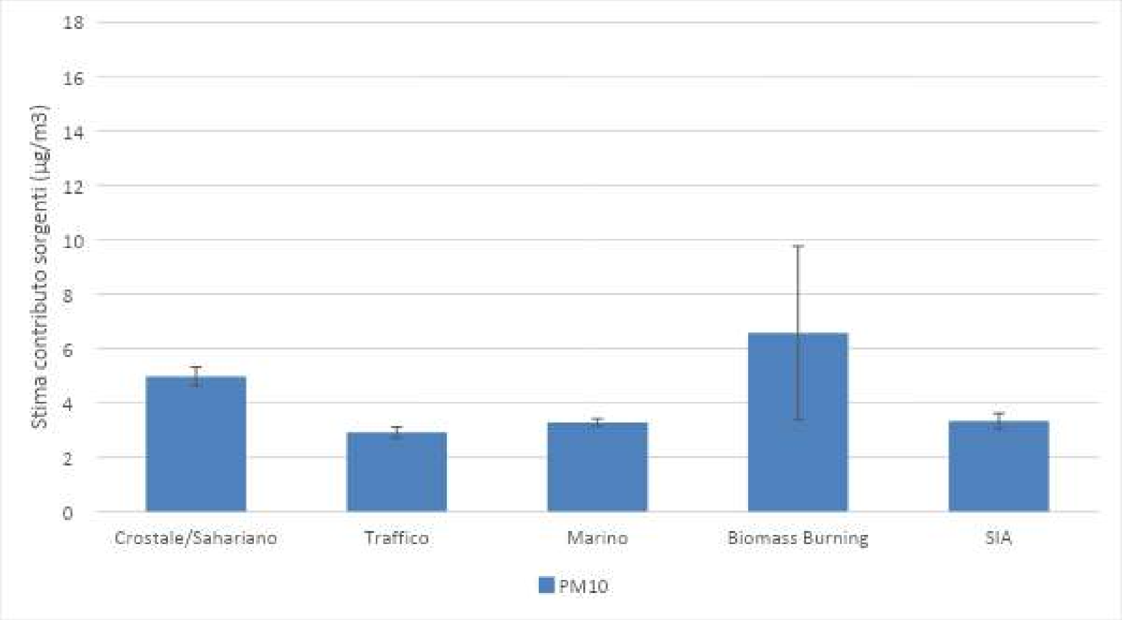
The sampling site of PM10 and PM2.5 is inside of the University Campus Ecotekne of Lecce, located in the Apulia region and it can be considered a suburban background station. While the depositions were sampled in the University Campus Ecotekne and at atraffic site in Lecce city. Soluble salts, metals and organic and elemental carbon were analysed. Source apportionment has been carried out with: the mass reconstruction method and the Positive Matrix Factorization (PMF) (Belis et al 2014).

2. Results and Discussion

In this study PM10 and PM2.5concentrations measured during the lockdown months of 2020 were compared to those measured during the same period in previous years (2007 and 2011) and in the following months of 2021 and 2022, showing a decrease in concentrations. Lowest monthly average PM10 values were observed in June 2020 (18±3 µg/m3) caused by limited number of people at University Campus Ecotekne and March 2021 (19±9 µg/m3), probably due to the introduction of strong restriction measures in "Red Zone". During Orange zone respect to No lockdown period, OC and EC showed an increase of 52% and 82%, while in Red zone, with the introduction of strong restriction measures on travels/movements OC and EC showed a decrease of 20% and 16%, respectively. Five factors were found by PMF: crustal/Saharan dust, total traffic, sea spray, biomass bourning and ammonium sulphate. Emission differences, among the different zone due to Covid19 restrictions, were mainly found in biomass bourning source, while the other sources did not show statistically differences. The same main sources were found in the studied depositions at both sites. The urban site is characterized by higher impact of anthropogenic sources. Different anthropogenic metals, such as Cu, Cd, Pb and V were found in higher amount in the acqueus phase, while Al, Fe, Cr and Zn are mainly present in the insoluble fraction. PAH are always higher in the urban site.

3. Conclusions

The present study has shown the decreasing of PM and of pollutants related mainly to combustions in relationship to the restriction introduced with Sars covid 19 regulamentations. The main sources affected by restrictions were combustion and resuspension one that lead to the decreasing of pollutants in air of the sub urban site. The urban site is characterized by higher impact of anthropogenic sources



Source apportionment of PM10

References

Belis C. A., Larsen B. R., Amato F., El Haddad I., Favez O., Harrison R. M., Viana, M., European guide on air pollution source apportionment with receptor models. Luxembourg: European Commission - Joint Research Centre, 2014.
Querol, X. et al. (2013). Atmos. Chem. Phys., 13 pp. 6185-6206

OP14

AN ANALYTICAL METHOD FOR THE ASSAY OF NITROPHENOLS IN INDOOR DUST USING MICROWAVE-ASSISTED EXTRACTION AND GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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1. Introduction

Phenolic compounds may be present in the environment due to contribution from different industrial sources including production of drugs, textiles, dyes and paper. Nitrophenols are among the most important organic compounds formed photochemically in the atmosphere from vehicle exhausts. They can have various effects on human health due to their estrogenic, anti-androgenic and vasodilatory activity. As a consequence, the US Environmental Protection Agency and the European Union have included nitrophenols in their list of priority pollutants [1,2], increasing the need for analytical methods for the determination of these compounds in different matrices. Indoor dust is a sink for many organic compounds and has been identified as a major source of environmental contaminants. Trying to meet the growing demand for new analytical approaches amenable to reduce organic solvent consumption in compliance with the principles of the Green Analytical Chemistry, a protocol based on the microwave-assisted extraction of 10 nitrophenols from the indoor dust followed by solid-phase microextraction gas chromatography-tandem mass spectrometry analysis (SPME-GC-MS/MS) was developed and optimized.

2. Results and Discussion

Microwave-assisted extraction (MAE) is a well-established technique for the extraction of analytes from solid matrices that is finding a growing use due to its advantages, including the reduced use of organic solvents and high productivity [3]. The studied analytes (4-nitrophenol, 2-methyl-4nitrophenol, 2,6-dimethyl-4-nitrophenol, 4-nitroguaiacol, 5-nitroguaiacol, 2,4-dinitrophenol, 3,4-dinitrophenol, 4-methyl-2,6-dinitrophenol, 4-nitrocatechol, 4-methyl-5-nitrocatechol) were extracted from indoor dust by MAE using environmentally friendly solvents and, subsequently, a derivatization step and the SPME extraction were performed directly on the MAE aqueous mixture eliminating additional sample clean-up steps. Due to the presence of the phenolic hydroxyl moiety on the target analytes a derivatization step was used prior to the gas chromatographic analysis. The classic acetylation reaction and the use, for the first time, of methyl chloroformate (MCF) and propyl chloroformate (PCF) leading to the formation of the corresponding carbonates were compared to obtain the best derivatization reagent. The results obtained showed that, for the analytes derivatized with PCF, the mass spectra gave more specific base peaks than the other two derivatizations tested. For this reason, a derivatization with PCF in presence of pyridine and in a basic reaction environment was selected. Both derivatization reaction and MAE extraction were optimized with the multivariate approach of "Experimental design". The central composite design (CCD) was used to optimize the volume of PCF, pyridine and derivatization time that were set at 439 µL, 219 µL and 5 minutes respectively. For the optimization of MAE extraction, a screening design was necessary, initially, due to the large number of significant variables. Among ramp time, hold time, water pH and ethanol concentration only the last two significantly influence the response of the monitored analytes. The best results in terms of chromatographic signal were obtained working at a water pH of 3 with an ethanol concentration of 50%. The use of GC coupled with a triple quadrupole mass spectrometry allows to combine the high separation efficiency of GC with a high selectivity and sensitivity of MS/MS. The signals were acquired in selected reaction monitoring (SRM) mode that allows the achievement of high specificity by selecting appropriate precursor–product ion couples.

3. Conclusions

The present work demonstrates that the use of microwave-assisted extraction (MAE) is a good choice to develop a green analytical method for the assessment of organic pollutants for monitoring purpose. The use of sustainable extraction mixtures allowed to interface the MAE technique with the solid-phase microextraction for the extraction of nitrophenols from indoor dust after a derivatization step, directly in aqueous extract, with propyl chloroformate. The experimental design was used to optimize the parameters that can influence the derivatization reaction and MAE extraction. The next step is to optimize SPME parameters and finally to evaluate the analytical performance of the method.

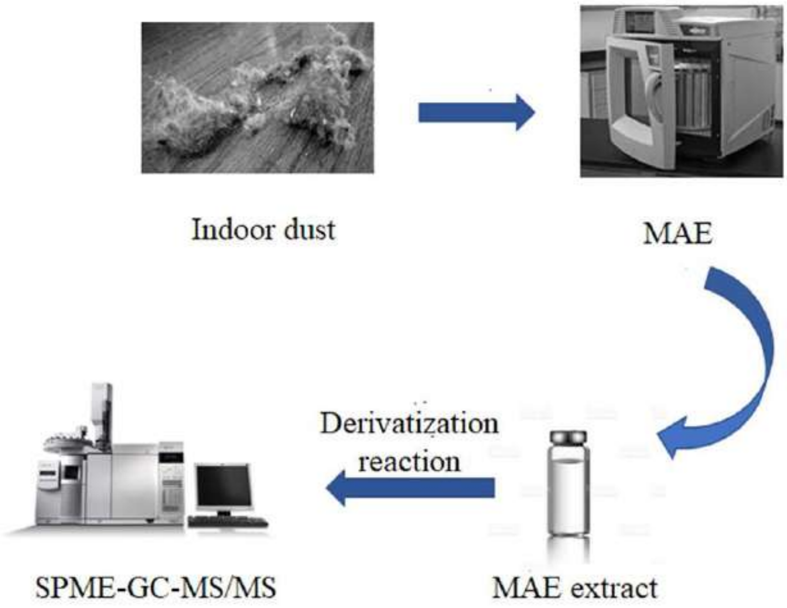

Figure 1: Schematic representation of extraction and analysis method.

References

[1] US Environmental Protection Agency. Environment Monitoring and Support Laboratory:Cincinnati, OH, USA, 1977.

[2] The list of priority substances in the field of water policy and amending directive,Council directive 2455/2001/ECC. Official Journal L331, November 20, **2001**, 1-5.

[3] A. Naccarato, A.Tassone, M. Martino, R. Elliani, F. Sprovieri, N. Pirrone, A. Tagarelli, Enviromental Pollution 285 (2021) 117487.

OP15

EXPERIMENTS IN ACCELERATED AGEING CHAMBERS TO UNDERSTAND THE SULPHATION PROCESS

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1. Introduction

This research focused on the process of black crusts formation, an important degradation phenomenon that affects much of the artistic heritage exposed outdoors. On this regard, heavy metals and carbon particles present in polluted environment seem to be involved as catalysts in the sulphation process. In this context, the present research work involved the exposure of Carrara marble samples treated with metal cation solutions in climatic chambers. In the "corrosion chamber" proper amounts of sulphur dioxide and humidity were set up; in the second chamber, xenon arc-UV radiation was supplied in order to simulate the sunlight irradiation naturally falling on monumental stone during the day. Properly treated marble samples were settled inside the chambers for assessing the catalytic action of metal cations commonly present in atmospheric particulate matter (PM 2.5). The first experimentation campaign involved a single exposure in accelerated aging chambers (4 weeks with high concentration of SO_2) which highlighted the complexity of sulphation process [1]. Although some conclusive considerations could be drawn, no univocal evidence on the role of the catalysts came out from this initial study.Therefore, we decided to carry out a second experimentation campaign (3 weeks, with a SO_2 concentration twenty-fold lower than the first one). The aim was to better discriminate the catalytic role of individual metals.Herein we report the novel results from the second exposure campaign. This research work is part of a broader interdepartmental project of the University of Milan, entitled SciCult.

2. Results and Discussion

In both the first and second exposure campaigns, the complexity of the sulphation process and the formation of black crusts was highlighted. It was observed that some metal cations activate the catalytic process faster than others. The different combinations of metal mixtures, with which some specimens were treated, show a high synergistic effect in terms of gypsum formation (mainly in the last weeks). The formation of gypsum over time affects the degradation of the stone substrate and this is higher for some specimens. Due to SO_2 concentration decrease, the sulphation process could be actually slow down and this allowed to distinguish the catalytic action of the individual selected metals better than during the first campaign. The results obtained using a stereomicroscope that almost all of the samples displayed the formation of gypsum crystals on the surface from the first and the second week. In the third week, the samples developed small variations in the formation of gypsum compared to the other weeks; in fact, compacted acicular crystals were observed that originated concretions scattered heterogeneously on the analyzed surface. In particular, the most evident results were obtained from the observations of the surface crystals performed by SEM-EDX. The analysis led to characterize the crystalline dress of the gypsum; in fact, the following crystalline dresses could be recognized: acicular, lamellar, swallowtail and rosette concretions. Colorimetric analysis, in terms of the change in ΔL^* (increase in brightness), displayed an increase in this coordinate, probably attributable to the formation of gypsum. An increase in the ΔL^* parameter was observed in all samples during the third week, ascribed to an increase in white gypsum crystals on the surface (as observed by stereomicroscope investigations). From ionic analysis is evident that all samples display high sulphate values as early as the first week. This seems to suggest that the various metals used, individually or in a mixture, activate the formation of gypsum on the surface early on. An increase in the concentrations of sulphate ions was observed in the last week of testing for some samples (Cu^{2+} and Cr^{3+}), suggesting that the catalytic effect of these metal cations may be long-lasting. A higher concentration of sulphate ions was registered for samples treated with the M1 mixture and lower for M3 differently from the first exposure campaign [1]. Under these new experimental conditions, the Fe^{3+} treated samples seem to be the most catalytically active, compared to the first monitoring campaign. Also, for this second exposure campaign, the samples treated with PM 2.5 show more sulphation than all the other samples. Finally, the XRPD analysis was performed to identify the crystalline phases present in the different samples. The results displayed that the powders have the mineralogical characteristics of calcium sulphate dihydrate with the relative characteristic peaks and calcium carbonate with less intense peaks.

3. Conclusions

This study focuses on the sulphation process evaluation by heavy metal catalysts triggering the formation of black crusts on marble samples inside climatic chambers. The ultimate aim of this research, in fact, is enablingthe prediction of outdoor damage on artistic heritage by mathematical modeling presently underway. The results so far achieved led to some important information on the sulphation process by metal catalysts such as: some metal cations activate the sulphation late but their action is constant over time (metal cations Cu^{2+}, Cr^{3+}); a different catalytic action of the mixtures was observed (M1 more active, M3 less active); Fe^{3+} appears to be the most catalytically active, compared to a previous monitoring campaign [1]. This could be attributed to the different experimental conditions, which were less harsh and more real; the most advanced sulphation process was observed for the samples treated with PM 2.5.

References

[1] V.Comite, A.Bergomi, C.Della Pina, C. Castellano, M. Borelli, C.A.Lombardi, M. Formenti, M.F.La Russa, C.Cavaterra, P. Fermo "Climatic chamber tests to evaluate the catalytic action of heavy metals in the sulphation process" (2022) 2022 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, MetroArchaeo 2022, pp. 294-299.

OP16

CW-EPR SPECTROSCOPY CHARACTERIZATION OF COPPER-ORGANIC BINDER COMPLEXES IN PICTORIAL LAYERS

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1. Introduction

The interactions between pigments and binders in painting layers are very relevant in the conservation of the cultural heritage, because these interactions induce the formation of metal-ligand complexes involved in degradation paths of the painted surface. These systems are usually characterized by optical (Raman, IR, etc.) spectroscopies or by spectrometric methods (LC-MS, GC-MS, etc.). Notwithstanding many techniques have been used in this field, a lack of understanding of painting layer formation and degradation is still present and characterization of the involved chemical species is not yet complete. Recently, a new spectroscopic tool has gained relevance in the cultural heritage field: the Electronic Paramagnetic Resonance (EPR) spectroscopy. This technique can give highly detailed information about magnetic species present in samples not compromising them. This study aims at characterizing the species formed by mixing verdigris (copper acetate) with many types of organic binders e.g., egg white, yolk, Arabic gum and rabbit glue by CW-EPR spectroscopy in the X-band (~9.5 GHz).

2. Results and Discussion

Figure 1a presents the spectra of the samples obtained by mixing raw pigment (verdigris) with different organic binders at a pigment/ligand ratio of 5% w/w. The spectrum is predominantly characterized by a prominent and broad signal centered at 330 mT, indicating the presence of a monomer copper species. This signal exhibits two distinct features: one in the lower field region (g parallel), displaying a quartet-type line shape, and the other in the higher field region (g perpendicular). The quartet-type line shape arises from the coupling between the unpaired electron and the nuclear spin of the copper nuclei, resulting in a signal with 2I + 1 lines ($I_{Cu} = 3/2$) [1]. Importantly, this signal is not associated with the verdigris pigment itself. As depicted in Figure 1b, the raw verdigris spectrum does not exhibit any signal around 330 mT. Instead, its spectrum is characterized by three distinct signals: one centered at 600 mT in the g parallel region, one centered at 500 mT in the g perpendicular region, and a broad signal in the 0 to 100 mT region, representing a forbidden transition only allowed in the X-Band [2]. These characteristics strongly suggest the dimeric nature of the raw pigment. In fact, verdigris consists of a bimetallic complex with two copper centers in a D_{4h} symmetry site bound by two acetate groups at the molecular level. The spectra were simulated using Easy Spin to determine key magnetic parameters such as the g-tensor, hyperfine couplings, and E and D values associated with the electron spin-spin coupling in the dimer structure of the pigment. In the latter case, the values obtained are highly consistent with those reported in previous literature [2]. According to Peisach and Blumberg [3], the number and nature of the donor atoms in monomer copper complexes can be determined by plotting the g parallel against the A parallel values. The calculated parameters were plotted accordingly. As expected, complexes with Arabic gum as the binder exhibit a 4O coordination, while proteinaceous media show a mixed oxygen-nitrogen coordination. However, due to the overlapping of the assignment regions, a systematic and precise determination of the first coordination sphere is currently challenging. Further experiments are necessary to obtain this information. To estimate the extraction efficiency of the different ligands, we propose using a coefficient (EE) calculated as the ratio of the double integral of the monomer signal to the double integral of the dimer signal. The double integral is proportional to the number of spins and, therefore, relative quantities of the species. Figure 1c illustrates the EE for each considered ligand. The graph clearly indicates a substantial difference between proteinaceous binder, mixed binders (yolk and egg white-yolk) and the oxygen-based binder (Arabic gum): the proteinaceous media more readily form complexes than other binders do. Hence, if the binder used is proteinaceous and the monomer complexes actually play a role in the degradation process, a correlation can be inferred. The spectra were acquired at 80 K to enhance signal to noise ratio, revealing the presence of several monomer species with the same ligand.

3. Conclusions

The results are highly intriguing for the field of cultural heritage, shedding light on the significant potential of the EPR technique in characterizing copper species. One notable observation is that the majority of the mixtures exhibit signals indicating the presence of copper monomers in the spectra. This suggests a substantial interaction between the pigments and the binders. It implies that the pigments are not merely dispersed within the binder matrices, but rather a portion of them actually dissolves to form Cu(II) complexes. Furthermore, it is evident that protein binders play a role in inducing the formation of more monomer copper complexes due to the chemical affinity between copper and nitrogen.

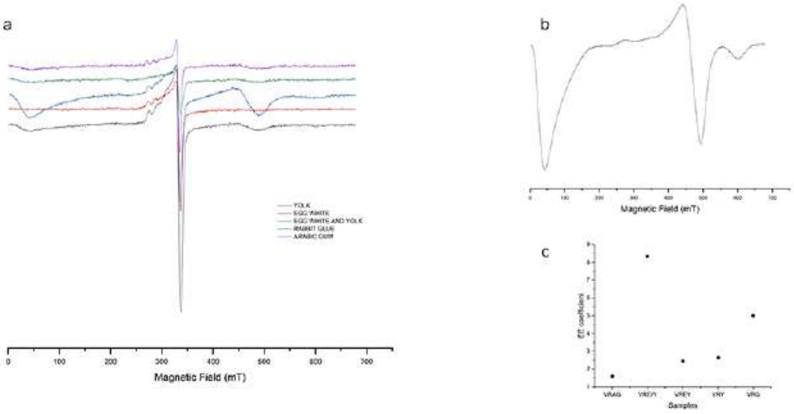

Figure 1: a) samples CW-EPR spectra, b) raw verdigris CW-EPR spectrum and c) EE coefficient diagram.

References

Zoleo A., Nodari L., Rampazzo M., Piccinelli F., Russo U., Federici C., Brustolon M., *Archaeometry.* **2015**, *56(3)*, 496-512.

Alter M., Binet L., Touati N., Lubin-Germain N., Le Ho A.S., Mirambet F., Gourier D., *Inorganic Chemistry.* **2019**, *59(19)*, 13115-13128.

Peisach J., Blumberg W.E., *Archives of Biochemistry and Biophysics.* **1974**, *165(2)*, 691-708.

OP17

BIOMONITORING STRATEGIES TO ASSESS METAL POLLUTION THROUGH ANALYSIS OF LEMURS BIOLOGICAL SAMPLES: A NON-INVASIVE APPROACH

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1. Introduction

Metal-contaminated environments are common in urbanized areas due to their proximity to emission sources. Organisms that populate those spaces can accumulate metals and other elements present in their habitat, mainly through ingestion and contact. In biomonitoring investigations, wild and domesticated mammals are frequently used. Animals housed in zoos and aquariums, instead of wild ones, provide excellent opportunities to study the potential of a particular species as bioindicator: living in limited areas, they are more likely to reflect the environmental conditions of a specific zone, while knowing their habits it is possible to exclude sources of contamination external to the environmental ones. The most commonly used methods are based on the quantification of elements in kidneys, bones, and liver of the target species, but such methods require the killing of the studied animals. (Lanocha et al., 2013) One possible alternative is to adopt non-invasive approaches for measuring animal exposure, quantifying the element content in matrices that can be sampled without harming the individuals under exam; in particular, fur and feces can be a good starting point for the development of alternative protocols. (Ferrante et al., 2018)

2. Results and Discussion

The aim of this study is to test new non-invasive approaches for biomonitoring element content in the environment using captivity Lemurs as a target animal. The investigated Lemurs are hosted in Zoom Biopark (Cumiana, Italy) in an area named “Lemurs’ Island”, an artificial island surrounded by a lake in which animals are free to move. The study was possible thanks to the collaboration with Fondazione Zoom, an institution promoting research activities in the Biopark. The animals’ matrices chosen for the project were feces, fur, and blood and the results obtained with the analysis of those samples were compared with the mineral element content in other environmental compartments, namely water and soil.

For the characterization of the environment, four samples of water were collected from the lake around the island, and soil was taken from seven points of the area to map the entire site, as shown in *Figure 1*. The zookeepers collected the animal matrixess with appropriate protocols, taking care to distinguish the samples from individuals of different species. The species included were four for the feces collection (*Eulemur mongoz, Eulemur rubriventer, Lemur catta, Eulemur macaco*) and only two for the fur samples because of the sensitivity of some individuals (*Lemur catta, Eulemur macaco*). Samples were pretreated differently based on their nature and then analyzed. After a pretreatment phase, soil, fur, and feces samples were mineralized with an appropriate acid solution by a microwave laboratory unit, while water samples were filtered with a filter at 0.45 µm, and 10% HNO_3 was added to the solution to stabilize the analytes. Then, total analyte concentrations in the solutions so obtained were determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS) based on their concentration range. Thirty-four elements were taken into consideration (Al, As, Ba, Ca, Ce, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Ti, V, Zn, Cd, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sr, Tb, Tm, Y, Yb). The results obtained were processed with chemometric techniques, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA), to understand the relationship between the environmental samples and the animal matrixes.

3. Conclusions

Multivariate analysis of the data made it possible to understand the relationships between the concentrations of the various elements in environmental compartments and animal matrices. The results highlighted the potential of using lemur feces and fur as bioindicators of element content in animal habitat, helping us to understand which matrix is best suited for the purpose. Biomonitoring studies can be used to identify polluted areas and to compare the conditions of different sites. In addition, the data collected will be helpful to detect nutrient deficiencies or potentially toxic metal accumulation in the investigated animals and take remedies, thus protecting their well-being,

In the next stages, analytes will also be quantified in Lemurs hosted in a botanic and zoologic park in Antananarivo, Madagascar. This new dataset will allow us to consolidate the results obtained from the data analysis carried out in Italy and detect the differences between the two geographical areas under study. Furthermore, blood samples of lemur specimens from the Italian park will also be collected and analyzed to compare another matrix type with those already under examination.

Figure 1 Aerial view of the Lemur Island, showing water (blue) and soil (red) sampling points.

References

Ferrante, M., Spena, M. T., Hernout, B. V., Grasso, A., Messina, A., Grasso, R., et al. (2018). Trace elements bioaccumulation in liver and fur of Myotis myotis from two caves of the eastern side of Sicily (Italy): A comparison between a control and a polluted area. *Environmental Pollution* 240, 273–285. doi: 10.1016/j.envpol.2018.04.133.

Lanocha, N., Kalisinska, E., Kosik-Bogacka, D. I., Budis, H., Sokolowski, S., and Bohatyrewicz, A. (2013). Comparison of Metal Concentrations in Bones of Long-Living Mammals. *Biol Trace Elem Res* 152, 195–203. doi: 10.1007/s12011-013-9615-x.

ARSENIC SPECIATION IN GRAPEVINE BY X-RAY ABSORPTION SPECTROSCOPY: IMPLICATIONS FOR FOOD SAFETY

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1. Introduction

Arsenic is a toxic metalloid that is ubiquitous in the environment due to its natural occurrence in the Earth's crust. It is reported that 1/60 people worldwide live in areas where the groundwater As contamination exceeds 5 times the recommended threshold value for drinking water. This is the case of the Rio Jáchal valley (Argentina), where As-contaminated groundwater is used for irrigation of grapevine and onion cultivations. Arsenic toxicity strongly depends on its speciation, which affects its solubility, bioavailability, uptake and transport pathways, and also the detoxification strategies enacted by the plant. However, plant As-tolerance can be improved by various amendments, among which the inoculation with plant growth promoting rhizobacteria (PGPR) is very promising[1].

In this work, we evaluated the effect of PGPR inoculation on arsenic uptake, accumulation, translocation and speciation in grapevine plants.

2. Results and Discussion

We compared As total concentrations, distribution and speciation in plantlets of grapevine grown in-vitro and subjected to four different treatments: As-only, PGPR-only, As+PGPR, control. Plantlets were grown for 40 days, and then dissected into leaves, stems and roots. Total As concentrations in the selected tissues were determined by Inductively Coupled Plasma - tandem Mass Spectrometry (ICP-MS/MS) after acid digestion. As speciation was investigated by synchrotron-based X-ray absorption spectroscopy (XAS) at the LISA beamline (BM08) of the European Synchrotron Radiation Facility (ESRF).

Plants inoculated with PGPR showed higher As-tolerance and lower total As concentrations. However, they also show a different translocation and accumulation pattern from roots to aboveground biomass. Arsenic speciation inside the plant tissues is also affected by inoculation.

3. Conclusions

The inoculation with PGPR improves the plant's As tolerance, however it seems to promote translocation and speciation changes that might pose a threat for food safety.

References

Pinter, M. I. F. et al. (2018) 'Plant growth promoting rhizobacteria alleviate stress by AsIII in grapevine', Agriculture, Ecosystems & Environment, 267, 100-108. doi: 10.1016/j.agee.2018.08.015

OP19

LIFE CYCLE ASSESSMENT OF RECIPES SERVED IN FOOD CANTEENS AND ELABORATION OF A NEW ENVIRONMENTAL INDICATOR

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1. Introduction

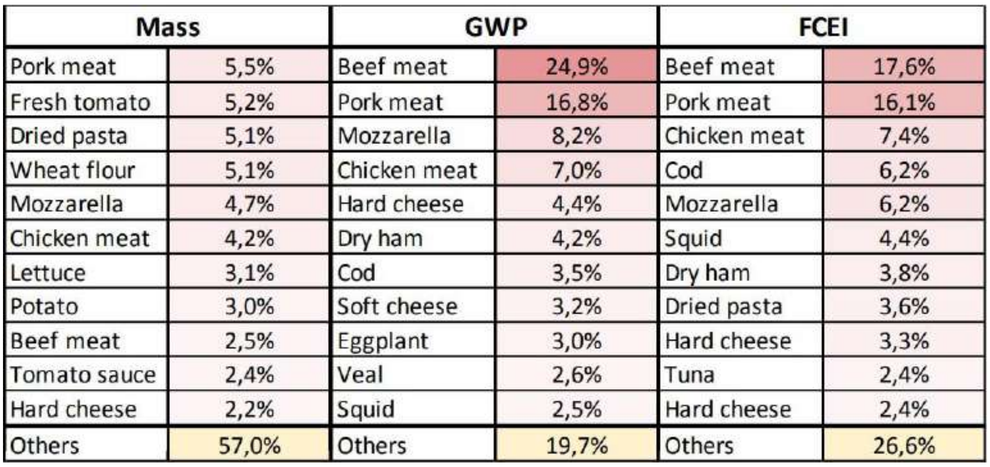
The world population growth brought to an increasing food demand and to a consequent higher concern related to the environmental burdens connected to the food sector[1]. Accordingly, many studies aimed at estimating the environmental impacts associated to the food supply chain, but most of the existing developed indicators limited the problem only to the climate change, while it is well-known that the food sector may extend its influence on a wider spectrum of environmental categories[2]. In addition, it has been noticed a divergence between the ethical sensitivity of consumers and the real environmental sustainability of their choices, in part due to the absence of exhaustive and widely accepted assessment schemes[3]. In this work, the Life Cycle Assessment (LCA) was applied to a list of 1001 recipes (LoR) for a food canteen, prepared with more than 150 ingredients by the company CAMST Soc. Coop. a r.l. The purpose was to develop a comprehensive environmental indicator (food canteen environmental indicator, FCEI), including in the evaluation all the environmental categories showing a significant contribution to the overall impact (single score) calculated with the ReCiPe 2016 method[4].

2. Results and Discussion

Among the 18 categories considered by the ReCiPe 2016 impact assessment method, five -identified in global warming (GWP), particulate matter formation (PMFP), land occupation (LOP), human non-carcinogenic toxicity (HTPnc) and water consumption (WCP)- contribute together to at least the 86% of the single score of each single dish of the examined LoR. Accordingly, a new single score based on the five selected categories (5-SS) was calculated. Since the obtained values of the 5-SS were not found to be normally distributed, results were first log-transformed and then scaled between an interval of 0 and 10, in order to establish an intuitive and circumscribed evaluation limit. Then, the contribution of the 150 ingredients on the LoR was estimated under three macro perspectives: mass, GWP impact and FCEI impact. The mass perspective indicates that the LoR contains a fairly balanced amount of ingredients (first column, Figure 1), pointing out a remarkable diversification of the menu in the examined canteen, since no ingredients contribute for more than the 5.5% of the total. However, despite the quite homogeneous employment of ingredients, moving from the mass perspective to the GWP and FCEI perspectives, it is evident how the environmental impacts are mainly related to meat-based and fish-based recipes (77% for GWP and 73% for FCEI), attributing to the vegetarian and vegan alternatives a lower responsibility to the whole impacts observed (second and third column of Figure 1), even if the latters are present for the 41% in mass. According to Figure 1, the main contribution to the GWP and FCEI environmental impacts is mainly due to few animal derivatives courses, dominated by beef meat and pork meat. However, even if GWP and FCEI elaborations present some common aspects, the adoption of the FCEI allows to capture some information which are neglected in GWP-based indicators. In particular, if meat-based dishes represent the 42% of the entire LoR in case of GWP, when adopting FCEI, their overall contribution is reduced to the 35%. Accordingly, the main percentage of FCEI is instead attributed to fish, raising from 31% (GWP) to 43%. Such variation demonstrated the relevance of the four additional selected categories for a final and comprehensive evaluation, proving that GWP-based indicators provide to the consumer only a partial representation of the issue. Of relevance here, when addressing food sustainability by removing or substituting critical ingredients from a menu, the adoption of the FCEI allows to support choices in a more correct way: : for instance, with the FCEI it is possible to include in the evaluation the effect on PMFP of fish-based products and the effect on HTPnc and WCP of dried fruit, discouraging, in the first case, the substitution of veal or dry ham with cod, which ranked as third worst option, and, in the second case, the substitution of pork meat with almonds (tenth worst option).

3. Conclusions

Some outcomes can be summarized as follows: i) the selection of 5 categories on which the FCEI in elaborated, allows both to provide the consumer with a synthetic, easily comprehensible, transparent and the same exhaustive information; ii) despite, in the case of GWP, meat-based foods were the main impacting items, when considering the FCEI, fish-based products dramatically increase their relevance; iii) FCEI is adaptable to every existing LoR and can be implemented in several catering context, by only revising the scaling step. Overall, the LCA methodology, demonstrated to be an essential tool for the evaluation of the environmental impacts of products and a promising option onto which develop metrics aimed at facilitating the interface between the consumer and the industry.



Mass		GWP		FCEI	
Pork meat	5,5%	Beef meat	24,9%	Beef meat	17,6%
Fresh tomato	5,2%	Pork meat	16,8%	Pork meat	16,1%
Dried pasta	5,1%	Mozzarella	8,2%	Chicken meat	7,4%
Wheat flour	5,1%	Chicken meat	7,0%	Cod	6,2%
Mozzarella	4,7%	Hard cheese	4,4%	Mozzarella	6,2%
Chicken meat	4,2%	Dry ham	4,2%	Squid	4,4%
Lettuce	3,1%	Cod	3,5%	Dry ham	3,8%
Potato	3,0%	Soft cheese	3,2%	Dried pasta	3,6%
Beef meat	2,5%	Eggplant	3,0%	Hard cheese	3,3%
Tomato sauce	2,4%	Veal	2,6%	Tuna	2,4%
Hard cheese	2,2%	Squid	2,5%	Hard cheese	2,4%
Others	57,0%	Others	19,7%	Others	26,6%

Figure 1: Ingredient contribution on the total LoR per mass, GWP and FCEI

References

1. Mancini, L. et al., Social footprint of European food production and consumption. Sustain. Prod. Consum. 35, 287–299 (2023).
2. Poore, J. & Nemecek, T. Reducing food's environmental impacts through producers and consumers. Science 360, 987–992 (2018).
3. Osman, M. et al., Sustainable Consumption: What Works Best, Carbon Taxes, Subsidies and/or Nudges? BASP 43, 169–194 (2021).
4. Huijbregts, M. A. J. et al. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int J Life Cycle Assess 22, 138–147 (2017)

OP20

THE SERVICES PROVIDED BY THE INTEGRATED PLATFORMS FOR THE EUROPEAN RESEARCH INFRASTRUCTURE ON HERITAGE SCIENCE (IPERION HS) PROJECT: TOWARDS THE ESTABLISHMENT OF A PERMANENT E-RIHS INFRASTRUCTURE.

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1. Introduction

IPERION HS project (Integrated Platforms for the European Research Infrastructure ON Heritage Science is a consortium of 24 partners from 23 countries that contributes, together with E-RIHS Implementation Phase project, to establishing a permanent European Research Infrastructure on Heritage Science (E-RIHS ERIC).

2. Results and Discussion

This lecture will provide with the overview of the IPERION HS/E-RIHS services with particular reference to the #HSAcademy training activities and access to a wide range of high-level scientific instruments, methodologies, data, and tools for advancing knowledge and innovation in heritage science. The aim of this lecture is to explain how researchers can benefit from the access to such expertise, facilities, and knowledge (#HS Academy and ARCHLAB, FIXLAB, MOLAB) offered, in the near future, by the E-RIHS ERIC.

3. Conclusions

In particular, the **2nd IPERION HS Doctoral Summer School** (HS-DSS) is aimed at providing examples of excellence in heritage science in the environmental impact on built heritage ad its digitalization. The HS-DSS comprises four full days of lectures, during which participants will become acquainted with the multidisciplinary skills of the IPERION HS consortium and knowledge accumulated by the partners. Issues such as materials and procedures for low environmental impacts, new methods for preservation of buildings and structures, digitalization and social and economical impacts will be presented and discussed. Lectures and study tours will be adapted to an interdisciplinary platea of learners by focusing more on problem solving than on the specific adopted scientific methods/techniques.

IPERION HS 2nd Doctoral Summer School "Environmental impact on built heritage and its digitalization"

References

https://www.iperionhs.eu/

OP21

DENTAL PROTEOMIC ANALYSES AND RAMAN SPECTROSCOPY FOR THE DETERMINATION OF BIOLOGICAL SEX AND AGE OF HUMAN REMAINS FROM HELLENISTIC CEMETERY IN REGGIO CALABRIA (ITALY)

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1. Introduction

Sex and age estimation is one of the most fundamental steps in mortuary studies and bioarchaeology. It is essential for a deeper understanding of ancient societies, and has wide applications in gender archaeology. The aim of this paper is to create a new and reliable protocol for unambiguous sex determination of the deceased, comparing proteomic analyses, archaeological evidence, and anthropological data from a Greek Hellenistic-Republican cemetery located in Reggio Calabria (the ancient Rhegion), as well as the first approach to determine the age of the deceased by Raman spectroscopy in archaeology. Excavations carried out in the San Giorgio Extra district by the Superintendence for the Archaeological Heritage of Calabria between 2004 and 2007, led to the discovery of the most significant Hellenistic cemetery in the city, specifically, thirty Greek inhumation burials and their related funerary objects. We provided a brief overview of the material assemblages discovered of the twelve Hellenistic-Republican burials that we choose for analysis and also attempted to infer the biological sex of the deceased based solely on their gender, which was derived from archaeological evidence.

2. Results and Discussion

We altered the typical research approach by starting with the definite data obtained from the results of the proteomic analysis. Subsequently, by comparing these data with the assumptions made by archaeological and osteological examination, we examined the agreements and disagreements in sex estimations between each method, both in terms of definitive and conditional estimates. This postdictive approach can be regarded as a validation test of the archaeological theories related to our specific site and material evidence [1]. It is important to note that this analysis was conducted on a limited sample of cases, which we believe is still valuable to highlight certain trends and tendencies. Despite the inherent numerical limitations, our analysis serves as a model for future researchers who wish to apply theoretical assumptions, either to confirm or refute our conclusions [2]. Through proteomic analyses, we monitored a total of eight characteristic peptides for the amelogenin isoform variants AMELX and AMELY from the dental enamel of twelve selected adult individuals. The presence or absence of the AMELY variant (exclusively present in male subjects, being encoded by the Y gene) allowed us to determine the sex of the analyzed individuals with high accuracy. Raman spectroscopy was also applied to study the enamel and dentine's crystallinity to determine other environmental and biological parameters. At the same time, archaeological studies based on artifacts discovered inside the graves and double-blind bio-anthropological sex estimation of the twelve subjects were performed in order to compare these evaluations with data from the proteomic analyses. Comparison between these different approaches produced congruent results. In addition, proteomic analysis allowed us to establish the sex of four poorly preserved subjects for whom sex estimation was somewhat doubtful, as well as that of one undetermined individual. Finally, proteomic results were produced here with a faster protocol than those found in the literature [3] and are potentially down-scalable to much lower sample amounts. However, it is important to note that only 12 out of 30 graves contained teeth with sufficient enamel for analysis, which constrained the application of proteomic techniques. On the other hand, archaeological evidence was available for 28 out of 30 tombs, but as previously mentioned, only a small portion of the funerary assemblages provided specific indications regarding the possible biological sex of the deceased, which was essentially assumed based on the gender of the artifacts included in the burials. However, the findings of this study demonstrate disparities in Raman spectroscopy results between archaeological retrieved teeth and recently explanted ones, specifically indicating minimal presence of residual collagen in the former. This variation in collagen content can be attributed to disparate environmental conditions that the teeth have encountered throughout their exposure period, and even dentin, which is usually not directly exposed to the environment, was degraded to the point that spectroscopic markers associated with collagenous tissues were barely detectable. By evaluating the overall quantity of carbonate apatite, particularly the level of A-substituted apatite, it was feasible to estimate that three individuals were significantly younger than the others, while four were potentially much older. All individuals, however, had reached skeletal maturity, which is indispensable to accurately assess biological sex [4].

3. Conclusions

Proteomic analyses have provided us with more reliable determinations of biological sex for all twelve individuals, overcoming the limitations of morphological approaches that may have produced unreliable results. The integration of osteological, archaeological, Raman, and proteomic data yielded highly confident estimations of demographic composition for the discussed burials. Accurate sex estimation holds a pivotal role in archaeological theories, and our holistic approach minimizes the occurrence of "indeterminate" classifications, a bias that often arises and limits archaeological interpretations. It is our hope that this pioneering research stimulates further discourse among archaeologists, chemists, biological anthropologists, and scientists in general.

References

[1] A. Gennaro et. al., GIS and remote sensing for post-dictive analysis of archaeological features. A case study from the Etnean region (Sicily), Archeol. e Calc. 30 (2019) 309–328. DOI: 10.19282/ac.30.2019.18.

[2] T. Buonasera et. al., A comparison of proteomic, genomic, and osteological methods of archaeological sex estimation, Sci. Rep. 10 (2020) 11897. DOI: 10.1038/s41598-020-68550-w.

[3] F. Lugli et. al., Enamel peptides reveal the sex of the Late Antique 'Lovers of Modena,' Sci. Rep. 9 (2019) 13130. DOI: 10.1038/s41598-019-49562-7.

[4] T. White, P. Folkens, The Human Bone Manual, Academic Press, San Diego, 2005. DOI: 10.1016/C2009-0-00102-0.

AMINO ACID PRESERVATION IN FOSSIL TOOTH ENAMEL UP TO 48 MILLION YEARS

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1. Introduction

Ancient biominerals represent potential time capsules for endogenous organic matter, locked into biogenic crystals during biomineralization processes surviving over time (1). Highly mineralized tooth enamel allows the long-term preservation of peptides and free amino acids (AAs), entrapped at the end of enamel mineralization. Whether primary AAs in fossils are preserved well enough to allow isotope and paleoproteomic analyses is still unclear. Indeed, protein preservation depends on different factors such as temperature, sediment, and matrix (2).

Here we explored how long back in time total hydrolysable amino acids (THAAs) could survive in fossil enamel, opening new research avenues for phylogenetic and ecological reconstructions of evolutionary processes back in deep time.

To characterize the AAs composition and its variation over time in enamel, modern and fossil samples (≈1 mg of powder) of different herbivorous large mammal taxa (Equidae, Rhinocerotidae, Proboscidea) back to ≈48 Ma have been analyzed through High-Pressure Liquid chromatography (HPLC) with a Diode Array Detector (DAD) using an Agilent AdvanceBio AAA LC column at the Max Planck Institute for Chemistry in Mainz.

2. Results and Discussion

The modern dataset includes enamel from 16 different large and small mammal taxa with different herbivorous and carnivorous diets to evaluate the impact of species and diets on AAs distribution. No significant difference in AA composition can be detected between the different species in this modern set, suggesting that taxonomy (at least among mammals) does not greatly affect the relative AAs abundance.

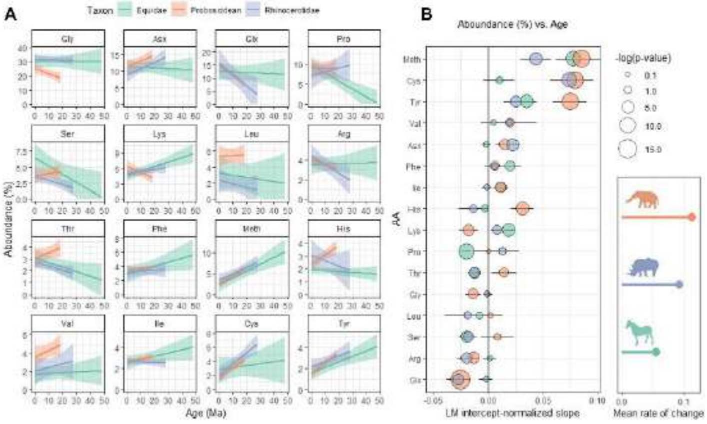
Modern tooth samples are essential to quantify potential changes in enamel AAs content and their relative abundances compared to fossil teeth through time. To minimize any phylogenetic effects fossil teeth of Proboscidea, Rhinocerotidae, and Equidae from different taphonomic settings (fluvial, limnic, carstic, permafrost, coal and peat deposits) have been compared with modern samples from the same taxonomic groups. All the large mammal species considered in this study revealed a strong decrease in the overall enamel AA abundance in the first 10 million years (down to one-third of the modern AA content), indicating that diagenetic alterations of AAs in enamel occur relatively early after burial.

To evaluate the changes of each AA more in-depth, their relative abundance with time for each taxonomic group was investigated separately through linear models (Figure). Despite the changes in absolute abundance, the results obtained in this study provided evidence that Rhinocerotidae and especially Equidae relative AA abundances overall change little throughout geological time with increasing age. Compared to Equidae, AAs of fossil Proboscidean enamel seems to be overall strongly affected by diagenesis over time, although the relative AAs content is similar to that of modern samples, thus indicating good preservation of the endogenous organic fraction, but worse than for the other two taxa. Some AAs revealed different responses to taphonomic alteration processes in the different species: Gly in Proboscidean (-0.347), Ser and Thr in Equidae (-0.126, -0.039) and Rhinocerotidae (-0.065, -0.035), and Pro in Equidae (-0.197) slope values decrease. AAs with a hydrophobic side chain were the ones best preserved in all the species (i.e. low or null linear slopes over time)

(Figure), while the hydrophilic ones showed remarkable variations. Differences in some AAs were detected through time in the three species. In particular, Gly showed a slope close to 0 in Equidae and Rhinocerotidae as expected due to its relative stability. However, Gly showed a negative slope in Proboscidea, which could suggest a decarboxylation reaction (4).
We used the ratio between Meth (positive slope) and Gly (close to null slope AA) as an alteration index to evaluate the AA preservation over time in all the species. Indeed, Meth has been demonstrated to be preserved in archeological bones (4), differently from other AAs which overall decrease. The threshold established (Meth/Gly ≈0.22) was referred to the maximum ratio obtained considering all the modern specimens. This ratio represents a threshold which is surpassed by a relatively high concentration of Meth that accumulates during diagenesis, while the other AAs (on average) degrade. The data demonstrated that Equidae and Rhinocerotidae Meth/Gly values were within (or close to) the modern range, revealing better preservation than for Proboscidea, which showed an increasing Meth/Gly ratio going back in time.

3. Conclusions

Despite the slight variations in relative AAs abundance in fossil teeth of different large mammal taxa, the results seem to indicate the preservation of the intra-crystalline organic fraction in tooth enamel at least up to 48 Ma. This demonstrates that enamel is a robust, highly mineralized and crystalline Ca-phosphate hard tissue in which potentially endogenous peptides, organic matter and ultimately AAs could be trapped and preserved at least in Cenozoic fossil mammal teeth and which can be used for paleoproteomics and isotope analyses. Moreover, it was possible to define a threshold of Meth/Gly derived from modern enamel samples, which can be used as a first screening tool to assess the degree of AA preservation in enamel of fossil teeth.



A) AAs variations according to the age. B) The slope-intercept ratio for each AA and taxon.

References

1. B. Demarchi, Amino acids and proteins in fossil biominerals. *Amin. Acids Proteins Foss. Biominer.* (2020) https:/doi.org/10.1002/9781119089537.
2. B. Demarchi, *et al.*, Protein sequences bound to mineral surfaces persist into deep time. *eLife* (2016), https://doi.org/10.7554/eLife.17092
3. D. Walton, Degradation of intracrystalline proteins and amino acids in fossil brachiopods. *Org. Geochem.* **28**, 389–410 (1998).
4. V. Rao Mundlapati, S. Ghosh, A. Bhattacherjee, P. Tiwari, H. S. Biswal, Critical assessment of the strength of hydrogen bonds between the sulfur atom of methionine/cysteine and backbone amides in proteins. *J. Phys. Chem. Lett.* **6**, 1385–1389 (2015).

ECOFOODFERTILITY RESEARCH PROJECT: THE ROLE OF HUMAN SEMEN AS AN EARLY AND RELIABLE TOOL OF ENVIRONMENTAL IMPACT ASSESSMENT

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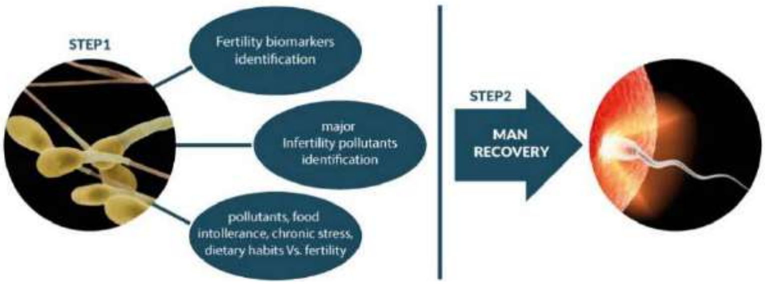
1. Introduction

The effects of chemical and physical pollutants, in addition to bad lifestyles, represent the most important threat to public health and the dramatic decline in fertility, especially in males. Even if pollution is widespread, there are areas of the same country or same region with high environmental and health criticalities. The EcoFoodFertility project is a human biomonitoring study, which started from "Land of Fires", an area in the Campania region (Italy), that has been plagued by significant environmental pollution issues for several decades. This project has omics multidisciplinary approach involving environment, lifestyle and diet, with two aims: i) developing a better understanding of the effects of environmental pollutants on human health considering reproductive biomarkers, especially human semen, as early flags of environmental pressure and enhanced risk of chronic adverse effects on health; ii) identifying dietary, nutraceutical and/or functional food approaches to reduce or modulate the effects of pollutants on human health. Currently, the project is in progress with a nationwide network of action in other environmentally-challenged areas of Italy.

2. Results and Discussion

The overarching aim of the project is to create a new tool for environmental health research to compare and integrate environmental monitoring, data from questionnaires and recently also using personal devices, biomonitoring, omics analyses and data science to identify relevant exposures to environmental contaminants in traditional biological monitoring matrices, blood, urine, and in highly environmental sensitive body fluid, semen, in order to study the pollutant determinants and elucidate the biological pathways and molecular actions through which they might contribute to the development of non-communicable diseases and impact on male gametogenesis. The project relies on a wide series of analyses (contaminants, oxidative, immunological, genetic, epigenetic, proteomic, lipidomic, metabolomic and other omics biomarkers) in cohorts of healthy young males homogeneous for lifestyles, living in areas with different environmental pressure on different biological matrices, identifying, in particular, human semen as an early and sensitive indicator of environmental exposure and health status (Human Semen "Sentinel" of Environmental and General Health).



Outline of the methodological approach applied in the EcoFoodFertility project.

In our biomonitoring studies more significant differences in accumulated pollutants were observed in semen than in blood, especially in heavy metals and some exogenous and endogenous volatile organic compounds

(VOCs). In addition, it has been observed a reduced total antioxidant capacity in samples from geographical areas with a high environmental impact, more evident in seminal plasma than in blood. Moreover, macro and trace elements in human semen and blood serum in highly polluted areas in Italy underline how semen is more sensitive than blood to accumulating pollutants. The sperm DNA fragmentation index (DFI) was also found to be higher in men living in more polluted areas, in the same way an alteration in the length of telomeres was observed in men living in polluted areas, and these differences appeared more significant in human spermatozoa rather than in blood lymphocytes. Semen analysis is a crucial tool for assessing male fertility and reproductive health, and alterations in semen parameters can provide insights into the impact of environmental pollutants. Research conducted in the Land of Fires and other regions (facing similar pollution issues) has suggested potential associations between exposure to environmental pollutants and adverse effects on semen quality. We have also observed a decreased sperm count, reduced sperm motility, abnormal sperm morphology, increased DNA sperm damage and altered sperm hystone/protamin ratio in men exposed to environmental pollution. The toxic substances can directly or indirectly affect male reproductive health. For example, heavy metals such as lead, cadmium, and mercury have been associated with decreased sperm quality and impaired fertility. These metals can accumulate in the testes and disrupt the normal functioning of sperm cells. Additionally, exposure to dioxins and furans, which are persistent organic pollutants, has been linked to reduced sperm quality and altered hormone levels.

Recently, we have also investigated the presence of microplastics in semen and urine samples and obtained interesting results. These types of pollutants have been gaining increasing interest in the last few years and deserve further attention.

3. Conclusions

A set of semen biomarkers is described for reproductive health effects in relation to environmental exposure. Environmental health should consider reproductive health and development, from intrauterine life to childhood and puberty: these are both vulnerable targets and high-value protection goals, in as much as they represent the future of our societies. Hence, biomarkers of reproductive health should be exploited as early signals of environmental pressure and increased risk of adverse chronic health effects so that the use of “human seminal model” might be the main objective to be considered in the agenda of public prevention policies for early detection and innovative programs of health surveillance in environmental risk areas.

References

1. Paolo Bergamo, Maria Grazia Volpe, Stefano Lorenzetti, Alberto Mantovani Tiziana Notari, Ennio Cocca, Stefano Cerullo, Michele Di Stasio, Pellegrino Cerino and Luigi Montano. Human semen as an early, sensitive biomarker of environmental exposure of healthy men living in highly polluted areas: a pilot biomonitoring study of trace elements in blood and semen and relationship with sperm quality and RedOx status. Reproductive Toxicology.2016. 66:1-9.

2. Luigi Montano, Paolo Bergamo, Maria Grazia Andreassi, Cecilia Vecoli, Maria Grazia Volpe, Stefano Lorenzetti, Alberto Mantovani, Tiziana Notari. The role of human semen for assessing environmental impact on human health in risk areas: Novels and early biomarkers of environmental pollution. EcoFoodFertility project. Reproductive Toxicology Vol. 72: 44-45. 2017 doi.org/10.1016/j.reprotox.2017.06.169

OP24

FIRST EVIDENCE OF MICROPLASTICS IN HUMAN SEMEN AND URINE SAMPLES

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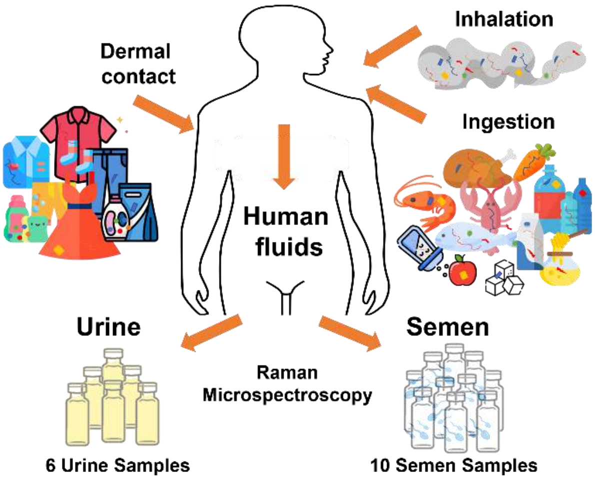
1. Introduction

In the last years, the number of studies on microplastic (MP) pollution has grown quickly due to the potential risks to human health associated with human exposure. The term microplastic is used to indicate plastic particles with a diameter lower than 5 mm. Based on their origin, microplastics can be classified as primary (intentionally manufactured particles) or secondary (derived from the deterioration of larger plastics) [1].
Microplastics reach the environment through various routes such as improper disposal of plastic waste, industrial and domestic discharge, atmospheric transport, wet and dry deposition, use of sewage sludge and plastic mulching in agricultural land. High microplastic concentrations were detected in all environmental matrices suggesting issues for human health. The human body's exposure to microplastics occurs through ingestion (seafood, drinking water and fruits), inhalation and dermal contact [2]. The present work is a preliminary study to assess the presence of MPs in particular human fluids such as urine and semen and to understand the evolution of MPs after the intake process and their possible accumulation in the human body.



Outline of the study.

2. Results and Discussion

Recent studies related to the presence of microplastics in the environment have highlighted the contamination of water, food, and soil, and, hence, it is not surprising to detect these pollutants in human samples, too. In the present study, urine and semen samples collected from volunteers coming from different cities in the south of Italy, have been investigated by Raman Microspectroscopy to highlight the presence of microplastics. In addition to the above-described semen and urine samples, environmental and procedural blanks were also analyzed to rule out any possible contamination during the analysis, and no MPs were found. Microplastics in urine samples ranged from 4 to 15μm, while smaller fragments (2–6 μm) have been found in semen. As regards the chemical composition, the most common polymers present in daily life were found, including polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyethylene (PE), polyoxymethylene (POM), polyvinylchloride (PVC), polycarbonate (PC) and polyvinyl alcohol (PVA). Moreover, we found a small but still noticeable relationship between MPs presence and the semen quality of participants, though we are aware that a higher sample size needs to be analyzed for a statistical correlation. Although it is possible to assimilate MPs to other various environmental pollutants and infer their toxicological impact on male fertility, this is the first study on this topic, so the observation of the relationship between MPs and sperm quality deserves further investigation.

3. Conclusions

The accumulation of MPs increases stress on human safety and health. In this preliminary study, for the first time, we assessed the presence of MPs in urine and semen samples collected from volunteers coming from different cities in the south of Italy. Raman microspectroscopy was efficiently used to identify the polymeric matrices, allowing the detection of PVA, PVC, PP, and PE fragments (4–15 µm) in urine samples and PE, PP, PS, PET, PVC, PC and POM (2–6 µm) in semen samples.

We believe that the scientific research should focus on new methodologies and analytical protocols able to evaluate the effects of MPs in humans and animals, to better characterize the level of risk and to understand the possible transportation routes in biological fluids and tissues.

References

[1] M. Ricciardi, C. Pironti, O. Motta, Y. Miele, A. Proto, L. Montano, 13 Water, 2021, 973.
[2] J.C. Prata, J.P. da Costa, I. Lopes, A.C. Duarte, T. Rocha-Santos, Sci. Total Environ. 2020, 702.

OP25

PY-GC-MS ANALYSIS OF MICROPLASTICS IN SEDIMENTS: EFFECTS OF MATRIX COMPONENTS

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1. Introduction

Microplastic (MP) pollution is acknowledged as an environmental and social issue. Nowadays an increasingly large number of studies is focused on detect MPs in environmental matrices, and different analytical techniques are currently applied and optimized for this purpose. When approaching MP analysis in environmental samples by analytical pyrolysis-based techniques (pyrolysis-gas chromatography-mass spectrometry, Py-GC-MS), sample pretreatment is crucial, and it frequently requires time-consuming steps. Sample preparation usually consists of subsequent purification steps such as physical separation, digestion, removal of organic interferents, and extraction prior to the actual analysis, with the aim of isolating MPs from the undesired organic and inorganic fractions of the matrix.

In this work, we evaluated the interference of inorganic and organic matrix components on the quantitation of synthetic polymers by Py-GC-MS. Marine sediment samples were taken as matrix and subjected to a multi-step sample preparation procedure which included pre-oxidation with H_2O_2, density separation with aqueous $ZnCl_2$, buffered multi-enzymatic digestion, and catalyzed Fenton oxidation(Figure) [1].

2. Results and Discussion

Marine sediments are very complex environmental matrix, consisting of different organic and inorganic components that could interfere in the analysis of MPs. Sediments were subjected to the sample preparation (Figure) and the three fractions obtained (the inorganic fraction, the untreated organic fraction, and the fully treated organic fraction) were used to evaluate matrix effect in the analysis of MPs. Moreover, two sets of these fractions were distinguished, by either performing or skipping the initial H_2O_2 pre-oxidation step. All matrices were obtained in triplicates for a total of eighteen samples. The matrix fractions were then spiked with six, previously milled, reference polymers: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), nylon-6,6 (Ny-6,6), and polyurethane (PU). Literature studies have reported that polycondensation polymers interact with each other during the pyrolysis step [2]. Therefore, in order to assess and study only the interference coming from the different components of the matrix, not all the polymers were added together in the same pyrolysis cup prior the actual analysis. In-matrix calibration curves were built by analysing the samples by Py-GC-MS, selecting a characteristic pyrolysis product for each polymer [3], and integrating the corresponding peak through the extracted ion chromatogram (EIC) of the chosen m/z. By definition, matrix effect is a change in the sensitivity of the analytical method, which is represented by the slope of the calibration curve. Therefore, the slopes of internal calibration curves were compared with the slopes of external calibration curves by statistical tests to assess the occurrence of matrix effect.

All curves were obtained with good fitting parameters for the majority of the polymers analysed ($r^2 > 0.87$). In general, polyolefins were less affected by the presence of the matrix fractions compared to polycondensation polymers. PU and PET underwent quantitative and partial hydrolysis, respectively, when pyrolyzed together with the matrix. This made it difficult to evaluate the matrix effects, requiring the necessity of choosing, if possible, different m/z quantification ions, from the ones used in the literature. Another very interesting effect was not only the confirmation of matrix effect for all the polymers due to the inorganic matrix, but also the fact that all the internal calibration curves built with the inorganic fractions showed higher slope values compared to the respective external calibration ones, suggesting some sort of catalytic effect promoted by the inorganic components of the sediments.

3. Conclusions

The results of this study helped to evaluate the effect of different steps of the pretreatment, when approaching MPs analysis of marine sediment samples by Py-GC-MS, and to obtain a better understanding of matrix effects in different environmental samples. Optimization of such sample pretreatment steps and evaluation of their actual necessity for the different environmental matrices has great potential to lead to significant improvements in MP analysis, by reducing the amount of time and reagents required.

This study was supported by the North Atlantic Microplastic Centre (NAMC, https://namc.no/), a research consortium coordinated by NORCE (Norway) of which the University of Pisa and Aalborg University are partners.

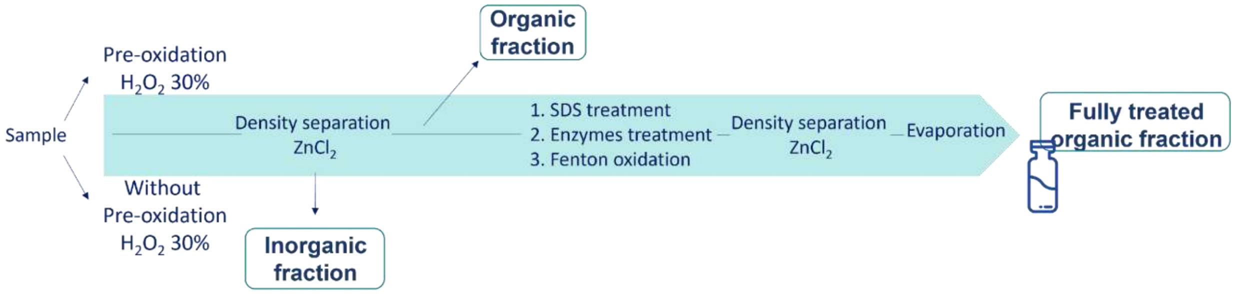

Figure. Sample preparation protocol applied to marine sediment samples.

References

[1] L. Simon-Sánchez, M. Grelaud, C. Lorenz, J. Garcia-Orellana, A. Vianello, F. Liu, J. Vollertsen, P. Ziveri, Environmental Science & Technology, 56, 16780-16788 (2022).

[2] I. Coralli, V. Giorgi, I. Vassura, A.G. Rombolà, and D. Fabbri, Journal of Analytical and Applied Pyrolysis, 161, 105377 (2022).

[3] M. Matsueda, M. Mattonai, I. Iwai, A. Watanabe, N. Teramae, W. Robberson, H. Ohtani, Y.-M. Kim, and C. Watanabe, Journal of Analytical and Applied Pyrolysis, 154, 104993 (2021).

OP26

AN ANALYTICAL APPROACH TO QUANTIFY NANOPLASTICS IN THE FOOD WEB: FROM VEGETABLE TO FISH

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1. Introduction

The presence and potential risks of nanoplastics (particles with sizes smaller than 1 µm) in the environment have raised serious concerns regarding their transfer from the environment into food webs. However, accurately measuring nanoplastics in complex matrices such as soil and organisms has been challenging due to the limitations of existing analytical methods. In this study, we present a novel approach that utilizes rare elements as tracers to investigate the uptake and biodistribution of nanoplastics in lettuce and their subsequent transfer to insects and from insect to fish. The objective of this study was to reveal how the variation in the chemical composition of nanoplastics modulates: (a) the particle uptake by plants from the soil, (b) their transfer in food chains, and (c) their possible accumulation and biodistribution in predators. We used 250 nm PVC and PS particles as our model nanoplastics. A rare element, gadolinium (Gd) was entrapped in the matrix of the nanoplastics and used as a proxy for tackling the challenges associated with tracking and quantification of particles in organisms' bodies [1].

2. Results and Discussion

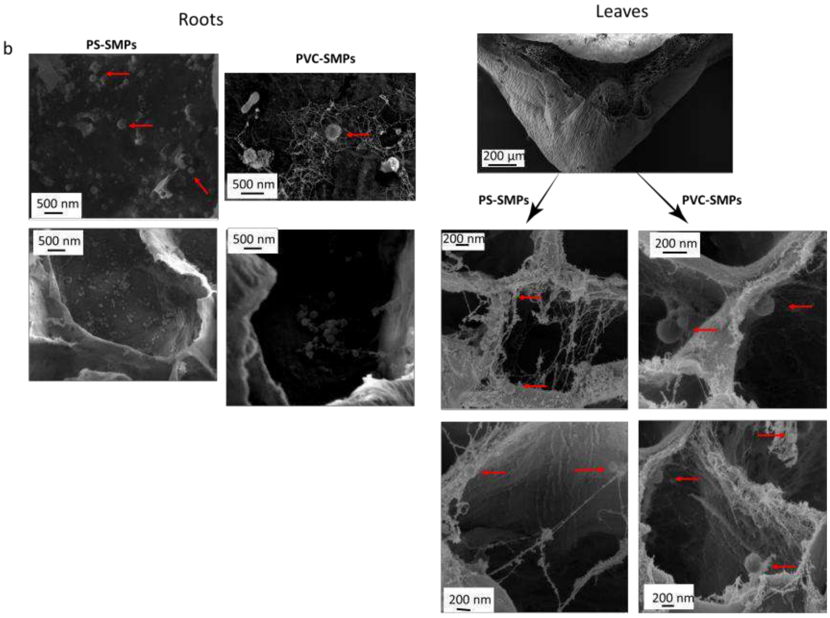
Our research findings provide new insights into the impact of chemical composition on the uptake, biodistribution, and transfer of nanoplastics in lettuce, insects, and fish. We observed that the chemical composition of the nanoplastics significantly influences their uptake and distribution within lettuce plants, as well as their subsequent transfer to insects and fish. Interestingly, our results show that regardless of exposure to clean feed after consuming treated lettuce, nanoplastics tend to accumulate in the digestive systems of insects. This suggests that once ingested, the nanoplastics persist within the insect's physiological system, potentially posing long-term risks. Furthermore, we found that the distribution pattern of nanoplastics in fish is also influenced by their chemical composition, indicating a complex interaction between nanoplastic properties and biological systems.

Crucially, our study demonstrates that no release of gadolinium (Gd), the tracer element, was observed from the particles during biotransformation processes that occurred within both plants and insects. This finding highlights the stability of nanoplastics within the organisms' physiological medium, suggesting that the particles retain their integrity.

These findings have significant implications for understanding the potential risks associated with nanoplastic pollution in ecosystems and the subsequent transfer to higher trophic levels, including fish that are part of human food chains. The stability of nanoplastics within organisms indicates a potential for bioaccumulation, raising concerns about long-term exposure and potential adverse effects on both wildlife and human health. Overall, our study underscores the urgent need for further research to assess the broader ecological and human health impacts of nanoplastic pollution.

3. Conclusions

Our findings indicate that lettuce plants are capable of taking up nanoplastic particles from the soil, which can subsequently enter the food chain. This highlights a potential health risk to herbivores and humans, assuming these results are applicable to other plant species, crops, and real-world field conditions. Different types of plastic exhibit distinct behaviors and fates within organisms and food webs. Consequently, data generated for one type of nanoplastics, such as PS commonly studied plastic-related research, cannot be directly extrapolated to other types of plastics. The methodology developed in our study provides a valuable approach for studying the bioaccumulation and trophic transfer of nanoplastics across different food webs, thereby contributing to a better understanding of the risks associated with these persistent materials in the environment.



SEM images showing the presence of PS and PVC nanoplastics in the root and leaves of the lettuces. The red arrows highlight the positions of some of the particles inside the plants, as examples.

References

F. Abdolahpur Monikh, M.G. Vijver, D.M. Mitrano, H.A. Leslie, Z. Guo, P. Zhang, I. Lynch, E. Valsami-Jones, W.J.G.M. Peijnenburg, The analytical quest for sub- micron plastics in biological matrices, Nano Today 41 (2021) 101296, https://doi. org/10.1016/j.nantod.2021.101296

OP27

ANODIC OXIDATION OF POLYSTYRENE: TREATMENT OF MICROPLASTICS IN WATER

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1. Introduction

Recently, plastics materials have gained a crucial role in the everyday life. Once their life cycle is over, they are released into the environment, contaminating soil and water. Due to various environmental processes, plastics can be transformed into smaller sizes. Microplastics (MPs) are tiny particles of plastic with a diameter of less than 5 mm. Microplastic contamination is common in aquatic ecosystems. MPs can be easily absorbed by many aquatic species and consequently absorbed by humans along the trophic chain. MPs have been shown to release toxic monomers and additives, resulting in cancer issues and reproductive abnormalities. From an environmental point of view, the type of plastic considered most dangerous is polystyrene (PS) due to its dangerous genotoxicity[1]. In recent years, electrochemical oxidation (EO), belonging to the class of advanced oxidation processes (AOPs), has been developed for the degradation of MPs from water[2]. This process is environmentally friendly as it could degrade organic contaminants into nontoxic molecules like water (H_2O) and carbon dioxide (CO_2) without addition of chemicals.

2. Results and Discussion

The effects of several operational parameters, such as electrolyte composition, electrolyte concentration and current intensity on the EO of a solution of PS (size 1 µm) monodispersed in water (25 mg L^{-1}), were investigated. The experiments were carried out in lab-scale reactor (250 mL), by means of two BDD electrodes (100 x 50 mm). Fig. 1A shows the impact of different electrolytes on the degradation of PS in terms of TOC removal %. As can be seen, a higher PS degradation efficiency (62.2 %) was obtained when Na_2SO_4 was used, rather than NaCl and $NaNO_3$. The presence of Na_2SO_4 as electrolyte can lead to the formation of strong oxidative species, such as $SO_4^{-}\cdot$ and $S_2O_8^{2-}$, which are capable to indirectly oxidize the PS molecules in solution[2]. Conversely, the use of NaCl leads to the formation of chlorine (Cl_2), hypochlorous acid (HClO), hypochlorite ion (ClO^-) which own a lower oxidative power than the sulphate species, results in a lower percentage of degradation (40.5 %). When $NaNO_3$ is present in solution, no oxidizing species can be generated in solution, involving that the degradation of PS can be ascribed only to direct oxidation (24.8 %).

Fig. 1B depicts the impact of Na_2SO_4 concentration on the process. The findings clearly indicate that the higher the salt concentration, the lower the PS removal. As reported previously by several authors, the increase of the sulphate concentration usually generates a positive effect on the degradation efficiency, but this happens up to an inhibition point, called optimal dose, starting from which the contaminant removal efficiency decreases. In fact, operating at high sulphate concentrations, like the experimental conditions investigated, a reduction of PS removal occurred due to parasitic side reactions and self-combination of radicals[3]. Moreover, high sulfate concentrations can block the anode surface, affecting the performances of the process[4]. The influence of the applied current intensity on the PS degradation process was shown in Fig. 1C. The PS removal efficiency increased by increasing the current intensity, in the experimental range between 0.1 and 0.5 A. The increase of current intensity leads to a greater presence of electrons directly available for anodic oxidation reactions and this translates into greater degradation efficiency[5]. Furthermore, the higher current intensity entails to oxidize more water molecules into $OH^{\cdot}$, enhancing the process. Anyway, it is important to stress that increasing the applied current intensity also involves an enhancement of side reactions, such as oxygen evolution reactions (OEP) which could affect the overall process, and drastically raise the treatment costs. For this reason, further investigations should be conducted to identify better operation conditions.

3. Conclusions

In the current study the electrochemical oxidation of 1 µm PS, considered borderline between micro and nanoplastics, in aqueous solution has been investigated. The presence of different electrolytes, salt concentration and current intensity were examined. The results highlighted that the highest PS degradation efficiency of 62.2% has been registered operating in presence of Na_2SO_4 0.02 M with current intensity of 0.5 A. The addition of Na_2SO_4 electrolyte in the process produce the formation of species with high oxidative power that can oxidize the compound. The EO could constitute a promising technique to face the worldwide current issue of the MPs in water bodies, but the possible intermediates generation and the high operational costs must be further evaluated.

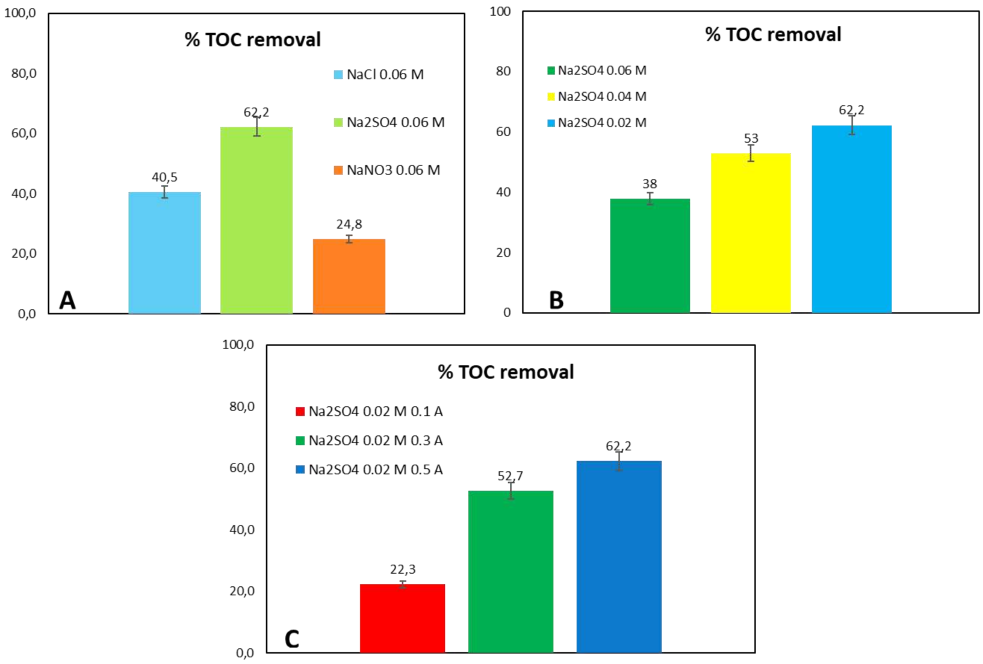

Fig.1*: Effect of (A) electrolyte composition, (B) electrolyte concentration, (C) current intensity on the PS removal %*

References

[1] Nugnes et al. 2022, Chemosphere, https://doi.org/10.1016/j.chemosphere.2022.134373
[2] Kiendrebeogo et al. 2021, Environmental Pollution, https://doi.org/10.1016/j.envpol.2020.116168
[3] Urán-Duque et al. 2021, Water, https://doi.org/10.3390/w13172445
[4] Rui et al. 2023, Chemosphere, https://doi.org/10.1016/j.chemosphere.2022.136993
[5] Iovino et al. 2023, Molecules https://doi.org/10.3390/molecules28031306

OP28

FATE OF SEMIVOLATILE POLYSTYRENE PHOTODEGRADATION PRODUCTS IN SURFACE WATERS AND THE ATMOSPHERE

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1. Introduction

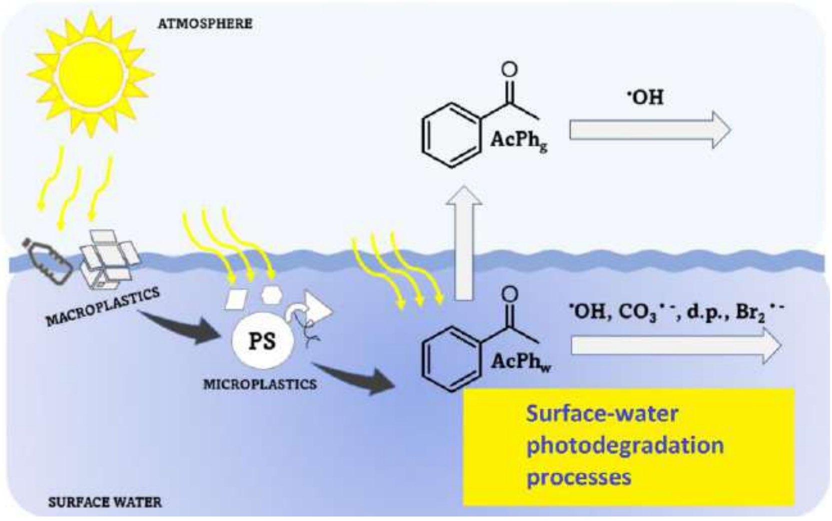
Micro- and nanoplastic particles are a considerable emerging problem in the environment because their small size facilitates interaction with living organisms, with harmful effects. Exposure of water-suspended plastics to sunlight may cause fragmentation, which is a source of microplastics and nanoplastics, but it may also induce formation of dissolved compounds [1]. The latter phenomenon is interesting because it could end up in eventual removal of plastic particles from environmental waters, thus its details deserve investigation. We have previously shown that exposure of polystyrene aqueous suspensions to sunlight produces a range of aromatic and aliphatic compounds that could derive either from the polymer skeleton, or from additives and plasticisers [2]. Among such compounds, benzene and acetophenone are semivolatile and could undergo either degradation in surface waters, or partitioning into the gas phase where they could react with gaseous $^{\bullet}$OH. This presentation will introduce an approach to predict the fate of the two compounds, as well as phenol (major benzene degradation product), using a two-compartment model that considers both surface waters and the atmosphere.

2. Results and Discussion

Acetophenone and benzene are important compounds deriving from the exposure of polystyrene to sunlight [2]. Experimental findings (irradiation with UV lamps followed by monitoring of the organic substrate by liquid chromatography) suggest that acetophenone in surface waters would mainly react with $^{\bullet}$OH and the carbonate radical ($CO_3^{\bullet-}$). On the other hand, benzene is well known to react selectively with $^{\bullet}$OH. On this basis, the photodegradation kinetics of the two compounds in different surface-water conditions can be predicted by using the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) [3]. However, as semivolatile molecules, acetophenone and benzene can also undergo gas-phase partitioning as competitive removal pathway from water. The respective first-order volatilisation rate constants from the aqueous phase, as well as the second-order reaction rate constants with gas-phase $^{\bullet}$OH were derived by using the EPIWEB 4.11 package (US-EPA) [4].

The overall processes involving acetophenone in the two considered environmental compartments (surface waters and the atmosphere) are depicted in the scheme below. Calculation results show that, for acetophenone, volatilisation kinetics would prevail over aqueous-phase photodegradation in the vast majority of environmental conditions. Therefore, with few exceptions, the main pathway to acetophenone removal from the aqueous environment would be volatilisation followed by reaction with gas-phase $^{\bullet}$OH.

Benzene is even more volatile than acetophenone, and the two compounds show similar photodegradation kinetics in the aqueous phase. Therefore, most benzene produced by irradiation of an aqueous suspension of polystyrene would end up in the gas phase, where it would react with gas-phase $^{\bullet}$OH. Phenol is the main product of the reaction between benzene and $^{\bullet}$OH in both water and air. In water, phenol would mainly react with the triplet states of chromophoric dissolved organic matter (^{3}CDOM*) [5]. In the gas phase, the main removal pathways of phenol would be reaction with $^{\bullet}$OH in daytime and with the nitrate radical ($^{\bullet}NO_3$) during the night [4].



Schematic of the formation of acetophenone (AcPh) from polystyrene (PS), and its environmental fate

However, gas-phase phenol could also undergo partitioning to atmospheric waters (e.g., cloud water), whence it could reach back surface-water environments by precipitation. This scenario was modelled by considering gas-water partitioning equilibrium as described by the Henry's law constant of phenol (K_H = 1.35×10^{-5} on a mol/mol basis) and the volume fraction of liquid water in the atmosphere (f_W = 5×10^{-7}) [4]. By so doing, it was possible to model the time evolution of aqueous-phase phenol by considering reaction of benzene + $^{\bullet}OH_{(w)}$ in water, followed by phenol degradation with $^3CDOM^*_{(w)}$, as well as phenol formation in the gas phase followed by liquid-water partitioning and precipitation.

This approach allows for an assessment of the relative contributions of the aqueous-phase and gas-phase pathways to phenol in surface-water environments. Moreover, it also gives insight into the possible contributions of polystyrene irradiation to the occurrence of carcinogenic benzene and toxic phenol in important environmental compartments.

3. Conclusions

Photochemistry plays an important role both in the formation of aromatic compounds from polystyrene in aqueous suspensions, and in the degradation of such compounds in surface waters and (when applicable) the atmosphere. Gas-phase partitioning followed by reaction with $^{\bullet}OH_{(g)}$ is a key pathway in the environmental fate of semivolatile plastic products such as acetophenone and benzene. In the latter case, phenol is the main transformation product of the reaction between benzene and $^{\bullet}OH$ in both surface waters and the atmosphere. Aqueous-phase phenol can either derive from benzene + $^{\bullet}OH$ in water, or be formed in the atmosphere and reach the water compartment upon partitioning into cloud water and scavenging by precipitation.

References

[1] Allen S, Allen D, Phoenix VR, Le Roux G, Durántez Jiménez P, Simonneau A, Binet S, Galop D. *Nat. Geosci.* **2019**, *12*, 339–344.
[2] Bianco A, Sordello F, Ehn M, Vione D, Passananti M. *Sci. Total Environ.* **2020**, *742*, 140413.
[3] Fabbri D, Carena L, Bertone D, Brigante M, Passananti M, Vione D. *Sci. Total Environ.* **2023**, *876*, 162729.
[4] US-EPA, **2021**. Estimation Programs Interface Suite™ for Microsoft® Windows, v. 4.11.
[5] Canonica S, Freiburghaus M. *Environ. Sci. Technol.* **2001**, *35*, 690-695.

ACCELERATED WEATHERING OF NANO-BASED FOOD PACKAGING MATERIAL: INVESTIGATION OF POTENTIAL MIGRATION INTO A FOOD SIMULANT

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1. Introduction

It has been estimated that insect pests annually infect up to 40% of global crop production, and more than 30% of cereals, rice, and legumes, which end up in huge loss of resources and money (each year, plant diseases cost the global economy over $220 billion)[1]. To tackle this challenge, the EU funded Horizon 2020 project SUNSHINE is working on the development of advanced multi component nanomaterials (MCNMs) to extend the shelf life of dry food. These MCNMs consist of either sepiolite or bentonite nanoclays encapsulating an essential oil (Fig. 1) to be added to a polyethylene film as anti-pest against the beetle within the Tenebrionidae family. As this MCNM is classified as food contact material (FCM), a complete consumer safety assessment of this nano-enabled product must be proven before the FCM reach the market, following the European Food Safety Authority (EFSA) regulations. In this regard, the potential migration of MCNMs or elements which constitute the MCNMs from the food packaging film was investigated into different food simulants, according to Regulation (EU) N°10/2011. Moreover, to simulate a natural weathering process, the potential migration of the same components was also studied after accelerated weathering of food packaging films loaded with MCNMs.

