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An Eco-Friendly Solution for the Efficient Elimination of Pentoxifylline from Water: An Operational Performance Investigation

LUCIAN GAVRILA[1], ANDREI-IONUT SIMION[1*], CRISTINA-GABRIELA GRIGORAS[1*], LIDIA FAVIER[2]
[1]University Vasile Alecsandri of Bacau, Faculty of Engineering, Department of Chemical and Food Engineering, 157 Calea Marasesti, 600115, Bacau, Romania
[2]Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

Abstract: *In recent years, more and more pollutants (including pharmaceuticals, personal care products, pesticides, herbicides, hormones, chemicals) are detected in the aquatic environment. Even if they are encountered in very low concentrations, the toxicological data reveal that they represent a major risk both for the water living organisms and for human beings. Moreover, an important resistance to the classical methods applied at wastewater treatment plants characterizes them. Aeration, coagulation, flocculation, sedimentation, filtration, adsorption, oxidation, activated sludge treatments are often either insufficient or completely ineffective. To overcome these drawbacks, many researches were dedicated to the development of new effective techniques for the removal of these water pollutants. Advanced oxidation methods are widely reported as being of the most efficient ones. In this article, we investigate the utility of the photocatalysis as a sustainable alternative for the enhanced elimination of an emergent water micropollutant. We evaluate here the impact of several parameters (catalyst type and concentration, contaminant concentration, radiant flux intensity) on the process efficiency. The targeted compound involved in the experiments was the pentoxifylline (a drug used in the treatment of diseases such as diabetic neuropathy, osteoradionecrosis or hepatic fibrogenesis). The registered pollutant removal rate under the selected reaction conditions (photocatalyst type: ZnO; photocatalyst concentration: 0.5 g/L; incident light flux: 9.52 mW/cm^2; natural pH) reached values near to 100 % providing new insights on the viability and the efficiency of the evaluated methodology.*

Keywords: *emergent water pollutant, photocatalysis, titanium oxide, zinc oxide*

1. Introduction

Water micropollutants are known as contaminants found in small concentrations (trace levels of ng/L to μg/L) in the aquatic environment [1]. They include various types of natural or synthetic substances such as drugs (antidiabetic medicines, anaesthetics, analgesics, anti-inflammatories, antihypertensives, antivirals, fungicides, antibiotics, diuretics, anxiolytics, anticonvulsants, antidepressants, antihistamines, lipid-regulators) [2-4], personal care products (fragrances, disinfectants, UV filters, repellents) [5, 6], hormones (estrogens, testosterone, progesterone, mestranol) [7-9], chemicals (plasticizers, surfactants, dyes) used in different industrial areas (food, textile, paint, polymers) [10, 11], pesticides (insecticides, herbicides, fungicides) [12, 13] etc.

Their significant toxicity, high persistency, reduced biodegradability and important bio-accumulative ability [14, 15] cause many difficulties in the efforts of removing them from the water matrices. Conventional physical, chemical or biological procedures as aeration, coagulation, flocculation, sedimentation, filtration, adsorption, oxidation, activated sludge treatments are often either insufficient or completely ineffective [16-19].

**email:asimion@ub.ro, cristina.grigoras@ub.ro*

Over the last years, numerous approaches focused on the development of efficient and environmental friendly alternatives for the classical wastewater treatment techniques. The advanced oxidation processes (AOPs) are listed as conducting to very good results. One of the most popular AOPs is the photocatalysis [20] and many researches consider it as green and sustainable alternative reporting good outcomes for its application in the elimination of organic water contaminants. Indeed, several studies report on the successful photocatalytic degradation of pollutants including dyes, pesticides as well as phenolic compounds or antibiotics [21-26]. The concept is based on the generation of highly reactive oxygen species (hydroxyl radical, superoxide anion radical, hydroperoxyl radical, alkoxyl radical), with the main feature consisting in their ability to mineralize unselectively the organic pollutants to carbon dioxide, water and inorganic ions or acids [27]. Hence, this process was successfully applied for the destruction of various dangerous organic substances from wastewaters [28-30]. It involves the pollutants transfer to the surface of a photocatalyst (titanium dioxide, zinc oxide, tungsten trioxide, strontium peroxide, zirconium dioxide, iron (III) oxide, cerium (IV) oxide etc.) where they are adsorbed and, under the action of photons, activated and decomposed [31]. A desorption of the reaction products and their removal from the photocatalyst surface complete the process [32].

