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To the Editor of Applied Catalysis B Environmental

Dear Editor,

we are herewith submitting, for publication in “Applied Catalysis B Environmental”, the article entitled: “An advanced oxidation process by photoexcited heterogeneous sodium decatungstate for the degradation of drugs present in the aqueous environment” by Luisa Pasti, Elena Sarti, Nicola Marchetti, Claudia Stevanin and Alessandra Molinari.

We believe that our contribution fits well with main topics of Applied Catalysis B Environmental. In fact, moving from a first research paper already published in Applied Catalysis B Environmental (2017, 203, 9-17), herein we improve the previous study considering two heterogeneous photocatalytic systems based on a polyoxoanion for the removal of drug molecules from water. In particular, in this manuscript we show for the first time the possibility to tune the photocatalytic activity of sodium decatungstate by varying the chemical-physical properties of the support.

The investigated photocatalytic systems still operate at ambient temperature, atmospheric pressure and at pH values similar to that of natural waters. ESR spin trapping and HPLC-MS investigation were carried out to elucidate the fundamentals of the photodegradation processes occurring in aqueous media.

To the best of our knowledge, we are unique in the scientific panorama to propose photocatalytic heterogeneous systems based on decatungstate anion for water remediation from contaminants of emerging concern.

Best Regards,

Luisa Pasti  
Alessandra Molinari

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## **An advanced oxidation process by photoexcited heterogeneous sodium decatungstate for the degradation of drugs present in aqueous environment.**

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### **Abstract**

The ability of decatungstate anion ( $W_{10}O_{32}^{4-}$ ) to photoproduce  $\cdot OH$  radicals from water is retained when the polyoxoanion is immobilized on solid supports and can be exploited as a heterogeneous photocatalytic process aimed to water remediation. However, we show that interaction between  $\cdot OH$  radicals and drug molecules depends on the physical chemical properties of the chosen support. In fact, we demonstrate that silica particles covered by decatungstate anions are not efficient in the degradation of carbamazepine and sulfamethoxazole (ubiquitary contaminants of natural waters) that are respectively neutral and negatively charged at operating pH of 6. On the contrary, entrapment of  $W_{10}O_{32}^{4-}$  inside a mesoporous organosilica matrix leads to a heterogeneous photocatalytic system with proper characteristic of hydrophobicity. Organic molecules enter mesopores and easily leave the aqueous environment. Inside pores, the reaction between photoproduced  $\cdot OH$  radicals is favored. Mono- and di-hydroxylated products precede fragmentation and degradation of the investigated drug.

### **Keywords**

Heterogeneous photocatalysis, sodium decatungstate, water remediation, drug mineralization,  $\cdot OH$  radicals.

### **1. Introduction**

Common emerging pollutants are pharmaceuticals, and among them, antibiotics and psychotropic drugs, largely employed worldwide, are very harmful since they can cause specific effects on biota even at low concentration levels. Most of these drugs have been detected in rivers and in influents and effluents of wastewater treatment plants of many countries [1, 2]. Their presence in the environment is mainly due to their incomplete removal by microbiological and/or conventional wastewater treatments. This aspect is relevant not only in environmental protection and restoration

but also for water reuse issues. Water scarcity is a well-recognized challenge to the sustainable development of many countries that claims for further efforts to develop and improve water treatment technologies. It is therefore necessary the development of processes capable to ensure the total elimination of trace of organic contaminants from waters.

The use of advanced oxidation processes (AOPs) has been demonstrated to be a possible approach for the remediation of contaminated waters [3, 4]. AOPs are based on the *in situ* production of free radical species, such as ( $\text{OH}^\bullet$ ), which being a strong oxidant characterized by a very high standard reduction potential ( $E^0 = +2.80 \text{ V vs. SHE}$ ) rapidly oxidizes electron-rich organic compounds up to their mineralization [5]. Among the large variety of oxidation processes, photochemical methods offers the advantage of energy efficiency, rapidness and limited use of chemicals (oxidants), which together concur to the sustainability of the process [5]. In particular, photocatalysis with  $\text{TiO}_2$  has been demonstrated to be an efficient method for the destruction of low amounts of water-soluble organic pollutants [6-8], even if other semiconductor materials, such as  $\text{WO}_3$ , have been recently successfully utilized [9].

In water decontamination issue, the applicability of polyoxotungstates for the degradation and mineralization of chlorophenols, chloroacetic acids and herbicide has been also explored [10, 11]. Among polyoxotungstates, decatungstate anionic cluster has light absorption properties very similar to those of  $\text{TiO}_2$  and for this similarity it can be considered a soluble analogue of the most employed semiconductor. In addition, it has been demonstrated that photoexcitation of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  dissolved in water produces  $\text{OH}^\bullet$  radicals from water oxidation [12]. The interest for heterogeneous decatungstate photocatalyst in advanced oxidation processes framework has led to the development of several heterogenization procedures, such as impregnation on a solid support [13] and ion exchange [14, 15]. Indeed, heterogeneous (photo)catalysis has the advantage of easy separation and recovery.

Recently, a heterogeneous photocatalytic system obtained by immobilization of the anionic decatungstate cluster on silica particles functionalized with  $-\text{NH}_2$  groups has been employed for the degradation of some contaminants of emerging concerns in aqueous matrix [16]. It was proved that the photocatalytic system was efficient and recyclable. The degradation process is achieved by photoexcitation of heterogeneous decatungstate that results in the formation of  $\text{OH}^\bullet$  radicals as revealed by EPR spin trapping spectroscopy.

In addition, studies on the reaction mechanism of heterogeneous polyoxotungstates indicate that the selectivity and efficiency of these photocatalysts depend on the support characteristics. In general, pore structures, distributions of the active sites and hydrophilic–hydrophobic interactions

with the substrate are key factors for the catalytic activity and selectivity of solid heterogeneous catalysts [17-19]. Therefore, the choice of support matrices is very important for highly efficient catalytic systems. In this paper, we show how support matrix properties can tune the degradation ability of immobilized decatungstate with respect to three target molecules in dilute aqueous solutions: propranolol, carbamazepine and sulfamethoxazole. These molecules are selected as probes since all of them are ubiquitous contaminants of natural waters. In particular, carbamazepine is a psychotic drug, resistant to conventional wastewater treatment and sulfamethoxazole is an antimicrobial largely employed, which has been detected in surface and drinking waters [20].

Two different heterogeneous catalysts, one obtained by immobilization of  $W_{10}O_{32}^{4-}$  by an ion exchange mechanism [16] and the other one obtained by encapsulation of the anionic cluster into a silicate structure [21], are investigated. In particular, their photocatalytic degradation activity is compared and related to both the support and the drug molecule physical chemical properties. EPR spin trapping technique and HPLC-MS analysis are employed to gain information about the operating degradative mechanism and the nature of reaction intermediates.