2. Results and Discussion

Besides a comprehensive physico-chemical characterization of both pristine MCNMs and LDPE films loaded with the MCNMs selected, this work focused on the accelerated weathering of these films according to ISO 4892-2-2/2013 method, already used in the literature[2] to perform UV weathering of nano-based plastic materials. After the accelerated weathering step, following the Regulation (EU) N°10/2011: i) the LDPE films, ii) the LDPE-MCNMs films and iii) the accelerated weathered LDPE-MCNMs films, were completely immersed into10% EtOH food simulant (i.e., to mimic fruits, vegetables, eggs, meat and fish) for 10 days at 40 °C and the potential release of any fragment (i.e., degraded matrix with embedded MCNMs or agglomerated MCNMs with some degradation debris attached or occasionally free MCNMs) was investigated by means of TEM-EDX, FT-IR and ICP-MS techniques. In general, only very few and only C-based fragments were observed for each sample investigated. Concerning the LDPE-MCNMs film samples and the corresponding accelerated weathered films, it seemed a very slightly increase in the degradation of the films after accelerated weathering. The released results by ICP-MS always showed very low concentrations, except for one LDPE-MCNMs film and one accelerated weathering LDPE-MCNMs film, for which Al concentration was higher than 1 mg/kg food simulant, which is the only threshold that should not be exceeded according to the Annex II, Table 1, Regulation 1245/2020 on plastic materials and articles intended to come into contact with food.

3. Conclusions

This accelerated weathering study showed no significant changes in the chemical structure of LDPE-MCNMs film when exposed to controlled UV light and water spray cycles. Very few fragments as degraded matrix with embedded MCNM have been observed in a µm size range and no free MCNM have been detected. Lastly, the investigation of inorganic elements migration into the food simulant mimicking fruits, vegetables, eggs, meat and fish highlighted that the threshold limit was exceeded for alluminum only by two samples, calling for further experiments to better clarufy the possibility of using this food packaging material in the market.

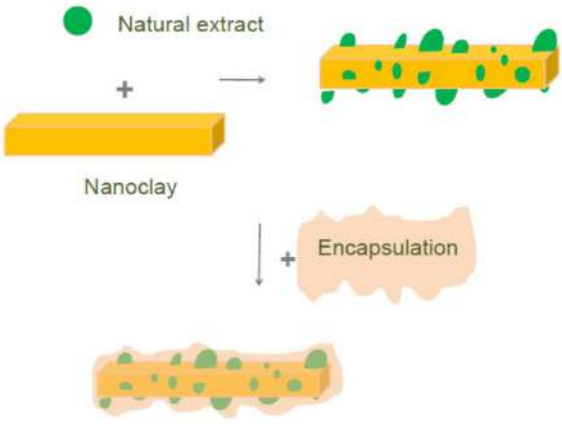

Fig. 1. The approach used to develop the multicomponent nanomaterial for food packaging

References

[1]https://www.fao.org/news/story/it/item/1402920/icode/

[2]Wohlleben and Neubauer (2016) 'Quantitative rates of release from weathered nanocomposites are determined across 5 orders of magnitude by the matrix, modulated by the embedded nanomaterial', NanoImpact, 1, 39-45. doi:org/10.1016/j.impact.2016.01.001

OP30

WILDLIFE AND LIVESTOCK ANIMALS AS SENTINELS OF ENVIRONMENTAL POLLUTION: QUANTIFICATION OF PERSISTENT, BIOACCUMULATIVE, TOXIC SUBSTANCES AND POTENTIALLY TOXIC ELEMENTS

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1. Introduction

The interest in a wide range of environmental contaminants, both of natural or anthropogenic origin, has raised in the last decades because of their adverse effects on human and animal health[1]. Environmental pollutants can exert their impact on vertebrates in two different ways: the direct exposure pathways, e.g., ingestion of contaminated water, soil, forage, and preys or by skin uptake subsequently to a spray event and the indirect effects associated with the loss in preys or through habitat modification[2-3]. Animals are exposed to a variety of environmental contaminants, and particularly wild mammals are well suited as biological indicators due to their relatively long lifespan resulting in higher contaminant accumulation compared to livestock [4-5]. The wildlife populations have been growing, and particularly wild boar and roe deer are among the most common wild mammal species in Europe, making wild meat increasingly available to consumers[6]. The accumulation of persistent, bioaccumulative, toxic substances (PBTs, e.g., dioxins, pesticides) and of potentially toxic elements (PTEs; e.g. chromium, cadmium, etc.) in the meat of these animals makes them excellent model animals for the study of environmental contamination in certain geographical areas.

2. Results and Discussion

The project aims to evaluate the interaction between wildlife and livestock living within the same geographical area, for the identification of potential chemical hazards induced by the ingestion of contaminated food and water due to environmental pollution The geographical area of relevance was centered in the northern section of the Apennine, called “Four Provinces Apennines”, In this area, a well-structured hunting activity is present and involves particularly wild boars (Sus scrofa) and roe deer (Capreolus capreolus), that present different feeding habits. In comparison, for livestock local specimens of Sus scrofa domesticus and cattle for meat production (Bos taurus) coming from grazing and not grazing farms (fed with forages and feeds from the geographical area) were considered.

Mass spectrometry hyphenated technologies(GC-MS, LC-MS/MS, ICP-MS) were used to investigate the contaminants’ accumulation in terms of PTEs’ and PBTs’ in different animal matrices. The methods for the detection and quantification of a large panel of pollutants belonging to different classes was developed considering the analytical parameters such as the linearity of the method, the intra-assay and inter-assay variations, the evaluation of the recovery value, the matrix effect, the limit of detection (LOD) and the limit of quantification (LOQ).

These results constitute the first step to evaluate the level of oral exposure to PBTs, PTEs, and antimicrobials in the different livestock species according to the content of their diet. Finally, the data from the quantification of contaminants in the different biological matrices together with the level of exposure of the domestic species, the productive, reproductive, and health data will be evaluated to study the toxicological implications of the substances.

3. Conclusions

Since wildlife and livestock are both exposed to different categories of PBTs, PTEs, and drugs depending on their geographical area and considered the likely correlation of contamination levels in animals that share water and dietary resources, studying rural ecosystems for identifying the chemicals that circulate into the water-soil-air-plants-animals system, in terms of a holistic One Health perspective, results particularly important.

The main goal of this ambitious project is related to providing information on the state of environmental contamination through the comparative study of the presence of contaminants in wild and farm animals, and their food, the consumer risk characterization.

References

1. Steffan, J.; Brevik, E.; Burgess, L.; Cerdà, A., The effect of soil on human health: an overview. *European journal of soil science* **2018,** *69* (1), 159-171.
2. Richard, F.-J.; Gigauri, M.; Bellini, G.; Rojas, O.; Runde, A., Warning on nine pollutants and their effects on avian communities. *Global Ecology and Conservation* **2021,** *32*, e01898.
3. Smith, P. N.; Cobb, G. P.; Godard-Codding, C.; Hoff, D.; McMurry, S. T.; Rainwater, T. R.; Reynolds, K. D., Contaminant exposure in terrestrial vertebrates. *Environmental Pollution* **2007,** *150* (1), 41-64.
4. Rhind, S., Anthropogenic pollutants: a threat to ecosystem sustainability? *Philosophical Transactions of the Royal Society B: Biological Sciences* **2009,** *364* (1534), 3391-3401.
5. Das, K.; Debacker, V.; Pillet, S.; Bouquegneau, J.-M., Heavy metals in marine mammals. *Toxicology of marine mammals* **2003,** *3*, 135-167.
6. Guardone, L.; Armani, A.; Mancianti, F.; Ferroglio, E., A review on Alaria alata, Toxoplasma gondii and Sarcocystis spp. in mammalian game meat consumed in Europe: Epidemiology, risk management and future directions. *Animals* **2022,** *12* (3), 263.

CONTEMPORARY MURALISM CONSERVATION: PRESERVING PAINTING MATERIALS OF A PILOT SITE IN MILAN

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1. Introduction

In the last years, contemporary mural artworks became very relevant as artistic and social expressions in urban contexts. Municipalities, the population, and Cultural Heritage experts started to care for their state of conservation and to set up strategies for their safeguard and preservation [1,2]. Within the framework of the PRIN 2020 SuperStar project [3], and in collaboration with the Municipality of Milan – (Direction of Public Art), a conservation and protection strategy, based on activities carried out on purposely selected pilot sites, has been established in order to analyze and monitor the degradation of contemporary muralism. The following research study focused on the characterization of the painting materials used in the artworks under investigation, evaluating the aesthetic and chemical alterations after the outdoor natural exposure, and proposing a testing protocol for the monitoring of selected protective coatings. The latter goal will be extensively studied in order to understand the protective behaviour and efficacy of each class of materials when applied in situ, their compatibility with different painting layers, and their durability over time.

2. Results and Discussion

The selected case study is the mural entitled *Musica popolare* realized by the OrticaNoodles group of artists in 2016, located in the Ortica neighborhood in Milan. This colourful mural is dedicated to the most prestigious and well-known performers of the Milanese music of the second half of 20th century, namely: Ornella Vanoni, Enzo Jannacci, Dario Fo, Ivan Della Mea, Giorgio Strehler, Giorgio Gaber, and Nanni Svampa [4].

Regarding the characterization of the painting materials and the study of their degradation phenomena and mechanisms, an initial survey of deterioration patterns has been carried out. Very different degradation phenomena were highlighted and defined according to the Capus Glossary [5].

It can be assumed that the peculiar location and exposition of the artwork play an important role in the observed degradation patterns. For this reason, the analysis was based on three portions of the wall with different environmental conditions (Figure 1): one is south-west-exposed (full sun exposure), one is partially sheltered by trees (mid-sun exposure), and the third one is located in the adjacent car tunnel, completely sheltered both from rain and direct solar radiation. As shown in other studies [6,7], the extent of degradation is related to the level of exposure to atmospheric conditions of walls, the most exposed one shows severe issues of color fading (whitening), detachments, painting cracks, scaling and flaking phenomena. On the other hand, the state of conservation of the wall portion located in the car tunnel still presents vivid colors and intact painting layers, although covered with extensive dust deposit.

From the color palette, the red paint was chosen to study the color fading and micro-sampling was carried out in the three portions of the wall. The degradation phenomena leading to whitening appearance, was investigated. The collected samples were characterized by using µ-FTIR and µ-Raman spectroscopies and by microscopic techniques to study the painting stratigraphy.

Subsequently, different commercial protective coatings have been applied in the three different wall sections. Protectives' performance has been evaluated by visual inspection, digital microscopy, colorimetry, and in-situ water absorption tests. The measurements were performed before and after the application of protective treatments. The assessment of the different properties of the coatings are [8]: protective efficacy from water action and UV radiation, and color stability.

The selection of the commercial protectives was carried out by interviewing different conservation experts, researching the available products on the market, and selecting them according to their chemical nature. Selected classes of protective coatings include acrylates, alkyl alkoxy silanes, fluorine-siloxanes, and siloxanes

[9]. The monitoring of the pilot site will continue for approximately 2 years starting from June 2023, performing periodic measurements, and comparing the protective performances.

3. Conclusions

The investigation carried out of the pilot site of the mural *Musica popolare* in Milan, allowed to in situ evaluate the conservation state of the painting materials and the protective performance of different selected commercial protective coatings. Moreover, the results will produce a reliable dataset concerning the behavior and durability of different classes of protective coatings, in order to define an effective conservation strategy for the protection of outdoor contemporary murals.

Figure 1: Musica Popolare by OrticaNoodles in Milan. Display of the three areas chosen for conservative strategy: a) sheltered; b) fully exposure; and c) mid-exposure areas.

References

[1] Cadetti, A., Conservare la street art. Le problematiche del muralismo contemporaneo in Italia, 2020, Florence (Italy).
[2] Mezzadri, P., Heritage, 2021;4:2515–25.
[3] https://prin2020superstar.dcci.unipi.it/.
[4] http://orticanoodles.com.
[5] https://capusproject.eu/glossary/.
[6] Cimino, D., et al., Heritage, 2022;5:581–609.
[7] Alonso-Villar, E.M., et al., Heritage, 2023;6:3475–98.
[8] Pagnin, L., et al., Proceedings Int. Conf. Metrol. Archaeol. Cult. Herit. 2023:80–3.
[9] Artesani, A., et al., Coatings, 2020;10:217.

OP32

CHARACTERIZATION OF A HIGH VISCOSITY POLIMER DISPERSION ENCAPSULATING ESSENTIAL OIL OF *GLYCYRRHIZA GLABRA* FOR THE CLEANING OF BIODETERIORATED STONES

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1. Introduction

The presence of biofilms on surfaces of cultural interest is a widespread and well-known phenomenon, leading to biodeterioration, which is a source not only of aesthetic, but also of structural and chemical damages on the colonized surfaces [1]. Soft matters and PVA-based materials, also thanks to their reversibility and eco-compatibility, are promising tools for restoration and cleaning purposes [2]. Indeed, between them, there are High Viscosity Polymeric Dispersions (HVPDs) that already showed to be suitable to confine chelators [3] and other substances, included natural biodices [4]. In this research it was studied a HVPDs obtained by the crosslinking reaction between Polyvinyl Alcohol and Borax and loaded with a commercial essential oil (EO) of *Glycyrrhiza glabra* L., selected for its biocidal and fungicidal properties [5]. Different formulations were characterized and tested, in presence and in absence of two concentrations of essential oil: 1.5% w/w e 2.0% w/w, with a PVA:B=4:1 ratio. Their properties were investigated with NMR relaxometry and molecular diffusion, MCR 301 rheometer, pH meter, FT-IR ATR, NETZSCH TG 209F3 spectrometer.

2. Results and Discussion

Three types of HVPDs were prepared, with the same ratio of PVA:B=4:1; sample 1 with no EO, sample 2 with 1.5% w/w of E.O, sample 3 with 2% w/w of EO The addition of EO lowers the pH by a few decimal units, always keeping it at high values, maintaining the basicity of the polymer, in a range between 8.95 and 9.15. Rheological analyses were performed, at constant temperature, beginning with a strain test, to investigate the behaviour of samples subjected to a rotational force, and to identify the frequency relative to the breaking point of each HVPDs; the G' and G" moduli, remain constant during all the experiment, indicating that the obtained materials are extremely viscous dispersions, with high resistance to deformation and do not present a shear point. The addition of EO does not change the behaviour of the soft matter. The samples were subjected to analysis of time sweeps of 1h each, at constant amplitude and frequency, to evaluate the stability of the product over time and the evaporation of the EO. It was noted that throughout the duration of the experiment, the products confirm their stability and no solvent evaporation is noted. To measure the viscoelasticity of the material, frequency sweep analyses were performed, by applying a stimulus whose frequency varies over time, maintaining its maximum intensity constant. The analyses confirmed the extreme viscosity of the samples. Isothermal thermogravimetric analyses were conducted with the aim to verify the ability of the product to retain its volatile fraction. A temperature range between 20°C and 800°C was used; all samples have a first decomposition temperature at 20°C, probably due to the evaporation of the weakly bound water, that could account for the rapid drying time of the soft matter; the second decomposition temperature is after 35°C, after which the samples begin to lose most of their mass due to water evaporation up to around 100 °C; the remaining residue is rather stable until 200 °C where a further decomposition occurs. FT-IR analyses were performed on Samples 1,2,3, identifying the classic peaks of a compound containing mostly water (3330 cm^{-1}, O–H stretching) and peaks related to presence of PVA, (3448 cm^{-1}, 2945 cm^{-1}, O–H bond stretching and C–H stretching of alkyl groups); in the region between 1333 cm^{-1} and 1416 cm^{-1} two peaks can be noted, which suggest that two types of complexation are formed between hydroxyl groups and borate. Numerous peaks can be noted (2937, 1603, 1513, 1416, 1077 and 1033 cm^{-1}), which confirm the presence of EO.

Diffusion NMR showed aging modality of HVPD which depends on PVA and water relative concentration. NMR relaxation times T_1/T_2 and diffusion quantified at different diffusion times and different magnetic gradient strengths showed useful information about the free and weakly bound water behaviour during time from the synthesis (aging) and during drying time. The peelability of the products was preliminary tested on sandstone specimens covered by biofilm, applying samples 2 and 3 with the aid of a spatula and removing them by peeling, as shown in Figure 1, after two drying times: 1h and 24h, to evaluate the ease of removal by peeling in both cases.

3. Conclusions

A thorough characterization of a HVPD, based on the cross-linking reaction between PVA and Borax and capable of encapsulating the commercial essential oil of *Glycyrrhiza glabra* L. has been performed. We established that the product is extremely viscous, it does not undergo to deformation or evaporation of co-solvent, thus retaining the essential oil. Moreover, the soft matter loses only the weakly bound water, at room temperature. Finally, NMR diffusion has proved to be a useful tool for monitoring the characteristics of HVDP as different parameters (time, drying time, relative percentage of PVA and water) vary. That information is very important in the field of cleaning porous surfaces, since it reduces the possibility of the product to leave residues, after an easy peeling action.

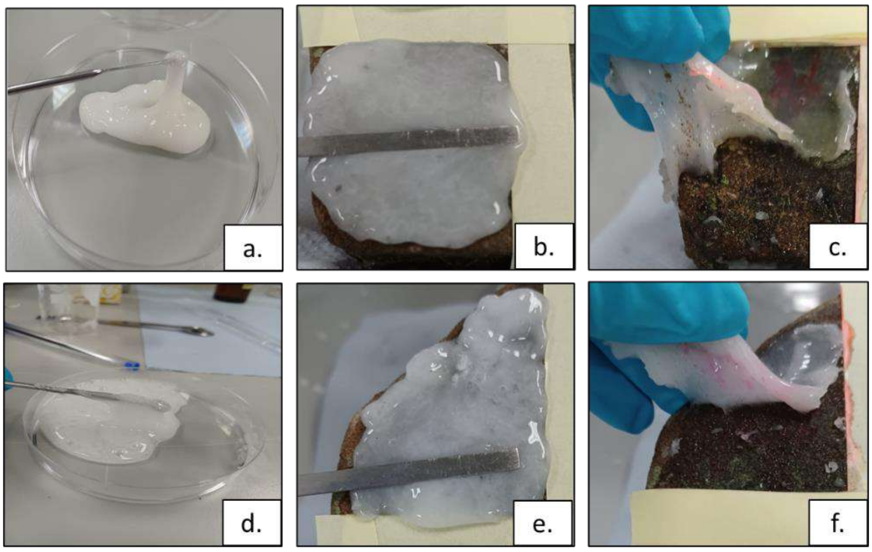

Figure 1. High Viscosity Polymer Dispersion: a. Sample 2,b. application of Sample 2,c. removal by peeling of Sample 2., d. Sample 3, e. application of Sample 3, f. removal of Sample 3.

References

[1] Ranaldi, R. et al., Int biodeterior biodegrad;172, 2022, 105436.
[2] Chelazzi, D. et al., ACS Symposium Series, 1296, 2018, 291–314.
[3] Berlangieri, C. et al.; Pure Appl Chem; 89(1), 2017; 97-109.
[4] Genova, C. et al., Coatings, 13(3), 2023, 520.
[5] Royani, A.; et al. Int J Corros Scale Inhib, 2022, 11(3), 862-888.

EVALUATION OF CLEANING METHODS ON DECORATED PLASTER IN ARTISTIC HISPANO-MUSLIM ARTWORKS

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1. Introduction

In this research, polychrome plasters were reproduced according to Hispano-Muslim techniques, made between the 12th and 15th centuries. The reproductions are made with plaster and tempera colours, using animal glue or gum arabic as binder. Three different pigments (vermilion, azurite and verdigris) were used for the color application. Subsequently, repaintings with oil colors were reproduced to simulate the repaintings on the original works that occurred over the centuries (Garcia, 2015). To evaluate the aging of the polychrome layers, an innovative aging protocol is proposed, designed according to the climatic conditions in which the real works are exhibited. It includes three daily phases for three weeks: freezer for 3 hours; humidification chamber with saline water (35g/l of NaCl in water) for 2 hours; UV lamp for 5 hours. Characterization measurements were performed by FTIR spectroscopy, GC/MS and colorimetry, before and after aging. For the cleaning of oily materials, different Agar-based gels have been tested, with the addition of hydrocarbons, alkalis and surfactants with a buffered aqueous solution at pH 7-7.6.

2. Results and Discussion

The results obtained by means of FTIR spectroscopy show that for animal glue a deterioration and denaturation of this type of protein binder is observed, due to the components such the amide A, I and II bands are reduced, and even the loss of the Amide B component. However, their chemical composition is not changed. For gum arabic there is also a decrease in the absorbance peaks of its main functional groups such as carboxyl and carbonyl groups (1600-1640 cm^{-1}) and the alkane groups (2900-2935 cm^{-1}) (Al-Gaoudi, 2020). The changes in both binders are more representative when mixed with the pigment verdigris, azurite and vermilion. Finally, for linseed oil new bands corresponding to the hydroxyl group are observed (3500-3430 cm^{-1}), the alkane group (2930-2855cm^{-1}/1463-1418cm^{-1}) and the significant band of the carbonyl group (1746 cm^{-1}) are reduced, and indeed the most intense characteristic band at ~1737 cm^{-1} is drastically reduced. This changes are observed specially with the pigments ultramarine blue and titanium white, the ochre pigment is more stable (Tammekivi et al., 2021).

GC-MS investigations on animal glue showed no changes in amino acid composition. No change in the composition of the monosaccharides is evident for gum arabic, while for linseed oil a loss of polyunsaturated fatty acids and the appearance of saturated dicarboxylic acids sebacic, azelaic and suberic (Tammekivi et al., 2021).

The chromatic variation is evaluated for the the pictorial layer of each probe and their repaints (binder and pigment) after the accelerated artificial ageing. It shows a yellowing of the arabic gum especially with the verdigris pigment, while in the case of the oil, a darkening and a yellowing is observed, especially aplicated with mixed of ultramarine blue and titanium white. In the case of animal glue, it shows a high darkening when is aplicated with azurite. For pigments, the colorimetric variation shows a photochemical alteration with darkening due to the UV rays in the case of vermilion applied with the gum arabic. Verdigris tends to turn yellow and a a more brownish tone in contact with oil colors, which is also caused by the pigment-binder ratio given thar verdigris has the finest grain size, so the mixture contains more binder than pigment. Azurite in contact with the oil repaintings layers leads to darkening, especially mixed with animal glue. And for repainted pigments, ochre is more stable applied mainly on animal glue with the thre original pigments than mixed ultramarine blue and titanium white.

The cleaning treatments are made to remove the oil painting. Here are proposed the use of 5% Agar gel with hydrocarbons heptane and acetone (50:50) (test 1); surfactant Triton-X (test 2); heptane and Triton-X (50:50) (test 3); NaOH (test 4); Agar gel at 5% made with Polyaminoamide and Glycine (test 5). These five cleanses are carried out in two phases, the first one of 30 min. and the second of 20 min.. The results obtained show that for the removal of both oil repaints, test 1 is the most effective on all binders and pigments. However, test 5 is effective for removing ocher overpaintings on vermilion with gum arabic, and on azurite with animal glue. The same result is obtained on repainting of ultramarine blue on vermilion with animal glue, and verdigris with gum arabic.

This study shows the importance of characterizing a work before selecting cleaning treatments, especially when they are repainted and require the removal of this overpainting. The ageing test has made it possible to study how the original materials and repaints behave. The results obtained showed that the verdigris pigment and the animal glue binder underwent the greatest changes during aging, as did the oil and ultramarine repaints. This has allowed the selection of specific treatments, based on rigid Agar gel and various detergents. The most effective treatment was the use of Agar, according to the protocols of test 1 and test 5.

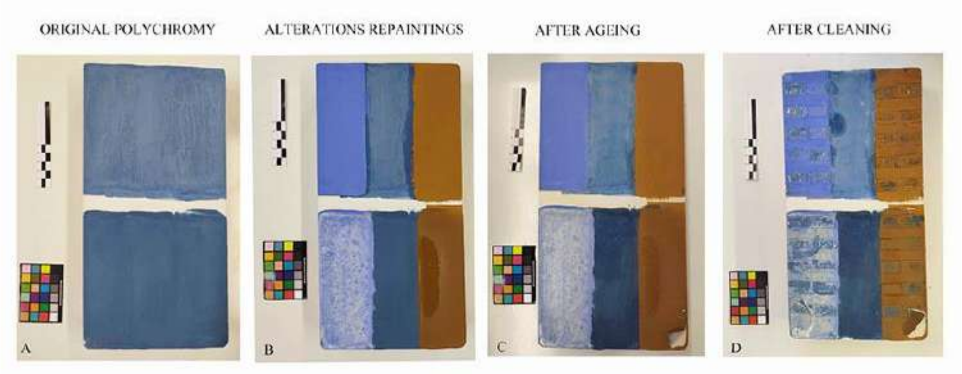

Figure 1. A. Top binder arabic gum, lower binder animal glue. B. Ultramarine blue and ochre oil repainiting. C. After ageing test. D. After cleaning treatments

References

Al-Gaoudi, A. (2020). Painted ancient egyptian mummy cloth of khonsuemrenep from bab el-gasus excavation: scientific analysis and conservation strategy. *SCIENTIFIC CULTURE*, *6*(2), 49-64.
García, A. (2015). *El Color en la Decoración Arquitectónica Andalusí.* Real Academia Bellas Artes San Fernando.
Tammekivi, E., Vahur, S., Vilbaste, M. and Leito, I. (2021). Quantitative GC–MS Analysis of Artificially Aged Paints with Variable Pigment and Linseed Oil Ratios. *Molecules*, *26*, 1-13.

NEW INSIGHTS IN THE PROTECTION OF WOODEN MATERIALS FROM FUNGAL BIODETERIORATION: CHITOSAN-BASED NANOPARTICLES LOADED WITH R-(+)-PULEGONE

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1. Introduction

A large part of cultural heritage is wooden made and one of the main causes of wood decay is given by fungal attack. This research aims to develop a biocidal product to prevent wood biodeterioration by employing sustainable reagents and harmless synthesis procedures. To this aim, R-(+)-pulegone (Pu), which is a main component of many essential oils that showed biocidal activities towards several microorganisms [1,2], was selected to be loaded in chitosan nanoparticles (ChNPs) and tested against *Aspergillus niger*, considered one of the main responsible of soft-rot decay [3]. Ionic gelation is the method used to obtain the ChNPs and is based on electrostatic interactions between the positively charged ammino groups of chitosan, a polysaccharide known for its biocompatibility, biodegradability and biocidal properties, and the negatively charged groups of sodium tripolyphosphate (TPP) [4]. The ChNPs have been morphologically characterized and their biocidal potential was evaluated towards *A. niger* in vitro and on artificially colonized wooden samples.

2. Results and Discussion

In the initial stages of the experiment, ChNPs loaded with Pu (Pu-ChNPs), at four Ch:Pu ratios (1:0; 1:0.25; 1:0.5; 1:1) were prepared following a two-step method for the formation of an oil-in-water emulsion and ionic gelation of chitosan with TPP.

Dynamic Light Scattering (DLS) allowed to calculate the hydrodynamic diameter (HD) and the polydispersity index (PDI) of the nano-systems dispersed in aqueous suspensions, confirming the presence of nanoparticles with different sizes, depending on the concentration of Pu present. According to DLS, the best result was obtained for Pu-ChNPs with a Ch:Pu ratio 1:0.25 (HD: 198 ± 4 nm; PDI: 0.39 ± 0.05).

Fourier-transform infrared spectroscopy (FTIR) was used to evaluate the encapsulation efficacy: variations of the spectral partner were observed and considered indicative of the efficient loading of Pu.

Multiwell Assay (MA) allowed to assess the inhibitory effect of Pu, chitosan and the four Pu-ChNPs systems at six concentrations (from 3 to 0.093 mg/mL) towards *A. niger*. The biological assays gave encouraging results, since the treatments based on Pu-ChNPs resulted more effective at lower concentrations than the ones obtained by employing the substances alone, active at higher concentrations.

Comparing the results from DLS and MA (inhibition at 0.75 mg/mL), the Pu-ChNPs system with a Ch:Pu ratio 1:0.25 was considered the best candidate for the following experimental steps.

In this regard, the synthesis protocol of the NPs was optimized considering a) the initial concentration of chitosan, b) the molar ratio between chitosan and TPP, c) the stirring speed during the ionic gelation and d) the pH conditions. The new systems gained better results, as confirmed by the DLS where NPs with smaller sizes (HD: 73.73 ± 0.10 nm) and lower PDI (0.31 ± 0.04) were obtained. The morphology of the NPs was observed by Scanning Electron Microscope (SEM) imaging, where the NPs appeared to be regularly distributed, well-separated and spherically shaped.

Two parallel experiments involved the treatment of wooden samples from three species (*Quercus petraea*, *Abies alba* and *Fagus sylvatica*) with an aqueous suspension of Pu-ChNPs (0.75 mg/mL), applied via spray. In the first case, the samples were preliminary treated with the solution and then inoculated with *A.niger* in laboratory conditions for two weeks. The treatments visually reduced the growth of the fungus, especially in the samples from *F. sylvatica*.

In the second experiment, the same treatment was applied on wooden samples previously subjected to a natural biocolonization. A colorimetric monitoring confirmed the progressive toning of the samples towards their original color after the treatment with the NPs. This result can be considered an indicator of the biocidal effect of the treatments, as a further confirmation of the potential of Pu-ChNPs for future applications.

3. Conclusions

R-(+)-pulegone was successfully loaded in chitosan spherical shaped NPs. The enhanced biocidal effects associated to the combination of chitosan and Pu towards *A. niger* could be explained taking into account that nano-encapsulation protects Pu from evaporation and oxidation, fostering its controlled release and improving its stability [5]. In this scenario, the promising results obtained suggest that such systems can represent a possible sustainable alternative to classical chemical biocides considered harmful for the environment and human health. Future applications will evaluate the combined biocidal and consolidant properties of Pu-ChNPs, in virtue of the recent applications of chitosan as a consolidant for archeological and waterlogged wood [6].

F.sylvatica treated (a and b) and untreated (c and d) with Pu-ChNPs after inoculation with A. niger.

References

[1] C. Genova, E. Fuentes, P.Sanmartin, G. Favero, B. Prieto, Coatings, 10(3), 2020, 295.
[2] M. Božović, R. Ragno, Molecules, 22(2), 2017, 290.
[3] S. A. M. Hamed, Int Biodeterior. Biodegrad., 78, 2013, 98-102.
[4] L. Keawchaoon, & R. Yoksan, Colloids Surf. B, 84(1), 2011,163-171.
[5] X. Wang, Y. Hu, Z. Zhang, B. Zhang, JCH, 53, 2022,206-211.
[6] M. Christensen, E. Larnøy et al., J. Am. Inst. Conserv., 54(1), 2015, 3-13.

ANALYTICAL EVALUATION OF THE EFFECTIVENESS OF LASER CLEANING IN THE CONTEXT OF CONTEMPORARY MURALISM

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1. Introduction

In recent years, the use of laser technology has increased significantly as a valid solution and alternative to traditional cleaning methods in the conservation of the cultural heritage, allowing to overcome some limits of the other cleaning methodologies. Despite the growing diffusion of laser systems and their use in very diversified contexts, there are objective difficulties in mastering the different modes of action and the settings of the many laser parameters. It is therefore very important to define protocols that allow for an accurate evaluation of the action of laser technology applied to cultural heritage. In this contribution, contemporary muralism was considered as case study, and especially the cleaning of wall surfaces painted with synthetic materials and later overpainted with vandalistic writing or drawings, made with the same graphic tools (e.g. spray cans) of the original paint layer.

2. Results and Discussion

Model samples of cement mortar were made on which: (I) two layers of paint were spread, (II) three types of paints were selected, namely an acrylic spray, an alkyd spray and an acrylic-styrene water-based paint to be applied by brush or roller, and (III) three colours, namely yellow, blue and fluorescent blue. The products to be used were selected following an accurate initial characterisation, excluding mixed binders, in order to better correlate the action of the laser to the type of binder. One set of specimens was used as it was, after at least one month of drying, while a second set with a single layer of paint was aged with artificial solar light. After 1000 hours of aging, a second layer of paint was applied on the samples. The cleaning tests, aiming to remove the overlying paint layer, were carried out using different types of lasers, on both sets of model samples, in order to evaluate the effectiveness of the treatment both in the case of a freshly made mural and in the case of a more dated one.

The effectiveness of the cleaning tests was first evaluated by constructing radar diagrams which represent the results of empirical evaluations of some particularly significant parameters for cleaning monitoring. In a subsequent phase, the same parameters were evaluated analytically through specific techniques whose instrumental responses made it possible to validate or not the initial empirical evaluations. In particular, we focused on the following parameters: presence of paint residues, surface roughness (topography integrity), color changes, cleaning evenness, cleaning effectiveness, pigment pickup during laser cleaning, UV fluorescence changes (if possible).

The analytical evaluation of the effectiveness of laser cleaning was carried out by adapting previously tested analytical protocols for both the use of lasers and gels [1]. These protocols are based on optical microscopy and SEM measurements, spectrophotometric analyses, FTIR and GC/MS, and aim not only to evaluate the ability of the laser to selectively remove the second layer of spray paint, but also to identify any processes and products of alteration due to the surface-laser interaction.

3. Conclusions

The research carried out so far constitutes the first part of a larger work which aims at identifying sustainable cleaning methods for contemporary muralism [2], and it also represents a starting point for a more ambitious project which aims at defining and standardizing the operative laser parameters in order to operate safely on a wider range of materials.

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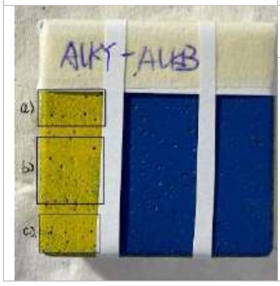
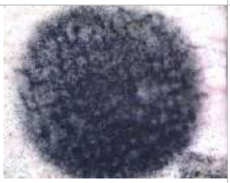
	Pwr 165	Pwr 181 with homogenizer	Pwr 181 second step
			

Left: Mock-up with a yellow alkyd paint at the bottom and a blue alkyd paint at the top. Right: Pigment pick-up during laser cleaning.

References

1. Bertasa M., Ricci C., Scarcella A., Zenucchini F., Pellis G., Croveri P., Scalarone D., "Overcoming challenges in street art murals conservation: a comparative study on cleaning approach and methodology", Coatings, 2020, 10, 1019.
2. https://prin2020superstar.dcci.unipi.it/

OP36

CLEANING TOOLS FOR REMOVING AGED POLYMER COATING FROM STONE ARTIFACTS

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1. Introduction

Stone artifacts represent an important part of our cultural patrimony, and they are continually subject to deterioration due to physical, chemical, biological, and air pollution factors [1]. Due to the ongoing threat of degradation of artifacts, the conservation aspects have recently gained prominence on a global scale. Finding suitable preservation products, assessment of their performance, including durability, and development of correct application techniques still represents crucially important research topics. Cleaning of artifacts from any undesired matter, such as decayed materials resulting from previous treatments, is a particularly delicate step of the conservation process. In fact, highly selective techniques must be applied, which should preserve the original nature and properties of the substrates [1,2]. Synthetic polymers have been largely employed in the traditional restoration practice as adhesives and conservation agents [1]. The removal of aged polymeric materials from the surface of artifacts is becoming a quite common cleaning operation in the conservation field. Hence, our research study was mainly focused on studying the removing process of decayed polymer coatings from stone surface by different cleaning tools. For instance, the removal of an acrylic polymer (Paraloid B-72) applied on two different porous stone substrates was investigated after application of nano-structured emulsions (NSE) supported on gels.

2. Results and Discussion

Different kinds of gel materials have been examined to find out the appropriate tool for removing aged polymer coatings from the considered stone substrates. For this purpose, three different gel materials were synthesized in the laboratory: (i) synthetic hydrogel obtained from HEMA-MBA (2-hydroxyethyl methacrylate/N, N-methylenebisacrylamide) copolymer and PVP; (ii) bio-degradable gel obtained from konjac glucomannan with sodium borate (KG+SB); and (iii) a new bio-degradable gel material prepared by modifying the natural konjac-based material with two different synthetic polymers (Polyvinyl alcohol and Polyvinylpyrrolidone, KG+PVA+PVP+SB). All the considered gel materials were characterized using different techniques to comparatively assess their properties that are relevant for cleaning purpose: gel content, equilibrium water content, retention capability, morphology, and durability [3]. The result indicated that both gels prepared by natural polymer (KG) have higher equilibrium water content (EWC ~96%) than the synthetic gel (HEMA-MBA/PVP, EWC ~81%). Consequently, the retention capacity has the same trend. Gels were loaded with appropriate amounts of nano-structured emulsions (NSE) containing cleaning agent (eco-friendly surfactant and/or organic solvents) and their performances tested after application on the surface of highly porous stone substrates Lecce stone (LS) and Arenaria stone (AS) used in historical buildings in Pavia and surroundings.

Different analytical techniques were used to investigate the performances of the cleaning tools: chromatic variations and contact angle measurements, optical microscopy, iodine vapour staining test, SEM-EDS, FTIR and micro-FTIR (in ATR mode). As shown in the SEM images taken on LS specimens (Figure 1), NSE-loaded synthetic gel (HEMA-MBA/PVP) was able to completely remove the aged polymer coating from the stone surface. Moreover, it needs only one cleaning step, while newly synthesized gel material (KG+PVA+PVP+SB) needs three cleaning steps for the same purpose. The gel prepared by KG with SB showed incomplete removing of aged polymer coating (after three cleaning steps) from the stone surface (Figure 1). The cleaning efficiency of different gel materials was quite similar (as Lecce stone) in the case of Arenaria stone, indicating that those cleaning tools can be used in both types of stones.

3. Conclusions

The experimental results suggested that NSE-loaded synthetic and modified natural gel materials can be used as promising cleaning tools for removing aged polymer coating from the stone artifacts. The synthetic gel (HEMA-MBA/PVP) showed the best performance in removing aged coatings from the surface of both LS and AS. The newly synthesized gel (KG+PVA+PVP+SB) also provided satisfactory cleaning results, although it requires more application cycles. Considering the sustainability of the conservation process, the bio-degradable konjac-based material should be considered, after all, more affordable for cleaning applications.

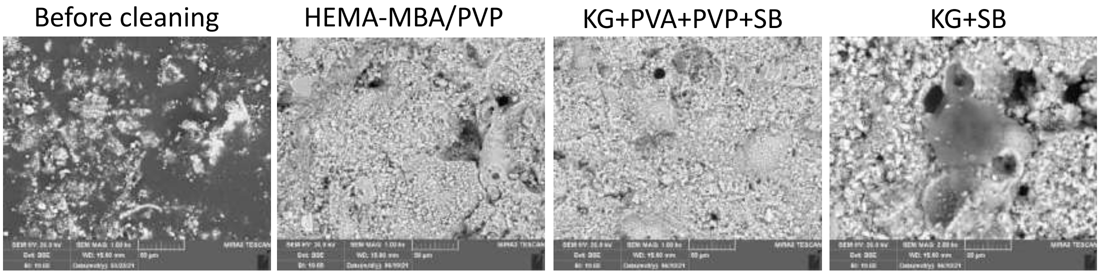
Before cleaning HEMA-MBA/PVP KG+PVA+PVP+SB KG+SB

Figure 1. SEM images of Lecce stone before and after cleaning by different gel materials

References

[1] M. L. Weththimuni, M. Licchelli, M. Malagodi, N. Rovella, M. La Russa, Measurement (2018) 127, pp. 396-405.
[2] P. Baglioni, R. Giorgi, Soft Matter (2006) 2, pp. 293-303.
[3] C. Lee, F. Volpi, G. Fiocco, M. L. Weththimuni, M. Licchelli, M. Malagodi, Materials (2022) 15, 1100, pp. 1-17.

HYDROPHOBIC MICROPARTICLES/HALLOYSITE NANOTUBES COMPOSITES: A VERSATILE MATERIAL FROM PICKERING EMULSION STRATEGY

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1. Introduction

Nowadays, Pickering emulsions are extensively employed in various applications due to their numerous advantages over surfactant stabilized droplets, such as low or no toxicity, ease of storage, low production costs, etc. In this regard, particles obtained from eco-sustainable sources have been employed for their design to satisfy the need for environmentally friendly materials. Among them, halloysite clay nanotubes can act as interracially active inorganic particles, and we recently proposed a protocol for the preparation of wax/halloysite based Pickering emulsions that can be used in a wide range of applications.

2. Results and Discussion

Microwax particles obtained from Pickering emulsions were embedded in halloysite-based geopolymers developing a new hybrid material with heat storage capacity and enhanced flexural performances [1,2]. The incorporation of microwax into the geopolymers was confirmed using various techniques, including thermal analyses, spectroscopies, microscopies, and contact angle experiments. The homogeneous dispersion within the geopolymeric network improved again the coating's physico-chemical properties by increasing the hydrophobicity. Furthermore, the Pickering emulsions were employed for the treatment of waterlogged wooden samples [2]. Compared to archaeological woods treated only with wax, the inclusion of nanotubes led to a notable enhancement in mechanical properties such as stiffness and flexural strength.

3. Conclusions

The discussed approaches suggest the development of wax/halloysite Pickering emulsions with versatile functions for both eco-friendly coatings and materials.

References

[1] Caruso M.R., Cavallaro G., Lazzara G., Milioto S. (2023). Materials Letters 333, 133567.
[2] Calvino M.M., Lisuzzo L., Cavallaro G., Lazzara G., Milioto S. (2022). Journal of Environmental Chemical Engineering 10, 108594.
[3] Lisuzzo L., Hueckel T., Cavallaro G., Sacanna S., Lazzara G. (2021). ACS Appl. Mater. Interfaces 13, 1651.

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Società Chimica Italiana
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Ambiente e Beni Culturali

OP38

A NEW USE OF FUNORI IN CULTURAL HERITAGE: PRELIMINARY THERMAL AND RHEOLOGICAL INVESTIGATIONS

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1. Introduction

The thermal properties and rheology of Funori, the polysaccharide derived from red algae *Gloiopeltis*, were investigated in this study. This polysaccharide is considerably used as an adhesive or thickening agent in several applications, especially in Japan, including the field of conservation of cultural heritage. It has been demonstrated how metal ions enhance funoran gelation with Ba^{2+} ions having a clearly higher gel-inducing effect [1]. For this reason, the aim of this work is to study the effects of the addition of $BaCl_2$ solutions at different molarities on 1% *w/w* Funori solutions studying the process of gelling kinetic at different temperatures, highly dependent both from the number of cations contained and cooling processes.

2.Results and Discussion

The samples were characterized by differential scanning calorimetry, dynamic rheometry and dynamic light scattering at different temperatures. $BaCl_2$ solutions exhibited a strong effect on the gelling formation: with enhancing salt concentration, storage modulus (G') and loss modulus (G'') increased in the selected concentration range (up to 0.2 M), but then gradually decreased with new additions in the salt content. Funori gelling kinetics at different molarities (0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.5 M) were measured at several temperatures (10, 12.5, 15, 20, 25 °C) for two hours: the gelling point is directly dependent by both concentration and temperature, reaching it first in time with enhancing concentration and decreasing temperature.

3. Conclusions

The addition of $BaCl_2$ and its relative sulfation remarkably affects Funori rheological properties. It does not gel without added ions, but it is able to form strong gels with a relatively high amount of inorganic cations. Decreasing temperature and enhancing concentration a strong gel is obtained. The good ability to form transparent and strong gels makes Funori a promising hydrocolloid for cultural heritage surface cleaning, especially in those cases where high temperatures must be avoided.

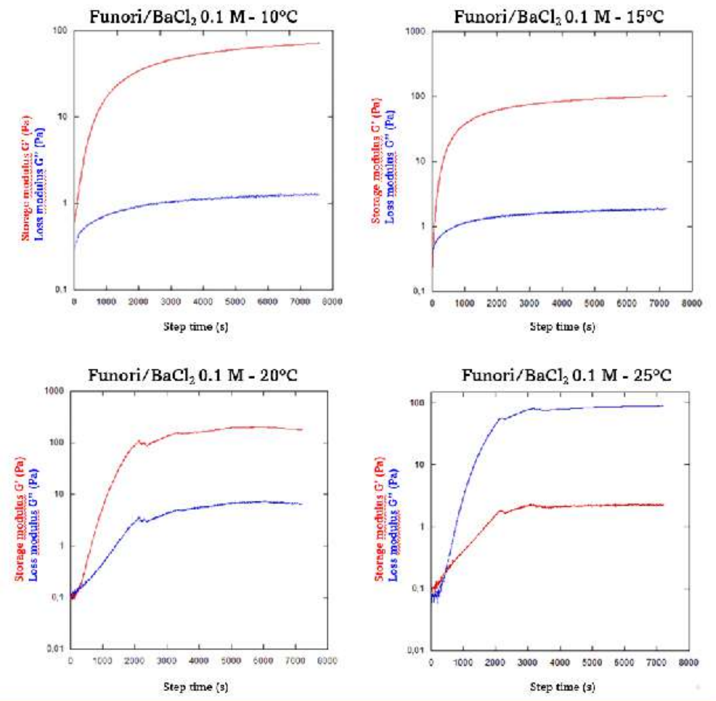

Figure 1. Gelling kinetics at different temperatures and concentrations

References

[1] Tuvikene, R.; Robal, M.; Mändar, H.; Fujita, D.; Saluri, K.; Truus, K.; Brenner, T.; Tashiro, Y.; Ogawa, H.; Matsukawa, S. Funorans from Gloiopeltis Species. Part II. Rheology and Thermal Properties. *Food Hydrocoll.* **2015**, *43*, 649–657.

PHOTOCATALYTIC DEGRADATION OF ACID ORANGE BY FE^0/ZNS AND EFFLUENT TOXICITY EFFECTS

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1. Introduction

Synthetic dyes have raised environmental concerns because of their contamination of water and soil, their toxicity and poor degradability. Azo dyes constitute about half of the dyestuff produced annually; due to their complex structures, they are recalcitrant to conventional wastewater treatment based on biological processes [1]. Acid Orange 7 (AO7) can be considered as a model molecule of many azo dyes. Zero valent iron (Fe^0) is an effective reducing reagent used for the treatment of several water pollutants, and its capability of removing AO7 molecules has been proved [1,2]. However, corrosion and loss of reactivity over time strongly reduce the practical use of Fe^0 in remediation processes. To overcome these limits, recently Fe^0 has been paired with a suitable semiconductor (ZnS), with high positive redox potential: when irradiated with UV light, ZnS provides electrons to reduce Fe^{2+} back to Fe^0, limiting the Fe^0 corrosion [3]. In this work, the removal of AO7 from water solutions using a Fe^0/ZnS composite was investigated. Additionally, ecotoxicity test was carried out on samples after the treatment, using *Artemia franciscana* as the target species.

2. Results and Discussion

For degradation experiments, 100 mL of AO7 solutions (20 mg/L) with a given amount of Fe^0/ZnS (0.25, 0.5, 1 or 2 g/L) were used. Suspensions were inserted in a 250 mL beaker and stirred for the entire duration of the test (160 minutes); samples were collected at regular intervals. The suspension was either irradiated with UV-A lights (365 nm) or kept under dark condition. Samples collected were centrifuged and AO7 residual concentration in the supernatant was monitored through UV-Vis spectroscopy, by following the intensity of its characteristic peak at 484 nm.

During the first minutes of the reaction, a rapid decolorization can be noted both under irradiated and non-irradiated condition, reaching a minimum after $\approx$ 10 minutes. During this phase, the Fe^0 causes the destruction of the azo dye chromophore through the cleavage of the -N=N- bond, and the subsequent decolorization [2]. The AO7 degradation improved with the increase of Fe^0/ZnS dosage, resulting equal to 55% (0.25 g/L), 85% (0.5 g/L), and 97% (1 g/L and 2 g/L) in irradiated condition, and 65% (0.25 g/L), 72% (0.5 g/L), 84% (1 g/L), and 97% (2 g/L) in dark condition, after 10 minutes of treatment (Figure 1A). Increasing the reaction time up to 160 minutes, a reduction of process efficiency could be observed for all catalyst concentrations except for 2 g/L. The overall degradation performance after 80 minutes is 24% (0.25 g/L), 49% (0.5 g/L), 90% (1 g/L) and 95% (2 g/L) in irradiated condition, and 28% (0.25 g/L), 35% (0.5 g/L), 68% (1 g/L) and 97% (2 g/L) in dark condition, reaching a plateau up to 160 minutes. Several explanation were proposed: (I) the first step of the reaction of AO7 with Fe^0 is reversible, and some of the unstable transitional compound returns to AO7 [2]; (II) the products of the AO7 degradation reacts together to form an imino compound similar in nature to AO7 [4]; (III) the further oxidation of the surface iron to Fe^{3+} causes the desorption of AO7 [5]. For all Fe^0/ZnS concentrations, irradiated conditions allow to achieve a more efficient degradation of the dye especially when longer times are considered, because of the ability of ZnS in the limitation of Fe^0 corrosion phenomena.

Ecotoxicity tests were carried out on samples from the experiments in irradiated condition collected after 10 or 160 minutes from the start of the tests, to monitor the toxicity of the sample after the treatment. The tests were carried out on *Artemia franciscana* nauplii, metanauplii, juvenile and adult according to standard methods [6] for assessing the mortality.

AO7 solution (20 mg/L) caused mortality (about 20-30%) in all life stages already at 6.25%, that was statistically significant respecting to control and all other concentrations. The mortality in all life stages at 100% solution involved all organisms. The treatment greatly reduces the toxicity of the starting AO7 solution for all *Artemia* stages, and in most cases, it can be considered residual toxicity due to the presence of Fe^0/ZnS (Figure 1B). However, it has been observed that the toxicity effect observed after 10 minutes of treatment is lower than the value after 160 minutes, considering the same concentrations of Fe^0/ZnS; thus, it can be concluded that the toxicity detected after 160 minutes of treatment was only partially related to due to the residual presence of Fe^0/ZnS.

3. Conclusions

The degradation of AO7 using a Fe^0/ZnS catalyst was investigated. A comparison between the results obtained under UV-A irradiated and dark conditions was carried out. Variable concentrations of Fe^0/ZnS (from 0.25 g/L to 2 g/L) allowed to reach a removal up to 97% of a AO7 solution of 20 mg/L, after 10 minutes of treatment. When longer treatment times were considered (up to 160 minutes), a reduction of process efficiency could be observed for all catalyst concentrations except for 2 g/L. UV-A processes allowed to achieve a more efficient degradation. Ecotoxicity test were also carried out to monitor the toxicity of the sample after the treatment, on *A. franciscana* specimens at various life stages. It was observed that the treatment greatly reduced the toxicity of the starting AO7 solution.

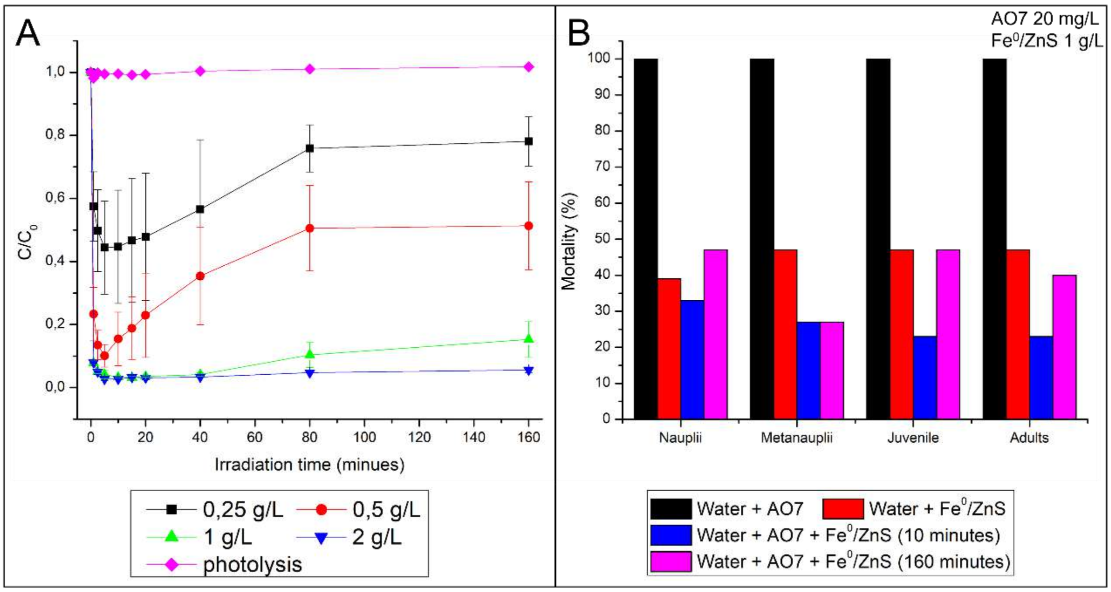

Figure 1 – A) Trend of AO7 concentration B) A. franciscana mortality in control and treated samples.

References

1. Zhang, Zhu, Zhang, Hu, 2012; J Environ Sci, 24, 1021-1026.
2. Cao, Wei, Huang, Wang, Han, 1999; Chemosphere, 38, 565-571.
3. Sacco, Vaiano, Navarra, Daniel, Pragliola, Venditto, 2021; Sep Purif Technol, 270, 118830.
4. Freyria, Bonelli, Sethi, Armandi, Belluso, Garrone, 2011; J Phys Chem C, 115, 24143-24152.
5. Freyria, Esposito, Armandi, Deorsola, Garrone, Bonelli, 2017; J Nanomater, 2017, 2749575.
6. APAT, ISRA, CNR, 2003; Metodi Analitici per le Acque, 3, 1043-1049.

OP40

GREYWATER TREATMENT AND DISINFECTION THROUG COMBINED FOAM FRACTIONATION AND PERSULFATE-IRON BASED FENTON PROCESS

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1. Introduction

Global water scarcity and increasing demand for freshwater have fuelled research into wastewater treatment for reuse[1]. Greywater (GW), from sources like showers and sinks, includes light (LGW) and dark (DGW) types, with lower contamination than municipal wastewater. GW composition varies by source, leading to differences in COD, BOD$_5$, total nitrogen (TN), total phosphorus (TP), and microbial content. Anionic surfactants, challenging to remove, pose environmental risks. Despite regulations, GW aligns with Agenda 2030's global wastewater reuse goals, requiring effective treatment methods[2].

Advanced oxidation processes (AOPs) like H_2O_2/Fe^{2+}, UV/H_2O_2, UV/$TiO_2/H_2O_2/Fe^{2+}$, and persulfate anion ($S_2O_8^{2-}$) show promise for organic and bacterial removal[3-5]. This study investigates real LGW treatment using foam fractionation (FF) as a primary method, with post-treatment Fenton processes (Fe^{2+}/H_2O_2 and $Fe^{2+}/S_2O_8^{2}$) to optimize contaminant removal for reuse. Factorial design and response surface methodology (RSM) were used to optimize parameters, ensuring efficient COD, surfactant, and bacteria removal.

2. Results and Discussion

In this study, the Fe^{2+}/H_2O_2 and $Fe^{2+}/S_2O_8^{2-}$ Fenton processes were optimized for LGW treatment using RSM analysis. Initially, the FF process was applied to synthetic LGW, showing significant removal of COD and TSU. Subsequently, Fenton processes were optimized through RSM to meet LGW reuse standards. ANOVA results validated the model assumptions, with perturbation plots revealing the effects of iron and oxidant concentrations and treatment time on COD and TSU removal. Fe^{2+} dosage had varying effects depending on the oxidant used, with Fe^{2+} positively influencing COD removal in the Fe^{2+}/H_2O_2 system but negatively in the $Fe^{2+}/S_2O_8^{2-}$ system. Three-dimensional response surfaces illustrated variable interactions.

The Fe^{2+}/H_2O_2 system achieved maximum removal efficiencies of approximately 72% for COD and 88% for TSU, while the $Fe^{2+}/S_2O_8^{2-}$ system achieved about 77% COD removal and 97% TSU removal. $S_2O_8^{2-}$ demonstrated higher removal rates than H_2O_2 for both COD and TSU. The optimal conditions were identified: for Fe^{2+}/H_2O_2, 50 mg/L Fe^{2+}, 157.6 mg/L H_2O_2, and 30 minutes of treatment; for $Fe^{2+}/S_2O_8^{2-}$, 12.5 mg/L Fe^{2+}, 185.6 mg/L $S_2O_8^{2-}$, and 30 minutes of treatment.

These conditions were applied to real LGW, resulting in slightly reduced COD and TSU concentrations. COD removal efficiencies decreased from 93% to 89% for $Fe^{2+}/S_2O_8^{2-}$ and from 88% to 78% for Fe^{2+}/H_2O_2, while TSU removal changed from 97.1% to 99.7% for $Fe^{2+}/S_2O_8^{2-}$ and from 88.2% to 96.6% for Fe^{2+}/H_2O_2.

The transition from synthetic to real LGW resulted in a slight decrease in COD and TSU concentrations. The COD removal efficiency decreased from 93% to 89% for $Fe^{2+}/S_2O_8^{2-}$ and from 88% to 78% for Fe^{2+}/H_2O_2. TSU removal changed from 97.1% to 99.7% for $Fe^{2+}/S_2O_8^{2-}$ and from 88.2% to 96.6% for Fe^{2+}/H_2O_2.

The optimized Fenton processes also achieved significant removals of BOD$_5$, TN, and TP. Fe^{2+}/H_2O_2 reached removals of 82% for BOD5, 86% for TN, and 80% for TP, while $Fe^{2+}/S_2O_8^{2-}$ reached removals of 93% for BOD$_5$, 79% for TN, and 70% for TP.

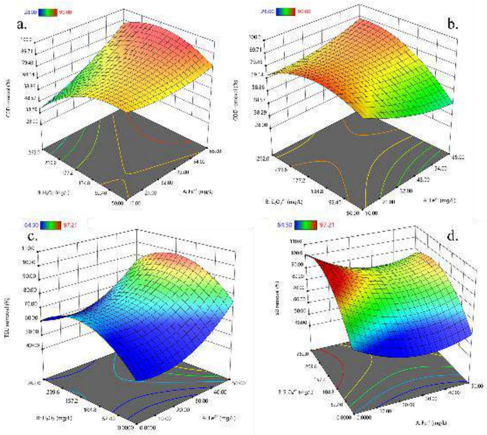
Sludge production was higher in the Fe^{2+}/H_2O_2 process (1.9 ± 0.3 mL/L) compared to the $Fe^{2+}/S_2O_8^{2-}$ process (0.4 ± 0.2 mL/L) due to different Fe^{2+} dosages. The $Fe^{2+}/S_2O_8^{2-}$ process showed higher removal efficiencies for organic matter and surfactants without significantly affecting sludge production.

For bacterial disinfection, the FF process achieved a bacterial removal of approximately 3 Log units for *Total coliforms (TC), E. coli, and P. aeruginosa*. Fe^{2+}/H_2O_2 achieved complete inactivation of *TC, E. coli, and P. aeruginosa* within 15 minutes, while $Fe^{2+}/S_2O_8^{2-}$ achieved complete inactivation within 10 minutes. Some bacterial regrowth was observed after FF, with minor regrowth between 24 and 72 hours. Fe^{2+}/H_2O_2 showed no regrowth for E. coli, minor regrowth of TC after 72 hours, and regrowth of P. aeruginosa at 48 and 72 hours. $Fe^{2+}/S_2O_8^{2-}$ also showed no regrowth for E. coli, minor regrowth of TC after 72 hours, and regrowth of P. aeruginosa at 48 and 72 hours.

Overall, the optimized $Fe^{2+}/S_2O_8^{2-}$ process demonstrated faster bacterial removal and disinfection kinetics compared to the Fe^{2+}/H_2O_2 process, with lower Fe2+ concentrations. $Fe^{2+}/S_2O_8^{2-}$ process shows promise for GW disinfection due to the effective activation of $S_2O_8^{2-}$ and generation of $SO_4^{\cdot -}$ radicals, even in the presence of organic matter, although further research is needed.

3. Conclusions

This study combines FF and $Fe^{2+}/S_2O_8^{2-}$ processes for efficient real GW treatment, achieving significant COD, TSU, and bacterial (*E. coli, P. aeruginosa, TC*) removals. FF attains 60-76% COD and TSU removal and over 50% bacterial reduction in 120 minutes. $Fe^{2+}/S_2O_8^{2-}$ outperforms Fe^{2+}/H_2O_2 with lower Fe^{2+} and higher removals, meeting strict reuse regulations and generating less sludge. Radical scavenging tests confirm $^{\cdot}OH$ and $SO_4^{\cdot -}$ radicals. A kinetic model fits data well. This sustainable technology has global potential but should address emerging contaminants and antibiotic-resistant bacteria for safe reuse.



Response plots for COD removal with H_2O_2 (a) and $S_2O_8^{2-}$ (b) as oxidant and TSU removal with H_2O_2 (c) and $S_2O_8^{2-}$ (d) as oxidant in 30 min of treatment time

References

1 P. Soriano-Molina, S. Miralles-Cuevas, I. Oller, J. L. García Sánchez and J. A. Sánchez Pérez, *Applied Catalysis B: Environmental*, 2021, **294**, 120251.

2 *I. N. Shaikh and M. M. Ahammed, Journal of Environmental Management, 2020,* ***261****, 110266.*

3 *A. Cibati, R. Gonzalez-Olmos, S. Rodriguez-Mozaz and G. Buttiglieri, Chemosphere, 2022,* ***290****, 133315.*

4 *A. Faggiano, M. Ricciardi, A. Fiorentino, R. Cucciniello, O. Motta, L. Rizzo and A. Proto, Separation and Purification Technology,* ***293****,121114.*

5 *A. Faggiano, M. Ricciardi, O. Motta, A. Fiorentino and A. Proto, Journal of Cleaner Production, 2023,* ***415****, 137792.*

OP41

COMPARISON EVALUATION OF TRIMETHOPRIM REMOVAL EFFICIENCY USING ADSORPTION AND ELECTRO-OXIDATION TECHNIQUES

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1. Introduction

Trimethoprim (TMP) is among the most widely used antibiotics worldwide. TMP is widely employed as feed additive in livestock industry. Since humans and animals can only metabolize about 20 % of TMP after ingestion, high amounts of this drug are excreted and detected in the aquatic ecosystems. Recently, various methods have been considered to treat TPM from water, including biodegradation, nanofiltration, reverse osmosis, adsorption, and advanced oxidation processes (AOPs), among others. Although these techniques have shown promising TMP removal efficiencies, some challenges still exist to select the best one, since all of them show both advantages and limitations. In this study we compared two of the most promising TMP removal techniques, such as adsorption and electrochemical oxidation (EO). The adsorption process of TMP was examined by investigating the use of two different adsorbents, such as a commercial activated carbon (F400) and a natural zeolite (NYT), and the impact of adsorbent dosage. For EO, the impacts of current density, electrolyte composition and concentration on the TMP removal were examined. Finally, the two techniques were compared in terms of treatment cost.

2. Results and Discussion

Fig. 1A shows that the rise in F400 initial dose consistently increased the TMP removal efficiency, achieving the highest value of 70.6 % when 50 mg of F400 were added. This result may be due to the microporous characteristics and the high surface area of F400 which implies the existence of a high number of available adsorption sites on the adsorbent[1]. However, the adsorption capacity decreased from 14.2 to 6.38 mg g^{-1} by increasing the adsorbent dosage. The outcome is likely due to phenomena of aggregation or overlapping of the adsorbent that occur at high F400 dosage, resulting in a reduction of the surface area available for TMP adsorption. Conversely, the NYT dosage displayed a less pronounced effect on the TMP removal. As illustrated in Fig. 1B, raising the initial amount of NYT a slight increase of TMP removal occurred. The adsorption capacity slightly decreased. This result may be ascribed to the low CEC of the NYT (1.90 meq g^{-1}), as well as to the weak electrostatic interaction between the negatively charged NYT-surface and the TMP molecules[2]. In aqueous media TMP is a weak base (pK_a of 7.3). Since the adsorption tests were carried out at pH of about 7, the TMP molecules are closed to their neutral form, so they cannot be strongly adsorbed to the negatively charged sites of NYT surface.

About EO, the degradation was higher operating with NaCl, rather than NaNO$_3$ (Fig. 2A). As broadly reported, the presence of Cl$^-$ in solution leads to the formation of strong chlorine reactive species (CRS) on the anode surface, which can degrade the TMP molecules through indirect EO [3]. As can be seen in Fig. 2B, the rate of TMP removal decreased as the concentration of NaCl increased from 0.04 M to 0.08 M. A rise of the electrolyte concentration, at constant current density, results in a decrease of the applied voltage. Thus, a corresponding drop in the anode potential may have caused a lower generation of CRS. Increasing the ionic strength of the solution may favor aggregation of antibiotics molecules, resulting in a lower sensitivity of the contaminants to EO. Moreover, high concentration of cations may substitute the H$^+$ of the acidic groups in organic contaminants, decreasing the effective hydrophobic surface area [4]. Fig. 2C exhibits that increasing current density from 40 to 120 A m^{-2} a significant rise of TMP removal was observed, likely because higher amounts of OH$^-$ and CRS species were generated in the system. Acting at 200 A m^{-2} no further increase in TMP removal was achieved, revealing a transition to mass transport-limited conditions, and a possible enhancement of parasitic reactions.

As shown in Fig. 3, the treatment cost of EO performed at 40 A m^{-2} with NaCl 0.04 M is comparable with the treatment cost of adsorption. EO operating costs are strongly influenced by configuration and scale of the reactor. For this reason, much attention and future investigations must be done to identify better operative conditions which can lead to more cost-effectively treatments. Although adsorption process demonstrated to successfully remove TMP, it simultaneously generates concentrated waste streams that need to be disposed of. Conversely, EO technology can mineralize the organic contaminants, producing H_2O and CO_2, which could be dispersed in atmosphere or capture and converted in valuable products [5].

3. Conclusions

Adsorption and EO were compared for TMP removal from water. The outcomes showed that the adsorption process using F400 produced better results than the use of zeolite. EO demonstrated to be also effective to remove TMP, and if Cl^- is present in decent concentrations it represents an energy and cost-saving strategy. Cost analysis indicates that adsorption is comparable with EO if the latter process is performed under low current density. In this case, EO is worth due to it does not produce any waste to dispose of. But EO may produce undesirable oxidation by-products that may have to be managed. In conclusion, the choice of right method will depend on a variety of factors, including the conditions of the wastewater, the desired level of TMP removal, the cost and availability of resources.

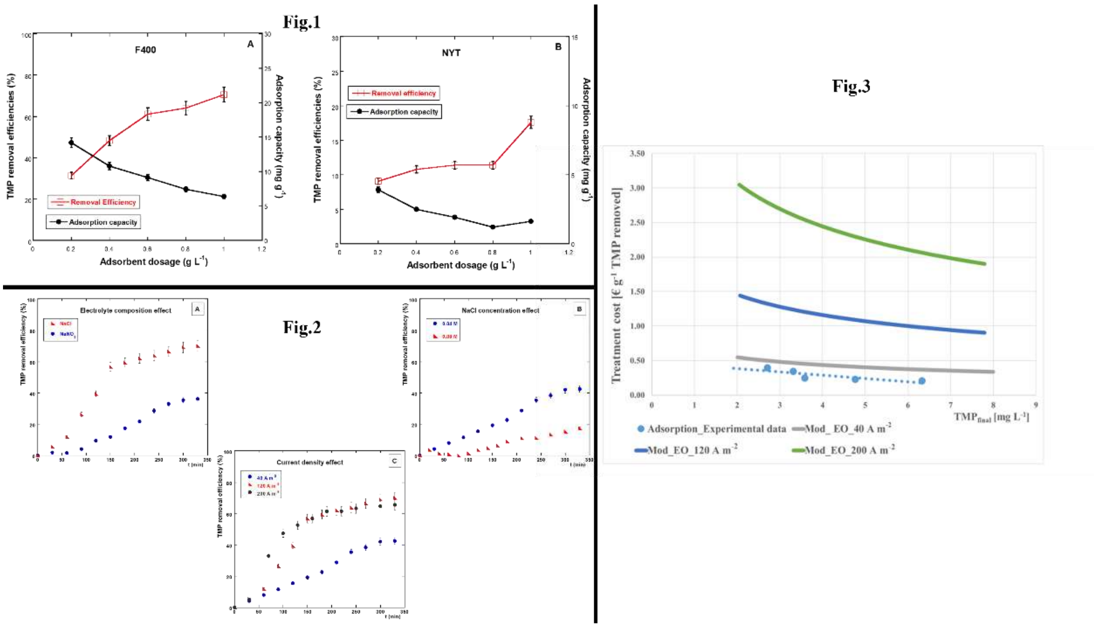

Fig: TMP Adsorption with test (1); TMP electro-oxidation test (2); Cost comparison assessment (3)

References

[1] Iovino et al. 2015, Chemical Engineering Journal, https://doi.org/10.1016/j.cej.2015.04.097
[2] Bekcy et al. 2006, JHZ; https://doi.org/10.1016/j.jhazmat.2005.10.029
[3] Abidi et al. 2022, Journal of Electroanalytical Chemistry, https://doi.org/10.1016/j.jelechem.2022.116584
[4] Li et al. 2017, Environmental Science and Pollution Research, https://doi.org/10.1007/s11356-017-9693-y
[5] Kah et al. 2021, Science of The Total Environment, https://doi.org/10.1016/j.scitotenv.2020.142770

OP42

ORGANIC MATTER, NUTRIENTS REMOVAL AND SLUDGE PRODUCTION MINIMIZATION IN LANDFILL LEACHATE TREATMENT BY FENTON PROCESS

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1. Introduction

Landfills have become a prevalent method for municipal waste disposal despite increasing recycling efforts. However, the generation of landfill leachate (LL) is concerning due to its potential to contaminate water sources. LL comprises wastewater from landfill moisture and rainwater. Its composition varies based on landfill factors like type, age, and temperature[1-2]. LL treatment involves physical-chemical, biological, and combined methods. Advanced oxidation processes (AOPs), generating highly reactive hydroxyl radicals (•OH), show promise in LL treatment[4]. The Fenton process uses H_2O_2 and Fe^{2+} to produce •OH but requires optimization for LL treatment[5-6]. This study focuses on optimizing Fenton treatment for mature LL to enhance pollutant removal, improve ratios like BOD_5:TN:TP, and reduce sludge production. The research employs a factorial design with response surface methodology to optimize H_2O_2 and Fe^{2+} doses while assessing key indicators like sludge-to-iron ratio (SIR) and organic removal-to-sludge ratio (ORSR). Overall, this study aims to refine the Fenton process for mature LL treatment, making it more efficient and environmentally friendly.

2. Results and Discussion

In this study, RSM coupled with a two-level factorial design was employed to optimize the operating conditions for the Fenton process. The perturbation plots and response surface plots revealed the effects of varying Fe^{2+} and H_2O_2 concentrations on the removal efficiencies of these parameters.

For COD removal, Fe^{2+} concentration had a slight positive effect, while H_2O_2 concentration had a strong negative effect. The oxidation effect generated by H_2O_2 seemed to prevail over the coagulation effect of Fe^{2+}. The maximum COD removal achieved was 72% at a Fe^{2+} concentration of 5000 mg/L and H_2O_2 concentration of 5000 mg/L. Similarly, BOD_5 removal was influenced by Fe^{2+} and H_2O_2 concentrations, with a maximum removal efficiency of 64% observed under the same conditions as COD removal.

Total nitrogen (TN) and total phosphorus (TP) removal efficiencies were also optimized using RSM. Fe^{2+} concentration showed a slight negative effect on TN removal, while H_2O_2 concentration had a positive effect. The maximum TN removal achieved was 98% at a Fe^{2+} concentration of 7000 mg/L and H_2O_2 concentration of 7000 mg/L. For TP removal, Fe^{2+} concentration had a strong negative effect until the midpoint, beyond which removal efficiencies worsened. H_2O_2 concentration had a strong positive effect, and the maximum TP removal achieved was 97% at a Fe^{2+} concentration of 3500 mg/L and H_2O_2 concentration of 7000 mg/L.

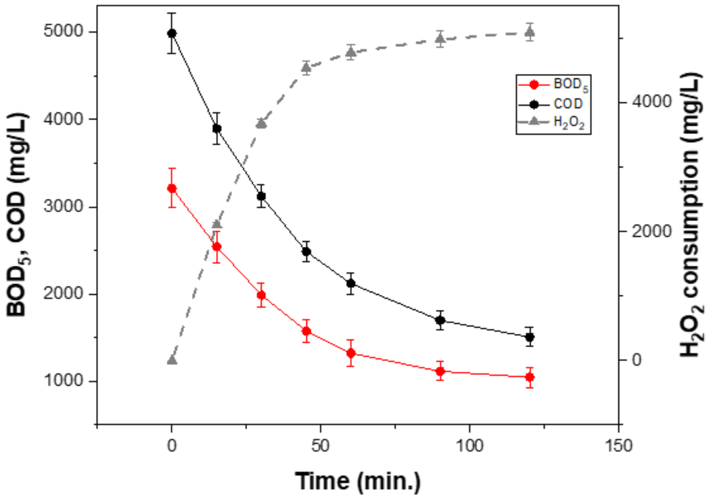
The effects of Fe^{2+} and H_2O_2 concentrations on sludge formation and organic matter removal were evaluated using the SIR and the ORSR. Both Fe^{2+} and H_2O_2 concentrations had negative effects on SIR, indicating reduced sludge formation at lower reagent concentration. Fe^{2+} and H_2O_2 concentrations had positive effects on ORSR, indicating enhanced organic matter removal at higher reagent doses. The optimization of the Fenton process showed that the highest removal efficiency and the lowest sludge generation were achieved in the same region, adjacent to the mid-levels of the factors.

According to RSM analysis, the optimized conditions for effective LL treatment using the Fenton process were Fe^{2+} concentration of 4262 mg/L and H_2O_2 concentration of 5104 mg/L (H_2O_2/Fe^{2+} molar ratio = 2). Three additional experiments were conducted to validate the models and optimization method. The optimized process achieved an average COD reduction of 70 ± 6% (final concentration: 1507 ± 112 mg/L) and an average BOD_5 reduction of 68 ± 8% (final concentration: 1047 ± 115 mg/L). The H_2O_2 consumption during the process was

97 ± 2%. Second-order kinetic models provided good fit for COD and BOD_5 reduction. TN and TP removal results confirmed oxidation followed by coagulation, with final concentration of TN equal to 61 ± 1 mg/L and TP equal to 12 ± 1 mg/L. The optimized process also achieved the desired BOD_5:TN:TP ratio for biological post-treatment (100:6:1). Fenton oxidation effectively reduced COD and BOD_5 before biological treatment. The process resulted in low sludge formation and high organic matter removal (SIR = 1.147 ± 0.06 L/mol, ORSR = 33.79 ± 2.2 g/L). The cost analysis showed that Fenton reagents accounted for the main costs, with total costs of \$22.22/m^3 of treated LL and \$6.39/kg of COD removed. Acidification and neutralization costs were relatively low. The results were comparable to other studies, emphasizing the importance of optimizing the Fenton process and minimizing sludge production to reduce overall costs.

3. Conclusions

This study evaluated the Fenton process for real LL treatment, focusing on organic matter and nutrient removal. It explored Fenton as a pre-treatment for biological processes. RSM analyzed H_2O_2 and Fe^{2+} dosages' effects on COD, BOD_5, TN, TP, SIR, and ORSR removal. Optimized conditions enhanced removal efficiencies and the BOD_5:TN:TP ratio, while minimizing sludge production. Ideal conditions were Fe^{2+} concentration of 4262 mg/L, H_2O_2 concentration of 5104 mg/L, and an H_2O_2/Fe^{2+} molar ratio of 2. This study showcases RSM's effectiveness in optimizing Fenton treatment, benefiting LL treatment economically and environmentally.



COD and BOD_5 removal kinetics of the Fenton process at the optimized conditions in LL treatment

References

1 *K. S. Rajoo, D. S. Karam, A. Ismail and A. Arifin, Environmental Nanotechnology, Monitoring & Management, 2020,* ***14****, 100372.*
2 *H. Luo, Y. Zeng, Y. Cheng, D. He and X. Pan, Science of The Total Environment, 2020,* ***703****, 135468*
3 *Y. Deng, Journal of Hazardous Materials, 2007,* ***146****, 334–340.*
4 *M. De Carluccio, A. Fiorentino and L. Rizzo, Journal of Environmental Chemical Engineering, 2020,* ***8****, 104444.*
5 *A. Faggiano, M. De Carluccio, F. Cerrato, C. A. Garcia Junior, A. Proto, A. Fiorentino and L. Rizzo, Journal of Environmental Management, 2023,* ***340****, 117950.*

OP43

ELECTRO-OXIDATION OF AMMONIA FROM LIVESTOCK FARM WASTEWATER (LWW): A PRELIMINARY INVESTIGATION

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1. Introduction

Recently, the huge population growth resulted in a higher worldwide food requirement. To address this need the number of livestock farms is drastically increased, causing water consumption and wastewater generation warming. These wastewater contain several contaminants, including high amount of nitrogen compounds, thus appropriate treatments are required before their discharge in water bodies. Excess of nitrogen in water causes environmental/health/social risks[1,2] such as eutrophication, risks of blood methemoglobinemia, and depletion of water quality, among others. So far various techniques have been developed to remove nitrogen compounds from wastewater such as physical, biological and chemical oxidation methods. Electrochemical oxidation (EO), belonging to the class of AOPs, is an innovative and promising method to treat nitrogen-impacted wastewater[3].

In this preliminary study, EO was used to remove total nitrogen (N_{TOT}) from a livestock wastewater (LWW) sampled in a farm located in Campania region. First, the effect of different electrode materials on N_{TOT} removal % was investigated by treating a synthetic sample. The optimized condition was adopted to treat the LWW.

2. Results and Discussion

EO experiments of the synthetic wastewater were performed at 25 °C in a lab-scale batch reactor of 0.250 L, by treating a 50 mg/L NH_4Cl solution, which contained an initial N_{TOT} concentration of 15 mg/L. The net treated working volume was 250 mL. The baseline experimental conditions were previously optimized by Iovino et al[4].The electrochemical apparatus consisted of two electrodes, with an active area of 50 cm^2 for each one and a gap of 1 cm. The electrodes were connected to a DC power supply BPS-305 (Lavolta, London, UK), allowing it to operate in amperostatic conditions. The effect of different type of anodes on the N_{TOT} removal % was investigated by operating with: 1) platinum coated titanium (Ti/Pt), 2) iridium/ ruthenium coated titanium (Ti/Ru-Ir), and 3) boron doped diamond (BDD). Consequently, the best anode type was used to perform a fourth EO by means of a stainless steel (SSL) cathode. NaCl with a concentration of 250 mg/L was used as electrolyte. The applied current intensity was 0.15 A and treatment time was 180 minutes. During, the second step, the optimized operative conditions, in terms of electrode materials, were adopted to treat the LWW. This real sample was collected from livestock farm located in Villa di Briano, CE, Campania, Italy (Fig.1a).

Fig. 1b shows the impact of the application of different electrode materials on the N_{TOT} removal efficiencies. As can be seen, the N_{TOT} degradation efficiency was roughly 0% (grey points), 64% (blue points), 79% (light-blue points), 96% (orange points), by operating with a pair of Ti/Pt, a pair of BDD, a pair of Ti/Ru-Ir, and with Ti/Ru-Ir as anode and SSL as cathode, respectively. Considering the first three experiments, the higher performances shown by the pair of Ti/Ru-Ir with respect to the pair of Ti/Pt and BDD is even clearer after only 60 min of treatment, where the maximum N_{TOT} removal was already reached. Although the mechanism of EO of nitrogen compounds removal from wastewater is complex, many researchers stated that the process takes place mainly through indirect oxidation by means of electrogenerated chlorine reactive species (CRS), in acidic conditions[5]. When NaCl is used as electrolyte, the generation of CRS (HClO, OCl^-, Cl_2) on the anode surface is obvious. The lower N_{TOT} degradation efficiency shown by BDD was due to the lower intrinsic capacity of *non-active* materials to generate *in-situ* CRS. The unexpected Ti/Pt inefficiency may be attributed to adsorption competition reactions between the nitrogen species, and oxidizing species on the anode surface, resulting in blocking effect of the active sites and hindering the oxidation efficiency of the anode. Finally, the highest N_{TOT}

removal achieved using Ti/Ru-Ir as anode and SSL as cathode may be ascribed to the high ability of SSL to produce H_2O_2, a weak oxidant that can be involved in the N_{TOT} degradation. Moreover, the SSL cathode allows to operate at lower applied voltages with respect to Ti/Ru-Ir, involving less undesirable side reactions and increasing the process efficiency.

Fig. 1C depict the results of the EO treatment performed on the LWW, by means of the optimized electrode configuration reported above. After 3 hours of treatment, about 67% of N_{TOT} degradation was obtained, implying the effectiveness of the technique in treating the real sample.

3. Conclusions

EO is an efficient process to remove nitrogen compound from wastewater. This study pointed out that the N_{TOT} removal is strongly affected by the material of the electrodes used. Ti/Ru-Ir, belonging to the class of *non-active* anodes, showed the highest N_{TOT} removal %, with respect to BDD and Ti/Pt electrodes. Indirect EO mediated by CRS may be the main degradation mechanism involved in the process. The soaring price of iridium hampers the spread of practical application of this material. So, the use of SSL as cathode material is a cost-friendly strategy, which allows to achieve even higher N_{TOT} degradation. Efficient treatments of livestock LWW constitutes crucial strategies to restore and reuse water in agriculture: a good circular economy practice.

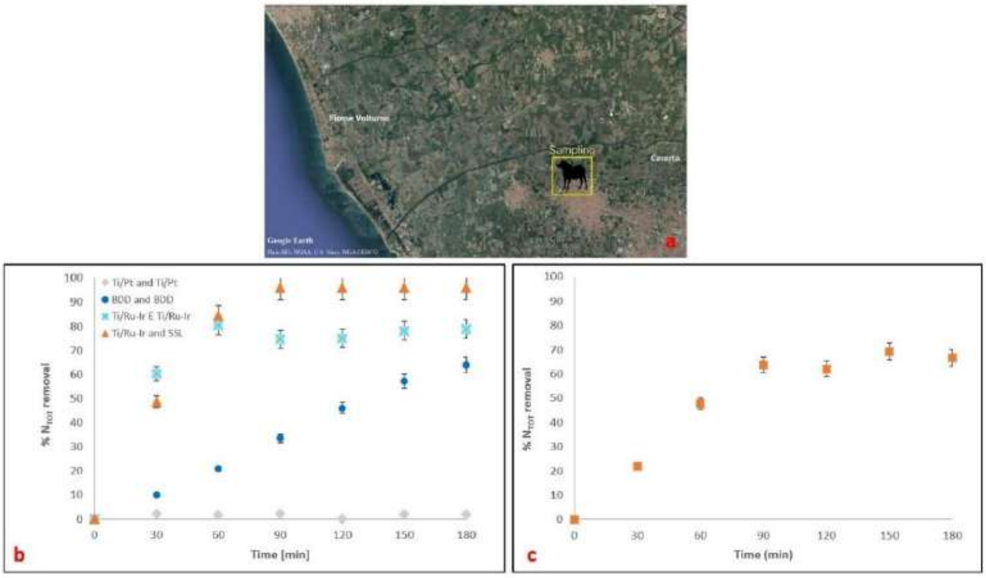

Fig. 1: a) LWW Sampling point; b) Effect of different electrodes materials on the N_{TOT} degradation; c) N_{TOT} Removal from the LWW using Ti/Ru-Ir anode and SSL cathode.

