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Influence of EfOM on the Oxidation of Micropollutants by Ozone and UV/H_2O_2 in Secondary Effluents

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Abstract: The aim of this work was to study the influence of effluent organic matter (EfOM) on micropollutants removal by ozone and UV/H_2O_2. To perform the experiments, deionized water and municipal secondary effluents (SE) were artificially contaminated with atrazine (ATZ) and treated by the two proposed methods. ATZ concentration, COD and TOC were recorded along the reaction time and used to evaluate EfOM effect on the system efficiency. Results demonstrate that the presence of EfOM can significantly reduce the micropollutant removal rate due to competition of EfOM components to react with radicals and/or molecular ozone. The hydroxyl radical scavenging caused by EfOM was quantified as well as the contribution of molecular ozone and ·OH radicals during the ozonation of SE. EfOM components promoted higher inhibition of ATZ oxidation by hydroxyl radicals than by molecular ozone.

Key words: Secondary effluents, effluent organic matter, UV/H_2O_2, ozonation, atrazine, pesticides.

1. Introduction

Micropollutants contamination and their potential effects on environment is currently a topic of great concern [1, 2]. Most of them, including pharmaceuticals and pesticides may have potential to cause effect on natural ecosystems [3] and to bioaccumulate [4, 5]. In this context, the treatment of secondary effluents appears as an alternative to minimize the discharge of these contaminants in receiving waters as well as to improve the water quality for a possible water reuse. However, when the secondary effluent (SE) is treated by methods based on oxidation such as ozonation and advanced oxidation technologies (AOPs) including UV/H_2O_2, the transformation of micropollutants depends on the matrix components, which determines the stability of the oxidant [6].

In this study, Atrazine (ATZ) was chosen as a model compound to represent micropollutant presence in SE. It is a water-soluble pesticide included in the European list of priority substances which represents a significant risk to the aquatic environment [7]. In 2004, ATZ was banned from the European Union (EU) due its persistent groundwater contamination. However, in the United States, Brazil and Argentine, it is one of the most widely used herbicides, being largely used in grain crops [8]. ATZ toxicity to microorganisms of biological treatments does not favor its removal by biological techniques frequently used in municipal wastewater treatment plants. Thus, due to its recalcitrant characteristic, it was found in surface and ground waters in concentrations of $\mu g \cdot L^{-1}$ [9].

The environmental occurrence of chemical substances presenting endocrine activity, named environmental estrogens, has been described on literature in the last three decades. Due to their potential toxicity and endocrine disruption effect, the triazinic compounds degradation methods and mechanism, mainly regarding ATZ, have been extensively studied. An endocrine disruption is the

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substance capacity of coupling with receptors and induces an endocrine response. Usually, the endocrine disruption test for one specific molecule is measured by the comparison with that measured for the 17β-estradiol. The YES assay (yeast estrogen-inducible expression system) uses genetically modified yeast, which contains the human estrogen receptor (HER). Thus, substances suspected to have estrogenicity are identified by their interaction with the receptor [10].

Advanced oxidation processes have been studied and applied as alternative methods to treat diverse types of recalcitrant compounds [11, 12]. Among them, UV irradiation in combination with hydrogen peroxide (UV/H_2O_2) produces hydroxyl radicals (OH) by the photolysis of hydrogen peroxide, which can degrade a large number of organic compounds [13-15]. On the other hand, ozonation can specifically react with micropollutants in water [16, 17] as well as promote the disinfection of effluents [18, 19]. Although the AOPs are established methods for the removal of organic compounds in drink and waste water, scientific literature dealing with their application in secondary effluents is nowadays limited [20, 21].

The aim of this study was to study the influence of the effluent organic matter (EfOM) on the removal of micropollutants in SE, specifically ATZ, by ozonation and UV/H_2O_2. For this purpose, secondary effluents samples of urban wastewater were spiked with 0.09 mmol (20 mg·L^{-1}) of ATZ and treated by ozonation and UV/H_2O_2. Total organic carbon (TOC), chemical oxygen demand (COD) and ATZ concentration were monitored along the reaction time and used to assess the system efficiency. To verify EfOM influence on ATZ oxidation, the results were compared with blank experiments using deionized water. As a complementary study, the estrogenic activity test YES was carried out in order to verify if the treatment would produce intermediates with estrogenic activity.

