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Research article

Selecting the best AOP for isoxazolyl penicillins degradation as a function of water characteristics: Effects of pH, chemical nature of additives and pollutant concentration

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ABSTRACT

To provide new insights toward the selection of the most suitable AOP for isoxazolyl penicillins elimination, the degradation of dicloxacillin, a isoxazolyl penicillin model, was studied using different advanced oxidation processes (AOPs): ultrasound (US), photo-Fenton ($UV/H_2O_2/Fe^{2+}$) and TiO_2 photocatalysis (UV/TiO_2). Although all processes achieved total removal of the antibiotic and antimicrobial activity, and increased the biodegradability level of the solutions, significant differences concerning the mineralization extend, the pH of the solution, the pollutant concentration and the chemical nature of additives were found. UV/TiO_2 reached almost complete mineralization; while ~10% mineralization was obtained for $UV/H_2O_2/Fe^{2+}$ and practically zero for US. Effect of initial pH, mineral natural water and the presence of organic (glucose, 2-propanol and oxalic acid) were then investigated. $UV/H_2O_2/Fe^{2+}$ and US processes were improved in acidic media, while natural pH favored UV/TiO_2 system. According to both the nature of the added organic compound and the process, inhibition, no effect or enhancement of the degradation rate was observed. The degradation in natural mineral water showed contrasting results according to the antibiotic concentration: US process was enhanced at low concentration of dicloxacillin followed by detrimental effects at high substrate concentrations. A contrary effect was observed during photo-Fenton, while UV/TiO_2 was inhibited in all of cases. Finally, a schema illustrating the enhancement or inhibiting effects of water matrix is proposed as a tool for selecting the best process for isoxazolyl penicillins degradation.

1. Introduction

The presence of antibiotics in the environment is a major cause of proliferation of both bacterial resistance and several human and animal illnesses (Korzeniewska et al., 2013; Rivera-Utrilla et al., 2013). Special attention has been given to the penicillin type antibiotics due to their extensive use in treating infections. An example is dicloxacillin (DXC), a isoxazolyl penicillin antibiotic widely used against *Gram*-positive bacteria (Raj et al., 2007). As a result of the inefficiency of conventional removal processes, DXC has been found in different water bodies (Homem and Santos, 2011; Rizzo et al., 2013).

Advanced Oxidation Processes (AOPs) are physicochemical techniques (De la Cruz et al., 2013, 2012; Rubio-Clemente et al., 2014), which have been applied to treat organic pollutants in both drinking water and wastewater (De la Cruz et al., 2013; Giraldo et al., 2010; Guzman-Duque et al., 2011; Velegraki and Mantzavinos, 2015). AOPs are characterized by the formation of oxidative species, mainly the hydroxyl radical (•OH), which degrades organic compounds with high reaction rates (Glaze et al., 1987). AOPs can be classified into photochemical and non-photochemical processes. Photochemical processes can be in turn grouped into heterogeneous and homogeneous catalytic techniques. Of these,

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photocatalysis with TiO_2 (UV/TiO_2) and the photo-Fenton reaction ($UV/H_2O_2/Fe^{2+}$), respectively, are among the most studied (Bernabeu et al., 2012; Lopez-Alvarez et al., 2012, 2011). On the other hand, one of the most promising non-photochemical processes is ultrasound (US), which is known to be an environmentally friendly technique due to the absence of chemical additives such as a catalyst or oxidants. This process is based on the cavitation phenomenon, then degradation can be by the interaction of high frequency ultrasound with aqueous media to produce •OH (Henglein, 1987) or via pyrolysis (Suslick et al., 1986).

Promising results have been obtained when using AOPs to eliminate pharmaceutical pollutants in waters, including isoxazolyl penicillins. A summary of the main works reported so far for the degradation of different isoxazolyl penicillins using AOPs is shown in Table SM 1 (See Supporting Material 1). These studies have suggested a strong influence exerted by the water matrix characteristics. However, few investigations deal with comparative issues and the variety of the tested chemicals components in the matrix remains scarce. Then, despite the available information, it is still difficult to select the most suitable AOP process for the treatment of waters contaminated with pharmaceutics such as isoxazolyl penicillins.

