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Chaima Brahmi, Mahmoud Benltifa, Mariem Ghali, Frédéric Dumur, Corine Simonnet-Jégat, et al.. Performance improvement of the photocatalytic process for the degradation of pharmaceutical compounds using new POM/polymer photocatalysts. *Journal of Environmental Chemical Engineering*, 2021, 9 (5), pp.106015. 10.1016/j.jece.2021.106015 . hal-03285144

HAL Id: hal-03285144

<https://hal.science/hal-03285144>

Submitted on 13 Jul 2021

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Performance improvement of the photocatalytic process for the degradation of pharmaceutical compounds using new POM/polymer photocatalysts

Chaima Brahmi^{a,b,c,d}, Mahmoud Benltifa^{*c}, Mariem Ghali^{a,b,c,d}, Frédéric Dumur^e, Corine Simonnet-Jégat^f, Monnier Valérie^e, Fabrice Morlet-Savary^{a,b}, Latifa Bousselmi^c, Jacques Lalevée^{* a, b}

^a University of Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

^b University de Strasbourg, France

^c Laboratory of Wastewaters and Environment, Center for Water Research and Technologies CERTE, BP 273, Soliman 8020, Tunisia

^d University of Carthage, National Institute of Applied Sciences and Technology, Tunis 1080, Tunisia

^e Aix Marseille Univ, CNRS, ICR, UMR7273, F-13397 Marseille (France)

^f Institut Lavoisier de Versailles, UMR CNRS 8180, Université Paris Saclay, Université de Versailles St-Quentin en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles cedex, France

*Corresponding author: Jacques.lalevee@uha.fr and mahmoud.benltifa@certe.rnrt.tn

Abstract:

In the last few years, pharmaceuticals compounds classified as emergent pollutants have attracted the attention of many researchers, due to their massive presence in soil, surface, sewage, groundwater and drinking water, and to their harmful impacts on human's health and environment. In this context, the degradation of four drugs with different chemicals structures which are Ciprofloxacin, Oxytetracyclin, Ibuprofen and Erythromycin was investigated. Indeed, in this paper, we studied the impact of the presence in the aqueous solution of a newly developed POM/polymer composites on the removal of these different drugs from water. Synthetic details and characterization of these materials were previously reported by our group. The different experiments done in this work revealed that the presence of the phosphomolybdic acid-based composite was not essential for the total degradation of

Ciprofloxacin and Oxytetracyclin which could be totally removed from water by simple photolysis under UV lamp irradiation. However, under the same experimental conditions, the use of this photocatalyst was indispensable for the total mineralization of Ibuprofen which is more recalcitrant than the other chosen drugs. In fact, just 16% of this pharmaceutical was degraded by simple photolysis vs. 100% and 94% under 90 min. of UV lamp and solar irradiation, respectively in the presence of the phosphomolybdic acid-based composite which was more pertinent than the usually used photocatalyst, namely titanium dioxide. Ibuprofen degradation pathway was identified thanks to mass spectrometry analysis, carried out at different times intervals. The obtained results demonstrated also that POM/polymer composite inhibits the degradation of Erythromycin by provoking the formation of more toxic intermediates than the original drug.

Keywords: photocatalysis, Polyoxometalate (POM) /Polymer composites, emergent pollutants...

1. Introduction

Recently, pharmaceutical products contaminating groundwater and threatening nature and human health have received intensive attention from scientists. These new pollutants enter the aqueous environment from domestic and industrial wastewater¹, affecting aquatic organisms² and causing diseases by promoting antimicrobial resistance³.

One of the most prescribed drugs worldwide, is Ibuprofen which is a non-steroidal anti-inflammatory used as a fever reducer and a pain killer in tooth aches, migraine, muscular pain and inflammation conditions^{4,5}. Antibiotics, are also excessively applied for humans and animal's medical treatments and additionally used in animals food to enhance their growth, to prevent and to control the apparition of serious diseases³. Indeed, Oxytetracyclin, Ciprofloxacin and Erythromycin are widely used antibiotics against numerous bacterial infections¹. These pharmaceutical compounds selected for this study have different stable chemical structures and these molecules are present in wastewater and rivers in non-negligible concentrations^{3,6}, since an important part of the initial drug dose administrated to humans and animal's is exerted to the environment. Indeed, based on previous studies, the concentration of pharmaceuticals present in groundwater and surface water were generally less than 0.1 µg/L and those in treated water were lower than 0.05µg/L⁷. The exposure to a

random combination between these different chemicals is a menace for humans' life. Therefore, researchers have concentrated their efforts on removing these toxic pharmaceuticals from water.

Conventional treatments such as physical and chemical methods, biodegradation, chemical and electrochemical oxidation have been applied for the degradation of these different drugs^{1,3,8}. However, these processes don't lead to a total mineralization of this products but most of the time transform them from one phase to another⁹. Hence, Advanced Oxidation processes (AOP), based on the production of highly reactive chemical including hydroxyl and superoxide anions radicals, have appeared as a new and performant technique for the total removal and mineralization of numerous emergent pollutants^{4,5,10}.