2. Materials and Methods

The pure atrazine 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. The effluent was collected from the wastewater treatment plant (WWTP) of Gava-Viladecans (Barcelona, Spain). The samples were preliminary filtrated and stored at 4 °C. Afterwards, the SE was spiked with 0.09 mmol·L^{-1} of ATZ and treated by the proposed methods.

UV/H_2O_2 experiments were carried out in a 2-L reactor containing 3 immersed UV-C (254 nm, 8 W) lamps. The actinometrical measurement used to determine the fluency and the photonic flux was based on the photochemical decomposition of oxalic acid in presence of uranyl nitrate. Thus, the incident photonic flux of 1.49×10^{-5} Einteins·s^{-1}, which corresponds to a fluency rate of 8.04 Wcm^{-2} for the three 254 nm lamps was obtained. To perform the runs, 1.47 mm·L^{-1} (50 mg·L^{-1}) of H_2O_2 was added to the sample and then the UV lamps were turned on. Samples were withdrawn in known intervals of time and the residual H_2O_2 was quenched by potassium bissulfite. Ozonation experiments were carried out in a 2-L reactor with an ozone flow rate of 0.87 g·h^{-1}. During experimentation, ozone was bubbled in the solution under continuous stirring and controlled temperature at 25 °C. Ozonation runs were carried out at pH 3.7 and 11 buffered with phosphates salts (KH_2PO_4, Na_2HPO_4) as well as at non controlled pH (~ 6). Ozone was generated by means of a Sander Labor Ozonizator (Germany) using pure oxygen as a feeding gas. The gaseous outlet from the reactor was conduced to an ozone depletion unit, where the remaining ozone stream was destroyed by a reaction with KI. The inlet and outlet ozone gas concentration were measured with a BMT964 ozone analyzer (BMT, Germany).

To assess the system efficiency, ATZ concentration was monitored along the reaction time. Moreover, the chemical oxygen demand (COD) (Standard method 5220 D) and the total organic carbon (TOC) were also recorded in order to evaluate the oxidation and mineralization of the dissolved organic matter in the medium. TOC measurements were performed by means of a Shimadzu 5000A TOC analyzer. To better asses the effect of EfOM on the stability of the oxidants, experiments in deionized water (DW) with 0.09 $mmol\cdot L^{-1}$ of ATZ at the same operational conditions for ozonation and UV/H_2O_2 were also carried out. UV_{254} absorbance was used as aromaticity indicator and it was measured using a Perkin Elmer UV/VIS Lambda 20 spectrophotometer. Total suspended solids (TSS) analysis performed following the guidelines given by the standard methods (APHA 1985, 2540D and 2540E) and turbidity measurements carry out using a HACH 2100P turbidimeter. pH and Redox were measured by CRISON glass electrodes. N-NO_3^- and alkalinity (HCO_3^- and CO_3^{2-}) were measure by a DIONEX ionic chromatograph.

To carry out the YES test, the genetically modified yeast strain (Saccharomyces cerevisiae) for the test used was donated by Prof. J. P. Sumpter of Brunel University, Uxbridge, UK. The experimental procedure for the estrogenic activity assay was performed using the method described by Routledge and Sumpter [22], where 17β-estradiol was used as control.

3. Results and Discussion

About an hour after being collected, SE samples were analyzed. Its physicochemical characteristics are presented in Table 1.

Table 1 Characteristics of the secondary effluent.

Parameter	Value
pH	7.9
SST ($mg\cdot L^{-1}$)	63.5
SSV ($mg\cdot L^{-1}$)	31.5
Turbidity (NTU)	13.6
UV_{254}	0.512
TOC ($mg\cdot L^{-1}$)	18.2
N-NO_3^- ($mg\cdot L^{-1}$)	0.13
COD ($mg\cdot L^{-1}$)	95
Redox (mV)	215.4
Alkalinity (mg $HCO^{-3}L^{-1}$)	507

3.1 ATZ Removal

In this work, in order to compare the degradation curves of atrazine in deionized water (DW) and secondary effluent (SE), the pseudo first order approximation method was used to calculate the apparent kinetic constants (k). To obtain the k values, the neperian logarithm of the normalised concentration was plotted against time, the slope of the resulting straight line represents k. On the other hand, lines were inserted on the graphics only for visual emphases of experimental data trends.