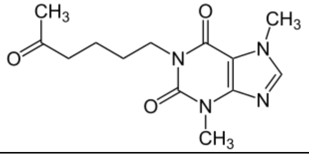
The photocatalytic reaction starts when the photocatalysts absorb photons with equal or higher energy than that of their band gap (which is for example of 3.2 eV for TiO_2 anatase form and of 3.5 eV for ZnO) leading to molecular excitation and charge separation. The generated mobile electrons (e^-) and holes (h^+) pairs can take part at an undesirable process of recombination and dissipation of the absorbed energy as heat or they can migrate to the catalysts surface. In the latter case, if the photocatalysis occurs in aqueous solutions, the electrons reduce oxygen into superoxide radical anions. In the same time, the holes react with water and hydroxide ions forming hydroxyl radicals that are responsible for the organic pollutants mineralization [33,34]. Keeping in mind all these considerations, the objective of this work was to evaluate the possibility of application of this eco-friendly process for removal of an emergent water contaminant named pentoxifylline (PTX). The considered target molecule is a methylxanthine derivative presenting properties comparable to theobromine, caffeine and theophylline and mainly used for the treatment of circulatory and cerebrovascular disorders, diabetic neuropathy, osteoradionecrosis and hepatic fibrogenesis [35]. Highly stable and soluble in water, PTX is a refractory and persistent compound which cannot be easily eliminated by the traditional water treatment methods. The process feasibility was firstly investigated in the presence of commercial photocatalysts under UV-A irradiation and then, in order to evaluate its potential application on the elimination of PTX, a detailed analysis of the effect of few of the main process parameters (photocatalyst amount, pollutant concentration, irradiation period and light intensity) was performed. The use of such strategy gives a better understanding on the existing correlation between these factors and the performance of degradation kinetics of the target molecule.

2. Materials and methods

2.1. Reagents

The pentoxifylline (PTX) (Table 1) was of analytical purity and procured from SIGMA (France).

Table 1. Pentoxifylline properties

Structure	
Formula	$C_{13}H_{18}N_4O_3$
CAS number	6493-05-6
IUPAC name	3,7-dimethyl-1-(5-oxohexyl)-3,7-dihydro-1*H*-purine-2,6-dione

Molecular weight, g/mol	278.31
Water solubility, mg/mL	43

ZnO (98 %, specific surface: 9 m^2/g, particle diameter: 110 nm), TiO_2 Cristalactiv® PC 500 (TiO_2 content: wt 85 %, specific surface: 350 m^2/g, particle diameter: 5-10 nm) and TiO_2 Kronos 7500 (specific surface: 250 m^2/g, particle diameter: 15 nm) used as photocatalysts were purchased from Alfa Aesar® (Kandel, Germany), Crystal (France) and Kronos (Germany), respectively.

Acetonitrile was supplied by Fisher Scientific (United Kingdom).

Ultrapure water (18.2 MΩ · cm; 25 °C; DOC < 5 µg C/L; *p*H = 6.5) used for PTX solutions preparation and for chromatographic analysis was obtained with a Purelab option-Q apparatus from Elga Labwater (Veolia, High Wycombe, United Kingdom).

2.2. Experimental setup

All the experiments on PTX removal were carried out at room temperature on a batch photoreactor system consisting in a cylindrical borosilicate glass reactor vessel of 1.5 L protected from sunlight and an UV-A lamp (PL-L 24W, Philips, Poland) with the main wavelength at 365 nm and two secondary wavelengths at 400 nm and 440 nm.

PTX aqueous solutions of different concentrations and various amounts of catalysts were added in the reactor and agitated for 30 min. Once the adsorption equilibrium was achieved, the UV lamp preheated outside for 30 min was introduced in the middle of the reactor.

The collected samples were filtered on Chromafil® Xtra H-PTFE 0.45µm syringe filters (Macherey-Nagel, Düren, Germany) prior to other analysis.

2.3. Chromatographic analysis

The residual concentration of PTX was established by high-performance liquid chromatography (HPLC) analysis. A Waters 600 system (Milford, MA, USA) equipped with a Waters 717 plus Autosampler (Milford, MA, USA) and a Waters^{TM} 996 photodiode array detector (Milford, MA, USA) set at 280 nm was used. The separation was performed at room temperature on a Symmetry C18 column (250 mm × 4.6 mm, 5 µm) from Waters (Ireland). The mobile phase was composed of water (solvent A) and acetonitrile (solvent B) and delivered in isocratic mode (70 % A, 30 % B) with a flow of 1 mL/min. The sample injection volume was of 50 µL. The recorded retention time of PTX was of 3.5 minutes.