Therefore, taking DXC as an isoxazolyl penicillin model, the aim of this research is to provide new insights toward the selection of the most suitable AOP for isoxazolyl penicillins elimination by photochemical and no-photochemical AOPs (ultrasound, photocatalysis with TiO_2 and photo-Fenton). The water matrix effects are comparatively investigated during the antibiotic elimination in synthetic and natural waters. The evaluation of initial pH and the effect of organic additives (glucose, 2-propanol and oxalic acid) are also investigated. Finally, comparisons between the antimicrobial activity, mineralization and the biodegradability of the treated solutions were also investigated. Results lead to a proposed illustration that allows to a better selection of a certain process to be applied according to the characteristics of the matrix components in the contaminated water.

2. Experimental stage

2.1. Reagents

DXC (99.9% purity) was provided by Syntofarma S.A. (Bogotá D.C., Colombia). Hydrogen peroxide (30% analytical grade) was provided by Panreac. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$, analytical grade), sodium bisulfite, sulfuric acid (96%), sodium hydroxide (analysis grade), 2-propanol, glucose, oxalic acid, sodium phosphate, acetonitrile (HPLC grade), potassium iodide and ammonium heptamolybdate were purchased from Merck. Titanium dioxide Evonik P-25 was used for the photocatalytical experiments. Distilled water and Milli-Q water were used for the test solutions and HPLC mobile phase preparations, respectively. Characterized natural mineral water was used to investigate DXC elimination in natural waters.

2.2. Reaction systems

Photocatalytic experiments (UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$) were carried out as described in SM 2. The DXC adsorption-desorption equilibrium was obtained after 60 min of constant stirring. In all cases, less than 10% of DXC was adsorbed onto the catalyst surface. Every experiment was duplicated at least once.

A cylindrical glass reactor was used for the sonochemical process and experiments were carried out as describe in SM 2 by using 60 W and 600 kHz of frequency. The reactor temperature was controlled at 20 °C by a thermostatic bath. The ultrasonic energy dissipated in the reactor (~58% of the electrical power input) was estimated by the calorimetric method (Vichare et al., 2001).

2.3. Analysis

DXC concentration was quantified using an Agilent 1100 series liquid chromatograph operated in isocratic mode (1 mL min^{-1}) with a RP-18 column (Merck LiChosphere). The quantification method was used as previously reported (Villegas-Guzman et al., 2015, 2014). Dissolved iron was quantified by atomic absorbance spectroscopy. The evolution of chemical oxygen demand (COD) was quantified according to the "Standard Methods for Examination of Water and Wastewater" (Method 5220) using a Spectronic Genesys 2.0 spectrophotometer. Biochemical oxygen demand (BOD_5) analyses were carried out using the respirometric method, in accordance with the "Standard Methods for Examination of Water and Wastewater" (Method 5210). For dissolved organic carbon (DOC) analyses, a Shimadzu TOC 5000A was used with a potassium phthalate solution as the calibration standard. Antimicrobial activity was determined using the Zone of Inhibition Test. For this test, *Staphylococcus aureus* (ATCC 6538) was used as the probe microorganism. 30 μL of sample solutions was seeded on Petri dishes containing 5 mL of potato dextrose agar and 10 mL of nutrient agar inoculated with 10 μL of *S. aureus* (optical density of 0.600 at 580 nm). After 24 h at 37 °C in a Memmert (Schwabach) incubator, confluent bacterial growth was observed, and the diameter of the inhibitory halo was measured.