Depending on the power and the emitting wavelengths of the irradiation sources, as well as the chemical structures and absorption spectra of the pollutants. Some of these chosen pharmaceuticals could be totally degraded with or without the presence of oxidative agents in the aqueous media. However, some others could require the presence of a photocatalyst to achieve a total mineralization. In this context, heterogenous photocatalysis based on semi-conductors appeared as one of the most pertinent techniques when photocatalyst presents stability, non-toxicity, low-cost and oxidizing power leading to a total mineralization of the pollutant without the generation of toxic by-products⁹. Recently, researchers have focused their interest on this degradation process which was demonstrated by the bibliometric analysis below (Figure 1). In fact, about 3634 articles have been published between 2000 and 2020, with an increase in the publications number every five years reaching 2611 papers published in the last five years (See Figure 1).

Figure 1. Bibliometric data using the keywords: Pharmaceuticals/Photocatalysis. Source: BibCNRS.

Titanium dioxide is the most used photocatalyst nowadays, however it absorbs only 4% of sunlight and is active in the UV range ¹. Polyoxometalates (POM) appeared as new visible-light photocatalysts thanks to their low toxicities and costs, their acidities and redox properties as well as their powerful absorptions of UV light at a longer wavelength than that done with TiO₂^{11,12}. However, these clusters are very soluble in aqueous solutions which limit their recyclability and their reusability^{12,13}. As a solution, several studies have reported the association of POMs with several materials as counter ion¹⁴, TiO₂¹⁵, silica gel¹⁶ and active carbon¹⁷.

Recent works realized by our group have reported the immobilization of this catalyst into a polymer. In fact, different regenerable POM/polymer composites were synthesized by photopolymerization under visible light. The successful hybridization of POM/polymer was proved by several characterization techniques including Electron Microscopy, Energy Dispersive X-Ray Microscopy^{17,18}. Moreover, these new developed materials were very efficient for the removal of Bisphenol-A from water under UV lamp and direct solar irradiation¹⁹.

In the present study, we have investigated the removal of four pharmaceutical pollutants from aqueous solutions using the newly developed POM/polymer composites under different sources of irradiation. The chemicals degradation percentages were determined by UV-visible spectroscopy via the monitoring of their absorbances at different irradiation times. The obtained degradation kinetics were confirmed by mass spectrometry analysis which was also carried out at different irradiation times in order to identify the degradation mechanisms and to prove the total degradation of these pollutants.

2. Experimental section

2.1. Chemical compounds

H₃PMo₁₂O₄₀²⁰, W₁₀O₃₂(Thianthrenium)₄²¹ were synthesized according to reported procedures. The monomer trimethyl-propane triacrylate (TMPTA) used for radical polymerization was purchased from Allnex. *Bis*(4-*tert*-butylphenyl) iodonium hexafluorophosphate (Iod orSpeedcure938) and *bis*(2,4,6-trimethyl-benzoyl) phenylphosphine oxide (BAPO or

speedcure BPO) were acquired from Lambson Ltd. Titanium dioxide used in this study and composed of a mixture of rutile and anatase, was obtained from TCI. Ibuprofen (α -methyl-4-(isobutyl)phenylacetic acid), Ciprofloxacin, Oxytetracyclin and Erythromycin were obtained from Sigma Aldrich. Chemical structures of the different reagents used in this study are shown in Figure 2. Physicochemical properties of the different pollutants studied in this work are presented in Table 1.

The synthesis of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer and $\text{W}_{10}\text{O}_{32}(\text{TH})_4$ /polymer composites was detailed in our previous work.¹⁸, as well as the dimension, the BET surface area and the energy bandgap of the different prepared materials are gathered in Table 2.

Figure 2. Chemical structures of the compounds used in this work.

Table 1. Physicochemical properties of the different pollutants degraded in this work.

Pollutants	Physicochemical properties						
	Molecular formula	Molecular weight (g/mol)	Water solubility (mg/L) at 25°C	Dissociation constant (pKa)	Max absorption (nm)	pH in water	Concentration ($\mu\text{mol/L}$)
Ibuprofen	$\text{C}_{13}\text{H}_{18}\text{O}_2$	206.28	21 ²²	4.52 ²²	222 ²³	7.2	72-74
Ciprofloxacin	$\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$	331.34	460 ²⁴	6.68-8.63 ²⁴	278 ²⁵	6.3	45-27

Oxytetracyclin	C ₂₂ H ₂₄ N ₂ O ₉	460.43	313 ²⁶	3.57-7.49- 9.44 ²⁷	380 ²⁶	6.1	32.57
Erythromycin	C ₃₇ H ₆₇ NO ₁₃	733.9	4.2 ²⁶	8.9 ²⁶	280 (pH=6.3) ²⁶	5	20.43

Table 2: Band gap energy and BET surface area of the different developed materials¹⁷.

Characteristics	Developed materials			
	H ₃ PMo ₁₂ O ₄₀ /polymer composite	W ₁₀ O ₃₂ (TH) ₄ /polymer composite	TiO ₂ /polymer	polymer
Band gap energy (e.V)	2.8	3.2	3.1	3.9
BET surface area (m².g⁻¹)	1.3 ± 0.11	5.4 ± 0.11	-	9.3 ± 0.37

2.2. Irradiation Sources

Photocatalytic degradation experiments were carried out under different light sources including, Light-Emitting Diodes (LED): LED@375 nm ($I_0 = 70 \text{ mW/cm}^2$), an Omnicure Dynamics lamp, Serie 1000 Lumen ($I_0 = 250 \text{ mW/cm}^2$, $\lambda=320\text{-}520\text{nm}$) and direct solar irradiation. The emission spectrum of the Omnicure lamp is shown in Figure S1 and the solar experiments were realized on July 24, 2019 at 2 PM, in Mulhouse, France, Northeast 30°, North 47°43'46'', East 7°18'35'' with an average intensity calculated for the entire solar spectrum of 682 mW/cm^2 provided by "Meteo Alsace"²⁸. However, the intensity absorbed by the developed photocomposites during solar photolysis corresponds only to a fraction of the total solar energy presented above.