## 2. Experimental

### 2.1 Materials

Propranolol (PRP, purity 99.8 %), carbamazepine (CBZ, purity 99.8 %), sulfamethoxazole (SMX, purity 99.8 %) and formic acid were purchased from Fluka (Fluka Chemie AG, Switzerland). Sodium hydroxide (Titolchimica, Rovigo, Italy), hydrochloric acid (Carlo Erba, Milano, Italy) of analytical grade were employed to adjust the pH of diluted drugs solutions. The pH was measured using an AMEL pHmeter (Milano, Italy). High-performance liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). The water was Milli-Q® grade (Millipore, MA, USA).

### 2.2 Photocatalysts preparation

Sodium decatungstate ( $Na_4W_{10}O_{32}$ ) was synthesized following reported literature procedures [22, 23]. The heterogeneous photocatalysts (silica- $NH_3^+ / Na_3W_{10}O_{32}^-$  and  $Na_4W_{10}O_{32}/SiO_2/BTESE$ ) have been prepared carrying out procedures already published [16, 21].

### 2.3 Photocatalytic experiments with homogeneous $Na_4W_{10}O_{32}$

An aerated aqueous solution (3 mL, final pH = 6) containing dissolved  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  ( $2 \times 10^{-4}$  M) and the drug of interest ( $C_0 = 10 \text{ mg L}^{-1}$ ) was put into a spectrophotometric cell (optical path 1 cm) and placed in front of a Hg medium pressure lamp (Helios Italquartz,  $15 \text{ W cm}^{-2}$ ). The solution is magnetically stirred and irradiation was carried out using a cut-off filter, placed between the lamp slit (1 cm x 3 cm) and the cuvette in order to select the suitable wavelength range (PRP,  $\lambda > 330 \text{ nm}$ , SMX  $\lambda > 335 \text{ nm}$ ; CBZ,  $\lambda > 300 \text{ nm}$ ). Selection of suitable cut off filter was performed in order to avoid direct photolysis of the drug compound. At the end of illumination, the sample was filtrated with  $0.22 \mu\text{m}$  PVDF membrane filters Captiva Econofilter Agilent Technologies (Santa Clara, CA, USA) and HPLC analysis was performed. Samples containing dissolved decatungstate anion have been kept in the dark and then analyzed.

#### *2.4 Photocatalytic experiments with heterogeneous $\text{Na}_4\text{W}_{10}\text{O}_{32}$*

In a typical photocatalytic experiment, the optimal amount determined elsewhere [16, 21] of silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  (5g/L) or of  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2/\text{BTESE}$  (500 g/L) was kept in suspension in aqueous solution (3 mL, pH=6) containing the drug of interest ( $C_0 = 10 \text{ mg L}^{-1}$ ) inside a spectrophotometric cell. Then, irradiation was carried out for the required period of time with the selected cut off filter (PRP,  $\lambda > 330 \text{ nm}$ , SMX  $\lambda > 335 \text{ nm}$ ; CBZ,  $\lambda > 300 \text{ nm}$ ) and then analyzed as described above.

After irradiation, the solutions were centrifuged to separate the heterogeneous photocatalysts and UV-vis spectra have been recorded to evaluate leaching of decatungstate anion. Moreover, these solutions have been subsequently irradiated to establish eventual photoactivity of traces of decatungstate cluster, leached into the solution and not detected by spectrophotometric analysis.

#### *2.5 HPLC analysis*

A HPLC/DAD (Waters, MA, USA pump: Waters 515, DAD: Waters PDA 996) was employed under isocratic elution conditions, reported in Table 2. The flow rate was  $1 \text{ mL min}^{-1}$ , while the column was thermostated at  $25 \text{ }^\circ\text{C}$ . The column was  $150 \times 4.6 \text{ mm}$  (Phenomenex, CA, USA) and packed with a C18 silica-based stationary phase with a particle diameter of  $5 \mu\text{m}$ . The injection volume was  $20 \mu\text{L}$  for all standards and samples.

#### *2.6 HPLC/MS analysis*

HPLC/MS analyses were carried out by means of Surveyor Plus micro-HPLC hyphenated to a linear ion trap mass spectrometer (LTQ XL Thermo Scientific, Waltham, MA, USA). The HPLC

apparatus was composed of a solvent delivery system, a quaternary pump (including a membrane degasser) and an autosampler (including a thermostated column compartment). The LTQ system was equipped with an electrospray ionization (ESI) ion source. The mobile phase was obtained as a mixture of ACN and formic acid 0.1% v/v: water formic acid 0.1% v/v. Chromatographic separation was performed under gradient elution conditions: 0-6 min 5% ACN, 6-14 min 5-70% ACN, 14-15 min 70% ACN, then held isocratically at 95% of ACN for 3 minutes before reconditioning the column. The flow rate was  $100 \mu\text{L min}^{-1}$ , while the column was thermostated at  $25 \text{ }^\circ\text{C}$ . The column was  $50 \times 2.1 \text{ mm}$  (Restek, Bellefonte, PA, USA) packed with a C18 silica-based stationary phase with a particle diameter of  $3 \mu\text{m}$ . The injection volume was  $5 \mu\text{L}$  for all standards and samples. MS experimental conditions were as follows: spray voltage  $4 \text{ kV}$ , capillary temperature  $275 \text{ }^\circ\text{C}$ , capillary voltage  $11 \text{ V}$  and tube lens  $25 \text{ V}$  for positive ESI conditions.

### 2.7 EPR-spin trapping experiments

EPR-spin trapping experiments were carried out with a Bruker ER200 MRD spectrometer equipped with a TE201 resonator (microwave frequency of  $9.4 \text{ GHz}$ ). The homogeneous samples were aqueous solutions containing 5,5'-dimethylpyrroline N-oxide (DMPO,  $5 \times 10^{-2} \text{ M}$ ) as spin trap and  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  ( $2 \times 10^{-4} \text{ M}$ ). In heterogeneous experiments, silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  was suspended in an analogous solution. When requested, CBZ ( $C_0 = 10 \text{ mg L}^{-1}$ ) was introduced together with the spin trap. The samples were put into a flat quartz cell and directly irradiated in the EPR cavity with a medium pressure Hg lamp equipped with cut off filter ( $\lambda > 300 \text{ nm}$ ). No signals were obtained in the dark or during irradiation of the solution in the absence of decatungstate.

## 3. Results and discussion

### 3.1 Sodium decatungstate heterogenized on modified silica particles (silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$ )

We recently demonstrated that a robust and recyclable photocatalytic system can be obtained by immobilization of the anionic cluster on silica particles functionalized with  $-\text{NH}_2$  groups [16]. Moreover, photoexcitation of heterogeneous decatungstate ( $5 \text{ g/L}$ ) suspended in aqueous solutions ( $\text{pH} = 6$ ) containing one among levofloxacin or trimethoprim or atenolol ( $C_0 = 10 \text{ mg/L}$ ) caused drug degradation mediated by  $\text{OH}^\bullet$  radicals, whose formation has been pointed out by EPR spin trapping spectroscopy [16].

