

A Comparison Study of the Removal of Selected Pharmaceuticals in Waters by Chemical Oxidation Treatments

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Abstract—The degradation of selected pharmaceuticals in some water matrices was studied by using several chemical treatments. The pharmaceuticals selected were the beta-blocker metoprolol, the nonsteroidal anti-inflammatory naproxen, the antibiotic amoxicillin, and the analgesic phenacetin; and their degradations were conducted by using UV radiation alone, ozone, Fenton's reagent, Fenton-like system, photo-Fenton system, and combinations of UV radiation and ozone with H₂O₂, TiO₂, Fe(II), and Fe(III). The water matrices, in addition to ultra-pure water, were a reservoir water, a groundwater, and two secondary effluents from two municipal WWTP. The results reveal that the presence of any second oxidant enhanced the oxidation rates, with the systems UV/TiO₂ and O₃/TiO₂ providing the highest degradation rates. It is also observed in most of the investigated oxidation systems that the degradation rate followed the sequence: amoxicillin > naproxen > metoprolol > phenacetin. Lower rates were obtained with the pharmaceuticals dissolved in natural waters and secondary effluents due to the organic matter present which consume some amounts of the oxidant agents.

Keywords—Pharmaceuticals, UV radiation, ozone, advanced oxidation processes, water matrices, degradation rates

I. INTRODUCTION

PHARMACEUTICAL compounds are extensively consumed annually in the world. Most of them are partially metabolized and excreted by humans and animals, and spilled into wastewaters that are later treated in municipal wastewater treatment plants (WWTP). However, some of these pharmaceuticals are not completely eliminated by the procedures applied in conventional water treatment processes, and consequently, are found in effluents exiting the plants. Thus, as it has been reported [1], several pharmaceuticals and their metabolites are partially removed, but other compounds persist after the treatment procedures, being returned to the environment, and could reach drinking water sources.

As a consequence of this problem, it is advisable to reduce their concentrations in wastewater purification plants by using different treatments, such as chemical procedures, which have demonstrated to be efficient to remove non-biodegradable pollutants. Among these techniques, UV radiation is widely used to induce photoreactions of pharmaceuticals [2]. Similarly, ozone is also an efficient oxidant for the purification of surface and drinking waters [3]. At the same

time, advanced oxidation processes (AOPs), which are based in the generation of hydroxyl radicals ($\cdot\text{OH}$) in solutions, have attracted great interest for the degradation of biorefractory or hazardous organic compounds in water systems.

Due to the interest of this research field, a global study was designed for the removal of four frequent pharmaceuticals dissolved in ultra-pure (UP) water or in different water matrices by using several oxidants and AOPs. The pharmaceuticals selected, which have been found in different aquatic environments at concentrations in the range ng L^{-1} to $\mu\text{g L}^{-1}$ [4], were: the beta-blocker metoprolol (Met), the nonsteroidal anti-inflammatory compound (NSAID) naproxen (Nap), the antibiotic amoxicillin (Amox) and the analgesic phenacetin (Phen). The degradation of these substances was conducted by single agents (UV radiation and ozone), as well as by several AOPs: Fenton's reagent, Fenton-like system, photo-Fenton system, and different combinations of UV radiation and ozone with H₂O₂, TiO₂, Fe(II), and Fe(III).

II. EXPERIMENTAL SECTION

The experiments were carried out in a 500 mL cylindrical glass reactor provided with inlets for feeding reactants and measuring temperature and outlets for withdrawing samples and exiting the effluent gas when ozone was used. The temperature was maintained at 20 ± 0.2 °C, and the reactor was also provided with the necessary elements for the development of the several processes performed: photochemical decomposition by single UV radiation, single ozonation, and different combinations of oxidants in the AOPs conducted. Thus, when UV radiation was used, either alone or combined with other oxidants, the radiation source was constituted by a low-pressure mercury vapour lamp (Heraeus TNN 15/32, nominal electrical power 15 W), which emitted monochromatic radiation at 254 nm. This lamp was placed axially within the reactor, and was protected by a quartz sleeve which housed the lamp.

Previous experiments based in the photolysis of H₂O₂ were also conducted in the form described in a former study [5], in order to determine the light intensity (radiation emitted) and optical path of the lamp, being the values obtained 1.81 $\mu\text{Einstein}\cdot\text{s}^{-1}$ and 5.09 cm, respectively. In processes where ozone was used, also alone or combined, it was generated from an oxygen stream in a commercial ozone generator, and the ozone-oxygen mixture (flow rate of 16 mg h^{-1} of ozone) was introduced into the reactor through a porous plate gas sparger that was located at the bottom of the reactor.