3.1.1 Ozonation

Fig. 1 shows ATZ ozonation in DW and SE during the first 10 minutes of treatment. DW solution was buffered to reach the same pH of SE samples (7.9). According to the results, the ozonation of ATZ DW solution promoted a fast ATZ removal since the first minutes of reaction. The complete ATZ removal was achieved after 19 $mmol\cdot L^{-1}$ of ozone dosage (45 min) in DW, while with the same quantity of ozone, about 90% of ATZ was removed in SE samples. EfOM presence promotes a small decrease on the ATZ removal rate by ozonation. The calculation of kinetic constants demonstrated that the present organic matter decrease in about 17% the ATZ removal rate. 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 molecular ozone. The calculation of the initial SUVA 2.81 (TOC/UV_{254} × 100) 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.

Since the pH of the reactions was 7.9 the OH radical contribution on ATZ oxidation during ozonation was expected to be considerable. Fig. 2 shows the variation on ATZ removal rate in DW when pH rises from 3 to 7. Although at pH 11 the experimental points did not allow the exact calculation of the oxidation rate, k values allows observing that ATZ removal rate was importantly increased when pH rises. Besides ozonation at buffered pH at 7 had similar ATZ degradation rate when compared with ozonation at non adjusted pH (5.8). Thus, the importance of OH radicals contribution during ATZ removal by ozonation at the used pH was confirmed. Therefore, the reduction of ATZ removal rate could be attributed to the sum of molecular ozone and OH scavenging promoted by different EfOM components.

3.1.2 UV/H_2O_2

The UV/H_2O_2 treatment using 1.47 $mmol \cdot L^{-1}$ (50 $mg \cdot L^{-1}$) of H_2O_2 was also able to remove ATZ in both DW and SE (Fig. 3). In this set of experiments, the decrease of ATZ removal rate caused by EfOM is also evident. The presence of EfOM reduced about 42% the ATZ removal rate during the UV/H_2O_2 degradation. This inhibition can be explained by synergic 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 DOC. As inorganic salts can also act as

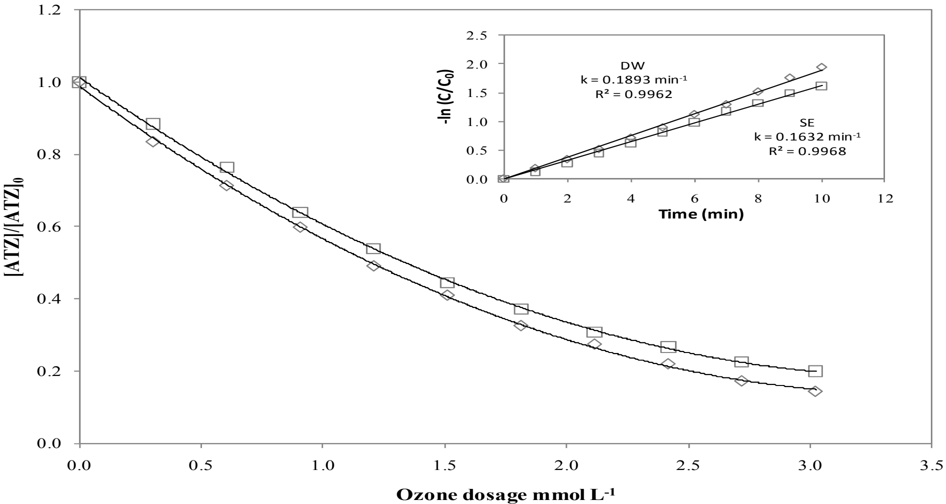


Fig. 1 Ozonation of ATZ. ATZ removal (◊)DW, (□)SE. $[ATZ]_0$ = 20 $mg \cdot L^{-1}$, pH without adjustment.