With the aim of evaluating the wide scope of the found method, we decided both to confirm the observed performance by using propranolol (PRP), another  $\beta$ -blocker similar in structure to the



previous studied atenolol, and to prove the photocatalytic method extending to other two drugs having different structure and physical chemical properties. In particular, we choose the antibiotic sulfamethoxazole (SMX, often used in combination with the studied trimethoprim) and the antidepressant carbamazepine (CBZ), which is known as a very recalcitrant drug. The degradation of each substrate is followed during irradiation time and it is expressed as ratio  $C/C_0$  (where  $C$  is the drug concentration at a certain time and  $C_0$  is the initial one). Interestingly, we observe (Figure 1) that PRP behaves similarly to atenolol and after 3h irradiation about 60-65% of degradation was obtained. On the contrary, irradiation of the silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  system does not cause any appreciable photocatalytic degradation of both SMX and CBZ.

Figure 1.

On the basis of these results, we propose that the inefficient degradation of both SMX and CBZ could be due to one of the following factors: i) low photoactivity of the polyoxoanion with respect to these molecules; ii) scarce affinity of the catalyst support for the two drugs; iii) combination of factors ascribable to decatungstate and its support.

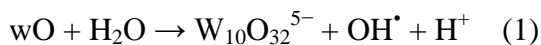
In order to evaluate the photocatalytic activity of decatungstate anion itself, experiments are carried out in homogeneous phase irradiating aqueous solutions containing dissolved  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  ( $2 \times 10^{-4}$  M) and CBZ, SMX or PRP ( $C_0 = 10$  mg/L). Obtained results are reported in Figure 2 (circles), together with control experiments in which analogous samples are kept in the dark (squares).

Figure 2

It is shown that around 90% of starting CBZ and PRP are degraded after 60 min of illumination in the presence of homogeneous sodium decatungstate, and a lower degradation efficiency is obtained with SMX that is, however, photodegraded of about 60% in the first hour of irradiation. This decrease is attributable to the photocatalytic activity of  $\text{W}_{10}\text{O}_{32}^{4-}$  since the decrease in the dark of CBZ, SMX or PRP never exceeds 10% (Fig. 2, squares).

Furthermore, EPR-spin trapping experiments support this statement. In fact, photoexcitation of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  dissolved in water in the presence of the spin trap DMPO causes the formation of a quartet 1:2:2:1 ( $a_N = a_H = 14.8$  G) ascribable to the paramagnetic adduct  $[\text{DMPO-OH}]^\bullet$  in

accordance to previous investigation [12]. As shown in Figure 3, the intensity of this signal increases by increasing the irradiation time, showing that reactions:



efficiently occur. Interestingly, addition of CBZ (10 mg/L) to the solution causes an important decrease of  $[\text{DMPO-OH}]^\bullet$  signal. This could be an indication that CBZ competes with DMPO in the reaction with  $\text{OH}^\bullet$  radicals, and probably this reaction is the first step of the photocatalytic drug degradation pathway.

Figure 3

Analogous EPR spin trapping experiments carried out irradiating silica- $\text{NH}_3^+$ / $\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  suspended in water containing DMPO show that the paramagnetic adduct  $[\text{DMPO-OH}]^\bullet$  is still formed, indicating that the primary photochemical process (reaction 1) that produces  $\text{OH}^\bullet$  radicals is operating also with the heterogeneous system. Contrarily to what observed for homogeneous decatungstate, the addition of CBZ does not cause any decrease in the intensity of the paramagnetic adduct (Figure 4). This indicates that  $\text{OH}^\bullet$  radicals generated by photoexcited silica- $\text{NH}_3^+$ / $\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  do not quickly react with CBZ, in agreement with the absence of degradation of this drug shown in Figure 1. Possibly, CBZ does not adequately approach the surface of the heterogeneous photocatalyst where  $\text{OH}^\bullet$  radicals are produced or CBZ concentration in the solution in contact with the particle is insufficient to favor the reaction between them two.

Figure 4.

The different behavior of silica- $\text{NH}_3^+$ / $\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  with respect to the studied drugs can be tentatively rationalized considering their distribution diagrams (Figure S1): at the operative pH of 6, while the  $\beta$ -blockers (PRP and atenolol, ATN) are mainly present in solution as cations, the same is not for CBZ and SMX. In fact, CBZ is in its neutral form and SMX presents an equilibrium between neutral and even negative form. Since the silica particles are covered by decatungstate

anions, it can be supposed that immobilized decatungstate anions and CBZ or SMX are not sufficiently close each other, a needed requirement for the reaction between drug molecule and photogenerated  $\text{OH}^\bullet$  radicals.

### 3.2 Sodium decatungstate heterogenized on hydrophobic mesoporous silica support ( $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ )

One of the main advantages of heterogeneous photocatalysis is the flexibility in choosing the support with the proper characteristics. Starting from the fact that silica- $\text{NH}_3^+/\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  is not able to perform efficient photocatalytic degradation of CBZ and SMX (Figure 1), we decided to improve the hydrophobicity of silica using a support obtained by direct hydrolysis of tetraethyl orthosilane (TEOS) and of an organotrialkoxy silane (1,2 bis(triethoxysilyl)ethane, (BTESE)). In the near past, morphological features of this system have been determined: a large surface area (about  $725 \text{ m}^2\text{g}^{-1}$ ) and an important mesoporosity (about 80% of the total pore volume) [21]. Sodium decatungstate is encapsulated inside this mesoporous network. Additionally, FTIR spectra clearly showed that organic fragments (coming from BTESE) and silica moieties are distributed within the framework and microgravimetric adsorption isotherms pointed out that  $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$  enhances adsorption of toluene vapors with respect to that of water [21].

Therefore, we decide to use this heterogeneous photocatalytic system for attempting the degradation of CBZ and SMX and, in a typical experiment,  $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$ , suspended in an aqueous solution containing the drug of interest, is irradiated for a desired time (see Experimental section). In parallel, samples prepared in an analogous way are kept in the dark for the same period. The degradation of each substrate is expressed, as before, in terms of  $C/C_0$  ratio vs time (Figure 5).

Figure 5.

One can observe that CBZ and SMX are now degraded upon photoexcitation of decatungstate. After 4 h illumination, more than 80% of CBZ and of SMX disappear from the aqueous solution. To verify the activity the eventual leached polyoxoanion, the solution after 1 hour irradiation was separated from the heterogeneous photocatalyst and directly irradiated for an hour. Analysis of these samples do not show a significant change ( $< 2\%$ ) in remained drug concentration indicating that release of decatungstate into the solution is negligible. These results allow us to infer

that this heterogeneous photocatalytic system is working and it is efficient also in the removal of CBZ and SMX, overcoming the obstacle of the charge taken by the drug molecule at pH 6 (Figure S1) and favors the adsorption of pharmaceuticals on the photocatalytic system facilitating the approach to OH<sup>•</sup> radicals.

In Table 1 the kinetic constants obtained by fitting the data with a pseudo first order kinetic model are reported. A comparison can be made between homogeneous samples and heterogeneous experiments. One can additionally observe that SMX degradation kinetic is the slowest also with homogeneous sodium decatungstate, reinforcing the idea that the ionic charge of the drug molecule at pH 6 has a relevant role for the beginning of the oxidation process.