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Finally, the required amounts of ferrous and ferric sulfate, hydrogen peroxide and TiO_2 were also introduced into the reactor in the AOPs where these oxidants were used. Specifically, the TiO_2 used was the powder standard material called P-25 Degussa, which has a relatively large surface area ($49 \text{ m}^2 \text{ g}^{-1}$).

In addition to ultra-pure water, four water matrices were used in order to study the oxidation of the selected pharmaceuticals under realistic water treatment conditions. Two of them were natural waters collected from locations in the Extremadura Community (southwest Spain): a groundwater (PZ), and a surface water from the public reservoir "Peña del Aguila" (PA). The remaining water matrices were secondary effluents collected from two WWTPs located in Extremadura Community: BA (from Badajoz) and LA (from La Albuera). The experiments were similar to those carried out in UP water, with an initial concentration of each pharmaceutical of $1 \mu\text{M}$.

Pharmaceutical concentrations in the samples withdrawn from the reactor at regular reaction times were measured by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column. The ozone concentration in the inlet gas ozone-air stream was determined iodometrically, the water quality parameters were analyzed according to the Standard Methods [6], and the total organic carbon (TOC) content was determined by an IO Analytical total organic carbon analyzer, based on the persulfate oxidation method.

III. RESULTS AND DISCUSSION

A. Degradation processes based in the use of UV radiation, Fenton's reagent and Fenton-like system in UP water

The photooxidation of the selected pharmaceuticals at 254 nm in UP water was initially carried out by using the monochromatic UV irradiation source previously described. Since the shape of the plots of the concentration decays vs. reaction times suggests a first-order reaction with respect to the pharmaceutical concentration, the pseudo-first order rate constants were evaluated and the values obtained are compiled in Table 1 (Expt. UV-1). They reveal the following trend of the degradation rate for the selected compounds: amoxicillin > naproxen > metoprolol > phenacetin.

The pharmaceuticals oxidation by hydroxyl radicals was initially investigated with these radicals being generated by the Fenton's reagent [7]. The Fenton process also follows first-order kinetics and their calculated rate constants are also compiled in Table 1 (Expt. F-1). A slight increase in the rate constant was obtained for the four pharmaceuticals in comparison to the previous single photochemical process, which reveals a more efficient oxidation role of the hydroxyl radicals than the direct UV radiation, and the same sequence of degradations is deduced: amoxicillin > naproxen > metoprolol > phenacetin.

TABLE I
 PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE DEGRADATION OF THE SELECTED PHARMACEUTICALS DISSOLVED IN UP WATER BY UV RADIATION, FENTON'S REAGENT AND FENTON-LIKE PROCESS (PH=3, INITIAL CONCENTRATION OF H_2O_2 , Fe(II) AND Fe(III) OF $10 \mu\text{M}$)

	Pharm.	k_F, min^{-1}
Expt. UV-1	Met	0.019
	Nap	0.054
	Phen	0.013
	Amox	0.109
	Pharm.	k_F, min^{-1}
Expt. F-1	Met	0.022
	Nap	0.068
	Phen	0.017
	Amox	0.117
	Pharm.	k_{FL}, min^{-1}
Expt. FL-1	Met	0.003
	Nap	0.004
	Phen	-
	Amox	0.028

The generation of hydroxyl radicals can be also performed by the Fenton-like process [8] that was also tested for the degradation of the selected pharmaceuticals. The pseudo-first order rate constants for this process are summarized in Table 1 (Expt. FL-1). An important decrease in the elimination rates of the pharmaceuticals in comparison to the preceding Fenton's reagent was observed, which is attributed to the fact that the Fe (III) reduction reaction with H_2O_2 is much slower.