Photocatalysis Experiments

The concentration of the pharmaceutical pollutants samples was fixed to 15 mg/L, which is a common concentration studied in literature, higher than those noticed generally in real effluents like mentioned in the introduction, and detectable by UV-visible absorption spectroscopy. Molar concentrations and measured pH of each pharmaceutical samples are presented in Table 2.

Photocatalytic degradation experiments were carried out directly in the photometer cell in the presence of 4 mL of the pharmaceutical pollutants and the POM/polymer composite shaped in the form of pellet. Monitoring of the chemicals concentrations was realized by following their absorbance over time with a JASCO V730 spectrophotometer.

Mass Spectroscopy Experiments

Analyses were carried out with a SYNAPT G2 HDMS (Waters) mass spectrometer equipped with a pneumatically assisted air pressure ionization (API) source. Mass spectra (MS) were obtained with a flight time analyzer (TOF). Exact mass measurement was done in triplicate with an external calibration. The sample provided in water at a concentration of 15 ppm is diluted 1/10 in a solution of methanol at 0.1mM of sodium chloride. The solution of the extract is introduced into the infusion ionization source at a flow rate of 10 $\mu\text{l}/\text{min}$. Such analyses were reported in our previous works¹⁸.

Results and discussions

1. Ciprofloxacin and Oxytetracyclin photocatalytic degradation

Photocatalysis tests were carried out under a UV-Visible lamp irradiation, emitting lights at wavelengths between 320 and 520 nm with an intensity of 250 mW/cm^2 .

UV-visible absorption spectra of Ciprofloxacin and Oxytetracyclin at different irradiation times with and without the presence of the phosphomolybdic acid-based composite are shown in Figure 3.

Figure 3. UV-visible absorption spectra of Ciprofloxacin (15ppm) in water at different irradiation time upon irradiation with a UV lamp light (A) in the presence of $H_3PMo_{12}O_{40}$ /polymer composite; (B) Without the composite. UV-visible absorption spectra of Oxytetracyclin (15 ppm) in water at different irradiation times under UV lamp light (C) in the presence of $H_3PMo_{12}O_{40}$ /polymer composite; (D) Without the composite.

Ciprofloxacin is characterized by two absorption peaks located at 272 and 330 nm corresponding respectively to $\pi \rightarrow \pi^*$ transitions of fluorobenzene and quinolone²⁹. These two bands gradually decrease by elongating the irradiation time (See Figure 3 (A, B)). ~~The non appearance of new absorption peaks reveals that no by products absorbing at analytical wavelength appeared during the degradation⁴⁹ (See Figure 3 (A, B)).~~ Similarly, Oxytetracyclin is characterized by two absorption bands localized at 269 and 354 nm which correspond respectively to the chromophore A and the system BCD (See Figures 1 and 3 (C, D))³¹. Intensities of these two absorption peaks undergo a gradual decrease with the appearance of a new peak at 260 nm, confirming the presence of intermediates during the degradation process. Disappearance of all absorption peaks reflects the mineralization of this organic pollutant (See Figure 3 (C, D)).

The pharmaceuticals concentrations were determined by monitoring the changes affecting the absorbance of the most intense peaks of Ciprofloxacin and Oxytetracyclin UV–visible spectra located respectively at 272 and 269 nm (See Figure 3). Therefore, as shown in Figure 4, the phosphomolybdic acid-based composite was not essential for the degradation of these pollutants, since high removal percentages were reached even in the absence of this photocatalyst. However, the final degradation percentages of Oxytetracyclin and Ciprofloxacin were slightly increased from 75 to 86% and from 88 to 90% in the presence of POM/polymer composite and after 75min of the UV-visible lamp irradiation. Kinetics of the photocatalytic degradation reactions were studied and the results are gathered in Table 3.

Figure 4. Monitoring of the concentration of (A) (1) Ciprofloxacin in the presence of the phosphomolybdic acid-based composite , (2) Ciprofloxacin and (B) (3) Oxytetracyclin in the presence of the phosphomolybdic acid-based composite, (4) Oxytetracyclin, in water, under UV-lamp irradiation light. [Oxy]₀=15mg/L, [CIP]₀=15mg/L.

Kinetics of Ciprofloxacin and Oxytetracyclin photocatalytic degradation in the presence or not of the phosphomolybdic acid-based composites were quantitatively determined by fitting the zero order, pseudo first-order and pseudo second-order equations to the experimental data. These models are given by the following equations³²:

$$C_0 - C = k_{app,0} t \quad (1)$$

$$-\ln(C/C_0) = k_{app,1} t \quad (2)$$

$$(C_0 - C)/(C \cdot C_0) = k_{app,2} t \quad (3)$$

C_0 and C designate respectively the pharmaceuticals initial concentrations and at time t , $k_{app,0}$ is the zero-order rate constant ($\text{mg L}^{-1} \text{min}^{-1}$), $k_{app,1}$ is the first-order rate constant (min^{-1}), $k_{app,2}$

is the second-order rate constant ($\text{L mg}^{-1} \text{ min}^{-1}$) and t the time. Therefore, k_{app} gives an indication of the activity of the catalyst. Results are gathered in Table S1.