References

[1] Val H. Smith et al. 2009, Trends in Ecology & Evolution, https://doi.org/10.1016/j.tree.2008.11.009
[2] https://www.airc.it/cancro/informazioni-tumori/corretta-informazione/nitrati-acqua
[3] Kwang-Wook Kim et al. 2006, Water research, https://doi.org/10.1016/j.watres.2006.01.042
[4] Pasquale Iovino et al. 2023, Molecules, https://doi.org/10.3390/molecules28031306
[5] Xuwen He et al. 2012, Chemical Technology and Biotechnology, https://doi.org/10.1002/jctb.4006

Funding: *Financial support for this research was provided by the Campania Region, Regional Law 29 June 2021, n.5-DRD n.410/2021, action B, under Project "RiduciN"and National Recovery and Resilience Plan (PNRR) "Digital and Environmental Transitions", D.M. 351/2022.*

OP44

Fe-IDS: A BIOMASS-DERIVED CATALYST IN PHOTO FENTON-LIKE PROCESSES AT CIRCUMNEUTRAL PH FOR THE DEGRADATION OF SURFACTANTS

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1. Introduction

Surfactants are widely used in detergent formulations for personal care, household cleaning products, and in different types of industries such as textile, polymers, cosmetics, pharmaceuticals, and oil recovery. The removal of surfactants from urban and industrial effluents is essential because they would cause severe issues to the environment, including foam formation, eutrophication, and toxicity towards some aquatic organisms[1]. However, surfactants are very difficult to be removed using conventional treatment methods. Due to their persistence and their harmful effects, they have been classified as CECs (Contaminants of Emerging Concern)[2]. To remove ubiquitous CECs, in recent years advanced oxidation processes (AOPs) have drawn much attention. Among AOPs, photo-Fenton process ($UV/H_2O_2/Fe^{2+}$) can be considered the most promising technology. Despite its efficiency, however, the high energy consumption and the need to reach strongly acidic pH have limited its feasibility on most wastewater treatment plants so far. For this reason, researchers have been working on the development of new catalysts capable of activating H_2O_2 in photo-Fenton processes even at circumneutral pH[3].

2. Results and Discussion

Thus, in this study a new, green, and fully biodegradable complex, ferric iminodisucinate (Fe-IDS), has been tested for the first time herein as catalyst in (photo) Fenton-like processes for the degradation of surfactants belonging to different classes. Fe-IDS catalyst proved to be effective in the degradation of each tested surfactants (>75% COD removed). Given those results, the TOF[4] of Fe-IDS catalyst have been calculated. Furthermore, the faith of the catalyst has been investigated within the photo Fenton-like process. Moreover, Fe-IDS-supported photo Fenton-like processes were performed also under visible light irradiation, to evaluate the possibility to replace the more energy-demanding UV-C irradiation source for the degradation of Sodium Dodecyl Sulphate (SDS).

3. Conclusions

Fe-IDS catalyst proved to be effective in the activation of H_2O_2 in photo-Fenton processes at neutral pH for the degradation of each targeted surfactant. Even under visible irradiation a high degradation of SDS (85% in 5 hours) was achieved at expense of a slower kinetics compared to UV-C irradiation (>95% in 2 hours).

The catalyst itself has been proved that it undergoes to complete mineralization within the photo Fenton-like process.

References

1. F. Freeling, N. A: Alygizakis, P. C. von der Ohe, J. Slobodnik, P. Oswald, R. Aalizadeh, L. Cirka, N. S. Thomaidis, M. Scheurer, *Sci. Total Environ.* **2019**, 681, 475-487. https://doi.org/10.1016/j.scitotenv.2019.04.445
2. F. Motteran, M. B. Amancio Varesche, P. A: Lara-Martin, *Environ Sci Pollut Res.* **2022**, 29, 84946–84961. https://doi.org/10.1007/s11356-022-21819-1
3. P. Prete, A. Fiorentino, L. Rizzo, A. Proto, R. Cucciniello, *Curr. Opin. Green Sustain. Chem.* **2021**, 28, 100451. https://doi.org/10.1016/j.cogsc.2021.100451
4. P. Prete, A. Fiorentino, L. Rizzo, A. Proto, R. Cucciniello, *Catal. Today* **2022**, https://doi.org/10.1016/j.cattod.2022.08.006

OP45

UPTAKE AND PHOTOINDUCED DEGRADATION OF PHTHALIC ACID ESTERS (PAES) IN ULVA LACTUCA HIGHLIGHT ITS POTENTIAL APPLICATION IN ENVIRONMENTAL BIOREMEDIATION

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1. Introduction

Phthalic acid esters (PAEs) represent a growing threat to human health and ecosystems due to their ability to bioaccumulate in the tissues of living organisms, resulting in several detrimental effects (e.g., hormone balance disorders) [1]. Despite restrictions to the use of PAEs as additives, their concentration in environmental and food matrices will certainly continue to increase due to the use of plastic materials which contain this class of compounds.

In this regard, monitoring of the distribution of PAEs along the trophic chains is needed, together with the identification and optimization of innovative and eco-sustainable processes for their removal from environmental matrices.

Based on previous studies of other persistent organic pollutants, seaweed-mediated phytoconcentration could represent a sustainable bioremediation solution [2]. *Ulva lactuca*'s ability to uptake PAEs over time has been assessed by exposure to different concentrations of contaminated sediments under controlled conditions for 31 days. Once the uptake from contaminated sediments was verified, the efficacy of the photoinduced degradation of the PAEs accumulated in algal matrices was evaluated.

2. Results and Discussion

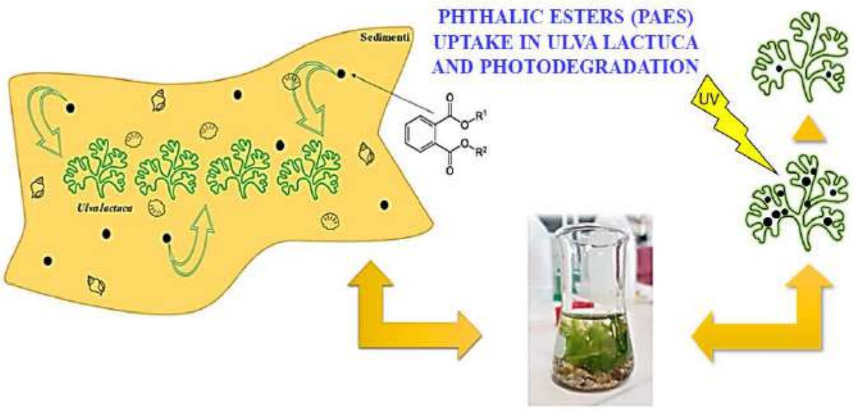
The experiment lasted 31 days and matrices of interest were analyzed at 5, 12 and 31 days. The analyses of the phthalic esters in both treated and control samples were carried out by gas chromatography coupled with mass spectrometry (GC-MS). Surprisingly, the highest concentrations of PAEs were found in algae exposed to sediments with the lowest analytes concentration. The control sediment also contained PAEs. During the experiments, the concentration of PAEs in the sediments showed a 95% decrease, whereas it showed a 14-fold increase in *U. lactuca*. Furthermore, this experiment recorded the highest values of the biota-sediment accumulation factor ($\log_{10}$BSAF). Similarly, the total PAEs in the sediments of the experiment at 5 ppm and 10 ppm showed a decrease of 53% and 64%, respectively. A high uptake rate by *U. lactuca* was recorded between the first and second day of sampling in microcosms where sediments were prepared at concentrations of 50 and 100 ppm. Instead, at the third sampling time, no increase in the concentrations of the six PAEs was observed in the algae. Indeed, between the second and third day of sampling, the total PAEs in the sediments did not change significantly for the experiment at 50 ppm, while they increased in the experiment at 100 ppm, probably due to the release of contaminants from the algal matrix to the sediments. It should be noted that in both microcosms all algal matrices died between the 2nd and 3rd day of sampling.

The danger of phthalates derives from their ability to interact with the organic components of cell membranes, depending on PAEs octanol-water partition coefficient (log K_{ow}) values. Consequently, algal matrices were richer in PAEs with the highest values of log K_{ow} and molecular weights (DEHP and DNOP). Considering the significant uptake of PAEs by algae, as recorded for all exposure levels, the first sampling point was chosen to perform photodegradation tests at different concentrations of PAEs (0, 10 and 100 ppm). In the control microcosms' seaweed, degradation of the six PAEs reached 26% after 30 minutes, 56% after 1.5 hours, and 75% after 8 hours of irradiation. In a similar manner, algae treated with 10 ppm showed increased degradation after 30 minutes, with total PAEs removal of 28%, while this percentage increased to 63% at 1.5 hours, and 79% after 8 h of irradiation. Algal matrices exposed to 100 ppm showed lower rates of PAE removal upon photodegradation. After 0.5 hours the total PAEs removal was 22%, reaching 55% at 1.5 hours and finally, after 8 hours of exposure to UV rays, 68%. In general, it was observed that a lower concentration of PAE in

U. lactuca corresponded to a higher efficiency of both accumulation (indicated by $\log_{10}$BSAF) and photodegradation (more than 70% removal of all phthalates in 8 hours).

3. Conclusions

These results, demonstrate the effective uptake capacity of *U. lactuca*, and related high rates of photodegradation at low PAEs concentrations (close to environmental ones). These results pave the way to future research in the development and optimization of environment-scale bioremediation processes. Furthermore, they suggest a potential use of algal matrices to mitigate the impact of ubiquitous pollutants such as PAEs and all those easily adsorbed and/or photosensitive. This approach could also form the basis of a virtuous cycle of reuse of algal biomass, where scientific research, development of green technologies and good practices in managing natural services play a fundamental role.



Ulva lactuca highlights its potential application in environmental bioremediation.

References

[1] Savoca, D., Arculeo, M., Vecchioni, L., Cambera, I., Visconti, G., Melfi, R., ... & Pace, A. (2021). Can phthalates move into the eggs of the loggerhead sea turtle Caretta caretta? The case of the nests on the Linosa Island in the Mediterranean Sea. *Marine Pollution Bulletin*, *168*, 112395.
[2] Cheney, D., Rajic, L., Sly, E., Meric, D., & Sheahan, T. (2014). Uptake of PCBs contained in marine sediments by the green macroalga Ulva rigida. Marine pollution bulletin, 88(1-2), 207-214.

OP46

LIGHT-INDUCED PHOTOREDUCTION OF Cr(VI) IN WASTEWATER BY VALUABLE BACTERIAL PIGMENTS

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1. Introduction

Cr(VI) is known to be a highly toxic, carcinogenic and non-biodegradable pollutant, that is massively used in different industrial processes and can be commonly found in industrial effluents. Different technologies have been investigated for Cr(VI) remediation and, in the last years, large interest has been demonstrated towards the photoreduction/photocatalysis of Cr(VI) species to environmentally friendly Cr(III) ions due to its efficiency, low cost and no dangerous chemicals production[1].

In this context, microbial biosynthesis processes constitute a cost effective and environmentally friendly alternative to produce biomolecules of technological interest[2,3].

This work shows new insight about UV-light driven photochemical degradation of fluorescent pigments produced by an Antarctic bacterium that, under UV-irradiation, was able to photo-reduce Cr(VI) to Cr(III), which is less toxic and easier to remove by precipitation. These pigments have been spectroscopically characterized and identified by HPLC-DAD-FLD and HPLC-MS-MS analyses. The Cr(VI) photoreduction and the pigments photo-oxidation were investigated by UV-Vis and photoluminescence spectroscopy, respectively.

2. Results and Discussion

A mix of fluorescent pigments, biosynthesized by an Antarctic salt tolerant *Pseudomonas* bacterium, were characterized as siderophores, that are typical bacterial metabolites produced during iron deficiency, due to their strong ability to chelate iron[4]. These biosynthesized pigments, in aqueous solution, showed a pale-yellow color and the pH was at around 6. The characterization by UV-Vis measurements showed the typical features of pyoverdine compounds with different spectral changes as function of the pH that can be attributed to the protonation and deprotonation of -OH groups of the dicarboxylic acid, and of the catecholate group present in the di-hydroxyquinoline structure, the fluorescent chromophore[4,5]. The fluorescence of the pigments solution changed as function of the pH showing different emission behavior at acidic, neutral and basic pHs.

Specific HPLC-DAD-FLD and HPLC-MS-MS methods were developed, and the best separation of the compounds was achieved by using the mobile phase: 90% (H_2O, 0.1% Formic acid) and 10% (MeOH, 0,1% Formic acid) with C-18 column; the DAD wavelengths were set at 306, 366 and 374 nm. The DAD chromatogram showed two main peaks at around 12 and 14 min, while the signal in FLD evidenced the high fluorescence of the compounds. The HPLC-MS/MS analysis allowed to detect the presence of three different pyoverdine molecules in the sample, in fact two pyoverdine coelute together, but by MS-spectrometer can be easily detected.

The properties of these pigments were therefore largely examined; in particular, the siderophores solutions were irradiated under UV-light and sunlight, and the ability to absorb photon was largely investigated and confirmed by UV-Vis spectral changes, demonstrating the photooxidation resulting in a fast degradation of the molecules.

The important perspective of the present finding was to use these pigments as potential photo-reducing molecules for the Cr(VI) under the presence of UV light. In that case, the mix of these pyoverdines was added to a synthetic contaminated Cr(VI) aqueous solution (15 ppm) and irradiated by UV-light (365nm). In these experimental conditions, Cr(VI) was present as $HCrO_4^-$ as the predominant form; a decrease in absorbance in the range between 350 and 400 nm during time, combined with diphenylcarbazide test[6] for the Cr(VI) detection, demonstrated the photodegradation/oxidation of the pyoverdines and the consequent reduction of Cr(VI) to Cr(III), confirming the ability of these molecules to photo-reduce the hexavalent form of chromium.

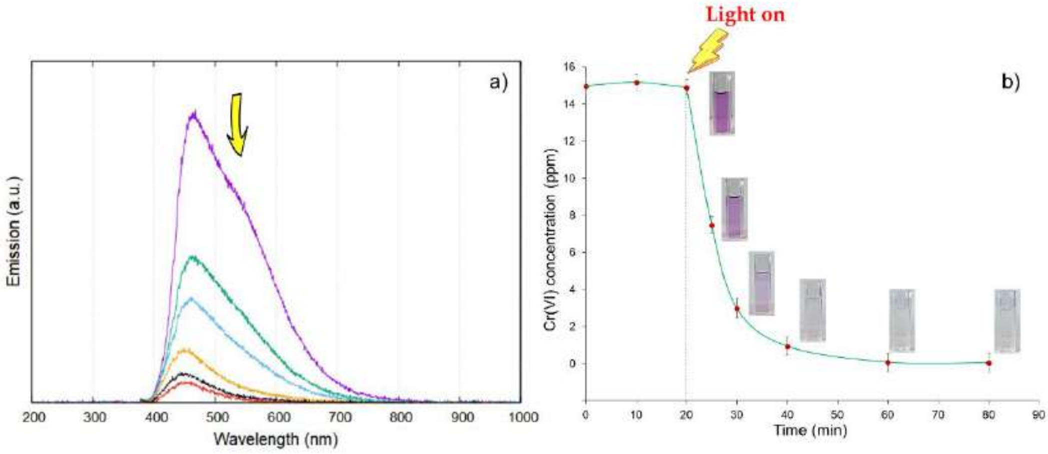
In addition, the further decrease of fluorescence demonstrated the pigment’s photooxidation; similar results were obtained when the same procedure was performed under natural sunlight exposure.

3. Conclusions

The present study investigated the features of a mix of bacterial pigments. A newer and green perspective has been reported regarding the use of these compounds that are able to perform the photoreduction of toxic Cr(VI) to Cr(III), with their complete photodegradation under UV-light or solar irradiation.

In fact, under UV-radiation or natural sunlight, a simple photocatalytic experiment revealed that very small quantities of these pigments are highly efficient for the quantitative reduction of Cr(VI) to Cr(III) in synthetic contaminated water containing 15 ppm of Cr(VI).

These results highlight the remarkable performance of these natural compounds and therefore represent a promising potential for purifying contaminated water resources.



a)Decrease of pyoverdines fluorescence under UV-light radiation; b) decrease of Cr(VI) (ppm) versus time.

References

1.E. T Anthony, N.A. Oladoja *Environ. Sci. Poll. Res.* 29 (2022) 8026-8053
2.Z. Roskova, R. Skarohlid, L. McGachy, *Sci. Total Environ. 819* (2022) 153144
3. M. Saha, S. Sarkar, B. Sarkar, B.K. Sharma, S. Bhattacharjee, P. Tribedi, *Environ. Sci. Pollut. Res.* 23 *(*2016) 3984-3999
4.H. Boukhalfa, S. D. Reilly, R. Michalczyk, S. Iyer, M. P. Neu *Inorg. Chem.*, 45 (2006) 45, 5607–5616
5.K. Rehm, V. Vollenweider, R. Kümmerli, L. Bigler *Anal. Bioanal. Chem. 414 (*2022) 2671-2685
6.S. M. Yousefi, F. Shemirani *J. Hazard. Mater*. 254-255 (2013) 134-140

INVESTIGATING THE EFFECTIVENESS OF CONSOLIDATION MATERIAL IN EARTHEN BUILDING HERITAGE

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1. Introduction

Earthen building materials have been used in various parts of the world throughout history. However, they are inherently vulnerable to degradation owing to environmental factors, and, therefore, the structural integrity and long-term durability of earthen structures are often compromised. This project investigated the effectiveness of silicate-based consolidants, specifically a nano-silica-based product, potassium silicate, and lithium silicates. Mock-ups miming an archaeological sample were subjected to treatment and comprehensive assessments. The effects due to the application of the consolidants were assessed considering possible chemical interactions with the clays (X-ray, ATR-FTIR, and Raman analyses) and the enhancement of the physical-mechanical properties. The latter were evaluated through water absorption measurements, surface abrasion and micro-drilling tests, and scratch tests. Furthermore, a preliminary sustainability assessment using open LCA software was conducted to assess the environmental impact and sustainable attributes of the consolidation materials.

2. Results and Discussion

The compositional analysis of the archaeological sample revealed its primary components as clay (70%), then sand (19%), straw (7.4%), and calcium carbonate (3.5%). Montmorillonite was identified as the predominant clay mineral present [1], and two sets of mock-ups were prepared using bentonite and sepiolite in addition to calcium carbonate, sand and straw in the same percentage present in the archaeological sample.

A commercial nano-silica-based consolidant (Nano Estel, CTS Italy), potassium silicate, and lithium silicate were applied with a SiO_2 concentration of 15% for the three consolidants. The study of a possible chemical reactivity of the consolidants with the earthen samples was initially performed by adding to the different clays (sepiolite and bentonite) the consolidants and comparing the XRD, ATR-FTIR and Raman spectra of the mixture with those of the single compounds. The X-ray diffraction showed slight variations in the clay, possibly related to changes in the silica patterns of the mixture, along with the formation of different silica phases following the curing period [2]. ATR-FTIR and Raman analysis indicated intensity and shape variations in different regions associated with stretching Si-O-Si and OH groups among the three products.

Colourimetric analysis, quantified through ΔE values before and after treatment, indicated noticeable chromatic modifications, detectable by the human eye ($\Delta E > 5$), except for lithium silicates on sepiolite. A general increase in L* and b* values indicated a lighting and yellowing effect after treatment [3].

Abrasion tests were conducted to evaluate the hardness of the post-treatment surface compared to untreated samples. Weight loss measurements were recorded at one-minute intervals over three total minutes. Nanosilica-based consolidant and lithium silicate exhibited lower weight losses compared to potassium silicate in bentonite, with losses of 0.8%, 0.9%, and 2%, respectively. Similar trends were observed with sepiolite samples, with weight losses of 0.4% for nano-silica, 0.8% for lithium silicate, and 0.3% for potassium silicate. Furthermore, the abrasion test, combined with the results obtained from the drilling test, provided insights into the ability of the consolidants to penetrate and homogenously distribute inside the samples. Capillary absorption tests demonstrated a moderate reduction in absorption for all the treated samples, resulting from decreased open porosity. The results were compared to the values of the untreated samples for accurate assessment [4].

The results were also evaluated alongside the findings obtained from the open Life Cycle Assessment (LCA) software to recommend the most ecologically sustainable product before and after application.

3. Conclusions

Nano-silica, potassium silicate, and lithium silicate as consolidants for earthen artifacts were investigated on laboratory specimens reproducing the composition of an archaeological sample, made of clay, sand, straw, and calcium carbonate, with montmorillonite as the primary clay mineral. Modifications on the treated samples were observed through XRD, ATR-FTIR, and Raman analysis with the use of silicate products and they suggest a chemical interaction with the sample materials. Noticeable chromatic changes were detected by colorimetric analysis, while abrasion and capillary absorption tests demonstrated better nano-silica-based consolidant and lithium silicate performance. The study provides valuable insights into the conservation and damage preservation of earthen heritage buildings.

References

1. A.S. Sheta1, A.M. Al-Omran1, A.M. Falatah1, et, International Conf. on Water Resources & Arid Environment (2004).
2. M. F. La Russa,N. Rovella,S. A. Ruffolo,et, *Archaeological and Anthropological Sciences* volume 11,4643–4652, 2019.
3. PanelIlaria Capasso [a], Abner Colella [b], Fabio Iucolano[c] Journal of Building Engineering volume 68, 2023, 106-124.
4. Kerstin Elert a, Fadwa Jroundi b, Cristina Benavides-Reyes c,et, Journal of Building Engineering Volume 50, 2022, 104-081.

OP48

NEW TREATMENT FOR THE CONSOLIDATION AND THE PROTECTION OF WOOL YARNS FROM A FLEMISH TAPESTRY OF THE XVITH CENTURY

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1. Introduction

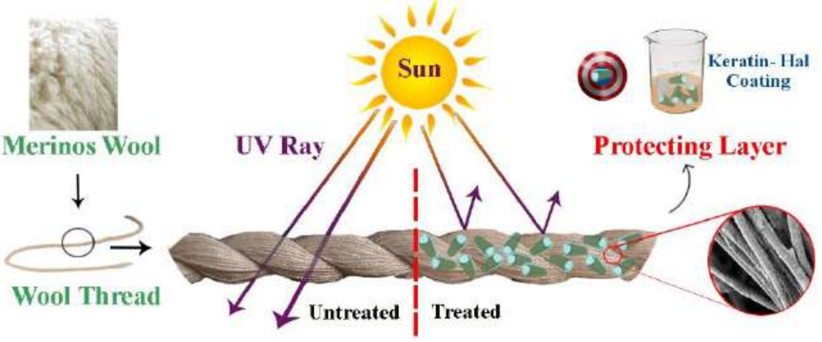
The degradation process of artwork on cultural heritage can be caused by environmental conditions, temperature, UV rays, and humidity, that accelerate the aging process by changing their chemical structure and starting biological attack, alteration, chemical modification, material loss, and interaction between different materials.

2. Results and Discussion

New sustainable material made with natural halloysite nanotubes and Keratin was studied for the protection and consolidation of artwork. This innovative green nanocomposite material was tested as a coating layer for the treatment of wool samples, keratin-based on cultural heritage. SEM and optical microscope analysis showed that treated samples were covered without creating any significant variations in the structural shape of the wool. The consolidation % effect of Hal/Keratin treatment was investigated by comparing treated samples at different concentrations of nanotubes with untreated samples. The amino acid cysteine, content on keratin, interacts with wool keratin and cross-links through disulphide bonds restoring wool degradation. After UV exposure of treated and untreated wool samples, the protective efficacy of Hal/Keratin treatment was investigated by mechanical analysis, and it was demonstrated an improvement of stress at breaking (average ca. 30%) and Young Modulus (average of ca. 58%) for treated samples related to the untreated wool sample. Hal/Keratin treatment ($R_{Hal:K}=0.5$) was applied to a wool historical yarn sample from a Flemish tapestry of the XVI century and analysing tensile properties of treated historical yarn compared to untreated sample, historical yarn acquired mechanical resistance after Hal/K treatment.

3. Conclusions

In conclusion, the application of Hal/Keratin dispersion on historical wool confirmed that is a promising consolidation and protective coating for wool samples. Keratin dispersion allows to create a film as a reinforcing coating for wool damaged, and halloysite nanotubes to enhance the mechanical resistance of wool sample.



Keratin/Hal consolidation and protection treatment

References

[1] Caruso, M.R.; Lisuzzo, L.; Cavallaro, G.; Mirto, G.; Milioto, S.; Lazzara, G. *Molecules*, **2022**, 27, 8450.
[2] Cavallaro, G.; Milioto, S.; Konnova, S., Fakhrullina, G.; Akhatova, F.; Lazzara, G.; Fakhrullin, R.; and Lvov, Y., *ACS Applied Materials & Interfaces*, **2020**, 12 (21), 24348-24362.
[3] Caruso, M.R.; Cavallaro, G.; Milioto, S.; Lazzara, G. *Applied Clay Science*, **2023**, Vol. 238, 106930, ISSN 0169-1317.

CONSERVATION OF WORLD WAR II AIRCRAFT HERITAGE: AN ASSESSMENT OF INNOVATIVE PROTECTIVE COATINGS THROUGH ACCELERATED AGEING TESTS

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1. Introduction

The PROCRAFT European project aims at developing conservation procedures for historical aircraft. In this framework, 3-mercapto-propyl-trimethoxysilane (PropS-SH) and Cutin coatings were tested as green alternatives to Paraloid B72 (PB72).

Two historical Al alloy (ca. 4 Cu, 0.6 Mg, 0.2 Si, wt.%) components were sampled: (i) One rolled fuselage plate retaining original paint with Zn and Ti pigments, and (ii) a wrought propeller blade with marine corrosion. Coupons from each one were investigated in uncoated, PB72-coated (benchmark), Cutin- or PropS-SH-coated conditions.

After documentation, the samples were artificially aged for a 20 days total under runoff conditions with synthetic acid rain (AR), to be followed by 14 days of climatic chamber ageing in the dark and under UV-A.

Documentation included weighting, profilometry, colorimetry, professional photography, 3-D digital microscopy, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), attenuated total reflectance Fourier transform infrared (ATR-FTIR) and Raman spectroscopies.

AR was analyzed by atomic emission spectroscopy (MP-AES) to measure metal release (Al for corroded and Zn for painted samples).

2. Results and Discussion

As regards metal release from corroded samples of the propeller blade, PB72 coating seems to lower the release of Al by almost an order of magnitude in respect to uncoated samples. Measuring Zn release from the painted samples proved less diagnostic, as Zn release from unprotected painted samples decreased and disappeared after the first dripping phases due to fast depletion by leaching.

Therefore, more attention was given to surface modifications in terms of chemical, topographic and mass changes. SEM-EDS proved particularly diagnostic: Unprotected corroded samples showed an increase in Al and Cu concentration, and a decrease in Ca, pointing to concretion dissolution. When these samples were protected with PB72, in addition to the C and O signals coming from the coating, low signals of Ca and Si from surface concretions were detected, as well as low Al signals coming from the substrate.

For unprotected painted samples, ageing led to an increase in Ti and Fe contribution on the surface, and a decrease in Zn (due to the higher solubility of Zn pigments). Instead, after ageing PB72-coated painted samples, the initial C and O signals coming from PB72 were modified by a higher contribution of Zn followed by Ti and S, pointing to the higher solubility of Zn compounds, and revealed the apparition of bubbling defects in the PB72 coating.

The aesthetic impact of the color change caused by coating and ageing was assessed by colorimetry and by processing professional registry images in ImageJ, considering only color changes above the relative standard deviation. For the corroded and painted uncoated samples, ageing caused a total color variation (ΔE) between 3 and 3.5.

Regarding PB72, coating created no significant difference in corroded and painted samples, as neither did PropS-SH coating on painted samples ($\Delta E < 1.7$). Even after ageing, these samples showed negligible color variations ($\Delta E < 3$).

Cutin application caused yellowing for both corroded and painted samples. Such color changes might be due to carotenoid impurities from the tomato source material for Cutin production. However, after ageing, samples coated with Cutin showed color variation always well within the acceptable threshold ($\Delta E \leq 5$), especially for painted samples.

Runoff ageing and testing is underway for samples coated with Cutin and PropS-SH, together with climatic chamber ageing of all samples. Metal release, SEM-EDS, color and mass variation evaluations, will allow to better understand the advantages and limitations of each protective coating.

3. Conclusions

Thus far, PropS-SH seems a good alternative to Paraloid B72. Cutin, due to its yellowish color contribution, does not seem recommendable yet for cultural heritage protection applications on white/silver metallic surfaces. Future improvements for the production of less-colored cutin polymer could solve this issue and enable its use as a naturally-sourced, non-hazardous alternative for heritage aluminium substrates, particularly when dark, heterogenous or exposed under irregular illumination conditions.

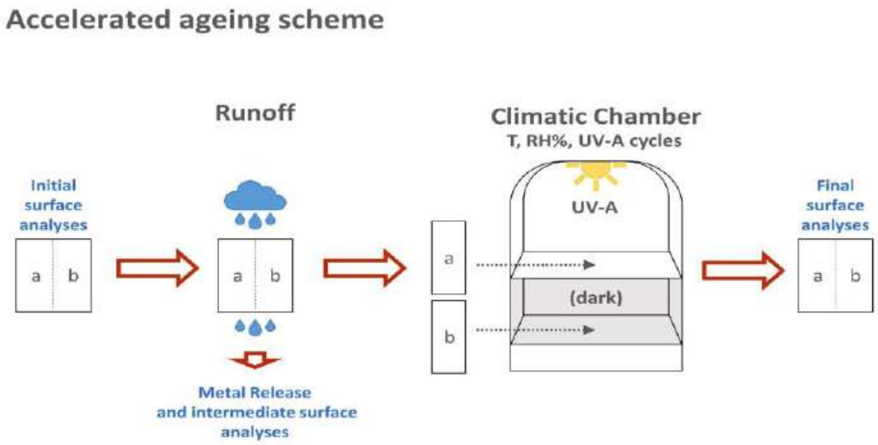

Fig 1.Artificial ageing scheme

References

1. Chiavari, C. *et al.* Organosilane coatings applied on bronze: Influence of UV radiation and thermal cycles on the protectiveness. *Prog. Org. Coat.* **82**, 91–100 (2015).
2. Benítez, J. J., Osbild, S., Guzman-Puyol, S., Heredia, A. & Heredia-Guerrero, J. A. Bio-Based Coatings for Food Metal Packaging Inspired in Biopolyester Plant Cutin. *Polymers* **12**, 942 (2020).
3. Corrosion of Aluminum and Aluminum Alloys. in *Corrosion: Materials* (eds. Cramer, S. D. & Covino, B. S.) 95–124 (ASM International, 2005).

OP50

JIN SHOFU STARCH NANOPARTICLES FOR THE CONSOLIDATION OF PAINT LAYERS

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1. Introduction

Matte and weakly bound paint layers represent nowadays a very difficult conservation challenge. These are typically found in modern and contemporary art since artists have used industrial paint formulations rich in additives and not conceived to last long. Paintings can exhibit fragile or powdering surfaces even before natural aging takes its course. Commonly used conservation practices lack satisfactory consolidants to target such demanding challenges. Traditionally, conservators apply natural and synthetic organic adhesives to re-adhere the powdering painted layers and strengthen the paint layers but these approaches prove detrimental as such materials can modify significantly the optical properties of the treated surfaces.

Alternatively, the development of tailored consolidants for art objects starting from renewable natural sources appears as a sustainable route, provided the new materials cope with specific requirements.

2. Results and Discussion

Starch is a promising candidate, being low-cost, renewable, and non-toxic. However, we expected that its effectiveness and applicability would be boosted if starch nanoparticles (SNPs), rather than the bulk polymer, were used. The reduced size of SNPs should allow efficient penetration inside the porous paint layers, avoiding the formation of thick surface coatings that provide only superficial consolidation and can alter the paintings’ appearance. Upon solvent evaporation, the particles are expected to form a homogeneous network through the paint section, and micro-junctions that strengthen the weak paint layers. The high surface-to-volume ratio of the SNPs is also expected to enhance the adhesivity of starch to the pigments, thanks to the great number of surface interactions via hydroxyl groups.

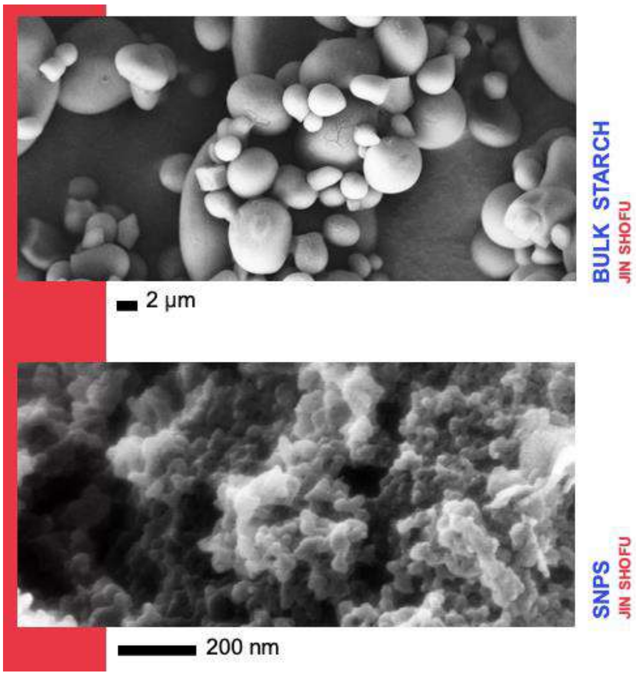
Acid hydrolysis is commonly used to obtain starch nanoparticles, as it removes the amorphous portion of the polymer ,but this method was not suitable for our purposes due to the high volumes of concentrated acid required, the low yield of the process (below 1 %), long preparation time (ca. 1 week), and high polydispersity of the obtained particles. Alternatively, a bottom-up method based on the dissolution of starch in alkali and the precipitation of the gelatinized polymer in a non-solvent (ethanol), was considered a promising approach being simple, robust, time-effective, and able to produce nanoparticles with desired size. Here, we changed and optimized this method, and selected “Jin Shofu” (an easily accessible gluten-removed and purified wheat starch) as the starting bulk material. The dry Jin Shofu Starch NanoParticles (SNPs) were analyzed by means of FTIR, XRD and DSC, before their re-dispersion and application. The obtained dispersions were also investigated to determine their stability. Ethanol was also considered, blended with water, to redisperse the SNPs. Even though its non-solvent character towards starch promotes some aggregation of the particles, the presence of ethanol in the dispersing medium favours the possibility to apply SNPs onto water-sensitive paint layers, which are frequently found in art conservation. Besides, this solvent is a good choice as a particle carrier, as it provides a good balance between surface wettability, volatility and low toxicity.

The amount of pigment removal from the mock-up surface, before and after the application of the SNPs dispersions, was determined. This value was semi-quantitatively measured by using an in-house micro-sampling protocol based on the controlled-contact and pigment-sampling by using a fiberglass filter (1 cm^2), that allowed us overcoming the limitations of traditional scotch tape and cotton swab tests. When no consolidation treatment is carried out on the paint, the average pigment coverage of the filter is ca. 44%, which is cut down to 1.5-3% when the paint layer is strengthened with the SNPs. This indicates that the starch particles effectively provided re-cohesion of the loose pigment grains, as both the water-ethanol and water dispersions proved highly beneficial; the latter is even more effective, consistently with the more complete particles’ penetration observed through the paint cross-sections.

3. Conclusions

Jin Shofu starch nanoparticles (SNPs) were obtained through an optimized bottom-up approach based on alkali dissolution and non-solvent precipitation. This method was applied, to our knowledge, for the first time for the consolidation of fragile, poorly bound paint layers. Our synthetic approach is robust and reliable (yield ≥ 97%), does not use additives potentially harmful to the paints, and can be tuned to obtain globular particles with different size distributions.

Testing of the newly developed formulation was applied to fragile, matte ultramarine blue paint layers, simulating the commonly found conservation issues of Edward Munch's works, which suffer from an extreme deterioration because of artistic experimentation and debatable handling and storage habits of the artist.



SNPs nanoprecipitation in ethanol

References

1. Casini, A.; Chelazzi, D.; Giorgi, R., Jin Shofu Starch Nanoparticles for the Consolidation of Modern Paintings, ACS Appl. Mater. Interfaces 2021, 13, 31, 37924–37936.
2. Gohde Sandbakken, E.; Storevik Tveit, E. Preserving a Master: Edvard Munch and His Painted Sketches; Vol.5, 2012, https://doi.org/10.14456/JUCR.2012.7.
3. Le Corre, D.; Bras, J.; Dufresne, A. Starch Nanoparticles: A Review. Biomacromolecules 2010, 11 (5), 1139–1153.
4. Gutiérrez, G.; Morán, D.; Marefati, A.; Purhagen, J.; Rayner, M.; Matos, M. Synthesis of Controlled Size Starch Nanoparticles (SNPs). Carbohydrate Polymers 2020, 250, 116938.

OP51

INVESTIGATION AND FORMULATION OF SUSTAINABLE PROTECTIVE COATINGS FOR OUTDOOR BRONZE ARTWORKS

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1. Introduction

Bronze outdoor statues are usually perceived covered by a patina resulting from their exposition to the environment. This patina has an important aesthetic and passivation role on the surface; however, it does not hamper the degradation processes promoted by external agents such as pollution, UV rays and relative humidity.[1] In these circumstances, it is important to find a suitable method to slow down these unwanted processes. The most employed protection methods are coatings. The most used ones, as waxes and Incralac®, have significant drawbacks: waxes' lifetime is short and their application is not reversible, while Incralac® is formulated with benzotriazole that is suspect of being cancerogenic. [2][3] Here it is described a multi-analytical study of the intrinsic properties of new types of coatings containing a combination of a corrosion inhibitor, a light stabiliser and an acrylic resin applied in solution with a non-toxic solvent. The approach we have used in this research is meant to identify the most light-stable coatings and then proceed in a subsequent phase to an in-depth study of their inhibition efficiency by applying them on the surface of patinated bronze mock ups.

2. Results and Discussion

This research focused on the study of several coating formulations composed of Paraloid® B44, (ethyl acrylate/methyl methacrylate copolymer) with different percentages of corrosion inhibitors, AEDTA (2-amino-5-ethyl 1,3,4 thiadiazole) and MPT (5-mercapto-1-phenyltetrazole), light stabilisers Tinuvin®312 and Tinuvin®5050, in solution with a green solvent, 1-methoxy-2-propanol. The obtained solutions were first applied on inert supports to study the coatings' light stability. They were artificially aged in a UV chamber for one thousand hours and they were regularly monitored by means of FTIR analyses in ATR mode and colorimetric measurements. At the beginning and at the end of the ageing process DSC analyses, double-shot py-GC/MS and determination of the insoluble fraction were performed. The multi-analytical approach allowed the study of the intrinsic properties of the coatings and of their single components: the outcomes suggested that AEDTA, MPT and the light stabilisers have a different behaviour under UV stressing. For what concerns corrosion inhibitors, the coatings containing AEDTA do not change colour over time whereas the ones with MPT yellows at the very beginning of the artificial ageing. Photostability was studied by means of FTIR and py-GC/MS analyses in double-shot mode. By monitoring the characteristic IR absorption peaks of both corrosion inhibitors, it was outlined that they do not last over time inside the coatings; however, py-GC/MS analyses pointed out a different behaviour: AEDTA is stable as its structure is unaltered after UV exposure while MPT showed degradation products after 1000h of ageing. The difference of glass transition temperature between unaged and aged samples highlighted that both the corrosion inhibitors are prone to embrittle the coating but with the addition of light stabilisers this drawback is reduced. The insoluble fraction is decreased as well by the addition of the two light stabilizers. This suggested that UV stabilizers are needed also to improve mechanical properties of the coatings. As a matter of fact, py-GC/MS unveiled that Tinuvin ® 312 is more stable than Tinuvin ® 5050: after ageing, the structure of the first one is unaltered while the latter is not present anymore. To further study the permanence of corrosion inhibitors in the coating during ageing, bronze mock ups were employed. Four types of coatings were selected and applied by brush. In addition to the all-in-one monolayer coatings, multilayer coatings were also prepared by dipping bronze mock ups in a solution of corrosion inhibitors and subsequently applying a film of Paraloid ® B44 by brush. They were aged at the same conditions of the previous samples and monitored through µFTIR in reflection mode and colorimetry; py-

GC/MS analyses were performed at time zero and after 1000h of ageing. Considering AEDTA, the two-step application gave worse results both from the photostability and from the colorimetric points of view; moreover, the inhibitor was clearly unevenly distributed. Even though MPT did not leave the coating and was homogeneously distributed, the change of colour was unacceptable. The all-in-one coatings containing AEDTA provided better results in terms of AEDTA distribution and permanence in the coating.

3. Conclusions

This research highlighted the major advantages and the drawbacks of multicomponent coatings and their single components, together with the most appropriate type of application. It was found out that AEDTA performs better than MPT: it does not change colour over time, it interacts preferably with the bronze surface and it is photochemically stable even if FTIR analyses show that is partially lost over time. It was demonstrated that the light stabilisers are needed for improving the mechanical properties of coatings, however Tinuvin ® 5050 is not stable after ageing, so Tinuvin ® 312 is the preferred one. Considering all the results and the application on bronze mock ups, a type of coating containing AEDTA and Tinuvin ® 312 was selected for further studies on anti-corrosive properties.

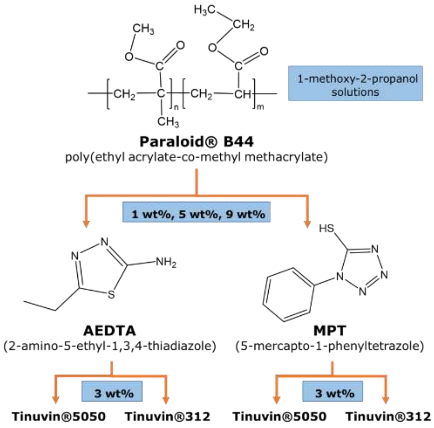

Fig.1 Composition of the formulated coatings

References

[1] A. Artesani, F. Di Turo, M. Zucchelli, and A. Traviglia, “Recent Advances in Protective Coatings for Cultural,” *Coatings*, vol. 10, no. 217, 2020.
[2] D. Mikić and H. Otmačić Ćurković, “Protection of Patinated Bronze with Long-Chain Phosphonic Acid/Organic Coating Combined System,” *Materials (Basel).*, vol. 16, no. 4, 2023.
[3] P. Letardi, “Testing new coatings for outdoor bronze monuments: A methodological overview,” *Coatings*, vol. 11, no. 2, pp. 1–16, 2021

OP52

PROPOSAL FOR A REMEDIATION METHOD FOR THE “VINEGAR SYNDROME” IN CELLULOSE ACETATE-BASED MOTION PICTURE FILMS

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1. Introduction

Motion picture films made of cellulose triacetate (CTA) are subjected to chemical degradation mainly due to the “vinegar syndrome”. It concerns the cleavage of the ester bonds between the acetate group and the cellulose chain through ester hydrolysis (deacetylation), with the formation of hydroxyl groups and the release of acetic acid [1,2]. It is strictly influenced by temperature, moisture and acidity: the released acetic acid acts as a catalyst for the reaction and induces an autocatalytic process. By-products of deacetylation can promote, also, the hydrolysis of the glycosidic bonds of the cellulosic backbone [3]. In addition to the smell, the deformation of the support and the detachment of the emulsion layer are the main macroscopic symptoms of this phenomenon and can strictly compromise the usability of the films [3,4]. On these bases, reducing environmental moisture and removing alteration by-products from the storing environment is mandatory to limit this degradation process. The most important goal of this project is to set-up up an innovative chemical approach to inhibit and/or prevent the vinegar syndrome through the use of soft matter and nanotechnologies.

2. Results and Discussion

The efficacy of various treatments based on sponge-like systems and metal oxide nanoparticles are evaluated by characterizing samples of motion picture films made of cellulose acetate on which the vinegar syndrome has been artificially induced. The idea was to set up systems able to neutralize acetic acid, which acts as a catalyst for the deacetylation reaction, and also as an alkaline reserve to prevent further degradation

Samples have been characterized before and after the aging, within and without the treatment, by different techniques. The decrease in the acetyl content has been monitored by Fourier Transform Infrared - Attenuated Total Reflected Spectroscopy (FTIR-ATR) in a non-destructive and non-invasive way: the ratio between the intensity of a peak associated with the acetyl group and the intensity of a reference peak, assuming that it does not vary during the aging, was calculated [5,6]. These data are validated by titration and free acidity tests [7]. In addition, the variation in mechanical and thermal properties was evaluated by Tensile Tests and Thermogravimetric Analysis (TGA).

In artificially aged samples, it has been possible to appreciate a decrease in the acetyl content, confirmed by both the titration tests and the spectroscopic data, an increase of the free acidity (which corresponds to the non-esterified acetic acid produced and adsorbed by the CTA film). These results prove that the deacetylation process has been induced on untreated cellulose acetate-based films. On the other hand, treaded samples showed an important slowdown in deacetylation, probably due to the neutralization of acetic acid due to the treatment: deacetylation content did not sensibly vary and the free acidity decreased during the aging.

Tensile strength measurements showed a decrease in Young's modulus up to the breaking in most degraded samples, compared to the starting polymer. This behavior may be due to various factors, such as the lowering of the average molecular weight of the polymer chains and the loss of plasticizers. By comparing the data obtained from untreated samples with those from treated samples, the decrease in Young’s Modulus appears less pronounced in the latter.

Also, from the DTG measurements, it is possible to observe a decrease in the pyrolysis temperature and a widening of this peak in the most aged, untreated samples [8]. On the contrary, in the treated samples, the temperature of degradation does not significantly change during aging. Therefore, is possible to hypothesize that, in the treated samples, the depolymerization process does not significantly occur.

3. Conclusions

In conclusion, through the use of a multi-analytical protocol, it has been possible to evaluate the efficacy of some treatments based on nanotechnologies and soft matter for the inhibition of the vinegar syndrome, which has been artificially induced on cellulose acetate-based motion picture films.

References

[1] N. S. Allen, M. Edge et al., Pol. Degrad. Stab., 1987, 19, 379.
[2] M. McGath, S. Jordan-Mowery et al., Restaur, 2015, 36, 333.
[3] J. Reilly, “IPI Storage Guide for Acetate Film”, Image Permanence Institute, 1993.
[4] P. Z. Adelstein et al., SMPTE J., 1992, 101, 336.
[5] P. Fei et al., Anal. Methods, 2017, 9, 6194.
[6] S. Nunes et al., Herit Sci, 2020, 8, 33.
[7] ASTM D871-96 (2004) Standard test methods of testing cellulose acetate (procedure B)
[8] Zhou, X. et al., Cellulose, 2016, 23, 811.

OP53

PRELIMINARY STUDY ON CONSOLIDATING PROPERTIES OF A MICROALGAE EXTRACT CALLED NYMPHA ON PAPER

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1. Introduction

During the last decades, the field of conservation faced the instance of finding alternative product and solution that are non-toxic and eco-friendly both for environment and human health with particular attention on product extracted from natural substrates [1].

In this paper we will discuss the properties of NYMPHA [2], a new polysaccharide product extracted from microalgae, to preliminarily evaluate its consolidating properties both for degraded paper supports and for fragile pictorial films on paper support. Two types of paper were used as test: a commercial type and a pure cellulose (whatman®), both in baseline condition and artificially aged by nitric acid immersion to provoke depolymerisation. Further samples of strongly unbound pigment layers were prepared for film consolidation tests with different pigments and binders.

Samples have been investigated by color measurements (spectrocolorimetry), microscope observation, scanning electron microscope (SEM-EDS) analysis and measurement of mechanical strength.

Results has been compared to those obtained with traditional consolidant products used in paper conservation such as crystalline nanocellulose (CNC), Klucel G and Funori.

2. Results and Discussion

Inspired from the experience with Funori [3], a product from seaweed that has been widely used by restores in consolidation practices for degraded paper and pictorial films, the project NYMPHA (Natural polysaccharides from Microalgae for the Protection of Cultural Heritage[4]) tested a new polysaccharide extract from microalgae. This work provides preliminarily results on the use of NYMPHA as consolidant in paper conservation issues and it is part of a bigger research project that involved several partners (Sapienza University of Rome, CNR crystallography institute and ICR) and it investigates properties of NYMPHA for the conservation and protection of different materials (paper, wood, stone). In this work we will discuss the consolidating capacity of NYMPHA on paper itself as well as on painting layers applied on paper.

To test paper consolidating properties, two different types of paper were investigated and the samples were obtained from commercial paper (plain paper, 100g) and pure cellulose paper (whatman®). First, the samples of paper underneath to a depolymerisation process by immersion in nitric acid to induce a hard- ageing artificial process. In order to establish the proper time of immersion we decided to conduct a series of preliminarily test to gain a reduction about 50% in mechanical strength. Results showed 6 days as minimum time required.

After that, the samples were treated with solutions of Klucel G 1% (w/V) in water, crystalline nanocellulose (CNC) 1 % (w/V) in hydro-alcoholic solution and NYMPHA 1% (w/V) in water.

Spectrocolorimetric measurements showed that ΔE values measured on the surfaces, before and after treatment with of all the product tested, were in the 0,7-1,7 range for the industrial paper and 0,2-0,7 range for whatman® paper so we can affirm that none of the product seemed to significantly alter the superficial color of the surfaces.

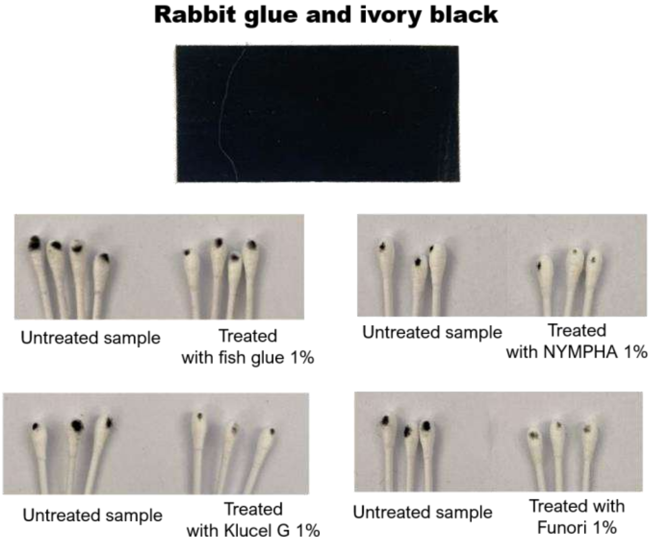
Scanning electron microscope (SEM_EDS) observation of samples before and after treatment, showed that CNC formed a superficial thin film that partially covered the fiber texture, which does not occur in samples treated with NYMPHA.

Mechanical strength increased more remarkably in depolymerized industrial paper samples treated with NYMPHA compared to CNC treated ones; industrial paper samples treated with Klucel G showed not completely clear results. Regarding whatman® paper samples mechanical strength, further investigation must be done due to controversial results obtained.

As far as the study of consolidating properties of loose paint layers, test samples were prepared with a white and a black paint film in a very diluted binder (rabbit glue and gauche binds). Before and after treatment with NYMPHA and other products tested, to evaluate consolidating properties a mechanical swab test was applied on black paint film, with a low-medium pressure, to evaluate the pigment loss. Test revealed interesting result on NYMPHA that showed a good consolidating capacity compared to common product used in painting on paper conservation treatment (fish glue, Klucel G, Funori). The ΔE values has been evaluated before and after application and they were largely below (ranging 0,8-1,6) the critical parameter (~5) so the product didn't affect significantly the color of the surfaces.

3. Conclusions

The results obtained on NYMPHA are encouraging: this product does not interfere with superficial color, it increases the mechanical properties of paper but does not form a thick layer on the surface that could interfere with the appearance of the artwork. NYMPHA also provided satisfactory results on consolidating properties on unbound painting layers on paper. In addition, it is completely safe both for the environment and the operator. While further investigation are necessary, this research provided promising results and set the stage for the evaluation of the new NYMPHA product for both paper substrate and painting layers consolidation. Further investigation on polysaccharide properties of NYMPHA will be included in Changes PNRR project activities as subject of main interest.



Mechanical swab test results on rabbit glue and ivory black samples.

References

1. Baudone Francesco, *Funori seaweed extracts as alternative material to semi-syntheticproduct used in paper conservation*, ECR-Estudos de Conservaçao e Restauro, 2019, 6-18
2. Antonacci A. et al., *Microalgae polysaccharides: a novel bio-material for cultural heritage preservation, Green Conservation of Cultural Heritage Conference*, Roma 3-4 febbraio 2022
3. Swider Joseph R., Smith Marta, *Overview of a 300-Year-Old-Consolidant,* Journal of American Institute for Conservation, (2005), 117-126
4. The project was possible thanks to a European and Lazio Region founding (POR-FESR Lazio 2014.20)

OP54

CRYSTALLINE NANOCELLULOSE IN THE RESTORATION OF HEMP STRINGS OF THE WORK "LA TORRE" BY ARTIST MARIA LAI

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1. Introduction

This research aims to evaluate the consolidating capacity of crystalline nanocellulose, in comparison with a commercial product already used in the restoration of cellulosic materials, in order to apply it on the hemp strings of the work "La Torre". The work, the subject of a vast restoration project, is a multi-material assemblage created by the artist Maria Lai, dated 1971-2002, which was kept until 2020 in the underground rooms of the Musma of Matera. The products selected for the consolidation of the fibers were Klucel G, which has already been used in the field of restoration due to its versatility and compatibility with cellulosic materials, and crystalline nanocellulose (CNC) whose physical-chemical characteristics are still under evaluation, but it is already used in other fields and is now being tested in the restoration of artworks of different nature both in wood and paper and also for other cellulosic supports.[1-3] CNC, in addition to the excellent optical and mechanical qualities and its close affinity with cellulosic materials, is also a non-toxic product, fully falling within the idea of eco-sustainable restoration.

2. Results and Discussion

The research, developed in a ICR thesis [4], included a phase of preliminary tests on the original pieces of string that could not be relocated, on which any dimensional and optical changes were investigated, through observations under the microscope, also repeated as a result of thermo-hygrometric stresses induced in a climatic chamber. Preliminary tests have made it possible to understand the applicability of the products at different concentrations and the way in which to carry out the consolidating treatment on such a non-homogeneous and hygroscopic material as twine. A hydroalcoholic mixture was chosen, given that the presence of ethanol favors faster evaporation, leaving the fibers moist for a shorter time and makes it easier for the consolidant to penetrate the twine. To facilitate penetration into the fibers, low percentages have been tested, starting from a minimum of 0.5% to reach deep into the depolymerized twines, restoring the twisting of the fibers, but also leaving the possibility of subsequent applications. Through SEM analyzes and EDS maps, the penetration capacity of the CNC was also ascertained, which inserts itself into the fibers of the original strings.

Samples prepared in new twine were subjected to optical evaluations and resistance tests, to a depolymerization process in nitric acid and to an artificially induced aging process, to compare the capabilities of the experimental CNC bioconsolidant with those of the commercial product Klucel G.

Analyzing the two consolidants, it can be said that satisfactory results were mostly found in the specimens treated with CNC, both in those subjected and not subjected to thermo-hygrometric stress. The effectiveness of CNC varies according to the concentration but compared with Klucel G, used under the same conditions (concentration, solvent mixture, application methodology and quantity), its superior consolidating capacity can be noted. This result is probably related to the compatibility of the CNC with the cellulosic material and also to its nanometric dimensions. However, as expected, neither of the two consolidants confers a mechanical strength comparable to that of the new material, i.e. undepolymerized, untreated and unaged string specimens. However, during the tensile tests, it was observed that for all the twine specimens treated with both consolidants, no clear breakage ever occurred. In fact, despite the dynamometer registering a decrease in resistance, the specimens inserted in the test bench seemed intact. The actual breakage of the external part of the string was found only following the release of the specimens from the clamps of the bench and subsequent traction exerted manually by pulling the two opposite ends. This aspect can therefore be reasonably interpreted as indication of an improvement in the mechanical strength conferred on the material by the two consolidating products, which led to the observation of only a partial yielding and not a total breakage.

Following the positive results obtained from the tests, it was decided to use CNC for the consolidation of some samples of twine from the work "La Torre". The bioconsolidant was applied with a pipette, following the established operating procedure and tested with positive results.

3. Conclusions

CNC hydroalcoholic suspensions were used as consolidant in the restoration of the hemp strings of the work "La Torre" by Maria Lai.

In the experiment, both the effectiveness in the structural reinforcement of new depolymerized cellulosic material and the optical properties of the material following the application of the bioconsolidant were evaluated. The effectiveness of CNC has been compared with that of the commercial product Klucel G resulting superior. The consolidating capacity of CNC was also evaluated by analyzing its degree of penetration into the internal structure of the fibers.

La Torre by Maria Lai (left), detail of the hemp strings of the work (right)

References

[1] Nechyporchuk, O. et al., (2018). On the potential of using nanocellulose for consolidation of painting canvases. Carbohydr. Polym. 194, 161-169.

[2] Basile, R. et al., (2018). Bio-inspired consolidants derived from crystalline nanocellulose for decayed wood. Carbohydr. Polym. 202, 164-171.

[3] Donati, S. *"La Torre" (197-2002) di Maria Lai: studio e restauro di un'opera polimaterica complessa. Ricerca di prodotti per il consolidamento dello spago e applicazione della nanocellulosa cristallina*, ICR-SAF Matera, PFP2, a.a. 2021-2022

OP55

CHEMICALDRIFT 1.0: A NEW OPEN-SOURCE LAGRANGIAN CHEMICAL-FATE AND TRANSPORT MODEL FOR ORGANIC AQUATIC POLLUTANTS: THE NORTHERN ADRIATIC SEA CASE STUDY

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1. Introduction

The negative effects of chemical pollution on the environment and human health have long been established, but only more recently has the need for integrated strategies and solutions for the simultaneous management of multiple stressors been widely recognized. In fact, one of the main challenges in assessing the impact of anthropogenic stressors on the environment, and especially on aquatic ecosystems, is to estimate the exposure to these contaminants while also keeping track of their origin, in particular when multiple sources of chemical pollution are considered. In this context, fate and transport modelling offers an effective way to estimate the contribution of emissions from various sources to the overall exposure to chemicals in transitional, coastal, and marine waters. In particular, in this work we will present the features of the Lagrangian model ChemicalDrift, a newly developed module of the OpenDrift suite (Aghito et al., 2023), and its application to investigate the impact of shipping in the Northern Adriatic Sea.

2. Results and Discussion

The chemical processes simulated in ChemicalDrift include degradation, volatilization, and partitioning between the different phases in the aquatic environment, (e.g. dissolved, bound to suspended particles, or deposited to the seabed sediments).

The dependencies of the chemical processes on changes in temperature, salinity, and particle concentration are formulated and implemented. Furthermore, chemical-fate modelling can be combined with a wide range of hydrodynamic data and information through the integration into the Lagrangian framework, which provides advection by ocean currents, diffusion, wind-induced turbulent mixing, and Stokes drift generated by waves. This tool is also easily adaptable to different spatio-temporal scales and areas with complex geometries such as coasts, lagoons and archipelagos.

The ChemicalDrift model was applied to investigate the contribution of shipping to the benzo-a-pyrene (BaP) and fluoranthene (Fl) pollution in the Northern Adriatic Sea. Shipping-related emissions of pollutants were simulated with the STEAM (Ship Traffic Emission Assessment Model) model (Jalkanen et al., 2020), based on Automatic Identification System data, while land-based emissions were quantified by combining daily river flow measurements with water chemical concentrations from routinely monitoring. The ChemicalDrift model was applied using 2018 data. The forcing data for the case study area were obtained from the SHYFEM model (ocean currents, temperature, and salinity) (Ferrarin et al., 2019) and Copernicus Marine Services (mixed layer depth and winds).

3. Conclusions

Preliminary results showed that shipping emissions can contribute significantly to the exposure to the selected contaminants, especially during the summer period when water flow from the tributaries reaches its minimum values and ship traffic increases.

The new Lagrangian model proved effective in simulating the environmental fate of different classes of chemicals and will be further tested on contaminants of emerging concern such as pesticides and pharmaceuticals.

Acknowledgements

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OP56

POLLUTANTS RELEASED FROM WASTES STORED IN ECO-CENTERS: DETECTION AND QUANTIFICATION

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1. Introduction

The different categories of waste delivered to the eco-centers are collected into containers according to the material type, waiting for the subsequent recovery or disposal steps. One of the main critical issues relating to the waste storage regards the potential release of contaminants from the containers exposed to atmosheric phenomena. Rainwater could potentially produce leachate from the stored waste that will consequently accumulate in various receptor bodies (i.e. surface waters, sewage systems, soils), specific for each eco-center. These runoffs, before being discharged into the eco-center's receiving body, are conveyed via drains towards an oil separator for the removal of sludge, oil and fat, and then disposed as wastewater according to legislative decree 152/2006.

In this context, this work aims at identifying the most critical types of waste - in terms of hazardous substances potentially released from the containers - in order to avoid exceeding the limits set by the legislative decrees and improve i) the sustainable management of the investigated eco-centers, and ii) the quality of the wastewater.

2. Results and Discussion

The study was initially carried out in different eco-centers located in the province of Treviso (North-East of Italy) in order to select the parameters to be investigated, to set-up the best conditions for the sampling procedure, and to choose target eco-centers. Two eco-centers were selected for the study, the first one was chosen among the newest eco-centers and the other among the oldest ones in term of construction age and technology used. COD, metals (Fe, Al, Zn, Cn, Pb, Cd, Cr, As, Ni, Mn and Sn), and surfactants (anionic, cationic and non-ionic) were selected as the main parameters/pollutants to be initially investigated.

As far as the sampling procedure is concerned, two different ways of sampling were followed (by means of a bucket or portable autosampler) and the results obtained from mass spectrometry and spectrophotometry analyses were compared to select the best option. The sampling was performed both in the containers and in the manholes below each container after meteoric events. Due to the complexity of the systems and the difficulties in interpreting the obtained data, experiments at lab scale have been performed by simulating the container use to store the small appliance of electric and electronic equipment (e-waste).

The preliminary results showed that the higher concentration of metals have been obtained between the 24 and 48 hours and that the more released ones are Zn, Sr, Al and Fe. Further studies are needed to ascertain that other typology wastes show the same behavior.

3. Conclusions

In this work, it is proposed a sampling methodology for the evaluation of the potential release of pollutants from different category of wastes when exposed to rainfall events. Compared to the periodic analyses required by the Legislative Decree 152/2006 in the Article 101 paragraph 3, which evaluate an average composite value of the pollutants contained on the wastewaters upstream at the entrance of the receptor body, this approach allows to obtain information on the leachate of the individual categories of waste collected by the eco-centers for a more sustainable management

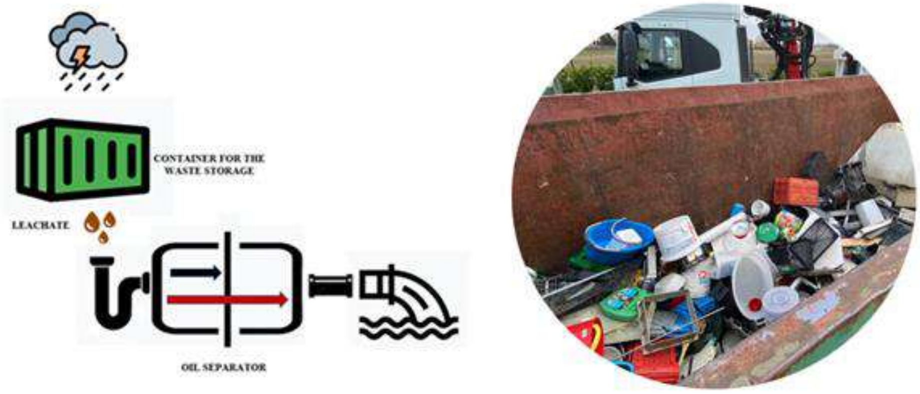

Figure 1 Schematic representation of the pollutant leaching process

References

Italian Council of Ministers, National Decree 152/2006 (in italian), (2006).
https://www.gazzettaufficiale.it/dettaglio/codici/materiaAmbientale

WORKFLOWS FOR ASSESSING PRESSURE, STATE AND IMPACTS OF ANTIBIOTICS RELEASED IN WASTE WATERS IN A COASTAL CITY (TRIESTE, NE-ITALY)

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1. Introduction

The emergence and spread of Anti-Microbic Resistance (AMR) in bacterial population is a relevant issue for health management [WHO, 2022] highlighting connection between human health, environmental quality, and animal health. Waste water treatment plants (WWTPs), beside intensive farming facilities, are potentially critical nodes for magnification of AMR genes [Ju, 20219], but their impact is not quantified yet. Attention is brought to the WWTP of the city of Trieste on the NE Adriatic sea, and a multidisciplinary task force has been established, for setting workflows producing data aiming at providing an assessment of pressures, state and impacts of antibiotic presence in treated urban wastewaters discharging in a low-depth coastal waters.

2. Results and Discussion

Databases collecting data on prescribed antibiotics for both non-hospitalized and hospitalized patients in the area served by the WWTP of Trieste (190000 equivalent inhabitants) from January 2022 to May 2023 have been retrieved from the Health Direction of Regional Administration of Friuli Venezia Giulia. allowing to quantify entity (as Defined Daily Doses and mass) and temporal variability of pressure from human antibiotics to the untreated waters, Analytical methods for both supervised screening of antibiotics considered in the national AR-ISS surveillance protocol [Istituto Superiore di Sanità, 2022] and unsupervised assessment of pharmaceuticals in wastewaters via LC-Orbitap technology have been developed by the regional EPA, allowing to distinguish among antibiotics that are present in free form from those that should be considered also in conjugate form. Preliminar I/O antibiotic concentration ratios in the considered WWT technology train have been identified. A procedure for extraction of adequate amount of genetic material from bacteria present in wastewaters has been set up, and bacterial DNA has been sent to NGS sequencing service. First results shows wide presence of genes associated to resistance to macrolides and in a lesser extent to tetraciclynes.
There is evidence of abatement of AMR genes in treated waters. Presence of bacteria in aerosols of the aeration tanks has been also considered and a procedure for bioaerosol sampling and 16S rRNA gene metabarcoding have been developed, not allowing metagenomic sequencing, due to low DNA concentrations in air.

3. Conclusions

A multidisciplinary set of workflows related to (i) monitoring of antibiotic consumption, (ii) analytical detection of pharmaceuticals, as well as (iii) metagenomic identification of AMR genes from bacteria, sampled in untreated and treated wastewaters, has been set up and it is available for deploying sound environmental assessment and relevance of AMR in wastewaters of a coastal city. Correlation among presence of antibiotics and AMR genes from water samples is currently addressed.

References

WHO Regional Office for Europe/European Centre for Disease Prevention and Control. Antimicrobial resistance surveillance in Europe 2022 – 2020 data. Copenhagen: WHO Regional Office for Europe, 2022.

Ju, F., Beck, K., Yin, X. et al.Wastewater treatment plant resistomes are shaped by bacterial composition, genetic exchange, and upregulated expression in the effluent microbiomes. ISME J 13, 346–360 (2019).

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OP58

GROUNDWATER QUALITY IN SOUTH APULIA PENINSULA

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1. Introduction

Seawater intrusion is a major problem which regards the coastal fresh groundwater and makes it unusable for human purpose. It has been established that intensive anthropogenic activities (such as overpumping or agricultural processes) usually, increase the risk of groundwater quality degradation. The principal aim of this study is to characterize the hydrochemistry of groundwater in Salento Peninsula, identifying the main processes that occur in three different areas (Adriatic, Inland and Ionian) and to determine the potential extent of marine intrusion in the aquifer. Hydrochemical investigations were carried out from 2016 to 2019 in groundwater samples collected by The Regional Environmental Protection Agency (ARPA Puglia, Dap of Lecce) in different wells of Salento Peninsula, in order to analyze the groundwater–seawater interactions.

2. Results and Discussion

In this study different techniques including Principal Components Analysis (PCA), tracers of SWI, ionic ratios, Seawater Mixing Index (SMI), Piper plot and Hydrochemical Facies Evaluation Diagram were applied to better understand the saline intrusion process. The Na/Cl molar ratio shows average values of 0.84, 0.83 and 0.85 in Adriatic, Inland and Ionian area, respectively. Furthermore the major parameters listed under PC1 (EC, Na^+, Cl^-, K^+, SO_4^{2-} and Mg^{2+}) contribute for 54,41% of the total variance (85,69%), showing the influence of "seawater intrusion factor". The SMI indices have been calculated for all the wells in order to know the average contribution of the mixing between saltwater- freshwater on each of the three analyzed areas (Adriatic, Inland and Ionian), comparing the values obtained with other models. Definitive results, shown by HFE-D plot than the Piper plot, indicate that of the 34 wells analyzed in the Salento Peninsula, 20 out of 34 (58.8%) are characterized by groundwater in freshening phase, while the remaining 14 wells are characterized by saline intrusion processes (41,2%).

3. Conclusions

The results found explain the impact of seawater mixing with fresh groundwater in a large part of Salento Peninsula.

References

Argamasilla, M.; Barberá, J.A.; Andreo, B. Factors controlling groundwater salinization and hydrogeochemical processes in coastal aquifers from southern Spain. Sci. Total Environ. 2017, 580, 50–68.

OP59

IMPROVING WATER QUALITY ASSESSMENT UNDER MULTIPLE STRESSORS: EXPLORING THE POTENTIAL OF AI-DRIVEN TECHNOLOGIES

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1. Introduction

Understanding and managing water quality under global changes requires a nexus approach that integrates various interconnected components of the water-energy-food-environment system (Hoff, 2011). This approach recognizes that water quality is influenced by a complex web of interactions among various processes, including physical, chemical, biological, ecological processes and human activities. Climate change can impact these components individually and interactively, leading to cascading effects. Only by considering the whole system, including both natural and human factors, we can capture complexity understanding multiple stressors and feedback loops that affect water quality (Sperotto et al., 2019).

One of the major challenges of adopting a system wise approach for water quality assessment is primarily represented by the need to access and combine data and model from many different scientific domains which often remains compartmentalized in silos, to pre-defined scales and fields, into a single, logically consistent integrated framework of analysis. Integrative technology such as Artificial Intelligence can offer a path forward to foster this integration permitting to maximize the value of available information.

2. Results and Discussion

A systemic integrated model for the assessment of climate change and anthropogenic activities conjoined impacts on water quality and related-Ecosystem Services supporting multiple sectors is currently under development and testing at the river basin scale in two case studies in Italy (i.e. Secchia river basin, Adige river basin).

The model is developed using ARIES (Artificial Intelligence for Environment and Sustainability), an open-source Artificial Intelligence modeler https://aries.integratedmodelling.org/. ARIES uses Artificial Intelligence, and in particular semantics and machine reasoning, allowing models and data developed by independent researchers, hosted on a network, to be integrated and automatically assembled into workflows running at the scale most appropriated for the context of analysis (Balbi et al. 2022, Villa et al. 2017).

Specifically, multiple type of data and models to describe different component and processes impacting water quality and related Ecosystem Services are derived from the context of interests. Climatic and hydrological model outputs, monitored data and EO (e.g. from Copernicus Data StoreCDS) are used to characterize changing conditions which could affect water yield and quality, while socio-economic census data, territorial information and sectoral models (i.e. type of land use, agricultural production data, environmental indicators) are used to disentangle the synergies and trade-offs between specific socio-economic activities and water and environmental quality.

All models and data are annotated semantically providing a standardized and structured representation of the domain knowledge, which facilitate the harmonization, integration and rescaling of diverse datasets. Ontologies are used to define the concepts, relationships, and attributes within each domain involved, enabling seamless integration and interoperability of available data across the system.

Once validated the model permits to simulate i) the impact of different climate change and land use scenarios of water and environmental quality indicators (e.g. nutrient loadings from different sources, water yield, water temperature, carbon stored in vegetation, soil retention); ii) spatially-temporally explicitly measure how such changes affects Ecosystem Services supporting key economic sectors; iii) test best practices permitting to reduce trade-offs between economic activities and ecosystem health.

3. Conclusions

The approach and preliminary results derived from two pilot case studies will be presented in light of discussing how AI-driven approaches can maximize data and model reusability and interoperability when assessing environmental quality problems and, more generally, in modelling complex anthropic and environmental interactions and their consequences.

Overall the outputs of the analysis will provide an actionable knowledge base to support policy making processes and enhance cooperation between sectoral policies to achieve EU targets related to the Water Framework Directive, the greener CAP (Common Agricultural Policy) and Green Deal ambitions.

References

Hoff, H. (2011). Understanding the Nexus. Background Paper for the Bonn 2011 Conference: The Water, Energy and Food Security Nexus. Stockholm Environment Institute (SEI), Stockholm.

Sperotto, A., Molina, J.L., Torresan, S., Critto, A., Pulido-Velazquez, M., Marcomini, A., 2019. A Bayesian Networks approach for the assessment of climate change impacts on nutrients loading. Environ. Sci. Policy 100, 21–36. https://doi.org/10.1016/J. ENVSCI.2019.06.004.

Villa F, Balbi S, Athanasiadis IN, Caracciolo C. Semantics for interoperability of distributed data and models: Foundations for better-connected information. F1000Res. 2017. May 17;6:686. doi: 10.12688/f1000research.11638.1.

EXTENDING A QUANTITATIVE WEIGHT OF EVIDENCE APPROACH TO INCLUDE ‘OMICS IN SEDIMENT QUALITY ASSESSMENT: THE CASE STUDY OF A VENICE LAGOON CANAL

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1. Introduction

In the context of ecological risk assessments, it is now well-established that ecosystem health status should be assessed on a broad range of indicators by bringing together different types of evidence via, for example, a quantitative Weight of Evidence (QWoE) approach. This holds also true in the sustainable management of dredged sediment, for which a thorough characterization is desirable so that neither the dredged area nor the destination site would result impaired.

To expand the existing knowledge on the quality of bed sediment from a canal subject to future dredging in the Venice Lagoon, a series of experimental investigations were carried out. Data from the chemical characterization of inorganic and organic contaminants in one-metre sediment cores converged into a line of evidence (LoE). Sampled sediment provided the exposure matrix for a battery of ecotoxicological bioassays, bioaccumulation tests, and biomarker analyses, constituting three more LoEs. With the intent of reaching a better-supported risk characterization, the QWoE methodology (Regoli et al., 2019) was extended to include analyses of transcriptional alterations, now forming a new LoE (Cecchetto et al., 2023).

2. Results and Discussion

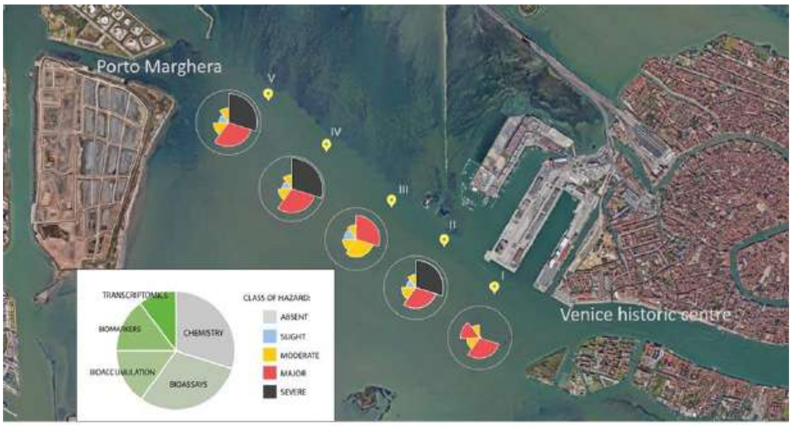
Results refer to the experimental investigation that comprises five sites along the Vittorio Emanuele III Canal (labelled consecutively with roman numbers from the historic centre of Venice to the industrial area of Porto Marghera, see figure below) at two different times, i.e. November 2020 and March 2021. A sixth site, far from pollution sources, was selected as a reference site based on previous evidence of its sediment good quality status.

For each of the five LoE, a set of algorithms helped in summarizing high dimensional data into synthetic hazard quotients with a relative class of hazard (from absent to severe), which are then aggregated to quantitatively infer the level of risk. The total hazard was finally expressed on a 0-100 scale, and associated class of hazard, by pondering on the relevance and reliability of each type of evidence.

Evaluation of the chemical hazard, by comparison of the measured concentrations with sediment quality standard values, revealed a worsening in sediment quality from the historic centre of Venice to the industrial area of Porto Marghera. This trend found confirmation in the hazard investigated via a battery of ecotoxicity tests, where the class is more often represented by a major hazard with no remarkable differences characterizing the two campaigns. Evidence gathered from the biological analyses (bioassays, bioaccumulation, biomarkers and transcriptomics) highlighted a potential hazardous situation at the organism level for site I (closer to the historic centre of Venice), especially in the first campaign, that the chemistry LoE did not reveal. Contaminants not measured in the analysis of sediment or the texture of sediment itself might have caused the observed discrepancy.

From the evidence integration, results confirmed the good quality status of the reference site. With regard to sites along Vittorio Emanuele III Canal, the integration of five types of evidence resulted in an overall hazard ranging from slight to major, with a quality worsening for sediment sampled closer to the industrial area. A slight difference characterized the hazard in the two campaigns, which likely stems from the higher concentrations of trace metals measured in the second sampling time, even if concentrations were within the variability range observed in the Venice lagoon sediments.

This stresses the importance of going back to the single evidence as an opportunity to better comprehend the driving factors of the overall hazard results. To this attempt, the figure below illustrates the contribution of each LoE to the overall hazard for all sites in the first campaign. This contribution depends on the hazard class estimated for each LoE, weighted according to the relevance and reliability attributed to that LoE.



Summary of the WoE-based evaluation of sediment quality along Vittorio Emanuele III channel in the first campaign.

3. Conclusions

The QWoE approach acted as an effective method to summarize and quantitatively integrate large and complex amounts of data and was flexible enough to include an additional line associated with transcriptional data, even if further testing is desirable. In the attempt of overcoming the "pass-to-fail" approach, where a single parameter could be responsible for the classification of the sediment, this approach promoted the evaluation and the interpretation of chemical data in the light of several biological types of evidence. The WoE methodology should also help assessors trace back to the linkages between data and the final hazard, to elicit possible causes and main driving factors of adverse effects to the ecosystem.

References

Regoli F, d'Errico G, Nardi A, Mezzelani M, Fattorini D, Benedetti M, Di Carlo M, Pellegrini D, Gordi S. 2019. Application of a Weight of Evidence Approach for Monitoring Complex Environmental Scenarios: the Case-Study of Off-Shore Platforms. Front. Mar. Sci. 6:377

Cecchetto M, Peruzza L, Giubilato E, Bernardini I, Dalla Rovere G, Marcomini A, Regoli F, Bargelloni L, Patarnello T, Semenzin E, Milan M. 2023. An innovative index to incorporate transcriptomic data into weight of evidence approaches for environmental risk assessment. Env. Res., Vol. 227

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OP61

LOW-COST AND UP-SCALABLE ADSORBENT HYDROGELS FOR ANIONIC DYES REMEDIATION AND INDUSTRIAL WASTEWATER DECONTAMINATION BY ELECTROSTATIC INTERACTIONS

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1. Introduction

Water pollution from dyes, deriving from the textile industry, food colorants, printing, and cosmetic manufacturing is harmful to the environment, plants, animals, and humans. Dyes removal from contaminated water is a daily challenge for experts in the field, often addressed using adsorption methods.

2. Results and Discussion

New low-cost and up-scalable adsorbent materials for anionic dye remediation and water decontamination by electrostatic interactions were developed.[1] To this end, two cationic resins (R1 and R2)[1,2] were synthesized by reverse suspension copolymerization of styrene-based monomers (M1 and M2) and dimethylacrylamide (DMAA), (Figure 1a).[1,2] Upon their dispersion in an excess of water, R1 and R2 provided hydrogels (R1HG and R2HG) with equilibrium degrees of swelling (EDS) of 900% and 1000% and equilibrium water contents (EWC) of 90 and 91%, respectively. They were characterized by ATR-FTIR analyses, rheological experiments, evaluation of content of cationic groups, crucial for the electrostatic-based absorbent activity, and by potentiometric titrations. In absorption experiments in batch, using methyl orange (MO), fluorescein (F), and their mixture (MOF) as dyes models, R1HG and R2HG showed high removal efficiency (RE) (97–100%), while R1HG and R2HG-based columns, mimicking decontaminating systems by filtration, were capable to totally remove from water (100%) all dyes and their mixture in different conditions of use (Figure 1b).

3. Conclusions

R1HG and R2HG represent low-cost and up-scalable column packing materials that are promising for application in industrial wastewater treatment.

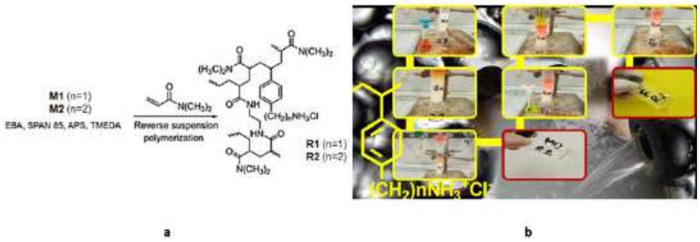

Figure 1: Synthesis of resins R1 and R2 (a); sequential removal of MO and F by filtration using R2 (b).

References

1. S. Alfei, F. Grasso, V. Orlandi, E. Russo, R. Boggia, G. Zuccari. Int. J. Mol. Sci. 2023, 24, 2948.
2. S. Alfei, G. Zuccari, E. Russo, C. Villa, C. Brullo. Int. J. Mol. Sci. 2023, 24, 1109.

MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF SLAG-BASED ONE-PART GEOPOLYMER BINDERS AND MORTARS

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1. Introduction

The building industry plays a vital role in community development, but it also has a great impact on the environment by consuming huge amounts of non-renewable natural resources and producing emissions that contribute to climate change. The great attention to environmental problems has forced the development of new eco-friendly materials. Alkali-activated materials (AAMs), such as geopolymers, are promising for the production of mortars and concretes. By using waste materials, as aluminosilicate precursors, the AAMs contribute to lowering energy consumption and CO_2 emission due to the cement production and minimize the environmental risks related to waste management [1].

Geopolymers are 3D inorganic polymers, usually obtained by reaction of solid aluminosilicate precursors (for example metakaolin) with an alkali activator solution, called *two-part* method [2]. The goal here proposed is the design of *one-part* geopolymer-like binders prepared starting from aluminosilicate waste precursors (blast furnace slag and steel slag) using solid alkali activators instead of alkali solutions. These binders are used for the development of sustainable mortars by adding sand and natural additives.

2. Results and Discussion

One-part alkali activated binders were prepared by mixing the precursors and the alkali activator (AA) with water/binder ratios ranging from 0.35 to 0.5 w/w, depending on the different reagents. In the development of the different formulations, slags (steel slag, SS and blast furnace slag, BFS) and metakaolin (MK) were tested as precursors and different combinations of hydroxide (Ca, Na, K), silicate (Na, K) and carbonate (Ca, Na, K), all in powder form, as alkali activators were experimented.

The SS (with grain dimension of about 0.5-0.2 mm) and BFS (rich in Si and Al) were the most reactive precursors as evidenced by FTIR spectroscopy: the geopolymerization reaction is confirmed by the strong band at about 950 cm^{-1}, attributed to the stretching vibrations of the Si-O groups, shifted at lower wavenumbers (at about 1050 cm^{-1}in the starting reagent) following the silicate dissolution and formation of Si-O-Al units of the geopolymeric network.

In the XRD pattern of the different formulations several large peaks are noticed due to the formation of new phases, characterized by low crystallinity, which emerge from a large amorphous background centered at about 30°, typical of geopolymers [3]. At $2\theta \approx 30°$ the main feature of calcite overlaps with that of the hydration product CSH (calcium silicate hydrate). Figure 1 reports the diffraction pattern of the formulation with BSF mixed with MK. The presence of CSH is also confirmed by Raman spectroscopy by the appearance of the peak at about 673 cm^{-1} [4].

The surface morphology of the binder samples, observed by SEM after 28 days of ageing, appears quite homogeneous and compact without evident micro-cracking, better for the formulation prepared with SS and K-based AA than for the formulation made with BSF and Na-based AA, where the surface appears spongy with micrometric pores and small and widespread micro-cracking.

