

Selective adsorption of toluene and n-hexane binary mixture from aqueous solution on zeolite ZSM-5: evaluation of competitive behavior between aliphatic and aromatic compounds.

E. Rodeghero^a, T. Chenet^b, A. Martucci^{a*}, M. Ardit^a, E. Sarti^b, and L. Pasti^{b**}

^aDepartment of Physics and Earth Sciences, University of Ferrara, Via Saragat, 1, I-44123 Ferrara, Italy

^bDepartment of Chemistry and Pharmaceutical Sciences, University of Ferrara, Via L. Borsari, 46, I-44123 Ferrara, Italy

Corresponding authors:

*Annalisa Martucci, mrs@unife.it

**Luisa Pasti, psu@unife.it

Keywords

ZSM-5, toluene, n-hexane, binary mixture adsorption, competitive behavior.

Abstract

In this study, high silica ZSM-5 was selected as an adsorbent for the removal of toluene (TOL) and n-hexane (HEX) binary mixtures from aqueous solution over a wide range of concentrations. In comparison with the single component systems, the binary mixture induced to a selective adsorption by the ZSM-5 zeolite. As a matter of fact, a selective adsorption, described by a competitive dual site Langmuir adsorption isotherm, is revealed where alkane compound is preferred to the aromatic one. Results from adsorption isotherm were related to the structural answer of the ZSM-5 framework as a function of a HEX-TOL equimolar binary mixture adsorption. Rietveld refinements provided information about the relative position of both molecules within the ZSM-5, and on the intermolecular distances between the adsorption sites of HEX and TOL. Residuals of electron density calculated by mean of delta Fourier maps indicated the presence of both guest molecules but with a clear indication of preferential towards n-hexane, and a clear differential adsorption site distribution. The occurrence of host-guest interactions in the narrow intracrystalline micropores between the solid catalyst and embedded molecules have been revealed.

1. Introduction

It's well known that zeolites represent a benchmark in the area of porous solid-state materials, with key applications in ion exchange (ion removal and water softening), adsorption, separation and gas storage, carbon dioxide sequestration, enhanced catalysis, smart sensors and drug delivery processes [1]. These functional solid-state materials comprise pure silica which can adsorb organic components from water as well as interact with guest molecules not only at the surfaces, but throughout the bulk of the material. Hydrophobic zeolites with modular compositions and tailorable cavities are very suitable for the encapsulation of non-polar guest molecules, thus allowing for their diffusion into porosities [2–7]. Microporous aluminosilicates with uniform and ordered networks and narrow intracrystalline micropores can strongly influence selectivity in catalytic reactions as well as diffusivity through their pore channels system [6]. Their application requires that these ~~catalysts~~ **materials** have to be active not only in a wide range of operative conditions but also during prolonged periods of time. Zeolites are relatively cheap adsorbents characterized by high stability in water, effectiveness towards aggressive chemical solutions, thus representing a viable alternative to other reactive media (e.g. carbonaceous resin, activated carbon, and ion-exchange resins) [3,8,9]. Both high surface area and pore volume combined with a specific shape selectivity, ability to host guest species, and a strong stability, make these solids suitable for the removal of environmentally concerned pollutants from water such as non-methane volatile organic compounds (NMVOCs) [10–15]. Adsorption is a rapid and economical method for NMVOCs removal from water and wastewater due to the universal nature of both soluble and insoluble contaminants removal. A wide variety of NMVOCs (i.e. aliphatic/aromatic hydrocarbons and their substituted compounds, organic acids and alcohols) is present in the environment and emitted from both anthropogenic (i.e. wastewater treatment plants (WWTPs), industrial and urban wastewaters, gasoline, solvents, urban and rural run-offs) and natural (i.e. vegetation and soil microbes, geogenic, lightning, and biomass burning) sources [16,17]. Different types of zeolites are efficient in non-methane volatile organic compounds adsorption (for instance, those with topology MFI, ITW, ERI, CHA, LTA, AFX, MOR, FER, BEA and silicalites). Their high efficiency (up to 90–99%) associated with low costs of maintenance and large functionality, make zeolites competitive towards other techniques and methodologies for NMVOCs removal from water bodies, such as reverse osmosis, ion exchange, electro-dialysis and electrolysis [10,12,16–35,37–43]. The adsorption efficiency of zeolites ~~as catalysts~~ could be improved or adjusted by controlling the hydrophobicity–hydrophilicity of the solid, the structure topology, the geometry of the environment of the active site and the chemical composition of the environment [6]. Due to the confinement effect, sorbate molecules in zeolites have been found to optimize van der Waals interactions with the zeolite walls by organising specific sites/microscopic cavity in order to match perfectly guests molecules size and shape to the zeolite

channel/cage size and shape [443]. Consequently, the comprehension of adsorption phenomena by combining batch adsorption and X-ray powder diffraction analyses can provide a powerful tool to understand the NMVOCs selective adsorption from aqueous on zeolites as well as microscopic details for the host-guest interactions governing the competitive behaviour in complex systems.

In this study we focus on the adsorption of two hydrocarbons: hexane (aliphatic) and toluene (aromatic) in order to: (i) evaluate ZSM-5 adsorption properties with respect to different type of hydrocarbons; (ii) evaluate the influence of adsorbent structure topology and NMVOCs size and shape on selectivity; (iii) gain information on location and orientation of organic compounds inside the zeolite frameworks.

ZSM-5 ~~catalyst~~ was selected as adsorbent medium due its characteristic three dimensional micropore system whose three dimensional channel structure ensures the accessibility of host selected molecules (size of the 10-ring micropores $\approx 5.1\text{--}5.6\text{ \AA}$) (Figure 1 a, b). Toluene (TOL) and n-hexane (HEX) are selected as NMVOCs representative of aromatic and alkanes hydrocarbon, respectively, as well as because of their amount, emissions and toxicity [454]. This information can help with the selection of optimal adsorbent material for water remediation technology as a function of the pollutants composition.

2. Material and methods

2.1 Materials

Hydrophobic ZSM-5 zeolite (code CBV 28014) supplied by Zeolyst International in its ammonium form was used as adsorbate in the present study. The characteristics reported by indicate a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 280, a NH_4^+ and Na_2O contents lower than 1% and 0.05 wt.% respectively, and a surface area of $400\text{ m}^2\text{ g}^{-1}$.