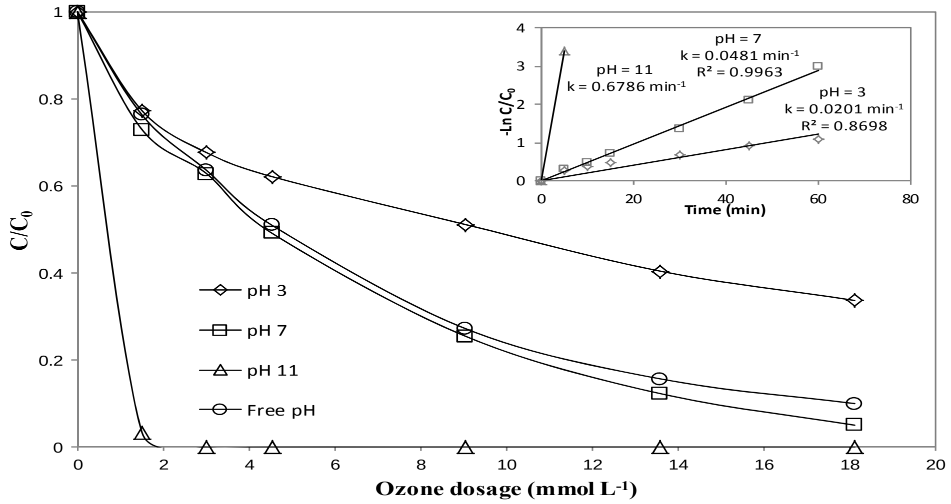


Fig. 2 Effect of pH on the ozonation of ATZ in DW. pH: (◊)3; (□)7; (○)free; (Δ)11. Solutions buffered with phosphates salts (0.1 $mol \cdot L^{-1}$).

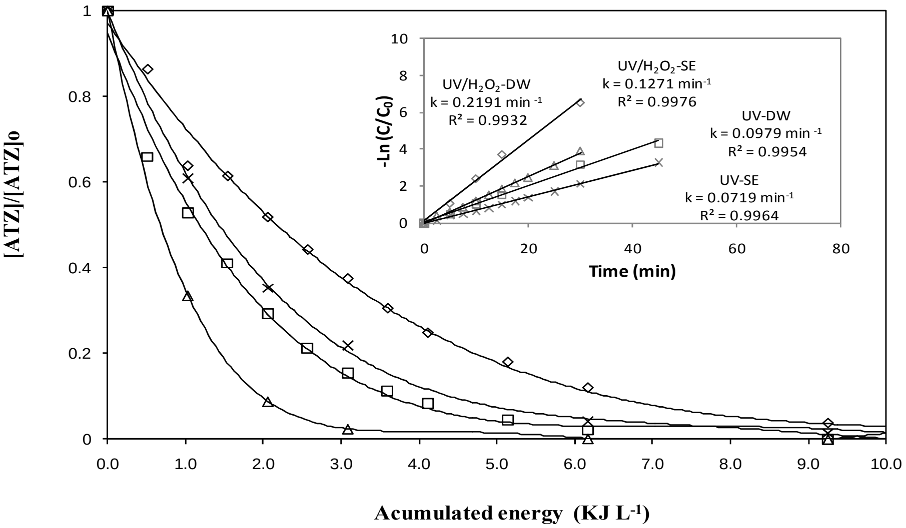


Fig. 3 ATZ removal by UV/H_2O_2 with $[H_2O_2]_0$ = 50 mg·L^{-1}; (□)SE by UV/H_2O_2, (◊)SE by UV, (Δ)DW by UV/H_2O_2, (x)DW by UV. $[ATZ]_0$ = 20 mg·L^{-1}, pH without adjustment.

hydroxyl radical scavengers, the high alkalinity (Table 1) [23] could be pointed as the main source of inorganic OH scavenging in both ozonation and UV/H_2O_2. At the used experimental conditions, EfOM caused higher inhibition on ATZ removal rate in UV/H_2O_2 than in ozonation. This difference could reside in the fact that hydroxyl radical has a non selective character, thus its consumption by the natural organic matter present in this type of effluents would be higher than the molecular ozone. The higher competition of hydroxyl radicals for other organic/inorganic compounds would cause higher inhibition of micropollutants removal. In the case of ozonation, although at the used pH the presence of hydroxyl radical is considerable, the concentration would be much less than those present during UV/H_2O_2 oxidation.

As reported also in Fig. 3, UV-C direct photolysis was also effective to remove ATZ, however EfOM interference on the UV incoming irradiation was observed. This effect might be related to SE turbidity (13.6 NTU) and color. A reduction of about 26% on ATZ transformation rate caused by the sole UV-C was observed, proving that turbidity and color should also be considered on the removal of microcontaminants in SE by photo-assisted oxidation methods.