Similarly to cementitious materials, also for geopolymeric binders the flexural strength is significantly low: all the specimens show strengths lower than 1 MPa except for the formulation obtained by *two-part* method with alkali activator in solution (as control). Regarding to the compressive strength, the two-part and the one-part formulations obtained starting from the blast furnace slag as aluminosilicate source have comparable values, in the range 23 - 28 MPa. The formulations made with SS with K-based AA and with BSF mixed with MK and Na-based AA exhibit higher strengths, 40 MPa and 54 MPa respectively. The addition of metakaolin is known to improve the mechanical properties and workability of the mixtures [5].

The *one-part* geopolymer binder with BSF mixed with MK was subsequently used for the development of a mortar by adding silica sand, as fine aggregate, and a natural polysaccharide (corn starch or cellulose) as additive to the mixture to investigate their influences. Two curing methods were tested at room temperature (T = 23±2 °C): in water and inside closed plastic bags. The mortar obtained by adding cellulose to the binder exhibits better workability while the mortar made by starch shows higher compressive and flexural strengths. After 28 days curing in sealed bags the mechanical properties are found to be better than in water.

3. Conclusions

New geopolymer-like binders are obtained starting from aluminosilicate waste precursors by the *one-part* method using different alkali activators. Their mechanical properties are generally better or at least comparable to those obtained with the traditional *two-part* method. The *one-part* binder formulated with blast furnace slag mixed with metakaolin and Na-based alkali activator has shown the best performances. Sand and additives have been added to the binder to give a mortar. Right workability and good mechanical properties of the mortar have been obtained with cellulose and corn starch as additives.

The obtained formulations have properties suitable for use as innovative and sustainable building materials.

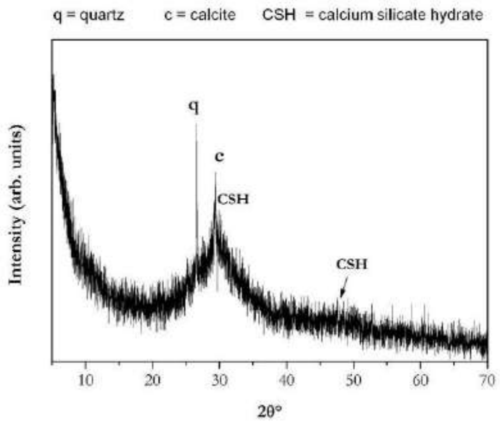

Figure 1 – XRD pattern of the binder obtained by mixing BSF and MK.

Acknowledgments

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References

[1] Nodehi, M., Taghvaee, V. M. (2022). Circ. Econ. Sust., 2, 165-196.
[2] Provis, J. L. (2018). Cem. Concr. Res., 114, 40-48.
[3] Bergamonti, L., Taurino, R., Cattani, L., Ferretti, D., Bondioli, F. (2018). Constr. Build. Mater., 185, 285-292.
[4] Mikhailova, O., Del Campo, A., Rovnanik, P., Fernández, J. F., Torres-Carrasco, M. (2019). Cem. Concr. Compos., 99, 32-39.
[5] Li, L., Xie, J., Zhang, B., Feng, Y., Yang, J. (2023). Constr. Build. Mater., 368, 130389.

OP63

ADSORPTION OF HUMIC ACIDS MONOMERS ONTO ZEOLITES: EFFECTS ON THE REMOVAL OF ORGANIC CONTAMINANTS

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1. Introduction

The contamination of natural waters still represents a problem of major concern not only for public health, but also for nature conservation. Wastewaters and contaminated natural waters may contain many different organic compounds originated form natural and anthropogenic sources.

Natural organic matter (NOM) is a complex mixture of organic compounds commonly found in surface and groundwaters; humic substances represent 40-80% of the NOM content and they are found in freshwater typically in a concentration range 1-25 mg/L [1]. Among this class of compounds, humic acids form a complex mixture of natural substances derived from the biodegradation of lignin; p-Hydroxybenzaldehyde (p-HBA) and caffeic acid (CA) are monomers of humic acids that are commonly found in natural waters.

Toluene is a contaminant belonging to the BTEX class which is frequently detected in all environmental compartments due to its wide use as solvent, antiknock agent in gasoline, and to produce benzene.

Among the available techniques for pollutants removal, adsorption is characterised by many advantages, including the use of eco-friendly adsorbents such as zeolites.

2. Results and Discussion

In this work, the potential competition between naturally found compounds and organic contaminants towards their adsorption onto zeolites was investigated. Indeed, high-silica zeolites have already been proven to be efficient eco-friendly adsorbents for the removal of several organic contaminants from aqueous solutions [2], but the presence of substances derived from the degradation of lignin could potentially reduce the efficacy of the adsorbent materials towards the removal of target contaminants.

In this study, two different zeolite topologies were chosen to investigate the adsorption of the selected organic compounds: zeolite ZSM-5 and Y, with MFI and FAU framework type topology and Si/Al ratio of 280 and 200, respectively.

Regarding the adsorption of the natural organic compounds, the systems zeolite - p-HBA and zeolite - CA were considered. The adsorption experiments were conducted using the batch method: an aqueous solution containing the natural substance at a known concentration was put in contact with a known amount of zeolite; the batch was kept at room temperature, under stirring, for 24 hours to ensure the equilibrium conditions were reached. The solution was then separated from the solid by centrifugation and analysed by HPLC-DAD to determine the concentration of the analyte. Both the initial solution (before contact with the zeolite) and the solution after equilibration were analysed to obtain the amount of substance adsorbed onto the zeolite.

Adsorption isotherms were determined at different pH values to establish the effect of this parameter onto the saturation capacity of the adsorbent materials.

At a pH near the pK_a of p-HBA (7.7) the adsorption for this humic acids monomer decreases, especially at lower concentrations, whereas at lower pHs, where the undissociated form of p-HBA is predominant, the adsorption increases. Rietveld refinements indicated that in both zeolites, p-HBA molecules can be connected by means of hydrogen bonds through co-adsorbed water, to form organic–water complexes.

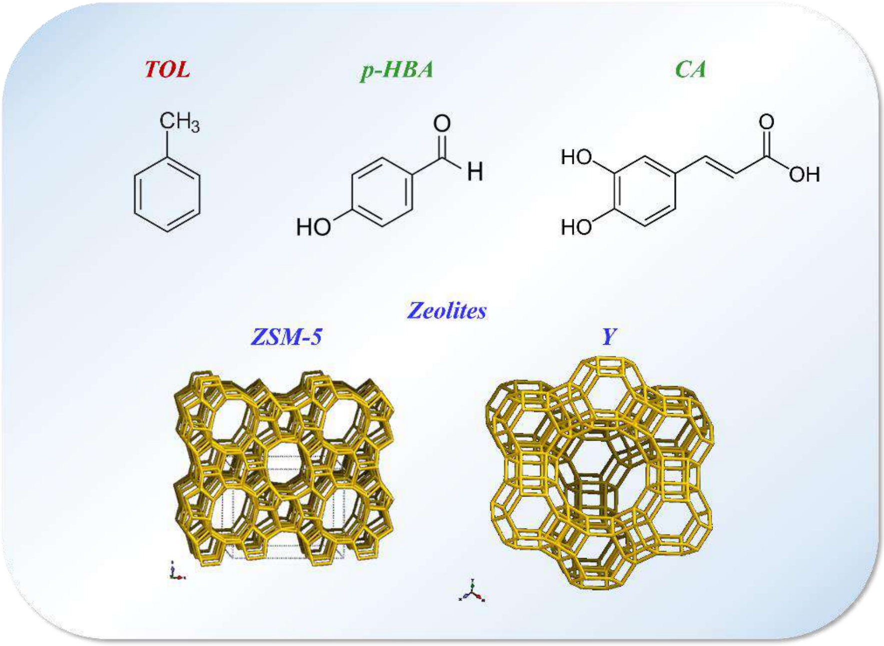
Also for CA, its uptake onto zeolites strongly depends on pH, the maximum saturation capacity was obtained at pH 4, corresponding to the nonionised form of caffeic acid [3].

Regarding the adsorption of the contaminant (TOL) from the aqueous matrix containing the natural humic acids monomer (p-HBA or CA), it resulted that the natural compounds do not show competitive behaviour: the adsorption of TOL was slightly affected by the presence of the humic acids monomers. The higher selectivity of ZSM-5 for TOL with respect to p-HBA and CA was also confirmed from structural investigation of the selected zeolite loaded with single component solution of TOL and p-HBA or CA, and from a binary mixture containing both the contaminant and the humic acids monomer (i.e., TOL and p-HBA, or TOL and CA). Strong similarities between the X-ray powder patterns after adsorption of the mixture and after only TOL adsorption, indicate that the zeolite adsorb preferentially and selectively toluene, also in the presence of the natural compounds.

3. Conclusions

In this study the mechanism of adsorption of lignin-derived compounds onto zeolites was investigated, the results obtained show an influence of pH on the uptake of these humic acids monomers onto the adsorbents. When binary mixtures containing the contaminant and the natural compound are considered, the uptake of toluene is only slightly affected by the presence of p-HBA and CA.

These findings confirm the high selectivity of zeolites for the removal of organic contaminants from waters in presence of natural components.



Organic contaminant (TOL), humic acids monomers (p-HBA and CA) and zeolites investigated.

References

[1] Uyguner Demirel, C.; Bekbolet, M.; Swietlik, J. Control of Disinfection By-Products in Drinking Water Systems, January 2007, 253-277.
[2] Sarti, E.; Chenet, T.; Pasti, L.; Cavazzini, A.; Rodeghero, E.; Martucci, A. Minerals 2017, 7(2), 22.
[3] Chenet, T., Sarti, E., Costa, V., Cavazzini, A., Rodeghero, E., Beltrami, G., Felletti, S., Pasti, L., Martucci, A. J. Environ. Chem. Eng. 2020, 8(5), 104229.

ADSORPTION OF TOXIC BIVALENT CATIONS Pb(II) AND Cd(II) ONTO HYBRID GEOPOLYMERS FROM ENVIRONMENTAL SAMPLES

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1. Introduction

Geopolymers are amorphous alumino–silicates characterized by a structure like tectosilicates, obtained through a polycondensation reaction of an alumino–silicate material, such as metakaolin as well as wastes deriving from thermochemical processes as ashes, in a strongly alkaline solution. By adding a silicone oligomeric resin through a crosslink reaction approach, a hybrid material with good mechanical properties as well as high fire resistance is obtained. This material has been used to remove from soils and water contaminated[2] metals as Pb(II), Cd(II), extremely dangerous to public health and the environment due to bioaccumulation.

2. Results and Discussion

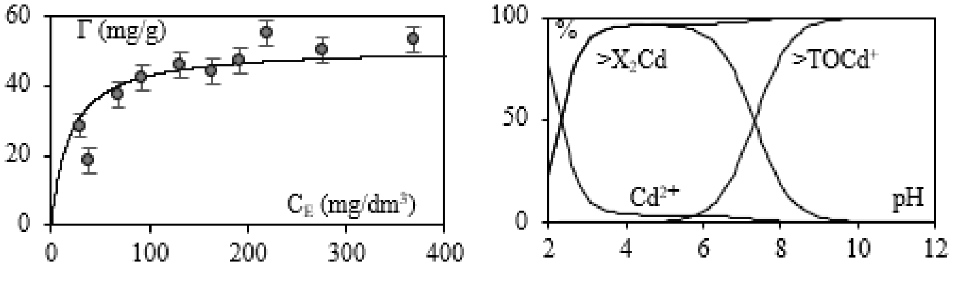
In the present work, the adsorption of toxic metals by using a hybrid geopolymer, obtained by co-reticulation reaction of metakaolin based geopolymer and polydimethylsiloxane[1] (10% by weight) at 25 °C in $NaClO_4$ as ionic medium has been studied. By potentiometric measurements it has been deduced that the solid presents superficial acid-base properties, (due to silanol and/or aluminolic groups) with the following surface acid constants :

$$>X^- + H^+ \leftrightarrows >XH \qquad \log K_X = 3.1 \pm 0.1$$
$$>TOH + H^+ \leftrightarrows >TOH_2^+ \qquad \log K_B = 5.2 \pm 0.2$$
$$>TOH \leftrightarrows >TO^- + H^+ \qquad \log K_A = -10.1 \pm 0.2$$

The solid shows a point of zero charge (PZC) of 6.9 ± 0.2.

3. Conclusions

Kinetic measurements show that adsorption process follows the pseudo-second order kinetic model.
From the adsorption isotherms the data collected are compatible with Langmuir's model. By the percentage of cadmium ions adsorbed on the solid sites involved, it is observed that for pH < 5.0 in 0.1 M $NaClO_4$ are involved the sites with fixed charge (X), as the pH increases, the acid−base sites are involved.



Isotherm (left) and superficial distribution diagram (right) of Geopol-Cd(II) system

References

1. G. Roviello, C. Menna, O. Tarallo, L. Ricciotti, C. Ferone, F. Colangelo, D. Asprone, R. Di Maggio, E. Cappelletto, A. Prota, R. Cioffi 'Preparation, structure and properties of hybrid materials based on geopolymers and polysiloxanes' Materials and Design, 2015, 87, 82-94.
2. G. Roviello, E. Chianese, C. Ferone, L. Ricciotti, V. Roviello, R. Cioffi, O. Tarallo 'Hybrid geopolymeric foams for the removal of metallic ions from aqueous waste solutions' Materials 2019, 12, 4091

OP65

LIGNIN - A HIGH POTENTIAL WASTE MATERIAL

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1. Introduction

Lignin is the second most abundant component of plant material, until now with limited applications due, above all, to its complex structure. This biopolymer is the main waste product of the paper and biofuel industries. Nowadays, over 90% of lignin is burned with very little efficiency. Part of the residual lignin from industrial processes also enriches cements and asphalts, products with a high diffusion but low added value[1]. The aim of this research is the characterization of two industrial lignins for their valorization. Different molecular characterization techniques have been applied, spectroscopic as UV-vis, FTIR, ^{31}P- e ^{13}C- NMR, thermal EGA-MS and chromatographic GPC as well as elemental analyses, - to have in-depth information on their different structure and their degree of molecular degradation caused by industrial treatments. Then, their efficient application as gate dielectric materials was demonstrated for organic field-effect transistors[2].

2. Results and Discussion

Two industrial softwood lignins from the same kraft pulping process were investigated and their characteristics were compared. Different degree of degradation and chemical composition due to the industrial process has been found. Also structural and physical-chemical properties determined were different, including their solubility. The most degraded lignin, with the lowest level of polymerization, showed a high percentage of phenyl enol ether and carboxyl groups and a high ash content. Those more degraded is dissolved in water while the other one, better preserved, requires the presence of a basic solution for complete dissolution.

To understand potentialities of application of both investigated lignin as gate materials for organic field effect transistors, dielectric spectroscopy investigations were carried out in a metal–insulator–metal (MIM) structure. The lignin with the highest degree of polymerization (better preserved) was found to be those with the best performance with lower hysteresis and higher charge carrier mobilities for both semiconductors.

3. Conclusions

Chemical structure and composition of two industrial lignins obtained by using various investigation techniques were compared. A correlation between the chemical structure of two kraft lignins and their performances as dielectric layers in organic field-effect transistors in the bottom-gate top-contacts device configuration for the first time was obtained.

The results obtained in this study set the bases for suitable renewable and cost-effective lignin materials deposited through solution methods for electronic devices fabrication.

References

1. Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G., A concise review of current lignin production, applications, products and their environmental impact. *Industrial Crops and Products* **2019,** *139*, 111526.
2. D'Orsi, R.; Irimia, C. V.; Lucejko, J. J.; Kahraman, B.; Kanbur, Y.; Yumusak, C.; Bednorz, M.; Babudri, F.; Irimia-Vladu, M.; Operamolla, A., Kraft Lignin: From Pulping Waste to Bio-Based Dielectric Polymer for Organic Field-Effect Transistors. *Advanced Sustainable Systems* **2022,** *6* (12), 2200285.

OP66

ADSORPTION KINETICS OF IOPAMIDOL ONTO ACTIVATED CARBON

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1. Introduction

Nowadays, a new class of emerging contaminants are pharmaceutical compounds such as X-ray contrast media that are widely used in the modern society [1].

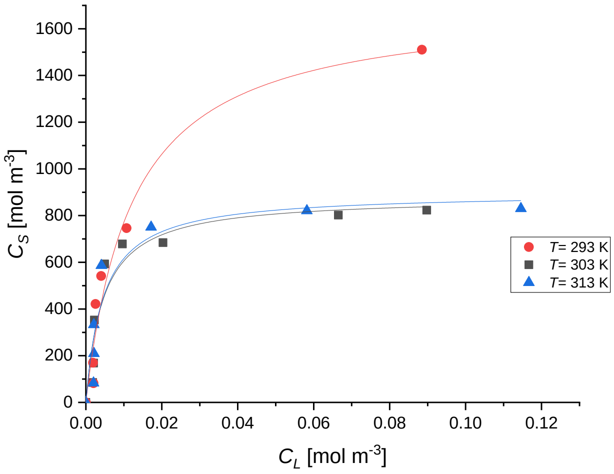
Iodinated X-ray contrast media (ICM), has become the focus of environmental concern because they are highly hydrophilic displaing high aqueous solubility, meaning that they are difficult to eliminate from water and wastewater [2]. Iopamidol ($C_{17}H_{22}I_3N_3O_8$) is a pharmaceutical compound beloging to the class of the non-ionic and monomeric iodinated constrast media. Conventional wastewater treatment processes are uneffective in removing these compounds leading to their appearance in surface water, effluents of wastewater, and groundwater. In this regard, different technologies have been developed for the treatment of wastewater. Adsorption is the best methods, thanks to its great applicability due to low cost, simplicity, and versatility [3]. In this study we used activated carbon to remove iopamidol from water.

2. Results and Discussion

The adsorbent was characterized by various analytical techniques such as thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET analysis, dynamic light scattering (DLS) and zeta potential measurements. Experiments were conducted in a batch apparatus and the effect of the initial concentration of iopamidol, the temperature and the adsorbent bulk density on the adsorption kinetics were investigated. The SEM micrographs show lamellar composition of the activated carbon Fluka while the TEM microphotographs reveal the presence of disordered and curled single carbon layers. The TGA analyses performed on the PAC samples after the adsorption test with iopamidol underline that significant weight loss at 300 °C was observed upon IPM adsorption. To describe how the adsorbate molecules are distributed between the liquid and the solid phases when the process of adsorption reaches an equilibrium state, the adsorption equilibrium are obtained. The trend of the adsorption isotherms of IPM on activated carbon follow the Langmuir model. The effect of sorbent load on the adsorption rate of the IPM was investigated at T= 303 K, v=800 rpm and by fixing the initial concentration of iopamidol at $C_{B,0}$=0.13 mol m^{-3}. The trend of iopamidol bulk concentration at different adsorbent bulk densities shows that by increasing the sorbent bulk density, an increase in the adsorption capacity is obtained. This is true from the bulk density value of 0.05 kg m^{-3}, since there is no effect on the iopamidol uptake between the experiments performed with 0.005 and 0.01 kg m^{-3} of adsorbent. Increasing the sorbent dosage at a fixed IPM initial concentration provided more available adsorption sites for IPM and thus increased the extent of IPM removal from the solution. As the temperature increase, a decrease in the iopamidol uptake is obtained, confirming the exothermic nature of the process as already reported in the previous paragraph. In fact, the iopamidol uptake is 33% higher at 293 K compared to that obtained at 303K and 313K.

3. Conclusions

The adsorbent characterization confirmed the high surface development and porosity typical of activated carbon. It has been seen that the zeta potential value of the adsorbent when placed in contact with the iopamidol increases by one unit. Studies at DLS showed the formation of aggregates between carbon and iodipamidol at acid pH. All kinetics and thermodynamics experiments were carried out in batch mode, and it was tested that the present adsorption process is exothermic. Furthermore, the adsorbent must be at least 0.05 kg m^{-3} to show a good removal capacity of the pollutant. The adsorption data at equilibrium follows the Langmuir model, showing the strong interaction between iopamidol and activated carbon.



Adsorption isotherms at different temperatures.

References

[1]Fonseca, E.; Hernández, F.; Ibáñez, M.; Rico, A.; Pitarch, E.; Bijlsma, L. Occurrence and Ecological Risks of Pharmaceuticals in a Mediterranean River in Eastern Spain. *Environment International* 2020, *144*, 106004.

[2]Mestre, A.S.; Machuqueiro, M.; Silva, M.; Freire, R.; Fonseca, I.M.; Santos, M.S.C.S.; Calhorda, M.J.; Carvalho, A.P. Influence of Activated Carbons Porous Structure on Iopamidol Adsorption. *Carbon* 2014, *77*, 607–615.

[3]Russo, T.; Fucile, P.; Giacometti, R.; Sannino, F. Sustainable Removal of Contaminants by Biopolymers: A Novel Approach for Wastewater Treatment. Current State and Future Perspectives. *Processes* 2021, *9*, 719.

POLYMER-DERIVED SIC/C AEROGELS FOR REMOVAL OF GLYPHOSATE HERBICIDE FROM WATER MATRICES

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1. Introduction

The issue of water pollution resulting from the release of herbicides and pesticides into the environment is a growing problem that requires the use of effective and sustainable depuration techniques, such as regenerable adsorbent materials. In this regard, this study focuses on the synthesis of a nanocrystalline silicon carbide aerogel and its application in the removal of glyphosate herbicide from contaminated water.

2. Results and Discussion

The aerogel was synthesized using allylhydridopolycarbosilane as a polymeric precursor via the Polymer-Derived Ceramic (PDC) route. Upon pyrolysis at 1500 °C in an argon atmosphere, the formation of β-SiC nanocrystals was observed, while the aerogel maintained a high specific surface area of 215 m^2/g. The nanostructured aerogel exhibited excellent adsorption capacity for glyphosate herbicide, with an adsorption capacity of 0.607 mg/g, resulting in a removal efficiency of 93% for the pollutant in solution.

The adsorption process of glyphosate onto the aerogel surface was found to follow the Elovich kinetics adsorption and Langmuir isotherm models, which effectively described the mechanism of glyphosate capture through adsorption. The adsorption data of the silicon carbide aerogels were compared adsorption data on glyphosate (C_e, q_e) available at the municipal drinking water plant of the city of Turin conducted on the activated carbon, here characterized for the purpose (SSA: 1073 m^2/g), predicting q_e values for the aerogel of one order of magnitude higher than those obtained with activated carbon.

3. Conclusions

These results confirms that Polymer Derived Ceramic aerogels are suitable materials for developing adsorbers to be intended for water purification.

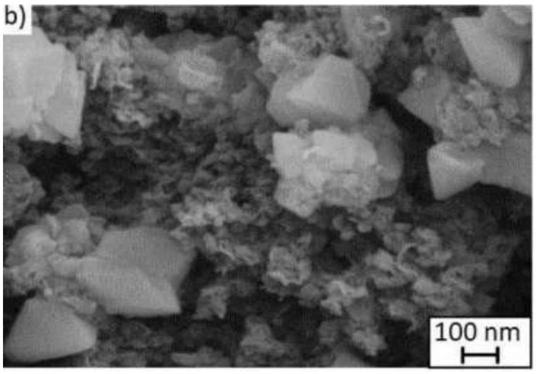

Figure 1. SEM acquisitions on the ceramic aerogel

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OP68

MIXED MATRIX MEMBRANES FOR THE REMOVAL OF PFAS FROM AQUEOUS SOLUTIONS

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic organo-fluorine compounds with hydrogen atoms on the alkyl chain replaced by fluorine atoms. Due to their unique chemical and physical properties such as hydrophobicity, oleophobicity and extraordinary chemical stability, PFCs have been widely used as surfactants, fire retardants, lubricants. The widespread industrial applications have released large amounts of PFAS into the aquatic systems. It is therefore really important to study new methods for the removal of pollutants from water environment, and membrane-based technology has rapidly become a competitive alternative with respect to traditional methods. [1]. In particular, mixed matrix membranes (MMMs), that are composed by a continuous polymer phase and a dispersed inorganic filler have gained importance due to their fouling, permeate quality and longevity characteristics. Different types of fillers had been utilized in MMMs, such as zeolites, mesoporous silica, carbon nanotubes (CNTs), montmorillonite, and metal–organic frameworks.

2. Results and Discussion

In this work nanostructured carbon material has been included in several formulations of hydrogels which differ in hydrophilicity, cross-linking and swelling, and the adsorption efficiency of all the formulations had been determined and compared to the adsorption of powder nanostructured carbon.

The hydrogel matrices were obtained using two different monomers of polyethylene glycol diglycidyl ether (PEGDE): PEGDE_Ethyl, that presents hydrophilic characteristics, and PEGDE_Propyl, which is more hydrophobic; these two PEGDE monomers were used in a mass polymerization reaction with other two different monomers having amine substituent groups, JEFFAMINE and polyethylene glycol amine functionalized, which give different types of cross-linking in the membranes; for each formulation, a percentage of carbon material 5% w/w, was added.

For all MMMs, the adsorption processes studies were carried out using the batch method. Batch experiments were performed by adding a certain amount of solid (adsorbent) into solutions containing known concentrations of contaminant with a specific solid/liquid ratio (1:1 mg/mL). The solution was constantly stirred at room temperature (25°C) for 24 hours. All the results obtained were compared with the values obtained for the powder of the carbon material. Kinetic studies showed that within 6 hours the kinetic equilibrium is reached for all the MMMs considered, while the swelling study was carried out by weight control at different contact times up to 24 hours. The isothermal study was carried out with a contact time of 24 hours, keeping the solution stirred at room temperature and evaluating, by LC/MS analysis, the change in concentration of the pollutant in the solution before and after the contact with the adsorbent material.

3. Conclusions

The data obtained showed that the MMMs has a higher adsorption efficiency than the powdered nanostructured carbon material. Furthermore, the different hydrophilicity, swelling and cross-linking characteristics play a fundamental role in the saturation capacity (qs) of different MMMs.

In fact, qs was improved of about 20 mg of PFAS per gram of adsorbent material, passing from qs = 30.1 ± 1.4 mg / g for powdered nanostructure carbon material to values higher than 50 mg/g for MMMs. Moreover, the results showed that the MMM with the highest saturation capacity was the membrane with higher hydrophobicity characteristics which presents more affinity for per- and polyfluoroalkyl substances. Kinetic studies showed that within 4 hours the kinetic equilibrium is reached for all the MMMs considered. The study of adsorption isotherms shows that carbonaceous material presents a Langmuir adsorption isotherm, while polymeric materials have been described using different adsorption isotherm models.

References

[1] A.E. Amooghin et al., *Progress in Materials Science*, **2019**, *102*, 222-295

OP69

SALINE POLLUTION ON THE ELECTRICAL SYSTEM INSULATORS: A CHEMICAL STUDY

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1. Introduction

In times of energetic transition, the preferred way to distribute energy is electricity. Insulators are a key part of electrical systems, thus their perfomance must be assured. It is known that particulate matter deposition together with high relative humidity can alter insulators' properties and cause flashovers [1]. This means that the infrastructure can be damaged, resulting in high maintenance costs and interruptions in electricity delivery, that can be prolonged in time. The majority of studies address the analytical problem of quantifying the risk of discharge only by a conductivity approach, even the technical standard [2]. This doesn't allow the in-depth understanding of the phenomenon. In this project, the attention was posed on the constituents of the deposit that cause this 'saline pollution' of the insulators. The objective is to use modelling tools to develop more effective and robust alert systems. The experimental set-up included the installation of insulators chains within RSE, in Milan, and was put in place to study the influence, to the properties of the deposit, of: weather conditions, vertical profile, insulator surfaces, coating effectiveness.

2. Results and Discussion

The set-up and the analyses were chosen because they can provide useful information for the model to be built. In 2020-2021, the installation consisted of three chains, one at *ground* level, one on a *roof* of a 40m building, and one in a *box*, to study dry deposition. From these, the deposit was sampled every two months for a year and a half, with the cleaning procedure described in the technical standard, distinguishing the top from the bottom. The first characterizations were the ESDD and NSDD indicators; their respective mean values were 0.01 and 0.02 mg cm^{-2}. These results proved the behavior of these chains to be comparable with the ones obtained during previous investigation campaigns. The attention was then put on the chemical composition of soluble and insoluble fractions of the pollutants, Ionic content was analyzed by Ion Chromatography. The main ions were ammonium, calcium, sodium, potassium, chloride, nitrate and sulfate: respectively, 36, 20, 14, 7, 9, 6 and 3%. Considering bicarbonates obtained by titration, ionic content was able to explain almost entirely the conductivity of the solutions. The main factor that could explain the concentrations found were weather conditions (as for all the other analytes). Almost all of the ions were present in higher concentration for the *roof* chain, except for bicarbonates. The upper surface was the most contaminated. Soluble metals and trace elements were evaluated using Optical Emission Spectroscopy (ICP-OES) technique. It is important to analyze both main and trace elements to obtain information on the sources. Total concentrations were found to be < 1 ppm. As for main ions, the upper face was the most contaminated. Regarding the vertical profile, some metals had unclear trends, like aluminum and chromium, while others, like copper, were preferentially found at ground level. The insoluble carbonaceous content was measured using Thermal Optical analysis in Transmittance mode (TOT), to obtain Organic Carbon (OC) and Elemental Carbon (EC). The mean surface densities were found to be 7.1 and 0.2 µg cm^{-2}, respectively. Up vs down surface factor was more important than vertical profile, unlike what was found for ions, especially for EC. The OC/EC ratio was significantly higher than the typical value of atmospheric particles, even not including the soluble OC, thus indicating evolution phenomena of the deposit and of the sources.

The study was continued with one-year 2022-2023 campaign in which two chains were added to the set-up:

one *ground* and one *box* type. These chains differ from the others because a hydrophobic coating, under study, was applied to them to evaluate its anti-pollution performances. The deposit was sampled in the same way of the previous campaign, every three months. ESDD and NSDD results showed the same order of magnitude of 2020-2021 campaign, as well as the results of the compositional analyses, with similar relative content in soluble and insoluble pollutants. The presence of the coating didn't seem to protect the insulator from the formation of the deposit, as the concentrations were similar to those found on uncoated insulators; more results must be studied to characterize the coating performances.

3. Conclusions

Air quality not only affects humans but also fundamental infrastructures for today's society. In fact, saline pollution of the electrical system insulators is a concerning problem. The aim was to add chemical information to the actual knowledge. Ionic content, soluble metals and traces, and the insoluble carbonaceous content were analyzed in deposits sampled from experimental insulators chains. The results allowed to highlight the role of weather conditions, vertical profile, insulator surface and coating, over the properties of the deposit. This work represents an essential novelty for Italy, and also internationally there are few works available [3], and is of crucial importance in developing alert systems based on models, that will have a concrete impact on our society.

References

[1] Mohammadnabi, S. et al. (2021) 'Influence of humidity and contamination on the leakage current of 230-kV composite insulator'. doi: 10.1016/j.epsr.2021.107083.

[2] International Electrotechnical Commission (2018) IEC 60815-1 'Selection and dimensioning of high-voltage insulators intended for use in polluted conditions'.

[3] He, Z. et al. (2019) 'Analysis of natural contamination components and sources of insulators on ± 800 kV DC lines'. doi: 10.1016/j.epsr.2018.10.033.

OP70

EVALUATION OF POLLUTANT EMISSIONS FROM A HYBRID OVEN (WOOD-FIRED AND GAS-FIRED)

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1. Introduction

Non-industrial combustion is amongst the macrocategories of anthropogenic emissions, as classified by the EEA. Within non-industrial combustion, wood burning contributes to the emissions of the major air pollutants, such as particulate matter (PM), carbon monoxide (CO), organic gaseous carbon (OGC) and polycylic aromatic hydrocarbons (PAHs) [1]. Emissions from this sector derive mainly from small-scale residential heating and cooking appliances. However, a non-negligible contribution has been estimated also for wood-burning ovens used in pizzerias [2]. This is especially the case in urban areas, where there is a higher concentration of establishments which make use of these devices, and population density is high, resulting in hot-spots of human exposure to wood burning. The interest of public administrations in pollutant emissions produced by pizzerias equipped with wood-fired ovens is therefore high, as these administrations are, on the one hand, driven to counteract a very relevant pollutant source, but on the other hand they are cautious about affecting a relevant economic sector and a product particularly appreciated by consumers and typical of Italian tradition.

2. Results and Discussion

Emission factors of the main air pollutants emitted by biomass burning (NOx, CO, PM, PAHs, OGC) were determined through the execution of experimental tests on an hybrid oven, which can operate both as a wood-fired oven and as a gas-fired one. Two different type of fuels were tested in the wood-fired operational mode: beechwood logs and beechwood briquettes. This essence was selected as it is currently the most widespread in Italian pizzerias, especially in the Northern part of the country. An ad-hoc sampling system was constructed by making reference to the UNI EN 16510-1:2019 technical standard and a new sampling protocol was designed to ensure reproducibilty of the tests. All the main phases of oven operation were investigated (cold-ignition, hot re-ignition, stationary cooking) and standard reference combustion cycles were defined for each one. The stationary phase was tested both with and without pizza cooking in order to evaluate the possible impact of this activity on the emissions of the oven.

Based on the data obtained from the experimental tests, the pollutant emissions of the hybrid oven operated with the wood-burning mode fall within the wide range of values observed in literature for other wood-burning appliances, such as stoves and fireplaces [3]. Instead, tests on the oven used with the gas-firing mode show comparable emissions of NOx and a significant reduction in the concentrations of CO and PAHs. Moreover, the use of the gas-fired system enabled to shed light on the effect of pizza cooking on the emissions of OGC and PM. Indeed, by removing the contribution of wood-burning it was possible to highlight the significant impact of pizza cooking on the emissions of OGC during the stationary phase. Moreover, unlike the tests conducted in the wood-fired mode, a significant degree of condensation of semi-volatile organic compounds was observed in the dilution tunnel, as observed by the difference in concentration between particulate matter sampled on the hot and on the cold fumes.

In the absence of specific legislation and/or regulations regarding the emissions of wood-fired pizza ovens, the experimental emission factors determined in this study were compared to the current EU policy regarding emission reduction from domestic combustion. Specifically, the observed values were compared to the 2020 emission requirements for open fronted solid fuel local space heaters. The emissions of both the wood-fired and gas-fired ovens are below the thresholds with regards to NOx and CO, whereas concentrations of OGC and PM often exceed the imposed limits. In both cases, the pizza cooking activity has an important contribution to the emissions for the considered parameters, clearly distinguishable from the emissions deriving from the combustion of the fuel.

3. Conclusions

The results of this study represent a significant step forward towards understanding the extent of the contribution of wood-fired pizza ovens to the emissions of the major air pollutants. Indeed, to the knowledge of the authors, this is the first-ever experimental determination of the emission factors of these devices. The data which is currently present in local emission inventories is based on estimates and modelling approaches and not on experimental testing. Hopefully, these results will help regulatory bodies to update the inventories and determine whether specific actions are necessary in order to limit the environmental impact of cooking ovens, whilst safeguarding a relevant economic sector and traditional product of the Italian culture.

References

[1] Bergomi A., Morreale C., Fermo P., Migliavacca G. Determination of Pollutant Emissions from Wood-Fired Pizza Ovens. Chemical Engineering Transactions 2022, 92, 499-504.
[2] ARPA Sicilia, 2018, Piano Regionale di Tutela della Qualità dell'Aria in Sicilia, Report, Regione Siciliana, IT.
[3] Tomlin A. S. Air Quality and Climate Impacts of Biomass Use as an Energy Source: A Review. Energy & Fuels 2021, 35, 18, 14213–14240.

OP71

LONG-TERM EMISSION ESTIMATES OF RADIATIVELY ACTIVE SPECIES AT THE REGIONAL SCALE USING INVERSE MODELLING TECHNIQUES: SCIENCE FOR SERVICE

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1. Introduction

Emissions of greenhouse gases (GHGs) reported by countries in their GHG inventories to UNFCCC (United Nations Convention on Climate Change) represent the central information used in international policies based on the Paris agreement to help curb global GHG emissions. Quantifying emission fluxes via atmospheric measurements and inverse modelling provides an independent assessment of the national inventories and can help determine their quality and make improvements. Here we present results based on atmospheric observations made at the WMO GAW (World Meteorological Organisation Global Atmosphere Watch) station of Monte Cimone (CMN) in the frame of the AGAGE (Advanced Global Atmospheric Gases Experiment) network for observation of ozone depleting and radiatively active gases. We focus on HFC-134a, whose emissions have been derived through a Bayesian inverse modelling technique by combining observations with an atmospheric dispersion model. Such estimates can help in improving the national emission inventories compiled annually by the Italian Agency for Environmental Research (ISPRA).

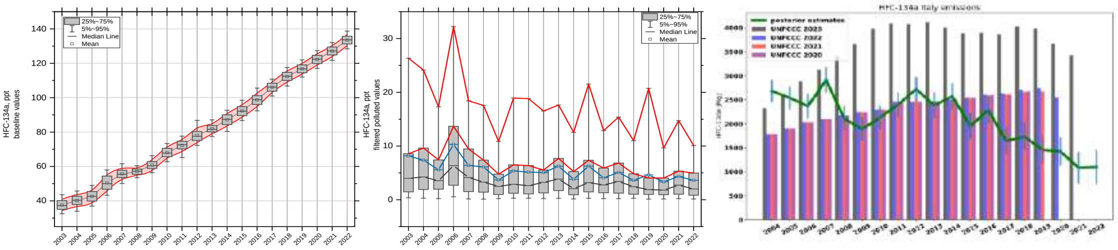
2. Results and Discussion

Long term measurement activities carried out at CMN provide a useful insight into the characterization of the composition of the Southern European atmosphere. Since 2003, ozone depleting substances (ODSs) and halogenated GHGs have been measured at CMN in the frame of the AGAGE programme (Prinn 2018), providing full traceability and harmonization of the measurement scale and protocols. This with the aim of tracking progress towards the implementation of the international treaties on stratospheric ozone depletion and climate and getting a better understanding of emissions both in terms of magnitude and localisation at the regional (EU) scale. By providing high quality, high frequency, continuous -almost uninterrupted- observations of the ozone depleting chlorofluorocarbons (CFCs)and hydrochlorofluorocarbons (HCFCs) and their radiatively active substitutes (HFCs) to modelers, the monitoring activities at CMN are crucial for improving the overall sensitivity of the inverse modelling techniques used to derive emissions, through the so called "top-down" approach, from the Southern EU/Mediterranean region. To verify the implementation of the several treaties involving the reduction on use of HFCs - such as the Kigali Amendment to the Montreal Protocol (2016), the EU F-gas regulation (2014), and the EU-MAC directive (2006)- we focus on HFC-134a, the most abundant HFC in the atmosphere, mainly used on the automotive air conditioning and domestic refrigeration. Measurements are performed with a gas chromatographic-mass spectrometric instrument (Agilent GC6820/ MS5975C) equipped with pre-concentration system that allows trapping compounds at -30°C in a multi-bed adsorbing trap (Markes International, UNITY2-Air Server2). Real air samples are analysed 12 times per day bracketed with working standard runs to calibrate each measurement on the SIO (Scripps Insitute of Oceanography, La Jolla, CA, USA) scale to harmonize results within the AGAGE network.

Time series at CMN show a steady increase of HFC-134a concentrations since the observations started in 2003, as worldwide demand raised, due to the ban of the ozone depleting CFCs. However, while background concentrations are still increasing at a constant pace, the statistical analysis of pollution events extracted from the record show their clear decline both in magnitude and frequency over the years, reflecting an underlying reduction of fresh emissions from the EU domain. A Bayesian inversion analysis is used to optimise the emission fluxes from the EU domain starting from the a-priori information fields based on the EDGAR (Emission Database for Global Atmospheric Research) inventory (Graziosi et al. 2016). The proposed method is based on Lagrangian Particle Transport model FLEXPART, driven by ECMWF-ERA5 meteorology data with 0.28x0.28 degree spatial and 3-hrs temporal resolution, to simulate 5-days backward air mass transport to the receptor, coupled with the analytical inversion algorithm FLEXINVERT+; results show that the optimized emissions for the EU, and in particular for Italy, are constantly decreasing over years. Conversely, NIRs (National Inventory Reports) based solely on statistical data (the so-called bottom-up approach) reported annually to UNFCCC by ISPRA show a different and not always coherent picture, reflecting some weaknesses of the bottom-up methods.

3. Conclusions

The use of the top-down approach to support and improve the quality of NIRs, has been first suggested by the IPCC (Intergovernmental Panel on Climate Change) 2006 national GHG inventory guidelines and reiterated in the 2019 refinement of the same guidelines. Supporting the scientific research at national level is a key step not only to improve the basic knowledge of the complexity of atmospheric science but also to provide a service for the worldwide community.



HFC-134a, statistical results on observations (baseline values, left panel, and pollution events, middle panel) and derived emission fluxes for Italy compared with NIRs (right panel)

References

Prinn et al “History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE)",2018, Earth System Science Data, 10, 2, 985, 1018, doi: 10.5194/essd-10-985-2018.
Graziosi et al.“European emissions of the powerful greenhouse gases hydrofluorocarbons inferred from atmospheric measurements and their comparison with annual national reports to UNFCCC",2017, Atmospheric Environment, 158, 85-97, doi: 10.1016/j.atmosenv.2017.03.029

OP72

CLIMATE CHANGE TRIGGER ATMOSPHERIC TRANSPORT OF NUCLEAR WASTE RESIDUALS TO THE ARCTIC

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1. Introduction

The primary environmental concern related to nuclear power is the production of radioactive waste hazardous to humans and the environment. The main scientific and technological problems to address this are related to the storage and disposal of the nuclear waste and monitoring the dispersion of radioactive species into the environment (Isogai 2002).We discovered anomalously high ^{14}C activity in Arctic snow sampled in spring 2019. We attributed the contamination to an intense episode of warm and humid air intrusion from lower latitudes were the air masses have uptake residuals from nuclear waste reprocessing materials.

In a scenario of a warming Arctic (Cohen 2014) these intrusions events are expected to increase in frequency and intensity (Dada 2022) therefore posing concerns about the contamination of a pristine environment with hazardous materials such as nuclear wastes and pollutants in general (Cappelletti 2023).

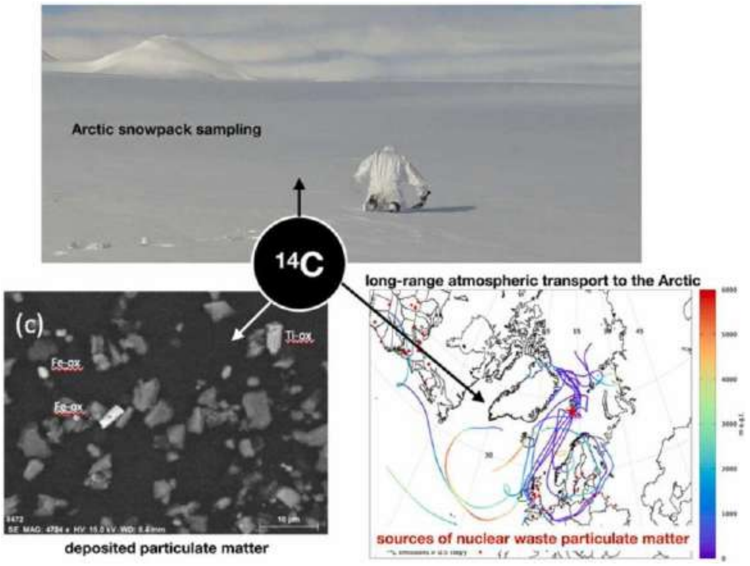
2. Results and Discussion

In this work, we determined an anomalously high 14C activity, well above the modern natural background, on surface and seasonal snow sampled in early May 2019 on glaciers in the Hornsund fjord area (Svalbard). Due to the lack of local sources, the high snow concentrations of 14C suggest long-range atmospheric transport of nuclear waste particles from lower latitudes, where nuclear power plants and treatment stations are located. The analysis of the synoptic and local meteorological data allowed us to associate the long-range transport of this anomalous 14C concentration to an intrusion event of a warm and humid air mass that likely brought pollutants from Central Europe to the Arctic in late April 2019. Elemental and organic carbon, trace element concentration data, and scanning electron microscopy morphological analysis were performed on the same snow samples to better constrain the transport process that might have led to the high 14C radionuclide concentrations in Svalbard. In particular, the highest 14C values found in the snowpack (> 200 percent of Modern Carbon, pMC) were associated with the lowest OC/EC ratios (< 4), an indication of an anthropogenic industrial source, and with the presence of spherical particles rich in iron, zirconium, and titanium which, altogether, suggest an origin related to nuclear waste reprocessing plants.

3. Conclusions

This study highlights the role of long-range transport in exposing Arctic environments to human pollution. Given that the frequency and intensity of these atmospheric warming events are predicted to increase due to ongoing climate change, improving our knowledge of their possible impact to Arctic pollution is becoming urgent.

OP72



Carbonaceous aerosol and mineral dust sampled in the Arctic snowpack revealed an anomalous ^{14}C contamination

References

K.Isogai et al. J. Environ. Radiol 59 (2002) 207-222
L. Dada, *et al.* Nat. Commun. 13 (2022) 1-15
J.Cohen et al., Nat. Geosci. 7 (2014) 627-637.
D. Cappelletti et al., J. Hazard. Mat. 452 (2023) 131317.

SPATIAL AND TEMPORAL VARIATION IN SURFACE SNOW CHEMISTRY ALONG A TRAVERSE IN THE EAST ANTARCTIC PLATEAU IN THE FRAMEWORK OF THE EAIIST PROJECT

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1. Introduction

Understanding the chemical variability of snow is key in the glaciological and glaciochemical studies since it allows to investigate both the past variations of snow from ice cores, but also to evaluate mass transport of chemicals, scavenging processes, wind distributions etc., fundamental parameters to characterize the unexplored areas of the Antarctic ice sheet from a climate perspective. Despite this, a large part of the East Antarctic plateau, especially the driest regions, is still unexplored. In the context of the EAIIST (East Antarctic International Ice Sheet Traverse) samples from the most arid places of Antarctica were collected and analysed with the goal of investigating these regions characterized by several unique geographical features (such as "megadune" and "wind crusts" areas) and where both physical and chemical processes of the snowpack are not yet fully understood.

2. Results and Discussion

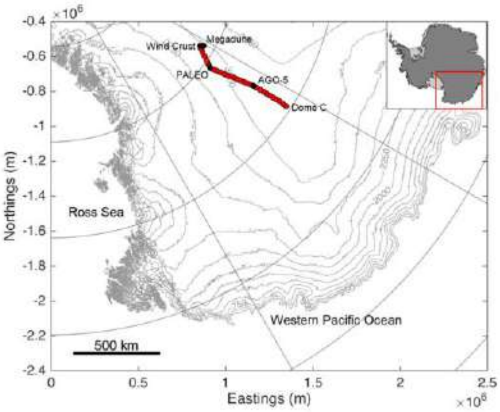
In this work 32 samples of surface snow and 5 shallow (approx. 2 m deep) snow pits were collected during the traverse following the 123° meridian moving from Concordia Station (75°05'S, 123°19'E). All samples were analysed once thawed by means of ion chromatography. Both cationic (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anionic (Cl^-, NO_3^-, SO_4^{2-}) content was determined working in a clean room (Class 10000) and under a class 100 laminar flow hood when possible. The chromatographic run was optimized taking into account for the extremely low concentration of the samples but also the absence of other ionic interference. This allowed to shorten the chromatographic run (5.5 min for both cations and anion) and, thanks to the high resolution, the volume of sample required was also reduced (200uL). The resulting concentration were plotted against the latitude and depth of the ice in order to study the temporal and spatial variability of chemicals across the plateau.

First, the non-sea-salt sulphate ($nssSO_4^{2-}$) stratigraphies from the shallow cores were used to date the ice using well known volcanic eruptions [1,2] and therefore obtain an estimate of the variation of snow accumulation rate across the plateau. This allowed to study not only the concentration of chemicals in the ice, but also their fluxes over Antarctica, which was used to study depositional and post-depositional processes occurring in the first layer of snows as a function of accumulation rate and glaciological features.

Sea-salt and non-sea-salt fractions for most ions were investigated and their ratios evaluated. For Na^+, more than 90% of the total budge of the ion was ascribed to a marine source, this was confirmed by the excellent correlation with other well-known marine ions such as Mg^{2+} and K^+, and more importantly, Cl^-. Ratios between Cl^- and Na^+, despite the correlation between the two, was found consistently higher than the one found in sea water, suggesting an alternative source for Cl^-. This was investigated by calculating the $nssCl^-$ fraction, mostly coming from the reaction with acidic species in the snow and correlating the variation in concentration in the surface snow with the distance from the sea. Both dry and wet deposition phenomena were found for the $nssCl^-$ fraction and this was highlighted by the trend in the shallow firn and ice core from the 5 inland sites. Similar considerations were done with other acidic species, such as NO_3^- that is known to have multiple sources, including the snowpack itself that acts as an accumulator of HNO_3 and its precursors [3]. The concentration found in the snow was compared with the one calculated considering the uptake of snow coming from both deposition and dry phenomena and the different processes occurring studied in the five different sites and correlated with their glaciological characteristics.

3. Conclusions

Sea-salt aerosol was proven to be mainly wet deposited in the Antarctic plateau despite the very low accumulation in the area. $NssSO_4^{2-}$ is mostly dry deposited, but it was noticed that the relative importance between biogenic and crustal contribution of sulphate changes with the distance from the sea, which could help explaining the discrepancy of biogenic activity as recorded from ice and marine sediments core [4,5]. Lastly, for Cl^- and NO_3^-, both affected heavily by post depositional processes, their re-emission in the first layers of snow was investigated especially in sites affected by wind scouring. The knowledge and quantification of these processes will allow to better interpret the chemical data in ice cores as a function of environmental and climatic variation of the past.



Snow surface samples (in red) and shallow snow pits (black) across the EAIIST traverse

References

[1] Castellano, E., et al., J. Geophys. Res., 110, D06114 (2005)
[2] Nardin, R., et al., Geosciences, 10(1) 1-15 (2020)
[3] Savarino, J., et al., Atmos. Chem. Phys., 7(8) 1925-45 (2007)
[4] Wolff, E. W., et al., Nature, 440(7083), 491-96 (2006)
[5] Kohfeld, K. E., et al., Science, 308, 74-78 (2005)

OP74

MICROWAVE-ASSISTED MINERAL CARBONATION OF BRUCITE AS A PROXY FOR CO_2 CAPTURE BY SERPENTINE USING AN EQUILIBRIUM MODEL TO VALIDATE EXPERIMENTAL DATA

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1. Introduction

Anthropogenic CO_2 emissions are responsible for global warming, problem that needs a solution. Among carbon capture and storage methods, mineral carbonation (MC) is very promising being irreversible. It is the reaction between CO_2 and Ca and Mg oxides (minerals) to form carbonates, stable compounds in which CO_2 is trapped. It takes place in the aqueous phase and involves mineral dissolution and CO_2 hydration, to give the active ionic species passing through chemical equilibria. MC is spontaneous, but has a kinetic problem being too slow compared to CO_2 emissions, thus it needs to be artificially accelerated and this costs energy. This PhD project studies microwaves (MW) as a new way to increase MC rate, activating the cleavage of the mineral, i.e. antigorite, a polymorph of serpentine, Mg phyllosilicate suitable for CO_2 capture due to its reactive cleavage surfaces. Given its complex structure, that alternates silica and brucite layers, this study involves only the active component towards MC: brucite. Results of experimental tests of brucite MC varying MW power supplied were compared with data from a chemical equilibrium model useful to describe the system evolution over time.

2. Results and Discussion

MC reactions were performed using a MW synthesizer capable of operating at high temperatures T and pressures p, with a teflon vessel which allows carbonations to be carried out in aqueous solution by controlling the atmosphere of the overlying gaseous phase. The instrumental output was a graph showing the reactor T and p versus time t, with p being used as an indicator of the reaction progress. This is because its variation over t was given by the only reactive species present in the gas phase: CO_2, so the greenhouse gas capture implies a decrease in p, which is measured continuously and instantaneously by the instrument.

A first set of tests was carried out at a fixed T (70 °C) to test the reactivity of the starting materials towards CO_2. The reagents tested were:

- deionized water (blank)
- talc (powder – Carlo Erba Chemicals), $Mg_3Si_4O_{10}(OH)_2$: representing silica, resulting inert (flat curve for p)
- brucite (powder – Sigma-Aldrich), $Mg(OH)_2$: two different grain sizes:
- as-is: 2.0 μm (DLS in water)
- grinded (mortar and pestle): 1.1 μm (DLS in water).

In both cases brucite was effective in CO_2 capture (drop in p curve), with MC reaction being faster for the grinded species (more rapid drop in p), as expected for smaller particles and thus with greater surface area.

Having identified brucite as the active component of the reference mineral for CO_2 capture, the second set of tests concerned MC of brucite at different T (from 40 to 145 °C, every 15 °C) thus varying the energy supplied by MW, keeping the other experimental conditions unchanged. The p curves showed that there was no clear activation effect of the reaction with T, as two antagonistic effects competed: CO_2 solubilization from the gas phase (favored at low T) and mineral flaking (favored at high T). Furthermore, analysis of the carbonation products by X-ray diffraction revealed that different hydrates of the generic $MgCO_3$ were formed: nesquehonite, $MgCO_3 * 3 H_2O$, ($T < 60$ °C) and hydromagnesite, $Mg_5(CO_3)_4(OH)_2 * 4 H_2O$, ($T > 60$ °C).

The subsequent phase of the work involved the study of a model based on thermodynamics and chemical equilibrium and its application to the group of thermal tests conducted on brucite to better understand the process and to compare the results obtained. The elaboration of the model was based on the writing of the chemical equilibria that regulate the entire MC reaction:

- CO_2 solubilization from the gaseous phase (Henry's law)
- CO_2 hydration to carbonic acid
- H_2CO_3 dissociation to bicarbonate ($K_{a,1}$) and carbonate ($K_{a,2}$) ions
- brucite dissolution
- dissolution of the carbonates produced, i.e. nesquehonite and hydromagnesite.

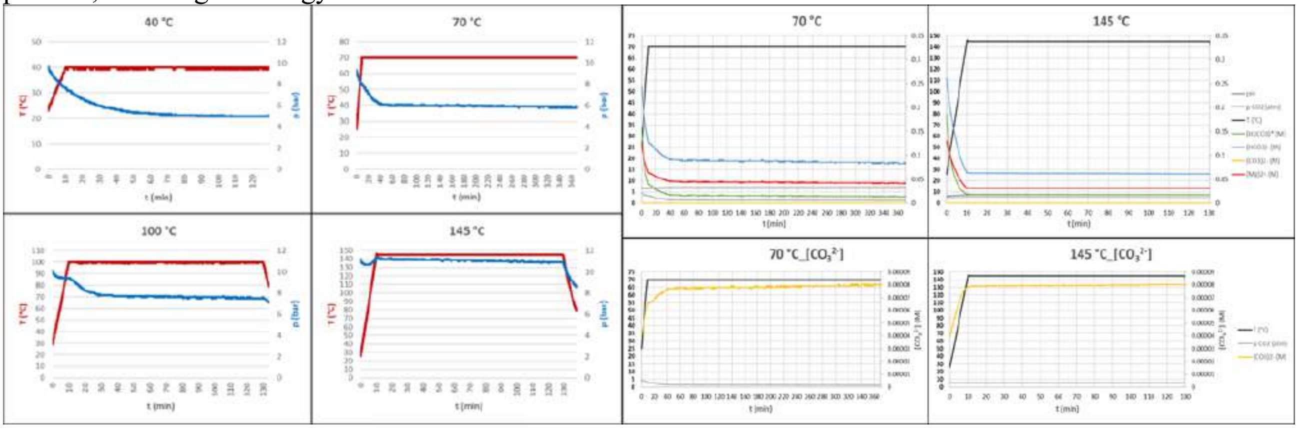
The use of equilibrium constants and the application of the electroneutrality condition allowed to write, as it evolves over t, the concentration of each single species present in solution involved in the brucite carbonation process, as a function of a single, experimental parameter, which is CO_2 partial pressure in the vessel atmosphere, obtainable from a simple calculation for each instant of the reaction.

The comparison between the data obtained in this way and the experimental ones proved to be good regarding:

- ✓ pH trend over t and its value before and after the reaction
- ✓ concentration of the single ionic species of interest over t with respect to expected trends
- ✓ trend of the product mass over t and order of magnitude of its final value.

3. Conclusions

The study of brucite as a proxy for CO_2 capture by serpentine proved to be effective as the formation of carbonates, compounds in which the greenhouse gas is permanently trapped, was obtained. The experimental system employed proved to be useful for real-time monitoring of the progression of the MC process, together with the use of the equilibrium model, which made it possible to describe the course of the reaction over t, confirming the data obtained experimentally. However the formation of product crystals does not occur at equilibrium, thus a kinetic study is needed to obtain accurate information on reaction rate. Moreover, experimental parameters, first of all T, need to be further investigated in order to optimize the speed of MC process, reducing its energy costs.



T, p vs. t for brucite MC (left). Antagonistic effects for T are shown, with no clear trend for p drop; Curves obtained from the chemical equilibrium model for two MC tests on brucite (right).

References

1. Harrison, 2019, Solubility of the hydrated Mg-carbonates nesquehonite and dipingite from 5 to 35 °C: Implications for CO_2 storage and the relative stability of Mg-carbonates, Chemical Geology
2. Gautier, 2014, Hydromagnesite solubility product and growth kinetics in aqueous solution from 25 to 75 °C, Geochimica et Cosmochimica Acta
3. Sanna, 2014, A review of mineral carbonation technologies to sequester CO_2, Chemical Society Reviews

OP75

NEW INSIGHTS INTO THE DEGRADATION PATH OF EMERALD GREEN IN OIL PAINTINGS

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1. Introduction

Emerald green (EM) is a copper acetate arsenite ($Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$) pigment, found in the palettes of famous impressionist and post-impressionist artists. It was introduced to improve the optical properties of its precursor, Scheele's green; a copper arsenite-based compound, characterized by variable stoichiometries [1].

EM undergoes degradation in oil painting as observed on a sample taken from a discolored area of the painting *"Descente des vaches"* by T. Rousseau [2]. Notably, FT-IR analysis and As K-edge XANES analysis have documented the presence of Cu^{2+}-soaps, As^{3+}-oxide and As^{5+}-compounds, respectively, which have been assumed as possible degradation products of EM [2,3].

The present contribution aims at describing the effect of environmental parameters on EM paint's stability, by presenting the vibrational spectroscopic and synchrotron radiation (SR)-based X-ray results (ESRF, Grenoble) collected from a set of artificially aged mock-ups. The resulting spectroscopic information was exploited to evaluate the degradation state of EM-containing areas of selected historical artworks. Indeed, the corresponding outcome of non-invasive in-situ analysis campaigns (in part carried out through the MOLAB platform within the Iperion HS project) will be also discussed.

2. Results and Discussion

To shed light on the factors affecting the degradation path of Cu-As oil paints, a laboratory work on paint mock-ups was carried out. After the accurate characterization of morphological, structural, and chemical properties of each pigment powder (in-house synthesized and historical), paints were prepared by mixing the pigment with linseed oil (4:1 weight ratio). Once the samples were dried, they were subject to artificial aging. The aging protocols were chosen to assess the separate effect of light (UVA-Vis) and relative humidity ($RH \geq 95\%$), as well as the combination of both on the pigment reactivity in the oil binder. The treatment of mock-ups was followed by bench-top and portable devices (operating both in point-analysis and imaging/mapping mode) with conventional and SR sources.

SR μ-XANES/μ-XRF measurements at As K-edge and reflectance FT-IR analysis revealed that the photo-aging (both at environmental and high humidity conditions) triggered the formation of As^{5+}-species at the surface. In the dark, high moisture conditions induced instead the formation of arsenolite (As_2O_3) across the entire paint stratigraphy. In all the employed aging conditions, copper did not show any change of its oxidation state, but Cu^{2+}-carboxylates (soaps) were developed in high humidity.

Overall, such outcomes clearly highlight that the oxidation of As^{3+} to As^{5+} is prompted by light exposure. In addition, the study of aged paint mock-ups allowed us to build a database of EM degradation products by portable non-invasive FT-IR spectroscopy, via identification of their characteristic spectral features. The knowledge so acquired was then exploited to interpret the corresponding data recorded from EM-containing areas of a selection of paintings by Robert Delaunay (1885-1941) and James Ensor (1860-1949).

3. Conclusions

In this research, the study of laboratory paint mock-ups allowed us to prove that the degradation path of EM (copper acetate arsenite) in the oil binder is favoured by the exposure to UVA-Vis light and humidity. While light promotes the oxidation of original As^{3+} to As^{5+}-compounds, moisture prompts the formation of arsenolite. Both compounds are responsible for the color change of the painted surface. The knowledge gained from the FTIR study of paint mock-ups was then used in-situ to evaluate the degradation state of EM-containing areas of historical artworks, by revealing the presence of degradation products, even when the discoloration of the paint is hardly visible with the naked eye. Warning conservators of ongoing degradation, prior to visible damage, together with the knowledge of the main environmental parameters which induce the degradation, are of key importance both to optimize the conservation conditions and, when necessary, to select the most appropriate conservation/restoration treatments.

References

[1] Fiedler, I. Bayard, M. A. In: *Artists' pigments, a handbook of their history and characteristics*. **1997**, *Vol. 3 (Ed. E. W. Fitzhugh)*, 219-271.
[2] Keune, K. Boon, J.J. Boitelle, R. Shimadzu, Y., *Studies in Conservation.* **2013**, *Vol. 58*, 199-210.
[3] Keune, K. Mass, J. Mehta, A. Church, J. Meirer, F., *Heritage Science*, **2016**, *Vol. 4 (n*. 10).

OP76

INTRA-SOURCE NON-DESTRUCTIVE PROVENANCE STUDY ON MONTE ARCI (SARDINIA) OBSIDIAN BY PXRF: A COMPARISON OF DIFFERENT ANALYTICAL APPROACHES

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1. Introduction

Obsidian is a natural nanocomposite,[1] whose extended use during the Neolithic and its good conservation over millennia in the archaeological sites make it a precious archaeological material to obtain information on its exchange/procurement routes and, consequently, on the organization of these ancient human communities. In the Western Mediterranean, only four geological sources were available in four Italian islands, among which Sardinia.[2] There, four primary subsources, named SA, SB1, SB2, and SC, in the Monte Arci were differently exploited even far away from their location, leading to evidence of selection criteria of the raw material and good seafaring abilities.[3,4] In the literature, different analytical methods have been proposed with the aim of discriminating the main obsidian sources based on its geo-chemistry, physical properties, or geological age, and in order to associate each artifact to the original raw material, in the so-called provenance studies. Intra-source studies are more challenging due to the higher similarities in the chemical and physical features, and the debate in the literature is still open.

2. Results and Discussion

In this work,[5] the Monte Arci obsidian geological sub-sources were characterised by portable X-ray fluorescence (pXRF) for a total of 68 samples, for the development of an X-ray fluorescence-based analytical standardless procedure and a nonconventional approach (in the framework of obsidian provenance studies) based on the direct multivariate analysis on XRF spectra.

The experimental conditions (analysis time, beamshutter aperture) for the analysis were carefully selected to improve the signal/noise ratio. Different softwares were adopted to obtain the mean values of intensity ratios accompanied by a standard deviation obtained from three independent measurements between discriminative elements for the bi-/trivariate method. In a blind test, this approach led to the correct assignment for the main SA, SB, and SC sub-sources, with an almost 13% of error in the assignment, 9 samples out of 68, for the durther distinction of the SB groups. The multivariate analysis on the XRF spectra provided a correct assignment for the SA, SB1, SC geological samples, while 71% of the SB2 samples were correctly identified. The as-developed approaches were also tested for the non-destructive provenance study on 14 archaeological samples from the archaeological site of Su Carroppu (Carbonia, southwestern Sardinia) rockshelter and from the Middle Neolithic (MN) 422 structure of the open-air dwelling site at Cuccuru is Arrius (Cabras, centralwestern Sardinia). A correct provenance assignment of all artifacts was obtained for the bi-/trivariate method, and of 12 samples out of 14 in the case of the multivariate one. The efficacy of the methods was verified by visual characterization and/or previous analyses by Particle Induced X-Ray Emission (PIXE).

3. Conclusions

The standardless analytical approaches proposed in this work both succeeded in the discrimination of the Monte Arci sources, in particular for the SA, SB1 and SC groups, while limits were observed in the identification of the obsidian samples from SB2, probably with an intrinsic higher compositional variability.

The proposed methods, besides the local impact, can represent a more general method exploitable for other provenance studies on materials of archaeological interest.

References

[1] Mameli, V., Musinu, A., Niznansky, D., Peddis, D., Ennas, G., Ardu, A., Lugliè, C., Cannas, C., 2016. J. Phys. Chem. C 120, 27635–27645.
[2] Francaviglia, V., 1984. Preist. Alp. 20, 311–332.
[3] Tykot, R.H., 2002. Acc. Chem. Res. 35, 618–627.
[4] Lugliè, C., Le Bourdonnec, F.X., Poupeau, G., Bohn, M., Meloni, S., Oddone, M., Tanda, G., 2006. Comptes Rendus - Palevol 5, 995–1003.
[5] Mameli, V., Sanna Angotzi, M., Farinini, E., Leardi, R., Lugliè, C., Cannas, C., 2023. Heliyon 9, e13958.

OP77

ACID DYES-BASED INKS: DISCLOSING THE DEGRADATION PATHWAYS OF MODERN INKS THROUGH AN OPTIMISED CHROMATOGRAPHIC METHOD

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1. Introduction

In the late 19th century, the introduction of synthetic organic pigments (SOPs) onto the market brought manufacturers into a new and fascinating landscape for ink's production, allowing to obtain high-performance and low-cost inks, and to explore a wide range of bright colours [1]. Thus, composition of inks dramatically changed in the early days of synthetic chemistry, encompassing complex mixtures of SOPs characterised by acid and basic functional groups [2]. Highly selective and sensitive methods, such as liquid chromatography coupled to diode array detector or tandem mass spectrometry (HPLC-DAD-ESI-Q-ToF), are necessary to characterise modern ink composition. However, the presence of acidic SOPs produces chromatographic fronting, leading to loss of resolution and sensitivity [3]. The characterisation of writing inks is further complicated by several issues, e.g. the variety of materials and recipes and the unreliability of commercial labels, and degradation processes. Thus, the chemical investigation of collections of historical-artistic materials is needed to improve our knowledge of technologies, synthesis, and ink composition of the early days of synthetic chemistry.

2. Results and Discussion

In the present work, a HPLC-DAD-ESI-Q-ToF method was specifically optimised for the analysis of acid dyes-based inks. Starting from an optimised chromatographic gradient for natural dyes analysis [4], different flow rates (0.4 and 0.6 mL/min) and formic acid percentage as mobile phase modifier (0.1%, 0.3% and 1%, v/v) were tested on standard natural dyes (carminic acid, alizarin and purpurin), and standard SOPs belonging both to acid (cotton scarlet, amido naphthol red G, and naphthol yellow S) and basic classes (methylene blue, methyl violet, and fuchsine). The data elaboration was performed in terms of number of theoretical plates, ionisation efficiency, limit of detection, and limit of quantification. The results obtained allowed us to determine an optimal chromatographic method with the following conditions: H_2O + 1% formic acid (FA); acetonitrile + 0.3% FA; flow rate = 0.6 mL/min. The optimised method was then applied to the analysis of a collection of modern inks produced in France in the late 19th- early 20th century, proving effective in improving both sensitivity and selectivity. The characterisation performed by HPLC-DAD-ESI-Q-ToF highlighted that the formulations from the early days of synthetic industry were mainly based on rhodamine B and 6G, eosin Y, rose Bengal, cotton scarlet and amido naphthol red G. Moreover, to predict possible degradation markers useful for dating and authentication, ageing tests were performed to simulate the ageing processes that could naturally occur in historical manuscripts and ink drawings. Thus, the most representative French ink formulations were selected, and their reference ink mock-ups (cast as water dispersion on Whatman filter paper, pure cellulose) were exposed at room temperature (T=25°C) to natural indoor light, and at RH c.a. 50%. Liquid chromatography coupled to tandem mass spectrometry enabled us to identify significative differences by comparing the unaged and aged ink's molecular profiles. Eosin Y-based inks show a general trend of decreasing relative percentage of eosin Y (EoY) and (3,5-dibromo-2,4-dihydroxybenzoyl)- benzoic acid (BHBA) formation in response to ageing (Figure 1), providing different fade kinetics depending on the ink formulation and whether other SOPs are present. Cotton scarlet-based inks are the most resistant to light fading mechanism amongst the set, showing significative changes only after two months of exposure to natural light. Finally, the ageing pathway of rhodamine B and 6G promotes consecutive N-deethylations reaction of the

SOPs backbones, proving that the photo-oxidation pathway already determined in the literature for historical textiles [5] also occurs during ink ageing.

3. Conclusions

The chromatographic method optimised in the present work allowed us to obtain the best compromise between number of theoretical plates and ionization efficiency for natural and synthetic dyes, resulting in an effective strategy for the analysis of historical and modern inks. The application to a collection of 19th – 20th century inks lead to a broad overview of the composition of inks in the early days of synthetic chemistry, and it could provide the springboard for a new way to investigate writing materials in historical samples by introducing ultra-sensitive chromatographic and mass spectrometric methods in the array of analytical tools. Our studies support art technological studies, and could bring important insights into the field of dye degradation in ink matrix.

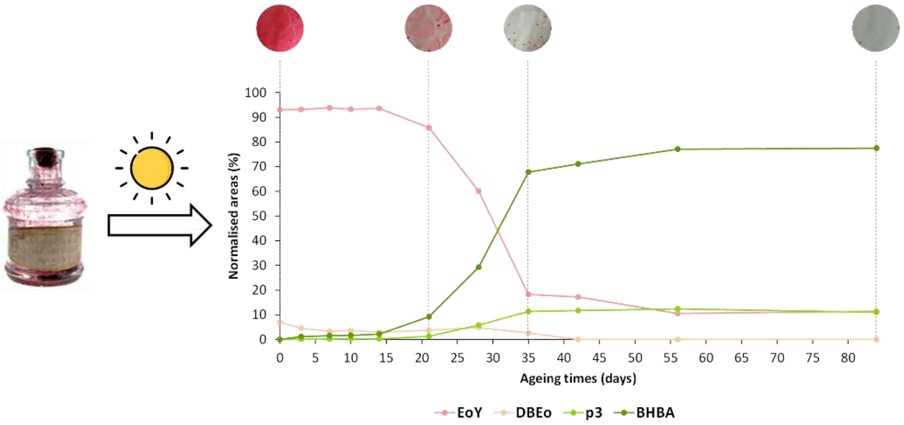

Figure 1: Semi-quantitative analysis results of French Ink 2 ageing.

References

[1] B. Reissland, A.N. Proaño Gaibor, F. Ligterink, J.G.Neevel, Exploring the Late 19th-Century Landscape of Ink Manufacturing via a Collection of 90 Bottles. *ICOM-CC 18th Triennial Conference*, **2017**.
[2] C. A. Mitchell, Inks: their composition and manufacture, **1904**.
[3] P.Jandera, J. Fischer, V. Stanek, M. Kucerova, P. Zvonicek, Separation of aromatic sulphonic acid dye intermediates by high-performance liquid chromatography and capillary zone electrophoresis, *Journal of Chromatography A*, **1996**.
[4] A. Ferretti, F. Sabatini, I. Degano, A Model Iron Gall Ink: An In-Depth Study of Ageing Processes Involving Gallic Acid, *Molecules*, **2022**.
[5] F. Sabatini, R. Giugliano, and I. Degano, Photo-oxidation processes of Rhodamine B: A chromatographic and mass spectrometric approach, *Microchem. J.*, **2018**.

OP78

BIOFILM FORMATION AND BIOCORROSION ON HISTORICAL OUTDOOR BRONZE ARTEFACTS

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1. Introduction

Microbial-influenced corrosion (MIC) on metal outdoor cultural heritage (CH) structures and in particular on historical bronze artefacts is still rarely studied, being mostly investigated in anaerobic environments, such as buried conditions. It is acquiring increasing importance due to the change in both bacterial compositions of biofilm and biodeterioration occurring on CH surfaces leading to biocorrosion as a result of climate and atmospheric composition changes. The study by (Timoncini et al., 2022) explored bacterial communities on outdoor bronze monuments, composed of mostly copper-resistant Methylobacterium. Only Cu-resistant bacteria can survive on these surfaces due to antimicrobial free-Cu ions (Lemire et al., 2015). The current changing environment imposes to consider not only the aerobic environmental conditions but also the biological agents involved, in order to understand and predict the decay of CH materials. Therefore, the aim of this work is an investigation of MIC on various bronze materials in outdoor conditions to fine-tune conservation and preservation strategies for bronze artefacts in the next years.

2. Results and Discussion

The present study investigates the growth of bacteria in both planktonic and biofilm forms attached to the bronze surface and the related corrosion. To do so we selected the following types of bronze (artistic casting alloy Cu-5Sn-5Zn-5Pb): (i) pristine and (ii) artificially aged (simulating wet&dry cycles of outdoor exposure to rainwater), with both materials coated with naturally sourced cutin-based anti-corrosion polyester-urethane coating derived from tomato peel waste. This allows us to assess: (i) how bronze surface conditions (pristine vs. aged) affect the bacterial colonization capacities and biocorrosion; (ii) the protective efficiency of the cutin-based coating from biocorrosion and (iii) how surface conditions (pristine vs aged) affect the protectiveness of this coating.

The study includes the use of environmental and metal-resistant bacteria strains, specifically: *Pseudomonas Putida*, *Pseudomonas pseudoalcaligenes* KF707, *Pseudomonas fluorescens*, *Cupriavidus metallidurans* CH3Y, and *Rhodococcus aetherivorans* BCP1. They have been chosen since they are common in soils, and have been studied for their biofilm and metal-tolerant properties. They can be transported to other places, like monument surfaces. The substrates were exposed for 6 days to the 5 bacterial strains in a media which simulate the rainwater composition typical of a polluted Mediterranean area, such as the Po Valley, under the climate change scenario (Timoncini et al., 2023). This rainwater was modified to include, besides the nutrients, firewood powder, and degraded crude oil to simulate pollutants from coal, wood and petroleum burning. Biofilm quantification is carried out using the crystal violet dye, which stains biological compounds. The supernatant is analysed via absorbance to get proxies for both bacterial growth and corrosion, at 600 and 575 nm respectively. Direct microbial counting of colony-forming units included both biofilm and supernatant to understand the distribution of living cells which induce the biofilm production. The corrosion will be quantified also via pickling and SEM-EDS surface observations.

The results show the capabilities of these bacterial strains to form biofilm on these substrates. In detail, on pristine bronze (Fig. 1), they show species-specific responses in terms of biofilm amount produced and regarding the proxy for both planktonic cell growth and corrosion. Indeed, strains KF707 and CH3Y show the highest biofilm mass, whilst the other 3 bacterial strains showed more reproducibility in trials. Here, the proxy for corrosion shows higher values for *P. fluorescens* and *P. putida* (Fig. 1).

In our closed assay system, no living cells were found inside the biofilm after the 6-day exposure, only some living cells were present in the supernatant, in particular for the CH3Y. At this point we can state that, this strain can thrive within the media composed of rainwater enriched in nutrients and pollutants and attach efficiently to the pristine bronze, subsequently starting to form biofilms.

We can postulate from our results to date that live cells in a polluted rainwater scenario (as in a puddle splashed onto a CH), may grow and attach to the bronze surface, leading to MIC. The corrosion products would include Cu ions that are antimicrobial active, eventually killing the bacteria but leaving organic biomass on the bronze surface.

3. Conclusions

This study investigates the biofilm formation and related biocorrosion, in aerobic conditions, produced by 5 robust soil bacteria on two types of bronze surfaces (pristine vs artificially aged to simulate outdoor exposure), subsequently coated for corrosion protection. We prove the capability of bacteria to form biofilm leading to biocorrosion on outdoor CH bronze surfaces, surprisingly, also on pristine ones. A species-specific response has been found. This work links the necessity of studying the biocorrosion on outdoor bronze surfaces and the effects of the current climate change on this CH material. Indeed it establishes the basis for future studies of biofilms on them in order to better fine-tune outdoor bronze preservation and conservation strategies for the coming decades.

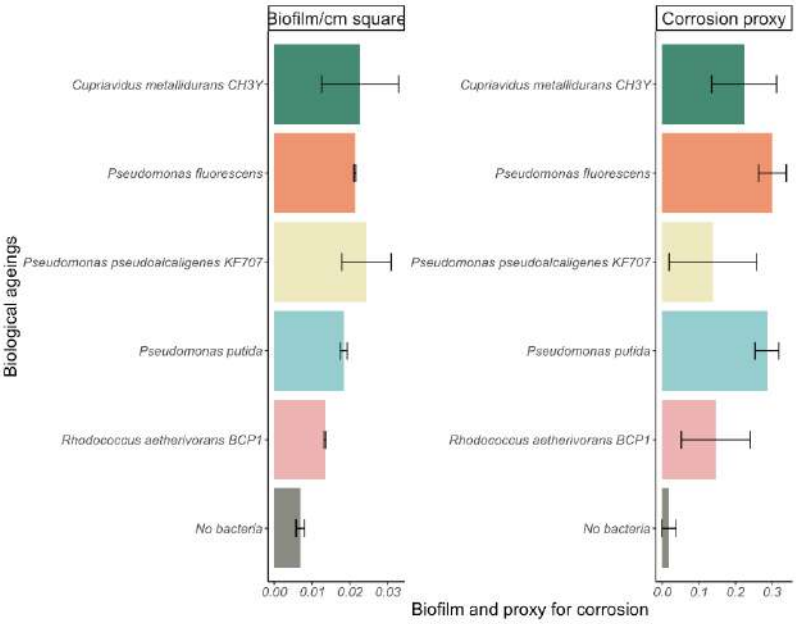

Figure 1. Biomass (organic material, live and dead cells in biofilm) quantification per cm square on pristine bronze n=4 (2 biological trials with two technical replicates) and corrosion proxy.

References

Lemire et al. 2013. Antimicrobial activity of metals: Mechanisms, molecular targets and applications. *Nat. Rev. Microbiol.* 11;371-384

Timoncini et al. 2023. Safeguarding outdoor cultural heritage materials in an ever-changing troposphere: Challenges and new guidelines for artificial ageing test. J Cult Herit 59, 190–201.

Timoncini, et al. 2022. Insight on bacteria communities in outdoor bronze and marble artefacts in a changing environment. Sci Tot Environ 850, 157804.

BLACK-APPEARING GLASS FROM IRON AGE CENTRAL ITALY: AN INSIGHT INTO THE MATERIAL THROUGH CHEMICAL ANALYSES

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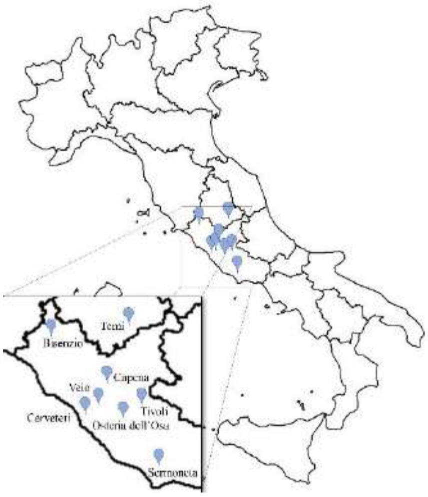
1. Introduction

Glass beads and other decorative glass objects are frequently found in archaeological excavations, although somehow overlooked by the archaeologists. Nevertheless, they keep the chemical fingerprint of the raw materials employed to produce and colour the glass, and chemical analyses can enhance their role as testimonies of regional and long-distance exchanges.

Here, we consider twenty-eight glass beads and two fibula bows from the collections of the Museo delle Civiltà in Rome, found in several archaeological sites in South Etruria and Latium (present Central Italy). They are dated from 900 to 625 BCE, when relevant changes occurred in glass technology. The focus is set here on the black-appearing glass, which was investigated in the frame of a broader interdisciplinary research project. The set of archaeological items includes mostly monochrome items, but several polychrome objects were also included. Digital microscopy, XRF, and FORS were used in the museum's premises to preliminary characterise the archaeological items. Then, some of them were transferred to the laboratory for further insight into their composition by means of SEM-EDS (one sample prepared as a polished cross section) and LA-ICP-MS (16 samples).



Map of the archaeological sites in which the glass items were found.

2. Results and Discussion

FORS was utilised to get information on the colouring species, although the low reflectance of such dark glass often prevented informative spectra from being collected. Some items featured strong absorption in the UV

region, possibly due to the high concentration of Fe(III). Cu(II) was detected in a few samples, and only one pear-shaped bead (possibly a small spindle whorl) showed the presence of Co(II) as the colouring agent.
Portable XRF highlighted the high-iron content that characterises all the black-appearing glass. As no significant correlation between ZrO_2 and Fe_2O_3 emerged, it was concluded that the source of iron was not linked with the quartz source. On the other hand, other compositional trends were highlighted: a group of samples featured K_2O above 2 wt. %, and these samples showed a positive correlation between K_2O and CaO. In addition, the majority of the samples aligned on the same CaO/SrO trend line, pointing to a common origin of the stabiliser, whereas a splitting was apparent when the concentration of TiO_2 and ZrO_2 were reported in a biplot, suggesting that samples might originate from different silica sources.
SEM images did not highlight the presence of dispersed particles acting as opacifiers, showing that the glass owes its black colour to the high concentration of iron (some 12% as Fe_2O_3 was detected in the sample analysed as a polished cross section).
LA-ICP-MS allowed us to go deeper into the composition of the beads: the high concentration of Fe_2O_3 was confirmed, with three groups possibly present (with <5%, c.a. 10% and >15% Fe_2O_3 wt. %). In the sample set considered here, Eu was strongly correlated with Al_2O_3, suggesting it originated from feldspars and supporting its role as a marker for provenance. Eu anomaly was therefore used to differentiate the silica sources on compositional bases, dividing them into samples with neutral Eu anomaly values and samples with negative Eu anomaly values. By comparing these two groups with external datasets, it emerged that the samples with neutral anomaly follow the trend found for glass of Levantine origin [1], with the samples with negative Eu anomaly fitting the composition of the majority of dark-appearing samples unearthed in Pella (Jordan) [2]. Interestingly, one biconical bead (possibly another small spindle whorl) showed the profile enriched in the heavy REE that was also found in the glass from Iron Age Sardis [3], which can also be the place of production of this glass, as suggested by its relatively high Al_2O_3 content.
A particularly relevant aspect was related to the raw materials employed for fluxing the silica, as during the period covered by the investigated items, a shift from plant ash to sodic evaporites occurred in the Mediterranean. Plant ash glass is normally recognised through its MgO content above 2% and K_2O content above 0.5%. The concentrations of these marker oxides would point to the use of plant ash in the present set of samples, but if we take into consideration the information related to the source of the network former, it is apparent that here the concentration of MgO and K_2O are, instead, related to the silica source. This leads to conclusion that the glass was obtained by employing a mineral flux instead of plant ash. In addition, the low concentration of CaO, and its relation with of K_2O, indicated that the Ca-bearing materials entered the glass batch as impurities of the sand, and that MgO and Fe_2O_3 also play a role in stabilising the black glass,

3. Conclusions

The chemical composition of the glass objects indicated that it was imported from several glassmaking centres of the Eastern Mediterranean. At least three sources of silica can be suggested for the set of dark appearing glass: one enriched in Ba with plagioclase with no negative Eu anomaly (probably Levantine), another Ba poor, with K-feldspar that adds negative Eu anomaly to the trace elements profile. One bead was produced using a different silica material, similar to the one used to make dark-coloured glasses found in Sardis. Iron from several sources was used to colour these samples. It is reasonable to assume that the glass was obtained by fluxing the silica with soda-rich evaporitic rocks.
This project has received funding from the EU H2020-MSCA (n. 754511). The contents of this abstract are the sole responsibility of the authors.

