Application of advanced oxidation for the removal of micropollutants in secondary effluents

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ABSTRACT

The aim of this work was to study the use of advanced oxidation technologies for micropollutant (atrazine, ATZ) removal in secondary effluents (SE). Experiments were carried out, for comparison purposes, in deionized water and in municipal SE. ATZ concentration, chemical oxygen demand (COD) and total organic carbon (TOC) were recorded along the reaction time and used to evaluate the system efficiency. Results demonstrate that the presence of effluent organic matter (EfOM) can reduce the effectiveness of the methods to remove ATZ due to the competition of EfOM components to react with OH radicals and/or molecular ozone. ATZ was more easily removed by hydroxyl radicals, however the presence of EfOM promoted higher inhibition of its removal by hydroxyl radicals than by ozone. The addition of Fe as catalyst in the UV/H_2O_2 system also increased the ATZ removal rate in SE. In addition, direct ATZ photolysis promoted by UV alone must be considered in the assessment of its degradation by UV-based methods.

Key words | advanced oxidation, atrazine, effluent organic matter, pesticides, secondary effluents

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INTRODUCTION

Micropollutants contamination and their potential effects on the environment is currently a topic of great concern (Eljarrat & Barcelo 2003; Ternes & Joss 2006). Most of them, including pharmaceuticals and pesticides, may have the potential to effect natural ecosystems (Cleuvers 2003) and bioaccumulate (Albanis *et al.* 1996; Isidori *et al.* 2007). In this context, the treatment of secondary effluents (SE) appears as an alternative to minimize the discharge of these contaminants in receiving waters as well as to improve the water quality for possible water reuse. However, when the SE is treated by methods based on oxidation, such as ozonation and advanced oxidation technologies (AOPs), the transformation of micropollutants depends on the matrix components (Lee & von Gunten 2010).

Atrazine (ATZ) was chosen in this study as a model compound. It is a water-soluble pesticide included in the European list of priority substances which represents a significant risk to the aquatic environment (European Union 2000).

In 2004, ATZ was banned from the European Union (EU) due its persistent groundwater contamination. However, in the United States, Brazil and Argentina, it is one of the most widely used herbicides, being largely used in grain crops (Rodrigues & Almeida 1995). ATZ toxicity to microorganisms of biological treatments does not favor its removal by biological techniques frequently used in municipal wastewater treatment plants (WWTP). Thus, due to its recalcitrant characteristics, it was found in surface and ground waters in concentrations of $\mu g\ L^{-1}$ (Sanches *et al.* 2003).

Advanced oxidation processes have been studied and applied as alternative methods to treat diverse types of recalcitrant compounds (Pera-Titus *et al.* 2004; Pignatello *et al.* 2006). Among them, ultra violet irradiation in combination with hydrogen peroxide (UV/H_2O_2) produces hydroxyl radicals ($^{\bullet}$OH) by the photolysis of hydrogen peroxide, which can degrade a large number of organic compounds (Ghaly *et al.* 2001; Muruganandham & Swaminathan 2004; Arslan-

Alaton *et al.* 2009). Besides, the use of Fe as catalyst is very common for this type of process to increase the quantity of formed OH radicals. On the other hand, ozonation can specifically react with micropollutants in water (Andreozzi *et al.* 2003; Dantas *et al.* 2008) as well as promote the disinfection of effluents (von Gunten 2003; Zuma *et al.* 2009).

The aim of this study was to study the use of AOP for the removal of micropollutants in SE, specifically ATZ. For this purpose, SE samples of urban wastewater were spiked with ATZ and treated by different AOPs. Total organic carbon (TOC), chemical oxygen demand (COD) and ATZ concentration were monitored along the reaction time. The influence of effluent organic matter (EfOM) on ATZ degradation rate was assessed by a comparison with blank experiments using deionized water (DW).

MATERIALS AND METHODS

The pure ATZ was supplied by Panreac (Barcelona, Spain). All identifications and quantifications were performed by a high performance liquid chromatograph (HPLC) supplied by Waters Corporation (Massachusetts, USA) equipped with a Teknokroma C-18 Tracer Extrasil ODS2 capillary column. The mobile phase used was a mix of H_2O:acetonitrile 40:60.