Table 1.

From these results, we suggest that the ability of SiO<sub>2</sub>/BTESE/Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> to photodegrade CBZ and SMX can be attributed to the hydrophobicity introduced by BTESE. Organic molecules present in water are prone to leave the aqueous environment and to enter the heterogeneous system, approaching the photoactive species and OH<sup>•</sup> radicals produced nearby.

In addition SiO<sub>2</sub>/BTESE/Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> maintains a very good performance also in the degradation of PRP, showing that hydrophobicity introduced in the support does not preclude positively charged molecules from approaching the polyoxoanion (Fig. 1S). This result is particularly relevant since drugs photodegradation can be performed despite the form (charged or not) mainly present at the working conditions and answers to the requirement of general applicability.

### 3.3 HPLC/MS analysis

Degradation mechanism of drug molecules by SiO<sub>2</sub>/BTESE/Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> was investigated analyzing irradiated solution by HPLC-MS. Identification of the degradation byproducts was based on the analysis of the total ion current (TIC) and on the corresponding mass spectra. The identified intermediates for the case of SMX and of CBZ are reported in Table 2 and 3 respectively.

Table 2

The intermediate with 301 m/z corresponds to a monohydroxylation of the aromatic ring and a nitration of the amino group of SMX. The product with 283 m/z derives from the oxidation of the amino group to nitro derivative, whereas the intermediate with 270 m/z correspond to the hydroxylation of SMX aromatic ring. Oxidation of the isoxazole ring of 270 m/z results in the formation of 288 m/z and 228 m/z intermediate and the intermediate with 216 m/z can derive from the opening of the isoxazole ring of SMX. The cleavage of bond between isoxazole ring and the amine group of SMX, can generate the 174 m/z by-product. The compound with 190 m/z was identified as an hydroxylated form of the amino group of 174 m/z derivative. Structures similar to those described were observed also in the photo-Fenton degradation of SMX [24].

From Table 2 it is seen that hydroxylation of SMX by hydroxyl radical ( $\cdot\text{OH}$ ) attack could be an important reaction for the subsequent degradation of SMX. Indeed, three mono-hydroxylated byproducts (i.e. 301 m/z, 270 m/z and 288 m/z) are revealed.

Mono and dihydroxylated intermediates were also identified in the CBZ degradation by photoexcited  $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$  catalyst in aqueous solution and they correspond to the intermediates 253 and 271 m/z respectively in Table 3. Further oxidation of both these compounds leads to the formation of 251 and 267 m/z intermediates. The detection of these intermediates indicates that hydroxylation and oxidation are the main reactions responsible for CBZ degradation.

Table 3.

On the basis of reported and previous results we propose a reaction mechanism for photoexcited  $\text{SiO}_2/\text{BTESE}/\text{Na}_4\text{W}_{10}\text{O}_{32}$  that can be considered general for pharmaceutical photocatalytic degradation. Photoexcitation of decatungstate anion dissolved or suspended in an aqueous environment causes the oxidation of water to  $\text{OH}^\bullet$  radicals [12], as shown in reaction 1. EPR spin trapping experiments and HPLC-MS point out that hydroxyl radicals attack drug molecules giving mono- or dihydroxylated intermediates. Their formation is the prelude to fragmentation.

#### 4. Conclusions

The ability of photoexcited sodium decatungstate to oxidize water producing  $\text{OH}^\bullet$  radicals, already observed in homogeneous conditions, is kept also when the polyoxoanion is heterogenized on siliceous supports. In this paper, we demonstrate that support characteristics are of paramount

importance when reaction between  $\text{OH}^\bullet$  radicals and the organic molecule is the first step of its degradative pathway. In particular, silica- $\text{NH}_3^+$ /  $\text{Na}_3\text{W}_{10}\text{O}_{32}^-$  system, constituted by particles covered by decatungstate anions, is not efficient in the degradation of carbamazepine and sulfamethoxazole, which are neutral or negatively charged at the operating pH. On the contrary, entrapment of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  inside a mesoporous organosilica matrix leads to a heterogeneous photocatalytic system with proper characteristic of hydrophobicity that is able to degrade not only carbamazepine and sulfamethoxazole but also all the other categories previously studied. In fact, the higher hydrophobicity of the organosilica support with respect to the aqueous environment favors adsorption of organic molecules, which enter the mesopores. Here, their proximity to photoproducted  $\text{OH}^\bullet$  radicals favors the hydroxylation of drug molecule. HPLC-MS investigation points out that mono- and di-hydroxylated products are formed and precede fragmentation pathways and degradation. Results obtained from the used independent techniques and methods allow us to formulate a general advanced oxidation process mechanism for the photocatalytic degradation of drug molecules by heterogeneous sodium decatungstate.

## **Acknowledgements**

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## Captions.

**Figure 1.** Degradation kinetics of drugs by photoexcitation of silica-NH<sub>3</sub><sup>+</sup>/ Na<sub>3</sub>W<sub>10</sub>O<sub>32</sub><sup>-</sup> (5g/L) suspended in an aqueous solution (pH 6) containing propranolol (PRP), or sulfamethoxazole (SMX) or carbamazepine (CBZ). C<sub>0</sub> = 10 mg/L. PRP, λ > 330 nm, SMX λ > 335 nm; CBZ, λ > 300 nm.

**Figure 2.** Degradation kinetics of carbamazepine (CBZ), sulfamethoxazole (SMX) and propranolol (PRP) by photoexcitation of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2 x 10<sup>-4</sup> M) dissolved in water at pH 6 (circles). Control experiments are carried out in the dark (squares). C<sub>0</sub>= 10 mg L<sup>-1</sup>. CBZ, λ > 300 nm; SMX, λ > 335 nm; PRP, λ > 330 nm.

**Figure 3.** Fixed-field signal intensity of the [DMPO-OH]<sup>•</sup> adduct in time upon irradiation (λ > 300 nm) of Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (2x10<sup>-4</sup> M) dissolved in water containing DMPO (5x10<sup>-2</sup> M): in the absence (full triangles) and in the presence (empty triangles) of CBZ (10 mg/L). Reported values are the mean of three repeated experiments. Errors do not exceed + 10%.

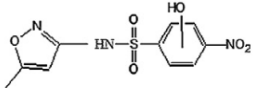
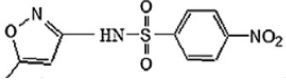
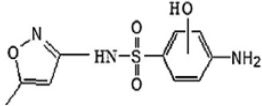
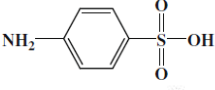
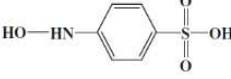
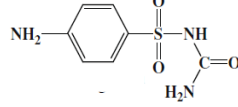
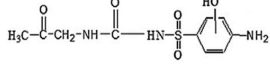
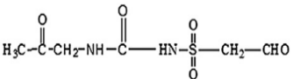
**Figure 4.** Fixed-field signal intensity of the [DMPO-OH]<sup>•</sup> adduct in time upon irradiation (λ > 300 nm) of silica-NH<sub>3</sub><sup>+</sup>/ Na<sub>3</sub>W<sub>10</sub>O<sub>32</sub><sup>-</sup> suspended in an aqueous solution containing DMPO (5x10<sup>-2</sup> M): in the absence (full symbols) and in the presence of CBZ (10 mg/L) (empty symbols). Reported values are the mean of three repeated experiments. Errors do not exceed ± 5%.

