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In situ generation of hydrogen peroxide from pharmaceuticals single ozonation: A comparative study of its application on Fenton like systems

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HIGHLIGHTS

- A mixture of two pharmaceuticals compounds has been completely removed by means of single ozonation.
- Single ozonation of a mixture of pharmaceuticals yields *in situ* generation of hydrogen peroxide.
- A response surface method was applied to optimize experimental conditions for hydrogen peroxide formation.
- Hydrogen peroxide formed was used for a second process (Fenton like systems) to improve the degree of mineralization.

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ABSTRACT

The oxidation of a mixture of two pharmaceutical compounds (sulfamethoxazole and acetaminophen) was carried out by means of single ozonation as initial process for *in situ* production of hydrogen peroxide and in a subsequent step this hydrogen peroxide was used for a sequential treatment in combination with Fenton or photo-Fenton systems. From single ozonation, fast and complete elimination of two pharmaceuticals were achieved but at the end of the ozonation time only a 10% of total organic carbon (TOC) was removed. The addition of ferrous ions (Fenton process) to the reaction media after single ozonation did not improve the extent of mineralization. The application of photo-Fenton process resulted in a markedly increase in the mineralization efficiency, nevertheless total mineralization was not attained. A simple kinetic model of the processes allowed the pseudo-first order kinetic constant calculations. Higher rate constants of the photo-Fenton system were due to photochemical regeneration of ferrous ions.

1. Introduction

Emerging contaminants are believed of causing adverse effects in humans and wildlife [1–5]. Surface water contamination by municipal and industrial sources is continuously increasing pollution levels in the environment [6–8]. Numerous field studies, designed to provide basic scientific information related to the occurrence and potential transport of contaminants in the environment are being continuously conducted with the aim to identify which contaminants enter the environment, at what concentrations, and in what combinations [9–11]. The major sources of environmentally relevant emerging contaminants are primarily wastewater treatment plant effluents that impact surface water quality with incompletely removed organic contaminants. Additional contamination comes from diffuse agricultural activities, in which over several million tons of fertilizers and pesticides are applied each year, and from atmospheric deposition. Many contaminants do not need to be persistent in the environment to cause negative effects since their high transformation/removal rate is compensated by their continuous introduction into the environment [12]. For most of the occurring emerging contaminants, risk assessment and ecotoxicological data are not available and therefore it is difficult to predict which health effects they may have on humans, terrestrial and aquatic organisms, and ecosystems [13]. Among emerging contaminants, pharmaceuticals constitute a growing group, since they are widely consumed all over the world and are not completely eliminated by conventional water treatment processes. Thus, there is a need to remove these compounds from water and tertiary treatment technologies are recommended for this purpose. Amongst these technologies ozonation and advanced oxidation processes (AOPs) have already been reported as the most appropriate ones for this task [14–17]. Nevertheless, in the case of ozonation, many works seem to point toward a rather quick destruction of the original contaminant when treated with ozone, but with a slower removal of the reaction intermediates that, in some cases, cannot be totally mineralized. This might not be a drawback if ozonation is applied as a previous step before a second treatment [18].

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On the other hand, some previous studies have demonstrated that ozonation of pharmaceuticals leads to the *in situ* generation of hydrogen peroxide [19] and in many cases to the fast removal of pharmaceuticals but to a very poor water mineralization. Hydrogen peroxide is a commonly used oxidant in water treatment technologies. Furthermore, H_2O_2 is normally applied in combination with other substances or catalysts. In this way, among advanced oxidation processes (AOPs), the Fenton (H_2O_2/Fe^{2+}) and photo-Fenton processes ($Fe/H_2O_2/UV$) are two technologies based on the generation of the highly reactive hydroxyl radicals. It is also known that AOPs may increase water mineralization because of the no selective reactivity of hydroxyl radicals with different organic compounds in water.

Thus, in this work the ozonation of a mixture of two very common pharmaceutical compounds (sulfamethoxazole and acetaminophen) has been applied as initial process for *in situ* production of hydrogen peroxide and removal of pharmaceutical compounds. These pharmaceuticals were chosen because of their continuous presence in many secondary wastewater effluents and the high rate constants of their direct reactions with ozone [20–23]. Sulfamethoxazole (SMT) is a sulfonamide type synthetic antibiotic used for the elimination of bacteria causing different illnesses. SMT is one of the most frequent sulfonamides in municipal wastewater and is persistent against conventional and biological treatments [24]. Acetaminophen (ACT) is a common analgesic and anti-inflammatory which is widely used for humans and animals but can cause serious liver and gastrointestinal side effects [25]. The abatement of SMX and ACT from water has been investigated using different advanced oxidation processes (AOPs) [26–29], which either eliminate or transform them into less toxic and or more biodegradable intermediates. However, no results have been found reporting the use of hydrogen peroxide obtained *in situ* (by means of ozonation of pharmaceuticals) in Fenton like systems. A response surface method (RSM) was adopted to optimize experimental conditions for hydrogen peroxide formation. In a subsequent step, this hydrogen peroxide was used for a second process (Fenton and photo-Fenton systems) to improve the extent of mineralization compared to that from ozonation alone.