The quantitative measurements were realized based on an external PTX calibration curve. To this purpose, a PTX stock solution (100 mg/L in acetonitrile) was prepared and then diluted to different concentrations (5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L, 80 mg/L). The calculated correlation coefficient (R^2) between the peak area and the pollutant concentration was 0.9999.

3. Results and discussions

3.1. Catalyst type effect

Three different catalysts, namely TiO_2 PC 500, TiO_2 Kronos 7500, and ZnO were tested in this study to evaluate their efficiency in the elimination of the target molecule. Our photocatalytic experiments were conducted with an initial pollutant concentration of 10 mg/L and a catalyst amount of 0.5 g/L in the presence of a maximal incident light flux (9.52 mW/cm^2).

As it can be seen in Figure 1, from the first minutes of photocatalysis, the degradation with ZnO is faster than that with TiO_2 Kronos 7500 and with TiO_2 PC500. In the case of ZnO, the pollutant degradation reached a removal yield of 55 % after only 10 min of irradiation while with TiO_2 PC500 and TiO_2 Kronos 7500 the observed photocatalytic efficiency was of 30 and 8 % respectively. It must be pointed out that with the last mentioned catalyst the target molecule is not completely removed even after an irradiation time of 150 min. The recorded data are consistent with those registered by Bansal and Verma [36] which reveal also only a low removal of PTX for the photocatalytic reaction with TiO_2.

Fenoll *et al.* [37] who studied the photo-oxidation of different insecticides in the presence of titanium and zinc oxides explain that the higher activity of ZnO can be attributed to its properties. In our case, ZnO is characterized by a reduced specific surface of 9 m^2/g and by a more important particles diameter (110 nm) compared to the other photocatalysts (TiO_2 Cristalactiv® PC 500 - 350 m^2/g, 5-10 nm; TiO_2 Kronos 7500 - 250 m^2/g; 15 nm). Moreover, according to Kitsiou *et al.* [38], zinc oxide possesses a higher electronic mobility, indicating lower charge recombination and therefore an enhanced reactivity.

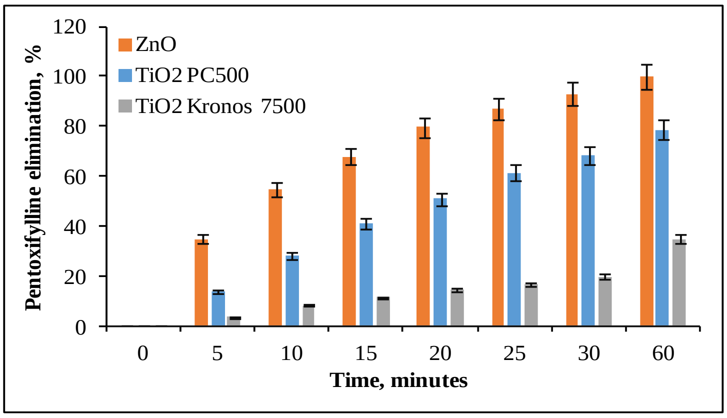


Figure 1. Influence of catalyst type on the elimination of the target molecule initial pollutant concentration: 10 mg/L; incident light flux: 9.52 mW/cm^2; catalyst concentration: 0.5 g/L; natural *p*H

3.2. Adsorption, photolysis and photocatalysis

After selecting the most appropriate catalyst, the influence of different conditions such as adsorption, photolysis and photocatalysis, on removing PTX from aqueous solutions was investigated. Several assays were carried out with an initial pollutant concentration of 10 mg/L, 0.5 g/L of catalyst, and an incident light flux of 9.52 mW/cm^2. Figure 2 illustrates the fact that PTX is not eliminated in the dark and highlights that the adsorption equilibrium was reached in less than 60 min. Similarly, a negligible pollutant removal was recorded during the photolytic reaction (data not shown). On the contrary, a significant reduction of PTX concentration was obtained when the system catalyst – UV-A was applied. Under these conditions, the target molecule was completely degraded in approximatively 60 min. Our previous studies conducted on 2,4-diclorophenol [39] and on clofibric acid [40] revealed comparable findings in terms of the reduced efficiency of adsorption and photolysis and of the high utility of combining the effect of catalyst with that of the UV-A irradiation.