2.2 Batch experiments

Adsorption isotherms were determined using the batch method. Batch experiments were carried out in duplicate in 20 ml crimp top reaction glass flasks sealed with PTFE septa (Supelco, PA, USA). The flasks were filled in order to have the minimum headspace. A solid/solution ratio of 1:2 (mg mL^{-1}) was employed, **a fixed adsorbent amount was placed in contact with solution at variable composition**. The samples were equilibrated for 24 hours at $20\text{ }^\circ\text{C}$ ($\pm 0.5\text{ }^\circ\text{C}$) by keeping the flasks into jacketed glass beakers connected to a thermostated water bath (Lab Companion RW-0525G). The samples were kept under stirring by a 10-place magnetic stirrer (IKAMAG RO 10 power, IKA, Stanfer, Germany) at a stirring speed of 500 rpm. After equilibration, the solids were separated from the aqueous solution by filtration trough $0.22\text{ }\mu\text{m}$ polyvinylidene fluoride (PVDF) membrane filters

(Agilent Technologies, Santa Clara, CA, USA). To determine adsorbed quantities (q) and equilibrium concentrations (C_e), concentrations of TOL and/or HEX were determined in solutions after equilibration with the zeolite and in equilibrated solution not containing adsorbent. All experiments were carried out in duplicates.

2.3. Gas Chromatography

The concentration of contaminants in the aqueous solution was determined by Headspace Gas Chromatography coupled to Mass Spectrometry (HS-GC-MS).

The analysis was carried out using an Agilent GC-MS system (Santa Clara, CA, USA) consisting of a GC 6850 Series II Network coupled to a Pal G6500-CTC injector and a Mass Selective Detector 5973 Network.

HS autosampler injector conditions are: incubation oven temperature 80°C, incubation time 50 min, headspace syringe temperature 85°C, agitation speed 250 rpm, agitation on time 30 s, agitation off time 5 s, injection volume 500 μL , fill speed 30 $\mu\text{L s}^{-1}$, syringe pull-up delay 5 s, injection speed 250 $\mu\text{L s}^{-1}$, pre-injection delay 0 s, post injection delay 2 s, syringe flush 30 s with nitrogen.

A DB-624 UI GC column ($L = 20\text{ m}$, I.D. = 0.18 mm, $df = 1.00\text{ }\mu\text{m}$ film thickness, Agilent, Santa Clara, CA, USA) was used. High purity helium was the carrier gas with a constant flow rate of 0.7 mL min^{-1} . The oven temperature gradient started at 40°C for 4 minutes and then ramped to 130°C at 15°C min^{-1} . The injector temperature was kept at 150°C. All samples were injected in split mode (10:1).

The mass spectrometer operated in electron impact mode (positive ion, 70 eV). The source temperature and the quadrupole temperature were set to 230°C and 150°C, respectively.

The mass spectra were acquired in full scan mode. The electronic scan speed was 1562 amu s^{-1} in a mass range from 30 to 300 amu . For identification and quantification of the target analyte, the SIM (selected ion monitoring) chromatograms were extracted from the acquired signal by selecting the most abundant characteristic fragments at m/z 41, 43, 57, 86 (HEX) and $m/z = 91, 92$ (TOL). Chromatographic peak of analytes was identified by comparison of the retention time and the mass spectrum with standard compound and library data; quantitative analysis was performed using calibration curves.

2.4 Thermal analyses

Thermogravimetric analysis (TGA), its derivative weight loss curve (DTG) and differential thermal analysis (DTA) on ZSM-5 before and after loading were performed using a STA 409 PC LUX[®] - Netzch

instrument, in order to follow pollutants mixtures release/decomposition process. The measurements were carried out at a fixed heating rate of 10 °C/min over a temperature range of 25-900°C (alumina powder as reference). The degradation runs were taken under an oxidizing atmosphere (flowing dry air) for gasification at a flow rate of 20 ml/min.

2.5 X-ray powder diffraction measurements and structure determination

X-ray powder diffraction data of ZSM-5 loaded with n-hexane and toluene mixtures (HEX-TOL-ZSM-5) were recorded on a Bruker D8 Advance Diffractometer equipped with a Si (Li) solid-state detector, (experimental setup: Cu K α 1,2 radiation, 3–90 2 θ range, counting time of 12 s per 0.02 2 θ step). Structural data of ZSM-5 after only unary mixtures (i.e. one component solution) of n-hexane and toluene adsorption are available from the literature [11,35,465]. Nevertheless, in order to have a direct comparison by means of the same experimental setup, additional X-ray powder diffraction data collections after only n-hexane and toluene adsorption (HEX-ZSM-5 and TOL-ZSM-5, respectively) were collected using the same strategy adopted for HEX-TOL-ZSM-5. All data processing was carried out by full profile Rietveld analysis using the GSAS package [476] with the EXPGUI interface [487], starting from the atomic model of Rodeghero et al. [35] in the monoclinic space group crystal system (s.g. P2₁/c). Lattice parameters and refinement details for TOL-ZSM-5, HEX-ZSM-5 and HEX-TOL-ZSM-5 systems are reported in Table 1.

The extra-framework sites of HEX-TOL-ZSM-5 were firstly located by difference Fourier maps and then optimized using the geometry optimization tool implemented in EXPO2014 [498] (by plane wave DFT with dispersion correction, DFT-D) in order to minimize the energy of the crystal structure and to provide reasonable bond lengths and angles for HEX and TOL molecules. The positions of H atoms were also calculated. The optimized structure was then refined again with GSAS and the final structural model showed the best agreement with the experimental data. In order to secure a stable refinement, the HEX and TOL molecule coordinates were fixed in the final cycles of Rietveld refinement thus limiting the number of refined atomic displacement parameters.

The fractional final coordinates with the hydrogens calculated as well as the main bond distances are listed in Tables 1-6 SI as Supplementary Information.