3. Results and discussion

3.1. Effects of water characteristics

3.1.1. Effect of the initial pH

Solution pH can entail into structural modifications of organic compounds, the catalyst properties and the oxidative species formed leading to important changes during organic pollutant degradation (Hazime et al., 2012; Ince et al., 2009; Lopez-Alvarez et al., 2011). Consequently, toward a better selection of the AOP, it is crucial to evaluate the influence of initial pH. Therefore, the DXC degradation by US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$ processes was tested at different initial pH values. Experiments were carried out using 0.00639 mmol L^{-1} (3 mg L^{-1}) of DXC in distilled water and three initial pH values: acidic (3.0), natural (5.8) and basic (9.0). In all cases, the pH drops at the end of the treatments. For instance, in the case of the natural pH (5.8), the pH drops to 2.9 in the sonochemical treatment; for UV/TiO_2 it drops to 3.7 and for the $UV/H_2O_2/Fe^{2+}$ process the final pH was 3.6. The initial degradation rate was calculated for each case (Fig. 1). The results showed higher degradation rates for $UV/H_2O_2/Fe^{2+}$ for all of the pH values tested, followed by US and then UV/TiO_2. In fact, the degradation rates for the photo-Fenton process were between one and two orders of magnitude higher than the others, while the degradation rates for ultrasound were between two and ten times higher than TiO_2 photocatalysis. These results can be attributed to the fact that while photo-Fenton and ultrasound are homogeneous processes where hydroxyl radicals are more likely to attain DXC molecules, UV/TiO_2 is a heterogeneous system with well-known limitations of mass transfer. Additionally, during US treatment the degradation rate depends on the degradation route, which can be via pyrolysis or •OH attack. Recently, it was demonstrated that DXC sonochemical degradation occurs via •OH radicals at the solution-bulk interface and in the bulk of the solution where not many •OH radicals are present (Villegas-Guzman et al., 2014). Then, degradation rate is lower than that reached by the photo-Fenton process.

Interestingly, Fig. 1 also shows that acidic media (i.e. pH 3) favors

US process. Here, a significant fraction of the pollutant molecules are protonated (pKa 2.8) increasing their hydrophobic character and getting closer to cavitation bubbles where the •OH produced can easier attack and enhance the degradation rate. At natural (5.8) or basic (9.0) pH values, the negative charge of the non-protonated DXC molecules increases their hydrophilic character. Then, degradation takes place with lower rate in the bulk of the solution where fewer hydroxyl radicals can persist before recombination.

On the other hand, for the photo-Fenton process a significant decrease in the degradation rates is observed when the pH changes from 3.0 to 5.8 or 9.0 (Fig. 1). The $UV/H_2O_2/Fe^{2+}$ system is known to be more efficient at pH values of around 3, where the reactive ferrous-hexaaquo complex $[Fe(H_2O)_6]^{2+}$ (represented as Fe^{2+}), able to promote •OH formation via the Fenton reaction, is predominant (eq. (1)). Additionally, at pH 3 ferric hydroxides ($Fe(OH)^{2+}$) are soluble and the regeneration of ferrous ions takes place leading to a concomitant formation of more •OH upon light irradiation (eq. (2)) (Pignatello et al., 2006), while natural and basic pH lead to insoluble ferric species limiting the catalytic process and consequently the degradation rate significantly deaccelerate. In fact, the amount of iron in the solutions drops to less than 0.0001 mmol L^{-1}, suggesting that at natural and basic pH values, almost 36 times less iron remains in the solution.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad k = 50 - 80\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe(OH)^{2+}\ h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \tag{2}$$

A different tendency was observed during the photocatalytic degradation with TiO_2, where the highest degradation rate was reached at natural pH (5.8). This is of special interest for the real-life application of the technology, since when using this system, adjustment of the initial pH will not be required. In order to understand this, the charge of the antibiotic and the isoelectric point of TiO_2 (IP ≈ 6.8) (Herrmann et al., 1993) have to be considered. Any pH value under 6.8 favors the predominance of positive charges on the catalyst surface. On the contrary, at a pH above 6.8, the TiO_2 surface gets negatively charged. Therefore, at a natural pH (5.8), attractive electrostatic forces between the negatively charged molecule of DXC and the catalyst take place (Villegas-Guzman et al., 2015). As a result, DXC molecules get close to the active sites of the catalyst and degradation is favored. At an acidic pH, a significant fraction of DXC molecules are in their neutral form and attractive forces are not predominant then degradation rate becomes lower. For a basic medium, both DXC and TiO_2 have negative charges resulting in repulsive forces inhibiting the degradation rate.