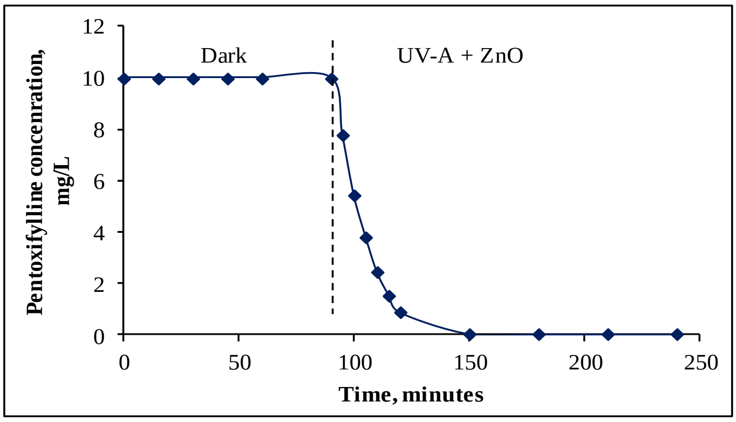


Figure 2. Influence of adsorption and photocatalysis on the removal of the target pollutant initial pollutant concentration: 10 mg/L; incident light flux: 9.52 mW/cm^2; catalyst concentration: 0.5 g/L; natural *p*H

3.3. Influence of photocatalyst concentration

In a photocatalytic process the degradation kinetics are significantly affected by catalyst load. Indeed, at low photocatalyst concentrations, there is a risk that the active sites will not be sufficient to efficiently remove the pollutant from the treated solution. In addition, the process can be adversely affected also when catalyst loading is higher than an optimum dosage. Light scattering, screening effects, catalyst particle agglomeration, solution turbidity etc. can be observed in this case along with a drastic reduction of the degradation efficiency. Therefore, an optimal catalyst mass in the medium should be established in order to avoid the catalyst excess and to guarantee a maximum of active sites on its surface area available for reaction, which will increase the number of hydroxyl and of superoxide radicals, and will ensure a rapid elimination of the target contaminant [28, 33].

In the present study, we focused our attention on the investigation of the effect of this factor on the degradation of the target molecule. Thus, different tests were performed for a constant initial pollutant concentration of 10 mg/L while the catalyst dose in the aqueous solution was varied from 0.1 g/L to 0.5 g/L. As depicted in Figure 3, more catalyst there is, faster the degradation occurs. 92.88 % of the pollutant was degraded after only 30 min when ZnO was used at a concentration of 0.5 g/L. Amounts of 0.25 g/L and of 0.1 g/L led to 76.69 % and 19.60 % of PTX removal, respectively. According to these data, the concentration of 0.5 g/L was considered as appropriate for the other experimental runs.

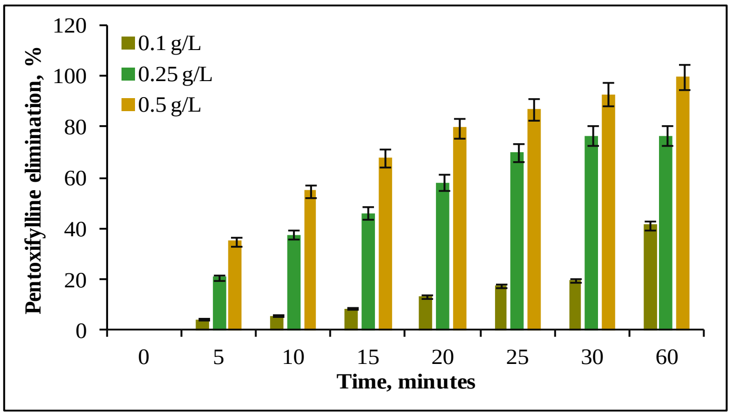


Figure 3. Influence of ZnO catalyst concentration on the pentoxifylline Elimination initial pollutant concentration: 10 mg/L; incident light flux: 9.52 mW/cm^2; natural *p*H