3. Results and Discussion

3.1 Adsorption

The TOL-ZSM-5 system has been already investigated [35], in a wide concentration range. In Figure 2 the adsorption isotherm of TOL on ZSM-5 in a low concentration range is reported together with that of

the HEX–ZSM-5. It can be observed that the adsorbed quantity from very diluted solution is proportional to the concentration for both the systems and can be described by an adsorption isotherm type-C [36]:

$$q = K Ce \quad (1)$$

Where q is the amount of solute adsorbed for unit weight of adsorbent at the equilibrium and Ce , the concentration in the solution at equilibrium, K is the partition constant. K is roughly double for HEX, then for TOL, thus indicating a more favorable adsorption of the linear alkane with respect the aromatic compound.

When a wider concentration range is considered, the TOL–ZSM-5 system is better described by a L-type isotherm, in particular a Langmuir isotherm model that has been previously employed to fit the adsorption data of various organic molecules onto zeolite.

For that which concerns HEX-ZSM-5, in this case too, Langmuir isotherm model:

$$q = \frac{q_s b Ce}{1 + b Ce} \quad (2)$$

where, q_s is the saturation capacity and b the binding constant, appears to fit well the data as can be seen in Figure 3 and from the determination coefficient in Table 2. The adsorption isotherm is characterized by a steep initial slope, which together with high q_s are desirable characteristics for adsorbent applications. In the adsorption of HEX on ZSM-5 both q_s and b are larger than those found for TOL in ref. [35], thus confirming what previously observed for the adsorption in the low concentration range. A similar behavior has been observed in the adsorption of n-heptane and toluene onto mesoporous ZSM-5 [5049]. To further investigate the selectivity of ZSM-5 with respect to HEX and TOL in aqueous solution, adsorption from equimolar binary mixtures were carried out (see Figure 3). The effect of HEX on the competitive adsorption of TOL can be evaluated from the adsorption selectivity (α) calculated as:

$$\alpha_{TOL/HEX} = \frac{x_{z,TOL}/x_{a,TOL}}{x_{z,HEX}/x_{a,HEX}} \quad (3)$$

where $x_{z,TOL}$ and $x_{z,HEX}$ are the adsorbed quantity per unit mass of adsorbent material, of TOL and HEX onto ZSM-5 and $x_{a,TOL}$ and $x_{a,HEX}$ are the **equilibrium** concentration of TOL and HEX in aqueous solution, respectively. For the adsorption from equimolar binary solution the selectivity is given by the ratio of the adsorbed quantities and it approaches a value of 3.6 at saturation Differences in the saturation capacity of ZSM-5 zeolites can be also inferred from the geometry of the channels. As a matter of fact, the analysis of shape and size of channels apertures (by means of ellipticity, ϵ , and Crystallographic Free Area, CFA, parameters, respectively) of straight and sinusoidal channels reveals that, HEX-TOL-ZSM-5 is

characterized by a CFA that in average is smaller than that of both unary mixture compounds, but a higher degree of departure from a circular shape of channel apertures (ϵ) (see Table 7 SI).

3.2 Characterization of TOL, HEX and HEX-TOL- loaded ZSM-5 by X-ray diffraction

The host–guest and guest–guest interactions governing the TOL, HEX and HEX-TOL mixture adsorption were investigated by X-ray powder diffraction (XRPD). According to Rodeghero et al. (2016) [35], toluene molecules in the TOL-ZSM-5 system are spread over two crystallographic independent sites: at the straight channel (TOL1 = C1, C2, C3, C4, C5, C6, C7 sites) and at the intersection between straight and sinusoidal channels (TOL2 = C8, C9, C10, C11, C12, C13, C14 sites), respectively. Refinements of the atomic occupancy factors confirm the presence of 6 toluene molecules per unit cell (corresponding to about 8% in weight). Moreover, as already highlighted by Rodeghero et al. [35], the occurrence of co-adsorbed-water-toluene oligomers interacting with framework oxygens was also confirmed (Figure 4a). Regarding the distribution of n-hexane molecules (Figure 4b), the refined atomic occupancy factors indicate 8 molecules per unit cell spread over two fully occupied crystallographic independent sites: the first (i.e., HEX1) hosts 4 molecules at the intersection of straight and sinusoidal channels (in analogous way to what reported by Fujiyama et al., 2014) [510]; the second (i.e., HEX2) is occupied by 4 molecules embedded in the sinusoidal channel. The refined total n-hexane amount (about 10.7 % in weight) well matches with the weight loss observed through the thermal analysis as shown in Figure 5a. The TG curve shows a gradual weight loss up to 300 °C, after which the instrument recorded a plateau with 11.14 % total weight loss until the end of the measurement. As regards the relation between the adsorbed organic and the ZSM-5 structure, the refined distances among the carbon sites and the framework oxygen atoms (C1-O31 2.58(1), C1-O44 2.32(1), C9-O25 2.77(1)) revealed the occurrence of host-guest interactions. No evidence of H₂O molecules is recognized, but the analysis of difference Fourier maps highlights slight disorder which could be attributed to the presence of co-adsorbed water. In both ZSM-5 loaded with unary mixtures a good correspondence with the saturation capacity estimated from the adsorption data was highlighted. After the analysis on the adsorption of samples characterized by a single organic component, attention was paid on the structural answer to organic adsorption of HEX-TOL-ZSM-5 sample, in order to test the possible competitive behavior during the adsorption in water solution. The first evidence of effective embedding of both organics was obtained by the comparison of the collected powder diffraction patterns (Figure 6 a, b) which show slight differences in both intensity and peaks position especially at lower 2theta values. Peaks position of collected patterns scale in the following order (moving toward high 2theta values): TOL-ZSM-5 > HEX-TOL-ZSM-5 > HEX-ZSM-5, meaning that a volumetric expansion occurs from TOL-ZSM-5 to HEX-ZSM-5 samples. On the other hand, HEX-ZSM-5 show pattern very similar to that of HEX-TOL-ZSM-5 and characterized by the same peaks