In a next step, the oxidation of the selected pharmaceuticals was performed by means of several AOPs constituted by the combinations of UV radiation with different oxidants. Thus, an enhanced degradation rate was observed for the UV/ H_2O_2 system, where OH generation is caused by the photolysis of H_2O_2 . Similarly, an important enhancement in the pharmaceuticals oxidation rate by the photo-Fenton system was appreciated, which is a consequence of an increasing contribution of the radical pathway due to an additional generation of OH radicals. Then, the presence of any second oxidant enhanced the oxidation rate in comparison to the single photolysis, which is due to the major catalytic effect because of the increase of the relationship active sites per organic molecule. This influence of the different processes can be observed in Figure 1, which represents the elimination curves of amoxicillin taken as example vs. reaction time by using the above mentioned oxidation procedures. Similar results were obtained for the remaining compounds. As can be seen, UV radiation alone presented the lowest degradation rate, while the system UV/ TiO_2 provided the highest oxidation rate. Intermediates rates were deduced for the combinations UV/ H_2O_2 , UV/Fe (II) and UV/Fe (III) with the oxidant concentrations used. It must be remarked that this lower efficiency of the UV radiation is due to the specific radiation source used in this work, consisting in a low-pressure mercury vapour lamp. The use of medium or high pressure mercury vapour lamps would lead to greater degradation rates and higher efficiencies.

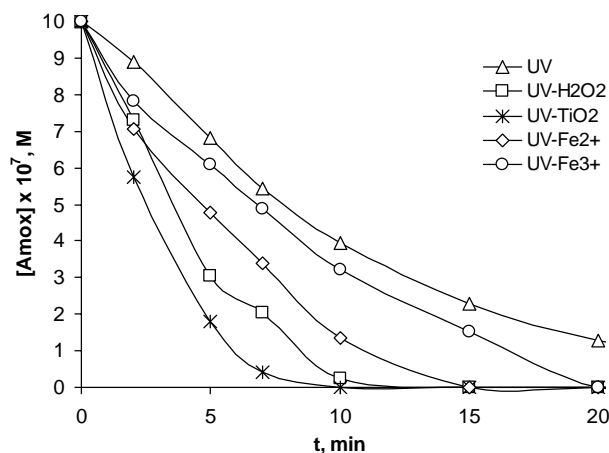


Fig. 1 Comparison of different oxidation systems used: evolution of concentration with reaction time for amoxicillin taken as example. Processes based in the use of UV radiation

B. Oxidation processes based in the use of Ozone in UP water

The removal of the pharmaceuticals by ozone alone was firstly studied in experiments carried out at pH 3 and 7. In a similar way as in the photodegradation processes, the overall ozonation reaction can be considered to follow first-order kinetics, and the following degradation sequence for the direct ozonation reaction was deduced: amoxicillin > naproxen > phenacetin > metoprolol. The pH effect on pharmaceuticals oxidation was positive, increasing the degradation rate at higher pH for amoxicillin, metoprolol and naproxen, which is due to the partial deprotonation of these ionic compounds.

The oxidation of the selected pharmaceuticals was later performed at pH=7 by means of the AOPs constituted by the systems O_3/UV , O_3/H_2O_2 , O_3/H_2O_2+UV , O_3/TiO_2 , and O_3/TiO_2+UV . Once again, the aim of these AOPs was the generation of OH radicals to enhance oxidation rates of these pharmaceuticals with respect to the single ozonation process.

The concentration decay curves revealed the significant increase obtained in the degradation rates with these AOPs when compared to the single ozonation reaction which is due to the contribution to the global reaction of the radical pathway. In effect, in the combinations of ozone with UV radiation, H_2O_2 and UV/H_2O_2 , a synergistic effect of several individual reactions takes place: direct ozonation, direct photolysis, and hydroxyl radical oxidation. These OH radicals are generated in the photolysis of ozone and/or H_2O_2 . Similarly, the additional presence of TiO_2 and TiO_2+UV enhanced the oxidation due to the formation of the ozonide radical, which also generates OH radicals [9].

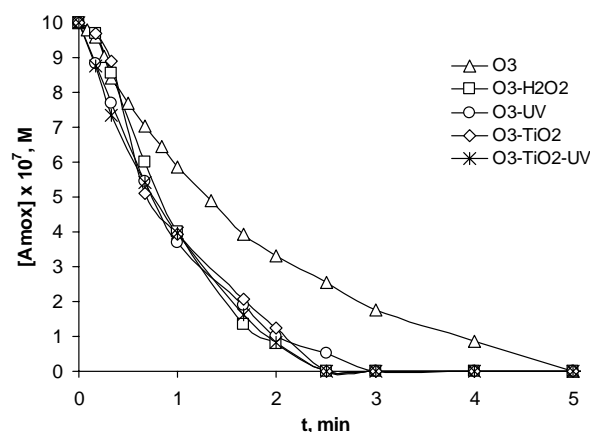


Fig. 2 Comparison of different oxidation systems used: evolution of concentration with reaction time for amoxicillin taken as example. Processes based in the use of ozone

These effects can be seen in Figure 2, which shows the degradation of amoxicillin in some oxidation systems based on the use of ozone. While ozone alone was the poorest oxidant system, its effectiveness was significantly improved by the addition of H_2O_2 , UV radiation or TiO_2 , as was discussed. On the other hand, it is also seen that the degradation rate for amoxicillin was similar in the different ozone-based AOPs applied. Therefore, the combinations of ozone with two oxidants do not present any advantage over the combinations with one oxidant.