As shown in Table S1, regression coefficients (R^2) calculated based on the zero order and first-order reactions, are very low and ranged from 0.407 to 0.780 thus demonstrating that degradation kinetics of these pollutants does not follow the zero-order and pseudo-first-order kinetics. Though, the regression coefficients calculated for the pseudo-second-order varying between 0.955 and 0.998 confirmed that these pharmaceuticals are degraded according to this kinetic model. Moreover, the obtained results confirmed also that the phosphomolybdic acid-based composite have slightly enhanced the degradation of the chosen two pollutants. Indeed, the second-order rate constants were increased from 0.113 to 0.243 $\text{L mg}^{-1} \text{ min}^{-1}$ and from 0.055 to 0.073 $\text{L mg}^{-1} \text{ min}^{-1}$, respectively in the cases of Oxytetracyclin and Ciprofloxacin (See Table S1).

In order to verify the obtained results by UV-visible absorption spectroscopy, the samples collected after 90 min of irradiation were analyzed by mass spectrometry. Figures 5 and 6 show that Ciprofloxacin ($m/z = 332.1$) is totally removed from water whether the presence or not of the phosphomolybdic acid-based composite in the aqueous solution. However, for the same irradiation time, the POM/polymer composite enhanced the mineralization of Oxytetracyclin. In fact, the disappearance of the characteristic peak of this pharmaceutical at $m/z=461.2$ after irradiation, in the presence of the photocatalyst, as shown in Figure 6 (B) confirms the total degradation of this pollutant. This peak persists in the absence of the composite proving that traces of this pollutant is still present in the aqueous media.

Figure 5. Positive electrospray mass spectrum of the Ciprofloxacin sample calibrated for exact mass measurement (targeted ion is detected at $m/z=332.1$), (a) before photolysis, (b) after photolysis in the absence of the $H_3PMo_{12}O_{40}$ /polymer composite under UV lamp irradiation (c) after photocatalytic degradation in the presence of the $H_3PMo_{12}O_{40}$ /polymer composite under UV lamp irradiation and (d) Positive electrospray mass spectrum of the analytical blank.

Figure 6. Positive electrospray mass spectrum of the Oxytetracycline sample calibrated for exact mass measurement (targeted ion is detected at $m/z=461.2$), (a) before photolysis, (b) after photolysis in the absence of the $H_3PMo_{12}O_{40}$ /polymer composite under UV lamp irradiation (c) after photocatalytic degradation in the presence of the $H_3PMo_{12}O_{40}$ /polymer composite under UV lamp irradiation and (d) Positive electrospray mass spectrum of the analytical blank.

2. Ibuprofen photocatalytic degradation

In contrary to Ciprofloxacin and Oxytetracycline which are totally decomposed under UV Lamp irradiation even in the absence of the POM/polymer composite, only 16% of

Ibuprofen is removed from water under the same time and irradiation source. Hence, the use of this photocatalyst was indispensable for the total degradation and mineralization of this recalcitrant pollutant.

Figure 7. UV-visible absorption spectra of Ibuprofen (15ppm) in water at different irradiation times upon UV lamp irradiation: (A) in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite, (B) Without the composite.

Progress of the photocatalytic abatement of Ibuprofen with the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite was followed by monitoring the characteristic peak of this pharmaceutical located at 220 nm by UV–visible absorption spectroscopy. Figure 7 shows that the absorption peak of this drug at 220 nm which is related to the benzene ring decreased rapidly by increasing the irradiation time, indicating the photocatalytic degradation process of this pharmaceutical pollutant (See arrow 1). Moreover, a new red-shifted band near 262 nm appeared which strongly indicates the formation of reaction intermediates (See arrow 2). This by-product is probably a changed aromatic molecule such as products hydroxylated in the aromatic, or intermediates with new functional groups on the benzene ring such as olefins, alcohols and ketones, which are promoted by the attack of Ibuprofen by strong oxidant species such as hydroxyl radicals^{19,20}. The formed band starts to arise immediately in the first period of photocatalytic treatment (after 5 min), and reaches a maximum after 30 min of photocatalytic treatment and then decreases with the irradiation time, suggesting the decomposition of these intermediates (See arrow 3). The band in the 250–300 nm range disappears, indicating the decomposition of the aromatic structure. A characterless absorption band however remains. It is probably due to the absorbance of other by-products formed by a secondary degradation of the primary by-product^{19,20}.

To study the effect of the type of irradiation sources on the Ibuprofen photocatalytic degradation, solutions containing 15 ppm of this pollutant in water were separately irradiated with a solar irradiation ($\lambda > 290$ nm, $I_0 = 682$ mW/cm²), a UV lamp (250 mW/cm², $\lambda = 320$ -550nm) and a LED@375nm (70 mW/cm²). The obtained results are presented in Figure 8.

Figure 8. (A) Conversion of Ibuprofen in the presence of the phosphomolybdic acid-based composite under (1) UV Lamp, (2) sunlight, (3) LED@375 nm, and without the composite under (4) UV Lamp, (5) sunlight and (6) LED@375 nm. [IBU]₀=15 ppm.