intensity, whereas the peaks of the TOL-ZSM-5 sample have lower intensity values. Strong similarity was also reported for lattice parameters (a , b , c , and β in Table 1) and this finding suggests a higher ZSM-5 adsorption affinity towards n-hexane. Rietveld structure refinements provided information about the relative position of molecules inside the structure after HEX and TOL binary mixture adsorption. Residuals of electron density calculated by mean of delta Fourier maps indicated the presence of both guest molecules but with a clear indication of preferential and differential adsorption site distribution (Figure 7). Toluene molecules are located only in the straight channel (TOL1 site, about 0.8 molecules, corresponding to approx. 1.2% in zeolite dry weight (dw)), whereas TOL2 site (located at the channels intersections) is now empty (Figure 7a). Molecules of n-hexane are always hosted at both HEX1 and HEX2 sites (7.2 HEX molecules per unit cell, corresponding to approx. 9.4% in zeolite dw) (Figure 7b). The concentration of n-hexane in HEX1 site is unchanged with respect after only HEX adsorption, whereas the short distances between HEX2 and TOL1 sites prevent their simultaneous presence at the intersection of straight and sinusoidal channels; the loading of n-hexane in HEX2 gives rise to 3.2 molecules per unit cell. Delta Fourier maps highlight the presence of 8 co-adsorbed H₂O molecules (W1 and W2 sites, respectively), corresponding to \approx 2.2% in zeolite dw. The total refined amount of adsorbed organic molecules is of about 12.5% in weight (Figure 5 a, b), in good agreement with the total weight loss (wt. %) that was estimated by means of thermal analysis as well as by adsorption methodologies. In particular, the ZSM-5-mixture DTA curve (Figure 5 c) shows a trend very similar to that obtained for HEX-ZSM-5 sample with a TOL desorption smaller contribute at the same time. The refined distances between the framework oxygen, water oxygen atoms and organic molecules suggested the occurrence of water-TOL (W1-TOL1 2.52 Å, W2-TOL2 2.96 Å) and water-HEX (W1-C3 2.94Å, W1-C9 2.87Å, W1-C12 2.72Å, W2-C4 2.94Å, W2-C9 2.83 Å, respectively) oligomers interacting with the framework (O20-C9-HEX2 2.89Å, O25-C12-HEX2 2.66Å, O26-C11-HEX2 2.34Å, O28-C9-HEX2 2.95Å, O31-C10-HEX2 2.84Å, O41-C11-HEX2 2.62Å, O44-C10-HEX2 2.94Å, respectively). In conclusion, the integration of these structural information to adsorption data allowed us to provide insights into zeolite selectivity for aromatic and alkanes hydrocarbon, respectively.

4. Conclusions

This work focused on the study of HEX and TOL absorption, in particular on the aspect of the selective behavior of zeolite ZSM-5 regarding the adsorption of aliphatic and aromatic compounds. The evaluation of adsorption isotherm data of HEX-TOL binary mixture have suggested a higher selectivity of ZSM-5 for the alkane with respect to aromatic compound a selective. Indeed, results pointed out that with respect to the single-component systems data (HEX-ZSM-5 and TOL-ZSM-5), the loading of both

compounds in a mixture reduces the absorption of the other one. These data were resulted in a very good agreement with that was obtained both from X-ray powder diffraction and from thermal analyzes. As a matter of fact, the study of residual intensities obtained through the difference Fourier maps and the Rietveld structural investigation provided information about the relative position of HEX and TOL molecules inside the ZSM-5 adsorption sites. In particular, the refined host-guests interactions revealed a more affinity towards HEX with respect to toluene TOL ones. This information can help with the selection of optimal adsorbent material for water remediation technology as a function of the pollutants composition.

Acknowledgements

Research funded by Research Center for Non-Conventional Energy, Istituto ENI Donegani-Environmental Technologies (San Donato Milanese, Italy).

References

- [1] M.E. Davis, Ordered porous materials for emerging applications, *Nature*. 417 (2002) 813. <https://www.nature.com/articles/nature00785>.
- [2] I. Braschi, S. Blasioli, L. Gigli, C.E. Gessa, A. Alberti, A. Martucci, Removal of sulfonamide antibiotics from water : Evidence of adsorption into an organophilic zeolite Y by its structural modifications, 178 (2010) 218–225. doi:10.1016/j.jhazmat.2010.01.066.
- [3] A. Martucci, I. Braschi, L. Marchese, S. Quartieri, Recent advances in clean-up strategies of waters polluted with sulfonamide antibiotics : a review of sorbents and related properties, 78 (2014) 1115–1140. doi:10.1180/minmag.2014.078.5.03.
- [4] A. Martucci, L. Pasti, N. Marchetti, A. Cavazzini, F. Dondi, A. Alberti, Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites, *Microporous Mesoporous Mater.* 148 (2012) 174–183. doi:10.1016/j.micromeso.2011.07.009.
- [5] B.A. Stein, Advanced Materials Progress Report on Advances in Microporous and Mesoporous SolidsDHlights of Recent Progress **, (2003) 763–775. doi:10.1002/adma.200300007.
- [6] A. Corma, No Title, *J. Catal.* 216 (2003) 298–312. [https://doi.org/10.1016/S0021-9517\(02\)00132-X](https://doi.org/10.1016/S0021-9517(02)00132-X).