**Figure 5.** Degradation kinetics of carbamazepine (CBZ), sulfamethoxazole (SMX) and propranolol (PRP) by photoexcitation of SiO<sub>2</sub>/BTESE/Na<sub>4</sub>W<sub>10</sub>O<sub>32</sub> (500 gL<sup>-1</sup>) suspended in water at pH 6 (circles). Control experiments are carried out in the dark (squares). C<sub>0</sub>= 10 mg L<sup>-1</sup>. CBZ, λ > 300 nm; SMX, λ > 335 nm; PRP, λ > 330 nm.

**Table 1:** Kinetic constants obtained by fitting the experimental data with a first order kinetic equation ( $C/C_0 = e^{-kt}$ ). Data in parenthesis are the confidence limits at 95% of probability.

| Photocatalyst  | Drug | k (h <sup>-1</sup> ) | R <sup>2</sup> |
|--|------|----------------------|----------------|
| Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub> solution   | CBZ  | 2.46 (2.10, 2.82)    | 0.9808         |
|  | PRP  | 2.94 (2.73; 3.05)    | 0.9934         |
|  | SMX  | 0.90 (0.89; 0.91)    | 0.9987         |
| silica-NH <sub>3</sub> <sup>+</sup> / Na <sub>3</sub> W <sub>10</sub> O <sub>32</sub> <sup>-</sup> | CBZ  | 0.024 (0.021; 0.027) | 0.9837         |
|  | PRP  | 0.35 (0.28; 0.42)    | 0.9867         |
|  | SMX  | 0.021 (0.018; 0.024) | 0.9881         |
| SiO <sub>2</sub> /BTESE/Na <sub>4</sub> W <sub>10</sub> O <sub>32</sub>                            | CBZ  | 0.97 (0.83; 1.11)    | 0.9977         |
|  | PRP  | 1.18 (1.08; 1.28)    | 0.9982         |
|  | SMX  | 0.48 (0.36; 0.60)    | 0.9825         |

**Table 2.** SMX: degradation intermediates, retention times, fragment ions and proposed structures.

| Precursor Ion<br>(m/z) | t <sub>r</sub><br>(min) | MS <sup>2</sup><br>(m/z) | Structure   |
|------------------------|-------------------------|--------------------------|---|
| 301                    | 9.18                    | 177<br>133               |    |
| 283                    | 9.18                    | 239<br>177<br>133        |    |
| 270                    | 10.25                   | 206<br>228               |    |
| 174                    | 10.20                   | 156                      |    |
| 190                    | 3.76                    | 158                      |   |
| 216                    | 13.54                   | 198                      |  |
| 288                    | 14.46                   | 270                      |  |
| 228                    | 14.70                   |                          |  |

**Table 3.** CBZ: degradation intermediates, retention times, fragment ions and proposed structures.

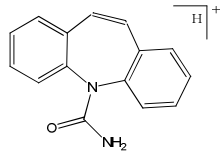
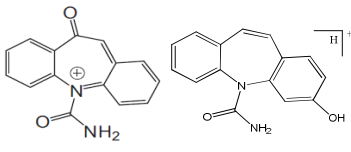
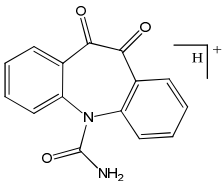
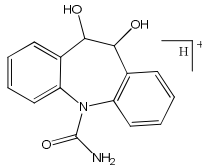
| Precursor Ion<br>(m/z) | Retention time<br>(min) | MS <sup>2</sup><br>(m/z) | Structure   |
|------------------------|-------------------------|--------------------------|---|
| 237.1                  | 14.35                   | 194.01<br>220.06         |    |
| 251.1<br>253.1         | 12.3                    | 208.0<br>210.0<br>236.0  |    |
| 267.1                  | 16.2                    | 168<br>196.1<br>211.1    |  |
| 271.1                  | 9.6                     | 210<br>253               |  |



Figure 1  
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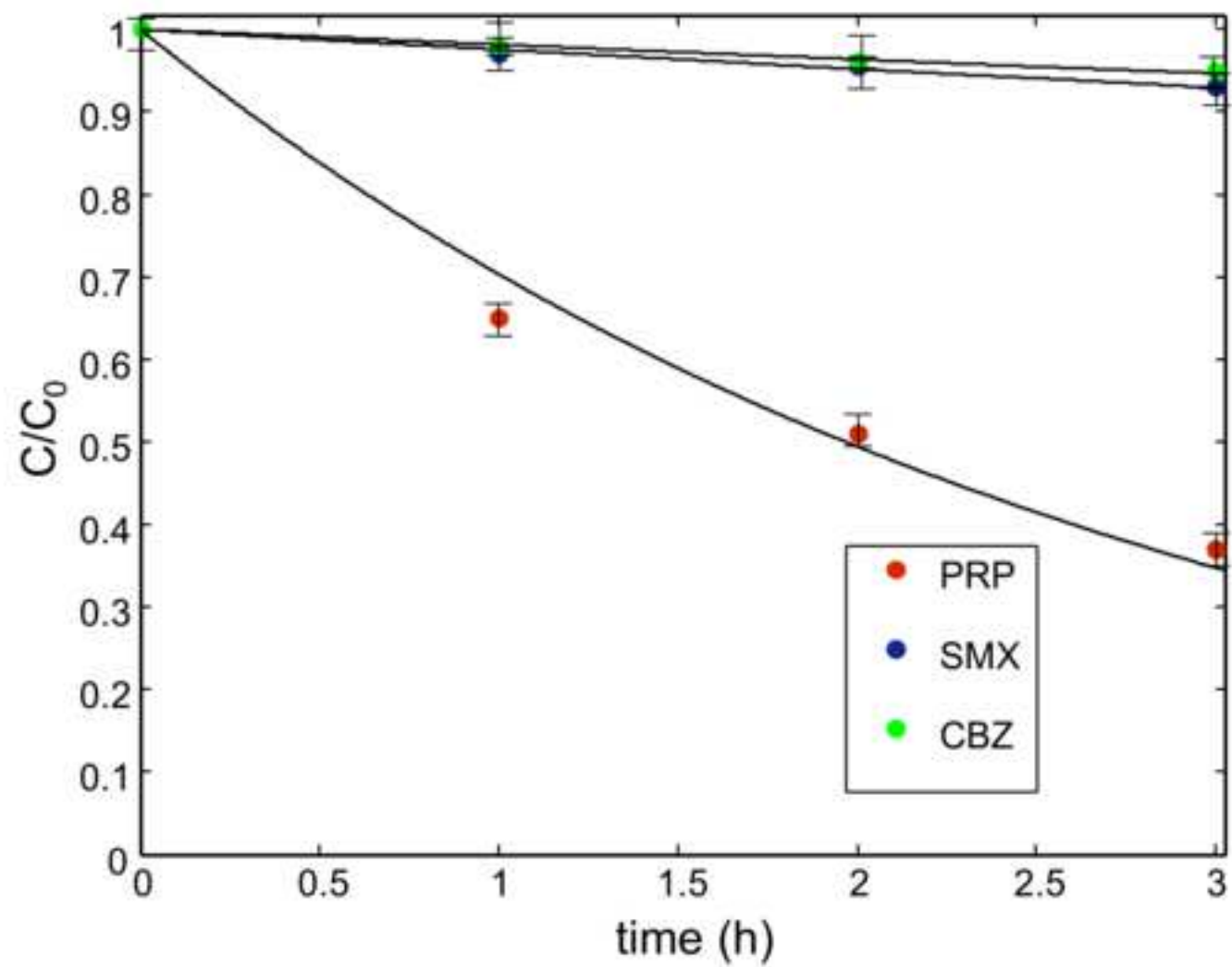