Figure 8 shows that the photolysis of Ibuprofen under the different irradiation sources and without the presence of any photocatalysts was low. Indeed, the concentration of this pharmaceutical hardly decreased by only 21%, 16%, 0.07% after 90 min of solar, UV lamp and LED@375nm irradiation, respectively. However, presence of the phosphomolybdic acid-based composite enhanced this pollutant conversion, reaching 94%, 100% and 69% under the same time and irradiation sources, respectively. These degradation percentages were confirmed by mass spectrometry analyses (See Table 3). Difference of efficiencies between the different irradiation sources can be explained by their irradiation intensities and their respective emission spectra. Indeed, the UV lamp and the solar irradiation are the most relevant ones thanks to their high irradiation power and the good overlap of their emission spectra with that of the composite absorption spectrum.

Table 3. Determination of Ibuprofen percentage removal from water by UV-visible absorption spectroscopy and mass spectrometry under different sources of irradiation.

Irradiation source	% of conversion of Ibuprofen after irradiation
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	UV-visible spectroscopy	Mass spectrometry
UV lamp	100	100
Solar irradiation	94	89
LED@375nm	69	60

Furthermore, the obtained results demonstrate that the composite has excellent photocatalytic activity for the degradation of Ibuprofen under different irradiation sources compared to other photocatalysts reported in the literature for the photocatalytic degradation of this pharmaceutical pollutant. In fact, Abdusalam and coworkers have degraded 99% of a 5 ppm ibuprofen solution in 200 min under visible light irradiation, using a surface modified TiO₂ nanoparticle immobilized on polyacrylonitrile/multiwall carbon nanotubes²¹. Moreover, 70 and 80% of Ibuprofen present in aqueous solutions could be removed from water after 90 min of solar irradiation. These percentages have been reported by Muhammad Tanveer and coworkers who used TiO₂ and ZnO photocatalysts respectively²².

The phosphomolybdic composite was selected as the photocatalyst model for the study of the effect of the irradiation sources on the removal of Ibuprofen and for the photocatalytic degradation of Ciprofloxacin and Oxytetracyclin, based on our previous works concerning the removal of Bisphenol-A from water in the presence of different POM/polymer composites, where the phosphomolybdic composite was identified as the most efficient one for this purpose¹⁹.

Therefore, in this paper, photocatalytic performance of the phosphomolybdic composite on the photocatalytic degradation of Ibuprofen ~~which was the most efficient one for the removal of Bisphenol-A from water deduced from our previous works,~~ was also compared to that of the decatungstate polyoxometalate and of the titanium dioxide in their powdered and composites forms, as TiO₂ is the most widely used photocatalyst nowadays under UV light. However, it was impossible to include the H₃PMo₁₂O₄₀ polyoxometalate in this comparison because of its high solubility in water and the superimposition of its absorption peak with that of the Ibuprofen pharmaceutical. All composites were synthesized under the same operating conditions. Obtained results are shown in Figure 9 and gathered in Table 4.

Figure 9. Ibuprofen photolysis (1) without photocatalysts presence and in the presence of (2) Suspended TiO_2 , (3) TiO_2 /polymer composite, (4) Polymer, (5) $\text{W}_{10}\text{O}_{32}(\text{TH})_4$ /polymer composite, (6) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite and (7) Suspended $\text{W}_{10}\text{O}_{32}(\text{TH})_4$, under UV lamp irradiation. $[\text{IBU}]_0=15\text{ppm}$.

Kinetics of the Ibuprofen photolysis and catalytic photocatalytic degradation by the different developed materials was quantitatively investigated by fitting the apparent first-order equation to the experimental data. This model is given by the following equation³²:

$$-\ln(C/C_0) = k_{\text{app}} t \quad (1)$$

C_0 and C designate respectively the Ibuprofen initial concentration and at time t , k_{app} is the first-order rate constant (min^{-1}) and t the time. Therefore, k_{app} gives an indication of the photocatalysis kinetic of the catalyst. Results are gathered in Table 4.

Table 4. Study of the Ibuprofen degradation kinetics by the different synthesized composites under UV lamp irradiation.

Materials	k_{app} (min^{-1})	R^2
$\text{W}_{10}\text{O}_{32}(\text{TH})_4$ (Powder)	0.073	0.964
TiO_2 (Powder)	0.013	0.965
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer	0.056	0.999
$\text{W}_{10}\text{O}_{32}(\text{TH})_4$ /polymer	0.027	0.846
TiO_2 /polymer	0.009	0.989
Polymer	0.009	0.990
Ibuprofen photolysis	0.006	0.945

Apparently, the polymer, the phosphomolybdic acid, decatungstate and titanium dioxide-based composites as well as the powdered samples showed low adsorption capacities of

Ibuprofen in the dark. Indeed, the low adsorption percentages of this pollutant ranged between 1% and 9% (See Figure 9). This could be explained by the small BET surface area of the different materials¹⁷ (See Table 2).