- [7] J. Pérez-Ramírez, C.H. Christensen, K. Egeblad, C.H. Christensen, J.C. Groen, Hierarchical zeolites: Enhanced utilisation of microporous crystals in catalysis by advances in materials design, *Chem. Soc. Rev.* 37 (2008) 2530–2542. doi:10.1039/b809030k.
- [8] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, *J. Environ. Manage.* 113 (2012) 170–183. doi:10.1016/j.jenvman.2012.08.028.
- [9] D.R. Rossner, A., Snyder, S. A., & Knappe, No Title, *Water Res.* 43 (2009) 3787–3796. <https://doi.org/10.1016/j.watres.2009.06.009>.
- [10] L. Pasti, E. Rodeghero, E. Sarti, V. Bosi, A. Cavazzini, R. Bagatin, A. Martucci, Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5, *RSC Adv.* 6 (2016). doi:10.1039/c6ra08872d.
- [11] K. Nishi, A. Hidaka, Y. Yokomori, Structure of toluene6.4-ZSM-5 and the toluene disproportionation reaction on ZSM-5, *Acta Crystallogr. Sect. B Struct. Sci.* 61 (2005) 160–163. doi:10.1107/S0108768105003186.
- [12] E. Sarti, T. Chenet, L. Pasti, A. Cavazzini, E. Rodeghero, A. Martucci, Effect of silica alumina ratio and thermal treatment of beta zeolites on the adsorption of toluene from aqueous solutions, *Minerals.* 7 (2017). doi:10.3390/min7020022.
- [13] A.A. Costa, W.B. Wilson, H. Wang, A.D. Campiglia, J.A. Dias, S.C.L. Dias, Comparison of BEA, USY and ZSM-5 for the quantitative extraction of polycyclic aromatic hydrocarbons from water samples, *Microporous Mesoporous Mater.* 149 (2012) 186–192. doi:10.1016/j.micromeso.2011.06.016.
- [14] P. Khalid, M., Joly, G., Renaud, A., & Magnoux, No Title, *Ind. Eng. Chem. Res.* 43 (2004) 5275–5280. <https://doi.org/10.1021/ie0400447>.
- [15] C. Perego, R. Bagatin, M. Tagliabue, R. Vignola, Zeolites and related mesoporous materials for multi-talented environmental solutions, *Microporous Mesoporous Mater.* 166 (2013) 37–49. doi:10.1016/j.micromeso.2012.04.048.
- [16] S. Atasoy, E., Döğeroğlu, T., & Kara, No Title, *Water Res.* 38 (2004) 3265–3274. <https://doi.org/10.1016/j.watres.2004.04.036>.
- [17] N.S. Chary, A.R. Fernandez-Alba, Determination of volatile organic compounds in drinking and environmental waters, *TrAC - Trends Anal. Chem.* 32 (2012) 60–75. doi:10.1016/j.trac.2011.08.011.

- [18] D. Makowski, W., & Majda, Equilibrated thermodesorption studies of adsorption of n-hexane and n-heptane on zeolites Y, ZSM-5 and ZSM-11, *Appl. Surf. Sci.* 252 (2005) 707–715. <https://doi.org/10.1016/j.apsusc.2005.02.052>.
- [19] B.H. Sun, X. Y., Li, J. W., Li, Y. X., Yang, S. C., & Chen, Adsorption of benzene and propylene in zeolite ZSM-5: Grand Canonical Monte Carlo simulations, *Chem. Res. Chin. Univ.* 25 (2009) 377–382.
https://scholar.google.it/scholar?cluster=6994539969316821427&hl=fr&as_sdt=2005&sciodt=0,5.
- [20] N. Floquet, J.P. Coulomb, J.P. Bellat, J.M. Simon, G. Weber, G. Andre, Heptane adsorption in silicalite-1: Neutron scattering investigation, *J. Phys. Chem. C.* 111 (2007) 18182–18188. doi:10.1021/jp0746502.
- [21] G. Floquet, N., Simon, J. M., Coulomb, J. P., Bellat, J. P., Weber, G., & Andre, Heptane adsorption in silicalite-1: Molecular dynamics simulation, *Microporous Mesoporous Mater.* 122 (2009) 61–71. <https://doi.org/10.1016/j.micromeso.2009.02.009>.
- [22] R. Krishna, S. Calero, B. Smit, Investigation of entropy effects during sorption of mixtures of alkanes in MFI zeolite, *Chem. Eng. J.* 88 (2002) 81–94. doi:10.1016/S1385-8947(01)00253-4.
- [23] L. Song, Z.L. Sun, H.Y. Ban, M. Dai, L.V.C. Rees, Benzene adsorption in microporous materials, *Adsorption.* 11 (2005) 325–339. doi:10.1007/s10450-005-5400-2.
- [24] S. Calero, M. Schenk, D. Dubbeldam, T.L.M. Maesen, B. Smit, The selectivity of n-hexane hydroconversion on MOR-, MAZ-, and FAU-type zeolites, *J. Catal.* 228 (2004) 121–129. doi:10.1016/j.jcat.2004.08.019.
- [25] J.F.M. Denayer, L.I. Devriese, S. Couck, J. Martens, R. Singh, P.A. Webley, G. V. Baron, Cage and window effects in the adsorption of n-alkanes on chabazite and SAPO-34, *J. Phys. Chem. C.* 112 (2008) 16593–16599. doi:10.1021/jp804349v.
- [26] J. Hibbe, F., Chmelik, C., Heinke, L., Pramanik, S., Li, J., Ruthven, D. M., ... & Kärger, The nature of surface barriers on nanoporous solids explored by microimaging of transient guest distributions, *J. Am. Chem. Soc.* 133 (2011) 2804–2807. <https://doi.org/10.1021/ja108625z>.
- [27] R. Krishna, B. Smit, S. Calero, Entropy effects during sorption of alkanes in zeolites, *Chem. Soc. Rev.* 31 (2002) 185–194. doi:10.1039/b101267n.