2. Experimental

2.1. Chemicals

Pharmaceuticals (sulfamethoxazol: CAS Number 723-46-6, SMT and acetaminophen: CAS Number 103-90-2, ACT) were purchased from Sigma–Aldrich, Madrid, Spain, and used as received. Iron (II) sulfate 7-hydrate (CAS Number 7782-63-0) was obtained from Panreac (Spain). Organic solvents were HPLC grade obtained from Panreac, Barcelona, Spain. Ultrapure water was obtained from a Milli Q water system.

2.2. Experimental setup

Experiments were carried out in 1-L capacity borosilicate glass cylindrical reactor equipped with mechanical agitation and an inlet for measuring temperature, ozone gas feeding and sampling. Oxidation was carried out at atmospheric pressure in 1 L of aqueous solution containing 30 mg L^{-1} as total pharmaceutical concentration with the aim of getting an appreciable quantity of hydrogen peroxide. For the ozone processes, an ozone–oxygen mixture was continuously bubbled into the aqueous solution through a porous plate placed at the bottom of the reactor. Ozone was produce from pure oxygen using a Sander Laboratory Ozone Generator, Barcelona, Spain. The gas flow rate was kept constant at 20 L h^{-1}. In photo-Fenton experiments, the reactor was situated in the middle of a wooden box (45 cm × 35 cm each wall) where four 15 W black light lamps, emitting mainly 365 nm radiation, were placed in each of the corners inside the box. Ferrioxalate actinometry [30] was used to determine the incident photon flux, I_0, in the photoreactor, that was found to be 5.4×10^{-8} Einstein·min^{-1} with four lamps simultaneously working.

Steadily, samples were withdrawn from the reactor and analyzed for parent compounds, total organic carbon (TOC), chemical oxygen demand (COD) and hydrogen peroxide concentration. In addition, in ozonation experiments ozone gas and dissolved ozone concentrations were also determined. When Fenton or photo-Fenton processes were applied ferrous ions and total iron concentrations were also quantified. In some cases, experiments were carried out in triplicate for experimental errors determination.

2.3. Analytical procedure

SMT and ACT were analyzed by high-performance liquid chromatography (HPLC, Elite La Chrom) with a GEMINI 5U C18 110R column. Elution of samples was initially made with a mixture of acidified water (1% phosphoric acid) and methanol (90/10 v/v) that was gradually changed to reach 40/60 v/v acidified water/methanol after 7 min. The flow rate was 0.5 mL min^{-1}. Quantification was made with L-2455 Hitachi Diode Array detector at 267 nm for SMT and 245 for ACT. Quantification limit for accurate measurements of concentrations was 100 μg L^{-1}. Analysis of standard solutions was repeated 10 times to establish the precision of the method that resulted to be +2% while accuracy was 1.2%.

The dissolved ozone concentration was determined by the indigo method [31]. Ozone concentration in the gas phase was monitored by means of an Anseros Ozomat (Tübingen, Germany) ozone analyzer. Hydrogen peroxide concentration was determined through the cobalt-bicarbonate method [32]. Total iron concentration was analyzed by the ferrozine method [33] and ferrous iron concentration by the phenantroline method [34]. Total organic carbon was monitored by a TOC-V_{SCH} Shimadzu carbon analyzer. Chemical oxygen demand (COD) was determined in a Dr. Lange (Düsseldorf, Germany) photometer, the method based on the dichromate standard procedure. Finally, the pH of the reaction media was followed by means of a Radiometer Copenhagen (Copenhagen, Denmark) pH-meter (HPM82).

3. Results and discussion

3.1. Optimization of hydrogen peroxide concentration

As mentioned before, one objective of this work was to optimize the operation conditions of hydrogen peroxide concentration produced during pharmaceuticals single ozonation [19]. Then, appropriate experimental conditions to obtain the maximum possible concentration of hydrogen peroxide were first established. Statistical experimental design is more practical compared to the conventional time-consuming one-factor-at-a-time methods. A response surface method (RSM) was adopted in this work in order to reduce the experimental workload. The RSM is an efficient approach for multivariate analysis with a minimum number of experiments and has already been used to optimize the operation parameters in wastewater treatments [35–39].

The RSM based on central composite design (CCD) was applied to optimize experimental conditions for hydrogen peroxide concentration. This design contains three kinds of points: cube points that come from factorial design, axial points, and center points. In the present investigation, three critical parameters affecting hydrogen peroxide generation were considered as follows: inlet ozone concentration (X_1, C_{O3}), pharmaceuticals ratio (X_2, C_{SMT}/C_{ACT}