UV/H_2O_2 and UV/H_2O_2/Fe experiments were carried out in a 2 L reactor containing three immersed UV-C (254 nm, 8 W) lamps. Initially, 50 mg L^{-1} of H_2O_2 was added to the solution and then the UV lamps were turned on. Ozonation experiments were carried out in a 2 L reactor with an ozone flow rate of 0.87 g h^{-1} ($\approx$0.85 mg L^{-1} of dissolved ozone concentration). The effluent was collected from the WWTP of Gava-Viladecans (Barcelona, Spain). The samples were preliminarily filtrated and stored at 4 °C. Afterwards, the SE was spiked with 0.1 and 20 mg L^{-1} of ATZ and treated by the proposed AOPs methods. During experimentation, the temperature was kept at 25 °C and no pH adjustment was carried out. To avoid ATZ degradation by biological reactions in SE or other reactions that could lead to experimental error, ATZ was added to SE immediately before initiating the experiments.

To assess the system efficiency, ATZ concentration was monitored along the reaction time. Moreover, the COD (Standard method 5220 D) and the TOC were also recorded

in order to evaluate the oxidation and mineralization of the dissolved organic matter along the reaction time. TOC measurements were performed by means of a Shimadzu 5000A TOC analyzer. To observe the effect of the organic matrix on the used oxidants, experiments in DW at the same operational conditions for ozonation and UV/H_2O_2 were also carried out.

RESULTS AND DISCUSSION

Effluent characterization

Experiments were performed in DW and SE artificially contaminated with ATZ. However, before the artificial contamination, the SE was previously filtered with a 10 μm filter in order to eliminate suspended matter that could disturb analytical measurements. This first step of filtration affected only suspended solids (TSS and VSS), turbidity and COD, which were reduced by 50, 20 and 10% respectively. Thus the filtered effluent was characterized and its physicochemical characteristics are presented in Table 1. Due to its low concentration when spiked in SE, ATZ presence did not affect organic matter measurements such as COD and TOC.

UV-based AOPs and Fenton

Figure 1 shows the degradation profile of 0.1 mg L^{-1} of ATZ promoted by some advanced oxidation processes.

Table 1 | Characteristics of the secondary effluent

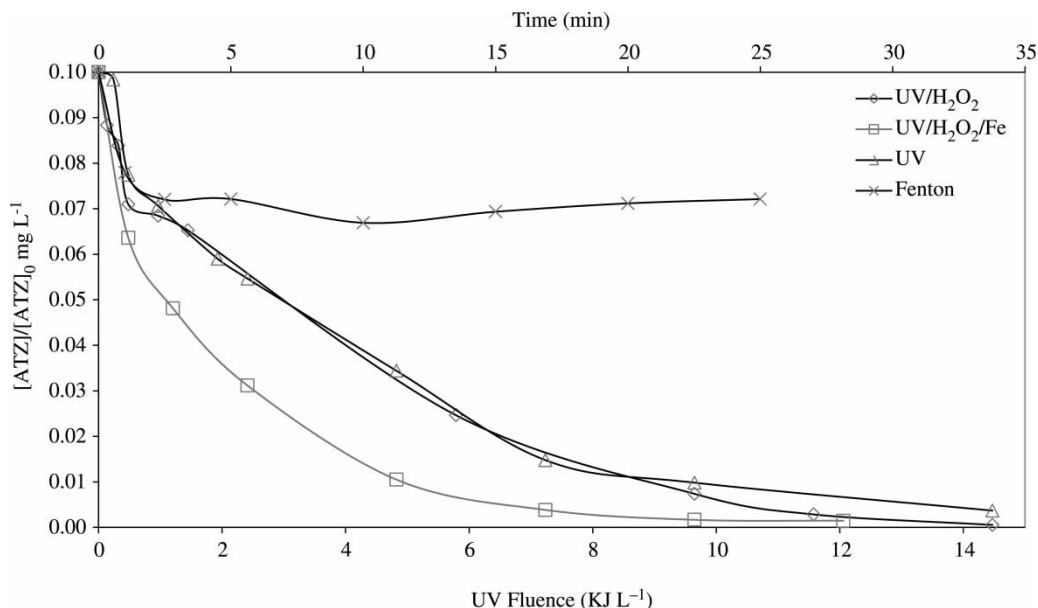| Parameter	Value
pH	7.9
TSS (mg L^{-1})	63.5
VSS (mg L^{-1})	31.5
Turbidity (NTU)	13.6
UV$_{254}$	0.512
TOC (mg L^{-1})	18.2
N-NO$_3^-$ (mg L^{-1})	0.13
COD (mg L^{-1})	95.4
Redox (mV)	215.4
Alkalinity (mg HCO$_3^-$ L^{-1})	507

Figure 1 | ATZ removal by AOPs in secondary effluent. $[H_2O_2] = 5$ mg L^{-1}.