References

[1] Panighello et al., *J. Archaeol. Sci.*, 39 (2012) 2945-2955.
[2] Reade et al., *Iron Age*, 38(16.69) (2009) 3-91.
[3] Van Ham-Meert et al., *J. Archaeol. Sci.*, 108 (2019) 104974.

OP80

AEROSPACE TECHNOLOGY AS PART OF OUR HERITAGE: CHARACTERIZATION OF AIRCRAFT MATERIALS AND STUDY OF THEIR DEGRADATION PROCESSES BY ANALYTICAL PYROLYSIS

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1. Introduction

Historical airplanes have entered museum collections to show the development of aviation and are part of our technical heritage. The period between the beginning of the aviation history and World War II is characterized by giant progressions in the chemical industry. During these years a wide increase in the production of new materials and coatings was observed, that replaced the natural materials used in the aircraft industries due to their improved properties. The study deals with the characterization of the materials used in the paint layers of three airplanes, an Ansaldo A.1 (Comune di Casale Monferrato, complete plane, 1918) and two Messerschmitt Bf 109 (Private owner, original cabin roof, 1937; Deutsches Museum, complete plane, 1938-repainted until 1975), including overpainting layers from later use and museum presentations [1,2]. The study is aimed at understanding the materials chosen in aviation technology, also in relation to the developing chemical industry, and to understand if and how the paint composition can be related to the conservation condition of the paint layers and of the aircrafts.

2. Results and Discussion

In this study we applied for the first-time analytical pyrolysis coupled with gas chromatography and mass spectrometry for the characterization of the painted layers. The analyses were carried out directly on the paint fragments, in some cases also with the use of hexamethyldisilazane as derivatizing agent. A selection of samples was also analyzed by infrared spectroscopy. The paint samples were characterized by a very complex stratigraphy, with extremely thin paint layers well-adhering to each other, and thus impossible to be mechanically separated. A careful sampling campaign allowed us to obtain information on the sample build up and the history of the planes. For the plane from the First World War the analyses allowed us to characterize the constituting materials and to highlight the ongoing degradation processes. The study carried out on samples from the two Messerschmitt planes allowed us to characterize the original materials used to produce the planes and to study those used in the different restoration campaigns which have been carried out until 1974.

3. Conclusions

The use of analytical pyrolysis was crucial to characterize a wide range of natural and synthetic materials, allowing to resolve complex mixtures. Data show an interesting evolution of the painting materials used in the two different historical periods, which include natural materials, as a drying oil and Pinaceae resin, but also several synthetic materials, including cellulose acetate, alkyd resin, nitrocellulose, phenol formaldehyde resin as original materials, and more than other six different synthetic polymers used during the restoration campaigns.

Airplanes subject to study

References

[1] J. La Nasa, C. Blaensdorf, E. Dolcher, S. Del Seppia, A. Micheluz, F. Modugno, M. Pamplona, I. Bonaduce, “Historical aircraft paints: analytical pyrolysis for the identification of paint binders used on two Messerschmitt Bf 109 planes”, Journal of Analytical and Applied Pyrolysis, 2022, Vol. 163, article number 105468

[2] J. La Nasa, A. Ceccarini, R. Ducoli, A. Manariti, J.J. Lucejko, I. Degano, N. Capra, L. Giovannini, M.L. Tomasi, F. Modugno, M.P. Colombini, I. Bonaduce. “The emergency landing of Ansaldo A.1 Balilla (1918) fighter aircraft: the role of early synthetic materials degradation in the downfall of this Italian World War I biplane fighter”, 2023, *submitted*

OP81

THERMODYNAMIC PROGNOSTIC MODEL ISORROPIA APPLIED TO INSULATOR FLASHOVER PREVENTION

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1. Introduction

Atmospheric aerosol plays a relevant role in the electric power system. Atmospheric aerosol is consisted of both soluble and non-soluble particles; under high ambient humidity the hygroscopic particles accumulated on insulators' surfaces dissociate into ions acquiring conductive properties, causing flashover accidents (Karady & Amarh, 1999). In this context, Milano-Bicocca University and RSE worked at the chemical characterization of aerosol deposits on Italian insulators and the determination of its phase transitions (deliquescence and crystallization relative humidity) with the related conductive effect, key issues for the prevention of these phenomena. To this aim, the thermodynamic code ISORROPIA (Nenes, 1998) was applied in order to simulate phase transitions of deposited aerosol particles. ISORROPIA is able to determine the thermodynamic behavior of aerosol as a function of its chemical composition and to identify the deliquescence relative humidity (DRH, i.e. the solid-to-liquid phase transition) which leads the deposit to assume conductive properties determining flashover events. Two different code versions are employed to predict the deliquescence phase: ISRP1.7 (which models the Na^+-NH^{4+}-Cl^--NO_3^--SO_4^{2-}-H_2O system) and ISRP2.1 (which also includes Ca^{2+}, K^+, Mg^{2+}).

2. Results and Discussion

ISORROPIA was widely applied to examine the behavior of different types of aerosol. For example, considering a standard urban aerosol system mainly composed of sulfate, nitrate and ammonium, the DRH curve predict by the model was consistent with the experimental one (Fig.1); while applying the model on the insulators deposit context, it showed irregular responses, alternating deliquescence and crystallization phases without a thermodynamic explanation. The chemistry of the insulators deposit differs from a standard sulfate-nitrate-ammonium aerosol system, since it was ammonium-poor and included a non-negligible fraction of crustal species (Ca^{2+}, K^+, Mg^{2+}). Despite these species are the main elements of mineral dust and sea salt aerosol, their thermodynamic behavior is not well understood yet. Ca- and Mg- containing salts are found to have a low deliquescence and they can alter the hygroscopicity of aerosol (Gou et al., 2019). Therefore, the parametrizations of ISORROPIA may didn't fit the contexts which include a relevant amount of crustal species. For all the aforementioned reasons, the model's behavior was investigated more deeply, starting from pure salts simulations. For some salts (e.g. sodium chloride), the predicted response of the model is consistent with the expected trend of the salt, while for other salts (e.g. magnesium sulfate, sodium sulfate) the model gave an unusual response, alternating deliquescence and crystallization phase or not predicting deliquescence at all (Fig.1). The thermodynamic behavior of these salts was studied in Aerosol Exposure Chamber (AEC) to make a comparison between the experimental and the modeling deliquescence phase; the deliquescence point (DRH) found in AEC is consisted with the DRH values in literature. Then a comparison was made between the ISRP1.7 and ISRP2.1, using the same composition for both versions (excluding the crustal species from ISRP2.1), with both balanced and unbalanced input, since excluding Ca^{2+}, K^+, Mg^{2+} the input resulted unbalanced in charges. While the same response was expected, differences in the identified deliquescence regions were instead observed. Finally, the linearity of the model was verified: the same input with different orders of magnitude was used to check that the model's response was the same. Using the whole chemical composition, the model gave the same response, while for sodium sulfate and magnesium sulfate, the model didn't respond in the same way to a change in the order of magnitude of the input. Lastly, the sensitivity of both versions of ISORROPIA at different temperatures (5, 30, 60, 80°C) was also tested. A low sensitivity to temperature was observed, in particular for ISRP1.7.

3. Conclusions

The present study aims to understand and investigate the effect if atmospheric aerosol deposited on insulator's surface along the Italian territory, since it is among the main causes of flashover accidents. In a preventive maintenance perspective, a prognostic model able to simulate the deliquescence phase of aerosol is an essential tool in identifying the critical phase transitions (solid-to-liquid) that gives conductive properties to the deposit layer, promoting the occurrence of flashovers phenomena. For this purpose, ISORROPIA was used, although its responses related to the insulators deposit weren't always consistent with the obtained experimental results. Therefore, an improvement in the model's parametrizations will be necessary in order to make the model more suitable for this specific application and for all cases in which the aerosol system includes a non-negligible amount of crustal species.

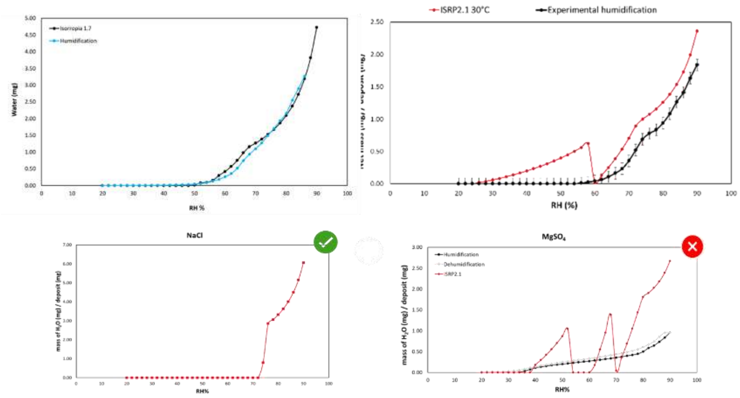

Figure 1. Experimental and modelling deliquescence phase; sodium chloride and magnesium sulfate.

References

Karady, G. G., & Amarh, F. (1999). Signature analysis for leakage current wave forms of polluted insulators. Proceedings of the IEEE Power Engineering Society Transmission and Distribution Conference, 2, 806–811.

Nenes, A., & Pandis, S. N. (1998). ISORROPIA: A New Thermodynamic Equilibrium Model for Multiphase Multicomponent Inorganic Aerosols. In Aquatic Geochemistry (Vol. 4).

Guo, L., Gu, W., Peng, C., Wang, W., Jie Li, Y., Zong, T., Tang, Y., Wu, Z., Lin, Q., Ge, M., Zhang, G., Hu, M., Bi, X., Wang, X., & Tang, M. (2019). A comprehensive study of hygroscopic properties of calcium-and magnesium-containing salts: Implication for hygroscopicity of mineral dust and sea salt aerosols. *Atmospheric Chemistry and Physics*, *19*(4), 2115–2133.

OP82

AEROSOL CHEMICAL COMPOSITION AND HEATING RATE FROM THE TROPICS TO THE NORTH POLE

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1. Introduction

Aerosols affect the climate both directly (absorption and reflection of sunlight) and indirectly (on cloud coverage and properties), triggering complex feedbacks at different spatial and temporal scales. For instance, absorbing aerosol species, such as Black (BC) and Brown (BrC) Carbon, are able to warm the atmosphere. They can act on the Arctic climate either as direct local forcers, or as indirect ones through the energy gradient induced by their forcing between lower latitudes and the North Pole. The role of aerosols is one of the least clear aspects in the so called "Arctic Amplification" (AA) and up to now this was mostly modelled [1,2]. AA is the phenomenon whereby in the Arctic region the rate of warming is four time faster than the rest of the planet. Therefore, the aerosol chemical properties are fundamental to describe its role on climate modifications. For this reason, we took part in four scientific cruises (AREX, Arctic-Expedition, summer 2018, 2019, 2021 and EUREC4A, 2020) in the North Atlantic, eastward and south-eastward of Barbados, aiming at the determination of the aerosol chemical composition and properties from the Tropics to the North Pole.

2. Results and Discussion

Regarding the chemical composition of both campaigns, the aerosol sampling was achieved by means of an high volume sampler (ECHO-PUF Tecora) while its chemical composition was inferred by analyzing aerosol samples collected on quartz filters via ion chromatography (for Water-Soluble Inorganic Ions), TCA (by Magee Scientific) for Total Carbon content, Aethalometer AE33 (for Black Carbon concentrations), ICP-OES for elements. The dominant aerosol chemical markers are related to primary marine emissions (most present ions are Cl^- and Na^+) followed by markers of several long range transport.

AREX chemistry clearly highlights the areas of anthropogenic influence along the cruise, and a clear latitudinal behaviour in Black Carbon concentrations, with the highest values at low latitudes (daily average BC concentration in Gdansk up to 1507 ± 75 ng m^{-3}) and a progressive decrease moving northwards and away from the big Arctic settlements (Black Carbon concentrations within the 81st parallel: 5 ± 1 ng m^{-3}). We demonstrated also that in the Arctic there are some important hotspots that can play a crucial role for AA.

In the EUREC^{4}A campaign the distinction between marine (ss) and non-marine (nss) origin of Ca^{2+} and K^+ ions and the nss- K^+/nss-Ca^{2+} ratio (as well as Black Carbon, elements, $PM_{2.5}$ and PM_1 measurements) made it possible to identify two main kind aerosol transport events: one mainly linked to Saharan Dust and one to Biomass Burning.

The Heating Rate (HR) was calculated under background conditions and transport events in different latitudes by means of an innovative methodology [3], obtained by cumulatively taking into account the chemical composition and associated optical properties, i.e. the absorption coefficients (measured by AE-33 Aethalometer) and incident radiation (direct, diffuse and reflected) across the entire solar spectrum. The HR computed along AREX and in Milan (in the same period) were used to estimate the energy gradient, due to the LAA induced heat storage at mid-latitudes, which contributes to AA through the atmospheric heat transport northward. According to the latitudinal behaviour of BC concentrations (decrease moving northward and away from big cities) and solar radiation (decreases towards the north while the diffuse component increases), HR decreases noticeably towards the Arctic: e.g. higher in the harbor of Gdansk (0.29±0.01 K/day) followed by the Baltic Sea (0.04±0.01 K/day), the Norvegian Sea (0.01±0.01 K/day) and finally with the lowest values in the pure Arctic Ocean (0.003±0.001 K/day). Accordingly, the energy density added to the system by the aerosol, a positive forcing that differs by 2 orders of magnitude between mid-latitudes and North Pole was found: 347.3 ± 11.8 J/m^3 (Milan), 244.8 ± 12.2 J/m^3 (Gdansk) and 2.6 ± 0.2 J/m^3 (80°N). These results highlight the presence of a great energy gradient between mid-latitudes and Arctic and thus of a transport of energy (heat) towards the north. Moreover this was strengthen by the HR value for EUREC^{4}A in Barbados that was 0.175 ± 0.003 K/day; hence, also the HR in the tropics is much higher than in the high latitudes contributing to energy transport towards the Arctic and enhancing its warming.

3. Conclusions

This study highlights the importance of absorbing species (e.g. Black Carbon, Brown Carbon, dust) in heating the atmosphere exerting a local atmospheric positive forcing able to act both locally at regional scale and globally affecting the energy gradients and thus receptor remote places, such as the Arctic where an excess of energy can promote complex feedback (e.g. sea-ice retreat, water-vapor cloud effects) amplifying the climate change

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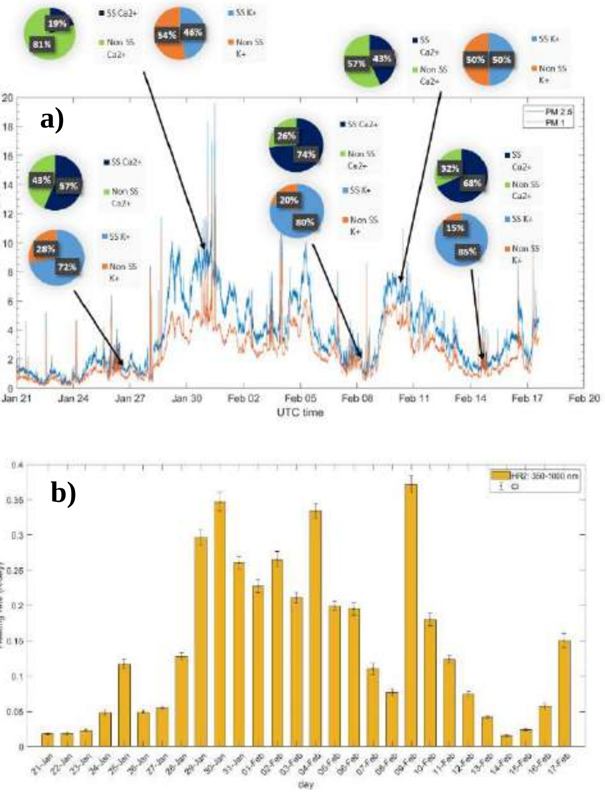

Figure 1. Sea salt and non-sea salt origin of Ca^{2+} and K^+ cations during the two events compared to the background in Barbados (a) and resulting heating rate (b) during 2020.

References

[1] Navarro, J. C. A. et al. (2016) *Nat. Geosci.* 9, 277–281.
[2] Shindell, D. and Faluvegi, G. (2009) *Nat. Geosci.* 2, 294–300. [3] Ferrero, L. et al. (2019) *Atmosphere*, 10.2, 54
[3] Ferrero, L. et al. (2018) *Environ. Sci. Technol.* 52, 3546 3555.

CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICULATE FROM URBAN ENVIRONMENT: THE MONAIR PROJECT

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1. Introduction

In the autumn of 2015, in some Municipalities of the Campania Region, the Regional Agency for Environmental Protection of Campania (ARPAC) recorded numerous breaches with respect to the legal limit of concentrations of atmospheric particulate matter (PM10) in the air. The Municipality of Pomigliano d'Arco, following the communication of the official data provided by ARPAC on air pollution, has decided to undertake a research collaboration with the Metrological and Advanced Technological Services Center (CeSMA) of the University of Naples Federico II for air monitoring through the MONAIR project. This project aims to monitor air pollution and identify, where possible, the nature and probable sources of atmospheric particulate matter and the related interventions to reduce the polluting phenomenon in the Municipality of Pomigliano d'Arco. Specifically, the study focused on the gravimetric determination of PM10 and PM2.5 and on the chemical speciation of the atmospheric particulate, with particular attention paid to the characterization of Polycyclic Aromatic Hydrocarbons (PAHs).

2. Results and Discussion

The environmental monitoring conducted in the Municipality of Pomigliano D'Arco over the years has provided a significant amount of data on the air quality of the Campania municipality. Specifically, the daily concentrations of the PM10 and PM2.5 particulate fractions, the daily concentration of benzo[a]pyrene and of the other 15 PAH congeners, defined as priorities by the EPA, were analyzed.

The monthly trends highlight the significant impact of meteorological conditions on the concentration of particulate matter. It is observed that, in the absence of precipitation, the concentration increases and, on the contrary, decreases in the presence of it, especially in the case of thunderstorms. Furthermore, as already verified in previous monitoring, it has been confirmed that the highest concentrations of PM10 and PM2.5, with related overshoots, occur in December, January, and February, i.e., the coldest months of the year. It is interesting to note that at the end of March, with the increase in average daily temperatures and the lesser need to use domestic heating, the cases of exceeding the pollution thresholds are drastically reduced and occur sporadically, i.e., in correspondence with events linked to particular conditions, such as Saharan events, or man-made events such as fires, demonstrations, etc. The calculated daily average value for PM10 with respect to the single sampling days was found to be 40.6µg/m3, while the estimate of the annual average, calculated based on the monthly averages, was found to be 40.9µg/m3. Therefore, for the year 2022 the limit established by Legislative Decree 155/2010 of 40µg/m3 per year has been exceeded.

As far as PM2.5 is concerned, it has been found that the annual average is 23.4µg/m3, therefore the annual limit of 25µg/m3 set by Legislative Decree 155/2010 has been respected. Subsequently, a chemical speciation of the particulate matter was carried out on the PM2.5 fraction, specifically the 16 PAHs, defined as priorities by the EPA, and methylated PAHs were determined, to identify the possible sources of particulate emissions. The total concentration of PAHs also shows a trend like that of particulate matter, i.e., higher concentrations are observed in the winter months, with an average monthly value of 76 ng/m3. The higher concentrations of PAHs during the months when temperatures decrease suggest a probable correlation with the use of domestic heating systems. The quantification of the concentrations of these species represents a fundamental aspect for identifying their origin and identifying their emission sources. In the literature, there are indices derived from the ratio between the concentrations of different congeners, which make it possible to determine the origin of the analyzed particulate, distinguishing between the pyrolytic origin, i.e., linked to combustion, and the petrogenic one, i.e., of natural origin. From the analysis of the indices, the nature of the particulate is predominantly pyrolytic. The calculation of the indices also showed that the results relating to 7.3% of the winter samples and 21.9% of the autumn samples are attributable to industrial emission sand vehicular emissions [1-3].

3. Conclusions

A monitoring was conducted to verify the air quality of the municipality of Pomigliano D'Arco (NA). The monitoring concerned the gravimetric determination of PM10 and PM2.5 and its chemical speciation, with particular attention to PAHs. The analyzes showed several exceedances of the daily and annual mean for PM 10 and PM 2.5, particularly in the winter months. Chemical speciation showed the prevalence of PAHs especially in the winter months, in agreement with PM10 and PM2.5. The calculation of the indices shows a prevalence of a pyrolytic origin deriving from vehicular traffic.

Environmental monitoring station installed in the Municipality of Pomigliano D'Arco

References

1. Zhang, J., Zhou, X., Wang, Z., Yang, L., Wang, J., Wang, W., Trace elements in PM2.5 in Shandong Province: Source identification and health risk assessment, Science of the total Environment 2018, 621, 558-577, doi: 10.1016/j.scitotenv.2017.11.292[1] Colbeck, I., (2008). "Environmental Chemistry of Aerosols". Blackwell Publishing Ltd.

2. Wheatley, L., Levendis, Y.A., Vouros, P., Exploratory study on the conbustion and PAH emission of selected municipal waste plastics, Environmental Science and Technology 1993, 27, 2885-2895, doi: 10.1021/es00049a032.

3. Ferrara, L., Trifuoggi, M., Toscanesi, M., Donadio, C., Barra, D., Aiello, G., Arienzo, M., Source identification and eco-risk assessment of polycyclic aromatic hydrocarbons in the sediments of seawaters facing the former steel plant ILVA, Naples, Italy, Regional Studies in Marine Science, Volume 35, 101097, ISSN 2352-4855, doi: 10.1016/j.rsma.2020.101097.

OP84

INNOVATIVE STRATEGIES TO ADDRESS ENVIRONMENTAL ISSUES: *CITIZEN SCIENCE* MONITORING APPROACHES

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1. Introduction

Recently in Italy Citizen Science (CS) is spreading more and more in academic environmental studies and it has been recognized as a valid scientific methodology by the official bodies in charge of environmental research and control (1). Despite this, CS is subject to a relevant "school educational void", as it is hardly ever included in science activities at school and only rarely mentioned in school textbooks. We have developed the program "CITISENS", including several projects and initiatives based on "citizens as sensors", to promote CS widespread as methodology of monitoring and research in environmental field. Within this program, partnership with schools is a core aspect to reinforce synergy between secondary and tertiary education, to foster introduction of innovative tools/skills in environmental science curricula at school and to turn schools themselves into reference centers for supporting dissemination of environmental culture in local communities and territories.

Among the activities performed, we highlight two air monitoring projects:

a. Particulate matter monitoring based on high space-time resolution sensors
b. Nitrogen dioxide monitoring based on diffusion tubes.

2. Results and Discussion

a. Particulate matter monitoring based on high space-time resolution sensors

In school year 2021-22, 20 sensors for continuous measuring of particulate matters (PM_{10}, $PM_{2.5}$, PM_1) and some meteo-climatic parameters have been installed outside the buildings of 9 schools in Salerno and Avellino, connected to a network platform for data collection and trending. More than 300 students and 20 teachers have been involved in sensors installation and, during the last two school years, have received specific training on data collection, statistical elaboration, comparison with official ARPAC values and law limits, possible interpretation of trends based on environmental/anthropic factors. An *Air Quality Observatory* has been constituted at each participant school, providing continuous monitoring and reporting of results in their respective territories, with possibility to gather large numbers of data also for scientific research and with implementation of information dissemination systems for local community.

b. Nitrogen dioxide monitoring based on diffusion tubes

We have developed and validated a new type of diffusion tube for air NO_2 sampling, based on the consolidated "Palmes tubes" and on the well-known principle of NO_2 absorption by TEA (triethanolamine) on a solid support (2), but with cheaper, more readily available materials and simpler assembling procedure: this allows self-production of the samplers by students at school, in order to actively involve schools in NO_2 monitoring campaigns with an approach "from A to Z". Besides the new sampling tool, we have developed an user-friendly App for smartphone, in order to collect on a platform real time information about sampling geo-localization, sampling periods and contact data of participants in the campaign: this updates and speeds up the traditional procedure based on paper forms filled in by the participants and further manual collection/organization of the data.

A successful experimentation has been performed involving 98 students from 5 upper secondary schools in March-April 2023. With support of university staff and instruction kits, students prepared 296 tubes in the school labs, exposed the samplers for 3 weeks outdoor in their towns (Salerno and Avellino areas) and, at the end of the sampling period, performed the chemical-spectrophotometric analysis (3) in the school lab, in order to obtain NO_2 concentrations in atmosphere (average value over the sampling period). Geo-localization of the sampling points allowed construction of an *NO_2 concentration map* in the investigated area.

3. Conclusions

These CS-based environmental monitoring projects have determined several benefits, improving synergies between school and university, increasing students' interest towards scientific research and making schools a reference point for environmental issues in the territory.

Innovative educational formats have been integrated in the school curricula, providing new skills and tools for students/teachers and fostering scientific inquiry at school.

A stable network has been constituted with the involved school.

CS has been promoted as a scientific research tool.

Dissemination systems have been implemented to raise public awareness towards environment study.

The realized activities can be reproduced at larger extent, in different areas and with larger number of schools and participants.

References

(1) Sistema Nazionale per la Protezione dell'Ambiente (SNPA) – Delibera n.60/2019

(2) E. D. Palmes, A. F. Gunnison, J. Di Mattio, and C. Tomczyk, Personal sampler for nitrogen dioxide. American Industrial Hygiene Association Journal 37 (1976): 570–577

(3) Atkins, D.H.F., Sandalls, J., Law, D.V., Hough, A.M. and Stevenson, K. The measurement of nitrogen dioxide in the outdoor environment using passive diffusion tube samplers. AERE R12133, United Kingdom Atomic Energy Authority, Harwell (1986)

OP85

METAL FRAGMENTS OF ROMAN FLUTES FROM POMPEII: INVESTIGATIONS ON COPPER-BASED ALLOYS, CORROSION PRODUCTS AND SURFACE TREATMENTS

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1. Introduction

This paper reports the study of 7 metal fragments (AN2, AN3, AN4, AN6, AN7, AN8, AN11) from roman flutes excavated from the Archaeological Park of Pompeii and preserved in the deposit of the Archaeological National Museum of Naples (MANN). The Roman flute, called *tibia*, is a wind musical instrument descended from the greek *aulos*: it can be made of bone, wood and/or metal. Materials consisting of metal alloys excavated from archaeological burial environments are characterized by significant corrosion phenomena due to the peculiar conditions of preservation. This research aims to identify the composition of the alloys, characterize the corrosion patinas and identify any ancient surface treatments on the fragments. Non-invasive and micro-invasive techniques were used to achieve this aim, i.e. optical microscopy, Raman spectroscopy (Renishaw Raman InVia, Laser Ar+), attenuated total reflectance Fourier-transform infrared spectrophotometry (Bruker Alpha, ATR mode with diamond crystal, spectral range 4000-400 cm^{-1}), scanning electron microscopy and energy dispersive spectrometry (Zeiss EP EVO 50 VP 100Pa with EDS INCA X-act Penta FET® Precision microprobe).

2. Results and Discussion

Alloy, corrosion products and surface treatments-related compounds were identified on *tibiae* fragments. Through SEM-EDS analysis on cross sections, two main alloy types were identified (Cu-Sn bronze and Cu-Zn brass) in the areas where some metal is still preserved. Specifically, in brass flutes (AN2, AN7, AN8, AN11), EDS analyses allowed the detection of Cu (about 89 wt.%) and Zn (about 11 wt.%) in the alloys. AN2 and AN7 showed a peculiar stratigraphy: the inner part of the fragments is mineralized while, in the outermost zones, thin metallic layers with a different composition were detected: in detail, Zn is significantly present only in the outer layers, whereas the core is rich in Cu (as evident in Figure 1). These layers could result from selective Zn leaching from the inner part or may be due to a decorative technique in which the bronze sheet may have been coated with a brass foil, in order to obtain a gold-like color. Bronze fragments (AN3, AN4, AN6) are more mineralized than brass fragments: tin contents up to about 11 wt.% were found. SEM-EDS analysis showed presence of other elements: Cl was detected on AN2, AN3, AN4, AN11 and its presence may be due to the type of excavation soil rich in soluble marine salts; P and Ca were found on AN11, probably due to contact with bones that were typically coated with metal sheets in *tibiae*; a considerable amount of Si derived from soil was found on AN3; Pb accumulation (in the form of an outer layer about 60 μm thick) was evident on AN4, as a result of a ternary alloy composition or, since it is present in a specific surface layer, of a decoration technique. Similarly to Pb, also the presence of Ag particles on AN2 could result from surface decorations.

As for the numerous types of patinas, corrosion products and other substaces related with conservation treatments, reflected light microscopy and micro-Raman provided decisive morphological and analytical information: cuprite, Cu_2O, is the most common corrosion product of Cu-based alloys and it was found on all the fragments; azurite $2CuCO_3(OH)_2$ was detected on AN2, AN4, AN6, AN7, AN11, while malachite $CuCO_3Cu(OH)_2$ was revealed on all the specimens. They are both typical corrosion products of Cu alloys in burial contexts. As for brochantite $Cu_4[(OH)_6|SO_4]$, revealed on AN2 and AN3, and posnjakite $Cu_4(SO_4)(OH)_6(H_2O)$ identified on AN2, the formation could result from the interactions with microorganisms or the presence of sulphurous compounds in the burial context. Presence of chloride-containing species in the soil led to the formation of clinoatacamite $Cu_2[(OH)_3|Cl]$ on AN4 and AN11; atacamite $Cu_2Cl(OH)_2$ was detected on AN6 and AN4. The presence of Zn in the alloy induced the formation of Zn-containing corrosion patinas, like aurichalcite $(Zn, Cu)_5(CO_3)_2(OH)_6$ detected on AN2, AN7, AN8 and rosasite $(Cu, Zn)_2[(OH)_2|CO_3]$ revealed on AN2. Hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ were detected on AN4 corresponding to the previously described Pb-rich layer. Coal particles were detected on all fragments, except on AN4. The FTIR-ATR analysis performed on AN4 and AN11 highglighted the characteristic bands corresponding to non-aged siccative oil, as well as the Raman signals of a natural wax peaks were recognized in AN3, AN6, AN7, AN8.

3. Conclusions

This study identified two main alloy types (brass and bronze) used in the construction of Roman flutes and revealed that brass fragments were more preserved than those made of bronze. Corrosion patinas contain different products depending on alloy type and soil components. Pompeii constitutes a *unicum* in conservation of archaeological artefacts: the eruption of Vesuvius in 79 B.C. generated a peculiar environment for artefacts preservation. Presence of organic substances on the surface suggests that surface treatments may have been carried out in ancient times as well as after excavation, through recent restoration interventions. Nevertheless, the peculiar stratigraphy of AN2 and AN11 and presence of Pb in AN4 suggests the execution of ancient decorative surface treatments coeval with the instruments: archaeological sources testify that the *tibiae* could have been richly decorated and painted.

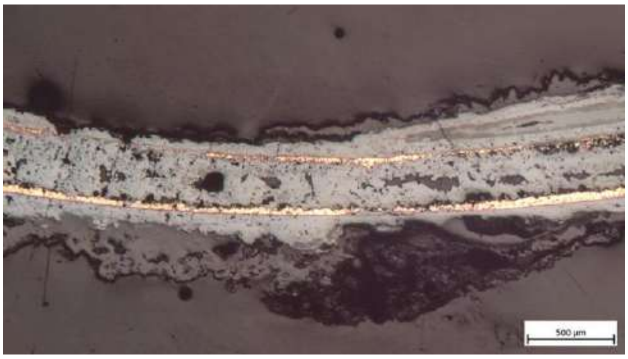

Fig. 1: AN2 stratigraphy.

References

H. Hassairi, L. Bousselmi, E. Triki, Bronze degradation processes in simulating archaeological soil media, Solid State Electr. 14,393–401 (2010)
G.M. Ingo, T. De Caro, C. Riccucci, S. Khosroff, Uncommon corrosion phenomena of archaeological bronze alloys, Appl. Phys. A 83, 581–588 (2006)
L. Pronti, A.C. Felici, M. Alesiani, O. Tarquini, M.P. Bracciale, M.L. Santarelli, G. Pardini, M. Piacentini, Characterisation of corrosion layers formed under burial environment of copper-based Greek and Roman coins from Pompeii, Appl. Phys. A 121:59–68 (2015)

OP86

ATTRIBUTING THE ORIGIN OF TWO MEDIOEVAL MUSICAL PARCHMENTS BY NON-INVASIVE ANALYSES

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1. Introduction

In Western Europe, the practice of dismantling obsolete books and recycling their pages for other purposes has been widespread in the Middle Ages until the 17th century. Consequently, durable and well-crafted parchments were frequently reused to cover paper books. This research discusses a scientific study on two ancient musical parchments discovered in renowned libraries in Pavia and Milan, Italy. The parchments served as covers for paper books and contained rare musical notes and lyrics from the Lombard tradition dating back to the Middle Ages (ca. 1400). The study aimed to determine: (i) the origin of the fragments assessing whether they came from the same manuscript and whether texts and notes were created during the same period; (ii) creating a consistent dataset and data treatment to study ancient inks; (iii) enhancing the legibility of the written parts for musicological and philological studies. Non-invasive and portable techniques were intentionally used: X-Ray Fluorescence (XRF) and External Reflection Infrared (ER-FTIR) spectroscopies addressed the chemical composition of parchments and inks, while multiband UV-vis-IR imaging helped reconstructing the deteriorated or detached parts of the musical text.

2. Results and Discussion

Analyses were conducted on two parchment fragments preserved at the University Library of Pavia (PV) and Trivulziana Library in Milan (TR), they were recycled as the cover of a book printed in 1601 and paper manuscript dating back to 15th century, respectively. Both fragments consisted in a bifolium with red pentagrams, musical notations, and polyphonic lyrics written with black inks both on recto and verso side, for which a coeval origin was researched. For comparison, the two manuscripts were analysed using the same analytical setup to reveal insights into their origin, as well as chemical and stylistic similarities among the different written sections.

Outputs of the examination so far revealed that the parchment substrate provided similar ER-FTIR spectra for PV and TR fragments, displaying the characteristic signals of collagen in the near-IR (combination bands and overtones from 5140 to 4260 cm^{-1}) and mid-IR regions (amide I, II, III at 1655, 1540, 1450 cm^{-1} after Kramers-Kronig transformation) [1]. Chemical analyses performed on the inked areas of PV fragment allowed a clear distinction between red and black inks. Both IR reflectography and IR-false colour identified the red ink as cinnabar, also confirmed by XRF a predominance of mercury (Hg) and sulfur (S). Conversely, only XRF analyses permitted characterizing the black musical notation and lyrics as iron-gall ink by detecting the major elements iron (Fe), copper (Cu), and zinc (Zn). The recognition of iron-gall ink was also supported by ER-FTIR spectra which showed a broadening of the band of amide I towards higher wavenumbers (1670-1700 cm^{-1}) due to carboxylic groups of tannic acid from the ink [2]. Occasionally, signals of oxalates were detected as a possible degradation product [3]. XRF data treatment highlighted the presence of three possible different gall-ink formulations not readily distinguishable by multiband imaging and ER-FTIR. Among them it was revealed that comparable formulation of iron-gall ink was used to write both musical notation and lyrics, either for recto or verso side of PV, implying that they originated at the same period but with different thicknesses.

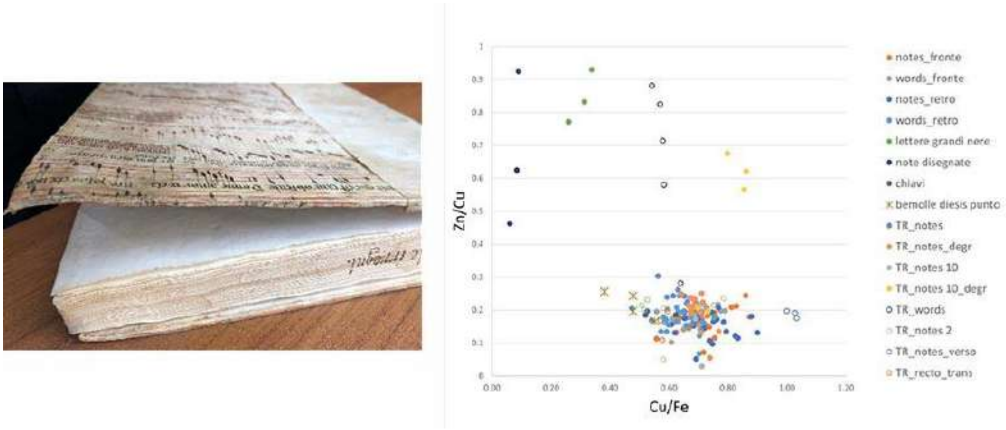
Furthermore, due to the chemical similarity between the ink used on the recto and verso, as well as the fact that they were written in different languages, it was suggested that there was a simultaneous presence of diverse linguistic influences in Northern Italy during that period.

Chemical analysis of TR parchment provided similar ER-FTIR spectra of those acquired on PV fragment, displaying collagen bands and more distinctive signals of calcium carbonate. Data treatment of XRF spectra acquired on red and black inks were found to be consistent with those observed for PV. The red ink resulted in HgS, as revealed also by multiband imaging, while black inks showed the composition of iron-gall ink with Fe>Cu>Zn. Differences in the chemical element ratios and multivariate analysis suggested multi-class distinction of iron-gall inks [4].

Finally, the acquisition of high-resolution photographs using UV, visible, and IR light sources enabled the non-invasive reconstruction of detached parts of the written content of the polyphonic music contributing to the deep understanding of the Lombard traditional music at that time.

3. Conclusions

The study addressed the origin of two parchment fragments, found in different libraries as cover of paper books, reporting musical notation and lyrics from the Lombard tradition dating back to the 13-14th centuries. By combining results from non-invasive and portable techniques like XRF, ER-FTIR, and UV-vis-IR multiband imaging, we assessed the composition of different inks and helped the reconstruction of missed or lost parts of the musical text. Outcomes of the study provided valuable insight into the polyphonic music of North Italy and the circulation of mediaeval texts, shedding light on the historical and cultural context of music during that era. Additionally, the significant dataset contributed to build a solid methodological approach to study ancient inks.



Left: Musical parchment fragment served as a cover book. Right: Preliminary biplot of black inks.

Acknowledgements – We thanks Dr. Antonio Calvia (project ERC Advanced Grant *Ars Nova*), Dr. Federico Saviotti (Pavia University), and Anne Stone (CUNNY) for offering the opportunity to collaborate and University Library of Pavia and Trivulziana Library in Milan to allow non-invasive analyses of the parchments.

References

[1] M. Vagnini et al., Anal Bioanal Chem (2009) 395:2107–2118
[2] M. Bicchieri et al., Vibrational Spectroscopy (2011) 55:267–272
[3] N. Ferrer, M. Carme Sistach, Restaurator (2013) 34(3):175-193
[4] P. Del Carmine et al., Physics Research B (1996) 13:354-358

IN SITU MICRO- AND NON-INVASIVE ANALYSES FOR THE STUDY OF CARTONNAGES FROM THE NECROPOLIS OF ASWAN (EGYPT)

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1. Introduction

The chemical-physical characterisation of artefacts of historical-artistic interest is important as it can provide valuable information about the painting techniques used, the availability of natural pigments and the technological skills of a population. Research studies conducted in this field were able to identify the range of colors available to the ancient Egyptians [1-3].

The following study aimed to investigate the nature and composition of the pictorial layers of four different Egyptian artefacts found in West Aswan, Egypt, in the framework of the excavation of EIMAWA (Egyptian Italian Mission At West Aswan), which is in the area surrounding the Mausoleum of the Aga Khan. The necropolis covers a period of around 1000 years (6th cent. BCE-4th cent. CE). The analyzed artefacts were three different cartonnages excavated during two different campaigns: the first carried out in June 2021 during which analyses were performed using ATR/FTIR and a portable colorimeter for in-situ analyses, and the second one (May 2023) when analyses were performed using a multispectral camera.

2. Results and Discussion

Using the ATR/FTIR technique, it was possible to highlight the nature of the compounds present on the cartonnages and thus investigate the nature of the pigments used to decorate these artefacts.

As is well known, strict Egyptian laws prohibit transporting any kind of artefact to other countries, so the use of portable instrumentation for in-situ analyses was mandatory. Investigations through portable ATR/FTIR spectroscopy were carried out in the storehouse where the items coming from the excavation are kept. Measurements were performed on fragments already detached from the cartonnages and found inside the paper packaging where they were preserved.

To identify the pigments, the collected spectra were compared with reference spectra present either in our database or in the literature. Calcium carbonate due to the substrate of the cartonnages was detected in all the spectra while the pigments were recognized as red ochre, yellow ochre, fine Egyptian blue and madder. The latter is a natural dye of organic origin coming from the root of the madder plant (*Rubia tinctorum*). This compound typically contains alizarin and purpurin, which are two anthraquinones,

Visible reflectance analyses were performed on-site, i.e. at the excavation, by means of a portable spectrophotometer. From the obtained spectra, it was possible to confirm homogeneity in the pigments applied on the cartonnages. In addition, the colorimetric data were also processed with PCA (principal components analysis) to highlight possible differences among the different hues.

With UVL (UV induced luminescence) imaging, it was possible to observe the distribution of the pigment of an organic nature on the surface of the artefacts together with the presence of organic binders. The VIL (Visible Induced Luminescence) technique, on the other hand, made it possible to immediately point out the presence of Egyptian blue on the artefacts, and finally, the IRR (IR reflectography) technique allowed getting a better understanding of the preparatory drawing hidden beneath the pictorial layer and to investigate the behavior of the different pigments when stimulated by infrared radiation.

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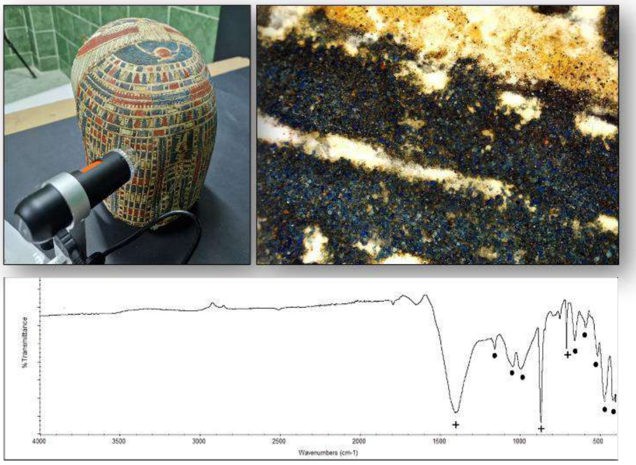
3. Conclusions

The analyses performed by ATR/FTIR revealed the presence of several pigments. Particularly interesting was the pink fragment: the spectrum itself was found to be different and it is suspected to be an organic dye, probably rose madder.

By studying the data obtained by reflectance spectroscopy, it can be stated that the pigments are the same for each color, and the palette remains confined to a limited range of minerals and dyes.

With UVL, VIL and IRR it was possible to observe the spatial distribution of some of the colors; specifically, areas mainly composed either of organic substances or of the abundant Egyptian blue were evidenced. Moreover, the drawing's shape hidden beneath the pigment layer was defined.

The investigation revealed the overall composition of the cartonnages' color palette, which was also found to be in line with the data in the literature.



Detail and ATR/FTIR spectrum of a blue fragment of cartonnage 1 (calcite (+) and Egyptian blue (•) bands).

References

[1] Hallmann, A., Rickerby, S., Shekede, L. (2021). Blue and green in the decoration of a Kushite chapel in Karnak, Egypt: Technical evaluation using low-tech, non-invasive procedures. *Journal of Archaeological Science: Reports*, *39*

[2] Lombardi, C. A., Comite, V., Fermo, P., Bergomi, A., Trombino, L., Guglielmi, V. (2023). A Multi-Analytical Approach for the Characterisation of Pigments from an Egyptian Sarcophagus Cover of the Late Dynastic Period: A Case Study. *Sustainability*, *15*

[3] Pozza, G., Ajò, D., Chiari, G., De Zuane, F., Favaro, M. (2000). Photoluminescence of the inorganic pigments Egyptian blue, Han blue and Han purple. In *Journal of Cultural Heritage*, *1*

OP88

RARE EARTH ELEMENTS IN THREE ABANDONED MINING SITES IN THE REGION OF PUGLIA

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1. Introduction

Rare earth elements (REEs) are necessary in the technology sector, as the production of many devices is based on their use. Due to this extensive use of REEs over the last years, concerns about their safety for human (Brouziotis *et al.*, 2022) and environmental health (Pagano *et al.*, 2019) have been raised. In addition, the demand for their production and utilization is continuously rising. Previous studies investigated the REE content on environmental matrices either on mining sites or on areas near these sites. In this research, environmental samples were collected from three abandoned mining sites in the region of Puglia, Southern Italy. Each mining site is in the region of Gargano, Otranto, and Spinazzola. Samples of soil, sediment, rock, water, and biota were collected and the REE content in them was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2. Results and Discussion

All 15 REEs (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) could be detected in all types of sample from all three abandoned sites, when analyzed by ICP-MS. Among all three sites, Spinazzola seems to be the richest site, containing higher concentrations of REEs with respect to Gargano and Otranto. Ce is the most abundant REE, followed by La, in all types of samples from all regions, except for the biota samples from Spinazzola region, where La was the most abundant REE, followed by Nd. Soil, rock, and biota samples from Spinazzola seem to contain a high amount of REEs, especially La and Ce. The mean concentration of Ce in soil samples is at 366 mg/kg, while in biota is at 130 mg/kg, and 116 mg/kg in rocks. On the same hand, the mean concentration of La is at 247 mg/kg, 66 mg/kg and 254 mg/kg in soil, biota, and rock samples respectively. Therefore, the environmental samples from the abandoned mining site from Spinazzola region, seem to be exclusively ideal for extraction of REEs. The correlation analysis between the REE-levels in the soil and biota samples from the same sampling point of each area, showed that there is correlation (Pearson $r>0.7$) of the REE-levels between the two types of samples for 13 REEs in Gargano, 11 in Otranto and 9 in Spinazzola. However, the small number of soil (9 from Gargano, 8 from Otranto and 10 from Spinazzola) and biota samples (5 from Gargano, 8 from Otranto and 9 from Spinazzola) obtained for this research makes the results having a big bias. Therefore, we can only have some first indications about the REE-levels and the correlation between soil and biota samples.

3. Conclusions

Cerium is the most abundant REE in all three regions. Spinazzola is the site containing the highest amount of these elements making it the most interesting among them for a possible process of REE extraction. REEs in environmental samples from abandoned mining sites in Southern Italy are not only in traceable levels, but in very interesting levels for a possible extraction. Since several previous studies have shown that they might consist of a threaten for human and environmental health, more investigations should be elaborated about their concentrations either near or further from mining sites.

References

1. Brouziotis A.A., Giarra A., Libralato G., Pagano G., Guida M., and Trifuoggi M. (2022), Toxicity of rare earth elements: An overview on human health impact. Front. Environ. Sci. 10:948041.
2. Pagano G., Thomas J.P., Di Nunzio A. and Trifuoggi M. (2019), Human exposures to rare earth elements: Present knowledge and research prospects. Environ. Res. 171:493-500.

Relazioni per il Corso di Aggiornamento dell' Ordine Regionale dei Chimici e dei Fisici

Ordine Regionale dei Chimici e dei Fisici

"Dal Rifiuto all'End-of-Waste: il recupero come reale spinta all'economia circolare"

Chairpersons: A. Tapparo, M. Di Serio

G. Stocco
Rifiuto e materia recuperata, il delicato intreccio tra le normative per la conformità dei processi e dei prodotti

A. Baldisseri
I criteri di autorizzazione degli impianti di recupero rifiuti per la produzione di End of Waste, alla luce delle nuove Linee Guida ISPRA

I. Fagiolino
Dal rifiuto ai materiali recuperati: l'importanza della caratterizzazione chimica

A. Tapparo
Tecniche analitiche di screening per caratterizzazione dei rifiuti e dei materiali recuperati

P. Mainolfi
Valutazione del rischio e comunicazione nei siti contaminati

S. Moro
Sostanze chimiche in articoli e materiali recuperati: la transizione verso materiali e prodotti più sicuri

M. Ortenzi
Plastica riciclata o bioplastica: problemi, opportunità e criticità a livello analitico

Poster Sezione Ambiente

POS01

BIOACCUMULATION OF TOXIC ELEMENTS ALONG THE TROPHIC CHAIN OF THE "OASI DI ALVIANO" (CENTRAL ITALY)

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1. Introduction

The presence of metals and metalloids in the environment can be determined by a variety of natural and anthropogenic sources. Toxic metals and metalloids, in particular, can affect all living organisms, producing accumulation and damage in the ecosystem. Bioaccumulation is thus a very effective tool to assess the quality of an ecosystem, by determining the concentrations of the elements of interest in the tissues of the studied organisms. Moreover, the bioaccumulation extent for each organism depends on exposure to pollution, growth stage and dietary habits. In particular, biomagnification is related to the placement of the organism in the food chain, and in particular to the prey-predator dynamics which are usually very complex and non-linear.

2. Results and Discussion

In this work, we characterized the aquatic ecosystem of the Alviano Lake (Central Italy). The "Oasi di Alviano" is a WWF reserve which hosts a great variety of habitats. However, the area shows mercury and arsenic contamination, due to old Hg mining activities upstream from the studied area (Amiata Mountain). The contamination extends from the Paglia River into the Tiber river and all the way to the Alviano basin. We evaluated the uptake, bioaccumulation and biomagnification of toxic elements along the trophic chain. We quantified 31 trace elements with triple quadrupole ICP-MS in environmental matrices (water, sediment), and selected tissues of several bioindicators belonging to different compartments of the trophic chain. In particular, we focused on honeybees[1] (*Apis mellifera*), dragonflies (*Orthetrum cancellatum*), crayfish (*Procambarus clarkii*) and fish (*Silurus glanis* and *Carassius auratus*).

3. Conclusions

This study allowed to identify the preferential target organs for each toxic element (e.g. muscle or liver/hepatopancreas) and to compare different species with complex prey-predator dynamics.

Sampling site: Oasi di Alviano

References

[1] Goretti et al. (2023). Bioaccumulation of Trace Elements along the Body Longitudinal Axis in Honey Bees. Applied Sciences, 13(12), 6918.

POS02

A COMPARATIVE LIFE CYCLE ASSESSMENT OF TWO TANNING PROCESSES: INNOVATIVE GREEN ORGANIC VS TRADITIONAL CHROME-BASED

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1. Introduction

In Valle del Chiampo area (Veneto, Italy), tanning companies are facing a challenge related to the conversion of the conventional chrome-based leather production throughout a more sustainable leather production based on vegetable and synthetic tannins. The proposed technology relies on the combination of polymer-based chemicals and protocols which allows to produce chrome-free high-quality leather, to reduce hazardous substances, environmental risks and to simplify the entire tanning process (Pasquale et al. 2019).

The achievement of this goal was supported by the LIFE GOAST (Green Organic Agents for Sustainable Tanneries) project.

The main aim of the LIFE GOAST project was to demonstrate the benefits of a new tanning technology on a semi-industrial scale. The technical feasibility of the technology was monitored in order to demonstrate the reduced environmental impacts of the new process, while producing comparable or better quality leather.

As part of this project, a Life Cycle Assessment (LCA) (ISO 14040-44) was performed to compare the innovative tanning process GOAST with the traditional tanning process TCTP (Traditional Chrome Tanning Process) environmental performance.

2. Results and Discussion

The LCA was performed, from a "gate to gate" perspective and taking 1 kg of tanned hides per year as the functional unit. The Impact Assessment (LCIA) has been performed using the Environmental Footprint (EF) method and database 2.0 and applying the Simapro 9.1 software.

The main result related to the LCA comparative analysis is that the innovative tanning process GOAST has lower environmental impact than the traditional tanning process TCTP.

As it can be seen from the characterized results, the GOAST process has a lower impact for 8 of 16 impact categories compared to the TCTP process. The percentage difference between the two processes is more evident in the impact categories related to toxicity, where the traditional tanning process (TCTP) is more impactful due to the use of chrome as tanning agent. On the other hand, the innovative GOAST tanning process is almost 70% more impactful in the Land use category due to the significant use of vegetable tannins. From these results, it can also be seen that most of the impacts comes from the tanning and retanning phases due to the significant use of chemicals.

By assessing single score results it is possible to investigate the overall generated impact and which impact category caused highest impairments. Considering all impact categories under the EF method, the overall impact of the GOAST tanning process is approximately 60% lower than the overall impact of the traditional tanning process TCTP.

The presented study is based on few limitations and assumptions which should be addressed to achieve a level of data quality necessary to procced with green labeling and certification.

The main limitation in comparing the two tanning processes TCTP and GOAST is that, at the moment, it is not possible to distinguish between the two production lines.

For this reason, many data related to the consumption of energy, water and waste streams produced are overestimated for the innovative tanning process GOAST.

Specifically, there is no differentiated water collection system for the two processes. For this reason, the sludge produced by the innovative tanning process GOAST has still high chromium concentrations caused by the mixing whit the sludge produced during the traditional tanning process (TCTP). The current situation therefore prevents the valorization of the sludge produced by the innovative GOAST tanning process. Additionally, is important to underline that the innovative tanning process GOAST is still in a development phase in comparison to the already optimized traditional tanning process.

3. Conclusions

The LCA analysis indicates the need for future optimization for the innovative tanning process (e.g., CO2 emissions, land use, water consumption. The overall results suggested that the innovative tanning process (GOAST) could reduce the environmental impacts related to the traditional, chrome-based, leather production. Indeed, the TCTP process is very impactful for the impact categories related to toxicity due to the use of chrome as tanning agent.

As these results suggest, the tanning process GOAST can in future improve its environmental performance. This can be achieved mainly by optimizing the innovative tanning process (GOAST) by allowing a lower tanning agents consumption.

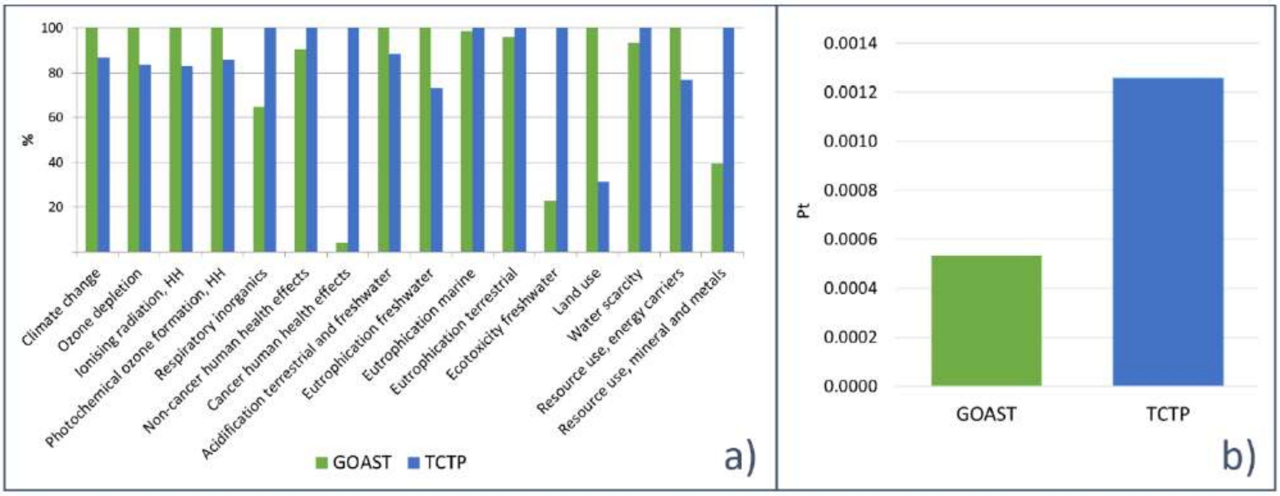

Figure 1: a) LCA characterized results at midpoint level; b) LCA single score results.

References

ISO 14040. 2021. “Environmental Management - Life Cycle Assessment - Principles and Framework ISO 14040:2021.”

ISO 14044. 2021. “Environmental Management - Life Cycle Assessment - Requirements and Guidelines ISO 14044:2021.”

Pasquale, R., C. Bortolati, F. Serafini, M. Signoretto, S. Tieuli, M. Silvestri, and L. Frighetto. 2019. “Life Goast Green Organic Agents for Sustainable Tanneries (LiFe16 Env/IT/000416).” in 35th IULTCS Congress 2019: “Benign by Design” Leather - The Future Through Science

POS03

BIOCAPACITY DISPLACEMENT AS A DRIVER OF GLOBAL NATURAL CAPITAL TRANSFER

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1. Introduction

Biocapacity is the ecosystem's capacity to provide biomass and fiber. It is related to the characteristics of the available ecosystem. Global ecosystems are heterogeneous and belong to different countries. High income countries with scarce biocapacity are pushed to match the domestic demand through the import of goods or the acquisition of land in foreign countries. When developed countries acquire land in developing ones, it is called land grabbing (Coscieme et al., 2018) and this kind of large scale land acquisitions often creates environmental degradation. Its environmental impact has been studied, though not from an ecosystem services perspective. Land grabbing is finalized to the appropriation of biocapacity. Though money should compensate for the value of the involved land, underestimations can derive from neglecting the economic value of biocapacity. Niccolucci et al., (2021) quantified the economic value of the biocapacity in each country. By comparing the transactions' biocapacity economic value (BEV) with the BEV of the grabbing countries it is possible to investigate the opportunity of such transactions and the reliance of such countries on outsourced BEV.

2. Results and Discussion

The analysis reveals that on a global scale the land grabbing phenomenon has marginal relevance in terms of BEV, i.e., the BEV of the globally grabbed land and forest is significantly lower than the BEV of the overall global land and forest. However, it is possible to identify all the entities involved in the land grabbing deals by backtracking the monetary flows from the final contract up to the original financial source (e.g., excluding financial intermediaries). Accordingly, by comparing the BEV of the countries involved in each individual land grabbing deal we revealed that in most cases there is a remarkable discrepancy between the price paid for the acquisition and the BEV of the land object of the deal. In most cases this discrepancy is favorable for the land grabbers. Consequently, in most cases, the land market failed to fully capture and internalize the actual value of the land. This ultimately incurs in the generation of inequalities or in a worsening of the existing ones. Considering that the land grabbing deals are commonly lasting few or several decades, it is immediately evident that the extent of the existing loss of value (the one not currently represented in the land market) is bound to severely exacerbate the previously existing inequality gap over the timespan of multiple generations. Furthermore, focusing on the land grabbers we revealed that they largely benefited from land grabbing ensuring a provision of unsustainably cheap biocapacity and coping with the scarcity of available domestic biocapacity – either due to physical unavailability, or due to unfavourable climate conditions. We further investigated this trend by comparing the BEV of the total grabbed land by each individual land grabber country with the BEV of a hypothetical domestic land of the same size – assuming that such land is available, though it is often not the case. This comparison allowed to estimate the overall land grabbers' opportunity to perpetrate land grabbing abroad. The results suggest that it has been much more convenient for land grabbers to acquire land abroad by paying a price that does not fully reflect the actual value of the land acquired.

3. Conclusions

The monetary transaction associated with large scale land acquisition deals corresponding to land grabbing fail to fully capture the value of the involved land when considering the corresponding BEV. The transfer often involves developed countries with scarce cropland and forest which seek for the provision of the related biocapacity beyond their territorial boundaries. In other cases, although countries have available forest and cropland, they resort to land grabbing driven by larger potential profit due to the price gap that neglects part of the actual value of the land.

References

Coscieme, L., Niccolucci, V., Giannetti, B.F., Pulselli, F.M., Marchettini, N., Sutton, P.C., 2018. Implications of Land-Grabbing on the Ecological Balance of Brazil. Resources 7. https://doi.org/10.3390/resources7030044

Niccolucci, V., Coscieme, L., Marchettini, N., 2021. Benefit transfer and the economic value of Biocapacity: Introducing the ecosystem service Yield factor. Ecosystem Services 48, 101256. https://doi.org/10.1016/j.ecoser.2021.101256

POS04

NANOFUN - NANOCELLULOSE-BASED MEMBRANES FOR WATER PURIFICATION WITH ENHANCED EFFICIENCY BY CHEMICAL FUNCTIONALIZATION

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1. Introduction

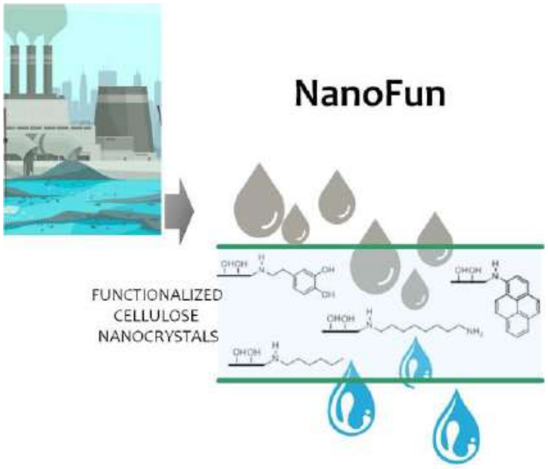
Water scarceness is a consequence of climate change and waste accumulation and represents an increasing threat for Italy and South Africa. The problem of water purification requires urgent solutions to ensure the wellness of our society and a more sustainable preservation of the environment. Potential contaminants are heavy metals and highly concentrated salts, microbes, oils, persistent and emerging organic pollutants (POPs and ECs) and microplastics.[1]

Absorption technologies for the purification of polluted water are usually considered less expensive and more efficient and can be engineered relying on the use of sustainable biopolymer aggregates for the preparation of purification devices. Cellulose-based nanomaterials have demonstrated their very high potential in materials preparation[2,3] and have already been proposed as absorbers for water contaminants.[4] Nanocelluloses display high mechanical strength and specific surface area, are inexpensive and biodegradable. Moreover, they are amenable to surface chemical functionalization, which can enhance their absorption properties. Finally, cellulose nanofibers (CNFs), in consideration of their high aspect ratio, are considerably suitable for the preparation of stable filtration membranes.

2. Conclusions

The NanoFun bilateral project (2023-2025) on functionalized nanocellulose membranes between Italy and South Africa aims to design innovative and sustainable membranes for water purification, based on cellulose nanofibers (CNFs) and/or nanocrystals (CNCs).

The CNF and CNC will be functionalized on the surface to modulate their ability to retain water contaminants: enrichment with negative surface charges or with lignin will be useful for retaining metal cations; functionalization with aromatic groups or lignin will serve to retain non-polar organic pollutants; ester groups (stearic transesterification with lipids) will be used to retain oils or emerging pollutants. The activities will include the preparation and functionalization of CNF and CNC, the preparation of the membranes, validation and the application to the purification of waters produced by companies or coming from polluted sites. Finally, a microfluidic filtration device will be assembled.



References

[1] M. M. Mekonnen, A. Y. Hoekstra, Sci. Adv. 2016, 2, No. e1500323N.
[2] F. Brunetti, A. Operamolla, et al. Adv. Funct. Mater. 2019, 29, 1806798.
[3] L. Spagnuolo, R. D'Orsi, A. Operamolla, ChemPlusChem 2022, 87, e202200204.
[4] R. Das, T. Lindström, P. R. Sharma, K. Chi, B. S. Hsiao, Chem Rev. 2022, 122, 8936-9031.

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Ministero degli Affari Esteri
e della Cooperazione Internazionale

POS05

ENVIRONMENTAL LIFE CYCLE ASSESSMENT APPLIED TO MEDICAL DEVICES

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1. Introduction

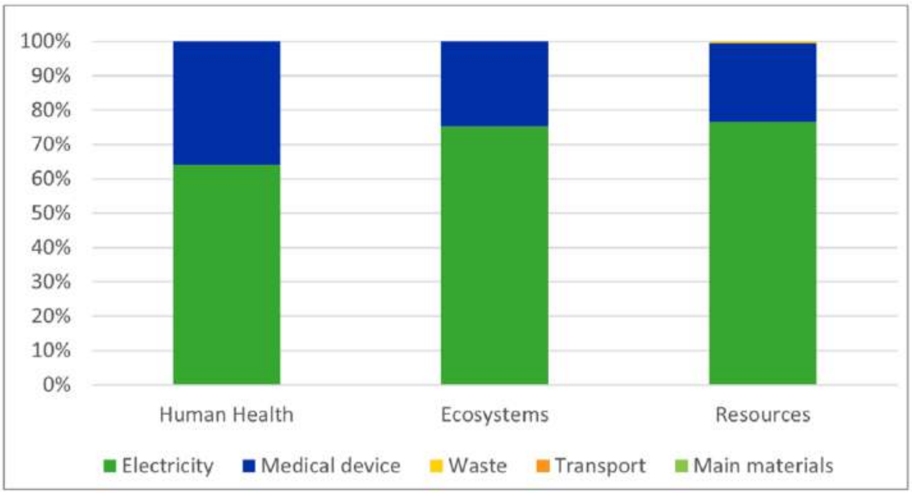
With the European Green Deal, the EU aim to reduce GHG emission by 55% by 2030, and to reach net zero by 2050. The healthcare sector is not an exception, indeed is responsible for 4-5% of global total carbon emissions. These impacts can be assessed by applying an LCA (Life Cycle Assessment), a methodology for the quantitative assessment of environmental impacts. This type of assessment is needed also for nanomaterials that are increasingly applied in many sectors such as medicine. To facilitate the fast transition to the market of new nanotechnology-based medical technologies, the SAFE-N-MEDTECH project offers to companies and laboratories the services required for the development, testing, assessment, upscaling and market exploitation of nanotechnology-based Medical and Diagnosis Devices. One of the objectives of the SAFE-N-MEDTECH is to assess the sustainability of nano-based medical technologies along their life cycle through LCA techniques. The topic of this contribution is to present the results of an LCA study for a nanotechnology-based medical device to prevent biological/microbial contamination to enhance MDs reprocessing developed by TECNAN and evaluated within SAFE-N-MEDTECH.

2. Results and Discussion

LCA has been applied to a nano-based medical technology, a forceps on which a nanocoating has been applied. The aim of nanocoating is to enhance the reprocessing chances of the medical device. LCA was carried out with the use of the SimaPro LCA software developed by PRé Sustainability and the database EcoInvent Version 3.6 (Wernet et al., 2016). ReCiPe 2016 Endpoint and Midpoint methods were jointly used to calculate environmental impacts (Huijbregts et al., 2017). Both Endpoint and Midpoint results are reported as percentage, where each impact category result is set at 100% and relative contributions of different materials/components/processes are presented. Midpoint results show the environmental impact due to the product under assessment for each impact category and main materials to produce the nanocoating (i.e., organometallic precursor, solvents), the material to produce the medical device, separated from the other main materials to better show the impact related to it, and specific process (i.e., electricity, waste, transport). For each impact category, the most relevant and practically the only contribution are provided by the electricity to produce the nanocoating and by the medical devices on which the nanocoating is applied. The significant impact arising from electricity consumption is the fact that a considerable amount of energy is required to produce even a small quantity of nanocoating. This heavily affects impact categories such as stratospheric ozonization, ionizing radiation, freshwater and marine ecotoxicity. Only for mineral resources and human carcinogenic toxicity impact categories, the medical device provides the highest contribution, mainly explained by the relevant energy consumption during the medical device production and the resources used to produce it (steel unalloyed). Indeed, to produce steel, materials such as iron must be extracted, and mixed with coke in furnaces that reach 1500 Celsius degrees. The main materials, waste and transport processes contributions are far less relevant (<3% each) and can be noticed only in a few impact categories: water consumption, fossil resource, global warming potential, ozone formation and terrestrial ecotoxicity. Endpoint results provide an overview of damages to ecosystems, human health, and resources, caused by environmental impacts of the life cycle of a nanocoated forceps. The normalized results of the three endpoint indicators are reported in the figure. Similar to the midpoint results, the largest contributions to the impacts are related to the electricity consumption to produce the nanocoating and the main material to produce the Medical device. Endpoint results better show that the large contribution is related to electricity consumption. In the next months, a comparative LCA will be carried out to assess the environmental impacts of forceps with and without nanocoating, looking at the water, material and energy consumption during the washing process.

3. Conclusions

The presented LCA study evaluated the environmental impacts of a nano-based medical technology, a forceps on which a nanocoating has been applied. It is specifically developed to prevent biological/microbial contamination to enhance MDs reprocessing. Regarding environmental impacts, both at the midpoint and endpoint level, the obtained results showed that the energy consumption to produce the nanocoating and the main material constituting the forceps provides the major contribution. Minor contributions are instead related to main materials, waste and the transport processes.



Nanotechnology-based medical device endpoint results

References

Huijbregts, M. A. J., Steinmann, Z. J. N., Elshout, P. M. F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., & Van Zelm, R. (2017). ReCiPe2016: A harmonised life cycle impact assessment method at midpoint and endpoint level. *The International Journal of Life Cycle Assessment*, *22*(2), 138–147. https://doi.org/10.1007/s11367-016-1246-y

Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., & Weidema, B. (2016). The ecoinvent database version 3 (part I): Overview and methodology. *The International Journal of Life Cycle Assessment*, *21*(9), 1218–1230. https://doi.org/10.1007/s11367-016-1087-8

POS06

RIDUCIN PROJECT: INNOVATIVE APPROACHES FOR REDUCING THE NITROGEN FRACTION IN LIVESTOCK WASTEWATER

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1. Introduction

In the last years, the increase in the number of farms in the Campania Region (southern Italy) has caused a drastic rise in water consumption, resulting in a high production of livestock slurry, characterized by a dry matter content of less than 7% and a limited soil amendment effect. Incorrect livestock wastewater management can lead to an augmentation of nitrogen pollution in water bodies through leaching phenomena. The RiduciN project, supported by the Campania Region, aims to develop and disseminate the contents of scientific knowledge of chemical-environmental and engineering character in the field of new and innovative processes for the treatment of zootechnical effluents, experimenting, developing, and industrializing emerging environmental technologies. Moreover, the project intends to provide valuable tools for the sustainable management of livestock wastewater, according to the goals of the 2030 Agenda of the Sustainable Development Agency[1]. The project focuses on developing a pilot plant that, leveraging the capabilities of natural zeolite adsorption and electro-oxidation technique, can be used effectively for treating liquid waste of livestock nature.

2. Results and Discussion

In order to achieve the project goals, preliminary lab experiments were carried out by treating real wastewater (RWW) sampled in a livestock farm located in the Campania Region (Fig. 1A). An initial sample characterization showed that the RWW contained about 1400 mg/L of total nitrogen (N_{TOT}), implying the demand for applying effective removal treatments before discharging it in water bodies.

Fig. 1B shows the preliminary results of EO experiments performed on the RWW sample by varying the initial N_{TOT} loads. Moreover, the effect of NaCl, a well-known reactive electrolyte, on the N_{TOT} removal has been examined. The EO tests have been carried out in lab-scale batch reactor[2]. The electrochemical apparatus consisted of two boron doped diamond (BDD) electrodes, with an active area of 50 cm^2 for each one and gap of 1 cm. The electrodes were connected to a DC power supply BPS-305 (Lavolta, London, UK), allowing it to operate in amperostatic conditions. The net working volume of RWW treated was 250 mL, and the process was carried out at 25 °C. As can be seen in Fig. 1B, in absence of NaCl (blue data), basically the same (N_{TOT}) degradation efficiencies of 2%, 5% and 3% were achieved, operating at different initial contaminant concentrations (1:1, 1:25 and 1:50, respectively). Conversely, when 250 mg/L of NaCl were present in solution (orange data), the N_{TOT} removal increased with an increase in the dilution rate of the RWW. In detail, 4%, 10%, and 31% of N_{TOT} removal were achieved, acting at 1:1, 1:25 and 1:50 RWW initial sample dilution, respectively. According to Iovino et al.[2], when NaCl is present in the system, high chlorine reactive species (Cl_2, HClO, ClO^-) are generated on the anode surface, which are further involved in the oxidation of the nitrogen species.

Fig. 1C reports preliminary outcomes of adsorption experiments performed by means of a Neapolitan yellow zeolitic tuff (PHIL75) as adsorbent, extracted from local zeolitic deposits. As known, natural zeolites have received high consideration as suitable adsorbents for contaminant removal from water due to their high cation exchange capacity. Natural zeolite is found in various concentrations in the pyroclastic rocks of volcanic origin; such materials show selectivity towards certain cations and this peculiar characteristic can be exploited for the removal of various chemical compounds present in an aqueous solution.

The adsorption tests were performed in three columns packed with 20 g of PHIL75 with three different initial particle sizes (0.5-0.2, 1.0-0.5, and a mixed condition with 1.0-0.5 and <0.2 mm). Five mL of the RWW sample were eluted through each column, the eluates were analyzed to assess the N_{TOT} removal efficiency of the process. The results indicated that the change in the initial adsorbent particle size does not impact N_{TOT} removal efficiency.

About 60 % of N_{TOT} removal was achieved operating under all the conditions investigated. These findings demonstrated the promising effectiveness of PHIL75 application for removing total nitrogen from impacted livestock wastewater.

3. Conclusions

Electrochemical oxidation and adsorption processes have shown promising results in the treatment of RWW samples affected by high N_{TOT} content. The RiduciN project aims to develop a batch-type reactor that has as a reference market is that of the treatment of wastewater produced by the livestock sector, widespread in the production reality of Campania, to guarantee the achievement of the regulatory limits [3] established by current legislation for discharge into the sewer. The coupling of both techniques can constitute an efficient tool for removing the nitrogenous load from zootechnical effluent, which allows the obtainment of a liquid phase with reduced nitrogen content at the outlet of the system, positively affecting the operating costs of wastewater purification.

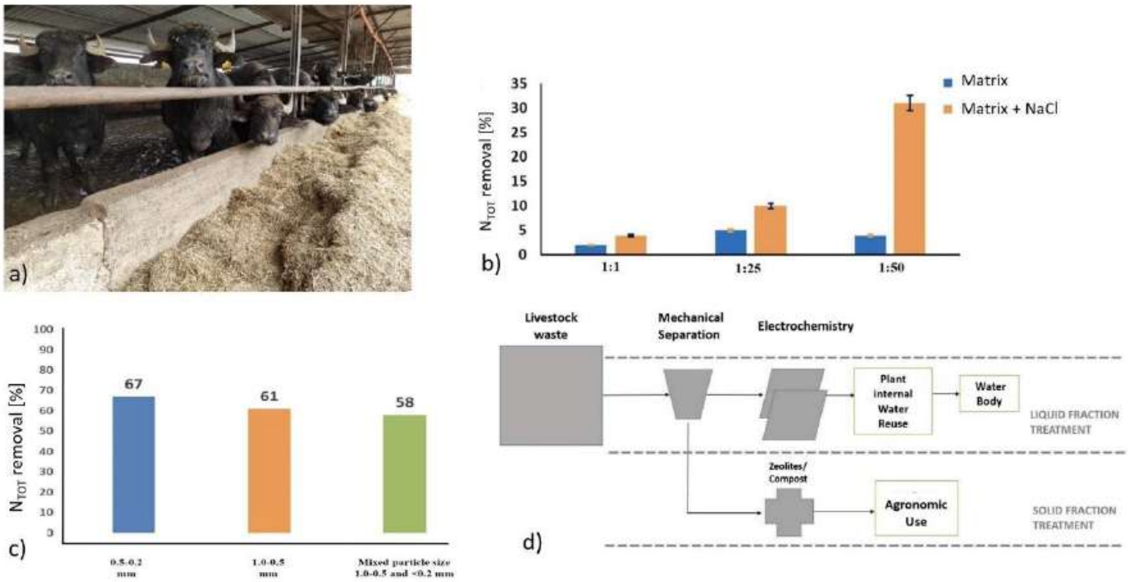

Fig. 1: a) RWW sampling point – livestock farm; b) EO preliminary results; c) Adsorption preliminary results; d) Pilot-scale plant schematization

References

[1] ASVIS, Sustainable Development Agency, https://asvis.it/
[2] Pasquale Iovino et al. 2023, Electrochemical Removal of Nitrogen Compounds from a Simulated Saline Wastewater.
[3] D.M. n. 260/2010 for groundwater.

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IRON IN WATER: A NEW PROCEDURE FOR ON-SITE MEASUREMENT USING VOLTAMMETRIC METHODS

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1. Introduction

Iron, a crucial element in our environment, plays a vital role in numerous natural processes. From supporting the growth of plants to facilitating chemical reactions, iron influences the balance and functionality of ecosystems. Understanding the presence and concentration of iron in the environment is very important, as it impacts various aspects of our planet's health. On-site detection and speciation of iron are significant for several reasons. Firstly, they allow for real-time monitoring and assessment of iron levels in a particular environment. Secondly, on-site detection facilitates research in several fields, like environmental science, biochemistry, and medicine. Studying the speciation of iron in different environmental compartments, such as water bodies or soil, can provide insights into its behavior, mobility, and potential interactions with other chemical species. In medical applications, on-site detection of iron speciation can aid in diagnosing and monitoring certain diseases, as abnormal iron levels or distribution can be indicative of underlying health conditions. Furthermore, on-site detection using voltammetry offers the advantage of convenience and cost-effectiveness. Traditional analyses often involve time-consuming sample collection, and expensive analysis, which can be impractical in some situations.

2. Results and Discussion

In this context, the present work aims at evaluating the applicability of voltammetry for on-site determination of iron and its possible speciation using a portable voltametric analyzer. For this purpose, a Glassy Carbon Electrode (GCE) was used, and the main focus of the work regarded the possibility of modifying the surface of the electrode in order to increase the sensitivity and the selectivity for iron (II) or iron (III). In this first step we focused on the development of the procedure for total iron and iron (III). The different species of iron were determined in synthetic solutions for optimizing all the procedure and the instrumental parameters.

For iron (III) determination we operated using a modification of the GCE with an antimony-bismuth film (SbBi-GCE) using acetate buffer (pH=4) as supporting electrolyte [1]. For the deposition of the film we worked in two steps: antimony was deposited in the first one, bismuth in the second one. The analyte was accumulated as the iron(III)-1-(2-piridylazo)-2-naphthol (PAN) complex, so we prepared a solution of this ligand and a standard 1000 mg L^{-1} solution of iron (III) from iron (III) nitrate nonahydrate salt, which was diluted to obtain test solutions; all analyses were carried out in acetate buffer (pH=4).

The technique adopted was Square Wave Adsoptive Cathodic Stripping Voltammetry (SW-AdCSV); the electrochemical parameters were optimized and consisted of a deposition step (120 s) at -0.40 V, followed by a scan from -0.3 V to -0.9 V. After that the linearity, the repeatability, the detection limit, and the accuracy were determined using synthetic solutions.

The new method was tested also with a Standard Reference Material (SRM) 1643f (Trace Elements in Water, iron certified concentration 93.44 ± 0.78 µg L^{-1}) for validation measurements.

After that the applicability of the proposed on-site technique for the determination of iron in real water samples was evaluated. Aliquots of tap water or lake water were acidified with nitric acid in order to have all the iron in the oxidized form III. 0.5 ml of sample were added with 9.5 ml of supporting electrolyte and PAN and analysed; the standard addition method was used to quantify iron concentration, as shown in Figure 1. The samples were also analysed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) in order to compare the total iron present; a good agreement between the results obtained with SW-AdCSV and ICP-OES was observed.

3. Conclusions

In conclusion, the results obtained demonstrated the good applicability of the on-site voltammetric technique proposed for determination of iron and its speciation in waters. By providing real-time monitoring, facilitating research, and offering convenience, on-site detection methods contribute to effective management strategies of environmental issues, cost-effective and versatile industrial practices, and enhanced scientific understanding of iron's role in various contexts. The next steps will concern the search for a modification of the electrode and related instrumental parameters suitable for the direct determination of the iron (II) content in synthetic solutions, followed by the test of the developed method with real water samples and biological fluids.

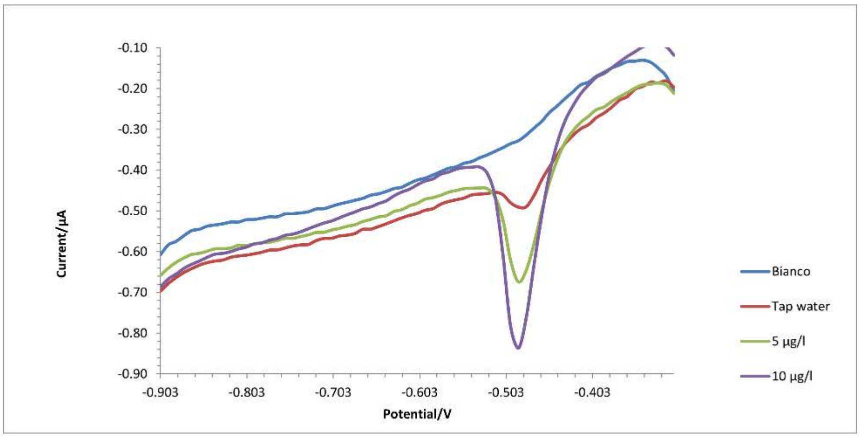

Figure 1- Voltammograms obtained by SW-AdCSV for a tap water sample and two standard additions (5 µgl-1 each) of iron (III)

References

[1] Segura, R., Toral, M. I., & Arancibia, V. (2008). Determination of iron in water samples by adsorptive stripping voltammetry with a bismuth film electrode in the presence of 1-(2-piridylazo)-2-naphthol. Talanta, 75(4), 973–977. https://doi.org/10.1016/j.talanta.2007.12.038

TRACE ELEMENTS AND NUTRIENTS EVALUATION IN THE CAOSTAL AREA OF ANCONA SUBJECTED TO DIFFERENT ANTHROPOGENIC PRESSURES

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1. Introduction

The city of Ancona lies on the mid-Adriatic coast and its port is an important junction for the distribution of goods and the transfer of passengers at European level. It is also dotted by several industries, mainly located along the Esino Valley and characterized by the presence of a big oil refinery in Falconara.

Trace Elements (TEs) (e.g. As, Cd, Hg, Pb) are persistent and naturally occurring elements, capable of generating toxicity for marine organisms by tissues bioaccumulation and - for Hg - even biomagnify. Anthropogenic pollution can release such contaminants in the environment, increasing natural concentrations [1]. Moreover, nutrients (N, P, Si) are essential for organisms' growth, but whenever high concentrations occur, may generate eutrophication, especially for a susceptible region such the Adriatic. The main sources for nutrients are riverine runoff and sewage discharge outflows, particularly if untreated [2].

The study aims to 1) evaluate the dissolved concentration of As, Cd, and Hg, investigating the possible sources and the differences between the sites; 2) assess the nutrients distribution, 3) chemically and physically characterize the coastal area of Ancona.

2. Results and Discussion

Seawater samples were collected monthly from March 2022 to March 2023 at three different sites of the coastal area of Ancona: Portonovo (PN), Marina Dorica (MD), and Palombina (PAL). These were selected as representative of three different levels and types of environmental impairment (Fig. 1). The anthropogenic pressure in the chosen sites is mainly due to maritime traffic for MD and PN, particularly during the summer season, and for PAL the proximity of untreated sewage discharge points and the refinery.

Samples has been collected in cleaned HDPE bottles, filtered immediately with Ø 0.45µm Mixed Cellulose Ester filters and then the filtered fraction was divided in two aliquots: one was reserved for colorimetric nutrient analysis, as described in [3], and another one was acidified with ultrapure HCl and reserved for dissolved As, Cd and Hg Atomic Fluorescence analysis, as described in [4].

Nutrients showed the following concentrations (values reported as mean ± SD): Si-$Si(OH)_4$ 100 ± 72 µg L^{-1}, N-NO_3 71 ± 79 µg L^{-1}, N-NO_2 8 ± 9 µg L^{-1}, and P-PO_4 4.2 ± 3 µg L^{-1}. Overall, nutrient concentrations between the sites were generally comparable, although MD had slightly higher results. Seasonal differences were observed for nutrients, primarily due to the effect of rain on riverine outflows. Lower concentrations were found during the summer, while higher concentrations were observed during the winter. This effect was more pronounced in the sites PAL and MD, which are closer to the Esino river and more subject to sewage discharge. In PN, there was a seasonal trend, but with more variability and apparently not related to salinity. The nutrient oscillations in PN could be more influenced by phenomena such as resuspension, driven by winter water column mixing.