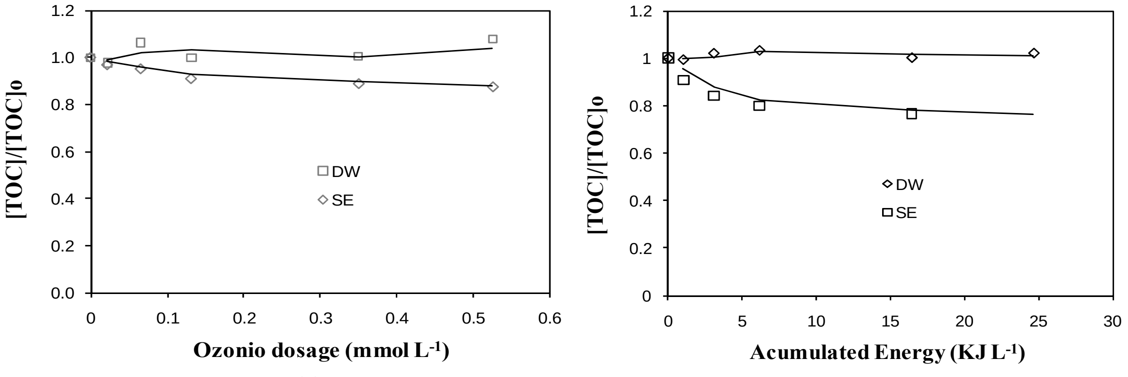
3.2 SE Mineralization and Oxidation

Concerning the mineralization of ATZ byproducts in DW promoted by ozonation, TOC analysis did not show any important variation at the end of two hour of treatment; instead, the spiked effluent achieved a mineralization in the vicinity of 10% after the same ozonation time (Fig. 4a). The occurrence of EfOM components mineralization confirms the competition of some natural organic compounds to react with ozone and hydroxyl radicals generated by ozone decomposition, thus decreasing the available dissolved ozone to react with specific micropollutants. Following the same trend, two hours of UV/H_2O_2 treatment (24.6 kJ·L^{-1}) in DW was not able to produce any appreciable change on TOC (Fig. 4b). However, a mineralization of EfOM higher than 20% was achieved after 80 min of SE treatment (16 KJ·L^{-1}). Thus it can be stated that hydroxyl radicals, molecular ozone and others related radicals produced during SE treatment are only able to transform ATZ molecule. Nevertheless, EfOM components undergo mineralization along the reaction time. The sole UV irradiation was not able to promote mineralization neither in SE nor in DW samples.

The organic matter oxidation, represented by COD analysis, in SE achieved by ozonation and UV/H_2O_2 is presented in Fig. 5. 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. Nevertheless, during SE ozonation, the ozone needed to remove 50% of the ATZ (4.5 mmol·L^{-1}) content in the sample promoted about 20% of COD removal, indicating that in early stage of micropollutant oxidation, EfOM undergo a considerable oxidation. As a result, the ozone dosage necessary to remove ATZ from SE samples has the potential to transform the more-reactive compounds present in EfOM. On the other hand, when 50% of ATZ was removed by UV/H_2O_2 (1 KJ·L^{-1}) only about 5% of EfOM undergo oxidation. Thus, by UV/H_2O_2 the removal of micropollutants could be accomplished with less organic matter transformation when compared to ozonation. This aspect is important if during micropollutants removal the augment of SE biodegradability is not desirable.

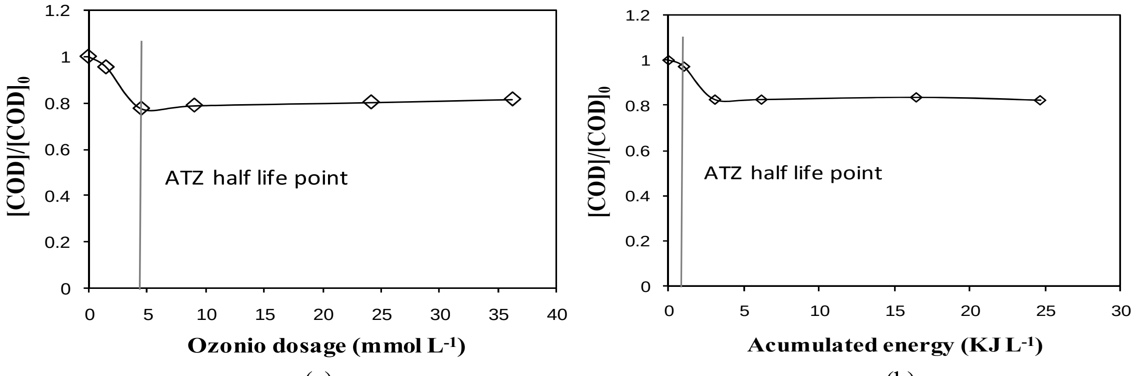
3.3 Oxidant Consumption

The SE composition can vary depending on the influent quality and WWTP level of efficiency. Thus, the inhibition of micropollutants removal caused by EfOM to different oxidants will depend of the quality and quantity of oxidable compounds as well as scavengers present in the medium. Since oxidant consumption is direct related to the cost of the system, the information about the increment of oxidant consumption in SE is considered in this section. In order to have an overall idea about the increment of oxidant consumption in SE samples due to EfOM presence, oxidants (O_3 and H_2O_2) consumption along