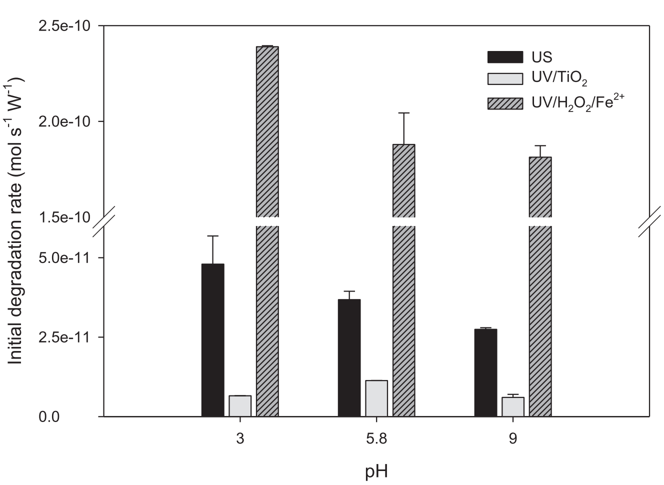

Fig. 1. DXC initial degradation rate as a function of the initial pH solution upon US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$ systems. **US**: 0.3 L; **UV/TiO_2**: 0.1 L and $[TiO_2] = 0.05$ g L^{-1}; **$UV/H_2O_2/Fe^{2+}$**: 0.1 L, $[H_2O_2] = 10$ mmol L^{-1} (180 mg L^{-1}) and $[Fe^{2+}] = 0.0036$ mmol L^{-1} (0.2 mg L^{-1}).

3.1.2. Effect of organic additives

In both natural waters and wastewaters, several types of organic species are commonly found which difficult the application and the understanding of AOPs in water remediation. In order to evaluate the effect of organic matter in the selected AOPs, three organic compounds, commonly used in pharmaceutical industry (Wirz et al., 2015) with different characteristics, were individually added (4.9 mmol L^{-1}) to a solution of DXC (0.213 mmol L^{-1}): (I) Glucose (Glu), a highly hydrophilic neutral compound widely used by pharmaceutical industries as an excipient and currently found in both pharmaceutical and hospital wastewaters (Legen et al., 2006). (II) 2-propanol, (2-prop), a primary solvent for topical preparations in pharmaceutical formulations (Rowe et al., 2009) with hydroxyl radical scavenger properties (Chen et al., 2005), whose volatility makes it a true model of volatile compounds. (III) Oxalic acid (OA), a dicarboxillic acid commonly found in natural waters coming from the decomposition of natural organic matter (NOM) (Espinoza et al., 2011), which is used in pharmaceutical co-crystal formulations to enhance the crystalline forms of therapeutic compounds (Jones et al., 2006). For the interpretation of the results, the ratio between DXC degradation rates in the presence of organic additives (r) and in the absence of such additives (r_0) were calculated. Fig. 2 shows the r/r_0 ratio for each additive using the US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$ processes indicating inhibition, enhancement or absence of effect on the evaluated systems. The results showed, for all of the tested AOPs, an inhibition of DXC degradation of between 30 and 40% when 2-propanol was part of the solution. These results are attributed to the 2-propanol •OH scavenger effect and suggest that under the working conditions, the DXC degradation route occurs via hydroxyl radical attack for all of the selected systems. Interestingly, the largest inhibition in the presence of 2-propanol was observed for the US system. In fact, it is the only substance that significantly inhibits the ultrasonic removal of DXC, which can be attributed to the volatile properties of the additive. Previous investigations have shown how the sonochemical degradation of 2-propanol is carried out via pyrolysis inside the bubbles (Mizukoshi et al., 1999). Then two facts are involved: 1) the presence of 2-propanol inside the bubbles decreases the amount of water inside and so less •OH radicals are produced. 2) The •OH radicals produce inside the bubbles can easily react with 2-propanol molecules instead of DXC molecules. Then, the available •OH radicals to promote DXC degradation are lesser. Fig. 2 shows that photocatalysis with TiO_2 was hampered in all cases and, in general terms, it was the system most negatively affected by organic additives. This behavior suggests a strong interaction between the catalyst and the additives. However, unlike the US system, 2-propanol was the additive that had the least impact which is a result of its lower adsorption onto the catalyst surface in aqueous media (Chen et al., 2005).