The dissolved fraction of TEs showed values ranging as follows: As 177 − 1208 ng L^{-1}, Cd 6.6 − 73 ng L^{-1}, Hg 2.1 − 53.3 ng L^{-1}.

The concentrations of dissolved Cd (Cd_{diss}) were comparable between PAL and MD (35 ± 20 ng L^{-1}), while PN had significantly lower concentrations (19 ± 7 ng L^{-1}). On the other hand, the concentration of dissolved Hg (Hg_{diss}) was higher in MD (27 ± 10 ng L^{-1}) compared to PAL and PN (16 ± 15 ng L^{-1}). The concentration of As was higher in PN (915 ± 235 ng L^{-1}) compared to MD and PAL (600 ± 200 ng L^{-1}).

Statistical analysis, performed with RStudio, showed significant negative correlation ($p<0.05$) between dissolved As_{diss} and salinity (S) in the PAL site. Positive relationships between As_{diss} and nutrients were found in all three sites, although only PN showed significant correlations with phosphates and ammonia ($p<0.05$). This suggests that the input of these compounds may have the same sources. Hg_{diss} in PAL exhibited a marked seasonality, with a significant negative correlation with T ($p<0.05$) and a weak negative correlation with S. No significant correlation was observed for Cd_{diss} and the other variables in PAL. However, a significant negative correlation with PO_4 ($p<0.05$) was observed in the MD site. In the PN site, Cd_{diss} showed a positive and significant correlation with NO_2 ($p<0.05$), but weak correlations with other nutrients.

In the month of July, a sample was taken at the PAL site while balneation (bathing) was closed due to untreated sewage discharge. This sample showed a peak in nitrates, ammonia, and Cd concentrations.

3. Conclusions

The results highlighted that hydrodynamics and geomorphology drive many site differences. Nutrients are well related to freshwater inputs, differently from TEs. While coastal sites concentrations seem to be more affected to freshwater inputs, the PN site (2 miles from the coastline) seemed to be more affected by resuspension phenomena. Dissolved TEs concentrations were far below the MAC-EQS for bathing waters (WFD 2008).

Further statistical analysis will be done in order to better understand the influence of freshwater inputs and to distinguish between the different inputs. The findings of the present work contribute to our understanding of the impact of factors such as bathymetry, proximity to freshwater discharge sources, and seasonal variability on the coastal marine environment.

Fig. 1. Map of the study area, main anthropogenic sources in evidence and sampling points in blue.

References

[1] Vareda, J. P., Valente, A. J., & Durães, L. (2019). *Journal of environmental management*, *246*, 101-118.
[2] Volf, G., Atanasova, N., Kompare, B., & Ožanić, N. (2013). *Journal of hydrology*, *504*, 182-193.
[3] Girolametti, F. et al., (2022). *Water*, *14*(4), 569.
[4] Fanelli, M. et al., (2022). *Water*, *14*(12), 1930.

CHEMICAL CHARACTERISATION IN ARCTIC MARINE SEDIMENTS IN KONGSFJORDEN

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1. Introduction

In recent decades, human activities have had a significant impact on the Arctic region. Climate change, caused by the fossil fuels burning and other human activities, has led to the warming of the Arctic at more than twice the rate of the rest of the planet. The global warming has been leading to the melting of sea ice, glaciers, and permafrost, with significant consequences for the Arctic's ecosystems and all the organisms depending on them. As the ice melts, new trade routes will be available, as well as the access to new fishing grounds and marine subsoil resources, e.g. oil and gas. These activities will also increase the pressure of anthropogenic impacts and further pollution risks on the Arctic's fragile ecosystems[1].

Within the framework of the project "Study of mercury in the Arctic marine sediments" in cooperation with the Norwegian University of Science and Technology (NTNU) and Università Politecnica delle Marche (DiSVA-UNIVPM), a research study on the elemental composition and the spatial distribution of elements in the surface sediments of Kongsfjorden area (Svalbard islands) has been carried out.

2. Results and Discussion

Surface marine sediments were collected along two transects consisting of five and six sites, respectively (Fig. 1). Marine sediments were lyophilized, and microwave digested in a HNO_3 solutions. Elemental composition was analysed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and by Direct Mercury Analysis System (DMA). TOC, ROC and TIC were also determined in order to characterize the collected marine sediments.

Element contents in the sediments of the Kongsfjorden were in agreement with previous studies carried out in the same study area and with other Arctic regions[2]. TOC% and TIC% were also determined in order to characterize the surface sediments. Both TOC and TIC decreased from the stations closer to the Ny-Ålesund harbour to the outer stations of the transect. Our data on %TOC and %TIC suggest that sediments in Kongsfjorden are influenced by glacial melting and by the biological activity, the latter influencing both TOC and TIC production.

The element contents in the sediments collected followed the decreasing order: Ca > Al > Mg ≅ Fe > K > Na > Si > S > P ≅ Ti > Mn > Ba > Sr ≅ Rb > Ce ≅ V ≅ Zn > Cr > La > Li ≅ Nd > Ni > Y ≅ Cu > Pb > Ga > Co > Sc ≅ Zr > Pr > As > Cs ≅ Sm > Gd > Dy > Th > Er ≅ Be > Yb > Eu ≅ Se > Sn ≅ U > Ho > Mo ≅ Tl ≅ Pd > Bi ≅ Tm ≅ Hf > Lu > Nb > Cd > Sb ≅ In ≅ Ag > Hg.

Four main spatial profiles of metal contents can be recognized from the inner fjord to the outer fjord: (I) decreasing distribution pattern (Na, Al, K, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Rb, Zr, Ag, In, Cs, Ba, Hf, Hg, Tl, Pb, Bi, Th, U), (II) increasing distribution pattern (S, Ca, Mo and Cd), (III) homogeneous distribution pattern (Mg, Si, P, As, and Sr) and (IV) undefined distribution pattern (Mn, Pd, Sn and Sb). As shown mostly of elements presented higher values near the harbour and lower values in the outer stations.

Enrichment Factors computed for each element by using Al as reference element of the average crustal composition gave information on possible sources of the elements determined in marine sediments. Most of the elements showed EF values <3 indicating no to minor enrichment in the Kongsfjord. Few metals (Li, Mg, S, Cr, Ni, Gd, Th, Bi) were presents with a moderate enrichment, As and Se showed a moderately severe enrichment and a very severe enrichment, respectively. The spatial distribution and the EF values highlighted the relative roles of several sources for elements in the Kongsfjorden, the glacial meltwater, the Bayelva river and physical conditions of the fjord.

The Arctic Sediment Quality Guidelines indicates Cr and Ni with values between the ASQG-low and ASQG-high, thus implying the possible occurrence of adverse effects on aquatic organisms. Cd, Cu, Pb, Zn and Hg are well below the ASQG-low at all sites, thus indicating that these metals can rarely cause adverse biological effects.

3. Conclusions

Element distribution exhibited considerable spatial variations within the study area. However, most of the elements here studied showed a decreasing spatial trend with concentrations in the inner stations higher than the outer stations of the transect. Enrichment Factors highlighted a moderately severe enrichment of As and the very severe enrichment of Se. assessments by the Arctic Sediment Quality Guidelines indicate that Cr and Ni are frequently associated with adverse ecological effects with values being above ASQG-low.

Our results highlight the need of constant and continuous monitoring programs in Kongsfjorden fjord to evaluate changes in the concentration of metals and protect the pristine environment.

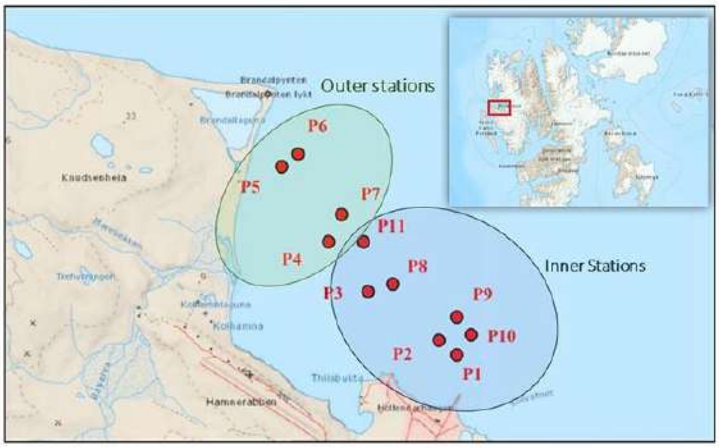

Fig. 1. Map of the study area, reporting the position of each sampling site in Kongsfjorden

References

AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), 1998, Oslo, Norway. pp. 859

Grotti, Marco, et al. Bioavailability of trace elements in surface sediments from Kongsfjorden, Svalbard. Marine pollution bulletin 77.1-2 (2013): 367-374.

POS10

POLYCYCLIC AROMATIC HYDROCARBONS, MERCURY AND SELENIUM DETERMINATION IN A COMMONLY CONSUMED MEDITERRANEAN ELASMOBRANCH (*MUSTELUS SPP.*)

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1. Introduction

The contamination of marine ecosystems by polycyclic aromatic hydrocarbons (PAHs) and mercury (Hg) has emerged as a significant concern due to their detrimental impacts on the health of marine organisms and humans. These contaminant sources come primarily from anthropogenic activities and bioaccumulate in tissues of predator species. Consequently, it can disrupt essential physiological functions and pose a substantial risk to consumers at higher trophic levels, including humans. Species from the genus *Mustelus* are common mesopredators with ecological and socioeconomic importance in the Mediterranean Sea. Their middle position within the food-webs make them crucial in regulating prey populations and acting as prey for larger predators [1]; but also, providing economic opportunities for coastal communities. The objective of this study was to evaluate the contamination levels of PAHs and Hg in the edible tissue of *Mustelus* spp. caught around the Egadi Islands in the central Mediterranean Sea. Additionally, risk indices such as the molar ratio of selenium (Se) to Hg and the selenium health benefit value (HBV_{Se}) were employed to assess the potential risks posed to consumers of this species.

2. Results and Discussion

This study analysed muscle tissue from 33 shark individuals (*Mustelus* spp.) opportunistically caught by artisanal fishermen. Individuals belong to the sympatric species *M. mustelus* and *M. punctulatus*. Samples were grouped into 16 pools based on sex, total length, and season of capture.

The PAHs extraction has been performed with the QuEChERS kit using acetonitrile as the reagent and the analysis carried out by UHPLC-FLD technique. Total PAHs in samples ranged from 1.04 to 1.35 µg kg^{-1} ww. Overall, concentration of major PAHs detected followed the order: acenaphthene > fluorene > naphthalene > fluoranthene > pyrene (**Figure 1A**). Our results indicate no difference between sex ($F_{1/14}$=0.18, p-value > 0.05) and size category ($F_{1/14}$ =1.11, p-value > 0.05). However, caution is needed since our low sample size in adult stages do not allows us to do proper conclusions for larger individuals.

Hg levels were measured using the thermal decomposition followed by amalgamation and AAS (TDA-AAS) technique, while Se levels were analysed using graphite furnace AAS (GF-AAS). Preliminary findings (only females) indicate an average Hg content ranging from 0.15 to 0.33 mg kg^{-1} ww, while Se levels ranged from 0.23 to 1.2 mg kg^{-1} ww in the samples (**Figure 1B**).

Considering the lipophilic nature of these contaminants, total intramuscular lipids were also measured to investigate possible correlations. Lipids were extracted by microwave-assisted extraction (MAE) and quantified gravimetrically. Lipid content was estimated at 0.7±0.2 (from 0.21 to 1.61) g $100g^{-1}$.

The European Union has set regulatory limits for Hg in fish tissue to ensure consumer safety. The maximum allowable limit for mercury in predatory fish intended for human consumption is outlined in Commission Regulation (EC) No 2023/915 [2]. According to this regulation, the maximum permitted level of total mercury in fish muscle tissue is 1.0 milligram per kilogram wet weight. The analysis of the fish samples revealed that the measured Hg content in the samples was found to be below the established European limit. Our results indicate that the commercial shark species known as "palombo" comply with the regulatory standards set by the EU. The antagonistic properties of selenium (Se) against the toxic effects of Hg have been extensively studied and documented in scientific literature [3]. Se acts as a protective element by forming stable complexes with Hg, thereby reducing its bioavailability and mitigating its adverse effects on biological systems. In this study, the molar ratio of selenium to mercury and the $\mathrm{HBV_{Se}}$ index were utilized as assessment parameters, calculated as follows:

$$\text{Molar ratio } = \frac{\mathrm{mol_{Se}}}{\mathrm{mol_{Hg}}} \qquad \mathrm{HBV_{Se}} = \left(\frac{\mathrm{Se} - \mathrm{Hg}}{\mathrm{Se}}\right) \times (\mathrm{Se} + \mathrm{Hg})$$

A molar ratio greater than 1 is considered safe, while a positive $\mathrm{HBV_{Se}}$ indicates a risk-free condition for consumers. Both the calculated values of the molar ratio (4.1±0.4) and the $\mathrm{HBV_{Se}}$ (4.5±0.5) index indicate that the consumption of this product does not pose any significant risk to consumers.

3. Conclusions

Overall, this study provides scientific evidence indicating that the examined shark samples meet the regulatory limits for the investigated substances set by the European Union. Additionally, this study highlights the importance of considering the protective role of selenium in assessing the risks associated with mercury contamination. These findings contribute to the understanding of the safety of consuming this product and can inform regulatory decisions and consumer choices. However, it is important to continue monitoring and research in this area to ensure ongoing consumer safety, especially for larger individuals from the genus *Mustelus*, which due to bioaccumulation, are expected to have higher concentrations of pollutants.

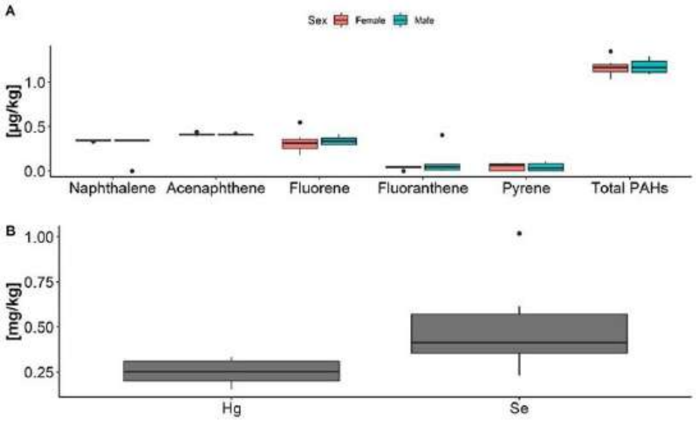

Figure 1. *Boxplot of PAHs (A), Hg and Se (b) concentrations in Mustelus spp. Solid line=median.*

References

[1] Woodland, R., et al. (2011). *Estuaries and Coasts*, 34, 391–404.
[2] Commission Regulation (EU) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing Regulation (EC) No 1881/2006
[2] Branco, V., et al. (2007). *Environmental Pollution 150*(3), 373–380.

HONEYBEE AND HONEY AS AN INNOVATIVE TOOL FOR THE MONITORING OF ENVIRONMENTAL HEALTH STATUS

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1. Introduction

In recent years, there has been an increase in the release of hazardous substances into the environment. Industrialization is the main contributors to pollution. Polycyclic aromatic hydrocarbons (PAHs) and heavy metals are concerning due to their toxic effects on organisms. Phthalic acid esters (PAEs) and bisphenol-A (BPA) are also harmful contaminants. Biomonitoring using living organisms has emerged as a cheaper method to assess environmental pollution. Honeybees are ideal bioindicators due to their sensitivity to pollutants and ability to collect samples environment. They cover a large territory and gather important samples for analysis. Beehives are economic devices for spatial and temporal surveys. Honeybees detect pollutants through their body surfaces and the collection of contaminated nectar, honeydew, and pollen. Assessing environmental pollution levels can be done through the presence of toxic molecules on bees. Honey can accumulate contaminants and act as a natural pollution-sensing drone. This study sought to evaluate honeybees and honey as indicators for environmental monitoring in the Molise region of Italy in different areas with varying pollution levels.

2. Results and Discussion

This study monitored heavy metals, polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), and bisphenol A (BPA) using bees and honey to assess the suitability of these matrices as bioindicators. The results showed higher levels of heavy metal contamination in honey samples compared to bees (average concentration of 48 $\mu g\ kg^{-1}$ compared to 25 $\mu g\ kg^{-1}$). However, higher concentrations of heavy metals were found in bees, except for copper (Cu) which accumulated more in honey. The authors hypothesize that the accumulation of Cu in honey could be due to the biology of bees, as only bees that leave the hive to collect pollen, nectar, resin, and water are affected by pollution phenomena. Furthermore, the possibility of analyzing pollen along with honey to better assess heavy metal accumulation was highlighted. As for PAHs, a higher level of contamination was observed in honey compared to bees, probably due to the presence of these pollutants in the nectar and pollen used by bees. It was also hypothesized that the accumulation of pollutants in the bee's body could influence transfer to honey. Finally, PAEs and BPA were also detected in honey, which are considered widespread contaminants in the environment. Overall, the results confirmed the suitability of honey and bees as bioindicators of environmental pollutants, although further research is needed to assess the accumulation and behavior of heavy metals, PAHs, and phthalate esters in honey.

3. Conclusions

The honey produced by *A. mellifera* has been found to be an effective and affordable bioindicator for both polycyclic aromatic hydrocarbons (PAHs) and heavy metals, making it a valuable tool in assessing environmental pollution. These bioindicators have proven capable of detecting variations in pollutant concentrations across different locations, as well as providing a preliminary assessment of the impact of weather conditions on their distribution. However, further studies are needed to fully understand how contaminants behave in response to changes in meteorological conditions. In summary, the use of *A. mellifera* and honey as bioindicators has provided valuable insights into environmental pollution.

Molise areas investigated in the present study.

References

Astolfi ML, Conti ME, Ristorini M, Frezzini MA, Papi M, Massimi L, Canepari S (2021) An analytical method for the biomonitoring of mercury in bees and beehive products by cold vapor atomic fluorescence spectrometry. Molecules 26:4878.

Martinello M, Manzinello C, Dainese N, Giuliato I, Gallina A, Mutinelli F (2021) The honey bee: an active biosampler of environmental pollution and a possible warning biomarker for human health. Appl Sci 11:6481.

Porrini C, Ghini S, Girotti S, Sabatini AG, Gattavecchia E, Celli G (2002) Use of honeybees as bioindicators of environmental pollution in Italy. In: Deville's J, Pham-Delegate MH (eds) Honey bees: estimating the environmental impact of chemicals. Taylor & Francis, London, New.

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POS12

CHEMICAL CHARACTERIZATION OF ARCTIC RESUSPENDED SOILS USING TRACE ELEMENTS AND STRONTIUM AND LEAD ISOTOPE RATIOS

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1. Introduction

Mineral dust emission and transport can occur at high latitudes, impacting the Earth's radiative budget and snow albedo. Even though the Arctic region is not often considered as a relevant dust source, in a context of arctic amplification, the importance of high latitude dust (HLD) sources is increasing. Although there is still a lack of knowledge concerning HLD sources and their impact, previous studies have shown how the dust produced there, affects the high Arctic.[1]

2. Results and Discussion

In this work, we have characterised both potential HLD source areas through the resuspension of soil samples and potential receptor areas through filtration of snow samples. The potential HDL sources considered are Iceland, Alaska and Svalbard Island (Norway), while the second ones, were obtained filtering snow, firn or ice sampled on different Svalbard glaciers.

31 trace elements (TEs) were quantified using tandem ICP-MS on the filters loaded by soil resuspension. Moreover, the Sr and Pb isotope ratios were measured on the whole set of samples using a MC-ICP-MS unit at the A&MS Lab at Ghent University. Specific TEs can be used to recognize different patterns in dust originating from regions characterized by a different geological composition and the analyses of two different isotopic systems is useful in order to differentiate eventual dust sources characterized by overlapping signatures for one of the two elements. [2,3]

3. Conclusions

The proposed methodology is therefore promising for tracing dust emission and transport in the high Arctic and potentially to reconstruct past circulation patterns by investigating the dust composition in ice cores.

References

(1) Meinander, O., et al. Newly Identified Climatically and Environmentally Significant High-Latitude Dust Sources. *Atmospheric Chem. Phys.* **2022**, *22* (17), 11889–11930. https://doi.org/10.5194/acp-22-11889-2022.
(2) Bazzano, A. et al. Potential Source Areas for Atmospheric Lead Reaching Ny-Ålesund from 2010 to 2018. *Atmosphere* **2021**, *12* (3), 388. https://doi.org/10.3390/atmos12030388.
(3) Conca, E. et al., Source Identification and Temporal Evolution of Trace Elements in PM10 Collected near to Ny-Ålesund (Norwegian Arc ic). *Atmos. Environ.* **2019**, *203*, 153–165. https://doi.org/10.1016/j.atmosenv.2019.02.001

POS13

OPTIMIZATION OF A GREEN QUECHERS BASED EXTRACTION PROTOCOL FOR THE QUANTITATION OF 34 MICROPOLLUTANTS IN TOMATOES BY EXPERIMENTAL DESIGN AND MULTIPLE RESPONSE APPROACH

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1. Introduction

The analysis of chemical contamination in highly consumed fruits and vegetables, such as tomatoes, is an analytical challenge due to the complexity of the matrix. The contamination by polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and nitro-PAHs raises serious health concerns due to their airborne deposition and uptake from polluted soils and water sources.The current analytical protocols used to investigate micropollutant contamination in tomatoes are time-consuming, non-simultaneous, and often not environmentally friendly. Furthermore, the study of nitro-PAHs in tomatoes has not been extensively explored.

2. Results and Discussion

On these premises, this research proposes a QuEChERS-based approach, combined with gas chromatography/mass spectrometry, to simultaneously detect 16 PAHs, 14 PCBs, and 4 nitro-PAHs in tomatoes. To determine the optimal conditions, this study examines the effects of dichloromethane, cyclohexane, and acetone as extraction solvents, as well as four d-SPE phases for the purification of the extract, utilizing advanced experimental design coupled with multiple response optimization. The optimized protocol involves cyclohexane extraction, followed by a double purification step using primary secondary amine and octadecyl silica, and sulfuric acid oxidation, allowing to achieve recoveries of 60-120% (RSD% < 15%). The method exhibits good repeatability (inter-day precision <15%) and minimal matrix effects (<16%). The greenness of the protocol over existing literature methodologies was assessed by a recently developed open-source tool (AGREE, Analytical GREEnness Metric Approach and Software). Finally, the developed protocol is successfully applied to the analysis of three authentic tomato samples (*Rio Grande, Beefsteak, and Vine* cultivars) purchased from a local market.

3. Conclusions

The method optimized within this study represents the first validated analytical approach specifically designed for the simultaneous analysis of PAHs and PCBs and nitro-PAHs in tomatoes. It offers a more environmentally friendly alternative compared to traditional preparation protocols. Additionally, the proposed method is characterized by its simplicity (reduced number of procedural steps) and reliability (with good intra- and inter-day precision). As a result, this method can be readily applied for routine analysis of PAHs, PCBs, and nitro-PAHs contamination in tomatoes, for example, in view of a future scenario of treated water reuse for irrigation.

Acknowledgements

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POS14

THE ROLE OF BIOENERGY IN THE PROCESS OF ECOLOGICAL TRANSITION: TRADITIONAL AND RENEWABLE ENERGY SOURCES COMPARED

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1. Introduction

In recent years, human population growth and overall industrial development have led to an exponential increase in global energy demand. The European economy still heavily relies on fossil fuels for its energy needs, but these will be depleted in the coming decades. An economy based on cheap and renewable energy sources, a clean environment and energy independence are characteristics of responsible societies. Commitments related to climate policy and the energy crisis have led to the search for alternative ways to obtain energy. Bioenergy is, in fact, considered the most consistent renewable energy source due to its economic and environmental advantages and its great potential to replace non-renewable fuel sources. The research and diffusion of alternative energy sources is therefore one of the key tasks of the energy transformation and the transition towards a zero-emission economy. This project aims to provide an overview of the role of alternative biofuels, through the achievement of carbon neutrality, for sustainable development.

2. Results and Discussion

European Union energy policy reform and subsequent legislation and regulation at the national level have provided a strong incentive for the development of increasingly competitive renewable energy generation technologies. One of the promising forms of renewable energy is biogas because it can be derived from widely available evergreen raw materials; it can use animal waste, agricultural waste, industrial waste, food waste as raw materials, thus supporting clean and sustainable energy. Biogas can provide an efficient means of generating energy that can be used as fuel in households, in vehicle power systems and as a source of electricity. Increasing the recycling, recovery and reuse of waste and its use as a resource should be the long-term goal of researchers. An emerging global trend is also to transform biogas into biomethane, which can be used as city gas or transport fuel. Rapid technological development has made it possible to identify new production sectors capable of generating value chains that replace traditional ones, maximizing the recovery and recycling of waste. Furthermore, recent energy crises and the prospect of near depletion of fossil or nonrenewable fuel reserves have led industrialized countries to promote renewable energy production, distributed generation, and energy efficiency interventions. The use of sustainable energy sources takes advantage of zero-emission resources (non-polluting and inexhaustible sources) whose availability is assumed in the future. The available studies in literature indicate a significant development of these resources, desirable due to the need to increase energy security, as well as for environmental and economic reasons.

3. Conclusions

The need for renewable energy sources that solve the intermittency problems seen by conventional renewable sources is unequivocal, and biofuels provide a solution to meet this requirement. Circular economy and bioeconomy are thus the prospects for addressing the challenges and achieving environmental and socioeconomic goals around the world. Energy generation from alternative sources will contribute to the mitigation of climate change and minimization of the alarms posed to the environment, so as to provide a clean and sustainable environment for our modern society.

References

Kang M.; Zhao W.; Jia L.; Liu Y. Balancing carbon emission reductions and social economic development for sustainable development: Experience from 24 countries. Chin. Geogr. Sci. 2020, 30, 379-396.

Kasinath, A.; Fudala-Ksiazek, S.; Szopinska, M.; Bylinski, H.; Artichowicz, W.; Remiszewska-Skwarek, A., Luczkiewicz, A. Biomass in biogas production: Pretreatment and codigestion. Renew. Sust. Energ. Rev. 2021, 150, 111509.

Pappalardo, G.; Selvaggi, R.; Pecorino, B. Biomethane production potential in Southern Italy: An empirical approach. Renew. Sust. Energ. Rev. 2022, 158, 112190.

POS15

REGENERABLE CATIONIC HYDROGELS AS NEW ADSORBENT MATERIALS TO ELECTROSTATICALLY REMOVE NITRITES FROM WATER

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1. Introduction

Metastable anions as nitrites, deriving from the oxidation of ammonia by agricultural pollution, sewage, decaying protein, and other nitrogen sources, are a recognized environmental issue, due to their role in eutrophication, surface and groundwater contamination, as well as toxicity towards almost all living creatures. Anyway, while several studies report on methods to remove nitrate from water, novel methods to remove nitrite are missing.

2. Results and Discussion

Two cationic resins found capable to form hydrogels (R1HG and R2HG) by dispersion in aqueous medium, and to remove anionic dyes from water by electrostatic binding,[1] were first tested in nitrite adsorption experiments in batch, to assess their removal efficiency by contact over time. Nitrites removal from samples of water appositely contaminated and containing 118 mg/L NO^{2-}, was monitored by UV–Vis methods, using the Griess reagent system (GRS).[2] The removal efficiency of R1HG and R2HG (89.2 and 89.6%), their maximum adsorption (21.0 and 23.5 mg/g), as well as the adsorption kinetics and mechanisms were evaluated.[2] R1HG- and R2HG-based columns, mimicking mini-scale decontamination systems by filtration under pressure, succeeded in rapidly and totally removing nitrites (99.5 and 100%) from volumes of nitrite solutions (NO^{2-} = 118 mg/L) 10 times the volumes of resins used.[2] When filtration was extended to increasing volumes of the same nitrite solution up to reach 60 times the volume of resins used, the removal efficiency of R2HG remained stable at over 89% (Figure 1a).[2] Interestingly, both the hydrogels were regenerable by 1% HCl washing, without a significant reduction in their original efficiency (Figure 1b).[2]

3. Conclusions

R1HG and especially R2HG represent low-cost, up-scalable, and regenerable column-packing materials, promising for applications in the treatment of drinking water contaminated by nitrites.

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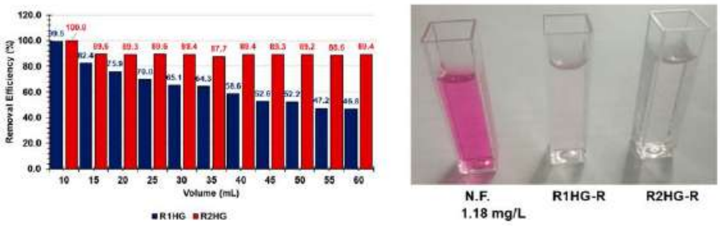

(a) (b)

Figure 1: Removal efficiency of R1HG and R2HG during filtration of increasing volumes of nitrite solutions (a); nitrite solution before filtration (N.F.) and filtrates by regenerated R1HG-R and R2HG-R (b).

References

S. Alfei, F. Grasso, V. Orlandi, E. Russo, R. Boggia, G. Zuccari. *Int. J. Mol. Sci.* **2023**, *24*, 2948.

S. Alfei, V. Orlandi, F. Grasso, R. Boggia, G. Zuccari. *Toxics* **2023**, *11*, 312.

POS16

ORGANIC COMPOUNDS IN GEOTHERMAL WATERS: ANTHROPIC CONTAMINANTS OR NATURALLY OCCURRENT?

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1. Introduction

Emerging contaminants, ECs, are residues of chemicals found in the environment at trace concentrations with potential, perceived, or real risk to the environment, human and animal health. They are compounds found in the environment whose presence was formerly not detectable or considered significant. The high demand for green energy resources has led to increased geothermal energy exploration, exploitation, and research. This has led to detection of emerging pollutants and priority organic pollutants in geothermal waters that were initially not taken into account in geothermal development.

Studies on the presence and effect of trace metal pollutants and non-condensable gases (CO_2, NH_3, H_2S, SO_2, and CH_4) in geothermal waters have extensively been carried out.[1] The high demand for green energy resources has led to increased geothermal energy exploration, exploitation, and research. This has led to detection of emerging pollutants and priority organic pollutants in geothermal waters that were initially not taken into account in geothermal development. Nonetheless, research on the presence of organic pollutants such as trace PAHs, and emerging contaminants in geothermal water and steam is scarce in literature. Geothermal fluids have diverse chemistries, which largely reflect the geological setting of the geothermal system. Many of these chemical differences largely depend on the source of recharge waters and the contribution of gases from magmatic or metamorphic sources. Furthermore, many hydro-chemical processes significantly affect the water composition during ascent to the surface, which can ultimately lead to pollution of the environment. These processes make the geothermal fluids acquire a unique chemical composition compared to the normal surface waters. This preliminary study aims to verify the presence of organic compounds, such as benzene and its higher homologues and polycyclic aromatic hydrocarbons (PAHs) in the geothermal fluids of Italy.

2. Results and Discussion

Few recent studies have demonstrated the significant presence of organic compounds in various geothermal fields worldwide. These molecules are ubiquitous and occur as volatile organic compounds (VOCs) at low but detectable concentrations in the hydrothermal fluids of volcanic and geothermal systems.[2] This preliminary study aimed to determine the presence of volatile organic compounds, such as benzene and its higher homologues, and polycyclic aromatic hydrocarbons in several geothermal water samples collected in different parts of Italy, near volcanic systems. The samples underwent analysis using gas chromatography coupled with mass spectrometry (GC-MS), preceded by sample pre-concentration through enrichment of volatile substances in the headspace (purge and trap) and solid-phase extraction for the determination of high molecular weight organic compounds like naphthalene and its higher homologues.

Preliminary analyses have revealed that the main classes of compounds detected are hydrocarbons, like alkanes, isoalkanes, isoprenes, alkenes and isoalkenes, polycyclic aromatic hydrocarbons, like phenanthrene and anthracene; BTEX, benzene, toluene, ethylbenzene, xylene.

To understand the obtained results, it is important to clarify that the natural origin of these compounds can be both abiotic and biogenic. The abiotic synthesis of alkanes and the presence of alkenes in hydrothermal environments have been attributed to Fischer-Tropsch-Type (FTT) reactions, a well-known process in industry and research that produces hydrocarbons and oxygen compounds from carbon monoxide and carbon dioxide.[3] Under geological conditions, the FTT reaction is proposed to occur through the reduction of CO_2 with H_2 in thermal fluids especially in the presence of water and ferrous ions from iron minerals.

The biogenic origin of such compounds is closely related to the presence of thermophilic (optimal growth temperature, OGT > 50°C) and hyperthermophilic (OGT > 80°C) organisms, which inhabit these springs as natural niches. Saturated hydrocarbons are biogenic compounds that are chemically stable and retain their chemical structure, as well as all biological and geochemical information.

However, benzene has been found to be relatively abundant in hydrothermal gases. This can be theoretically attributed to reversible catalytic reforming processes, i.e., multi-step dehydrogenation reactions involving saturated hydrocarbons.[4] Benzene can also be effectively produced under hydrothermal conditions through the dehydrogenation of saturated cyclic organic compounds in the presence of catalytic sulfide minerals (sphalerite and pyrite) and iron oxide minerals (magnetite and hematite). The relative amounts of cyclic organics and aromatic compounds in geothermal waters strongly depend on the physicochemical conditions of the deep reservoirs, with increasing temperatures favoring the conversion of cyclic organics into aromatics. The stability of benzene is favored by high temperatures, as both cyclization and dehydrogenation processes are endothermic, while benzene hydrogenation to produce cyclohexane is favored by low-temperature geothermal regimes.

3. Conclusions

In conclusion, this study has achieved its objective of determining the presence/absence of organic compounds in geothermal systems. It lays the foundation for subsequent studies that will focus on the nature of these contaminants, with the aim of answering the question: anthropogenic or naturally occurring contaminants?

The technique employed has proven to be sensitive and advanced, allowing for the detection of hydrocarbons, like alkanes, isoalkanes, isoprenes, alkenes and isoalkenes; Polycyclic aromatic hydrocarbons, like phenanthrene and anthracene; BTEX, benzene, toluene, ethylbenzene, xylene.

at concentrations on the order of µg/L.

Furthermore, it is important to conduct detailed assessments of the environmental impact of geothermal systems to inform health and safety considerations in the development and utilization of geothermal resources. Dynamic geological and climatic changes, coupled with increased exploitation of geothermal resources, necessitate ongoing research and monitoring of potential environmental degradation.

At present, thermal waters containing even minimal traces of organic compounds are by law considered as polluted; based on this and other studies, the parameters for assessing water quality could be reconsidered.

Hot spring of Terme di Saturnia – Tuscany, Italy.

References

Wang, M. *et al.* (2020). Major, trace, and rare earth elements geochemistry of geothermal waters from the Rehai high-temperature geothermal field in Tengchong of China. Applied Geochemistry, 119, 104639.

Venturi, S. *et al.* (2017). Mineral-assisted production of benzene under hydrothermal conditions: Insights from experimental studies on C6 cyclic hydrocarbons. Journal of Volcanology and Geothermal Research, 346, 21-27

Mißbach, H. *et al.* (2018). Assessing the diversity of lipids formed via Fischer-Tropsch-type reactions. Organic Geochemistry, 119, 110- 121.

Bockisch, C. *et al.* (2019). Selective hydrothermal reductions using geomimicry. Green Chemistry, 21, 4159-4168.

POS17

PHYTOREMEDIATION POTENTIAL OF EPIPHYTIC TILLANDSIA (BROMILIACEAE): EVALUATION OF REMOVAL EFFICIENCY OF FORMALDEHYDE

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1. Introduction

Extensive research has been made over the past years to evaluate the phytoremediation potential of pollutants in several environmental matrices. In this wide research context, the exploration of indoor plants' role (adsorption and absorption mechanisms) in the abatement of airborne pollutants concentration and, as a result, in improving indoor air quality (IAQ) has recently become a matter of interest within the international scientific community [1-3]. Based on the current level of knowledge on the plethora of airborne pollutants indoors and the awareness on the potential risks for human health due to inhalation exposure, the interest on phytoremediation is mainly justified by the need of applying effective strategies for indoor pollution containment and priority pollutants removal. Formaldehyde (FA) is a priority pollutant for the proven potential adverse effects on human health; it is an ubiquitous chemical compound inside indoor environments, emitted by building materials and products or generated by human activities (e.g., smoking cigarettes). Epiphytic Tillandsia species, object of investigation in the present study, show to uptake compounds directly from the gas phase via their leaf trichomes for sustainment and growth, therefore they may play a key role in the removal of airborne pollutants including FA.

2. Results and Discussion

The present study was performed with the main objective to investigate whether Tillandsia species can efficiently adsorb FA and remove it from the gas phase. For comparative evaluation, the adsorption capacity of two different Tillandsia species, e.g., *Tillandsia Velutina and Tillandsia Ionantha*, was assessed. Static experiments with and without plants were carried out inside a test chamber (Perspex globe box: dimensions 85 x 61 x 63.5 cm, volume equal to 0.33 m^3) under controlled microenvironmental conditions (temperature, relative humidity) and lighting (natural or artificial). At each experimental step (preliminary background, introduction of plants, introduction of FA source), the temporal variation of FA concentration into the gas-phase was constantly monitored by means of FA-selective high-temporal resolution detector (*Formaldemeter Htv-M*, *PPM Tecnologies*). Moreover, in order to deepen the effect of FA absorption on plant cellular metabolism and to understand the fate of FA once absorbed, the monitoring into the gas-phase of FA concentration was coupled with investigations onto Tillandsia leaves, pre- and post- exposure to FA. More specifically, glutathione (substrate of formaldehyde dehydrogenase) and soluble protein contents were measured. The comparison of the experimental outcomes e.g., temporal variation of FA concentration observed during the experiments without and with plants, demonstrated that both Tillandsia species investigated were able to remove FA with a high efficiency. FA removal was also promoted when artificial lighting was applied, suggesting that a controlled lighting in a selected spectral range result in a stimulated plant metabolism. The extent of FA removal was shown to be related with plant dimensions: the removal capacity increased with the increase in leaf surface and number of absorbing trichomes. FA, probably due to a fast metabolism and reutilization, was not accumulated in the leaves. This conclusion can be drawn taking into account that, after FA exposure, the glutathione content significantly decreased in both the species (suggesting the occurrence of oxidative stress) and the content of soluble proteins simultaneously increased.

3. Conclusions

In conclusion, the experimental outcomes obtained in the present study combining test chamber investigations, e.g., monitoring of FA concentration into the gas-phase, with foliage investigations suggested that *Tillandsia Velutina* and *Tillandsia Ionantha* were both capable of absorbing FA via the specialized trichomes located onto the leaves' surface. Moreover, the absorbed FA is likely to be quickly metabolized and used for plant growth.

References

[1] Kim K.J. et al., 2018. *Phytoremediation of volatile organic compounds by indoor plants: a review.* Horticulture, Environment and Biotechnology 59, 143-157.

[2] Ravindra K. and Mor S., 2022. *Phytoremediation potential of indoor plants in reducing air pollutants*. Frontiers in Sustainable Cities 4, 1039710.

[3] Li P., Pemberton R., Zheng G., 2015. *Foliar trichome-aided formaldehyde uptake in the epiphytic Tillandsia Velutina and its response to formaldehyde pollution*. Chemosphere 119, 662-667.

POS18

INDOOR AIR QUALITY IN THE SCHOOLS: EVIDENCE TOWARDS AND NEW PERSPECTIVES

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1. Introduction

Indoor air quality in schools is an issue of growing concern given the large number of hours that students and school staff spend inside these buildings. The most fragile individuals are certainly the children, whose organs are most vulnerable to airborne pollutants because of their higher respiratory rate and their still-developing respiratory and immune systems [1]. In fact, prolonged exposure to indoor environments with poor air quality can lead to serious side effects such as asthma, allergic disorders, and other respiratory diseases. In addition, prolonged exposures to high concentrations of Volatile Organic Compounds (VOCs) could also have a direct impact on pupils' school performance as well as impair their proper development [2]

2. Results and Discussion

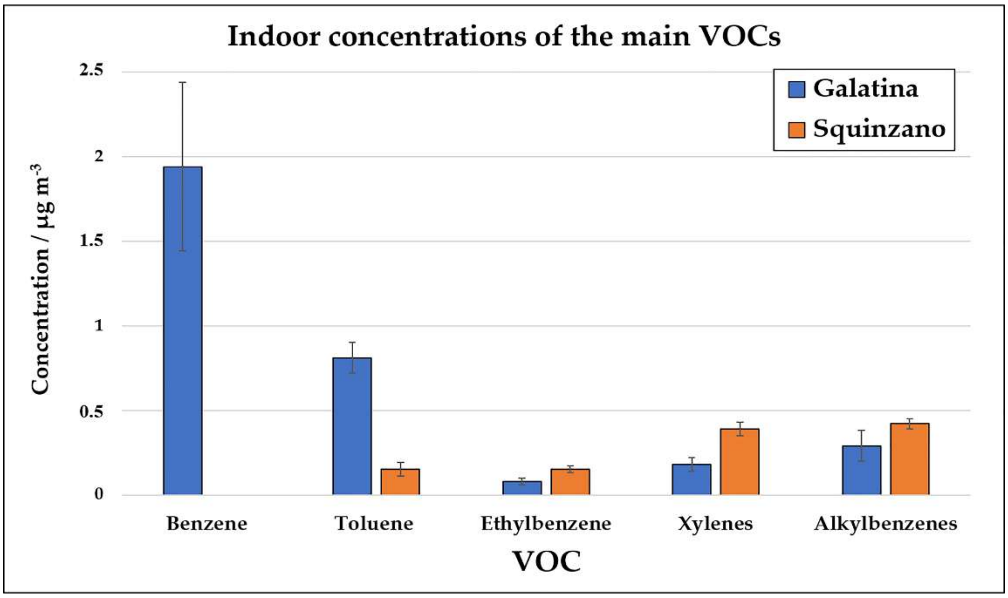
In this study a comparison of the indoor and outdoor concentrations of VOCs in two different schools of the Puglia region (Southern Italy) was performed. Volatile organic compounds were sampled using passive diffusive samplers (Radiello®, Fondazione Salvatore Maugeri-IRCCS, Padova, Italy). Diffusive samplers were placed in four different locations within the school: the women's bathroom (B1), the men's bathroom (B2), a classroom (4B), and outdoors (O). Campaign in Galatina was carried out from February 1st to March 12th, 2019 as reported in the work of Ielpo et al. 2021, while the monitoring campaign in Squinzano was performed from May 13th 2019 to June 3d 2019 continuously.

Moreover real-time monitoring of TVOC concentrations was carried out. Overall, the results highlighted a good air quality in both schools in terms of VOCs, with concentrations below the levels considered harmful for human health. Differences within the school environments monitored were due to specific activities, such as cigarette smoking in the classrooms of Galatina (Ielpo et al. 2021) or solvent use in the bathrooms of Squinzano (Ielpo et al. 2023, submitted). Instead, differences between the two schools were due to geographical location and monitoring period. The figure shows the average concentrations registered in the classrooms of the two sites. The main difference is represented by the levels of benzene: in Squinzano it was detected above the LOD in only two out of the twenty-seven samples analyzed (for this reason no average value are shown in the figure), whereas in Galatina this was the main VOC (1.94 mg m-3). Toluene showed a similar trend: once again the average indoor concentrations were lower in Squinzano with respect to Galatina. Regarding other species, no significant differences were observed between the two sites and in both cases the average concentrations were always below 0.5 µg m-3. About alkylbenzenes, 1,2,4-trimethylbenzene was the main compound in both schools, which accounted for more than 50% of the total amount.

The relevance of this work stems from the fact that, the topic of VOCs and generally indoor air quality in school environments has not been exhaustively studied and there is a lack of monitoring data in many areas, especially in southern Italy, because of the large number of types of indoor pollutants. Hopefully, this work will pave the way towards a more complete and in-depth analysis of the air quality within schools, aimed at the safeguard of the children’s health. In the frame of this approach, it will be briefly explained the objectives of the PNC MISSION (Monitoraggio abbattImento riSchi Sanitari InquinamentO iNdoor) project funded by the Italian Ministry of Health in the frame of Italian National Recovery and Resilience Plan, in which some of the authors of this work take part.

3. Conclusions

The information collected in this study may also be useful in mapping the air quality conditions (in terms of VOCs) in Italian schools, considering that literature data pointed out high concentration variability among schools of the same country. For this reason, some of the main objectives of the Mission PNC project are in fact: review of scientific literature on health effects associated with short- and long-term indoor pollution in school settings; implementation of an indoor monitoring program in a sample of schools and implementation of a health monitoring program and creation of a platform for data collection.



Average concentrations of the main VOCs in the two classrooms of schools in Squinzano and Galatina

References

Rivas, I.; Viana, M.; Moreno, T.; Pandolfi, M.; Amato, F.; Reche, C.; Bouso, L.; Àlvarez-Pedrerol, M.; Alastuey, A.; Sunyer, J.; et al. Child Exposure to Indoor and Outdoor Air Pollutants in Schools in Barcelona, Spain. *Environ Int* **2014**, *69*, 200–212

Al-Awadi, L. Assessment of Indoor Levels of Volatile Organic Compounds and Carbon Dioxide in Schools in Kuwait. *J Air Waste Manage Assoc* **2018**, *68*, 54–72.

Ielpo, P.; Mangia, C.; de Gennaro, G.; Gilio, A. di; Palmisani, J.; Dinoi, A.; Bergomi, A.; Comite, V.; Fermo, P. Air Quality Assessment of a School in an Industrialized Area of Southern Italy. *Applied Sciences (Switzerland)* **2021**, *11*.

POS19

PY-GC-MS ANALYSIS AND QUANTIFICATION OF MICROPLASTICS IN SEWAGE SLUDGE

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1. Introduction

Microplastics (MP) are emerging pollutants of main interest due to their widespread occurrence and the risks they may cause to the environment and to human health [1]. MPs generated from human activities are mainly collected in domestic wastewaters, including both primary (e.g., from personal care products) and secondary (e.g., from washing machines) MPs. Although the removal rate of wastewater treatment plants (WWTPs) is rather effective, MPs can be retained in sewage sludge (SS) during water depuration processes. SS can be employed in agriculture as soil conditioners, becoming an indirect contamination source of MPs in soils [2]. The analytical issue behind their quantification is quite complex and standardised analytical methods for MPs quantification are still missing. The thermoanalytical technique of pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) can provide qualitative and quantitative information about several polymers within MPs.

The study aimed at the optimization and application of Py-GC-MS technique for the qualitative and quantitative analysis of MPs in SS from municipal WWTP. For this purpose, two quantitation methods were compared: internal standardisation and standard addition.

2. Results and Discussion

SS from a WWTP was oven-dried, ground and sieved to 0.3 mm. The homogenized samples were oxidized with Fenton's to reduce the organic load and filtered on quartz fiber filters (0.3 µm). This pre-treatment allowed the determination of the micrometric portion of MPs. The filters were folded and inserted directly into the pyrolysis cups, where the internal standard (tri-*tert*-butylbenzene, TTB) and reagent (tetramethylammonium hydroxide, TMAH) were also added prior to the Py-GC-MS analysis. In order to assure the quality of the provided results, quartz fiber filters were pre-treated in muffle at 600 °C for 4 h and reagent and solvent were pre-filtered before the oxidation procedure. Moreover, procedural blanks were performed to take into account the possible contamination. Polymers were quantified by calibration curves with internal standard. Another quantification was performed for each polymer using the method of standard additions, for the validation of the MP analysis method.

In the present study, the considered polymers were polypropylene, polyethylene, polyammide-6, polyethylene terephthalate, polycarbonate and polystyrene (PP, PE, PA-6, PET, PC and PS, respectively). During pyrolysis, polymers fragmentation generates new characteristic molecules. Among these, polymer-specific markers were selected to be used for polymer detection and quantification (Figure 1).

The standard addition method produced results in agreement with those obtained by internal standard calibrations, therefore we can consider the method validated for the quantification of MPs in SSs.

Results obtained after data processing indicated PE as one of the most abundant polymers in the analyzed sludge samples, with concentrations greater than 1300 $\mu g_p/g_{dry\ sludge}$. Appreciable concentrations of PET were also found, amounting to about 400 $\mu g_p/g_{dry\ sludge}$. These data can be considered plausible as PE is the polymer most produced on a global scale and used mainly in packaging, while PET is the main component of synthetic fabrics. Conversely, PS concentrations did not exceed 110 $\mu g_p/g_{dry\ sludge}$ and PA-6 was not detected.

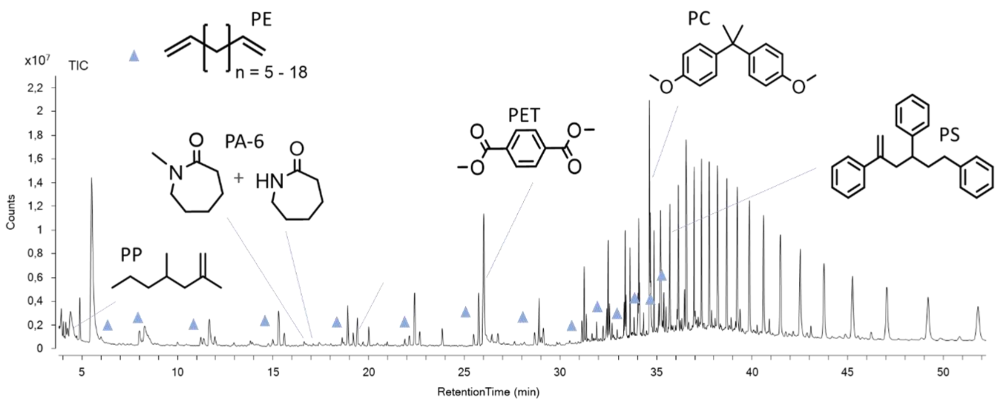

Figure 1. Example of pyrogram of a standard mix of polymers and their specific markers.

3. Conclusions

The study provided an example of method validation and application for the quantification of MPs in a complex matrix using the thermoanalytical technique of Py-GC-MS. Based on the comparison of the results obtained by the standard addition method with those obtained by internal standard calibrations, it can be concluded that the presence of a complex matrix did not affect the capability of the proposed method to quantify PP, PE, PA-6, PET, PC, PS within MPs.

Despite the analytical quantification of polymers within MPs in complex matrices is still challenging, this method was validated and then applied for the study of MPs loading in municipal SS.

References

[1] Hao Du, Jun Wang – Characterization and environmental impacts of microplastics, 2021

[2] Theresa Schell, Rachel Hurley, Nina T. Buenaventura, Pedro V. Mauri, Luca Nizzetto, Andreu Rico, Marco Vighi – Fate of microplastics in agricultural soils amended with sewage sludge: Is surface water runoff a relevant environmental pathway?, 2022

POS20

A MULTIPARAMETRIC STUDY FOR THE MONITORING OF CONTAMINANTS IN MILK

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1. Introduction

Environmental pollution caused by anthropogenic activity is the subject of constant study and monitoring. Various classes of pollutants are known nowadays, such as persistent bioaccumulative toxic substances (PBTs), potentially toxic elements (PTEs), and antimicrobials. PBTs and PTEs are classified as "endocrine disruptors", i.e., they own the capacity of interfering with all endocrine systems (reproductive system, immune system, ecc.) by mimicking or blocking the activity of hormones. Thanks to their abilities, these contaminants cause both acute and chronic toxicity and can bioaccumulate through the food chain, posing a risk also for human consumers. Indeed, several studies have demonstrated that the main route of exposure to these compounds for humans is the oral route, and in particular through foods, namely meat and milk.

2. Results and Discussion

The study of rural ecosystems in terms of One Health, i.e., under a holistic view, which also consider the presence of human consumer of the product of animal origin, assumes thus a particular importance. This project aims at the determination of the contamination levels in terms of heavy metals and mycotoxins contamination in cow's milk samples from different Italian dairy farms. Metals analysis was performed by inductively coupled plasma-mass spectrometry after mild digestion, while mycotoxins determination was conducted by high performance liquid chromatography coupled to mass spectrometry in Multiple Reaction Monitoring, taking advantage by sensitivity and specificity of this tandem mass spectrometry technique.

3. Conclusions

The positive impacts expected from the research are in line with EU Green Deal policies; in addition to providing information on the state of environmental contamination through the study of the presence of different class of contaminants in farmed animals, and their products, the consumer risk characterization will be made. Moreover sensitive, specific, and robust methods for the determination of contaminants will be developed and validated, and new data for use in epidemiological studies will be available.

Reference

1. Thompson LA, Darwish WS. Environmental Chemical Contaminants in Food: Review of a Global Problem. J Toxicol. 2019 Jan 1;2019:2345283. doi: 10.1155/2019/2345283. PMID: 30693025; PMCID: PMC6332928
2. Nunzio AD, Giarra A, Toscanesi M, Amoresano A, Piscopo M, Ceretti E, Zani C, Lorenzetti S, Trifuoggi M, Montano L. Comparison between Macro and Trace Element Concentrations in Human Semen and Blood Serum in Highly Polluted Areas in Italy. Int J Environ Res Public Health. 2022 Sep 15;19(18):11635. doi: 10.3390/ijerph191811635. PMID: 36141930; PMCID: PMC9517217.
3. Leite, Marta, Andreia Freitas, Jorge Barbosa, and Fernando Ramos. 2023. "Mycotoxins in Raw Bovine Milk: UHPLC-QTrap-MS/MS Method as a Biosafety Control Tool" *Toxins* 15, no. 3: 173. https://doi.org/10.3390/toxins15030173

POS21

MORPHOLOGICAL AND CHEMICAL CHARACTERIZATION AND NUMERICAL SIZE DISTRIBUTION OF PARTICULATE MATTER IN THREE AREAS OF LECCE

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1. Introduction

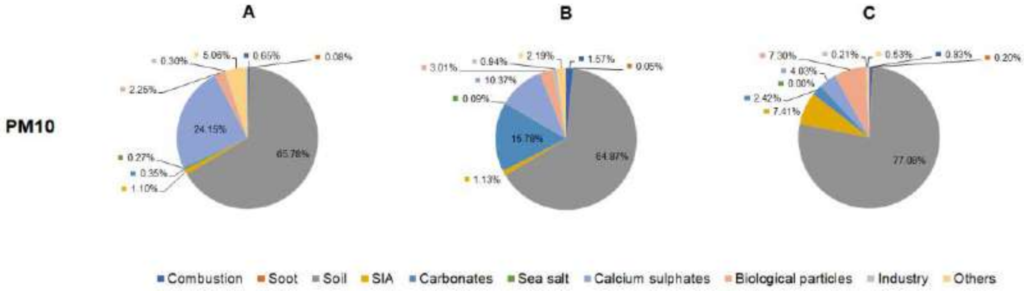
Air pollution is one of the most discussed global problems with serious effects on the health of the population of all ages living in both urban and rural areas. Children are especially affected by the risks caused by atmospheric pollutants as they breathe faster than adults by inhaling a greater quantity of air and consequently more pollutants. Moreover, they live closer to the ground where some pollutants reach higher concentrations and spend more time outside where they play sports (WHO, 2018). For these reasons, in three areas of Lecce (city in the Apulia region, Italy) where three primary schools are located, the air quality was assessed. The conventional source apportionment methods are based on bulk chemical analysis and require the specification of emission sources and information on the elemental composition of particles from each of the emission sources. In this work, we applied individual particle analysis to sources apportionment of particulate matter using scanning electron microscopy coupled with energy dispersive analysis (SEM-EDS). In this way, each aerosol particle is supposed to have unique information about its emission source.

2. Results and Discussion

Single particle analysis was performed on PM10 samples collected on polycarbonate membranes exposed to air for 6h, using a low volume sampler operating at a flow rate of 2.3 m^{3}h^{-1}. The samples collected on 4 June 2015 in the garden of school A, on 29 May in school B and on 12 May in school C were analyzed with the SEM. The wind blows mainly from the N at the A and B sites, and from N-NE sector at the C site with an average speed, in the sampling hours from 10:30 am to 4:30 pm, of 2.7 ms^{-1} and of 3 ms^{-1}, respectively. Based on the chemical composition and morphology of the particles, it was possible to identify the following groups: aluminosilicates, silicates, aluminosilicates with sulphur, calcium sulphates, silicate-sulphate-mixed particles, phosphate-sulphate mixed particles, iron oxides, metal oxides, iron mixtures, irregular silicates, aluminosilicates with sulphur, irregular Fe particles and secondary particles (Genga et al. 2018). At the three sites, the number size distributions of both irregularly shaped aluminosilicates and silicates, aluminosilicates with sulphur, carbonates, carbonates-silicates, secondary particles, aged sea salt, fluorides, soot, biological particles and remaining carbon-rich particles. All particles, which could not be classified into one of the previous groups because they were formed by clusters of different particles, were included in the group labeled "others". At the A and B sites the relative numerical abundance of particles as a function of their size has a similar trend with a higher percentage of particles in the PM1 fraction; in the C site about 50% of the analyzed particles has an equivalent spherical diameter between 1 and 2.5 μm. At the A site calcium sulphates are the largest group of particles; at the C site there are more irregular aluminosilicates, silicate sulphate mixed particles, phosphate - sulphate mixed particles silicates, irregular Fe particles and secondary particles. The number size distributions of irregular aluminosilicates, irregular silicates, aluminosilicates with sulphur, calcium sulphates and irregular carbonaceous particles are similar with a peak in the range 0.6 -0.8 μm. The numerical concentration of the phosphate-sulphate mixed particles is negligible in the A and B sites, while in the C site it follows a bimodal trend with a small peak around 1.5 μm and another more pronounced in the coarse fraction around 3.5 μm. To distinguish the anthropogenic sources from the natural ones, the source apportionment was performed for each measurement site (Siciliano et al. 2021). The following sources have been identified: combustion, industry, soil, SIA (Secondary Inorganic Aerosol), sea salt, soot, carbonates, calcium sulphates, biological particles and others. As regards the PM1 fraction, in the B and C sites, the soil contributes to the source apportionment with about 50%, followed by calcium sulphates, combustion, carbonates and SIA. In the A site the calcium sulphates have a greater effect with more than 60% followed by the soil and combustion sources. In the PM2.5-1 and PM10-2.5 fractions, an increase in soil and a decrease in calcium sulphates were observed for each site. In the three sites, the greatest contribution to PM10 is provided by soil with more than 65% followed by calcium sulphates for site A, by carbonates and calcium sulphates for site B and by SIA and biological particles for site C.

3. Conclusions

Based on the morphological and chemical properties of the particles analyzed with the scanning electron microscope, the source apportionment identified ten sources for each site. In the three sites the major contribution to PM10 is given by the soil source and this is probably due to the characteristics of the sites located in peripheral areas of the city. Low levels of anthropogenic sources, such as soot, industry, and combustion, have an impact on the three sites. This last result is in agreement with the study conducted by De Donno et al. (2016) in which it is shown that the biological effects on school-age children living in Lecce is mainly due to lifestyle and cigarette smoke inhaled at home, while the effect of air pollutant concentrations is not evicted.



Average contribution of the sources to PM10 at the measurement sites: A, B and C

References

De Donno, A., et al., 2016. Int. J. Sus. Dev. Plann. 11 (4), 500–510.

Genga, A., Siciliano, T., Siciliano, M., Aiello, D., Tortorella, C., 2018. Environ. Monit. Assess. 190, 456–469.

Siciliano, T., Giua, R., Siciliano, M., Di Giulio, S., Genga, A., 2021. Atmos. Res. 251, 105416 1–14.

WHO, 2018. Air pollution and child health: prescribing clean air. Summary. Geneva: World Health Organization; 2018 (WHO/CED/PHE/18.01). Licence: CC BY-NC-SA 3.0 IGO.

POS22

BACTERIAL GROWTH ON LOW DENSITY POLYETHYLENE (LDPE) AND MINERAL OIL

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Introduction

All organics are potential carbon and/or energy sources for microorganisms. Most can be partially or completely degraded by naturally occurring microorganisms [1]. Complete biodegradation is referred to as mineralization. The degree and speed of degradation varies depending on a variety of factors. Bioremediationis the use of biological processes for the removal or detoxification of pollutants in polluted environments [2].Recent studies on plastic degradation have provided compelling evidence regarding the potential of microorganisms to biodegrade both plastics and microplastics (MPs) found in polluted environments. There is a possibility that strains capable of degrading LDPE may also have the potential to degrade mineral oil (MO) due to their shared linear hydrocarbon nature and the potential bioavailability of oil. We are currently studying 40 potentially LDPE degrading strains. The ability to grow and metabolise on MO or LDPE were investigated using viable counts, ATP measurements, and CO_2 measurements. Furthermore, this offers the opportunity to better understand the role of bacterial metabolism in the breakdown of different classes of MPs.

Results and Discussion

The initial experimental design demonstrated that the bacteria feeding on LDPE continued to grow and effectively degrade the material even after 12 weeks. Furthermore, the new experimentation on MO shed light on a particular bacterial strain that exhibited exceptionally vigorous metabolic activity. This finding strongly suggested that this strain exclusively relied on MO as its sole carbon source, continuously utilising it for sustenance.This aforementioned evidence emerged both from the bacterial cultures in petri dishes carried out at regular intervals to constantly monitor growth or any variations and from the specific ATP test to confirm a regular degradative activity carried out by the microorganisms. Another test,conducted to evaluate the CO_2 production capacity, gave in most cases a positive result.

Conclusions

From a Bioremediation perspective, harnessing the potential of microorganisms as a tool to restore environments contaminated by emerging pollutants like MPs holds significant promise. Several studies, including the research conducted by [3], have already demonstrated the remarkable capability of certain bacterial species in degrading the carbon chain through the activation of specific enzymes. Our findings haveprovided valuable insights for the selection of bacterial species with the highest degradation capacity, Furtherinvestigation is warranted to delve deeper into their mechanisms and fully understand their potential in environmental remediation.

References

Duque, Estrella et al. “Providing octane degradation capability to Pseudomonas putida KT2440 through the horizontal acquisition of oct genes located on an integrative and conjugative element.” Environmental Microbiology Reports 14 (2022): 934 - 946
Bhandari, Sobika et al. Microbial Enzymes Used in Bioremediation. Journal of Chemistry 2021 (2021): 1-17 [3]Yoshida S, et al. A bacterium that degrades and assimilates poly(ethylene terephthalate). Science. 2016 11;351(6278)

PRIORITIZATION OF CONTAMINANTS OF EMERGING CONCERN FOR A SCREENING STUDY IN THE VENICE LAGOON – A METHODOLOGICAL APPROACH

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1. Introduction

Understanding the occurrence and behaviour of contaminants of emerging concern (CECs) in transitional environments is essential to complement the knowledge of "traditional" and regulated pollutants and achieve a thorough evaluation of the environmental quality status. Since the risk posed by CECs in the Venice lagoon (Italy) has been poorly investigated, in the framework of the Venezia2021 research programme a screening study was conducted to provide some preliminary knowledge and propose chemical candidates for a more comprehensive monitoring plan of the lagoon.

The inclusion of new chemical substances in local monitoring programmes asks for a robust prioritization approach (Carvalho et al., 2015), suitable to integrate diverse typologies of data and effective in supporting environmental management decisions in data-poor contexts. For this purpose, a risk-based methodology was developed to identify emerging contaminants that either are expected to pose a significant ecological risk or need to be further investigated due to the high uncertainty in the available data.

2. Results and Discussion

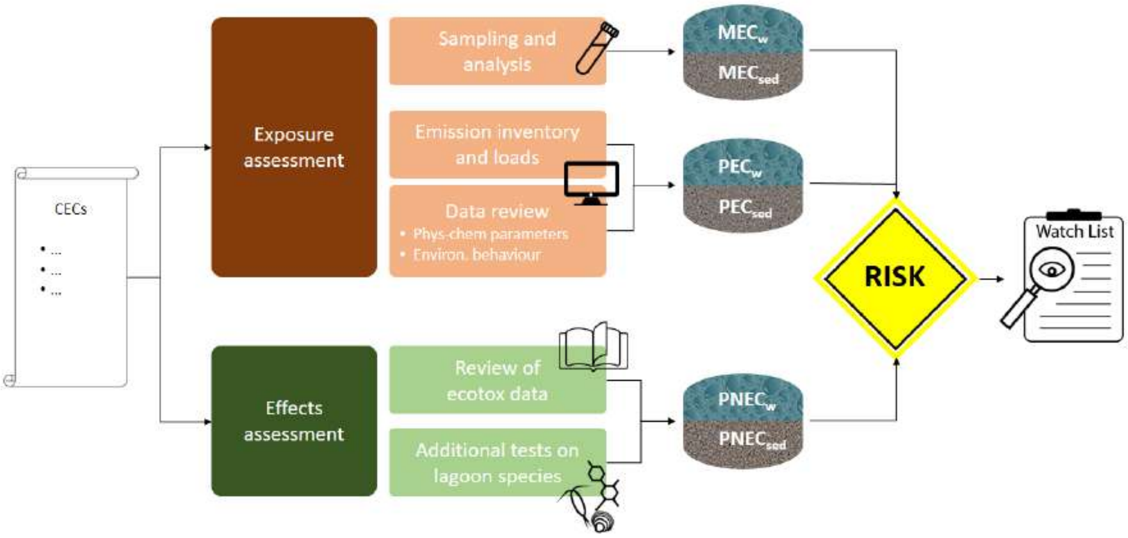
The proposed methodology is based on the integration of i) experimental exposure data from a field campaign in the Venice lagoon, addressing both water and sediment contamination (Measured Environmental Concentrations, MECs); ii) modelled exposure data simulated through a multi-media fate model (Predicted Environmental Concentrations, PECs); iii) ecological effect thresholds (Predicted No Effect Concentrations, PNECs) derived from literature ecotoxicological data on marine species, complemented with the results of additional bioassays performed on lagoon species for a sub-set of contaminants (Picone et al., 2021, 2022).

Integration of exposure and effect information in this screening assessment is based on the Hazard Quotient (HQ) method, where exposure concentrations, being them MECs or PECs, are divided by an ecotoxicological benchmark concentration, i.e. PNEC. Risk is then deemed significant when the ratio exceeds the threshold value of 1.

With the aim of making the most of available exposure and effect data, a decision tree was built on a set of criteria to guide the assessment and prioritization of CECs, so that decisions could be made about the inclusion of considered chemicals into a "Watch List" for the Venice lagoon. The decisions behind inclusion or not into the Watch List are based on the HQ, which, in a protective way, was also calculated for the maximum measured concentration and the 95th percentile of the predicted exposure concentrations.

This decision tree was applied to a set of 29 CECs considered in the project, including plant protection products, pharmaceuticals, personal care products, and industrial chemicals. Results proved that the decision tree can differentiate chemicals that, based on the estimated risk, should be included in future monitoring plans from those contaminants with great data uncertainty requiring additional investigation efforts. Among those, EE2, Amoxicillin e Triallate should be flagged as they were never quantified in water samples, but their quantification limits exceeded the PNEC values. In this case, the recommendation concerns new ecotoxicity tests on marine and estuarine species or refinement of analytical methods to reach lower quantification levels in environmental matrices. Out of the 29 CECs, 14 chemicals made it into the Watch List for future water monitoring plans.

Similarly to water, the decision tree was applied to the sediment matrix. However, results should be cautiously handled. Given the scarcity, or even the complete lack, of data available from ecotoxicological tests, PNECs for sediment were calculated from the respective values for marine water. With the intent of limiting the uncertainty around the resulting Watch List for sediment, we advocate for further investigations on the effect of CECs to marine and estuarine species.



Conceptual framework for the definition of the CECs Watch List

3. Conclusions

The expected outcomes of a screening assessment include the identification of further assessment needs, recommendations to guide data collection in subsequent tiers as well as information to define the scope of a definitive assessment. In this context, the proposed approach proved effective to differentiate contaminants to be included in future monitoring plans from those requiring additional investigation efforts. The decision tree integrates experimental and modelling results, favouring the inclusion of all available information that can concur in a more thorough assessment.

Most importantly, the proposed approach is eligible for iterated applications in case new exposure and effect data will become available in the future and can be used to evaluate extended/different sets of contaminants.

References

Carvalho, R. N., Ceriani, L., Ippolito, A., & Lettieri, T. 2015. Development of the first watch list under the environmental quality standards directive. JRC Science Hub.

Picone M., Distefano G. G., Marchetto D., Russo M., Vecchiato M., Gambaro A., Barbante B., Volpi Ghirardini A. 2021. Fragrance materials (FMs) affect the larval development of the copepod *Acartia tonsa*: An emerging issue for marine ecosystems. Ecotoxicology and Environmental Safety, Volume 215

Picone M., Distefano G.G., Marchetto D., Russo M., Baccichet M., Zangrando R., Gambaro A., Volpi Ghirardini A. Inhibition of Larval Development of Marine Copepods *Acartia tonsa* by Neonicotinoids. Toxics. 2022; 10(4):158. https://doi.org/10.3390/toxics10040158

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MICROPLASTICS IN THE SEA, CARRIERS OF METALS IN THE FOOD CHAIN

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1. Introduction

Plastics are one of the major global environmental issues of the 21st century. The term microplastics (MP) refers to plastic debris with dimensions less than 5 mm. It has been highlighted that a wide range of commercially important fish species are often contaminated with microplastics, providing a route for human exposure to these particles and the chemicals they contain. These observations raise particular concerns about the potential effects on humans. In addition, contaminants carried by microplastics can be transported through the food chain to humans. The chemicals found in microplastics include those added during their manufacture (additives) and those present in water and adsorbed on the surface of microplastics, such as persistent organic pollutants, pharmaceuticals, pesticides or herbicides, or metals. Among the pollutants that microplastics can accumulate, metals such as chromium, copper, nickel, lead and zinc have been widely studied. In addition, some metals are often added as catalysts, pigments and stabilisers during the production of plastics.

2. Results and Discussion

Our research focuses on the characterisation of MP from several marine areas close to the Calabrian coast. Samples are collected by the Regional Agency for the Environment (ARPACAL) in the following areas: Cetraro (Cosenza), Vibo Marina (Vibo Valentia), Gioia Tauro (Reggio Calabria) on the Tyrrhenian coast; mouth of the river Crati (Cosenza), mouth of the river Corace (Catanzaro), mouth of the river Neto (Crotone) on the Ionian coast. For each area, MP samples were collected at three different distances from the coast (0.5; 1.5; 6 nautical miles). Each sample was subjected to several analyses. To characterise the quantity of plastic particles, their size, shape and colour, a visual analysis was carried out using the naked eye and a stereomicroscope. Infrared spectroscopy (FT-IR) analysis allowed the bulk composition of all fragments to be identified. Scanning electron microscopy coupled with EDS analysis (SEM-EDS) was used to observe the surfaces and make a semi-quantitative assessment. The results suggest that the most common colour of plastic debris is white with a fragment shape, while the most common polymer is represented by polyethylene. This is also due to the fact that sampling was carried out on the surface and the density of polyethylene, which floats easily on water, even when loaded with heavy additives such as metal oxides. In terms of metal content, iron, titanium and aluminium are the most common metals found in plastic fragments. Many other metals such as Mn, Cu, Pb and Ni were also detected.

3. Conclusions

It has carried out a preliminary characterisation of MP from several areas in the Calabria region. The analytical plan foresees a more accurate analysis of the metals in the plastics using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In addition, the release of metals from MP will be assessed using a fish digestion model.

References

Godoy V. et al. The potential of microplastics as carriers of metals (2019) Environmental Pollution, 255, art. no. 113363.

Chen H. et al. Investigation of Microplastics in Digestion System: Effect on Surface Microstructures and Probiotics (2022) Bulletin of Environmental Contamination and Toxicology, 109 (5), pp. 882 – 892.

Marrone A. et al. Microplastics in the center of mediterranean: Comparison of the two calabrian coasts and distribution from coastal areas to the open sea (2021) International Journal of Environmental Research and Public Health, 18 (20), art. no. 10712.

POS25

CHARACTERIZATION OF CO_2 AND CH_4 GAS HYDRATES: A RAMAN OBSERVATION OF CO_2 SEQUESTRATION VIA GAS HYDRATES

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1. Introduction

Gas hydrates (GHs) or clathrates, are crystalline structure where water cages host gas molecules. The cage is formed by water molecules keep together by hydrogen bond interaction, while host molecule is free to rotate inside the structure. GHs structure possesses some similarities to the ice structure of water since it is composed by 85% of water. Natural GHs (NGHs) represents an energy resource for CH_4 that is distributed evenly around the world and near the cost, making recovery action easier and less expensive. The most important and promising strategies to collect CH_4 are related to the CO_2 replacement that allows permanent storage of CO_2, as reducing greenhouse gas without additional energy[1].

In the contest of the PRIN Project "Methane recovery and carbon dioxide disposal in natural gas hydrate reservoirs", some marine sediment samples that contained NGHs, were chemically analyzed to obtain indications for the synthetic reproduction of GHs in laboratory.

Different CH_4, CO_2 and CO_2/CH_4 GHs, prepared with two different apparatus, were ex situ analyzed by using Raman-spectroscopy and morphological characterized by low-temperature SEM (LTSEM) measurements.

2. Results and Discussion

The chemical composition in seawater of marine sediments, as well as the physical properties and chemical composition of soils, influence the phase behavior of NGHs by disturbing the H-bond network in the water-rich phase before GH formation. The salts influence the formation of NGHs and their nucleation occurs preferentially in a region with low ions concentration; for these reasons, the investigation about the chemical composition of seawater containing NGHs is very important to obtain useful data for the comprehension of their formation mechanisms in the natural environment. To this purpose, water inside some marine sediment samples that contained natural GHs, sampled in the Antarctic Peninsula during the summer of 2003–2004 by Italian National Antarctic Research Program[2], were chemically analyzed (by ICP-MS and ionic chromatography) to obtain the indications for the synthetic reproduction of GHs. The obtained results show that 1 kg of water contained about 4.7% of salts; these results show an enrichment of ions with respect to the seawater because the sediments, sampled at different depths, can accumulate different quantities of salts during the formation.

The application of the replacement strategies in NGHs reservoirs, always leads to the formation of "mixed" hydrates, whose mechanical and chemical properties are different from those of pure CH_4 and CO_2 hydrates[3]. In this study, the process of the replacement of CH_4 with CO_2 molecules into hydrates was described at a molecular level by studying with Raman measurements different laboratory reproduced GHs; the obtained data permitted to evaluate properties and behavior of the different GHs through the study of fingerprint of host molecules and of water OHs bands.

Specifically, the results showed that the CO_2 hydrates showed a less ordered structure in the presence of sand but however, thanks to the interaction between water and silanol groups of sand particles, their stability was maintained with the variation of temperature, favoring the expansion of the cages that was highlighted by the Raman shifts of the CO_2 Fermi diad. The observation of the water OHs bands, interpreted by S_D indices[4] showed that these parameters correlated perfectly with the increase of temperature and also provided information about the characteristics of water inside GHs, showing that the least ordered water structure was present on CO_2GHs in the presence of sediments, while the most ordered one was that of (CH_4/CO_2)GHs.

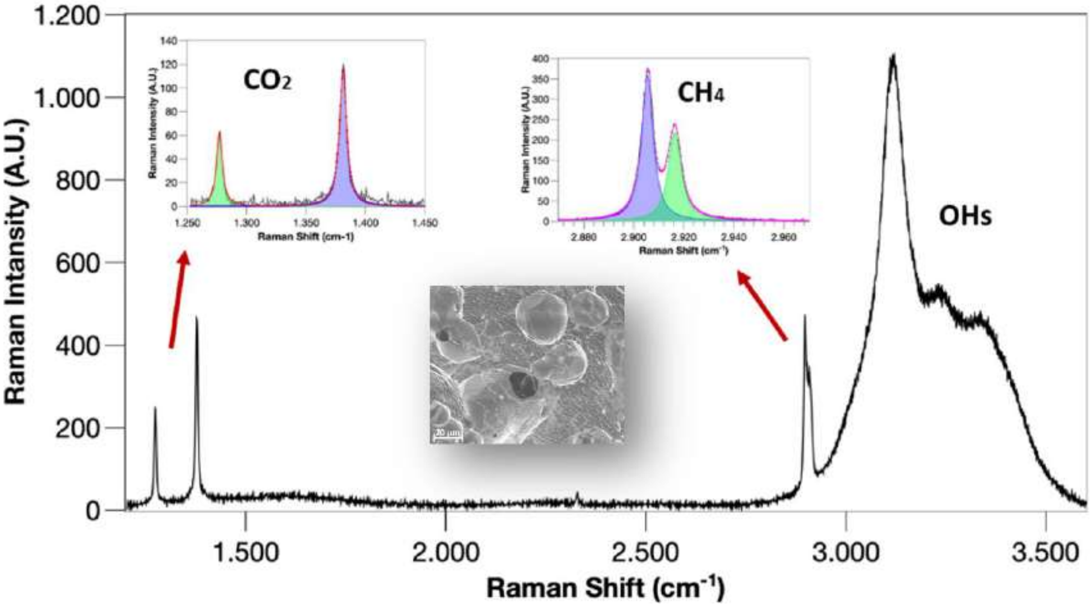
By these measurements, (CH_4/CO_2)GHs was proved to contain the most quantity of CO_2 confirming therefore a favorable replacement of CH_4; these results were in accordance with larger surface morphology observed in the

LTSEM images. The LTSEM analysis highlighted clear differences in the micro-shapes between the various GHs samples, displaying changes in the surface morphology related to specific hydrate composition.

3. Conclusions

The results related to the composition of seawater clarified the chemical conditions under which NGHs are formed and was used to reproduce synthetic GHs. The collected information by the Raman spectra of synthetic reproduced GHs improves the knowledge on the complex phase behavior, on the specific occupation of the cages of external host molecules and on the characteristics of the mixed gas hydrates.

The analysis of water OHs bands of the different GHs permitted to describe the relation between symmetric and asymmetric water OHs bands, but also provided information about the characteristics of water inside the different GHs, showing that the least ordered water structure was that of GHs containing sand, while the most ordered one was present on binary CO_2/CH_4 GHs.



Raman spectrum of (CH_4/CO_2)GHs and LTSEM image showing the surface morphology.

References

1. A. Hassanpouryouzband, E. Joonaki, M. V. Farahani, S. Takeya, C. Ruppel, J. Yang, N. J. English, J. M. Schicks, K. Edlmann, H. Mehrabian, Z. M. Aman, B. Tohidi *Chem. Soc. Rev.*, 49 (2020) 5225-5309.
2. U. Tinivella, F. Accaino, B. Della-Vedova, *Geo-Mar. Lett.* 28 (2008) 97–106.
3. R. Giovannetti, A. M. Gambelli, A. Rossi, B. Castellani, M. Minicucci, M. Zannotti, A. Nicolini, F. Rossi, *J. Mol. Liq.* 368 (2022) 120739.
4. I. Đuričković, M. Marchetti, R. Claverie, P. Bourson, J-M. Chassot, MD. Fontana *Appl. Spectrosc.* 64, 8 (2010) 853-857.

MICROPLASTICS: ADSORPTION OF HEAVY METALS ON POLYSTYRENE PARTICLES

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1. Introduction

Microplastics (MPs), usually defined as small plastic particles with a size of less than 5 mm (Thompson et al., 2004). They have received global attention due to their ubiquitous presence in the environment. MPs can be accumulated due to their inert nature, and they can absorb a large number of environmental pollutants (such as heavy metals) due to the high fugacity capacity and large specific surface area.

Heavy metals are soluble trace elements, and their concentration has increased with the advancement with human progress. Some heavy metals such as Pb, Cd, Ni, Zn are released by vehicle exhausts and roadside soils are commonly enriched with them. After a rain, these metals released into the environment by anthropic activities, can easily reach nearby watercourses. Subsequently they can be adsorbed by MPs present in the water and when plastic particles loaded with pollutants are ingested by organisms, they pose a potential threat to biota.

To date, only few studies have revealed the property of MPs to adsorb heavy metals in the environment, therefore the aim of our study was to evaluate the adsorption of some heavy metals on microplastics.

2. Results and Discussion

In our experimental work we used a solution of microplastics (5µm diameter polystyrene particles) with a concentration of 0.04 mg/L (sub-toxic conditions per ecotoxicological studies), and we put them in contact separately with Cu (0.5 mg/L), Pb (0.5 mg/L), Cd (0.25 mg/L) and with a mix containing the three metals simultaneously (Cu 0.5 mg/L, Pb 0.5 mg/L, Cd 0.25mg/L), in order to quantify the adsorption capacity and to compare the interaction with each metal here considered.

The MPs in solution were kept in contact with the heavy metals under stirring for one week. Every day we took a sample from each solution to evaluate by means of polarographic analysis (Metrohm - Model 797 VA – Computrace) the possible variation in the concentration of the metals present in the solution, in order to quantify the quantity of metal which was adsorbed by MPs.

Polarography is an electroanalytical technique that allows you to conduct qualitative-quantitative analyzes by measuring the current flowing in an electrochemical cell during electrolysis at controlled voltage. It is based on the recording of a redox potential signal, i.e., it records the presence of an element (a metal) based on the redox potential.

At time 0 the initial metal concentration was 0.5 mg/l for Pb, 0.5 mg/l for Cu and 0.25 mg/l for Cd. After 24 h the concentration value of Pb was 0.3 mg/l, while the Cu value was 0.4 mg/l. After 48h, 72h, 96h and 168h the concentration of the two metals analyzed did not undergo significant variations.

This demonstrates the absorption capacity of polystyrene (PS) for Pb and Cu but also shows that the saturation level of microplastics had already been reached after 24h. Instead for Cd, no significant concentration variations were found in any of the times considered, this shows a lower affinity of PS for this metal. The results found in our study are in agreement with the experimental works of Yuan et al. in 2020 and by Barus et al. in 2021 that in both studies they observed a greater adsorption on PS MPs of Pb and Cu and a lower one of Cd.

In the solution containing the MPs and the mix of the three metals with an initial concentration of 0.5 mg/l for Pb and Cu and 0.25 mg/l for Cd, we observed that after 24h the concentration of Pb and of Cu was 0.4 mg/L. After 48h, 72h, 96h and 168h the concentration of the two metals analyzed did not undergo significant variations. The simultaneous presence of several metal species in solution probably led to the adsorption of lower quantities of Pb and Cu on the MPs.

Again, we have not observed any significant changes in the cadmium concentration. This shows a lower affinity between polystyrene and Cd compared to Pb and Cu (results are reported in Figure 1).