(a) (b)

Fig. 4: (a) TOC removal during ozonation □ = DW, ◊ = SE. $[ATZ]_0$ = 20 mg·L^{-1}, pH without adjustment; (b) TOC removal during UV/H_2O_2 ◊ = DW, □ = SE, $[H_2O_2]_0$ = 50 mg·L^{-1}, $[ATZ]_0$ = 20 mg·L^{-1}, pH without adjustment.



(a) (b)

Fig. 5: (a) Organic matter oxidation in SE by ozonation, $[ATZ]_0$ = 20 mg·L^{-1}, pH without adjustment; (b) Organic matter oxidation in SE by UV/H_2O_2, $[H_2O_2]_0$ = 50 mg·L^{-1}, $[ATZ]_0$ = 20 mg·L^{-1}, pH without adjustment.

the time was plotted in Fig. 6. In the case of ozonation, the consumed ozone was calculated by the difference between the inlet and outlet measured ozone concentration along the reaction time (Fig. 6a). This graphic shows that the presence of EfOM appreciably increased the consumed ozone. In average, the system consumed about two times more ozone per minute treating SE when compared with runs using DW. The ozone consumption in both DW and SE decreased with ozonation time due to the formation of more-oxidized and less-reactive compounds. On the other hand, the hydrogen peroxide consumption in UV/H_2O_2 behaved in a different way. The increment of H_2O_2 consumption during reaction was not significant compared to that observed in ozonation. Therefore, it can be assumed that variation on SE composition would not affect the cost of UV/H_2O_2 treatment to remove micropollutants.

3.4 EfOM Scavenging Quantification

In order to quantify the EfOM inhibition on ATZ removal during ozonation and UV/H_2O_2 in secondary effluents, the contribution of hydroxyl radical and molecular ozone on ATZ removal in DW and SE were calculated. For ozonation runs, the oxidant contribution was determined by the ratio of ozone and OH radical oxidation and the total oxidation using the corresponding kinetics. The overall degradation rate (r_{tot}, $mol \cdot cm^{-3} \cdot s^{-1}$) of a compound is the sum of the contributions of the reaction rate of molecular ozone (r_{mol}, $mol \cdot cm^{-3} \cdot s^{-1}$) and reaction rate via ·OH radicals (r_{rad}, $mol \cdot cm^{-3} \cdot s^{-1}$). Thus, this relationship is described by Eqs. (1) and (2) [24].

$$r_{tot} = r_{mol} + r_{rad} \quad (1)$$

$$r_{tot} = k_{mol}[A][O_3]^m + k_{rad}[A][\cdot OH]^n \quad (2)$$

Where, k_{mol} and k_{rad} are the second-order kinetic constants of rate in $(mol \cdot cm^{-3})^{-1} \cdot s^{-1}$, m and n are the orders of reaction with respect to O_3 and ·OH radical reactions, respectively. Therefore, Eq. (2) can be written as follows:

$$r_{tot} = k'_{mol}[A] + k'_{rad}[A] \quad (3)$$

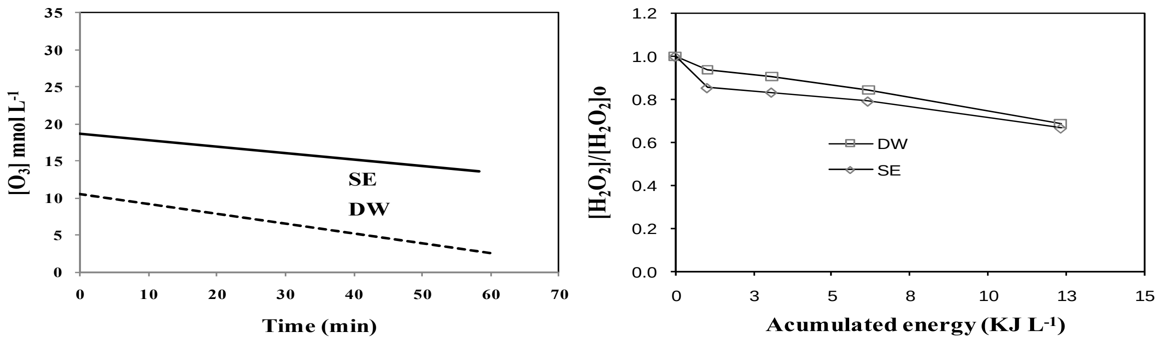
$$r_{tot} = (k'_{mol} + k'_{rad})\,[A] \quad (4)$$