According to the results, the Fenton reaction promoted the lowest ATZ removal rate, achieving only 30% of ATZ removal after 10 min of treatment. The UV/H_2O_2 and UV/H_2O_2/Fe treatments were more effective and able to completely remove ATZ in SE. UV radiation alone was also very effective to promote the direct photolysis of ATZ, suggesting that during UV/H_2O_2 treatment using UV-C radiation, the ATZ photolysis is more important than its oxidation by the formed ·OH. However, in the presence of catalyst (Fe), an important increase on the ATZ degradation rate was observed.

Another set of UV/H_2O_2 experiments was performed increasing the ATZ and H_2O_2 concentration. In this case, the runs were performed in SE and DW to observe the organic matrix effect. The UV/H_2O_2 treatment using 50 mg L^{-1} of H_2O_2 was also able to remove ATZ in both DW and SE (Figure 2). In this set of experiments, 1 mol of H_2O_2 was capable of removing 1.34 and 0.42 mol of ATZ in DW and SE, respectively, thus, the presence of EfOM tripled the hydrogen peroxide quantity required to remove ATZ. This inhibition can be explained by sinergical effects related to hydroxyl radical scavenging by some inorganic components of the EfOM, such as ammonia and nitrites, as well as by its consumption by natural dissolved organic carbon (DOC). As inorganic
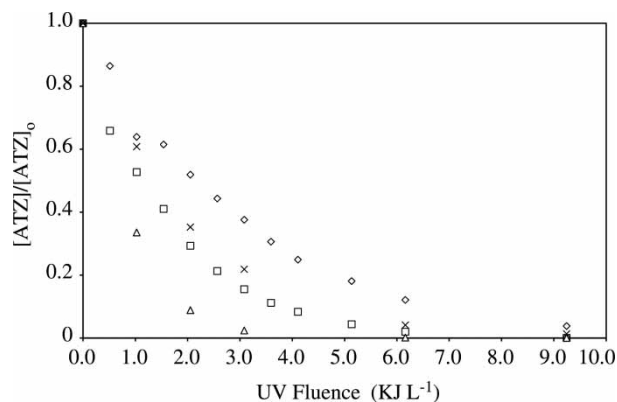

Figure 2 | ATZ removal by UV/H_2O_2 with $[H_2O_2] = 50$ mg L^{-1}. □ = SE by UV/H_2O_2, ◇ = SE by UV, △ = DW by UV/H_2O_2, x = DW by UV. [ATZ] = 20 mg/L, pH without adjustment.

salts can also act as hydroxyl radical scavengers, the high alkalinity in this wastewater also contributes to the scavenger effect. Since the hydroxyl radical has a nonselective character, its consumption by the natural organic matter present in this type of effluent is significant.

UV radiation alone was also effective in promoting the direct photolysis of ATZ, however EfOM interferences, mainly related to the SE turbidity (13.6 NTU) and color, increased the needed radiation in SE by about 65% compared to DW (Figure 2), proving that these parameters

should also be considered on the removal of microcontaminants by photo-assisted oxidation methods due to the difficulty of irradiating H_2O_2 molecules.

Concerning the mineralization of ATZ byproducts induced by UV/H_2O_2 in DW, 2 hours of treatment (24.6 kJ L^{-1}) was not able to produce any appreciable change on TOC (Figure 3). However, a mineralization of EfOM higher than 20% was achieved after 80 min of treatment (16 kJ L^{-1}). Thus, it can be stated that the hydroxyl radicals and other related radicals produced during the UV/H_2O_2 treatment would only promote the first step of oxidation of the ATZ; afterwards, the radicals are mainly consumed by some compounds from the EfOM. The sole UV irradiation was not able to promote mineralization, neither in SE nor in DW samples.
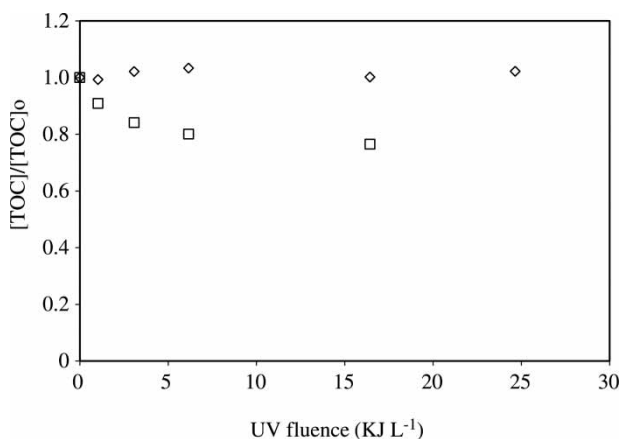

Figure 3 │ TOC removal by UV/H_2O_2 with $[H_2O_2]$ = 50 mg L^{-1}. □ = SE sample, ◇ = DW sample. [ATZ] = 20 mg/L, pH without adjustment.

