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# Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices

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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 $H_2O_2$, $TiO_2$, 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/$TiO_2$ and $O_3$/$TiO_2$ 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.

## 1. 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.

Due to 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].

On the other hand, advanced oxidation processes (AOPs), which are based in the generation of hydroxyl radicals ($^{\bullet}OH$) in solutions, have attracted great interest for the degradation of biorefractory or hazardous organic compounds in water systems. These substances are oxidized by the free oxidant radicals and mineralized to water, carbon dioxide and mineral salts. A great number of studies have shown the potential for using AOPs, based on the combinations of ozone and/or UV radiation with different catalysts, to eliminate micro-pollutants in general, and pharmaceutical substances in particular [4,5]. Similarly, the Fenton's reagent (Fe(II)/$H_2O_2$), and Fenton-like system (Fe(III)/$H_2O_2$) have also demonstrated a great efficiency in treatment of non-biodegradable wastewater [6,7], although they have two limitations in their applications: a large production of iron sludge, and a slow reduction of ferric ions by $H_2O_2$ [8]. Then, the use of UV was suggested as a good solution for the limitations of the Fenton systems, because the photoreduction of various ferric species contributes to the production of ferrous ions and radical species [9].

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 $\mu g\,L^{-1}$ [10], were: the beta-blocker metoprolol (Met), the nonsteroidal anti-inflammatory compound (NSAID) naproxen (Nap), the antibiotic amoxicillin (Amox) and the analgesic phenacetin (Phen), whose chemical structures are shown in Fig. 1. And 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 $H_2O_2$, $TiO_2$, Fe(II), and Fe(III).

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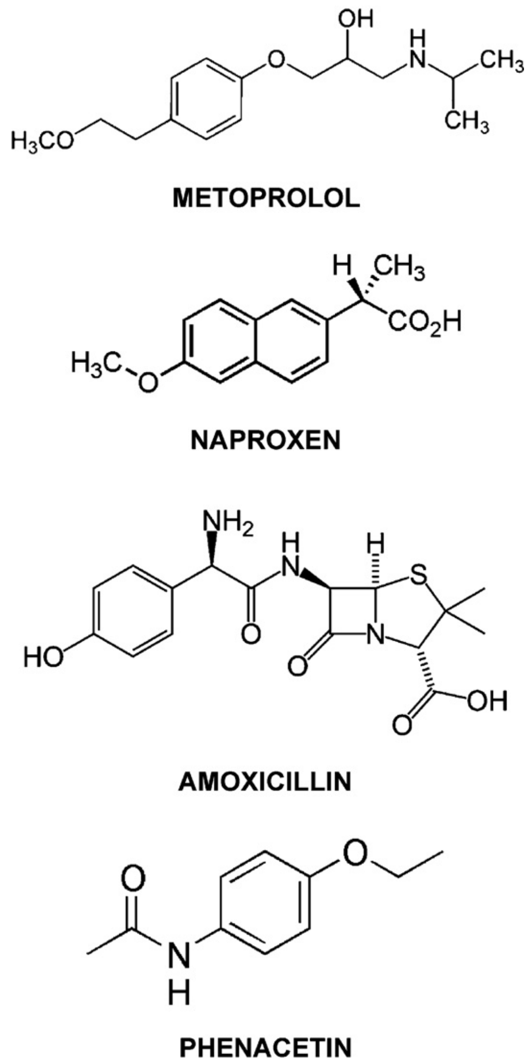
METOPROLOL

NAPROXEN

AMOXICILLIN

PHENACETIN

**Fig. 1.** Chemical structures of the selected pharmaceuticals.

More specifically, the objectives pursued in the present work were to provide data on the removal obtained in each process, to determine values of the apparent rate constants for each procedure tested, and to establish the enhancements reached in the degradation levels by the presence of the free hydroxyl radicals when compared to the single degradation processes. Finally, experiments were carried out with the pharmaceuticals present in several water matrices (a reservoir water, a groundwater, and secondary effluents from two municipal WWTP) in order to reproduce conditions that take place in real oxidation treatment processes.

## 2. Materials and methods

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. At the same time, an external jacket surrounded the reactor, and a water stream was pumped from a thermostatic bath in order to maintain the temperature at the constant value of 20 ± 0.2 °C.

It 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 $H_2O_2$ were also conducted in the form described in a former study [11], in order to determine the light intensity (radiation emitted) and optical path of the lamp, being the values obtained 1.81 microEinstein $s^{-1}$ 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. 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 $m^2\,g^{-1}$).

In the first group of experiments, the reactor was filled with 350 mL of a solution of the four selected pharmaceuticals simultaneously dissolved in UP water, and the pH was adjusted by adding phosphoric acid/phosphate buffer (0.05 M). The initial concentration of each pharmaceutical was 1 $\mu$M.

In the second group of experiments, 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). These samples were shipped overnight from each utility in 20 L bottles and stored in a refrigerator at 4 °C until the experiments were performed. Their main quality parameters are compiled in Table 1. Chemical oxygen demand (COD), total organic carbon (TOC) and absorbance at 254 nm ($A_{254}$) constitute a significant indication of the total dissolved organic matter (DOM) present in these waters. The experiments were similar to those carried out in UP water, with an initial concentration of each pharmaceutical of 1 $\mu$M. More concretely, while natural waters were treated with UV based AOPs and Fenton's reagent, secondary effluents were treated with more powerful ozone based AOPs. These experiments were carried out at the natural pH of each water, except Fenton's reagent and photo-Fenton experiments that were performed at pH 3.

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 [12], and the total organic carbon (TOC) content was determined by an IO Analytical total organic carbon analyzer, based on the persulfate oxidation method.

## 3. Results and discussion

The degradation of the four selected pharmaceuticals, simultaneously dissolved in UP water, was firstly performed by means of UV radiation alone, the combinations of $H_2O_2$ plus Fe(II) (Fenton's reagent) and plus Fe(III) (Fenton-like system) and by the following AOPs based in the use of UV radiation: UV/$H_2O_2$, UV/$TiO_2$, UV/Fe(II), UV/Fe(III), UV/Fe(II)/$H_2O_2$ (photo-Fenton system). Similarly, in a