On the other hand, the detrimental effect of glucose was also seen during the application of the photo-Fenton system (Fig. 2). Like many organic compounds, glucose can compete with the pollutants for the •OH produced, thereby inhibiting the degradation process. The relatively higher inhibition of Glu in the UV/TiO_2 system (r/r_0 0.3) can be attributed to the formation of hydrogen bonds between the catalyst and the hydroxyl groups of the glucose molecules (Zhou et al., 2012). These strong intermolecular forces provoke a reduction in •OH formation, and as a result DXC degradation is significantly lowered. In contrast, the absence of effect during US is a consequence of the lower water solubility

(0.00767 mmol L^{-1} or 3.6 mg L^{-1}) and high hydrophobic character of DXC compared to glucose (water solubility, 5055 mmol L^{-1} or 9.1×10^5 mg L^{-1}). Hence, DXC molecules are relatively closer to the cavitation bubbles than glucose, and hydroxyl radicals can easily react with the pollutant without interference. For a better understanding of the effect of oxalic acid, additional tests using an equimolar concentration of OA and the antibiotic (0.213 mM) were also carried out. No inhibition of ultrasonic action was observed, which can be explained by the relatively high hydrophilic character and high water solubility of this additive (1.59 mmol L^{-1} or 143 mg L^{-1}). However, a strong inhibition was found during the application of the UV/TiO_2 system. Under the working conditions (pH 5.6), the catalyst surface has positive charges, and according to the OA pKas values (1.27 and 4.27), there are strong attractive electrostatic forces between the OA and the TiO_2 surface. Therefore, hydroxyl radicals predominantly react with OA molecules instead of DXC molecules. Additionally, it has been shown (Quici et al., 2005) that oxalic acid can be adsorbed at the catalyst holes and oxidative decarboxylation of this additive, via the photo-Kolbe reaction, occurs. Both, the scavenger effect of OH radicals and adsorption onto the TiO_2 surface cause a detrimental effect on the DXC degradation. As a result, OA in TiO_2 photocatalysis provokes the inhibiting effect which increase when OA concentration increases (Fig. 2).

The effect of OA during the photo-Fenton DXC degradation is quite interesting. In the presence of the concentrated OA, a detrimental effect is observed, which could be attributed to the fact that the additive must compete for the hydroxyl radicals. On the contrary, a remarkable enhancement (~80%) was observed when OA was in an equimolar concentration with the substrate. This improvement can be mainly attributed to the formation of two iron-oxalate complexes:

(i) The highly soluble and photoactive complex between oxalate ions and Fe^{3+} (eq. (3)), promotes the formation of new reactive species able to degrade the substrate (Spuhler et al., 2010) and regenerating Fe^{2+} (eqns. (4) and (5)). It is worth remarking that Fe^{3+} ions are produced from the Fenton reaction (eq. (1)) or the oxidation of Fe^{2+} with dissolved oxygen (eq. (6)) (Feng et al., 2012; Pignatello et al., 2006).