C. Oxidation of pharmaceuticals dissolved in real water matrices

The following stage was focused on the application of AOPs to the elimination of the selected pharmaceuticals when they were present in several water systems, in order to reproduce some real conditions that are found in water purification plants. The four water matrices used were described in the Experimental Section, and the procedures followed were similar to those applied in UP water.

Regarding to the AOPs based on the use of UV radiation, degradation experiments were carried out with the groundwater PZ and with the reservoir water PA. Once again, it is considered that the process globally follows first-order kinetics, and after regression analysis, the slopes were evaluated and provided the pseudo-first-order rate constants k for the selected pharmaceuticals.

A comparison between these rate constants and those obtained in the equivalent oxidation processes in UP water was conducted and it was observed a much higher removal rate in the UP water when compared to the real water matrices. These results are explained by the fact that the dissolved organic matter (DOM) present in both water matrices could consume some amounts of the oxidant agents for the elimination of other compounds which are also present in addition to the pharmaceuticals; and consequently, less oxidant is available for the pharmaceuticals degradation. This effect took place in a higher extent in the reservoir water due

to a higher content in DOM. On the contrary, UP water does not contain any amount of organic matter, and therefore, the radiation emitted is almost totally consumed in the degradation of the pharmaceuticals, leading to a higher elimination rate. At the same time, the same sequence of degradations than in UP water was obtained: amoxicillin > naproxen > metoprolol > phenacetin.

Similarly, the degradation of the selected pharmaceuticals present in both secondary effluents (water matrices denoted LA and BA) was performed by means of ozone and ozone combined with H₂O₂, which are more powerful oxidation systems than the UV based AOPs applied in natural waters. Figures 3 and 4 show the comparison between the rate constants obtained in these experiments and those determined in the equivalent experiments conducted in UP water:

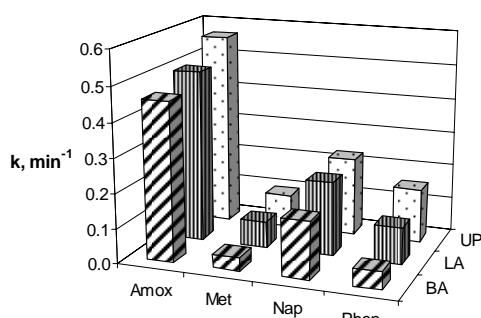


Fig. 3 Comparison of pseudo-first-order rate constants obtained in the degradation of pharmaceuticals in UP water and BA and LA secondary effluents by using different ozone alone

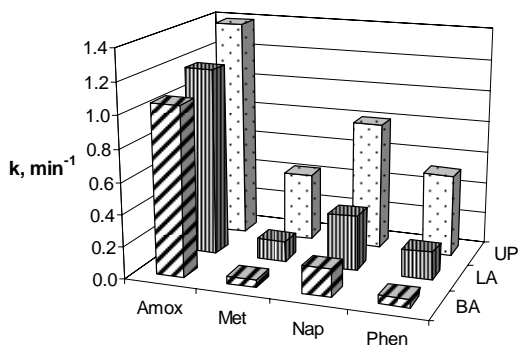


Fig. 4 Comparison of pseudo-first-order rate constants obtained in the degradation of pharmaceuticals in UP water and BA and LA secondary effluents by using the O₃/H₂O₂ system

On one hand, it can be clearly seen that the combination of ozone with hydrogen peroxide provided higher rate constants than the single ozonation in the water matrices tested, as could be expected. On the other hand, it is also observed that the degradation rate was again higher in the UP water than in the secondary effluents, as a consequence of the DOM present, which consumes part of the oxidant in the oxidation of other substances present. At the same time, the DOM content was lower for LA than for BA, and consequently, the degradation

rates were higher for LA wastewater in both processes (O₃ and O₃/H₂O₂).

In conclusion, in water systems with higher content of DOM, the amount of oxidant available to react with micropollutants is lower, and thus, higher doses of oxidants are required to reach the desired level of pollutant elimination.

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