Ozonation

To compare the ATZ removal by OH radicals and ozonation, SE samples spiked with 20 mg L^{-1} of ATZ were also treated by ozonation. In Figure 4(a), the ozonation of ATZ in DW solution promoted a fast ATZ removal after the first minutes of reaction, achieving complete ATZ removal after 45 min (0.9 g L^{-1} of ozone dosage). In contrast, the ozonation of SE samples needed 1.8 g L^{-1} of ozone to promote its total removal (Figure 4(a)). Although ozone is a very selective oxidant, reacting mainly with specific groups such as aromatic rings and deprotonated amines, the EfOM may contain numerous organic compounds with functional groups that would be attacked by the molecular ozone. The calculation of the initial SUVA ($TOC/UV_{254} \times 100$) (2.81) indicates the presence of organic compounds with functional groups which can absorb UV at 254 nm, such as aromatic rings. These types of organic compounds are reported to be strongly reactive with ozone. Thus, the presence of natural organic matter on ozonation experiments decreased the ATZ degradation rate 2.5 times. Furthermore, the presence of EfOM doubled the amount of inlet ozone needed to remove all ATZ content (approximately 2 and 4 mmol of O_3 in DW and SE, respectively). Concerning the mineralization of ATZ byproducts, the TOC analysis did not show any important variation when ATZ was oxidized in DW for 2 hours, instead, the mineralization of the spiked effluent achieved about 10% after 2 hours of ozonation (Figure 4(b)). The mineralization of some EfOM components confirms the competition of some natural organic compounds to react
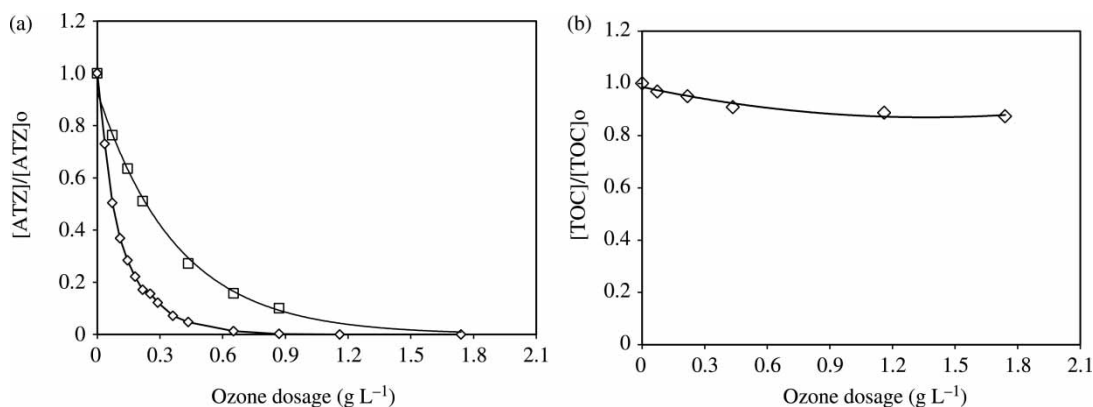

Figure 4 │ Ozonation of ATZ. (a) ATZ removal ◇ = DW, □ = SE; (b) TOC removal on SE. [ATZ] = 20 mg/L, pH without adjustment.

with ozone and the hydroxyl radicals generated by ozone decomposition, thus decreasing the available dissolved ozone to react with specific micropollutants.

It is important to point out that at neutral and basic pH, the contribution of hydroxyl radical on the ATZ oxidation is considerable. Figure 5 shows that the oxidation rate doubled when pH rises from 3 to 7. Although at pH 11 the experimental points did not allow the exact observation of the oxidation rate, ATZ was removed approximately 10 times faster than at neutral pH. SE pH was 7.9 and, therefore, the indirect ozone attack via hydroxyl radicals would have an important contribution on the ATZ oxidation.