- [28] A. Martucci, L. Pasti, M. Nassi, A. Alberti, R. Arletti, R. Bagatin, R. Vignola, R. Sticca, Adsorption mechanism of 1,2-dichloroethane into an organophilic zeolite mordenite: A combined diffractometric and gas chromatographic study, *Microporous Mesoporous Mater.* 151 (2012) 358–367. doi:10.1016/j.micromeso.2011.10.010.
- [29] R. Arletti, A. Martucci, A. Alberti, L. Pasti, M. Nassi, Location of MTBE and toluene in the channel system of the zeolite mordenite : Adsorption and host – guest interactions, (2019).
- [30] L. Pasti, A. Martucci, M. Nassi, A. Cavazzini, A. Alberti, R. Bagatin, The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites, *Microporous Mesoporous Mater.* 160 (2012) 182–193. doi:10.1016/j.micromeso.2012.05.015.
- [31] L. Martucci, A., Leardini, L., Nassi, M., Sarti, E., Bagatin, R., & Pasti, Removal of emerging organic contaminants from aqueous systems: Adsorption and location of methyl-tertiary-butylether on synthetic ferrierite, *Mineral. Mag.* 78 (2014) 1161–1176.
- [32] Y. Kamiya, N., Oshiro, T., Tan, S., Nishi, K., & Yokomori, Adsorption process of phenol on silicalite-1 and crystal structure of phenol8. 0–silicalite-1 using a single crystal X-ray diffraction method, *Microporous Mesoporous Mater.* 169 (2013) 168–175. <https://doi.org/10.1016/j.micromeso.2012.11.006>.
- [33] A. Martucci, E. Rodeghero, L. Pasti, V. Bosi, G. Cruciani, Adsorption of 1,2-dichloroethane on ZSM-5 and desorption dynamics by in situ synchrotron powder X-ray diffraction, *Microporous Mesoporous Mater.* 215 (2015). doi:10.1016/j.micromeso.2015.05.035.
- [34] N. Kamiya, W. Iwama, T. Kudo, T. Nasuno, S. Fujiyama, K. Nishi, Y. Yokomori, Determining the structure of a benzene7.2-silicalite-1 zeolite using a single-crystal X-ray method, *Acta Crystallogr. Sect. B Struct. Sci.* 67 (2011) 508–515. doi:10.1107/S0108768111038560.
- [35] E. Rodeghero, A. Martucci, G. Cruciani, R. Bagatin, E. Sarti, V. Bosi, L. Pasti, Kinetics and dynamic behaviour of toluene desorption from ZSM-5 using in situ high-temperature synchrotron powder X-ray diffraction and chromatographic techniques, *Catal. Today.* 277 (2016). doi:10.1016/j.cattod.2015.11.031.
- [36] C. H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, *J. Colloid Interface Sci.* 47(3) (1974) 755-765.
- [37] I.J. Gomez, B. Arnaiz, M. Cacioppo, F. Arcudi, M. Prato, Nitrogen-doped Carbon Nanodots

for bioimaging and delivery of paclitaxel, *J. Mater. Chem. B.* 6 (2018).

doi:10.1039/x0xx00000x.

- [38] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, *Nat. Protoc.* 1 (2007) 2661–2667. doi:10.1038/nprot.2006.370.
- [39] S. Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A., & Agarwal, No Title, *RSC Adv.* 2 (2012) 6380–6388. 10.1039/C2RA20340E.
- [40] C.T. Laurencin, S.F. El-Amin, S.E. Ibim, D.A. Willoughby, M. Attawia, H.R. Allcock, A.A. Ambrosio, A highly porous 3-dimensional polyphosphazene polymer matrix for skeletal tissue regeneration, *J. Biomed. Mater. Res.* 30 (1996) 133–138. doi:10.1002/(SICI)1097-4636(199602)30:2<133::AID-JBM1>3.0.CO;2-S.
- [41] I. Ali, Water treatment by adsorption columns: evaluation at ground level, *Sep. Purif. Rev.* 43 (2014) 175–205. <https://doi.org/10.1080/15422119.2012.748671>.
- [42] & S. Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., Low-cost adsorbents: growing approach to wastewater treatment—a review, *Crit. Rev. Environ. Sci. Technol.* 39 (2009) 783–842. <https://doi.org/10.1080/10643380801977610>.
- [43] L.M.T. Smith, Berend; Maesen, Commensurate Freezing of Alkanes in Channes of Zeolite.Pdf, (1995).
- [44] E.G. Derouane, The energetics of sorption by molecular sieves: surface curvature effects, *Chem. Phys. Lett.* 142 (1987) 200–204. [https://doi.org/10.1016/0009-2614\(87\)80922-3](https://doi.org/10.1016/0009-2614(87)80922-3).
- [45] R.G. Dollard, G. J., Dumitrescu, P., Telling, S., Dixon, J., & Derwent, Observed trends in ambient concentrations of C2–C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, *Atmos. Environ.* 41 (2007) 2559–2569. <https://doi.org/10.1016/j.atmosenv.2006.11.020>.
- [46] H. Morell, H., Angermund, K., Lewis, A. R., Brouwer, D. H., Fyfe, C. A., & Gies, Structural investigation of silicalite-I loaded with n-hexane by X-ray diffraction, ²⁹Si MAS NMR, and molecular modeling, *Chem. Mater.* 14 (2002) 2192–2198. <https://doi.org/10.1021/cm011267f>.
- [47] A.C. Larson, R.B. Von Dreele, L. Alamos, Laur 86-748 ©, *Structure.* (2000).
- [48] B.H. Toby, EXPGUI , a graphical user interface for GSAS , *J. Appl. Crystallogr.* 34 (2001)

210–213. doi:10.1107/s0021889801002242.

- [49] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, EXPO2013 : a kit of tools for phasing crystal structures from powder data , J. Appl. Crystallogr. 46 (2013) 1231–1235. doi:10.1107/s0021889813013113.
- [50] R. Zhao, H., Ma, J., Zhang, Q., Liu, Z., & Li, Adsorption and diffusion of n-heptane and toluene over mesoporous ZSM-5 zeolites, Ind. Eng. Chem. Res. 53 (2014) 13810–13819. <https://doi.org/10.1021/ie502496v>.
- [50] Y. Fujiyama, S., Seino, S., Kamiya, N., Nishi, K., Yoza, K., & Yokomori, Adsorption structures of non-aromatic hydrocarbons on silicalite-1 using the single-crystal X-ray diffraction method, Phys. Chem. Chem. Phys. 16 (2014) 15839–15845. doi:10.1039/C4CP01860E.

Figures captions

Figure 1. Three dimensional micropore system of ZSM-5 viewed along [100] (a) and [010] (b), respectively.

Figure 2: Adsorption isotherms (a) ZSM-5-TOL in low concentration range, ZSM-5-HEX in: (b) low concentration range, (c) wide concentration range.

Figure 3: Adsorption isotherms of binary equimolar mixtures of HEX-TOL on ZSM-5: a) HEX; b) TOL.

Figure 4. Rietveld structure refinements of single component systems: a) adsorption sites of TOL in ZSM-5 structure; b) adsorption sites of HEX in ZSM-5 structure.

Figure 5. Simultaneous Thermogravimetry (TG) (a); Differential Thermogravimetry (DTG) (b) ; Differential Thermal analyses (DTA) (c) of ZSM-5 in the temperature range 25–900 °C.