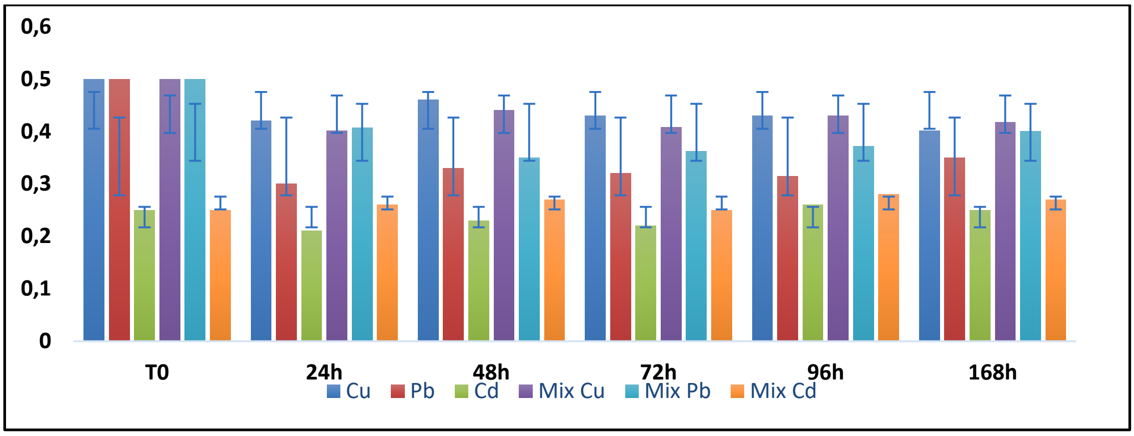

Figure 2 Adsorption by MPs of heavy metal (Cu, Pb, Cd and mix Cu, Pb and Cd)

3. Conclusions

Microplastics (MPs) have received much attention in recent years due to the ubiquitous distribution in the environment, the biological hazard to the organisms, and the non-degradable properties (Thompson et al., 2004). Due to its unique physicochemical properties, MPs are considered potent adsorbents for environmental pollutants and can influence their fate and toxicity in the environment. In this study, we observed the adsorption of three typical heavy metal ions (Pb, Cu and Cd) by MPs. The results of our study showed the achievement of a saturation level by MPs already in 24 hours and demonstrate a higher adsorption by PS MPs for Pb and Cu and a lower affinity by MPs for Cd. Finally, our findings highlight that PS particles can act as carriers for heavy metals in the aquatic system.

References

Abbasi, S., et al. (2020). PET-microplastics as a vector for heavy metals in a simulated plant rhizosphere zone. Sci. Environ. 744, 140984.
Barus B., et al. (2021). Heavy metal adsorption and release on Polystyrene Particles at various salinity. Frontiers in Marine Sc 8.
Thompson, R.C., et al. 2004. Lost at sea: where is all the plastic? Science, 838.
Yuan W.,et al. (2020). Toxicological effects of microplastics and heavy metals on the Daphnia magna. Sci of Env. Vol 746, 141254.

POS27

SPECTROSCOPIC INVESTIGATIONS OF PIGMENTS ON ROCK ART OF THE MOUNT TYNDALL 2, SOUTH AFRICA

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1. Introduction

In this work, preliminary investigations were carried out on South African rock paintings, from Mount Tyndall 2, Eastern Cape Drakensberg. Mount Tyndall 2 is a rock shelter measuring approximately 25 m (L) x 3 m (H) x 6 m (D). Paintings are found throughout the shelter, although most are concentrated in two panels towards its center [1]. Paintings are deeply damaged: parts of the rock face have collapsed and many fragments are detached.

A total of 10 collapsed painted fragments were studied (Figure 1). The analyses are performed on dark red, light red, white and black areas by means of Raman and FTIR spectroscopies. In addition to the spectroscopic investigations, SEM-EDS and GC-MS measurements were carried out.

2. Results and Discussion

Raman measurements confirm the use of iron oxides as pigments: in all red samples, as expected, the main chromophore detected is haematite (Fe_2O_3), recognizable by the characteristic peaks at 220, 289, 404 and 609 cm^{-1}. Quartz (464 cm^{-1}), albite (479, 507 cm^{-1}) anatase (144, 396, 515, 638 cm^{-1}), weddellite (907 cm^{-1}), whewellite (1460 and 1485 cm^{-1}) and gypsum (1008 cm^{-1}) have also been detected [2]. Gypsum, found in the white and in the colored areas, suggests that it was used as pigment, also mixed with haematite. Gypsum was also detected in white surface areas along with oxalates. It cannot be excluded that it is due to a degradation process. Quartz, feldspar and titanium dioxide are from the rock substrate, having also been found in the back of the samples.

The black areas are composed of amorphous carbon, as clearly revealed by Raman spectroscopy by the typical features at about 1350 and 1590 cm^{-1}. The absence of a peak at about 960 cm^{-1}, due to phosphate group, even if difficult to observe, does not allow to attribute the black colour to bone black or ivory black. The black pigment is more likely to be lampblack, as already found in rock paintings of the same area [3].

The surface of the samples is rough and irregular. Black crusts are extensively found on the surface of the samples and on the coloured layers, both in red and white areas. They are composed of gypsum and calcium oxalate. Ca-oxalates (whewellite and weddellite) are mainly of biogenic origin (metabolic activity of lichens, fungi or bacteria). In addition, oxalates could be formed by the degradation and alteration of organic materials.

Rock fragments RP 15, RP 20 and RP 50 were analyzed by means of GC-MS after gently scrubbing through cleaning swabs: long chain saturated fatty acids from C12 to C18 are detected. The lipidic fraction could be due to animal fat and/or wax, probably used as binders for the pigment.

3. Conclusions

Rock paintings fragments from South African cave paintings, from Mount Tyndall 2, Eastern Cape Drakensberg have been investigated by different techniques.

By Raman spectroscopy, the pigments found are mainly haematite on the red areas and gypsum on the white parts. The black areas are probably based on lampblack.

The surface of the samples shows black crusts composed of gypsum and oxalate, as evidenced by reflectance FTIR spectroscopy. GC-MS investigation revealed the presence of long-chain fatty acids (C12-C18).

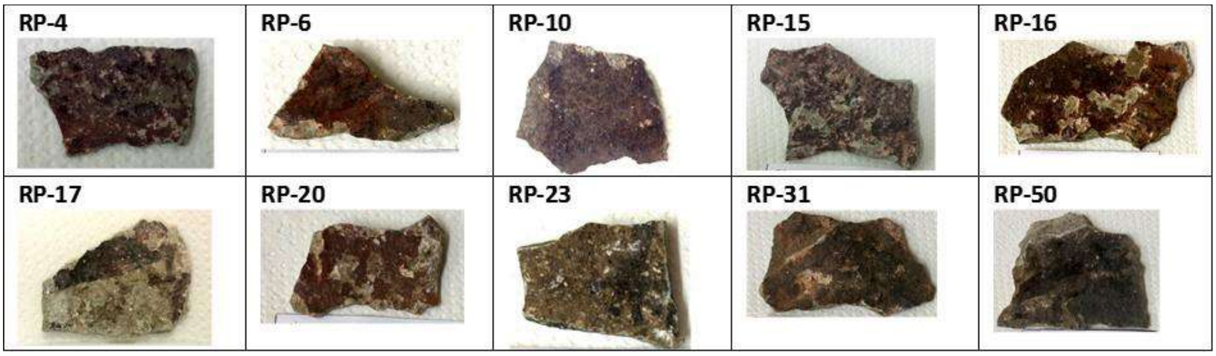

Figure 1 – The rock fragments analysed. Sample sizes are about 2 cm x 1.5 cm

References

[1] Pearce, D. G. (2010). Conservation and management of collapsing rock paintings: three sites in Maclear District, Eastern Cape Province, South Africa. South African Archaeological Bulletin, 65(191), 96-103.

[2] Rousaki, A., Vargas, E., Vázquez, C., Aldazábal, V., Bellelli, C., Calatayud, M. C., ... & Vandenabeele, P. (2018). On-field Raman spectroscopy of Patagonian prehistoric rock art: Pigments, alteration products and substrata. TrAC Trends in Analytical Chemistry, 105, 338-351.

[3] Bonneau, A., Pearce, D. G., & Pollard, A. M. (2012). A multi-technique characterization and provenance study of the pigments used in San rock art, South Africa. Journal of Archaeological Science, 39(2), 287-294.

Poster Sezione
Beni Culturali

POS28

FORMULATION OF SYNTHETIC ATMOSPHERIC PARTICULATES AND DEVELOPMENT OF A DEPOSITION TECHNIQUE FOR CORROSION STUDIES

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1. Introduction

Particulate matter (PM) is considered one of the main air pollutants and a danger for human health, ecosystem, and materials too. In particular, PM can affect cultural heritage by processes of soiling and physical-chemical damage that deserve further investigations[1,2]. This topic is challenging because of the high degree of variability in PM composition and size, which depend on the environmental conditions of the site. Tests in laboratory-controlled conditions can contribute to overcome this difficulty by investigating the impact of different PM amounts and compositions on material decay, also in relation with different climate scenarios, as well as to assess the efficiency of new protective treatments with respect to this aggressive factor. Therefore, the aim of this work were (i) to formulate a representative synthetic PM and (ii) to develop a replicable methodology for accelerated dry deposition of synthetic PM on specimens. A quaternary bronze (Cu-5Sn-5Zn-5Pb) was chosen as a reference substrate for the development and validation of the methodology.

2. Results and Discussion

First, a representative formulation of PM_{10}, based on PM compositions available in literature for urban and non-urban sites around the world, was defined. In this phase of the project, inorganic soluble and insoluble fractions, as well as elemental carbon, were considered for that formulation. Each compound was ground to a particle size consistent with its presence in fine or coarse PM_{10} fraction. Particle size control was conducted by acquiring and processing multiple images for each compound at different grinding times until the optimal size was reached. Afterward, the resulting compounds were mixed according to the previously defined proportions. The influence of each fraction in the formulation, deposition and ageing steps was evaluated by preparing and depositing three different mixtures: the first containing only the soluble inorganic fraction (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, NH_4^+), the second containing both the soluble and insoluble (Al_2O_3, SiO_2) inorganic fractions and the third including also elemental carbon (carbon black). These mixes were prepared by keeping constant the amount of soluble component to be deposited, as this fraction is considered the most relevant in corrosion phenomena. For this reason, the amount of mix to be deposited has been increased appropriately whenever a more complex mix was to be deposited. Subsequently, the dry deposition was simulated by blowing the synthetic PM on the specimens with the aid of an airbrush, after using an organic solvent to promote the powder adhesion on the bronze surface. This technique has been standardized and the sample-airbrush distance has been optimized to obtain reproducible and homogeneous depositions. The deposition process was validated by ion chromatography analysis to verify that the ionic ratio of the powder deposited on the specimens matched with the one of the starting mixtures. The results obtained for each mixture deposited were consistent. Finally, to test that the mixtures used could promote the evolution of corrosion products compatible with those found on real outdoor bronzes, the specimens were submitted to accelerated ageing for three weeks in a climatic chamber by setting up a cycle simulating day-night conditions with environmental parameters representative of winter and summer days. The morphological and chemical evolution of the surface was followed mainly by SEM-EDS and Raman analyses performed after each week of ageing. Results obtained on the different replicates were consistent with each other (figure 1). SEM-EDS analyses revealed an increase in the area affected by corrosion with the ageing time and, at the end of the aging, all specimens showed sulfate and chloride corrosion products that, according with the literature[3], tend to form after months or years on bronzes exposed outdoor. Moreover, the presence of the water insoluble fractions favored both the deposition phase and the development of corrosion products.

3. Conclusions

The mix containing all the considered PM components (soluble and insoluble inorganic fractions and elemental carbon) provided the better results in terms of deposition efficiency and homogeneity, as well as in promoting the development of corrosion products representative of long-term outdoor bronze corrosion (e.g. brochantite). In conclusion, a replicable methodology to create and deposit synthetic PM mixtures was developed and validated on bronze substrates, paving the way for the introduction of PM in artificial ageing protocols.

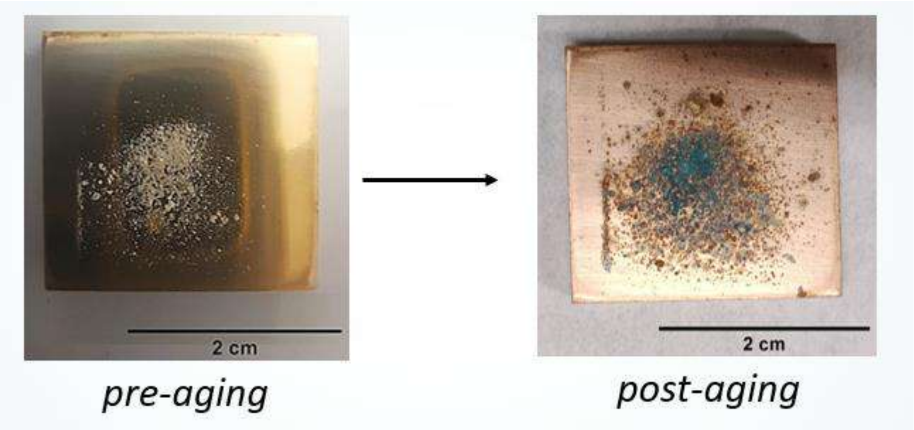

Figure 1. Sample evolution during the aging

References

[1] Vidović, K. et al. (2022), Impact of air pollution on outdoor cultural heritage objects and decoding the role of particulate matter: a critical review, Environmental Science and Pollution Research, 29, p. 46405–46437.

[2] Bernardi, E. et al. (2020), Influence of inorganic anions from atmospheric depositions on weathering steel corrosion and metal release. Construction and Building Materials, 236, pp. 1-12

[3] Kratschmer, A. et al. (2002), The evolution of outdoor copper patina, Corrosion Science, 44, p. 425-450.

POS29

CHEMICAL CHARACTERIZATION OF A FUNERAL EQUIPMENT FROM A HELLENISTIC YOUNG WOMAN TOMB FOUND IN BATTIPAGLIA

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1. Introduction

The study of ancient ceramics includes the characterization of chemical and mineralogical composition to reconstruct their life cycle from production to use. A complete investigation of these manufacts involves the analysis of the ceramic matrix and their content to identify eventual residues left (Papadopoulou et al., 2006). These data can be obtained via an interdisciplinary approach based on archaeological classification coupled to experimental techniques (Colomban, 2004). In the present work, six samples from a young woman tomb of the Hellenistic age were investigated to find out their possible use during the ceremonial burial. They are part of the funeral equipment stored at the Archaeological Museum of Eboli and Middle Sele Valley. The samples were collected under the supervision of Director Dr Scarano and listed as follows: *i) bombylios* T2.2; *ii)* two *skyphos* T2.5 and T2.6; *iii)* two jugs T2.1B and T2.7; *iv)* a sample of woody appearance (T2.1A) found in T2.1 container (Figure 1). To achieve these results a multimethodological approach combining optical microscopy, Raman micro-spectroscopy and chromatographic techniques coupled with mass spectrometry was performed.

2. Results and Discussion

The samples were taken from the bottom of the ceramic container, originally found nearby the human remains of the young woman. The approach adopted combines optical microscopy, spectroscopies and chromatographic techniques coupled with mass spectrometry. Raman micro-spectroscopy is a non-destructive technique and allowed to obtain results on the inorganic components of the ceramic matrix. Raman spectra clearly identified hematite, used as red pigment in the *skyphos* T2.5 and T2.6 content, and present in the ceramic matrix to obtain the characteristic red color. Also, a black pigment was identified as amorphous carbon in samples T2.5 and T2.6. In T2.2 sample, small hexagonal prismatic crystals of organic nature were assigned to an indigo-like compound used as blue pigment. Moreover, Raman spectra of T2.6 and T2.7 show peaks attributable to Sn-based compounds (confirmed by SEM-EDS), probably a yellowish pigment used to obtain an orange shade. The organic components present in the samples were analyzed using chromatographic techniques coupled to mass spectrometry. First, a multistep extraction protocol that uses different solvents was applied to separate sugars, lipids, and proteins. Each molecular fraction extracted was then treated differently: the lipid and sugar fractions were derivatized to be analyzed by GC-MS, while proteins were reduced, alkylated, digested with trypsin, and then analyzed by LC-MS/MS. The GC-MS analysis on samples T2.5 and T2.6 showed similar results. In the sugar fraction, different monosaccharides were identified with a preponderance of two hexoses: glucose and galactose. The analysis of the lipid fraction allowed the identification of saturated fatty acids, with hexadecanoic (palmitic) and octadecanoic (stearic) acids as the most prominent. Based on the composition found in samples T2.5 and T2.6, it was hypothesized the presence of milk since glucose and galactose are components of lactose, and the composition of fatty acids is compatible with that of milk. This hypothesis was confirmed by proteomic analyses conducted on samples T2.5 and on a casein standard. Three proteins from bovine milk were unambiguously identified, alpha-S1 casein (*Bos Taurus),* beta-casein (*Bos Taurus)* and alpha-S2 casein (*Bos taurus)*. Regarding samples T2.2, T2.1B and T2.7, the analysis of the sugar fraction by GC-MS has highlighted the presence of monosaccharides with glucose and/or galactose as principal components. Several fatty acids were identified in the lipid fraction, with prevalence of palmitic and stearic acids. Also, vaccenic acid and some cholesterol derivatives were identified suggesting the hypothesis that these samples may contain milk. Further investigations on the protein fraction for samples T2.2, T2.1B and T2.7 will provide additional elements to validate the hypothesis of milk. Interestingly, the GC-MS analysis also highlighted the presence in samples T2.2, T2.1B and T2.7 of several tricyclic diterpenoid acids with abietane skeleton, characteristic of pine resin. Its use is documented in antiquity as sealant but also as medicine, antiseptic, or ritual balms. Considering the variety of pigments and binders preliminary found, it is possible to hypothesize that the ceramic containers were filled with cosmetics and ointments for the young woman corpse.

3. Conclusions

The chemical characterization of the ceramic containers analyzed allowed to identify the inorganic components (through Raman micro-spectroscopy) and organic binders, both of vegetal and animal origin (through chromatographic techniques coupled with mass spectrometry). The results obtained suggest the possible use of vegetable and animal derivatives to prepare pigmented and shimmering (due to the basaltic rocks found) ointments or cosmetics probably to sprinkle the corpse of the young woman. A further verification of the milk proteins and elemental chemical composition of the ceramic matrix will be performed using LC-MS/MS and SEM-EDS.

Figure 1. Six samples from a young woman tomb of Hellenistic age. A, B. Skyphos T2.5 and T2.6; C) Bombylios T2.2; D) jug T2.7; E) jug T2.1 Caption (max 100 charcters - spaces included)

References

Colomban, Ph., 2004. Raman spectrometry, a unique tool to analyze and classify ancient ceramics and glasses. Appl. Phys. A 79, 167–170. https://doi.org/10.1007/s00339-004-2512-6

Papadopoulou, D.N., Lalia-Kantouri, M., Kantiranis, N., Stratis, J.A., 2006. Thermal and mineralogical contribution to the ancient ceramics and natural clays characterization. J Therm Anal Calorim 84, 39–45. https://doi.org/10.1007/s10973-005-7173-y

POS30

MULTI-ANALYTICAL STUDY ON THE STUFFED CROCODILE OF CASTEL NUOVO IN NAPLES (ITALY): CONDITION ASSESSMENT AND CONSERVATION

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1. Introduction

The specimen of crocodile object of this study, treated with the taxidermy technique, was once affixed to the outside of the second entrance portal of the Arc de Triomphe of Alfonso I of Aragon, at the Castel Nuovo in Naples and now preserved at the Certosa and National Museum of San Martino (Naples, Italy), in whose deposits it was found only in 2018 as certified by some unpublished official documents.

The presence of the animal, dead and stuffed on the castle door, which dates back to the first quarter of the seventeenth century, was fundamental for the birth of the legend about the Crocodile Pit of Castel Nuovo in Naples and, over the centuries, a strongly characterizing theme of Neapolitan folk culture, inspiring the other both literary and artistic works (Settembrini, 1934). Its sudden disappearance from the Castel Nuovo portal, in the last quarter of the nineteenth century, resulted in an increase in its popularity, prompting many scholars to search for this animal believed to be lost, and attributing connections with the famous crocodile to any naturalistic finding within the area surrounding the castle.

2. Results and Discussion

The crocodile was subjected to a complex multi-analytical study to evaluate the preservation state, the methodology of the taxidermy technique, and conservation treatments. The conditions of conservation were extremely worrying, after about four centuries spent on the door of the castle, completely vulnerable to atmospheric conditions, and after a period in the museum deposit in an unfavorable storage situation.

Despite the lack of material related to the stuffing and the loss of parts of skins and skeleton, the analyses were focused on the six fragments identified as: upper mandible fragment, maxilla with portion of nuchal shields, constant back of about thirteen consecutive rows of dorsal shields, a leather element with small bony shields between the dorsal section and the tail, a fragment of the tail and a small fragment of some spiers belonging to the single caudal crest. From the individual fragments, a series of samples were taken for non-destructive investigations through observation in light microscopy and analysis of elemental composition by X-Ray Fluorescence Spectroscopy (XRF) and for subsequent micro-destructive analysis, by Scanning Electron Microscopy (SEM) and dispersive energy X-ray microanalysis (EDX), ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS) and microwave plasma atomic emission spectroscopy (MP- AES). In addition, some materials taken from the surfaces during cleaning and prior to disinfection treatments were analyzed.

Biomolecular investigations of ancient DNA, made by Polytechnic University of Marche, led to recognition of the species Crocodylus niloticus, and the results of radiocarbon dating (Fioravanti et al., 2020), which placed it between 1296 and 1419 A.D., made it the testimony of the oldest taxidermy preparation present in Europe (Bertelli, 2018; Poliquin, 2011). Taxidermy was a technique for preparing animal skins for its long-term conservation, consisting in two main operations. The first leather phase, messa in pelle, consists in separating the skin from the body, while the second one, messa in posa, consists in stuffing the skin and giving it realistic features (Gestro, 1925). The leather phase consists mainly of two important operations: skinning and tanning. The latter is often secret between the various preparers and therefore differs both for the raw materials used to obtain the tanning solution, and for the maceration times.

To understand the tanning material, several samples including muscle fibers, dermis and epidermis were analyzed by XRF M6 Jetstream (Bruker), finding the presence of high quantity of calcium, up to 50%, confirmed also by SEM-EDX microanalysis performed with NOVA NANOSEM 450 (FEI, Thermo Fisher). Numerous mechanical damages were found, including lesions and crack in the bone material, superficial delamination and defibration of the skin caused by dehydration and subsequent contraction of the leather, confirmed by determination of pH according to UNI EN ISO 4045:2018 and determination of the moisture content. Furthermore, the preliminary study on incoherent deposits revealed that the dust present consisted of the deposition of particulate pollutants of organic and inorganic origin, with high concentration of K, Fe, Pb and Ti. Finally, ICP-MS analysis on cleaning pads detected the presence of a significant percentage of Al, Fe, Pb and Ca.

3. Conclusions

The autoptic-perceptive analysis and the diagnostic investigations, performed on the specimen of crocodile, have tried to recognize the taxidermic technique adopted, therefore, identifying at the elemental level the materials used for tanning hides, those present in the form of preservatives and the natural fibers associated with the internal filling. On the other hand, it aimed to examine and catalogue conservation problems by first taking an interest in a superficial analysis of the deposits and microbiological forms found, and then to extend research to a specific investigation aimed at determining the state of deterioration of skin and bone tissues. A final role was to verify the effectiveness of the products selected for conservative treatments.

Fig. 1. Robert Rive - No. 68. Bronze door of the triumphal arch of Alfonso of Aragon

References

Bertelli, P., 2018. La Vergine e il drago. Universitas Studiorum, Mantova.

Fioravanti, T., Casafredda, E., Splendiani, A., Caputo Barucchi, V., 2020. The stuffed crocodile of “Castel Nuovo” in Naples (Italy): new insights from ancient DNA and radiocarbon. Eur. Zool. J. 87, 452–458. https://doi.org/10.1080/24750263.2020.1800840

Gestro, R., 1925. Il naturalista preparatore, VI Edizione. ed. Hoepli, Milano.

Morris, P., 2011. A history of taxidermy: art, science and bad taste. Arch. Nat. Hist. 38, 371–372. https://doi.org/10.3366/anh.2011.0056

Settembrini, L., 1934. Ricordanze della mia vita. Gius. Laterza & Figli, Bari.

POS31

PRELIMINARY LIFE CYCLE INVENTORY OF CHICHEN ITZA: THE SCORE PROJECT

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1. Introduction

Vast research efforts have been made worldwide for the conservation of Built Cultural Heritage (BCH) [1], but more work must be done, involving all stakeholders, to include the sustainability of the materials and methods employed during conservation works. Sustainable interventions for the conservation of cultural heritage should consider socio-cultural, economic and environmental factors simultaneously, but these are often overlooked due to a lack of proper methods to handle all of them [2]. In order to propose solutions for a large variety of built cultural heritage, the SCORE (Sustainable COnservation and REstoration of built cultural heritage) project [3] intends to analyze two kinds of application cases, archaeological sites in Yucatan peninsula with an equatorial climate and vernacular built cultural heritage in different types of warm temperate climates in Europe, using different building materials and techniques. Life Cycle Assessment (LCA) methodology will be used to understand and possibly prioritise conservation and restoration interventions using more sustainable materials and techniques according to the different climatic conditions. In the present contribution, a preliminary Life Cycle Inventory on two selected sites of Chichen Itzà is presented.

2. Results and Discussion

Chichen Itza, a world heritage site (850-1200 CE), is the most representative archaeological site in Yucatán (Mexico) with two different architectural styles (Puuc and Toltec) and characterized by the presence of impressive iconographic representations carved in limestone, stucco plasters and polychrome finishes. In order to prevent the loss of architectural surfaces, SCORE aims to experiment innovative conservation methodologies and materials compatible with the original substrates and in full respect of the local constraints. On site visits were performed in order to obtain detailed information on the conservation procedures and the materials employed. Thanks to a strong collaboration with the Instituto Nacional de Antropologia e Historia (INAH) that is responsible for the protection, conservation, research and dissemination of the paleontological, archaeological and historical heritage in the country, a selection of the Chichen Itza site restauration/conservation processes that will be assessed by LCA methodology was defined.

In agreement with UNI EN ISO 14040–14044 regulations, ad hoc questionnaires related the north or east outside facade of the «casa de las Monjas» and the south west facade on top of the «Tempio del Chac Mool» were distributed (Figure 1). Flow diagrams reporting the input and output flows of the considered systems were defined. Particularly, for the «casa de las Monjas» the mortar suspension preparation, its application on the selected surface were considered, together with all the activities related to the set-up of the scaffolding and the cleaning of the surfaces to be treated.

For the «Tempio del Chac Mool» an alternative ZnO nanoparticles suspension was tested on the south west façade of the top floor. Therefore, the inventory analysis included the synthesis of the nanoparticles, the preparation and packaging of the suspension and its application after an opportune cleaning/treatment of the surface to be treated.

3. Conclusions

The preliminary life cycle inventory phase performed on selected sites of Chichen Itza allowed to model the performed restoration and conservation activities in a reliable way, within the LCA calculation tool (SiMaPro v. 9.3.0.2). This detailed inventory will allow the quantification of the related environmental and human health impacts in a trustworthy and objective manner.

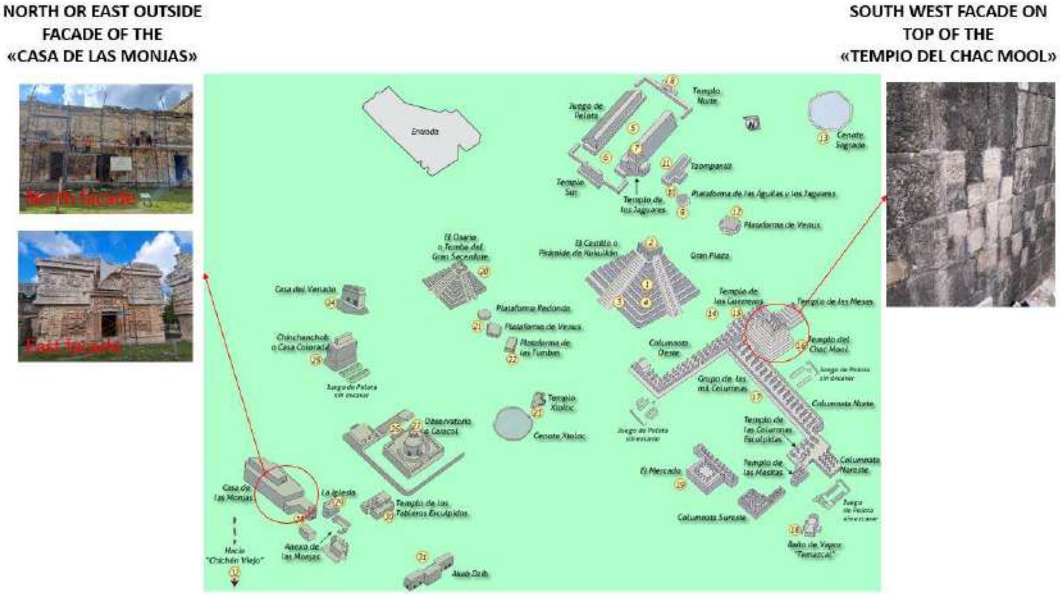

Figure 1. Chichen Itza archeological sites selected for the LCA study

References

[1] Bonazza A., Sabbioni C., Messina P., Guaraldi C., De Nuntiis P., (2009a). Climate change impact: mapping thermal stress on Carrara marble in Europe. Science of the Total Environment, 407, 4506-4512.

[2] Balliana E, Ricci G, Pesce C, Zendri E. (2016). Assessing the value of green conservation for cultural heritage: Positive and critical aspects of already available methodologies. International Journal of Conservation Science, 7, Special Issue 1: 185-202.

[3] https://score-project.net/en

Acknowledgements

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POS32

THERMAL AND MECHANICAL PROPERTIES OF POLYCAPROLACTONE-BASED COMPOSITES WITH DIATOMACEOUS EARTH AND HALLOYSITE NANOTUBES

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1. Introduction

The biodegradable polymers have been attracted interest for the design of green composites in recent decades to face the urgent environmental issues.

Polycaprolactone (PCL) is one of the most promising environmentally friendly polymers. Recent studies have reported that blending PCL with different types of fillers may affect its physic-chemical properties and crystallization rate.

Halloysite nanotubes (HNT) and diatomaceous earth (DE) have been recently investigated for the preparation of PCL-based composites with appealing performances[1],[2]. Both are naturally occurring materials with nanoscale dimensions and a structure that lend them also absorbent properties. Potentialities of such materials in polymer composites need to be further developed for environmental remediation applications[3].

For the study, binary blends of PCL with HNT and DE were prepared by melt mixing, starting from 5 w/t% of filler to the maximum miscible concentration to the polymer. The thermal and mechanical properties of the obtained composites were investigated. Thermogravimetric analysis, differential scanning calorimetry and dynamic mechanical analysis were employed for the research purposes.

2. Results and Discussion

Thermogravimetric analysis (TGA): The measurements were carried out by using the Q5000 IR instrument (TA Instruments) under nitrogen flow of 25 cm^3/min by heating the samples from 20° to 800 °C. with a rate of 1°C/min. The degradation temperature of the pristine materials and their composites were taken at the maximum of the first order derivative curves of mass percentage vs. temperature.

It was observed that concentration of HNTs up to 15 w/t% did not affect the thermal stability of PCL. The recorded T_{max} values show no significant variations compared to pristine PCL. Higher content of HNT, beyond these levels, leads to a significative decrease in the thermal stability of the PCL matrix, resulted in a lower onset decomposition temperature.

The addition of DE did not significatively affect the thermal stability of the composites, with a similar onset temperature for all of composites as the DE content increased.

Graphs of the residue vs filler concentration showed a good dispersion degree of the filler particles throughout the polymeric matrix.

Differential scanning calorimetry (DSC): The melting and crystallization behaviour testing of the composites and of pristine materials were carried out by using the differential scanning calorimeter TA Instrument DSC (2920 CE). Samples of approximately 5 mg were heated from 25°C to 80°C at a rate of 1 °C/min, under nitrogen atmosphere. The melting temperatures at the onset (T_{mi}), at the peak (T_{mp}) and the enthalpy of melting (ΔH_m) per gram of PCL in the composites were calculated.

The heating thermograms showed melting temperatures values constant for both PCL-based composites as compared to the neat PCL. The crystallinity degree (χ_c) of PCL did not change for blends with DE while significant variations were observed in PCL/HNT nanocomposites. The results showed that, up to the filler concentration of 15 wt%, χ_c increase, indicating that the well-dispersed HNT acted as nucleating agents in the PCL matrix. At higher concentrations, the crystallinity degree decreased, affected by the achievement of the percolation threshold of HNT and by the consequent decrease in molecular mobility of the PCL chains in the nanocomposites.

Dynamic mechanical analysis (DMA): Dynamic mechanical measurements were performed by using the DMA Q800 (TA Instruments). The temperature range was 30° to 80°C with a scan rate of 2°C/min, at an applied oscillation frequency of 1 Hz and strain of 0.5%. The shear gear method with samples of a surface of 100 mm^2 were employed to measure the elastic (storage modulus) and the viscous (loss modulus) components and tan delta parameters. For the study, the peak maximum of the loss modulus curves was considered. It was observed that these values reduced in the filled system as compared to the pristine counter parts, which is due to the reduction of viscous component of the polymer matrix by the presence of HNT and DE.

3. Conclusions

Well-dispersed binary blends of PCL with HNT and DE were prepared by melt mixing. Composites with the maximum miscible concentration to the polymer were obtained since there is a lack of information in the literature on the evolution of crystallization rate in PCL composites containing high percentages of fillers.

TGA and DSC analysis evidenced that the thermal properties of the polymer are mostly affected by the HNT addition and that the HNT concentration of 15 w/t% represents a sort of critical threshold after which a change in the behaviour of the composites occurs.

Viscoelastic measurements showed that both fillers increase the capacity of PCL to store energy during mechanical stress as their content percentage increases.

The reported data are the result of a preliminary characterization of sustainable composites whose potential for environmental remediation applications is currently being studied.

References

1. Kassa, A.,et al. Effects of montmorillonite, sepiolite, and halloysite clays on the morphology and properties of polycaprolactone bionanocomposites. Polym.Compos. 28(2020)
2. Oun, A. A.,et al. Comparative study of oregano essential oil encapsulated in halloysite nanotubes and diatomaceous earth as antimicrobial and antioxidant composites. Appl. Clay Sci. 224(2022)
3. Cavallaro, G.,et al. Organic-nanoclay composite materials as removal agents for environmental decontamination. RSC Adv. 9(2019)

CALCIUM CARBONATES BIOPRECIPITATION: CHEMICAL AND MICROBIOLOGICAL CHARACTERISATION AND POTENTIAL APPLICATIONS FOR CULTURAL HERITAGE

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Introduction

Conservation, protection and restoration are the three fundamental actions for the correct management of cultural heritage.

In this work, the bio-precipitation capacity of carbonates for marble restoration was evaluated.

Bio-consolidation is a procedure that uses specific non-pathogenic bacteria for production of calcium carbonate. This procedure is used for consolidating calcareous materials such as marble.

Microbially induced calcium carbonate precipitation is a naturally occurring biological process in which microbes produce inorganic materials as part of their basic metabolic activities. This technology has been widely explored and promising with potential in various technical applications. (Reddy et al., 2013)

Bio-consolidation improve the characteristics of cohesion and adhesion between the constructive particles of a material through biocalcification or carbonatogenesis or bacterial precipitation of calcium carbonate.

The bio-precipitation can produce Calcite or Aragonite base on the environmental conditions of formation as minerals.

The calcium carbonate crystals can be produced by the metabolites of microorganisms, which react with the microenvironment rich in Ca^{2+} ions, pH, and availability of nucleation sites the key factors of the whole process.

Results and Discussion

Bacteria and Culture Medium

C 1-8, F3, Bet Calc, MT19, MT10, Sporosarcina pasteurii, Bet2, Bac2-2, Bet 5 are used as bacteria. These bacteria were cultivated using the 30g\L of urea, 27,4 g\L of $CaCl_2$, 20g\L of NaCl and the nutrient broth wassterilized by autoclaving at 121 °C for 15 min.

Then, the bacteria were inoculated into the sterilized medium and cultivated for 24 h at 30 °C.

Once calcium was added to culture medium.

After 0h, 48h and 192h samples are analysed at ion exchange chromatography.

Quantitative analysis of precipitate-Chromatography

Ion Chromatography is a sensitive and powerful analytical method for determining inorganic anions and cations, as well as selected organic substances which can existing in the ionic form. In many cases, it has replaced the conventional wet chemical methods, which often are labor-intensive and time-consuming. (Paullet al.,2019)

Ion Chromatography two eluents are needed, one for the anions and one for the cations for respective two columns.

For the anions, a solution of carbonate and bicarbonate with negative charges is used as eluent because attracting the negative charges.

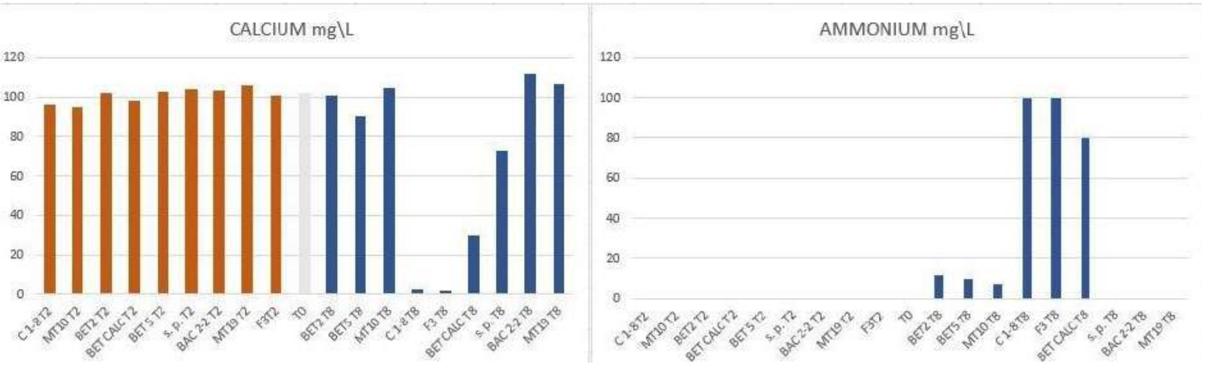
For the cations a solution of methane sulphonic acid is used because attracting the positive charges.

The anion and cation columns are based on a stationary phase and a mobile phase which allow charge separation.

The IC is controlled by Chromeleon software. The sample before chromatography is pre-treated.

Pre-treatments include dilution because the samples rich in organic material hinder the effectiveness of the measurement, and then they are filtered with 0,20μm diameter filters.

Nine different types of samples with bacteria were tested by chromatography and only three (Bet Calc, C1-8and F3) gave a good result.

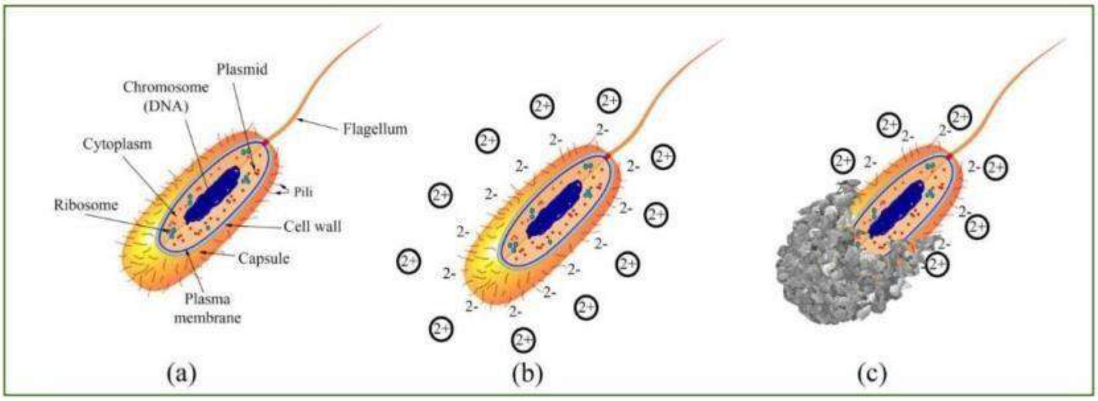


Graphs: calcium and ammonium at chromatograph analysis

In the graphs it is clearly show that after 192h for bacteria C1-8, Bet Calc and F3 the ammonium in solution increases while the calcium decreases because it has precipitated.
This happens because the precipitation of carbonate depends on bacteria's metabolic activities such as hydrolysis of urea, that produce ammonium in solution.
These bacteria were selected for the next phase and were then put in contact with a break in the marble, withina week the bacteria precipitated the carbonate inside the break healing it.
The last phase was a characterization of the precipitate to evaluate the mineralogical composition of the precipitate produced by the bacteria, and then evaluate how the precipitate adheres to the surface.

Conclusions

In conclusion, this technique can be useful as an alternative to traditional restoration methods.
The bacteria tested proved to be excellent for bio-precipitation and resistant over time.
This technique is easy to use and has not toxic effects for the operators, and it is safe for the work of art.
The precipitate is compatible with the marble construction material is a long-lasting technique and also is safe for the environment.



-Process of bio-precipitation induced by bacteria

References

Bred Paull, Rajmund Michalski, Ion Exchange | Ion Chromatography Principles and Applications,
Editor(s): Paul Worsfold, Colin Poole, Alan Townshend, Manuel Miró, Encyclopedia of Analytical Science (Third Edition), Academic Press, 2019, Pages 178-189.

Reddy M. Sudhakara, Biomineralization of calcium carbonates and their engineered applications: a reviewFrontiers in Microbiology (Fourth Edition), 2013

NEW HYDROPHOBIC TREATMENT BASED ON ORMOSIL AND NANO-$Mg(OH)_2$ FOR THE PROTECTION OF “STUCCO” ARTIFACTS

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1. Introduction

From the Middle Ages to the Baroque age, stucco was the preferred binder for masonry mortars and decorative plasters. Gypsum has played an important role in the traditional and monumental architecture of many areas of the Mediterranean, where there are examples of high architectural splendor [1]. The term stucco was widely used by Giorgio Vasari and it is meant any plaster intended for decorative purposes, low or high relief, but also plaster walls and ceilings, especially when gypsum is used as the binder fraction [2]. Due to its low water resistance and low mechanical strength, gypsum can be subject to physical, chemical and biological degradation.

To improve the preservation of gypsum and gypsum-based plaster artifacts here we propose the synthesis of a new hybrid inorganic-organic hydrophobic treatment based on nanometric magnesium hydroxide ($Mg(OH)_2$) and organically modified silica (OrMoSil), a class of materials with intermediate performance between "pure ceramic" and "pure polymers".

The hydrophobic product was tested for a possible application in the conservation of ancient and contemporary architecture as surface coating and as consolidant added to the mixture of gypsum-based mortar and plaster.

2. Results and Discussion

The OrMoSil was synthesized by sol-gel method, using tetraethyl orthosilicate (TEOS) as inorganic precursor and hydroxyl-terminated polydimethylsiloxane (PDMS-OH) as organic precursor. Ethanol and deionized water were used as solvents, while oxalic acid dihydrate was used as a catalyst.

Nano-$Mg(OH)_2$ was prepared starting from $MgCl_2$ as precursor and urea as templating agent, by precipitation in an alkaline medium. The final hydrophobic sol was obtained by mixing OrMoSil and nano-$Mg(OH)_2$ in a volume ratio 1:1.

The crystalline nature of $Mg(OH)_2$ powder was confirmed by Raman spectroscopy and XRD analyses. The size of the $Mg(OH)_2$ crystallites, obtained from TEM investigations, is about 15-20 nm. The characteristic vibration bands of magnesium hydroxyde and hydrophobic siloxane are clearly evident in Raman and FTIR spectra of the final product.

The pure gypsum samples were made by mixing gypsum powder with a water/solid ratio 0.7 for 3 min and the slurry was poured into 5x5x1.5 cm3 silicone moulds. The moulds were stored for 24 hours at room condition, then the specimens were demoulded and cured in a dryer.

The gypsum-based plaster specimens were obtained by mixing gypsum and calcium hydroxide in weight ratio 1:1. Animal glue was also added to the mixture [3]. Samples were cast into 4x4x16 cm3 mold, demoulded after two days and cured for 28 days in plastic bags.

The surface morphology of the coated samples has a homogeneous microstructure characterized by a microporosity with pores of about 30-50 micron in diameter as given by SEM measurement. The treatment is nearly homogeneously distributed on the surface as shown by EDS elemental Si and Mg maps.

Capillary water absorption and static contact angle measurements on gypsum coated with the hydrophobic suspension confirm the effectiveness of the treatment: the capillary water coefficient decreases by more than 50% and the contact angle is greater than 150°. The coating does not alter the aesthetic appearance of the samples: $\Delta E = 1.2 \pm 0.3$.

The influence of the new hybrid hydrophobic treatment on the mechanical properties of plasters was demonstrated by flexural and compressive strength measurements. The mechanical properties significantly improved, showing an increase in flexural and compressive strength of about 25% and 30%, respectively, compared to the raw gypsum plaster and of about 10% and 15%, respectively, compared to reference commercial plaster samples. To evaluate the carbonation front, the surfaces of the samples, just broken, were sprayed with phenolphthalein (1%) alcoholic solution. The depth of carbonation in the treated material is a few millimeters, while in untreated samples it is evident in almost the entire section.

3. Conclusions

As demonstrated by the capillary water absorption and the static contact angle, the new hydrophobic protective coating proved to be very effective. The treatment does not alter the aesthetic appearance of the surface as verified by colorimetric measurements. The new treatment added to the plaster paste is effective as a consolidant: the mechanical properties improve significantly and the depth of carbonation decreases.
The new hydrophobic nanocomposite product, both as a coating and as an additive, is therefore a promising material for the protection and consolidation of monuments and buildings of cultural interest.

Acknowledgments

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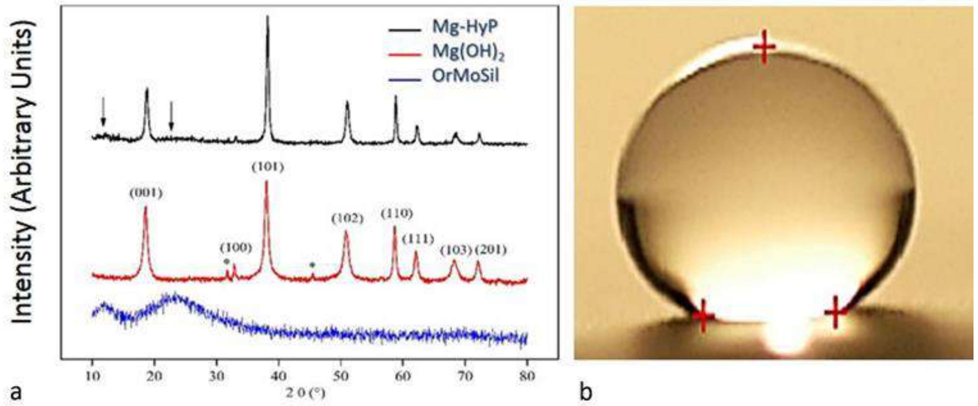

Figure 1. a) XRD pattern of the hydrophobic (Mg-HyP);b) static contact angle on coated gypsum sample

References

[1] Cotrim, H., do Rosário Veiga, M., & de Brito, J. (2008). Freixo palace: Rehabilitation of decorative gypsum plasters. Construction and Building Materials, 22(1), 41-49.
[2] Gapper, C. (1999). What Is “Stucco”? English Interpretations of an Italian Term. Architectural History, 42, 333–343.
[3] Salavessa, E., Jalali, S., Sousa, L. M., Fernandes, L., & Duarte, A. M. (2013). Historical plasterwork techniques inspire new formulations. Construction and Building Materials, 48, 858-867.

POS35

POLY(DIMETHYLSILOXANE) ORGANOGEL SPONGES: SYNTHESIS, CHARACTERISATION, AND APPLICATION IN CLEANING WORKS OF ART

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1. Introduction

Polydimethylsiloxane (PDMS) organogels and sponges were studied with the aim of possible applications for cleaning works of art. In particular, PDMS sponges were produced according to the sugar leaching technique, leading to two sponges differing in porosity, pore size distribution, and solvent absorption and retention capability [1]. The sponges were characterized by Fourier Transformed Infra-red spectroscopy in the attenuated total reflectance mode and compared with the PDMS slabs that do not contain pores. Scanning Electron Microscopy provided information about their morphology. X-ray Micro-Tomography allowed us to ascertain the form of the sugar templating agent. Measurements of absorption by ten solvents covering a wide range of polarities [2] were in the order: PDMS slab < PDMS (powdered sugar template) << PDMS (sugar cube template). Rheology data established that solvent absorption did not change appreciably, suggesting that the gel-like properties of the sponges have strong potential for applications in cultural heritage conservation as cleaning tools for degraded surfaces.

2. Results and Discussion

The first aspect to be discussed was the result of the two synthetic routes selected to obtain the two POPs PDMS differing for total porosity and pore size distribution. The results confirmed what is reported in the literature in the case of using a sugar cube, but the novelty was succeeding in obtaining also a PDMS more compact with much lower porosity using powdered sugar. The FTIR-ATR analysis was fundamental to establish that the two porous PDMS sponges have exactly the same IR spectra as non-porous PDMS, and that no sugar residues were present. This was an important preliminary test to the base of all the subsequent comparing data.

From the comparison of the morphology and porosity data, it was evident that the two sponges, even if they are chemically identical, are characterized by a completely different porosity: the PDMS_SC has a much higher porosity than PDMS_PS according to the large dimensions of the grains constituting the sugar cube

The swelling kinetics of the PDMS slab, PDMS_SC and PDMS_PS sponges was clearly the mirror of such strong difference in porosity among the three materials. Fig. 4.5 shows that PDMS_SC presents both the fastest kinetics of solvent absorption and the largest amount of swelling at the asymptote. This was ascribed to its very high porosity compared to PDMS_PS and also to the non-porous PDMS. It is worthwhile to recall that the solvent absorption by the copolymer was due to simple swelling phenomena for the PDMS slab, whereas for the POPs PDMS sponges two synergistic effects were present, i.e. swelling of the copolymer enhanced by capillary suction mediated by the pores. The results agreed with the literature [3] showing the driving factor for solvent absorption by PDMS is the hydrophobic interaction which is maximum for solvents with the lowest dielectric constant: indeed, according to this consideration, the behavior reported in Fig. 4.5 completely matched the data reported in Table 3.3.1. This is a key point in the view of thinking these systems for possible applications as cleaning tools for works of art surfaces. The swelling/adsorption data indicate that they are suitable as possible supports for cleaning solvents because can release them in a controlled way, avoiding at the same time both their spreading into the work of art porous support and any water contamination that is typical for most of the commonly used chemical hydrogels

The last aspect to be investigated is their rheological properties which are reported in section 4 and Supplementary File data. All the investigated systems are characterized by a solid-like behavior, so it is possible to classify them as chemical organogel/sponges. As far as we know these peculiarities, these systems could represent a truly innovative tool for the cleaning of works of art, especially where the presence of traces of water during the cleaning procedure represents a serious damaging drawback. The very interesting finding was also that the solvent absorption did not meaningfully change the viscoelastic behavior of PDMS sponges and slabs, so the application tests could open new perspectives for cultural heritage conservation in the field of selective cleaning.

3. Conclusions

The investigated systems presented in this work were potentially useful to be tried in cleaning tests for works of art conservation enabling to ascertain the role of porosity and pore size in determining solvent/release retention, its spreading within the works of art support, and solubilization ability against coatings to be removed.

References

[1] J. González-Rivera et al., Structural and thermoanalytical characterization of 3D porous PDMS foam materials: the effect of impurities derived from a sugar templating process, Polymers 10 (2018) 616
[2] T. T. Duncan et al., Maximizing contact of supersoft bottlebrush networks with rough surfaces to promote particulate removal, ACS Appl. Mater. Interfaces 11 (2019) 45310
[3] J. Ng Lee et al., Solvent compatibility of poly(dimethylsiloxane)-based microfluidic devices, Anal. Chem. 75 (2003).

MULTIANALITICAL APPROACHES FOR THE INVESTIGATION OF STREET ART: THE PAINTING OF BERLIN WALL

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1. Introduction

In this study fragments of the pictorial surface of the Berlin Wall have been analyzed as a case study for the development of a multi-analytical and non-invasive approach able to identify the materials, pigments and binders, used for the painting. The characterization of the used colors could be fundamental in planning suitable strategies for the restoration and conservation over time of these works which are subject to constant anthropic and atmospheric degradation. Recently the most used technique for the unequivocal identification of the main components, is Pyr-GC/MS, which however is micro-destructive [1]. We propose a non-destructive analytical approach to carry out the investigation of wall street art. Multispectral imaging, fiber optic reflectance spectroscopy (FORS), XRF, FT-IR and Raman investigations were performed. The same analytical techniques were applied on five commercial acrylic colors [2], used as standards the identified pigments. The dilution of these colors with the titanium white of the same brand simulates the practice of color mixing very common among painters and allowed the realization of a semi-quantitative calibration by using the same techniques.

2. Results and Discussion

From XRF, Ca and Ti are the main constituents in all the samples. The presence of Ca is justified by the use of calcite as mineral filler in paints, and its presence is confirmed by both infrared spectroscopy, which shows three peaks centered at 1412, 872, and 712 cm^{-1} (the latter peak is often overlapped by peaks due to the binder) and Raman spectroscopy, which shows a characteristic peak at 1086 cm^{-1}. The abundance of Ti justifies the presence of TiO_2 as the main white pigment. The presence of titanium dioxide is confirmed by two characteristic peaks in Raman spectra at 445 and 610 cm^{-1} [3]. Regarding the almost ubiquitous presence of Fe, it is unlikely that this element is characteristic of a pigment. Instead, it is more probable that this element is present in mortar underlying the paint film or as a result of anthropogenic deposition on the surface. Chromium and lead are only present in the sample named GN1, which is green. Therefore, it can be confirmed that they are characteristic elements of the color of the fragment. The inorganic pigment containing both chromium and lead is lead chromate ($PbCrO_4$), which is yellow in color. Additionally, traces of copper can be observed in both some of the blue samples and the green sample.

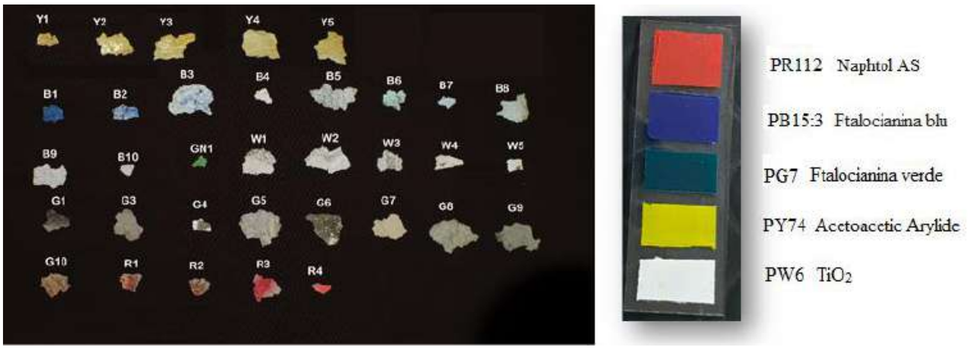
The FT-IR spectra samples compared with the literature data [4] show the main peaks attributed to the acrylic binder. In detail, include the C=O stretching band, typically appearing around 1720-1740 cm^{-1}, which signifies the presence of the carbonyl group in the acrylic polymer, the C-H stretching bands, observed between 2800-3100 cm^{-1} associated with the carbon-hydrogen bonds present in acrylic polymers and, the presence of the C-O stretching band, typically observed around 1100-1300 cm^{-1}, which indicates the presence of ester groups in the acrylic polymer structure.

From the comparison of Raman spectra with the spectral library of literature [5], it was possible to identify four pigments belonging to two classes of synthetic organic pigments: phthalocyanines and azo pigments. The spectra show a high similarity both in terms of the number of peaks and the broadening of the bands.

We prepared standard samples using commercially available colors, and their analysis using XRF, FTIR, and Raman spectroscopy enabled us to establish calibration curves. For XRF and Raman spectroscopy, the calibration curves correlating the ratio between titanium oxide and pigment signals, followed exponential trends. This means that as the concentration of the analyzed element or compound increased, the XRF and Raman signals exhibited a non-linear response, showing an exponential relationship between signal intensity and concentration. Interesting results for the ftalocianine mixture with TiO_2 provide exponential trend for the correlation between Ti and Cu with the same decay factor. On the other hand, the calibration curve obtained from FTIR spectroscopy correlating the ratio between the acrylic binder and the pigment, exhibited a linear trend. This implies that the FTIR signal response was directly proportional to the concentration of the analyte, resulting in a linear relationship between signal intensity and concentration. By establishing these calibration curves, we can now use XRF, FTIR, and Raman spectroscopy to quantitatively analyze similar samples and determine the concentration or presence of specific elements or compounds of interest.

3. Conclusions

The developed approach permits the identification of the binder and the pigments of some berlin wall paintings. The XRF investigation allowed to identify and/or exclude the presence of inorganic pigments; with FT-IR spectroscopy the type of binder was identified as acrylic, highlighting also the aging. Raman spectroscopy allowed the identification of some pigments thanks to the comparison with the few databases present in the literature. The analysis mixtures of commercial acrylic colors provide useful calibrations for the determination of pigment-binder ratio, of titanium oxide-pigment ratio, and clarify the problem of the identification of ftalocianine pigment by the determination of cupper presence with XRF measurements.



Fragment of the berlin wall painting and identified pigment with commercial colors

References

Pellis, G., Bertasa, M., Ricci, C., Scarcella, A., Croveri, P., Poli, T., & Scalarone, D. (2022). A multi-analytical approach for precise identification of alkyd spray paints and for a better understanding of their ageing behaviour in graffiti and urban artworks. Journal of Analytical and Applied Pyrolysis, 165, 105576.
https://www.schmincke.de/en/products/health-safety/all-mediums/italian.html
Germinario G, van der Werf ID, Sabbatini L. Chemical characterisation of spray paints by a multi-analytical (Py/GC–MS, FTIR, μ-Raman) approach. Microchem J. 2016; 124: 929-939.
Wiesinger R., Pagnin L., Anghelone M., Moretto L. M., Orsega E. F., and Schreiner M., Pigment and Binder Concentrations in Modern Paint Samples Determined by IR and Raman Spectroscopy Angew. Chem. Int. Ed. 2018, 57, 7401– 7407
Nadim C. S, Zumbuehl S, Delavy F, Fritsch A, Kuehnen R, Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection, Spectrochimica Acta Part A 73 (2009) 505–524

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POS37

PRELIMINARY RESULTS OF MULTI-TECHNIQUE ANALYSES ON GLASS BEADS FROM A SCYTHIAN TOMB ON THE KHORTYTSIA ISLAND (UKRAINE)

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1. Introduction

This work focuses on 12 glass items (whole beads and beads' fragments) retrieved from a looted 4th century B.C Scythian tomb at the Kanfarka necropolis (Khortytsia island, Zaporizhzhia region, Ukraine).

Khortytsia is the largest island of the Dnipro River. It has played a prominent role in the exchange of people and goods in the Northern Black Sea region since ancient times and the traces of past human activities are abundant in the area, therefore it received the status of the National Reserve in 1993.

Four types of glass beads remained after the looting of the tomb, and they were investigated through stereomicroscopy (SM), fibre optics diffuse reflectance spectroscopy (FORS), scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS), micro-X ray diffraction (m-XRD) and X-ray fluorescence spectrometry (XRF).

One type consists of cubic black beads with yellow zigzag decorations; another type includes slightly flattened spheres of black glass, decorated with white, yellow, and red uneven spots placed on the surface; the last two types are barrel-shaped green or black beads with a yellow stripe decorating their largest diameter.

Types of glass beads included in this study (courtesy of Khortytsia National Reserve. Photos: D. Nykonenko).

2. Results and Discussion

The first results of the investigation come from a thorough inspection under the stereomicroscope of the whole beads and of several fragments. The conservation state of the surface, and some features related to the forming technique and the tools employed by the bead maker, clearly emerged. In particular, extensive crizzling characterises the green beads, and evident traces of the tool(s) used to "comb" the yellow decoration on the cubic beads and to detach the bead from the mandrel were documented.

The black-appearing glass of the cubic beads revealed to be yellow translucent when thin fragments are observed with transmitted light. The same observation setting performed on a fragmentary green bead showed abundant bubbles entrapped in the glass, contributing to its opaque appearance.

FORS detected Cu(II) as the primary colouring agent of the green glass; on the other hand, the very dark colour of the black-appearing beads did not allow this technique to retrieve any information on the colourants. Finally, reflectance spectra recognised iron red oxides in the reddish deposit in the beads' hole, supporting the hypothesis that it is some kind of clayey material, which can be tentatively liked to the bead making process.

SEM-EDS performed under low vacuum conditions on the whole beads enabled a closer look at the surface, highlighting extensive pitting and a variety of superficial deposits at the micro-scale.

Two fragments were also prepared as polished sections. A chip from a cubic black bead showed rare (rounded) silica grains and numerous small bubbles a few microns across dispersed in the glass matrix, with no evidence of crystalline opacifiers. The composition was characterised by an elevated concentration of iron (some 6% in weight as FeO). Both the intense absorption of Fe(III) ions dissolved in the glass matrix under oxidizing conditions, and the Fe(III)-S chromophore that develops in a reducing atmosphere would explain the yellow translucent colour [1], therefore further analyses would be necessary to clarify how the colour is obtained in this bead. SEM-EDS data from the fragment of the green barrel-shaped bead confirmed that copper is the responsible for the green colour, with lead also playing a role in the development of the hue. Sporadic particles of lead antimonate were also detected in the green glass matrix.

Further information on the composition of the beads was obtained from XRF analyses. Copper was confirmed in all the green beads, with lead concentration of about 3% (wt PbO). The concentration of iron clearly separated the black beads into two clusters, dividing the cubic and the barrel-shaped ones from the round ones, as these latter featured significantly higher concentrations. On the other hand, the barrel-shaped black bead contained significant concentration of lead (some 3 wt% as PbO) that differentiated its composition from that of the cubic beads.

SEM-EDS elemental data – in combination with the outcomes of micro-XRD analyses - gave some indications to characterise the phases that give colour (and opacity) to yellow, white and red decorations. Both elemental data and diffraction patterns indicated that lead antimonate is present in the yellow decorations. The high concentration of iron in the red spots of the round black beads would suggest that iron(III) oxide could play a role in the colour; however, the XRD patterns revealed the reflections of face-centred cubic crystals of elemental copper, which give the glass an opaque-red appearance. As for the white decorations, the elemental composition determined by SEM-EDS in low vacuum mode highlighted elevated concentration of antimony (and, possibly, of calcium), that would indicate the presence of calcium antimonate. Several antimony-rich phases emerged from the micro-XRD patterns of the white spots, among which orthorhombic $Ca_2Sb_2O_7$. These crystals, along with quartz grains, can be therefore indicated as the white opacifiers in the decorations.

3. Conclusions

Khortytsia was the link between the Mediterranean and the deep steppe regions of the Northern Black Sea. The transit of goods in the steppe took place mainly along the river arteries. Such key points on these routes as Khortytsia were places of lively cultural contacts. Finds of similar beads are known at a distance of up to 2,000 km from the Black Sea to the east deep into the Great Steppe. They are found at the sites of different nomadic cultures along the banks of the Don, Volga, and Urals and are indicators of the ancient system of steppe trade routes. Chemical analyses on the glass finds can give information to support archaeologists in interpreting these contacts and exchanges. As a relevant example, evidence of glass production on the Black Sea coast emerged by combining archaeology and archaeometry to study the glass finds from the 6th century BC Greek settlement of Yahorlyk [2]. The present work is a further step towards a broader application of multidisciplinary investigation of glass finds from the lower Dnipro region.

References

[1] W.A. Weyl, Coloured glasses, Society of Glass Technology, 1981 (reprinted).
[2] A. Kolesnychenko, O. Yatsuk. Glass-making or glass-working? Yahorlyk settlement in the light of recent research. Eminak, 33 (2021) 144-156.

POS38

FLUORESCENT CHEMICAL MARKER: A NEW TOOL AGAINST ILLICIT TRAFFICKING OF ARTWORKS

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1. Introduction

Artifacts are constantly threatened by anthropogenic actions. Looting, smuggling, and illicit trade of cultural goods pose major risks to our cultural goods and our cultural identity. One of the major consequences of these illegal activities is the dissociation, meaning the loss of information associated with an object, such as provenance, identification, or location information, without which the object loses significance or is lost. Thus, art property marking and tracking are crucial to ensure the object identification, collection management and protection, while maintaining their state of conservation. Several actions have been adopted during the years to strengthen the protection of cultural property and cultural heritage, but they often lack effectiveness.

The AURORA project (Artwork Unique RecognitiOn and tRacking through chemicAl encoded data, miniaturized devices and blockchain alliance – GA 101094245 - HORIZON Europe) aims filling this gap by demonstrating how chemical marking as anticounterfeiting tool, miniaturized device, art deep-scan technique, cloud and blockchain based platforms can be combined to create a cost-effective, non-destructive, and non-invasive countermeasure against illegal activities while preserving artifacts.

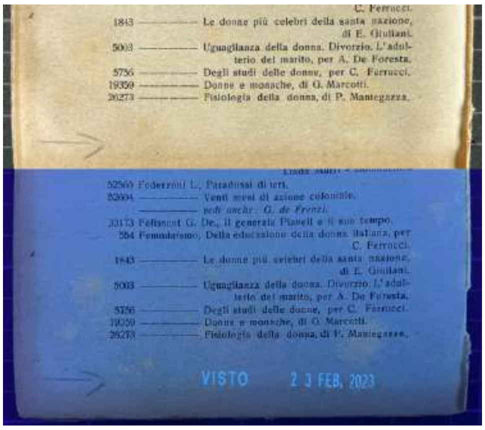
2. Results and Discussion

The technologies researched and implemented in AURORA are converging in a digital tool allowing relevant stakeholders, art dealers, curators, auction houses, logistic services, and enforcement agents, to easily verify artwork authenticity and provenance, enabling art piece movement tracking. In close collaboration with relevant cultural institutions partners, AURORA will showcase real setting applications to validate the non-invasiveness, low-cost, long-term stability, confidentiality, and data security features of the proposed solutions.

In this contribution, the very recent achievements, in the synthesis of ZnO nanoparticles and their compatibility with chitosan, proposed as a binder to create stable film shaped as a QR-code, will be presented. The fluorescence response of ZnO has been investigated and optimized by controlling the synthesis parameters. Chitosan stability was also studied, under different accelerated aging procedure, to determine the ideal concentration and the optical effects on the anticounterfeiting marker. Different application techniques (e.g. stamping, direct printing, writing, dry transfer labels, etc) are under investigation to fulfill the requirements connected with the artwork typology, the chemical and morphological properties of the surface, and the acceptable size of the marker.

3. Conclusions

Preliminary formulations based on ZnO NPs/chitosan nanocomposite provide promising nanoinks, not visible at naked eye, which show under UV light an intense and stable fluorescence, easily readable using digital cameras.



C. Ferrucci.
1843 ———— Le donne più celebri della santa nazione, di E. Giuliani.
5003 ———— Uguaglianza della donna. Divorzio. L'adulterio del marito, per A. De Foresta.
5756 ———— Degli studi delle donne, per C. Ferrucci.
19359 ———— Donne e monache, di G. Marcotti.
26273 ———— Fisiologia della donna, di P. Mantegazza.

52560 Federzoni L., Paradossi di ieri.
52604 ———— Venti mesi di azione coloniale.
———— *vedi anche: G. de Frenzi.*
33173 Felissent G. De, Il generale Pianell e il suo tempo.
554 Femminismo, Della educazione della donna italiana, per C. Ferrucci.
1843 ———— Le donne più celebri della santa nazione, di E. Giuliani.
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VISTO 23 FEB. 2023

Fluorescent ink (commercially available) applied on paper under normal (top) and UV light (bottom)

References

- Xi Chen, Qi Wang, Xiao-Ju Wang, Jie Li, Guo-Bin Xu, Synthesis and performance of ZnO quantum dots water-based fluorescent ink for anti-counterfeiting applications, Scientific Reports (2021) 11:5841.
- Kai-Kai Liu, Chong-Xin Shan, Gao-Hang He, Ruo-Qiu Wang, Zhi-Peng, Quan Liu, Lin Dong, De-Zhen Shen, Advanced encryption based on fluorescence quenching of ZnO nanoparticles, J. Mater. Chem. C, 2017, 5, 7167.
- Illicit trade in cultural goods in Europe Characteristics - criminal justice responses and an analysis of the applicability of technologies in the combat against the trade, EUROPEAN COMMISSION, 2019; doi:10.2766/183649.

I PROMESSI SPOSI BY ALESSANDRO MANZONI: NON-INVASIVE ANALYTICAL STUDY OF THE ORIGINAL MANUSCRIPTS THROUGH XRF AND ER-FTIR

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1. Introduction

"I Promessi Sposi" were written by Alessandro Manzoni between 1821 and 1842, when the final version called "Quarantana" was published. During this twenty-year period, Manzoni returned to the original manuscripts several times to add, remove, and modify parts of the text. The project, at its preliminary stage, is aimed at investigating and characterizing the composition of the inks used in the writing of the original text, preserved in the Biblioteca Braidense in Milan, as well as studying the erasures and notes that Manzoni added on his manuscripts.

A selection of manuscripts including parts of the introduction and chapters 2, 7, and 9 of "I Promessi Sposi" novel written between 1821 and 1825 were selected for the study. In addition, other rare writings, named "Modi di dire irregolari" and "Frammenti d'un libro d'avanzo", dated between 1823 and 1824, were studied to compare the inks and possibly understand the evolution of writing.

To these purposes, X-Ray Fluorescence (XRF) and External Reflection-FTIR (ER-FTIR) spectroscopies [1,2] were performed in-situ to obtain molecular and elemental information together with UV-Vis-IR multiband high-resolution imaging [3] to highlight specific manuscript features related to writing media, erasures and paper conservation.

2. Results and Discussion

The non-invasive investigations carried out on selected areas of the manuscripts showed, in all the parts, the presence of iron-gallic ink, clearly characterized by XRF signals associated with iron (Fe), potassium (K) and sulphur (S) [4]. This finding was confirmed by ER-FTIR investigations, which highlight the characteristic absorption due to carboxylic groups of tannic acid in the range 1700-1600 cm-1 [2,4]. It is important to point out that the metal-organic ink used by Manzoni lacks the typical signals related to copper (Cu) and zinc (Zn), typically present in the Roman vitriol (a mixture of ferrous and copper sulphates) used for centuries as a raw material for ink production [1,2]. This aspect may be related to the use around the mid-19th century of more pure and selected materials, a procedure closely linked to the development of technology also in the field of chemistry and materials production.

Regarding the identification of possible different sets of iron-gall inks useful for highlighting different stages of writing, the analyses seem to show the presence of four different sets, each related to a chapter. Looking at the results, it seems also that the corrections were made with the same type of ink as the main text. This result would suggest that the original drafting and the related corrections, erasures and changes made by Manzoni on the different parts of the text took place within a tight time frame. In addition, the probable absence of different ink sets on individual chapters excludes the possibility that Manzoni returned during the years to the same manuscript.

A first comparison with the results obtained on the inks of the other manuscripts written in the same years of chapters 7 and 9 (1823-1825), namely "Modi di dire irregolari" and "Frammenti d'un libro d'avanzo", seem to confirm the presence of the same ink.

Unfortunately, the absence of the typical Cu and Zn signals limits the opportunity to obtain more in-depth information regarding the different compositions of the iron-gall ink used over the years, allowing only an interpretation of the data for Fe, K, and S.

3. Conclusions

By combining results of the non-invasive, multi-analytical and portable techniques, relevant information about the composition of the different inks used by Manzoni in the manuscripts were achieved, shedding light on the inks and on the presence of different sets of inks used by Manzoni during the writing. This information that will help Manzoni scholars to deepen and resolve some outstanding doubts concerning the writing and evolution of the "I Promessi Sposi" by Alessandro Manzoni. At a later stage, further processing of the analytical data (i.e., chemometrics tools, machine learning) will be tested to try to overcome the limitation given by the absence of Cu- and Zn-related signals.

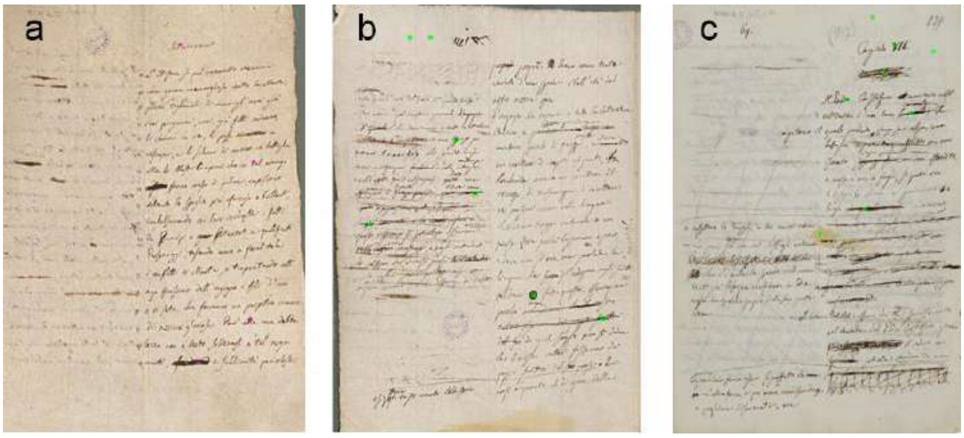

Figure 1. Visible light images of the (a,b) Introduction, and (c) Chapter 7 selected by Manzoni for the final version of "I Promessi Sposi".

References

[1] Bicchieri M., Monti M., Piantanida G., Sodo A., Vib Spectrosc, 39, 2008.
[2] Díaz Hidalgo, R.J., Córdoba, R., Nabais, P. et al., Herit Sci, 6, 2018.
[3] Dyer J., Verri G., Cupitt J., Multispectral Imaging in Reflectance and Photo-induced Luminescence Modes: A User Manual, British Museum, London, UK, 2013.
[4] Adami G., Gorassini A., Prenesti E., Crosera M., Baracchini E., Giacomello A., Microchem J, 124, 2016.

POS40

EVALUATION OF THE EFFICACY OF PROTECTIVE COATINGS FOR CULTURAL HERITAGE MATERIALS UNDER CLIMATE CHANGE: AN ARTIFICIAL AGEING METHODOLOGY.

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1. Introduction

Tangible Cultural Heritage (CH) exposed outdoor interacts with atmospheric, physical, chemical, and biological factors that cause degradation and are evolving due to Climate Change[1]. The unprecedented rates of environmental change lead to changes of the average climatic conditions, and can induce, accelerate or amplify loss by affecting frequency and intensity of said changes[2].

Non-climatic stressors should also be considered, namely variations of atmospheric concentration of pollutants and particulate matter as a result of environmental policies[3]. It is evident how tangible CH interacts with interrelated mutable factors and how these new conditions must be considered to understand degradation processes and test protective products.

Green, eco-friendly coatings allow to implement sustainable treatments with low impact on the environment and operators[4]. Their efficacy can be assessed via accelerated ageing tests representative of current environmental conditions. In order to do so, an artificial ageing methodology was developed by taking into account updated environmental parameters (T, RH, UV radiation, rain, pollutants), and applied to various types of CH materials.

2. Results and Discussion

The work hereby presented focuses on the study of inorganic materials such as metals, glass and stone commonly used for the production of artefacts, sculptures, architectonic elements and built heritage. Quaternary bronze, sodic glass, and marble were chosen as representative materials and mock-ups were obtained.

For each material, two kinds of substrates are considered: unaltered i.e. the new, non-degraded material, and pre-aged i.e. patinated bronze, corroded glass, and weathered marble. The second substrate serves the purpose of having starting conditions similar to those met during a realistic conservation treatment.

An innovative coating and a commercial coating were then selected for each material, with the aim of evaluating the new coating's performance and comparing it to commonly used products.

Following a multi-analytical approach, the materials are characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray fluorescence spectroscopy, infrared spectroscopy, Raman spectroscopy, and UV-Vis spectrophotometry for colour analysis. Additionally, electrochemical measurements are performed on bronze samples, while X-ray diffraction, microindentation hardness test, ultrasonic pulse velocity test, and peeling test are performed on marble samples. The preliminary characterization allows to gather information about the materials at the initial stage, and is repeated after each step of the ageing procedure in order to observe the evolution of the degradation processes.

The artificial ageing phase is carried out in two steps: the first one simulates the effects of rainwater, while the second simulates the effects of environmental parameters such as temperature, relative humidity and solar radiation. With the purpose of imposing ageing conditions as representative as possible of real conditions, the chosen environmental parameters are based on current environmental monitoring data. Notably, particular attention is paid to the chemical composition of rainwater with the aim of reproducing in laboratory a synthetic rain as close as possible to the real one.

The impact of rainwater is replicated through the implementation of two methods in order to simulate the effect of both stagnant rain and runoff conditions. In both cases, the solutions in contact with the mock-ups are analysed by inductively coupled plasma atomic emission spectroscopy in order to know the concentrations of ions coming from the substrates, whose presence is diagnostic for the corrosion process. These information, alongside the surface analyses performed after this step, allow to understand the mechanisms of the degradation processes and the efficiency of the protective products against the action of water.

The subsequent step of the accelerated ageing is carried out in a climatic chamber simulating daily variations of T, RH and UV irradiation. Surface and cross-section analyses performed after this step allow to observe the state of the coating after the combined effects of water and exposure to environmental conditions varying cyclically.

3. Conclusions

Preliminary results from the proposed accelerated ageing methodology were presented. This constitutes a systematic approach that could allow to better understand the degradation mechanisms of bronze, glass, and marble exposed outdoor in light of the new climatic conditions brought by climate change, as well as to assess the efficacy of traditional and innovative protective coatings in said conditions.

The employment of environmental parameters based on monitoring data enhances the procedure's reliability and decreases potential discrepancies between the predicted behaviour of protective treatments in traditional ageing tests and their performance in real conditions.

References

1. Sesana, E. et al. Climate change impacts on cultural heritage: A literature review. *Wiley Interdiscip. Rev. Clim.* **12**, e710 (2021)
2. Bertolin, C. Preservation of Cultural Heritage and Resources Threatened by Climate Change. *Geosci.* **9**, 250 (2019)
3. EEA. *European Union emission inventory report 1990-2019 under the UNECE Convention on Long-range Transboundary Air Pollution (*2021)
4. Artesani, A. et al. Recent Advances in Protective Coatings for Cultural Heritage–An Overview. *Coat.* **10**, 217 (2020)

POS41

AN INTEGRATED DIAGNOSTIC APPROACH FOR THE STUDY OF THE INTERACTION OF THE ORGANIC COMPONENTS OF OIL PAINTINGS WITH INORGANIC PIGMENTS ON A 16TH CENTURY PANEL DEPICTING THE MADONNA AND CHILD WITH ST. JOHN.

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1. Introduction

The artwork analyzed in this study is an oil painting on panel, depicting the Madonna and Child with St. John. After a careful historical-artistic research [1], the painting can be dated in the last quarter of the 16th century, a period of great changes in the perception and meaning of pictorial genres and in political and ideal movements, characterized by a need for 'devout' painting imposed by the new post-Tridentine scenarios [2].

The numerous restorations that the work has been subject to over the centuries have made it possible to explore the articulated theme of 'Restoration of Restoration' and the superimposition of various interventions. This reflects a context related to the interactions between the various interventions considered 'posthumous', as opposed to a physical consistency of the 'original' work of art [3].

Here, we present a study on the identification of the causes of the progression of degradation of materials and techniques used in previous interventions. We used high-resolution analytical methods (XRF, FT-IR and GC/MS).

Results and Discussion

The taxonomic analysis established the wooden species of the support to be of the *Populus* genus, while the wooden species *Junglans Regia*, also known as walnut for the support structure [4].

XRF was used to identify the pigments used. Components such as iron (Fe), calcium (Ca) and lead (Pb) were identified in the preparation, confirming the pigmentation of the priming layer. Moreover, XRF analysis led to the identification of traditional pigments and more modern elements within the paint layer, tracing the succession of the various repaintings. In particular, the pigments in the Madonna's cloak revealed the history of previous restorations and the actual state of preservation; three points on the cloak area were examined. Potassium (K) and cobalt (Co) based pigments were identified, confirming the use of enamel blue; in the same area we could identify a red pigment, corresponding to the original layer of the underlying mantle, covered in the past by the repainting of enamel blue, which affected the entire area. The cause of the degradation would go back to the interaction of the components of the glaze in an oily binder, which undergoes an alteration process due to the reaction of the potassic, alkaline glass with the carboxylic acids of the oil, leading to the formation of potassium fatty acid soaps [5,6].

To obtain a complete description of the paint layers, an FT-IR chemical investigation was carried out, which led to the identification of linseed oil as the binder. Subsequently, to confirm the nature of the binder used for the polychromy samples were taken and subjected to GC/MS analysis [7] showing a high level of deterioration of the film.

Finally, a study of the protective layer was carried out using UV analysis. On a large part of the panel, particularly in the background, the light-blue hue registered the presence of an uneven layer of varnish, applied in larger quantities than on the figures and the result of an earlier restoration. Furthermore, we identified the nature of the varnish on the original coat and the one of the restoration by FT-IR survey and the GC/MS. The results led to the identification in both cases the presence of Dammar.

The blue enamel pigment, also known as blue pigment smalt or cobalt blue, was the primary focus of our computational analysis. It is a type of alkali silicate glass with general formula (K2O)x-(Cu2O)y-(SiO2)(1-x)+y.

Point defects in the structure, such as Al3+instead of Si4+, are also likely because these pigments were obtained by mixing cobalt oxide with molten glass. Our goal, however, is to provide an explanation for the discoloration that occurs. The physical-chemical process that is responsible of this process is related to the transformation of tetrahedral Co(II) sites into octahedral coordination complexes upon migration of K ions across the materials bulk and surfaces [8,9]. In other words, the change of color is triggered by K cations, which act as bond-breaking agents into the silica glass network, converting some of the bridging oxygens into nonbridging ones. Along these research direction, ongoing ab initio molecular dynamic simulations combined to Artificial Intelligence tools for analysis and predictions will provide further insights on the structural and chemical stability of the inorganic pigment and its complex chemical environment.

3. Conclusions

The study and restoration work carried out on the painting of the Madonna with Child and St. John have made it possible to obtain important information regarding the interventions undergone by the work under examination and the technique of the support, preparatory layer and paint film.Taken together, our results made it possible to highlight the state of degradation of the pictorial binder, probably connected to interactions between identified fatty acids and the pigments present.

Fig.1 Unknown painter from the late 16th century, Madonna and Child with St. John, 85.7x72 cm, University and Ente Morale Suor Orsola Benincasa - Depots, Naples.

References

[1] P. Leone de Castris, Pittura del Cinquecento a Napoli: 1540-1573. Fasto e devozione, Napoli, Electa Napoli;
[2] F. Bologna, Roviale Spagnuolo e la pittura napoletana del Cinquecento, Napoli, Edizioni scientifiche italiane, 1958;
[3] Restaurare i restauri: Metodi, Compatibilità, Cantieri, Atti del convegno di studi Bressanone 24-27 giugno 2008, Venezia, Edizioni Arcadia Ricerche, 2008, a cura di Guido Biscontin e Guido Driussi;
[4] G. Fatigati, Le arti del legno. Natura, proprietà e problemi della materia nella conservazione delle opere, Napoli, Università Suor Orsola Benincasa, 2010;
[5] Spring, M., Higgitt, C., Saunders, D. "Indagine sui processi di interazione pigmento-medio in pittura a olio contenente smalto degradato". Bollettino tecnico della National Gallery Vol. 26, pp. 56–70.
[6] Poldi, Gli azzurri perduti nei dipinti del Tintoretto. Ri- vedere le cromie grazie alle analisi scientifiche, in La Crocifissione di Tintoretto. L'intervento sul dipinto dei Musei Civici di Padova, atti della giornata di studi (Venaria Reale, 11 ottobre 2012), a cura di S. Abram, Torino 2014.
[7] Melchiorre C., Palmiero S., Fatigati G., Amoresano A., Marino G., Carpentieri A. "A procedure for combining the removal and the identification of a patina on a 15th century byzantine icon". International Journal of Conservation Science, 2019.
[8] Cianchetta I., Colantoni, I., Talarico, F., d'Acapito, F., Trapananti, A., Maurizio, C., Fantacci, S., Davoli, I. "Discoloration of the smalt pigment: experimental studies and ab initio calculations". J. Anal. At. Spectrom., 27, 1941-1948, 2012
[9] Vaselnia S. Y., Khajeh Aminian M., Dehghan Banadaki, R. "Experimental and theoretical study on the structural, electronic, and optical properties within DFT+U, Fxc kernel for LRC model, and BSE approaches. Part II: CoSiO3 and Co2SiO4 pigments". Powder Technology, 397, 116999, 2022.