Figure 2  
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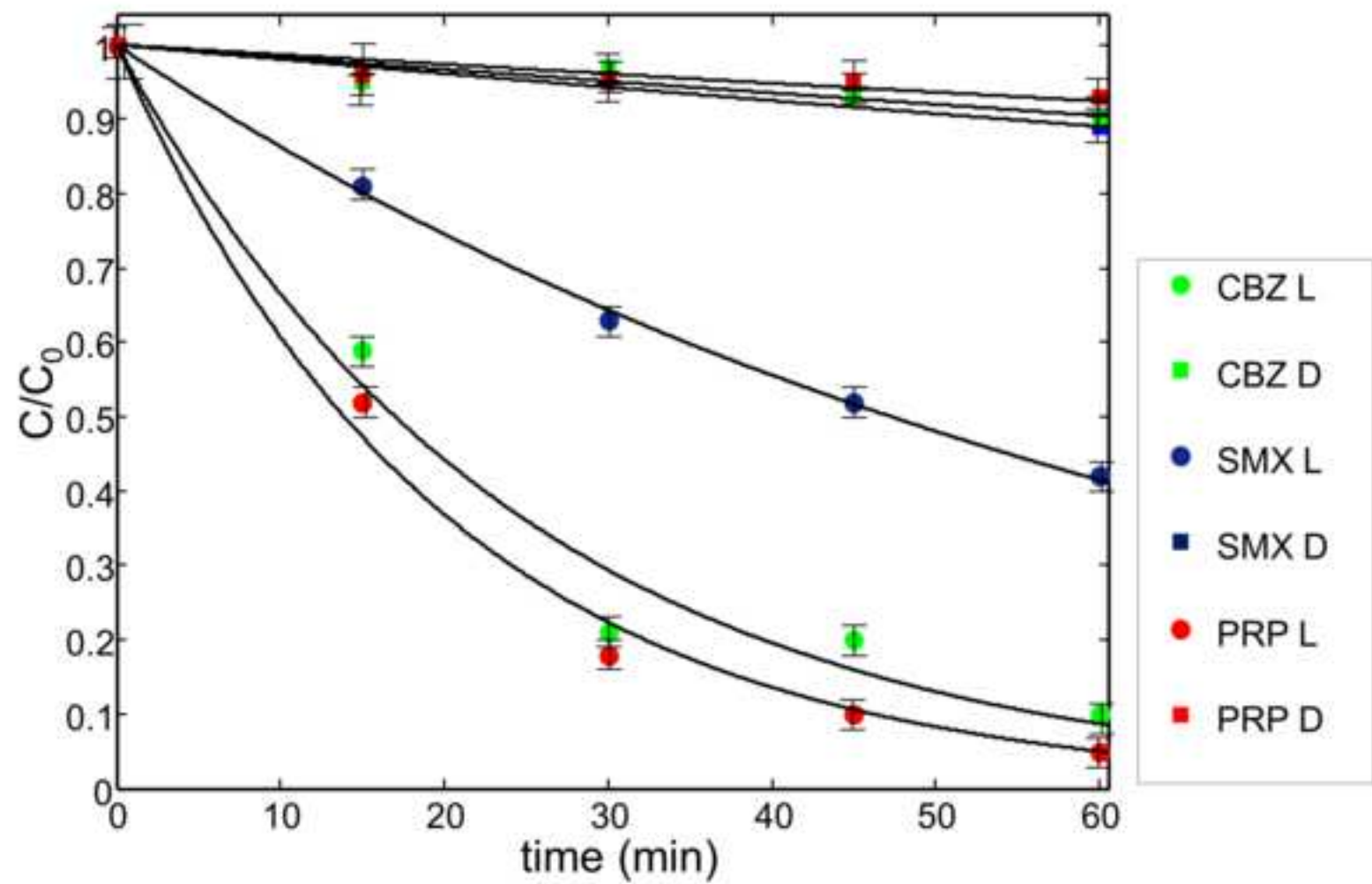