$$r_{tot} = k'_{tot}[A] \quad (5)$$

Where, $k'_{mol} = (k_{mol}[O_3]^m)$ and $k'_{rad} = (k_{rad}[\cdot OH]^n)$ are the pseudo first order kinetic constants in s^{-1} for the reactions via molecular ozone and ·OH radical, respectively. k'_{tot} (s^{-1}) is the pseudo first order kinetic constant of the overall ozonation reaction. Thus, the kinetic constant equation can be described by Eq. (6)

$$k'_{tot} = k'_{mol} + k'_{rad} \quad (6)$$

To obtain the experimental data needed to calculate k'_{mol} and k'_{rad}, ATZ solutions at concentration of 0.09 $mmol \cdot L^{-1}$ were prepared in both DW and SE. Afterwards, DW solutions were buffered at the same pH of SE samples (7.9) with phosphate salts at 0.2 $mol \cdot L^{-1}$. The strategy consisted in add an OH radical scavenging (t-butanol 0.1 $mL \cdot L^{-1}$) to prevent the indirect (OH) mechanism and thus determine k'_{mol} assuming that only the molecular ozone attack would occur. Another run without the presence of the ·OH scavenging was performed and the data was used to



(a) (b)

Fig. 6 (a) Oxidant consumption during ozonation, DW = dashed line, SE = full line; (b) Oxidant consumption during UV/H_2O_2, □ = DW, ◊ = SE.

calculate k'_{tot}. k'_{rad} was calculated using Eq. (6). Once performed the runs, ATZ concentration was measured in the first 10 minutes of reaction and the neperian logarithm (ln) of the normalised concentration (C/C_0) was plotted against time, the slope of the resulting straight line represents k'. This strategy was used for DW and SE spiked solutions and to ensure reproducibility all experiments were carried out in triplicate. For UV/H_2O_2 runs the ATZ removal was completely attributed to OH radicals (Eq. (7)):

$$r_{tot} = r_{rad} \tag{7}$$

Fig. 7 presents ln (C/C_0) versus time for a set ozonation experiments used for k' calculation.

Fig. 8 shows the block diagram with the average values of k'_{tot}, k'_{mol} and k'_{rad} for ozonation and UV/H_2O_2 experiments carried out in DW and SE samples.

According to Fig. 8, the ATZ degradation rate during ozonation represented by k_{tot} is reduced about 17% by the presence of EfOM. When ATZ is oxidized in DW, as expected, OH radicals are more reactive than molecular ozone and ·OH radicals contribution is very important, representing about 74% of k_{tot}. On the other hand, when ATZ was treated in SE samples, the specific character of the molecular ozone favored the main oxidation pathway via direct ozonation (63%). The reduction of ·OH contribution between runs in DW and SE, represented by k'_{rad}, can be attributed to OH scavenging promoted by EfOM, which in this case was around 60%. This high percentage of radical scavenging caused by EfOM presence is attributed to the non-specific character of OH radical along with the presence of oxidable organic compounds and the high alkalinity of the used SE sample. In the case of ATZ removal rate reduction in UV/H_2O_2, as commented before, the reduction of about 42% is due to both OH radical scavenging and reduction of incoming light irradiation caused by EfOM components.

3.5 Estrogenic Activity Test (YES)

To asses the possibility of formation of more biologically active intermediates during the treatment of waters containing ATZ, the estrogenic activity of the samples was measured according to YES method procedure. The results demonstrated that 0.09 mmol·L^{-1} ATZ solution did not present estrogenic activity, however, 3 min of ozonation promoted the formation of intermediates which have a weak estrogenic response for YES assay. After the treatment by ozone and UV/H_2O_2, the estrogenic response decreased. Afterwards, their oxidation reduces this activity. Although, it can be stated that the YES test was inconclusive for assessing the estrogenic activity of ATZ, since it was observed a weak estrogenic response to a wide range of concentrations (0.5, 16, 50