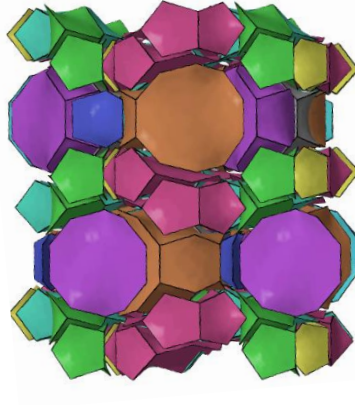
Figure 6. Cascade plot of ZSM-5 samples in selected angular ranges (7–17 °2 θ , (a); and 19–28 °2 θ , (b) at room temperature.

Figure 7. Adsorption sites for HEX and TOL in binary mixture along the c axis.

Figure 1



a)



b)

Commentato [U1]: Nel testo si è perso il riferimento a questa figura.
Va tolta o si aggiunge il richiamo?

Figure 2.

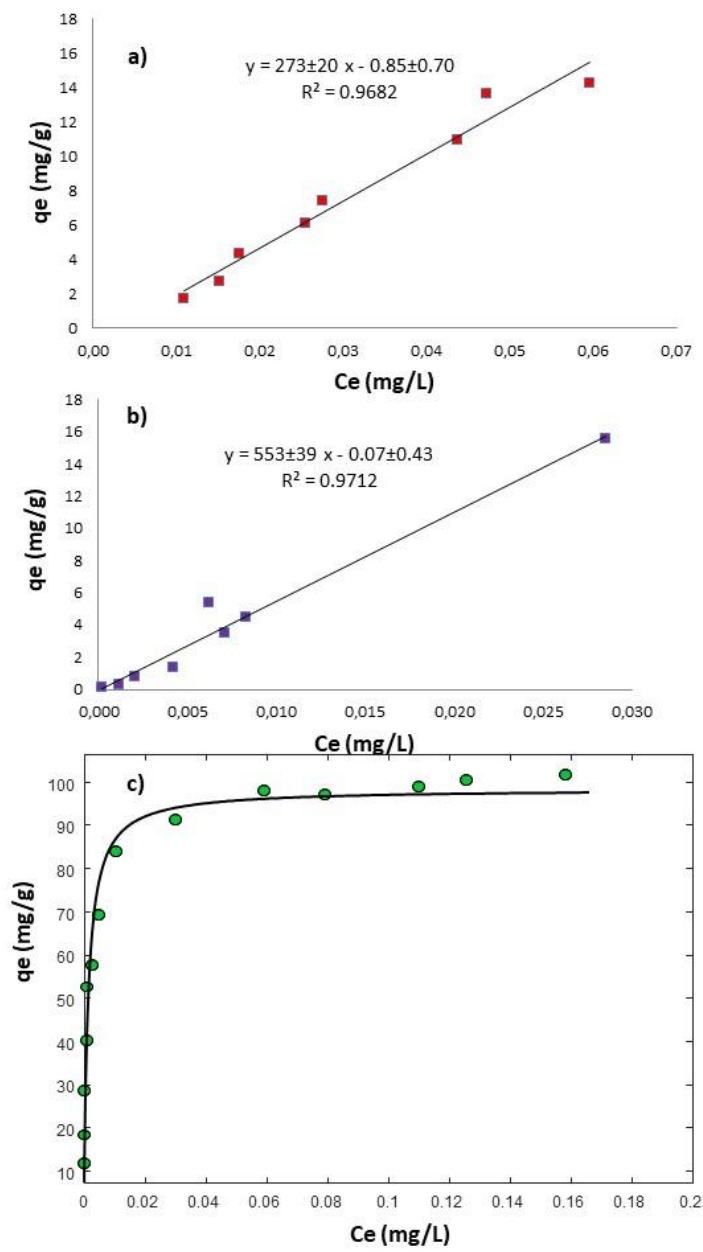


Figure 3.

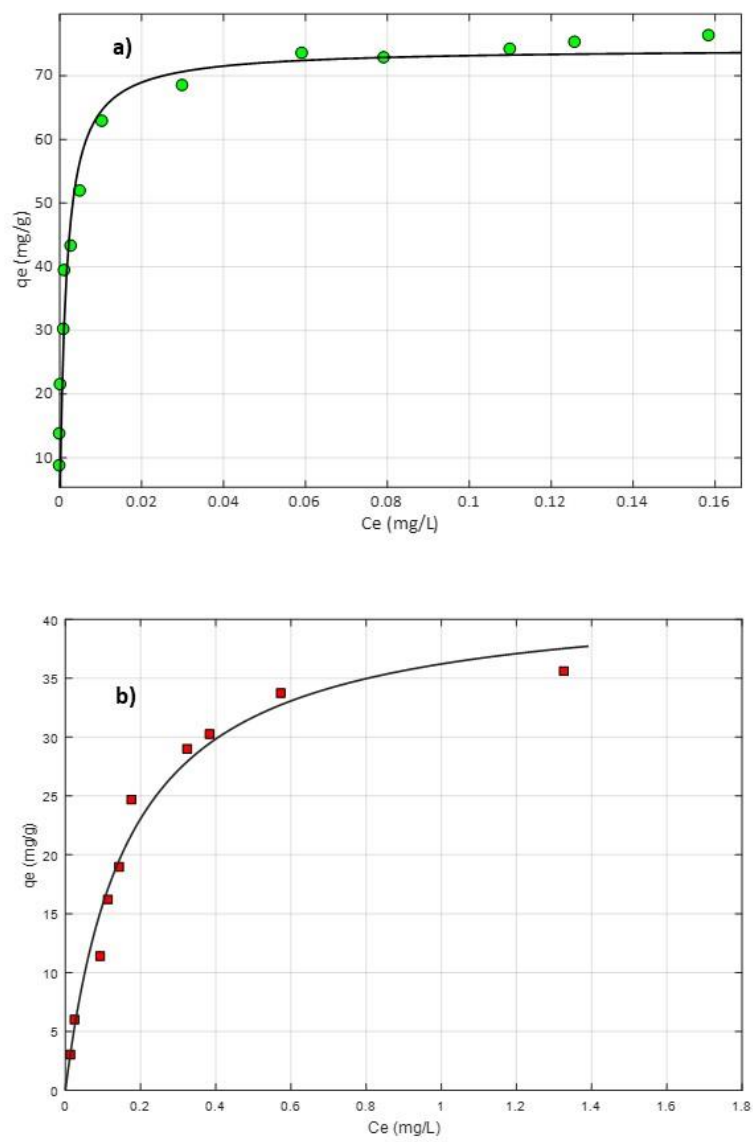


Figure 4.