Figure 3  
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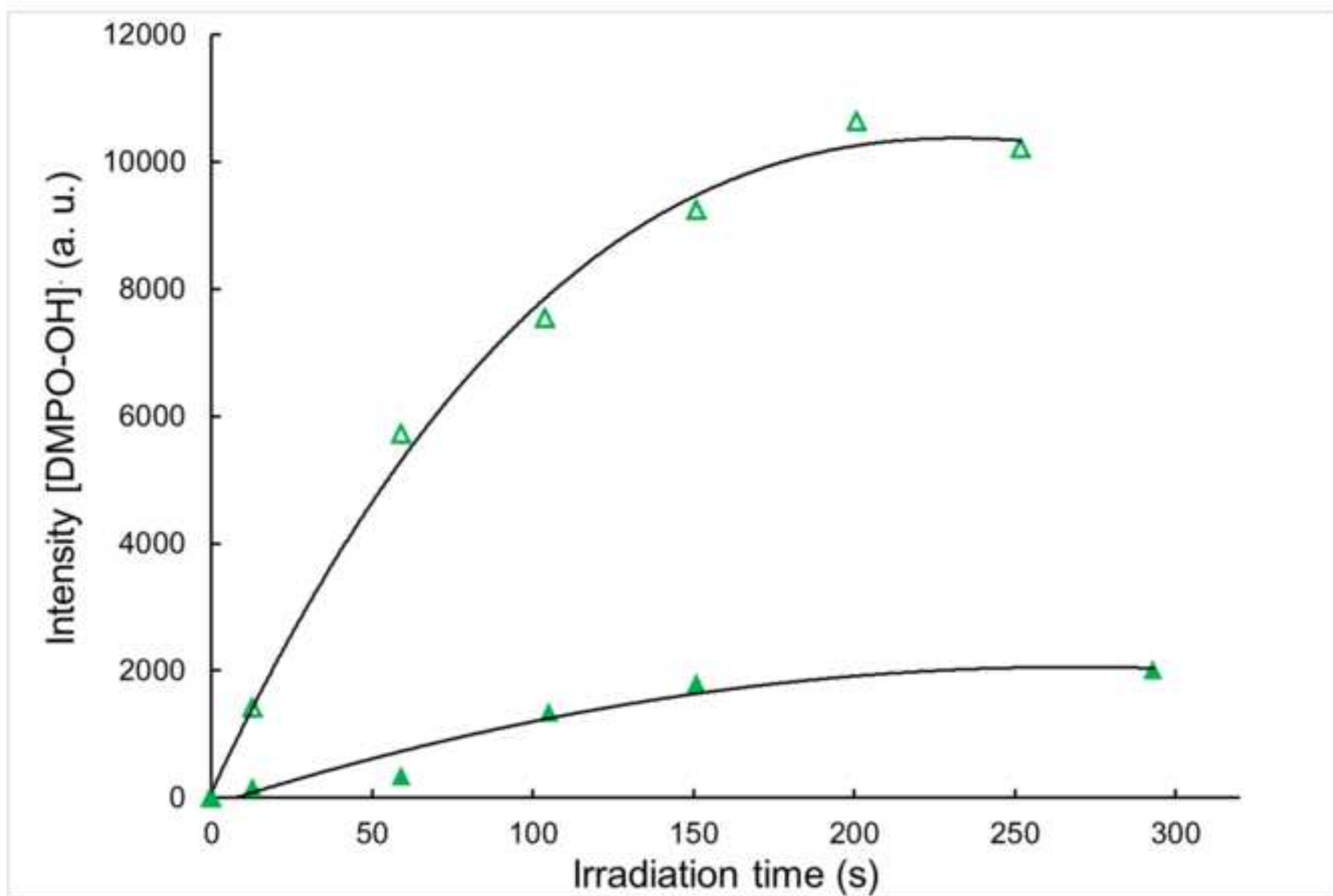