Similarly, Rajeev *et al.* [41] demonstrated in their paper that, in the tested experimental conditions, the acetophene was efficiently removed by photocatalysis on ZnO only at the optimal catalyst concentration. For chlorpyrifos degradation Kanmoni *et al.* [42] used ZnO concentrations between 0.1 g/L and 1 g/L and showed that the best results were at a ZnO dosage of 0.75 g/L. Burbano *et al.* [43] quantified the elimination of dimethylamine salt of 2,4-dichlorophenoxyacetic acid by photodegradation and reported as appropriate a zinc oxide concentration of 0.35 g/L. Ceretta *et al.* [44] coupled the bacteria effect with that of a composite containing ZnO and polypyrrole and concluded that the adequate catalyst dosage for Direct Black azo dye degradation was of 2 g/L. On the contrary, when the concentration of the photocatalyst exceeds the optimal value, less light is allowed to pass through the photocatalyst surface, a light screening effect appears and the reaction rates descends [33, 45].

3.4. Influence of initial pollutant concentration

The initial pollutant concentration also affects the photocatalytic reaction efficiency. An augmentation of the target molecule concentration conducts to an increase of the absorbed substance on the catalyst active sites and consequently to a higher request of oxidizing species. Since the catalyst surface area remains the same for fixed photocatalytic conditions (catalyst load), at some point, the generation of hydroxyl radicals is unsatisfactory because there are only a few active sites available for the adsorption of hydroxyl ions. Additionally, the photons are no longer able to reach the catalyst surface [40, 46]. Hence, all these aspects have a negative impact on the pollutant elimination.

In this regard, the photocatalytic degradation with different initial pollutant amounts was also examined in this work. A series of photocatalytic tests were conducted for different pollutant concentrations (ranging from 5 mg/L to 50 mg/L) and for a catalyst load of 0.5 g/L. As expected, at lower initial concentration, the degradation rate was significantly increased (Figure 4). It was found that after 15 minutes of irradiation, the removal efficiency was 97.38 % when the initial pollutant concentration was of 5 g/L compared to 67.99 % for a PTX load of 10 g/L and to 28.04 % for 50 g/L. After a reaction time of 30 min, PTX elimination reached values of 100 %, 92.88 % and, respectively, 50.10 %.

Analogous influence of the initial emergent compounds concentration on the photocatalytic process efficiency was confirmed by other previous reports. In their work, Wang *et al.* [47] reveal that the ibuprofen photodegradation percentage decreases with the increase of its concentration in the aqueous solutions. Mahalakshmi *et al.* [48] who carried out experiments on removing carbofuran by photocatalysis with zinc oxide varying the contaminant concentration from 50 mg/L to 250 mg/L reported a similar behavior. In their work, Choina *et al.* [49] highlighted as well that the substrate concentration is one of the key factors affecting the water decontamination. They reported that the initial amount of tetracycline and ibuprofen existing in the solutions submitted to photocatalysis over ZnO nanoparticles contributes significantly to the process efficiency.

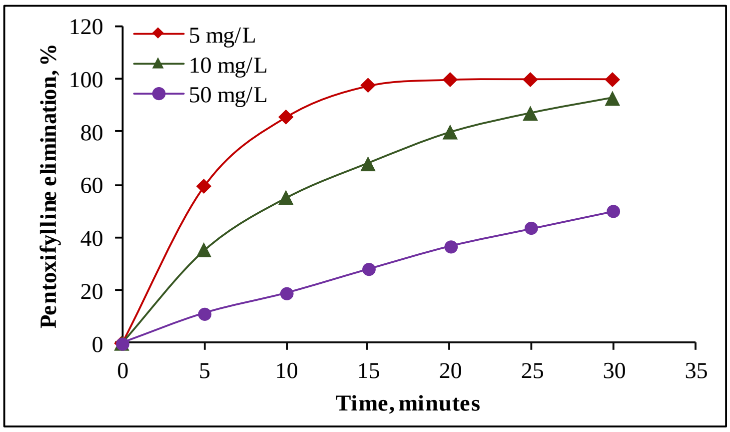


Figure 4. Influence of initial pollutant concentration on its eliminationZnO catalyst concentration: 0.5 g/L; incident light flux: 9.52 mW/cm^2; natural *p*H

3.5. Influence of light intensity

The photodegradation of a PTX solution of 5 mg/L at a catalyst concentration of 0.5 g/L was also carried out at three different values of light intensity in order to evaluate the effect of this process parameter on the compound degradation. The data obtained for each of investigated conditions were fitted as pseudo first order kinetics and the rate constants were determined as negative slope of linear regression of $ln(C/C_0)$ over reaction time. For calculation purpose, C was the pollutant concentration at a time t and C_0 was its initial concentration.