Furthermore, the comparative study between the different synthesized materials used for Ibuprofen removal from water presented in Figure 9 and Table 4, showed that the phosphomolybdic acid and decatungstate composites exhibit the highest Ibuprofen photocatalytic degradation under UV lamp irradiation. In fact, approximately 100% ($K_{app} = 0.056 \text{ min}^{-1}$) and 92% ($K_{app} = 0.027 \text{ min}^{-1}$) of this compound was removed by these two photocatalysts respectively, after 90 min of irradiation (See Figure 9 (curve 5, 6)). The better photocatalytic activity of the phosphomolybdic acid-based composite compared to that of the decatungstate composite was probably due to its lower energy bandgap (2.8 eV) (See Table 2) and to its higher redox potential and therefore to its easiness to be reduced (approximately a difference of 0.4 V between the two composites)^{37,38}. Indeed, a molybdate Keggin type polyoxometalate could accept between 1 e^- and 12 e^- . However, the decatungstate polyoxometalate can accept only 1 or 2 e^- ³⁸. Furthermore, thanks to their excellent redox properties as well as the lower energy bandgap in the case of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite, these two composites were more efficient than titanium dioxide/polymer composite. In fact, only 55% ($K_{app} = 0.009 \text{ min}^{-1}$) of the initial Ibuprofen concentration could be removed from water in the presence of the TiO_2 /polymer composite compared to POM/composites (84% ($K_{app} = 0.027 \text{ min}^{-1}$) and 97% ($K_{app} = 0.056 \text{ min}^{-1}$)) (See Figure 9 (curves 3, 5, 6)). Moreover, in the presence of the neat polymer, approximately 55% ($K_{app} = 0.009 \text{ min}^{-1}$) of this pharmaceutical was degraded. This could be due to the presence of the oxidant iodonium salt into the polymer, used as co-initiator for the free radical polymerization.

Remarkably, the photocatalytic performance of the different photocatalysts used in this work was reduced by their immobilization in the polymer. This was confirmed in the case of the decatungstate POM and TiO_2 , which have respectively removed 100% ($K_{app} = 0.073 \text{ min}^{-1}$) and 56% ($K_{app} = 0.013 \text{ min}^{-1}$) of Ibuprofen after 60 min of UV lamp irradiation when they were used in suspension (See Figure 9 (curves 7, 2)) vs. 84% ($K_{app} = 0.027 \text{ min}^{-1}$) and 50% ($K_{app} = 0.009 \text{ min}^{-1}$) in composite (See Figure 9 (curves 3, 5)). This was probably due to the decrease of the photocatalysts active sites.

In order to evaluate the newly synthesized POM/polymer composites photocatalytic performances on the Ibuprofen removal from water under UV lamp and solar irradiation, the average degradation reached by these materials, the active and specific surface area as well as the apparent kinetics constants ($K \text{ min}^{-1}$) were compared to those of the most relevant immobilized photocatalysts reported in the literature (between 2000 and 2020 (See Table 5)). To facilitate the comparison, a coefficient D^* representing the ratio between average degradation rate and the active surface area of the immobilized photocatalysts, was calculated (Table 5: coefficient D^*).

Table 5. Comparative study of the different immobilized photocatalysts used for the Ibuprofen photocatalytic degradation .

Photocatalyst	Light source	Average degradation/Material active surface ($\text{mg.min}^{-1}.\text{cm}^{-2}$) (D^*)	Specific surface area (m^2/g)	$k_{\text{app}} (\text{min}^{-1})$	References
H₃PMo₁₂O₄₀/polymer composite	UV light (250 mW/cm ²)	3.55×10^{-4}	1.3	7.9×10^{-2}	This work
	Sunlight (682 mW/cm ²)	3.35×10^{-4}	1.3	3×10^{-2}	This work
W₁₀O₃₂(TH)₄/polymer composite	UV light (250 mW/cm ²)	3.29×10^{-4}	5.4	2.75×10^{-2}	This work
TiO₂/polymer composite	UV light (250 mW/cm ²)	2.16×10^{-4}	-	9.4×10^{-3}	This work
Self-assembled films of PAA/PAH/TiO₂	Xenon solar simulator (350 mW/cm ²)	1.67×10^{-4}	-	-	39
TiO₂ activated borosilicate tube	Solar simulator (50 mW/cm ²)	1.22×10^{-5}	-	3×10^{-3}	40
Immobilized TiO₂/ZnO sensitized copper (II)	365 nm UV light (1200 mW/cm ²)	2.67×10^{-5}		7×10^{-3}	41
PAN-MWCNT/TiO₂-NH₂ nanofiber membrane	UV-A lamp (315-400nm), 40W	2.18×10^{-5}	-	-	5
Immobilized TiO₂ in a pilot plant	Solar light	4.03×10^{-6}		4.8×10^{-2}	42
TiO₂-rGO (reduced Graphene Oxide)	Visible light irradiation	6.74×10^{-7}	-	7×10^{-4}	43
	UV light irradiation	4.85×10^{-6}	-	-	
TiO₂-Fe	Visible light irradiation	1.73×10^{-6}	-	1.85×10^{-3}	
	UV light irradiation	1.60×10^{-6}	-	-	

D^* was calculated by this paper's authors.

Interestingly, the developed POM/polymer composites displayed better ratios between the average degradation and the active catalysts surface area which corresponds to the calculated D^* , than those calculated for the most pertinent fixed catalysts already

reported in the literature (Table 5). A factor of 10 to 100 differentiates the average degradation achieved by the materials studied in this work from those identified from the bibliographic research (See Table 5). Other factors can have a drastic effect on D^* and are not considered here such as the intensity of the light source or the energy bandgap of the developed photocatalysts. However, we can assume that our newly synthesized photocatalysts have high efficiencies and performances for Ibuprofen photocatalytic degradation compared to those reported in Table 5.