POS42

THE SUSTAINABILITY OF BIOCOLONIZATION REMOVAL: THE CASE OF THE *CASA A PONENTE* OF *PALAZZO ROCCA COSTAGUTA* IN CHIAVARI (GENOVA, ITALY)

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1. Introduction

Microorganisms often grow as colorful sub-aerial biofilms (SABs), forming complex communities on mineral surface exposed to the atmosphere, such as the masonry of historic buildings. Traditionally, the interactions between SABs and heritage stone surfaces have been considered detrimental to the substrates, leading to biodeterioration. However, recent studies have highlighted that SABs can have a neutral or even protective role in certain situations [1,2].

The plastered wall of the *Casa a Ponente* of *Palazzo Rocca Costaguta* is partially covered by patchy green SABs. It is the result of biological recolonization after a recent biocidal/cleaning treatment. The option of not pursuing further removal actions is therefore actually under evaluation. Preliminary investigations using contact angle measurements have demonstrated the near hydrophobic characteristics induced by the SAB on the masonry surface. On-going analyses aim to investigate the nature of the interactions between the biofilm and the substrate. In the present study, in addition, the sustainability of the biocolonization removal will also be addressed.

2. Results and Discussion

Areas of the biocolonized wall were selected and treated with common biocidal products: benzalkonium chloride, essential oils and hydrogen peroxide. A comparative LCA analysis between the treatments has been considered, to assess the environmental effects related to the different chemicals used for the biocidal treatment. The functional unit chosen is the volume of chemical (in the liquid, applicable form) employed for the treatment of a unitary surface (namely, 1 cm^2). The life cycle boundaries of the system are "from cradle to gate", i.e. from the raw materials to the production of the chemical, without considering neither the use stage (the application on the surface), nor the end of life of the packaging containing the products.

Moreover, additional investigation on the wall surface were carried out before and after treatment. An untreated (NT) area and an uncolonized area (NC) were also characterized as reference surfaces. The measurement after biofilm removal were performed one month after the treatment, to evaluate the impact of the chemical cleaning on the state of conservation of the plaster and the efficacy of the biocide action against SABs. Measurements will be repeated approximately one year after the treatment to evaluate the efficacy in terms of prevention of recolonization. The on-site investigation was made by portable digital microscopic observation using a digital microscope DinoLite Premiere AM7013MT. The percentage of colonized surfaces was also calculated with the freely available software GIMP (GNU Image Manipulation Program, Berkeley, California) and the obtained results pre- and post-treatment were compared for a preliminary evaluation of the treatment efficacy. The extent of biocolonization was reduced by above 90% for benzalkonium chloride and hydrogen peroxide, with hydrogen peroxide<benzalkonium chloride and around 70% for essential oils. Only in the case of hydrogen peroxide, the

application of the product was followed by mechanical cleaning using a sponge and brush. From these preliminary results benzalkonium chloride appears the most efficient biocide in terms of biofilm removal. Moreover, the surfaces treated with benzalkonium chloride and hydrogen peroxide appear to have greater roughness compared to non-biocolonized area. Microscopic observation suggests that the treatment, in these cases, leads to a relevant selective removal of the binder from the surface.

3. Conclusions

The results suggest that the removal of biofilm with chemical products, benzalkonium chloride and hydrogen peroxide, may also have an impact on the state of conservation of the substrates. On the other hand, essential oils did not completely remove the biofilm. Therefore, it is important to also consider the option of preserving the biofilm instead of removing it. This aligns with the criteria of safety, health, reversibility and minimum intervention that drive the conservation of built heritage.

A case-by-case approach should be used, when dealing with cultural heritage, considering the type of microorganisms, the lithotype, the environment and the cultural context. LCA is becoming an important support tool, to assess the sustainability of the products of art conservation employed, that could integrate information deriving from the application of risk assessment methodologies, which describe a more direct effect on the operator or on the substrate. In the view of complying in all human activities with the “Do No Significant Harm” principle, also wider environmental categories (global warming, energy and water consumption, etc.) deserve to be considered.

References

1. Villa, F., Stewart, P. S., Klapper, I., Jacob, J. M., & Cappitelli, F. (2016). Subaerial Biofilms on Outdoor Stone Monuments: Changing the Perspective Toward an Ecological Framework. *BioScience*, *66*(4), 285–294. https://doi.org/10.2307/90007580
2. Gulotta, D., Villa, F., Cappitelli, F., & Toniolo, L. (2018). Biofilm colonization of metamorphic lithotypes of a renaissance cathedral exposed to urban atmosphere. *Science of the Total Environment*, *639*, 1480–1490. https://doi.org/10.1016/j.scitotenv.2018.05.277

POS43

RESISTANCE OF GLAZED TILES FOR ROOF COVERING IN ALPINE CLIMATE: A CASE STUDY FROM THE 18TH CENTURY

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1. Introduction

The 18th century roof tiles from the "Casa delle vigne", located in Aosta region (north-east Italy), were investigated as an example of ceramic tiles with a lead-based glaze finishing used to create colorful patterns [1].

The main degradation agent for ceramic materials with open and interconnected porosity is water that can reach the material due to capillarity from rain, fog, condensation and freeze causing cracks, new pores, and delamination of the surface [2,3]. The use of glazed tiles is peculiar of Aosta region, characterised by an alpine climate, with frequent alternation of freeze-thaw in fall-winter, and thermal inversion at the valley floor leading to low temperatures and high humidity conditions [4]. Nevertheless, the tiles demonstrated outstanding resistance, but the failing of nails caused the tiles fall. A conservation project proposed the integration of the original tiles with new ones, produced according to traditional methods in the adjacent Piedmont. Original and new tiles were analysed with Fiber Optics Reflectance, μ-Raman, IR spectroscopy, X-Ray Fluorescence, and Thermogravimetry to understand their composition and production technology. Their resistance to freezing was also evaluated[2].

2. Results and Discussion

The "Casa delle vigne" tiles are constituted of a ceramic body, a white slip (optional), and a coloured glaze in green, yellow or natural red. Microscopic observation pointed out that the ceramic bodies is characterized by an intense red paste with small white and black aggregate inclusions (< 100 μm), or a light-coloured paste with bigger inclusions (>100 μm). Micro-Raman, performed on the cross sections of representative samples, and FTIR-ATR, performed on powdered samples, were combined to study the chemical composition. The paste, considering the micro-Raman and the FTIR results, seems to be mainly composed of aluminosilicates, in particular albite and orthoclase, feldspars, kaolin, hematite and quartz; the presence of carbonates was not detected. According to TG-DSC and spectroscopic analysis, the original clay was probably fired in an oxidizing atmosphere at around 900°C. The glaze, as clearly visible in the cross sections, is either laid directly on the ceramic body or on a white slip, applied probably to enhance the colour of the glaze. The slip contained less feldspars and hematite than the ceramic body, and a higher amount of quartz and kaolinite responsible for the light colour. The interface between the glaze and the body or the slip is mainly composed of orthoclase crystals.

The glaze is a lead-based mix with a low alkali content and can be transparent, yellow, or green. The glaze colour is given by the presence of transition metals: green is obtained with the addition of a copper-based pigment (ramina), while yellow is probably obtained from an iron-based pigment (i.e. ochre). Moreover, it is possible that some green-yellowish colours were obtained mixing yellow and green pigments. The glaze of the old tile is extremely compact and adherent to the ceramic body, despite showing a dense network of micro-cracks. Surface opalization, iridescence, and pitting are also present and mainly concentrated in areas of low wash-off, where rust and atmospheric deposition can easily accumulate.

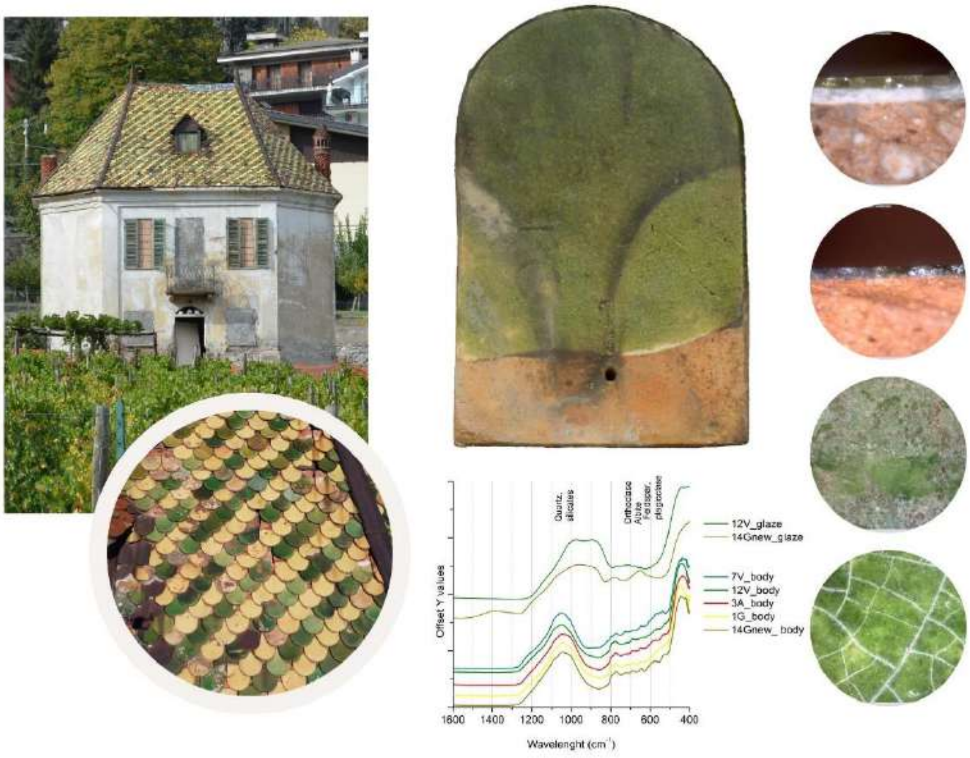
The new handmade tiles, selected for the restoration, have a different composition respect to the original ones. The ceramic body shows higher calcium content. Probably, clay rich in calcium aluminates and silicates were used. The glaze presents a higher content of calcium and a lower percentage of lead; most probably, CaO was used as a flux. Tin was added to obtain the lemon-yellow hue of the glaze.

Twenty freeze-thaw cycles were performed to evaluate the resistance and behaviour of the new tile in comparison to an old one. Each cycle is composed of 3 hours of capillary absorption followed by 3 hours at -15°C, drying at 19°C±2°C and 60%±5% relative humidity overnight. Freeze-thaw resistance was considered as Aosta region experiments cold and humid winter. Both the original and new tiles resulted to be extremely resistant to freeze-thawing cycles in terms of glaze delamination and formation of new cracks. Possible colour variations, determined according to Cie L*a*b* system, were difficult to evaluate due to the high variability among the glazes. Nevertheless, the blue-yellow b* resulted to be the more affected chromatic coordinate for both tiles.

3. Conclusions

In this research work, the first aim was to understand the materials and characteristics of original 18th glazed tiles from Aosta and the newly produced. The second was to compare the resistance of the new versus the original tile when subjected to freeze-thawing cycles in terms of durability.

The use of pure clays with low calcium contents, high firing temperature and lead-rich glazes were found in the original tiles, able to outstand several freezing-thawing cycles without damage. Iron and copper pigments were used in old yellow and green glazes. Zinc based pigment, low lead and calcium-rich glazes are employed for producing the new ones; the glaze remained mainly coherent to the ceramic body during freeze-thaw test. The restoration intervention with the new tiles maintains the original aspect and behaviour of the original roof and contribute to support the local product and expertise.



Left: Casa delle Vigne and roof detail; right: green tile and details, stratigraphy, FT-IR spectra

References

Casasola, R., et al., *J Mater Sci* **2012**, *47*, 553–582, doi:10.1007/s10853-011-5981-y.
Porfido, C. Rizzo, R.E. et al., *Mater Charact* **2021**, *177*, 111185, doi:10.1016/j.matchar.2021.111185.
Colomban, P. In *Conservation Science: Heritage Materials,* P. Garside, E. Richardson, Eds. RSC, 2020; p. 978.
Https://Www.Arpa.Vda.It/It/Relazione-Stato-Ambiente/Archivio-Rsa/Xv-Relazione-Sullo-Stato-Dell-Ambiente-2020/1344-Rsa-2020-Ambiente-Naturale/Rsa-2020-Atmosfera/. (10-07-2023)

CURRENT ANALYTICAL CHALLENGES FOR THE IDENTIFICATION OF ORGANIC RESIDUES IN ARCHAEOLOGICAL POTTERY

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1. Introduction

Proteomic approaches based on mass spectrometry (MS) have been used successfully in the recent past for the molecular characterisation of art works and archaeological objects.[1] However, there are still relatively few examples of the successful recovery and detection of proteins from archaeological pottery. This is mostly because ceramics often contain a much lower amount of proteinaceous material, that is also highly contaminated and degraded, thus making proteomic analyses quite challenging.[2,3]

In the attempt to address this issue, we herein report efforts in developing new methods for the characterisation of protein residues deposited in pottery. Deep eutectic solvents (DESs) have been recently proposed as promising media to extract proteins from ceramics.[2] In this work, the feasibility of a DES-based extraction strategy will be explored as a promising alternative for the traditional protein extraction protocols. Preliminaryexperiments will be performed on test specimens, namely modern ceramics on which known foodstuffs were artificially deposited. The optimized protocol will be then applied to a set of historical samples coming from the archaeological site of Pani Loriga.

2. Results and Discussion

Preliminary characterisation studies have been conducted on historical samples coming from Pani Loriga. In particular, GC-MS analyses allowed for the classification of the samples based on their lipid and sugar compositions. On the basis of the GC-MS profiling, some of the samples were selected and investigated for their protein component. These samples were subject to a standard 6M Urea-based protein extraction protocoland then analysed by LC-MS/MS. As successful example, we report the case of sample PLB17.S6N.1519.13,a pitcher on which proteomic analysis enabled to identify several bovine serum proteins (Fig.1).

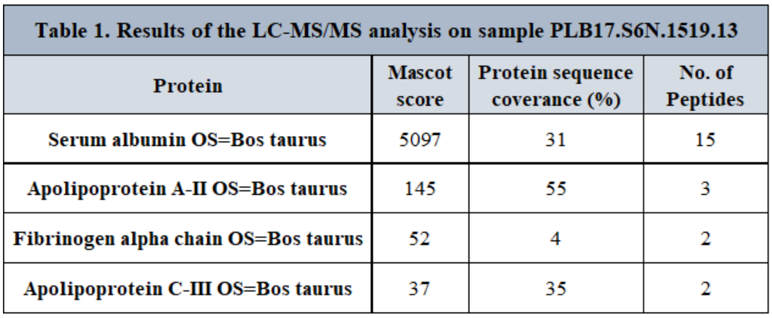

Table 1. Results of the LC-MS/MS analysis on sample PLB17.S6N.1519.13

Protein	Mascot score	Protein sequence coverance (%)	No. of Peptides
Serum albumin OS=Bos taurus	5097	31	15
Apolipoprotein A-II OS=Bos taurus	145	55	3
Fibrinogen alpha chain OS=Bos taurus	52	4	2
Apolipoprotein C-III OS=Bos taurus	37	35	2

Fig. 1. Results of the identification of proteins obtained by LC-MS-MS analysis for sample PLB17.S6N.1519.13.

These results were consistent with the hypothesis proposed based on previous GC-MS analyses. Indeed, the simultaneous identification of animal fatty acids, animal-type steroid hormones and bovine serum proteins suggests that the vessel might have been used to contain beef or beef broth. However, only in very few cases successful protein recovery and identification were obtained, prompting for the search of further extraction strategies. This emphasises how critical it is to design novel experimental strategies dedicated to a sensible and reliable diagnosis in the field of cultural heritage.[3]

In the framework of this project, the feasibility of a DES-based extraction strategy will be explored as a promising alternative for the traditional protein extraction protocols.

To this purpose, data collected with the DES-based extraction strategy proposed by Chowdhury et al. will be shown in comparison to other establishedextraction protocols as controls.[2] In particular, the 6M GuHCl-based protocol by Chowdhury et al. will be usedto confirm the control proposed by the authors.[2] Moreover, a 6M Urea-based extraction protocol, that is our standard procedure, will be considered as additional internal control.[4] To evaluate the best protocol for analyses, preliminary experiments will be performed on test specimens, namely modern ceramic fragments onwhich known foodstuffs (milk or meat) were artificially deposited. For each test specimen, sampling was carried out by scratching the surface of the fragment where the different substances had been placed, similar to how sampling takes place on archaeological objects.

Once optimised the extraction procedure, the developed protocol will be applied to a set of historical samples.In particular, ceramic samples coming from the collection of the archaeological site of Pani Loriga will be analysed as extremely interesting case studies.[5] Pani Loriga is a Phoenician-Punic settlement located in southwestern Sardinia, being active from the late VII century to the first half of the IV century BC. During twoexcavation campaigns on this site, we collected a significant set of samples, which include (i) scratched parts from different sides of the ceramic vessels and (ii) internal powders recovered near the bottom of the pots andtherefore most likely assumed to have been in direct contact with foods.

Proteomic characterisation, integrated with GC-MS analyses of lipid and saccharide fractions from the same samples will hopefully significantly support historical and archaeological interpretations, revealing new insights into the customs and habits of the Sardinian Phoenician-Punic population.

3. Conclusions

We expect the novel protocol set-up in this work will provide new insights into the proteomic analysis of pottery-absorbed residues, a still extremely challenging issue in the panorama of cultural heritage diagnosis. The application of this procedure to case studies from Pani Loriga will provide a strong validation of theproposed strategy. In addition, the obtained results will provide keys to deciphering ancient ceramics materials,revealing new insights into ancient peoples' uses, customs and habits that preceded us.

References

1. C. Warinner et al., Chemical reviews vol. 122,16 (2022): 13401-13446.
2. M.P. Chowdhury et al., J. Proteome Res. 2022, 21, 11, 2619–2634.
3. D. Tanasi et al., Amino Acids. 53, 2021, 295–312.
4. R. Vinciguerra et al., Microchem. J. 126, 2016, 341–348.
5. M. Botto et al., Publications du Centre Jean Bérard. 2021, 273–292.

POS45

MOLECULAR CHARACTERIZATION OF COLLAGEN-BASED ANIMAL GLUES BY PROTEOMICS AND SPECTROSCOPIC ANALYSES

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1. Introduction

Animal glues prepared from connective tissues are widely used in restoration as adhesives, binders and consolidants for organic and inorganic materials. Collagen in its natural state is a triple helix protein characterized by a Gly−X−Y repetitive sequence and a unique high content of Proline and Hydroxyproline thatmake collagen easily recognizable in the protein universe. Upon treatment with acids or alkalis in hot water, the otherwise insoluble collagen becomes a soluble gelatin to be used as animal glue. The performance of theglue strongly depends on the original source of collagen but is also influenced by the extraction and preparation procedures.[1] Thus, a systematic molecular characterization of animal glues is crucial to help restorers in selecting the most appropriate materials to be used in conservation treatments.[2] In this work, a multi-analyticalapproach based on proteomics and spectroscopic analyses is used to characterize animal glues from different sources provided by restoration workshops. Special attention is paid to the study of chemical modifications and conformational changes that occur in collagen upon glue preparation from natural materials.

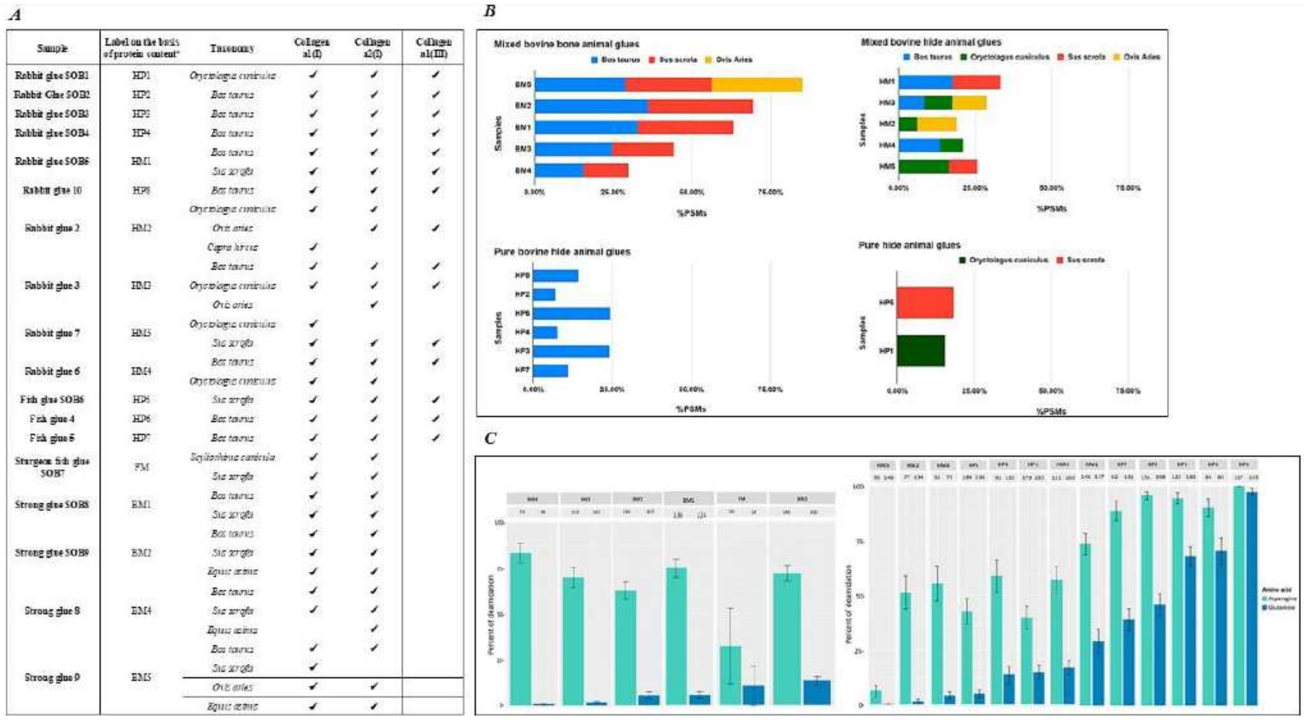
2. Results and Discussion

Proteins in samples were identified by a shotgun proteomics approach by LC-MS/MS. This analysis allowed to establish the glue source and distinguish between hide and bone glues. The discrimination between animal species in the case of collagen is challenging as it relies only on the detection of a very few unique peptides. To simplify species assignment, the search space was reduced to sequences of collagen type I and III of the common domesticates generally used for animal glues.[2] In particular, the detection of collagen alpha 1(III) was used to distinguish between hide and bone glues, as this molecule is abundant in soft connective tissues and skin, while it is poorly synthetized in bones.[3] Following the identifications, samples were clustered basedon the proteins content as bone (B) and hide glues (H) and subdivided in Pure (P) and Mixed (M) (Fig.1A).[2]

Proteomics and analytical pyrolysis coupled to GC-MS were used to analyse chemical modifications in collagen. First, backbone cleavage of the polypeptide chain was considered as an expected degradation featurein proteins from animal glues. Collagen is insoluble in cold water and is transformed into soluble gelatin by denaturation and partial hydrolysis, which is achieved by hot water extraction (hydrolytic breakdown).[4] Such damage at the backbone can be evaluated as semitryptic peptides that will be generated upon trypsin hydrolysis,with a trypsin cleavage site only at one end.[4] The occurrence of semitryptic peptides was semi-quantitatively evaluated by counting peptide to spectrum matches (PSMs) and dividing the PSMs of semitryptic peptides with the total PSMs of identified peptides, including both tryptic and semitryptic peptides.[2] To further investigate the degree of backbone cleavage, analytical pyrolysis coupled with GC-MS was carried out.[2] The most characteristic pyrolysis products of proteins are cyclic dipeptides, 2,5-diketopiperazines (DKPs), whoseformation is hypothesized to be a depolymerization involving the cyclization of neighbouring amino acids in a polypeptide chain. A relatively high yield of DKPs might be ascribed to a high degree of protein hydrolysis.

Data obtained reveal that generally bone glues are more fragmented than hide ones (Fig.1B).2

Also, deamidation was evaluated as relevant chemical modification in collagen, as it is expected to strongly influence the rheological properties of the adhesive material by changing collagen pI. During glue processing,the acidic or alkaline treatments favour hydrolysis of the amide groups in collagen to a greater or lesser extentby deamidating the lateral chain of Glutamine (Q) and Asparagine (N).[5] Thus, harsher conditions of collagen extraction in the preparation of glues might have been imprinted also in the profile and level of collagen deamidation. Deamidation was evaluated from raw LC-MS/MS data by MaxQuant software with an in-housescript based on PSMs intensities for semiquantitative evaluation.[2] Data collected showed that on average boneglues are less deamidated than hide glues, while mixed-collagen glues are overall less deamidated than pure glues (Fig.1C).[2] How these molecular details are reflected in the three-dimensional structures and in the rheological propertiesof animal glues is currently under investigation by a combination of thermalgravimetric analysis (TGA), differential scanning calorimetry (DSC) and spectroscopic techniques.



Sample	Label on the basis of protein content*	Taxonomy	Collagen a1(I)	Collagen a2(I)	Collagen a1(III)
Rabbit glue SOB1	HP1	*Oryctolagus cuniculus*	✓	✓	✓
Rabbit Glue SOB2	HP2	*Bos taurus*	✓	✓	✓
Rabbit glue SOB3	HP3	*Bos taurus*	✓	✓	✓
Rabbit glue SOB4	HP4	*Bos taurus*	✓	✓	✓
Rabbit glue SOB6	HM1	*Bos taurus*	✓	✓	✓
		Sus scrofa	✓	✓	✓
Rabbit glue 10	HP8	*Bos taurus*	✓	✓	✓
Rabbit glue 2	HM2	*Oryctolagus cuniculus*	✓	✓	
		Ovis aries		✓	✓
		Capra hircus	✓		
Rabbit glue 3	HM3	*Bos taurus*	✓	✓	✓
		Oryctolagus cuniculus	✓	✓	✓
		Ovis aries		✓	
Rabbit glue 7	HM5	*Oryctolagus cuniculus*	✓		
		Sus scrofa	✓	✓	✓
Rabbit glue 6	HM4	*Bos taurus*	✓	✓	✓
		Oryctolagus cuniculus	✓	✓	
Fish glue SOB5	HP5	*Sus scrofa*	✓	✓	✓
Fish glue 4	HP6	*Bos taurus*	✓	✓	✓
Fish glue 5	HP7	*Bos taurus*	✓	✓	✓
Sturgeon fish glue SOB7	FM	*Scyliorhinus canicula*	✓	✓	
		Sus scrofa	✓	✓	
Strong glue SOB8	BM1	*Bos taurus*	✓	✓	
		Sus scrofa	✓	✓	
Strong glue SOB9	BM2	*Bos taurus*	✓	✓	
		Sus scrofa	✓	✓	
		Equus asinus	✓	✓	
Strong glue 8	BM4	*Bos taurus*	✓	✓	
		Sus scrofa	✓	✓	
		Equus asinus		✓	
Strong glue 9	BM5	*Bos taurus*	✓	✓	
		Sus scrofa	✓		
		Ovis aries	✓	✓	
		Equus asinus	✓	✓	

Fig. 1. Results of the LC-MS/MS analyses for the animal glue samples. A. Collagen chains identified. B. Occurrence of backbone cleavage. C. Overall percentage of deamidation for N, Q residues for the collagen chains identified in bone (left) and hide (right) glue samples.[2]

3. Conclusions

In conclusion, although much attention has been devoted to physical properties of collagen-based animal glues,a systematic characterization of molecular properties of animal glues is still lacking. This work strives to address this issue by providing a molecular characterization of a set of 19 animal glues produced for restorationpurposes. Data herein presented confirm the heterogeneity of collagen-based animal glues at the molecular level. This heterogeneity is strongly increased by preparation and manufacturing procedures that affect the properties of the glue, possibly more than the collagen origin itself. These data pave the way to a correlation between molecular modifications and material performances in animal glues.

References

1. G. Ntasi et al., J. Prot. Res. 2022, 21, pp. 2173–2184.
2. H. Kuivaniemi et al., Gene, 707, 2019, pp.151–171.
3. T.P. Cleland et al., Proc. R. Soc. B Biol. Sci. 2015, 282, p. 0150015.
4. G. Leo et al., Anal Chem, 2011, 83, pp. 2056-64.

ANALYTICAL PYROLYSIS FOR THE CHARACTERIZATION OF PAINT MATERIALS IN STREET ART IN THE PRIN PROJECT “SUPERSTAR - SUSTAINABLE PRESERVATION STRATEGIES FOR STREET ART”

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1. Introduction

In the last decade, works of street art, located outdoors in urban contexts, have received increasing attention from citizens, institutions, art historians and conservators, due to their acknowledged social and cultural relevance [1]. The ephemeral character, free access, and exposure to the environment and anthropic actions, make indeed public paintings vulnerable to neglect, removal, vandalism, and degradation. Beyond that, the strategies aimed at their preservation and fruition are rather unclear or lacking. The Italian project Prin2020 “Superstar-Sustainable Preservation Strategies for Street Art” sets as a goal the definition of innovative guidelines for a sustainable preservation strategy of street art, aimed at safeguarding its powerful social and cultural message in the urban context (https://prin2020superstar.dcci.unipi.it).

2. Results and Discussion

The availability of effective analytical tools for the identification of artwork materials is thus crucial to support defining the best preservation practices. The cooperative consortium for the project is composed of University of Pisa (project coordinator Prof. Francesca Modugno); University of Bologna (Prof. Silvia Prati), Politecnico di Milano (Prof. Lucia Toniolo), University of Turin (Prof. Dominique Scalarone) and CNR -Perugia (Dr. Laura Cartechini).

Superstar project case studies include two prominent public mural paintings located in Milan, selected with the support of Comune di Milano (Area Museo delle Culture, Progetti Interculturali e Arte nello Spazio Pubblico, Dr. Marina Pugliese and Dr. Alice Cosmai): Or.Me by Orticanoodles in Via S. Faustino (2017) and Necesse by SMOE in via Ludovico di Breme (2021). The two murals have been the object of study of an extensive in-situ non-invasive campaign of measurements carried out by CNR-Perugia [2]. Within this analysis campaign, it was possible to collect some samples from damaged and altered areas in the mural paintings.

The poster describes the results obtained in the analysis of the paint samples by analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), applied to characterise paint binders and organic additives in the paint formulations [3].

3. Conclusions

The analyses allowed for the identification of paint binders in the two murals and were interpreted contextually with the results of non-invasive external reflectance Fourier transform infrared spectroscopy (FT-IR). In particular, polyvinyl acetate plasticised with Veova and styrene-acrylic resins were detected in Or.Me, while a nBA/MMA acrylic resin was the binder in Necesse.

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Mural paintings object of the study (Necesse by SOME, above; Or.Me by Orticanoodles, below)

References

[1] Ross et al, In search of academic legitimacy: The current state of scholarship on graffiti and street art, *The Social Science Journal* 54, 2017, 411.
[2] Brunetti et al, Non-invasive investigations of paintings by portable instrumentation: the MOLAB experience, *Topics in Current Chemistry* 374, 2016, 10.
[3] Degano et al, Advances in analytical pyrolysis to investigate organic materials in heritage science. *Angewandte Chemie*, 57, 2018, 7313.

POS47

LABEL-FREE ELECTROCHEMICAL IMMUNOSENSOR FOR NON-INVASIVE DETECTION OF PROTEINS IN PAINTING

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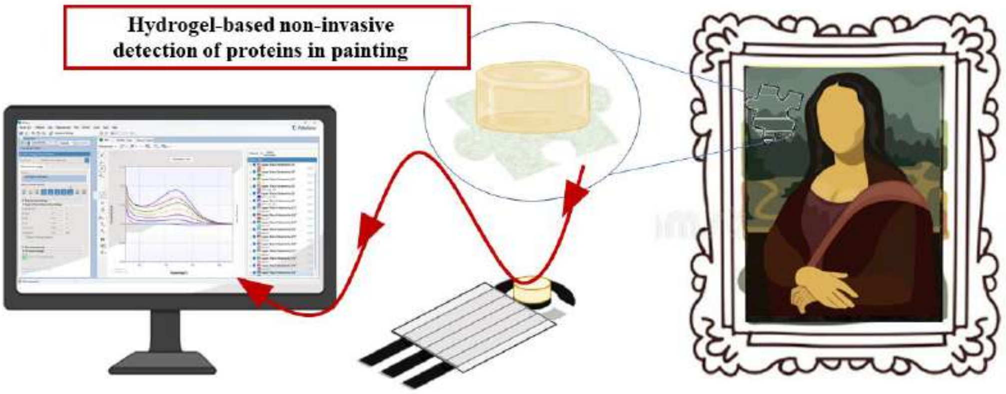
1. Introduction

In the cultural heritage field, there is a growing interest in the development of new non-invasive analytical strategies capable of obtaining a comprehensive characterization of painting components without causing damages. In particular, the selective and non-invasive recognition of organic substances, used in paintings as binders and adhesives, still represents an open research issue. Nowadays, researchers are forced to face between analytical selectivity/sensitivity and non-invasiveness towards the artwork. In particular, a key research issue is related to the identification of proteinaceous materials, such as ovalbumin, collagen, and casein. These materials are extensively employed as binders and/or coatings in ancient paintings. Accurately identifying them is of utmost significance in determining artistic techniques and conducting attribution studies. In the last decades, analytical strategies based on immunochemical methods have been implemented, to provide a highly sensitive approach to the identification and localization of proteins. . Despite these methods overcoming the traditional drawbacks of spectroscopic investigations in terms of selectivity and sensitivity, as well as the drawbacks associated with chromatographic techniques in terms of cost, time consumption, and loss of spatial information, immunochemical methods typically require the collection of samples for analysis.

To address the need for sustainable and efficient analytical approaches for non-invasive protein analysis, the current study focuses on the development of label-free electrochemical miniaturized immunosensors coupled with a biocompatible gellan gel for non-invasive protein sampling and on-site selective identification.

2. Results and Discussion

In this research work, a portable, flexible, and low-cost system is implemented using an immunosensor based on screen printed electrodes (SPEs). The system enables fast, direct, and on-site protein recognition, with proteins being captured by gellan gel during the sampling step. To achieve this, a working electrode (WE) is functionalized with a primary antibody (anti- ovalbumin) for the specific recognition of ovalbumin (OVA). When OVA is present, the antigen-antibody reaction occurs, resulting in the formation of an immunocomplex on the WE. The immunocomplex is then detected by measuring the current variation of a reversible electroactive probe, such as $[Fe(CN)6]^{3-/4-.}$ In this approach, the concentration of the immunocomplex formed is inversely proportional to the recorded current. This means that as the OVA concentration increases, the immunocomplex formation increases, resulting in greater steric hindrance and lower diffusivity of the redox probe, leading to a decrease in the recorded current (see Fig. 1).



To guarantee a sensitive and reproducible immune-complex formation, a careful optimization of each step of the immunosensor fabrication was carried out starting from the concentration of primary antibody (Ab_1) and the blocking solution.

The performances evaluation of the immunosensor, in terms of sensitivity, was obtained by constructing a calibration curve with aqueous ovalbumin solution at different concentrations (between 0 and 10 µg/mL) obtaining a LOD 10^{-3} µg/mL (RSD 5%).

The selectivity was assessed by testing the biosensor in presence of different proteins solutions (casein, collagen, bovine serum albumin), at a concentration of 0.1 µg/mL, directly applied on the SPE. The results revealed that the immunosensors was not significantly affected by cross-reactivity with other proteins or by non-specific interaction by assay reagents to the electrodes.

To assess the applicability of the developed immunosensor on real samples, the device was employed for investigation of paint mock-ups. Particular attention was devoted to the possible presence of spurious materials on the painting surface, such as dust and/or pigment particles, which may be entrapped into the gel and interact with the electrodes, inducing not specific variation of the current signal. The results indicated that the tool successfully detects OVA albumin in samples where egg is used as a binder. The capability to extract proteins from the painted surface without compromising their stability was thoroughly evaluated, taking into account two potential effects: i) removal of pigments and ii) presence of gel residues on the surface.

3. Conclusions

The developed biosensor enabled non-invasive extraction and identification of ovalbumin, which is used as a binder and coating in paintings. his achievement was accomplished by employing a combination of Gellan gel with electro-immunochemical detection. This research thus represents a step towards the development of a new generation of simple analytical devices suitable for performing sensitive and quantitative on-site analyses, leading to future multiplex-systems for a simultaneous detection of different binders.

References

K. Retko *et al.*, “*Herit. Sci.*, 8, 1, 1–13, 2020
R. Vinciguerra *et al.*, *Microchem. J.*, 144, 319–328, 2019
G. Sciutto *et al.*, *Anal. Chim. Acta*, 831, 31–37, 2014
L. Micheli *et al.*, *Microchem. J.*, 138, 369–378, 2018

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CODEX4D – 4D VOYAGE IN THE MANUSCRIPT

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1. Introduction

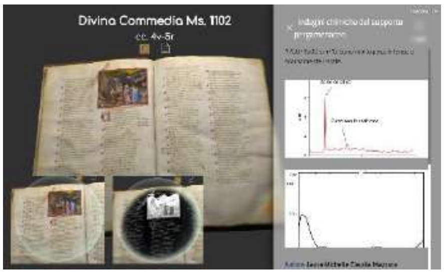
The ancient codex is a complex object with a living body composed of many materials, an organism that must be protected and exploreted. The manuscript is in fact the fruit of craft skills that may have been censored, hidden and dismembered. All these stories are imprinted in its material and are part of its value as a testimony. This is the context for the Codex 4D project, conceived by the CNR's ISPC and the Department of Industrial Engineering of the University of Rome Tor Vergata, in collaboration with the Biblioteche Angelica and Casanatese (Rome)[1]. The project aims to develop a methodology that, starting from the digital acquisition of the book, develops solutions for its 3D visualisation. The aim is to add the fourth dimension, that of depth in the artefacts, revealing elements that enhance knowledge of the property, such as the chemical, physical and biological state of the constituent materials, thus enabling a multidisciplinary experience with the manuscript.

2. Results and Discussion

As part of an experimental effort, manuscripts that are among the most priceless in the collection kept at the Angelica Library have been analyzed to date, including the De Balneis Puteolanis, Divina Commedia manuscript 1102, and the Libro d'Ore[1]. Obviously, the determination of the composition of the materials as well as their state of degradation is a necessary step to determine the suitable restoration and conservation processes of artworks. The most cutting-edge methods for documenting were employed, starting with colorimetry, X-ray fluorescence, infrared reflectance, and Fourier-transform infrared spectroscopy performed right in the restoration labs. In parallel, using dry cleaning sponges, particular areas of the manuscripts have been cleaned, and the elements that have been removed are analyzed at the labs of "Tor Vergata" University using destructive methods such as high-performance liquid chromatography and non-destructive methods such as FT-IR-ATR[2]. In this way, we were able to characterize the paper support without harming the manuscript.

3. Conclusions

In conclusion, for the ancient code model in 4D a non-invasive sampling approach has been developed based on an analysis of the substances that cleaning sponges absorbed when dry cleaning paper. The spectroscopic analysis was done to validate the chromatographic results using portable equipment. Additionally, the composition, degree of deterioration, and ink composition of the manuscripts have all been determined.



The 4D model of the manuscript.

References

codex4d.https://codex4

Titubante, M., Giannini, F., Pasqualucci, A., Romani, M., Verona-Rinati, G., Mazzuca, C., & Micheli, L. (2020). Towards a non-invasive approach for the characterization of Arabic/Christian manuscripts. *Microchemical Journal*, *155*, 104684.

POS49

TEMPORAL MONITORING OF DETERIORATION INDUCED BY ATMOSPHERIC AGENTS ON CALCARENITE ROCKS USING XPS DATA AND CHEMOMETRICS

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1. Introduction

Calcarenites are sedimentary rocks widespread in the Mediterranean area, used for centuries as a construction material thanks to their conjugation as 'soft rocks' of sufficient mechanical strength and good workability. The Gravina calcarenite played a crucial role in the construction of the historic *Sassi* district in Matera: initially favoring the settlements of cave-dwelling civilizations was then extracted and utilized for the urban expansion of this magnificent heritage, UNESCO site since 1993. However, calcarenite as a carbonate rock always faces challenges related to its weathering susceptibility. To preserve the historic fabric of the *Sassi* of Matera, conservation initiatives are focused on structural reinforcement, surface treatments to protect against weathering, and monitoring systems to assess the condition of the assets.

In this study, a block of calcarenite bricks was utilized as a model construction for investigating surface degradation, using X-ray Photoelectron Spectroscopy (XPS) as the characterization technique. The data sets obtained from the detailed analysis were employed to perform Principal Component Analysis (PCA) to evaluate the deterioration trend over time.

2. Results and Discussion

The Gravina calcarenite is a carbonate rock primarily composed of calcium carbonate in the form of calcite ($CaCO_3$) and small percentages (around 4%) of dolomite ($CaMg(CO_3)_2$). Additionally, small amounts of iron oxides, pyroxenes, micas, and apatite may be present [1].

In order to assess the early progression of alterations and the subsequent modifications of the calcarenite surfaces, a reference cube (approximately $1m^3$) made of calcarenite stones (33x15x15 cm), sourced from a local quarry, was located in a rural site of Basilicata, geographically not far from Matera [2], for the permanent exposition to outdoor conditions.

Samples for XPS analysis were suitable amounts of surface powders scraped from the calcarenite stones, collected at selected heights of all the exposed walls, signed by the cardinal directions, at regular time intervals of outdoor exposure for 6, 9, 12, 21 and 52 months.

As regards the reference samples, the initial analysis of the wide spectra showed the same photoelectron peaks from the powders collected along the four walls, as expected. Thus, they were considered four replicates of the same sample and the main signals of the detected elements were reported with the associated standard deviations. Qualitatively, the presence of carbon, oxygen, calcium, silicon, and aluminum, which are the elements constituting the rock, has been confirmed. Subsequently, higher-resolution detailed regions representative of each element identified in the wide spectrum were acquired and resolved into their constituent peaks using the curve-fitting program 'NewGoogly'[3].

During the first three months of exposure, there is no evident variation in the composition of the stone. After 6 months of exposure, the specimen already shows signs of degradation affecting the calcarenite walls. There is a discrepancy between the percentage of calcium related to calcium carbonate ($CaCO_3$) and the percentage of carbon related to carbonate (CO_3^{2-}). The excess carbonate could be attributed to the formation of calcium bicarbonate ($Ca(HCO_3)_2$) as well reported for carbonate stones affected by acidic rains [4]. As the exposure time increases, due to the deposition of particulates, the contribution of carbonate to the C1s total area decreases compared to the other carbonaceous components. No apparent forms of degradation of the aluminosilicate components have emerged, until 21 months, seemingly more resistant to degradation than calcite, as evident from the graph in **Figure 1,** where the averaged values of each component are reported with the relative standard deviation.

The Principal Component Analysis (PCA) was then applied on the data matrix related to powdered samples, including 18 samples collected at regular time intervals, the reference specimen and 8 variables, i.e. the different percentages of calcium, iron, silicon, aluminum, oxides and carbonate components. A total variance higher than 65% was explained by PCA, with the two first components able to explain the compositional variation of calcarenites under environmental exposure and extract the main indicators of degradation. The synergic investigation on XPS data, based on spectra curve-fitting and chemometrics, is promising and is currently in progress on a larger set of results.

3. Conclusions

An interesting interplay between XPS data elaborated by curve-fitting and their chemometric interpretation is shown in this work, to study calcarenite degradation over time. The XPS technique represents a useful investigative tool in addition to the most commonly used techniques in the field of cultural heritage. Furthermore, the information obtained from the chemometric analysis is consistent with the classic reprocessing of XPS data. This demonstrates how PCA, applied to XPS datasets, can be useful for the construction of models for the study of degradation processes, also applicable to real monumental heritages.

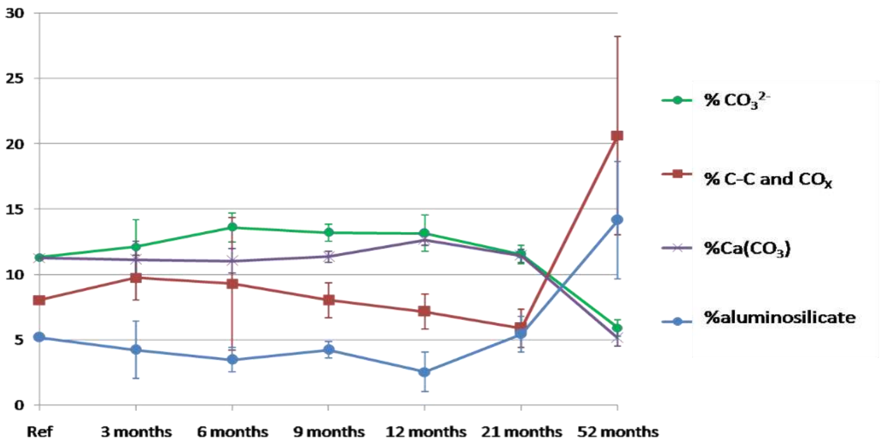

Figure 1. *The relative change of stone components of the calcarenite cube over 52 months of outdoor exposure*

References

[1] A.E. Bonomoet al.,Journal of Cultural Heritage 42 (2020) 191–201
[2] L. Scrano et al., Karaelmas Science and Engineering Journal 1/2 (2011) 1-14 and references therein.
[3] J.E. Castle and A.M. Salvi, Journal of Electron Spectroscopy and Related Phenomena 114 (2001) 1103-1113
[4] S.L. Stipp et al., Geochimica Acta 55(1990) 1723-1736

POS50

A REVIEW ON INORGANIC GASEOUS POLLUTANTS IN INDOOR SPACES HOUSING CULTURAL COLLECTIONS

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1. Introduction

The preservation of cultural collections is directly and indirectly affected by environmental conditions (both climate and pollution). If the monitoring of climate conditions is becoming a common practice and regolated by EU standards and guidelines, gaseous air pollution concentrations are rarely monitored in indoors. For this reason, the present contribution aims at providing a scientific literature review on gaseous inorganic pollutants monitored in spaces housing cultural collections. To the best of our knowledge, such a review has not been conducting so far.

2. Results and Discussion

Sixty-six scientific articles were selected through the PRISMA methodology (Page *et al.*, 2021) over the period 1984-2021 for a total number of 80 case studies mainly located in Europe (64%). The monitoring was mainly performed in museums and galleries (61%), specifically in exhibition rooms (79%). Active devices were rarely employed, whereas passive samplers, exposed *in situ* and then laboratory-analysed, were mostly used for nitrogen dioxide and sulphur dioxide monitoring. Direct-reading continuous devices were widely used for ozone. It was found that average concentrations of ozone were below 5 ppb in only 50% of cases, nitrogen dioxide below 10 ppb in more than 60% of cases, nitrogen monoxide below 5 ppb in 30% of cases, nitric and nitrous acid below 1 ppb in less than 50% of cases, sulphur dioxide below 2 ppb in more than 60% of cases, hydrogen sulphide below 0.1 ppb in only 25% of cases. The lowest concentration values were usually associated with the use of mechanical ventilation systems equipped with air filters and with non-urban case studies.

3. Conclusions

The low number of scientific articles and case studies can be due to the difficulties to perform monitoring in spaces housing cultural collections with the features of current sensors, usually developed for outdoor air pollutants measurements.

References

Page, M. J., McKenzie, J. E., Bossuyt, P. M., Boutron, I., Hoffmann, T. C., Mulrow, C. D., Shamseer, L., Tetzlaff, J. M., Akl, E. A., Brennan, S. E., Chou, R., Glanville, J., Grimshaw, J. M., Hróbjartsson, A., Lalu, M. M., Li, T., Loder, E. W., Mayo-Wilson, E., McDonald, S., … Moher, D. (2021). The PRISMA 2020 statement: An updated guideline for reporting systematic reviews. The BMJ, 372, 1–9. https://doi.org/10.1136/bmj.n71

POS51

THE ART OF WAR FRIEZE IN THE DUCAL PALACE OF URBINO: MATERIAL, EXECUTIVE TECHNIQUES AND CONSERVATION ISSUES

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1. Introduction

The Art of War frieze (Fig. 1) is formed by 72 stone bas-reliefs that in the late 15th century were positioned on the plinth running along the sides of the facade of the Urbino Renaissance Ducal Palace (Marche Region, Italy). The frieze, probably elaborated by Federico da Montefeltro around 1474, illustrates a rich iconographic repertoire depicting numerous engineering machines and symbols related to the military and political spheres (Petrini et al. 2022). There is no certain information regarding the design of the frieze, its chronology, the order of the bas-reliefs arrangement and the debate concerning their execution appears even more complex (Petrini et al. 2022). Regarding the stone material, Baldi (1590) mentioned the use of local *Travertine of Piobbico* (Amadori 1985). The bas-reliefs originally decorated the facade from its creation until 1756 when they were positioned in the Soprallogge for conservation purposes (Bernini Pezzini 1985). This paper aims to clarify the debate concerning the original arrangement of the bas-reliefs, the constituting material and the executive technique Some aspects concerning conservation issues were also considered.

2. Results and Discussion

Nine representative samples were collected from the frieze (Fig. 1) and investigated using polarized light microscopy (PLM), scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM/EDX), Fourier Transform Infrared spectrometer (FTIR). A microclimate measurement campaign was carried out in the Chancellery room from November 2019 to December 2020 using data loggers to collect temperature (T) and relative humidity (RH) values. On the basis of PLM investigation, the samples can be classified as packstone (Dunham 1962) attributable to the Calcare Massiccio A Formation, locally known as *Female Travertine* of Piobbico (Amadori 1985; Bani1989). According to the traces observed in the bas-relief's surfaces, cord/running drill, roundel chisel, claw chisel, point chisel, channeling tool, tooth chisel and rasp were probably used. In most cases, the technique used for the surface finishing is rather quick and inaccurate. By distinguishing various bas-relief groups on the basis of specific features and by comparing the same subject (flowers, leaves, etc.) carved in different panels, it was possible to highlight certain differences in both style and execution. SEM investigation highlighted the presence of fissures and microcracks confirming the decohesion phenomena observed in most of the bas-reliefs surface. Fe-based red traces covered both the patina and the deteriorated surfaces of a few bas-reliefs. FTIR analysis of yellowish external patinas (Fig. 1) detected calcium oxalate (predominantly trihydrate, monohydrate and dihydrate), sulphates, and silicates. Caoxite, a rare trihydrate Ca-oxalate, was identified due to both the strong signals at ~1323-1324 cm^{-1} and the OH stretching at 3526, 3422 and ~3270 cm^{-1} (Contia et al. 2015). The Ca-oxalates presence could be related to a consequence of the oxidative degradation of ancient organic treatments applied on the stone surface during the centuries (Camaiti et al. 1996) or they could be a product of past lichen colonization (Cariati et al. 2000). In addition to gypsum, an acrylsilane resin (Wu et al. 2014) was detected in two samples, while dialkyl silane oligomer (Launer and Arkles 2013) was identified in one sample. As Ducal Palace is located on the top of one hill (450 m altitude), the climate conditions of the area mainly caused the various deterioration typologies that affected the Frieze even if it remained there for ~200 years. Moreover, anthropic factors and the frequent displacement of the stone panels also contributed to the worsening of their state of conservation. The main decay typologies are loss of parts, abrasion, differential erosion, alveolization, detachment, mechanical damage, patinas and rare biological attacks. According to microclimate monitoring carried out in the Chancellery room, major variations in temperature occurred especially between April and November but this parameter always remained below 30°C. Compared to T, RH is characterized by greater fluctuations, mostly between July and November with an average value of 50-60% (therefore respecting the recommended range) that in some cases reached even 70% and 30%.

The anomalous trend of T and UR, such as in November, can be explained by the outdoor Urbino climate condition as this month is the wettest and rainiest month of the year.

3. Conclusions

The Renaissance Art of War frieze was carved by different sculptors using Calcare Massiccio (type A), locally called *Female travertine of Piobbico*, excavated from the quarries located 35 km away from Urbino. The main tools used in the various stages of execution were cord/running drill, different typologies of chisels, channelling tool and rasp. The presence of calcium oxalate may be related to conservation treatment or/and to a lichens/fungal biological activity. The decay typologies are mainly due to weathering phenomena that occurred at the frieze during the two centuries of its exposure on the façade. T and RH parameters detected in the Chancellery room respected the recommended range but as the data variations did not always occur in a constant manner this could compromise the stone surface integrity.

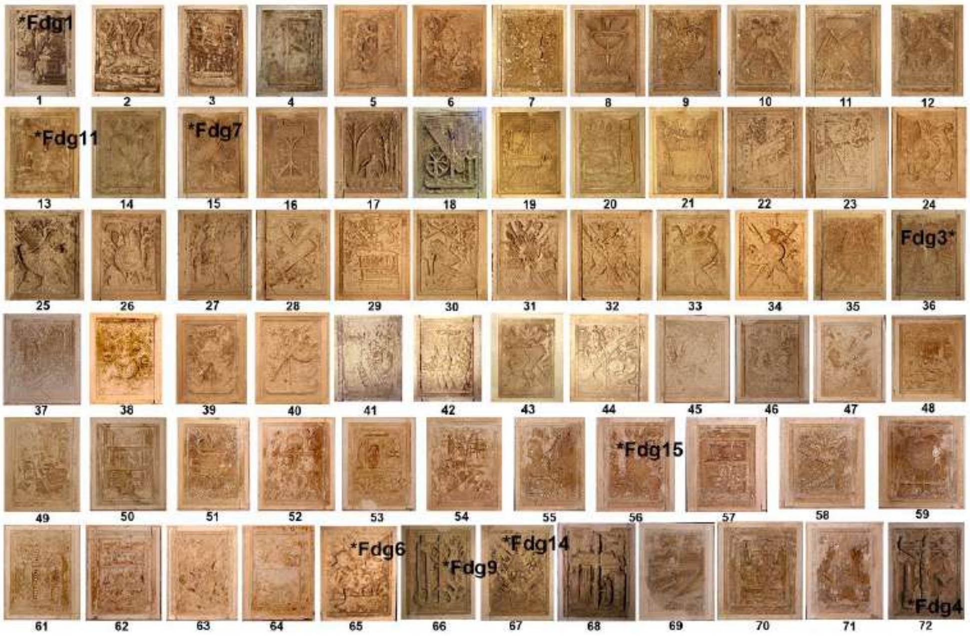

Fig. 1 Bas-reliefs of the War Frieze, Ducal Palace of Urbino, progressive number and sampling location

References

Amadori ML (1985b) Studi e Ricerche sulle Pietre del Palazzo Ducale. In: Polichetti ML (ed) Il Palazzo di Federico da Montefeltro, Quattroventi, Urbino, 1, pp 715-727.

Camaiti M, Fommei C, Giammello M, Sabatini G, Scala A (1996) Trattamenti di superfici lapidee secondo antiche ricette: primi risultati sulla formazione di ossalati di calcio. In: Realini M, Toniolo L (eds) The oxalates Films in the Conservation of Works of Art, Editeam, Castello d'Argile (BO), pp 285-298.

Cariati F, Rampazzi L, Toniolo L, Andrea Pozzi A (2000) Calcium Oxalate Films on Stone Surfaces: Experimental Assessment of the Chemical Formation. Stud. Conserv. https://doi.org/10.2307/1506764

Conti C, Casati M, Colombo C, Possenti E, Realini M, Gatta GD, Merlini M, Brambilla L, Zerbi G. (2015) Synthesis of calcium oxalate trihydrate: New data by vibrational spectroscopy and synchrotron X-ray diffraction. Spectrochim Acta A Mol Biomol Spectrosc. https://doi.org/10.1016/j.saa.2015.06.009

Dunham RJ (1962) Classification of Carbonate Rocks According to Depositional Texture. In: Ham, W.E., Ed., Classification of Carbonate Rocks, AAPG, Tulsa, 108-121

Launer P, Arkles B (2013) Infrared Analysis of Organosilicon Compounds. In: Arkles B, Larson GL (eds) Silicon Compounds: Silanes & Silicones. Gelest Inc. Morrisville, PA, pp. 175-178.

Pietrini D, Graziani P, Sorini L (eds) (2022) Libro de viva pietra: Studi sul fregio della facciata del Palazzo Ducale di Urbino. Urbino University Press, Urbino. https://press.uniurb.it/index.php/urbinoelaprospettiva/catalog/view/25/33/192

Wu J, Ma G, Li P, Ling L, Wang B (2014) Surface modification of nanosilica with acrylsilane-containing tertiary amine structure and their effect on the properties of UV-curable coating. J. Coat. Technol. Res. https://doi.org/10.1007/s11998-013-9552-9

POS52

ADVANCE IN LEAD-ZINC-BARIUM TYPE GLAZED WARMING BOWL RELATED TO THE XUANDE EMPEROR (1426-1435)

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1. Introduction

A rare Chinese polychrome glazed warming bowl related to the reign of the Xuande emperor (1426-1435 AD) was investigated using: digital microscope, portable X-ray fluorescence spectrometer, X-radiography, micro-computed tomography (CT) and scanning electron microscopy with energy dispersive X-Ray detector (SEM/EDS). According to the results, the chemical composition of the ceramic glaze belongs to the lead-zinc-barium-silicate (PbO-Zn-BaO-SiO2) system. This unexpected data is in contrast with the common knowledge attesting that the addition of barium in the making of glass and ceramic disappeared soon after the Han dynasty (206 BC-220 AD). Moreover, the combination of PbO-Zn-BaO seems to be rare both in ancient pre-Han and during the Ming and Ching dynasties. Therefore, this paper aims to demonstrate that (a) the use of barium for glaze and glass, which seems to have its roots in Taoist alchemy, wasn't totally halted in later periods respecting to Han dynasty; b) lead-zinc-barium glaze was used during Xuande emperor.

2. Results and Discussion

The glazed Chinese polychrome ceramic is a double-walled bowl with a circular hole at the foot that was used to fill the inner part with hot water, keeping both the ceramic and the content warm. Probably this cavity also allowed the gas leak during the firing process avoiding the ceramic breaking (Figure 1a,b,c). Three dragons with five claws decorate the front of the Xuande bowl and six dragons on the back. According to an imperial edict, this iconography was related to the Emperor of the Yuan Dynasty (1279-1368) (Y. Lu et al. 2014). The blue mark on the back of the bowl indicates that it was made between 1426 and 1435, during the reign of emperor Xuande belonging to the Ming dynasty. X-radiography and X-ray micro-computed tomography were valuable tools for understanding the structure and the different materials used in the glaze decoration (Fig. 1b,c). ED-XRF analysis of the white glaze showed the presence of Si, Pb, Ba, Ca, Al, K, Fe and Zn (Fig. 1d). The green areas are mainly based on Cu; Fe is very high in red and yellow details; as expected Mn and Fe were detected in the blue mark; Mn was also used to obtained grey hue. SEM/EDX analysis (Fig. 1e) confirmed that the ceramic glaze belongs to the lead-zinc-barium-silicate (PbO-Zn-BaO-SiO2) system (Wood 2023). This unexpected data is in contrast with the common knowledge attesting that the addition of barium in the making of glass and ceramic disappeared soon after the Han dynasty (206 BC-220 AD) (Ma et al. 2021). The addition of barium-bearing material to achieve a jade-colour opacity is attested in the early Chinese glasses (Živković 2019) and the low-fired barium-lead glazed pottery is documented in China during the early Warring States period (453-221 BC) but it disappeared soon after the Han dynasty (206 BC-220 AD) (Kim 2012 and references therein). According to the literature data, the combination of PbO-Zn-BaO seems to be rare both in ancient pre-Han and during the Ming and Ching dynasties (Wood 2023). The presence of Pb-Ba-Zn glazes was also detected in Jingdezhen blue and white porcelains from the Yuan dynasties, Ming and Qing (Wu et al. 2000) and in an imported ceramic from Bahlā, a large oasis town in central Oman, dating back to the 17th century AD (Živković 2019). Anyway, Pb-Zn presence could suggest the exploitation of a single source for the lead-zinc raw material (Klein 2023 and references therein). According to three Chinese dictionaries ("Kāngxī zìdiǎn", "Guǎngyùn" and "Jíyùn") the "Kāngxī zìdiǎn" (Kangxi Dictionary) the use of barium (鋇 bèi) in ceramics and therefore the presence of this ancient manufacturing technique is mentioned in subsequent periods very distant from the early Warring States period and the Han dynasty (Yushu et al. 2016) and its importance is recalled in numerous sources from the XVI to XIX centuries, with the indication that only men of a certain rank and social influence could possess similar riches (Yuan 1989). Moreover, the mines of barium and other metals were under imperial control and there were very severe edicts that prevented their access (Rickett, 1985). Minerals containing lead, barium and zinc are found in several deposits such as those of Jinding, Lehong and Huize (Tang 2017; Li 2023; Yang 2023).

3. Conclusions

The Chinese ceramic could be associated with models called Zhūgé (诸葛) and Kǒngmíng (孔明), referring to the warming bowls (碗 wǎn) made during the period of the Ming (1368-1644) dynasties. The ceramic glazes belong to the lead-zinc-barium-silicate (PbO-Zn-BaO-SiO2) system suggesting a particular production prospered during the brief reign of the Xuande emperor. The green colour can be attributed to the dissolution of Cu in the glass matrix; iron was used to obtain red and yellow hues; Mn was used in the grey detail and together with Fe in the blue mark. Starting from the review of ancient Chinese literary sources we found a lot of unpublished information on the use of barium and lead/zinc in the production of glazed ceramics during the age and also on the ancient mines located in the Yunnan area.

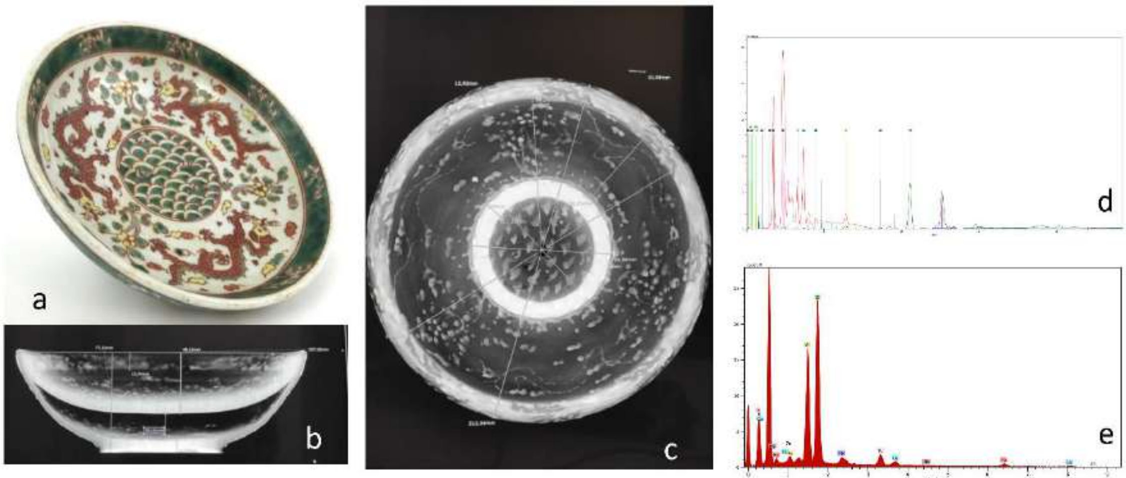

Figure 1 (a) Xuande ceramic warming bowl; (b, c) X-ray radiography; (d) ED-XRF spectrum of the glaze; (e) SEM/EDX spectrum of the glaze.

References

Klein S., Fischer-Lechner S., Berthold C., Sessing J., Kirnbauer· T., Zeiler M., Essling-Wintzer W. (2023) Lead-Glazed Ceramic Fragments: Intentional Glazing or Metallurgical Accident?, Metallography, Microstructure, and Analysis.

Kim F.C. (2012), Early Chinese lead barium glass: its production and use from the Warring States to Han periods (475 BC-220 CE). Dissertation, John Brown University: 12

Lu Y., Qian C., He H., (2014), A history of Chinese science and technology, Volume 2, Heidelberg, p. 392.

Li Y., Kong Z., Zhang C., Wu Y., Yang X., Wang Y. Chen G., (2023), Pore Variation Characteristics of Altered Wall Rocks in the Huize Lead–Zinc Deposit, Yunnan, China and Their Geological Significance, Minerals 2023, 13, 363, 3,7,8.

Ma Q., Braekmans D., Shortland A., Pollard A. M. (2021), The Production and Composition of Chinese Lead-Barium Glass through Experimental Laboratory Replication, Journal of Non-Crystalline Solids 551, 2.

Rickett W. A. (1985),《管子》 "Guǎnzǐ", (1995), Taipei. Guanzi, Political, Economic and Philosophical Essays from Early China, Princeton University Press, Princeton.

Tang Y., Bi X., Fayek M., Stuart F.M., Wu L., Jiang G., Xu L., Liang F., (2017), Genesis of the Jinding Zn-Pb deposit, northwest Yunnan Province, China: Constraints from rare earth elements and noble gas isotopes, Ore Geology Reviews 90, 976.

Wood N. (2023), Chinese Glazes. Their Origins, Chemistry and Re-creation, Herbert Press, London, 187.

Wu J., Leung P. L., Li J. Z., Stokes M. J., Li M. T.W (2000), EDXRF studies on blue and white Chinese Jingdezhen porcelain samples from the Yuan, Ming and Qing dynasties, X-Ray Spectrom 29, 239–244.

Hao Zou Y.L., Said N., Liu H., (2023), A new classification of barite deposits in China, Ore and Energy Resource Geology 14, 7.

Yuan W., Changling H. (1989), "Huángcháo jīngshì wén biān" 《皇朝經世文編》, 台灣大學 (Taiwan University).

Yushu Z., Tingjing C. et al. (2016),《康熙字典》 "Kāngxī zìdiǎn", by, 吉林文史出版社 , Jilin Literature and History Publishing House.

Živković J., Power T., Georgakopoulou M., Carvajal López J.C. (2019), Defining new technological traditions of Late Islamic Arabia: a view on Bahlā Ware from al-Ain (UAE) and the lead-barium glaze production, Archaeological and Anthropological Sciences 11, 4705.

POS53

BIOTIC TRANSFORMATION PRODUCTS OF SULFONAMIDES IN ENVIRONMENTAL WATER SAMPLES: HIGH-RESOLUTION MASS SPECTROMETRY-BASED TENTATIVE IDENTIFICATION BY A SUSPECT SCREENING APPROACH

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1. Introduction

The presence of pharmaceuticals in the aquatic environment is mainly due to their release from the effluents of the wastewater treatment plants (WWTPs), which are unable to completely remove them and their transformation products (TPs). Sulfonamides (SAs) are synthetic antibacterial drugs used to treat both human and animal infectious. In particular, SAs are widely used in veterinary medicine, due to their low cost and high efficacy against some common bacterial diseases; in 2018, they were the third most sold veterinary antibiotic class in Europe [1]. SAs can undergo several transformation pathways, which are further affected by environmental factors, and for these reasons both parent compounds and their TPs have been detected in surface water as well as in the WWTP effluents [1], at concentration levels from ng L^{-1} up to µg L^{-1}. Acetylation is one of the most studied transformations and it can stem from the metabolism of organisms or SA degradation in municipal WWTPs or in the environment [2]; furthermore, an acetylated SA could transfer back to its parent SA [1]. However, many TPs are still unknown, and the impact on the environment and human health of the known TPs is still unclear since ecotoxicity data on single TPs are lacking [1].

Monitoring SA TPs should be important as well because they could still exert some pharmaceutical activity; however, many TPs are still unknown since several transformation processes are possible (e. g. human and animal metabolism, WWTP activities, environmental factors etc.). In this work [3], three of the most used SAs, i.e., sulfamethoxazole (SMX), sulfapyridine (SPY), and sulfadiazine (SDZ), were incubated for 20 days in a batch reactor with activated sludge under controlled conditions. Then, the experiment was stopped, and the water sample was subjected to SPE. Two sorbents, i.e., Oasis HLB and graphitized carbon black (GCB), were tested. The ultra-high performance liquid chromatography-HRMS analysis was carried out in untargeted detection mode, whereas the software-assisted tentative identification of the most abundant SA TPs was performed following a suspect screening workflow based on the literature data. Finally, the m/z values of the identified TPs were used to create an inclusion list for the HRMS-based suspect screening of WWTP effluent samples.

2. Results and Discussion

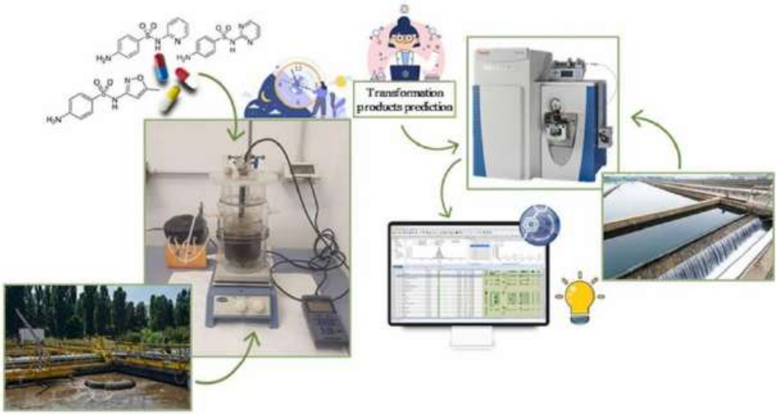
The extraction protocol was optimized for the simultaneous analysis of SAs and their TPs. Sorbent choice was necessary because SAs and their TPs can have a wide range of polarity and structural differences. Two different sorbent materials were tested for this purpose, i.e., GCB and Oasis HLB, using a mixture of 10 compounds chosen from the SA class and the related TPs, for which analytical standards were commercially available. Oasis HLB is a hydrophilic/hydrophobic polymeric material very popular in environmental applications because of the sorption affinity for diverse compounds in a wide polarity range and the stability from pH 0–14. GCB is a non-porous carbon material made up of interconnected and layered graphitic sheets; the peculiar structure allows different kinds of interactions, both hydrophobic and polar ones, with a wide range of analytes and can, therefore, be used for both polar and non-polar compound extraction and clean-up [4]. The results showed that both sorbents yielded high recoveries, consistent with the literature, but GCB gave better results at lower concentrations, which is mandatory in environmental studies due to the complexity of the matrix and the extremely low abundance of TPs. The better RE of the GCB sorbent could be explained by the different pH of the extraction procedures because SAs have pK2 values around 2.5 [5]. Therefore, the GCB sorbent was selected for sample preparation.

The raw data files were processed with Compound Discoverer, and 44 TPs (18, 13, and 13 TPs for SMX, SPY, and SDZ, respectively), including multiple TPs, were manually validated. To overcome the limitation of the DDA, the identified TPs were used in an inclusion list to analyze WWTP samples by a suspect screening approach. In this way, 4 SMX TPs and 5 SPY TPs were tentatively identified together with their parent compounds. Among these TPs, 5 of 9 were acetylated forms, in agreement with previous literature reporting that acetylation is the predominant SA transformation.

3. Conclusions

In this work, an analytical workflow for SAs and their TPs monitoring has been developed; as these analytes are diverse but also possess a similar core structure, the method allows to search for an entire class of compounds by combining the untargeted MS analysis with the suspect screening identification approach. By knowing the potential sites of derivatization, and collecting knowledge of the possible transformation reactions, it was possible to search the experimental MS/MS data for the resulting compounds. The approach was applied to three main SAs and studied in simulated laboratory conditions. The advantage of this approach is that precursor compounds and their TPs are present in a considerable amount and can be detected by the automated software processing with Compound Discoverer and manually validated. The results of this study provided that of all the potential compounds, 18 for SMX and 13 for both SPY and SDZ were detected in the batch reactor simulation. These compounds were then used to generate an inclusion list for MS/MS acquisition, so to bypass the sensitivity problems often observed in the environmental analysis of these compounds. The method was finally tested on WWTP samples and confirmed that acetylated products are indeed the most common TPs observed in these samples. Also, compounds such as TP 256 and TP 284, as well as TPs that were never reported before (e.g. TP 274), could be tentatively identified by the developed approach.

Applying this analytical strategy to other relatively homogeneous classes of contaminants will open a way to improve the knowledge of TPs by an automated and systematic screening of potential compounds. Manual validation is necessary only at the end of the analytical workflow, with optimization of knowledge over analysis time.



Graphical Abstract

References

[1] N. Puhlmann, O. Olsson, K. Kümmerer, Transformation products of sulfonamides in aquatic systems: lessons learned from available environmental fate and behaviour data, Sci. Total Environ., 830 (2022), Article 154744, 10.1016/j.scitotenv.2022.154744

[2] H. Cui, H. Chang, H. Zheng, Y. Wan, Determination and occurrence of sulfonamide transformation products in surface waters, Sci. Total Environ., 779 (2021), Article 146562, 10.1016/j.scitotenv.2021.146562

[3] C.M. Montone, B. Giannelli Moneta, S.E. Aita, A.L. Capriotti, A. Cerrato, A. Laganà, A. Marchetti, S. Piovesana, M. Villano, C. Cavaliere, Biotic transformation products of sulfonamides in environmental water samples: High-resolution mass spectrometry-based tentative identification by a suspect screening approach, J. Pharm. Biomed. Anal., 227 (2023), Article 115292, 10.1016/j.jpba.2023.115292

[4] C.M. Montone, B. Giannelli Moneta, S.E. Aita, F. Aulenta, C. Cavaliere, A. Cerrato, S. Fazi, A. Laganà, V. Paolini, F. Petracchini, S. Piovesana, A.L. Capriotti, Untargeted analysis of contaminants in river water samples: comparison between two different sorbents for solid-phase extraction followed by liquid chromatography-high-resolution mass spectrometry determination, Microchem. J., 172 (2022), Article 106979, 10.1016/J.MICROC.2021.106979

[5] M.E. Lindsey, M. Meyer, E.M. Thurman, Analysis of trace levels of sulfonamide and tetracycline antimicrobials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry, Anal. Chem., 73 (2001), pp. 4640-4646, 10.1021/ac010514w

POSSP1

RAMAN SPECTROSCOPY IN ARCHAEOLOGICAL STUDIES

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1. Introduction

Chemical identification is an important part of the study of archaeological artefacts and artworks. This information can be obtained through nondestructive Raman analysis directly within the environment in which the artefacts are discovered. This information is extremely helpful in forming the basis of identifying pigments, dyes and paints used; thus indicating when and how a piece was made, giving insight into the time period of creation, and suggesting the authenticity of the object.

Raman spectroscopy can be used to measure lower frequency vibrations (than, for instance, FTIR) and this region below 500cm-1 provides rich information for characterization of minerals and inorganic materials, such as pigments. By analyzing the Raman spectrum, we can also determine differences in polymorphic forms of pigments. The instrument portability allows for on-site analysis without the need to remove samples and disrupt important archaeological sites. Portable Raman instruments such as the i-Raman® series are equipped with a fiber optic probe, which makes it easy to reach samples in different environments.

2. Results and Discussion

The instrument portability and fiber optic probe can be used to measure samples of different shapes and sizes, without requiring sample preparation. The system laser power can be adjusted at 1% increments, allowing for use of low laser power (3mW). Such versatility with the laser power control makes this system ideal in work with difficult samples such as dark pigments.

A recent study used portable Raman in the characterization of prehistoric paintings on the Abrigo de los Chaparros (Albalate del Arzobispo, Teruel) on the Iberian Peninsula.1 The rock paintings were found in open-air shelters, making Raman measurements challenging due to sunlight and wind, as well as dust and crusts that have developed on the surface which can obscure the Raman signal of the pigments. A flexible foam rubber cap (Càrol's cap) was designed and utilized in the study to minimize these environmental interferences on the Raman spectra. A spectrum collected in daylight of finger dots in the cave is shown in Figure 1, where peaks of haematite (h) can be seen in addition to those attributed to crusts containing whewellite (w) and gypsum (g).

B&W Tek's portable Raman spectrometers are also being used in a comprehensive study of the materials used in the plasterwork in vaults of the Alhambra Hall of Kings, one of Spain's most important cultural sites2, 3. This work which has been ongoing for several years is the study of the material in the plasterworks, focusing on the technologies in the application of the plasterworks and the decay they have undergone over the centuries. Figure 2 shows a schematic of the Hall of Kings indicating the location of the Raman instrument coupled to a microscope head on the scaffolding 12m above ground, as well as pictures of the instrumentation and the video microscope with a motorized stage on a tripod mounting.

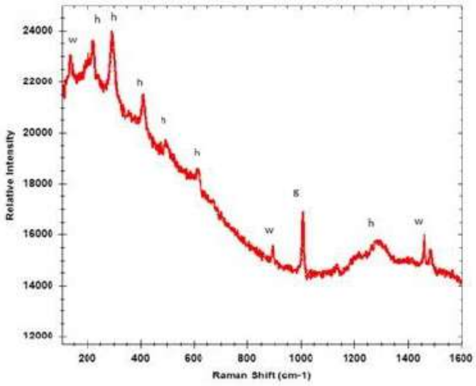
Raman spectra were measured on the decorations of the stalactite vaults of the Alhambra without removing samples, thus maintaining the integrity of this important cultural heritage site while being able to study a larger area of the site. These decorations are built in gypsum and decorated in many colors reflecting the Islamic style. Different typical antiquity pigments have been identified, and from the details of the spectra of lapis lazuli the geographic origin can also be identified. Blue is a predominant color in Islamic art, and originates from the mineral lazurite to form lapis lazuli pigment. Figure 3 shows spectra of blue decorations in the vault and natural and synthetic blue pigments, all of which have the characteristic peak of the lazurite mineral at 548 cm-1.

The pigments cinnabar and minium provide the red color in the vaults' decorations. These were found in different parts of the vaults, and appear to be used together in some decorative motifs. Spectra of the cinnabar were collected over the gypsum substrates. From the collected data, not only are the pigments able to be identified, but also the degradation that they are undergoing. White coloring due to the degradation product calomel is present and detectable in the cinnabar Raman spectra as seen in Figure 4, which also include signal at 1009 cm-1 from the gypsum over which the pigments are applied.

Many of the gilded parts of the decorations have suffered from decay, and are not as widely present, so in situ analysis is often the only means of characterizing these limited (and often difficult to access) sample regions3. Black area in the vaults near the gilding are consistent with tin oxides, suggesting that tin foil was used in place of gold in the gilding, perhaps during later restorations.

3. Conclusions

Portable Raman spectroscopy is an invaluable tool in the study of archaeological sites, allowing for in situ analysis which minimizes the impact of such studies on important cultural sites. The flexibility of the use of a fiber optic probe and tripod-mounted video microscope with a light weight instrument reduces the need for sampling, and increases the ability to make representative measurements over what can be very large sample areas. With laser power adjustable to low levels, there is flexibility and control to work with difficult dark pigment samples. The information content of Raman spectroscopy is assisting in the understanding of the materials used in the construction and restoration of important archaeological sites, and in understanding the degradation that is occurring which should aid in preservation and restoration work.



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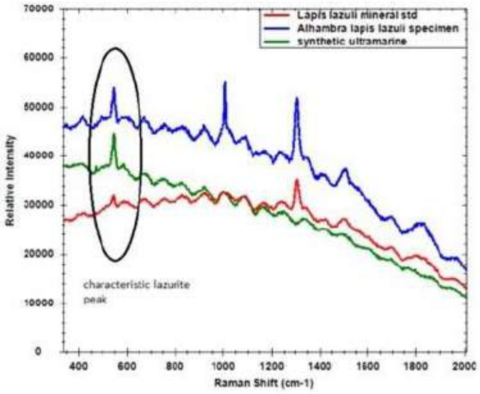

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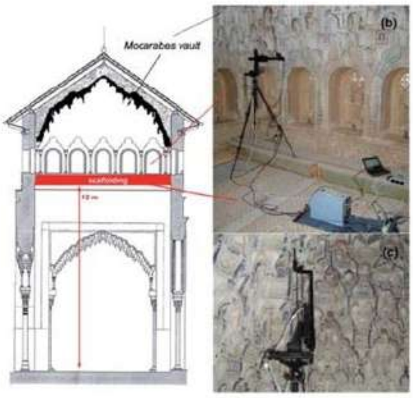

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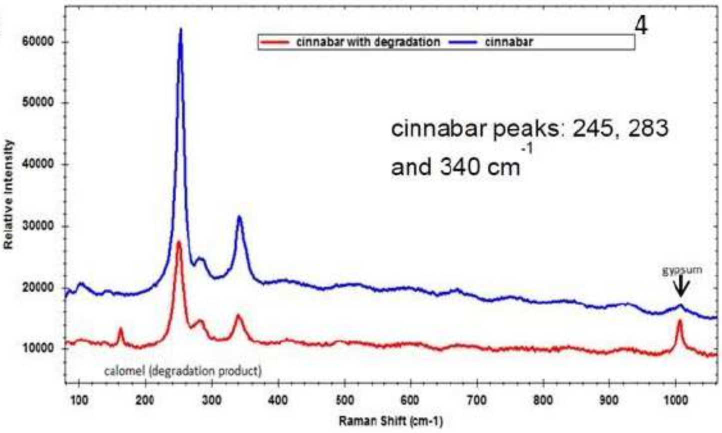

4

QUANTIFICATION OF MICROPLASTICS IN AIRBORNE PARTICULATE - A COMMON SAMPLE PREP PROTOCOL SUITABLE FOR MASS AND MORPHOLOGY IDENTIFICATION

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1. Introduction

The increasing use of synthetic materials has made plastic pollution an important environmental problem, including microplastic particles in various environments. These pollutants pose risks to human health and ecosystems. A major concern is the possibility of plastic particles being dispersed into the air as particles and inhaled by humans, which can harm respiration and other body systems, so it is important to study microplastics as an air pollutant. In this work is proposed a mass quantification through pyrolysis GCMS preceded by a dedicated sample preparation. Sample prep described in this work does not involve, as final step, filtration which let to analyze an aliquot of microplastics with a spectroscopy technique like LDIR (laser direct infrared).

2. Results and Discussion

The Py-GC-MS analysis performed on the powder recovered was characterized by around 45% of NP species, and by PS (41.7 %) and ABS (6.2 %) as the most abundant polymers. The analysis also highlighted the presence of significative amounts of PVC (4.7 %) and PC (1.9 %). Only traces of PP and PMMA were detected, with values below 1 %. The results obtained by Py-GC-MS analysis on the indoor particulate recovered from two filters at different sizes fractions were significatively different, both in terms of amount of NP residues and of polymer distributions, thus suggesting a size distribution of the typologies of materials/polymers. Sample preparation is detailed described and tested. Spectroscopy data are under development but sample preparation is perfectly suitable for both techniques.

3. Conclusions

The proposed method was found to be efficient in detecting both microplastics and polymer additives in airborne particulate matter. Sample preparation protocol can be used not just for detecting airborne particles but also microplastic in general coming also from other matrixes.

References

1 - Pomata, Donatella and La Nasa, Jacopo and Biale, Greta and Ceccarini, Alessio and Di Filippo, Patrizia and Riccardi, Carmela and Buiarelli, Francesca and Modugno, Francesca and Simonetti, Giulia, Plastic Breaths: Quantification of Microplastics and Polymer Additives in Airborne Particulate. Available at SSRN: https://ssrn.com/abstract=4421205 or http://dx.doi.org/10.2139/ssrn.4421205

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