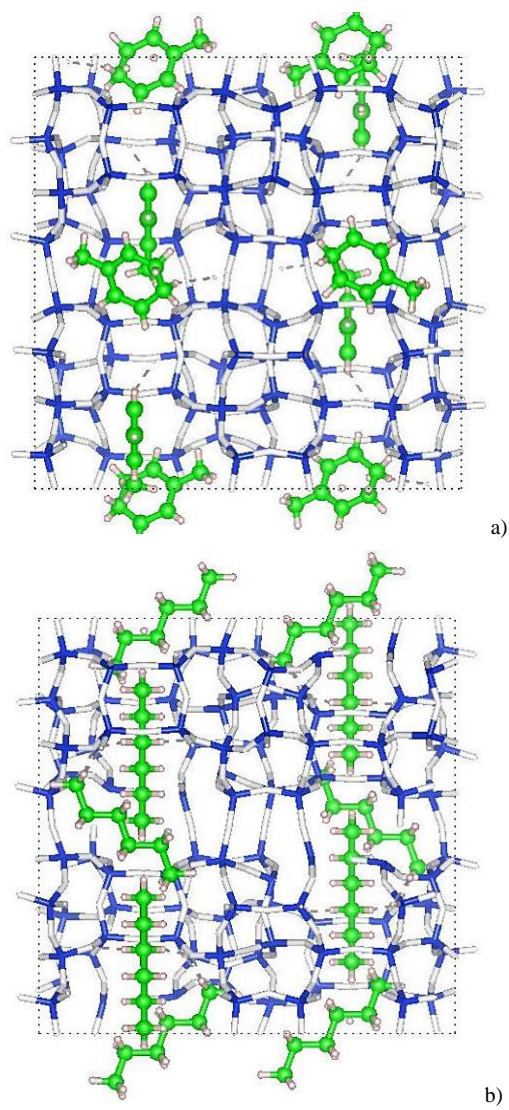


Figure 5.

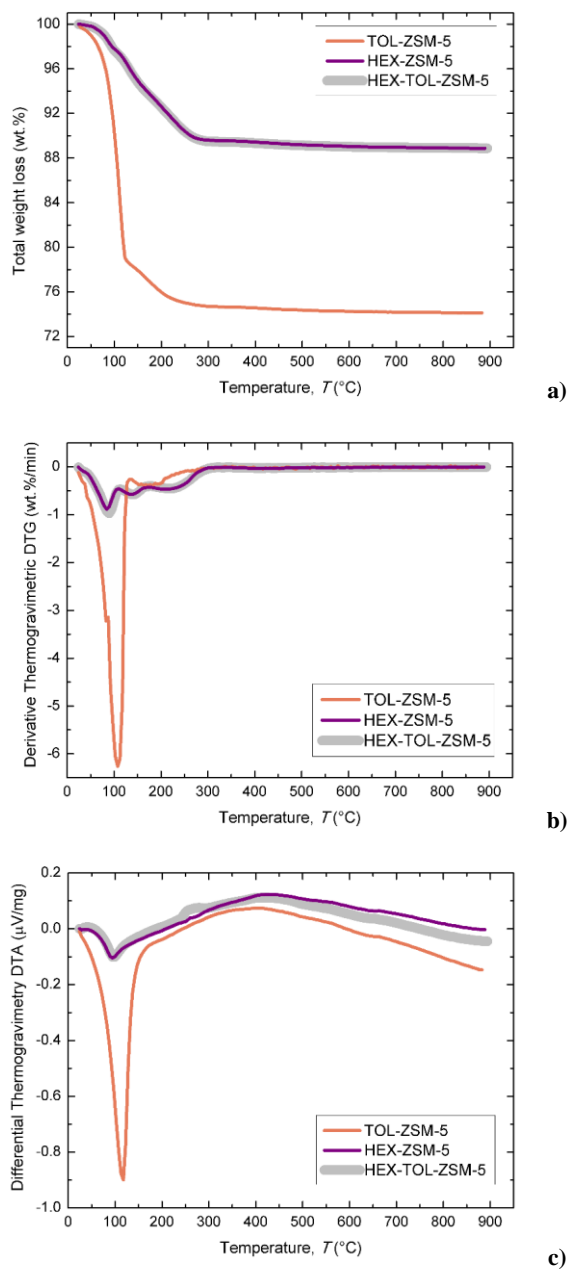


Figure 6.

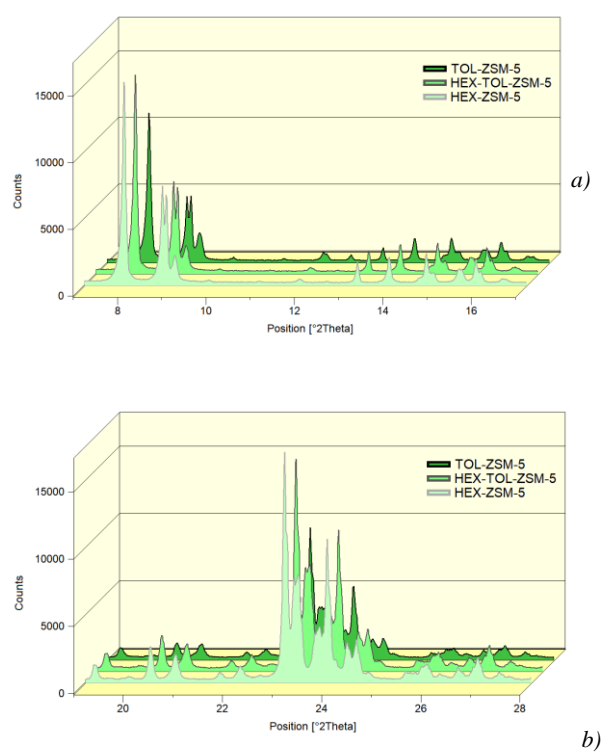


Figure 7.