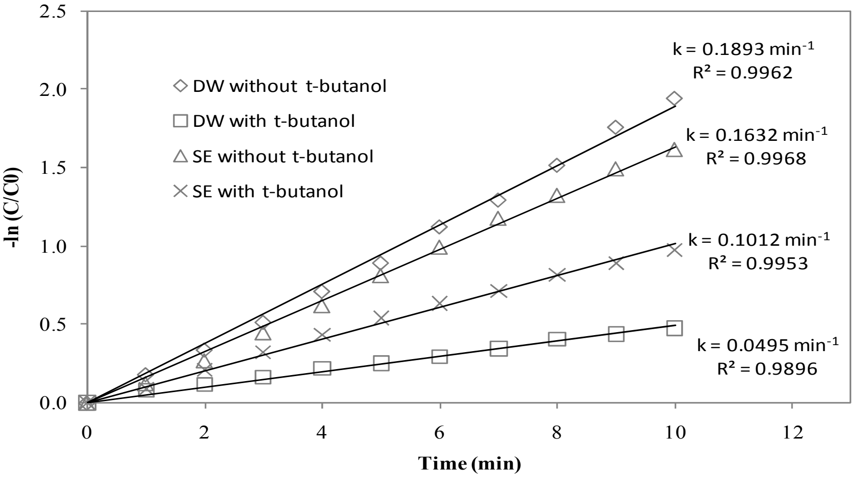


Fig. 7 Rate constants of individual contributions, molecular reaction (k_{mol}) or radical reaction (k_{rad}), and overall reaction (k_{tot}) for the ozonation systems.

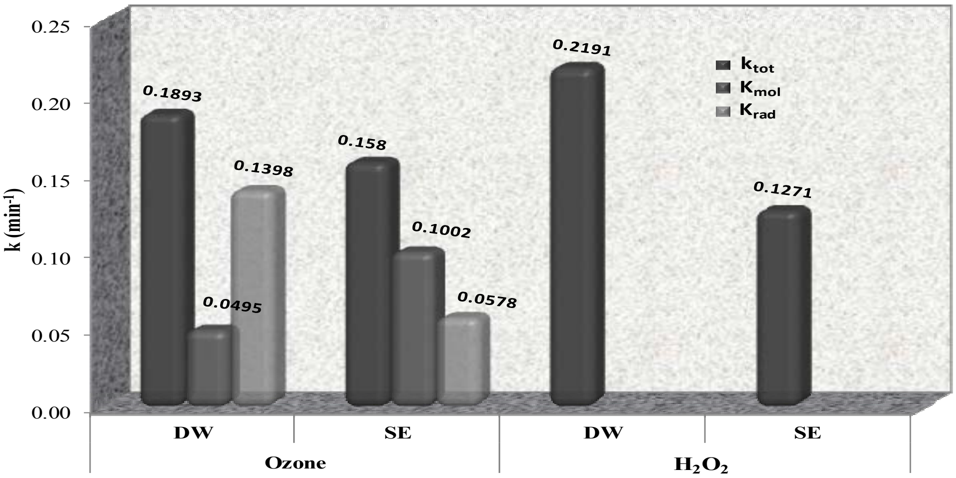


Fig. 8 Individual oxidant contributions on ATZ oxidation. Molecular reaction (k_{mol}), radical reaction (k_{rad}) and overall reaction (k_{tot}).

and 100 mg·L^{-1}). It can be suggested that ATZ treatment by advanced oxidation could induce to the formation of intermediates with a weak strogenicity. Besides, a possible antiestrogenic activity of ATZ intermediates is supported by Orton et al. [25] where the author reports that Atrazine showed response to the test for antiestrogenic activity (YAS) and showed no response to the test of estrogenic activity (YES).

4. Conclusion

The preliminary assessment of the ATZ treatment in secondary effluents proved the efficiency of ozone and UV/H_2O_2 to remove specific micro-contaminants. The presence of effluent organic matter 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. During ozonation of ATZ in SE the direct oxidation pathway prevails, while in DW the major ATZ oxidation is accomplished by hydroxyl radicals. At the point of total ATZ removal, ozonation promoted about 20% of EfOM oxidation in front of 5% obtained by UV/H_2O_2. Moreover, EfOM presence raised increment of oxidant consumption in ozonation, while in UV/H_2O_2, its influence was not significant. According to the YES test, the ozonation of SE containing ATZ could lead to the formation of intermediates with low estrogenic activity.

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