Ibuprofen degradation percentages obtained by UV-visible absorption spectroscopy were confirmed by mass spectrometry (See Table 3). Moreover, the realization of mass spectra at different irradiation times during the Ibuprofen photocatalytic process allowed the identification of the different steps of the photocatalytic degradation mechanism (See Figure 11). Confirmation of the degradation kinetics was investigated under UV lamp irradiation via UV-visible absorption spectroscopy (See Table 6).

Table 6. Study of the Ibuprofen degradation kinetics by two different analysis methods: Mass spectrometry vs. UV-visible absorption spectroscopy, in the presence of the phosphomolybdic acid-based composite. $[IBU]_0 = 15$ ppm.

Methods	kapp (min^{-1})	R ²
UV-visible spectroscopy	0.056	0.999
Mass spectrometry	0.049	0.939

Table 6 showed the monitoring of the Ibuprofen photocatalytic degradation via two different methods, namely UV-visible absorption spectroscopy and mass spectrometry. Apparent kinetic first order constants reached by the two analysis methods were almost similar (0.056 min^{-1} vs. 0.049 min^{-1}).

The mineralization of Ibuprofen was verified by mass spectrometry analyses of different samples collected at the end of the photocatalytic process in the presence of the phosphomolybdic acid-based composite under UV lamp irradiation. Results are presented in Figure 10.

Figure 10. Negative electrospray mass spectrum of the Ibuprofen sample calibrated for exact mass measurement (targeted ion is detected at $m/z=205.1$), (a) before photolysis, (b) after catalytic photocatalytic degradation in the presence of the $H_3PMo_{12}O_{40}$ /polymer composite under 90 min of UV lamp irradiation and (c) Negative electrospray mass spectrum of the analytical blank.

Figure 10 shows that the heterogeneous photocatalytic degradation of Ibuprofen operating under UV lamp irradiation promoted the total removal and the mineralization of this compound. In fact, disappearance of the Ibuprofen characteristic peak at $m/z=205.1$ after the irradiation confirms the total degradation of this pollutant. Moreover, the total degradation of by-products formed during the photocatalytic process demonstrates the mineralization of this pollutant.

Mechanism of the photocatalytic degradation

In order to identify the Ibuprofen degradation route, the samples collected during the degradation experiments at different time intervals were analyzed by mass spectrometry. The HRMS data and the obtained mass spectra shown in Table 7 allowed to identify some intermediates arising from the photocatalytic degradation of Ibuprofen based on the literature, which are I_2 , I_3 and I_4 . I_1 , I_5 and I_6 .

Based on previous studies concerning ibuprofen mineralization, I_1 ($C_{13}H_{18}O_3$), which could be represented as two isomeric forms: α -hydroxycarboxy-IBP and α -hydroxy-isopropyl-IBP), is formed by a hydroxyl radical attack and add to the ring or the side chain of Ibuprofen^{6,44,45}. Subsequently, the decarboxylation of primary intermediate I_1 results in the formation of 4-isobutylacetophenone (I_2) which was identified by experiments analysis and previously reported in many works^{34,46–48}.

By extending the photolysis duration, the secondary by-product formed, undergoes continuously attacks by hydroxyl radicals leading to the formation of the intermediate I_3 . Therefore, the decomposition of the compound I_3 forms two intermediates I_4 and I_5 ⁴. I_3 and I_4 are identified by mass spectrometry experiments and based on our knowledge, they are reported for the first time in this work. The repeatedly electrophile addition of hydroxyl radicals to the formed by-products induced benzene ring opening and then the mineralization of the initial pharmaceutical product by producing linear carboxylic acids with low molar mass and CO_2 ⁴. The different identified intermediates via experimental mass spectrometry analysis and those deduced from the literature are gathered in Table 7.

The degradation mechanism presented in Figure 11, based on mass spectrometry analyses and deduced from the literature was in line with our previous work in which we have reported the photocatalytic POM/polymer composite mechanism based on hydroxyl radical production¹⁸.

Table 7. Identification of the formed Intermediates during the Ibuprofen photocatalytic degradation.

	Compound name	Formula	Theoretical m/z	Measured m/z	Δ (pp m)	reference
I	Ibuprofen	$C_{12}H_{16}O_4$	224.16	224.16	0.9	
I_1	Hydroxy Ibuprofen	$C_{13}H_{18}O_3$	222			¹⁵
I_2	4-isobutylacetophenone	$C_{12}H_{16}O$	177.12	177.12	3	⁴⁵
I_3	1-[4-(1,2-dihydroxy-2-methylpropyl)-2-hydroxyphenyl] ethanone	$C_{12}H_{16}O_4$	225.11	225.10	1	
I_4	2-Hydroxyisobutyric acid	$C_4H_8O_3$	103.04	104.04	10	
I_5	Phloracetophenone	$C_9H_8O_4$	125.02			⁴
I_6	1,6-Dideoxyhexo-2,5-diulose	$C_6H_{10}O_4$	146			⁴

Figure 11. Ibuprofen proposed degradation mechanism.