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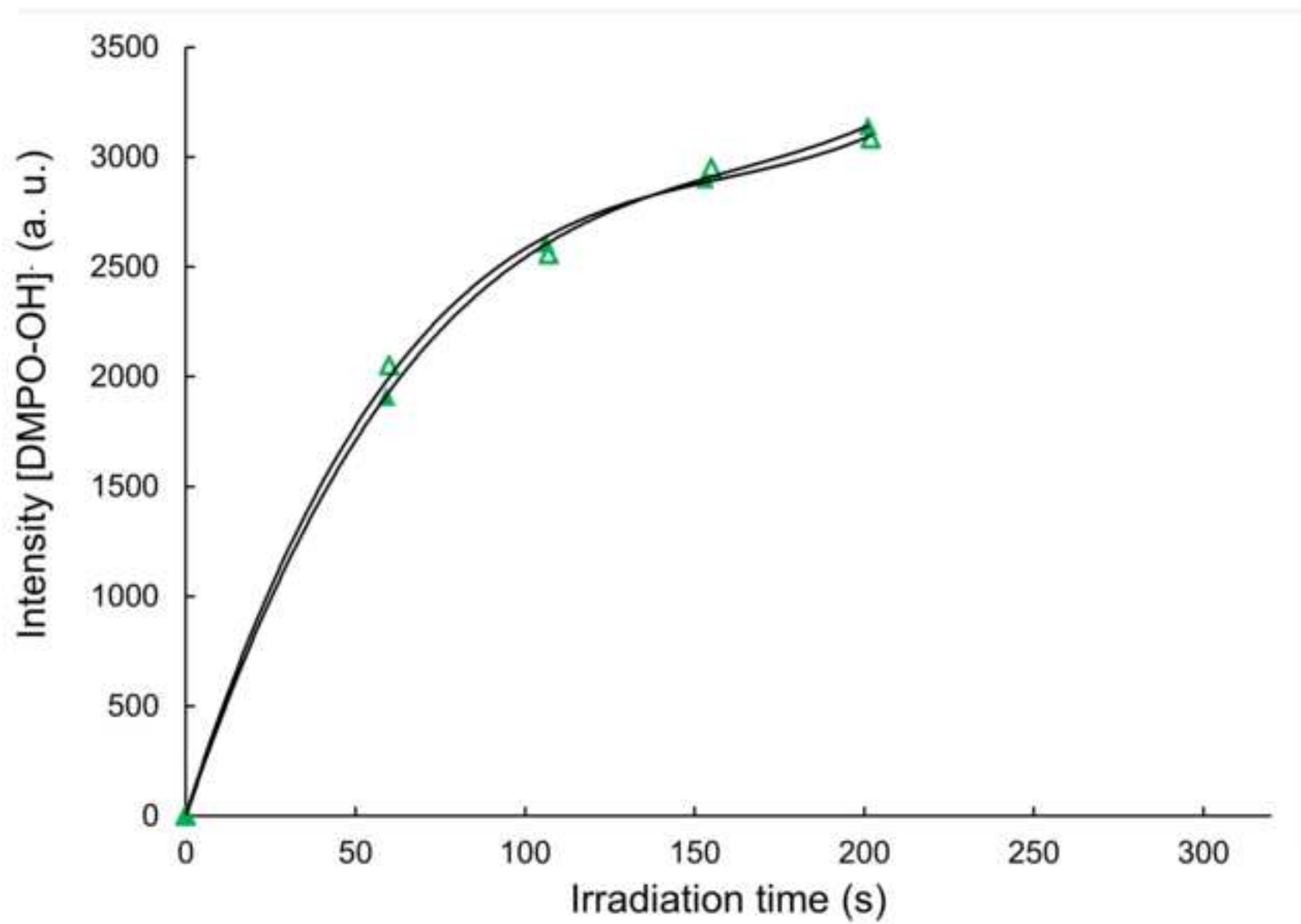
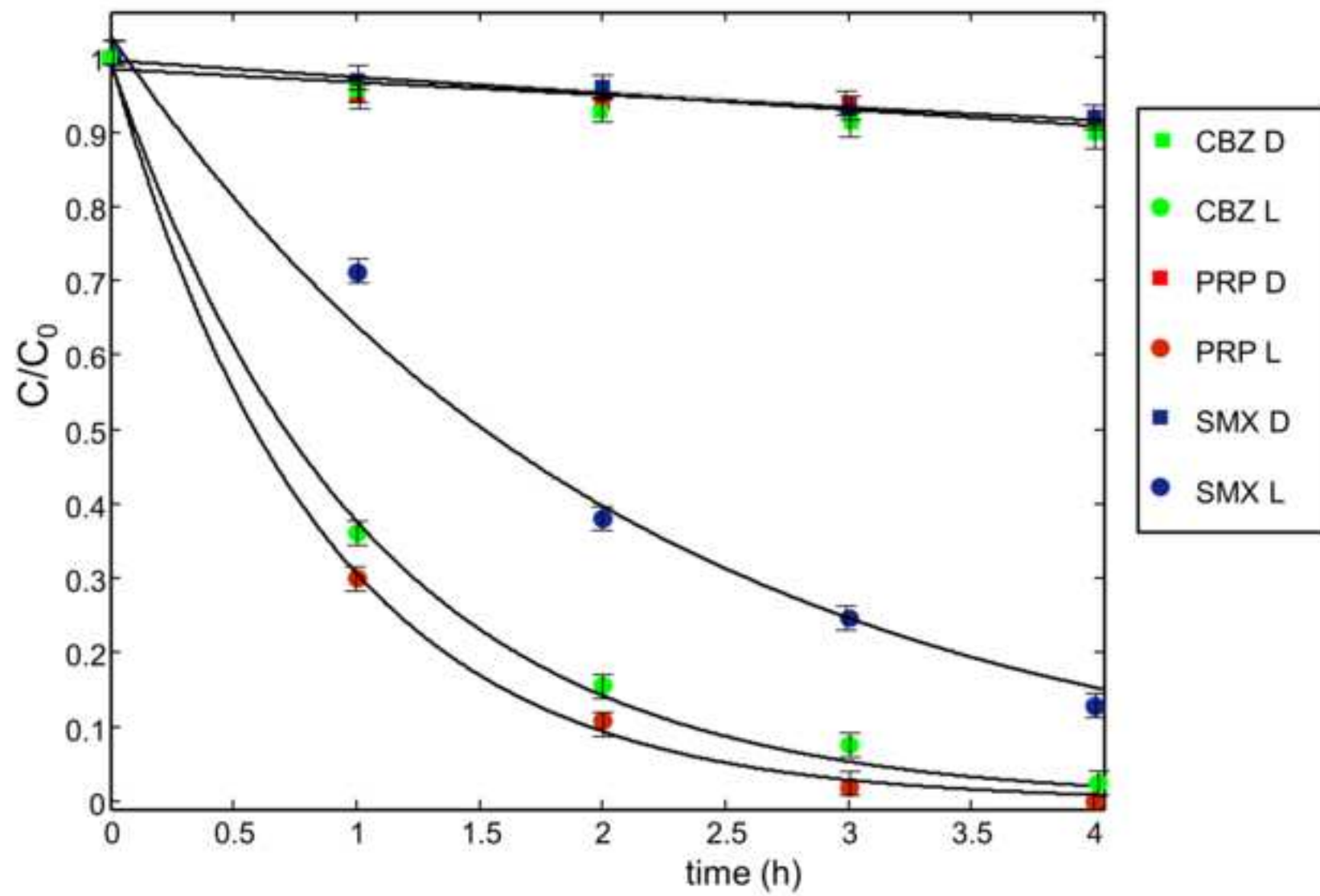
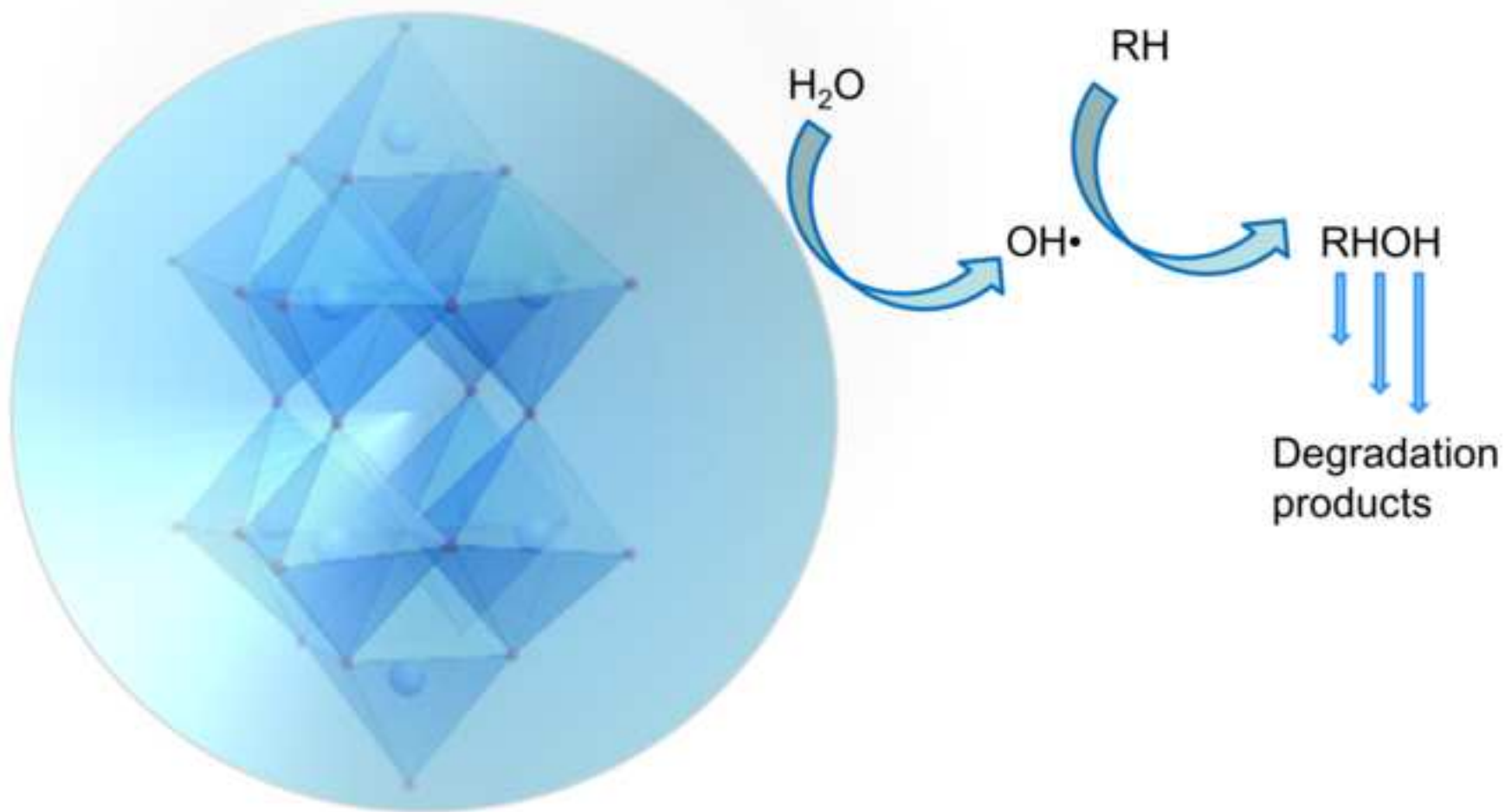


Figure 5  
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## **Highlights**

A heterogeneous photocatalytic system for water remediation is proposed.

Photoexcited sodium decatungstate oxidizes water producing  $\text{OH}^\bullet$  radicals which oxidize drugs.

The drug degradation ability of decatungstate strongly depends on the catalyst support.

Proper characteristics of the support can be successfully combined with decatungstate photoactivity.

**Supplementary Material**

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