As shown in Figure 5, at the maximal incident light flux (9.52 mW/cm^2) used in our experiments, the total degradation of PTX takes place in the first 20 minutes.

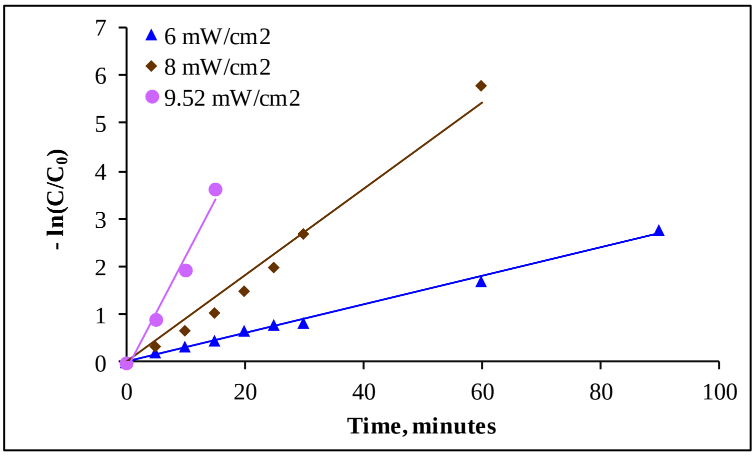


Figure 5. Influence of incident light flux on the photocatalytic degradation of the target pollutant catalyst concentration: 0.5 g/L; initial pollutant concentration: 5 mg/L; natural *p*H

On the contrary, when the light intensity decreases at 8 mW/cm^2 and at 6 mW/cm^2 the required time to reach the same pollutant elimination yield is three times and respectively six times more important. Thus, our results clearly demonstrates the beneficial effect of the incident light intensity on the elimination of the considered pollutant.

It is known that if the photocatalytic process is conducted under a certain light intensity an amelioration of the reaction rate can be remarked [50]. Such behavior can be explained by the fact that when the light intensity increases there is a higher probability that the number of active species (electron-holes pairs) formed increases correspondingly conducting to an augmentation of the photodegradation rate. The calculated values corresponding to kinetic rate constants obtained as a function of incident light flux used in our study as well as the obtained correlation coefficients are presented in Table 2. It can be observed that the degradation rate constants notably increase with the applied incident light intensity.

Table 2. Pseudo first order rate constants obtained for the degradation of the target molecule at different light intensities

Incident light flux, mW/cm^2	**Kinetic constant, min^{-1}**	**Correlation coefficient (R^2)**
6	0.0299	0.9945
8	0.0902	0.9778
9.52	0.2244	0.9699

Similar results about the existing correlation between the light intensity and the elimination rate were also reported by several studies carried out on different organic water pollutants. Nishio *et al.* [51] specify that the decolorization rate of Orange II solutions linearly increased with the increase of UV light intensity from 0 W/m to 19.8 W/m. Other works showed that rhodamine B degradation rate constant increased with augmentation of light intensity from 10 mW/cm^2 to 60 mW/cm^2 [52]. Moreover, in their work, Elsellami *et al.* [53] demonstrated that the phenylalanine is faster degraded when the radiant flux varied from 0 mW/cm^2 to 10 mW/cm^2. These results are consistent with our data confirming the positive role of incident light flux on the photocatalytic process.

4. Conclusions

The registered data reveal that the photocatalysis can be successfully employed to remove refractory contaminants from aqueous solutions.

Among the three catalysts tested (TiO_2 PC 500, TiO_2 Kronos 7500 and ZnO), zinc oxide had the utmost photocatalytic performance in terms of the elimination of pentoxifylline (the target compound). The experiments indicated that photolysis and adsorption mechanisms had a negligible influence on the removal efficiency, both UV-A and catalyst being necessary for the molecule degradation.

The photocatalytic process was considerably affected by the initial catalyst dosage and by the starting pollutant concentration. A major importance had also the value of the used radiant light flux, the best results being recorded at its maximum value (9.52 mW/cm^2). The assays carried out established that a pseudo-first-order kinetic model can describe the degradation of the studied micropollutant.

Our findings demonstrated that the photocatalytic process using UV-A and ZnO photocatalyst could be a potential technique for the elimination of emergent water contaminants.

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