3. Erythromycin photocatalytic degradation

Erythromycin is one of the most prescribed antibiotics worldwide, used for the treatment of different infections⁴⁹. Due to its toxicity and abundant presence in groundwater, removing it from water by our new developed POM/polymer composites seemed to be an interesting approach. Obtained results are shown in Figure 12.

Figure 12. UV-visible absorption spectra of the Erythromycin (15ppm) in water at different irradiation times upon UV lamp irradiation: (A) in the presence of the $H_3PMo_{12}O_{40}$ /polymer composite and (B) Without the composite.

Figure 12 (A) shows that the modification of the absorption spectra of Erythromycin with increasing the irradiation time in the presence of the $H_3PMo_{12}O_{40}$ /polymer composite clearly indicates the formation of reactions intermediates. In fact, the absorbance at 210 nm starts to arise immediately at the beginning of the photocatalytic treatment and reaches a maximum after 15 min of irradiation and then decreased, due to the decomposition of the formed by-product.

However, the Erythromycin photolysis absorption spectra in water in the absence of the composite (Figure 12 (B)), haven't undergone the same spectral changes. Indeed, a slight increase in the absorbance at 210 nm was noticed. These results suggest that this antibiotic dissolved in pure water did not photodegrade in the same way under UV lamp irradiation in the presence or not of the phosphomolybdic acid-based composite.

As the UV-visible absorption spectra cannot be used to monitor the degradation of the pollutant as the newly formed intermediaries are absorbing in the same range than the phosphomolybdic acid-based composite. In order to confirm the Erythromycin photocatalytic degradation and to identify the formed intermediates, mass spectrometry analyses were carried out before and at the end of the irradiation process. Results are shown in Figure 13.

Figure 13. Positive electrospray mass spectrum of the Erythromycin sample calibrated for exact mass measurement (targeted ion is detected at $m/z=734.5$), (a) before photolysis, (b) after photocatalytic degradation in the absence of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite under 90 min of UV lamp irradiation, (c) after photocatalytic degradation in the presence of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite under 90 min of UV lamp irradiation and (c) Positive electrospray mass spectrum of the analytical blank.

Figure 13 (b) shows that the Erythromycin photolysis under a UV lamp irradiation without the POM/polymer composite presence, promoted the total removal and the mineralization of this compound. In fact, the disappearance of the characteristic peak of Erythromycin at $m/z=734.5$ after the irradiation confirms the total degradation of this pollutant. However, in the presence of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ /polymer composite, only 94% of this

antibiotic was removed from water (See Figure 13 (c)). Moreover, the Erythromycin A dihydrate and the Erythromycin F have been identified by mass spectrometry analyses as by-products with a mass error less than 1ppm. These intermediates were previously reported by Voigt and coworkers who studied the photocatalytic degradation kinetics of azithromycin, erythromycin and tylosin and their transformation products⁵⁰. Tae-Kyoung Kim and coworkers have also reported the generation of these two by-products during the photocatalytic treatment of Erythromycin with chlorine. Furthermore, they studied their toxicities and noticed that Erythromycin A dihydrate (by-product 1) has higher toxicity than Erythromycin whereas Erythromycin F (by-product 2) has lower toxicity⁴⁹. Therefore, presence of the phosphomolybdic acid-based composite in solution decreased the Erythromycin mineralization rate and led to the production of toxic intermediates after 90 min of treatment. Consequently, the heterogenous photocatalytic treatment of this antibiotic is less effective than its simple photolysis. A partial degradation pathway of Erythromycin in the presence of the POM/polymer composite and under Omnicure lamp irradiation is proposed in Figure 14 based on mass spectrum analyses and the literature^{49,50}. By-product 1 is a result of a dehydration of the initial compound and by-product 2 is formed by a hydroxyl attack.

Figure 14. Suggested photocatalytic degradation pathway of the Erythromycin under UV Lamp irradiation, in the presence of the phosphomolybdic composite.

Conclusions

Since the presence of pharmaceuticals compounds in groundwater is a serious problem threatening human health and environment, the degradation of Ciprofloxacin, Oxytetracycline, Ibuprofen and Erythromycin was investigated in this work based on UV-visible absorption spectroscopy and mass spectrometry analyses.

In this study, the effectiveness of our new developed POM/polymer composites for the removal of the different pharmaceuticals from water was investigated. Synthesis details and characterization of this photocatalyst material have been previously reported by our group^{18,17}.

Experiments have proved that Ciprofloxacin and Oxytetracyclin are totally degraded under UV lamp irradiation even without the POM/polymer composites presence. However, only 16% of Ibuprofen was removed from water under 90 min of the same irradiation source. Hence, the use of this photocatalyst was indispensable for the total degradation and mineralization of this recalcitrant pollutant under different irradiation sources including solar irradiation, UV lamp and LED@375nm. Degradation mechanism of this pharmaceutical have also been identified by realizing mass spectrometry analysis at different irradiation times during the photocatalytic process. Furthermore, the obtained results demonstrate also that the POM/polymer composites were not essential for the complete degradation of Erythromycin. In fact, no enhancement of the photodegradation kinetics was observed in the presence of this photocatalyst which leads also to the formation of more toxic intermediates than the original drug.

In conclusion, heterogenous photocatalytic treatment is a powerful way to mineralize some recalcitrant pollutants such as Ibuprofen. However, depending on the target pollutant absorption area and the irradiation sources emission spectrums, simple photolysis could be more effective to obtain total mineralization.

TOC graphic

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