Oxidation of the organic matter

The oxidation of the organic matter in SE by ozonation and UV/H_2O_2 is presented in Figure 6. COD removal profile in
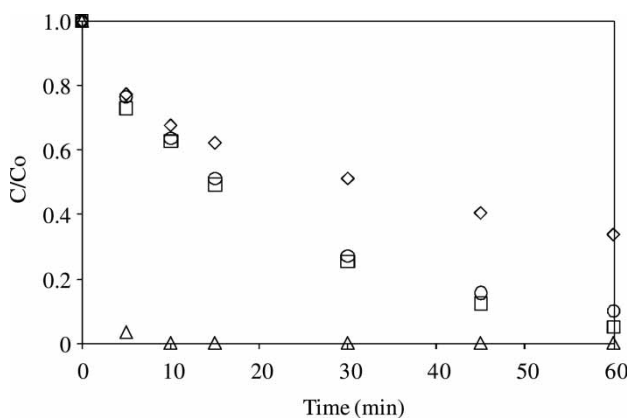
both treatments showed similar behavior, achieving about 20% of oxidation in the first minutes of reaction and remaining at the same level during the remaining reaction time. In the case of ozonation, the ozone needed to remove 50% of the ATZ content in the sample also promoted about 20% of COD removal, indicating that in the early stage of micropollutant oxidation, the EfOM undergo a considerable oxidation. Therefore, the ozone dosage necessary to remove ATZ from the SE sample would have also the potential to transform the more reactive compounds present in the EfOM. On the other hand, when 50% of ATZ was removed by UV/H_2O_2 (1 kJ L^{-1} = 5 min of treatment) only about 5% of the EfOM undergo oxidation. Thus, hydroxyl radicals promoted a fast micropollutant removal (ATZ) with lower subsequent EfOM oxidation.

CONCLUSIONS

- The preliminary assessment of the ATZ treatment in SE proved the efficiency of ozone and advanced oxidation technologies to remove specific micro-contaminants.
- The presence of EfOM can reduce the effectiveness of the methods to remove ATZ due to the competition of EfOM and inorganic components to react with radicals and/or molecular ozone.
- ATZ was easily removed by UV/H_2O_2, however the presence of EfOM promoted higher inhibition of ATZ removal by hydroxyl radicals (UV/H_2O_2) than by ozone.
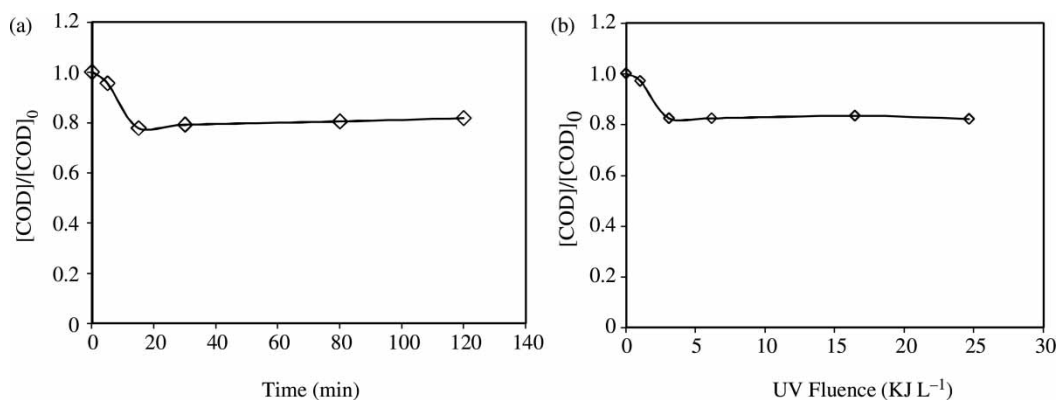

Figure 5 │ Effect of pH on the ozonation of ATZ in DW. pH : ◇ = 3; □ = 7; ○ = free; △ = 11. Solutions buffered with phosphate salts (0.1 mol L^{-1}).

Figure 6 │ Organic matter oxidation in SE. (a) ozonation (b) UV/H_2O_2. [H_2O_2] = 50 mg/L. [ATZ] = 20 mg/L, pH without adjustment.

- Since the ATZ is significantly removed by UV direct photolysis, its contribution must be considered in the assessment of its degradation by UV/H_2O_2.
- In the point of ATZ removal, ozonation promoted about 20% of EfOM oxidation in front of 5% obtained by UV/H_2O_2.
- EfOM presence promoted high increment of oxidant consumption in ozonation, instead, in UV/H_2O_2, its influence was not considerable.

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