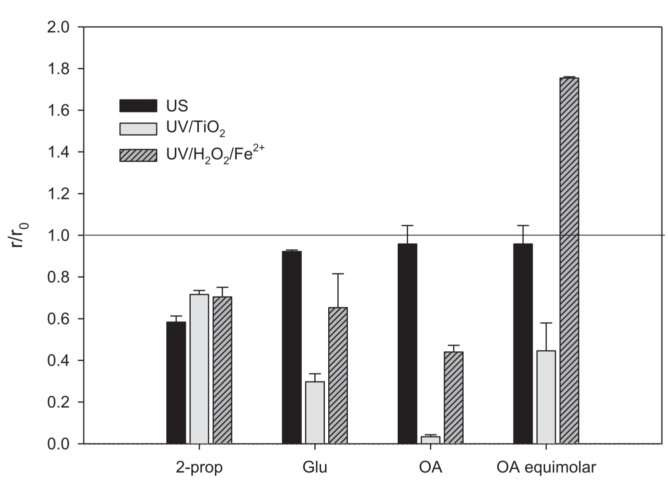

Fig. 2. DXC degradation rate ratio by US, UV/TiO_2 and UV/H_2O_2/Fe^{2+} systems in presence (r) and absence (r_0) of: glucose (Glu), 2-propanol (2-prop) and oxalic acid (OA) at natural pH. [DXC] = 0.213 mmol L^{-1} (100 mg L^{-1}), [organic additive] = 4.9 mmol L^{-1} and $[OA]_{equimolar}$ = 0.213 mmol L^{-1}. **US**: 0.3 L, 60 W; **UV/TiO_2**: 0.1 L, 60 W and [TiO_2] = 0.05 g L^{-1}; **UV/H_2O_2/Fe^{2+}**: 0.1 L, 30 W, [H_2O_2] = 10 mmol L^{-1} (180 mg L^{-1}) and [Fe^{2+}] = 0.0036 mmol L^{-1} (0.2 mg L^{-1}).

$$Fe^{3+} + 3C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_3]^{3-} \quad (3)$$

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{\bullet-} \quad (4)$$

$$C_2O_4^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + 2CO_2 \quad (5)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet-} \quad (6)$$

(ii) The oxalate-Fe(II) complex (eq. (7)) has a higher kinetic rate with H_2O_2 (1×10^4 M^{-1} s^{-1}) (Park et al., 1997) than the ferrous-aquo complex (50-80 M^{-1} s^{-1}) (Barb et al., 1950; Rigg et al., 1954) (eq. (1)). Therefore, it is a better provider of hydroxyl radicals.

$$Fe^{2+} + C_2O_4^{2-} \rightarrow Fe^{2+}[C_2O_4^{2-}] \quad (7)$$

3.1.3. Effect of inorganics species in natural water at different isoxazolyl penicillin concentrations

Recent investigations have shown that inorganic species in natural waters have inhibition and enhancement effects during the degradation of organic pollutants by AOPs (Costa and Olivi, 2009; Frontistis et al., 2014; Guzman-Duque et al., 2011; Hazime et al., 2012; Lipczynska-Kochany and Kochany, 2008; Merouani et al., 2010; Torres et al., 2007). In order to evaluate the effect of inorganics species commonly found in natural waters, experiments were carried out using characterized (Table 1) natural mineral water (pH 6.2). In addition, three different initial DXC concentrations were evaluated to determine its impact in the tested AOPs in both natural water (NW) and distilled water (DW): 0.00639 mmol L^{-1} (3 mg L^{-1}), 0.213 mmol L^{-1} (100 mg L^{-1}) and 0.426 mmol L^{-1} (200 mg L^{-1}). The degradation rates (r) were calculated for both water types and the ratio between them (r_{NW}/r_{DW}) for each DXC initial concentration is plotted in Fig. 3.

During UV/TiO_2 degradation, significant inhibition effects of the natural water were observed for all of the tested DXC concentrations. In fact, the lowest r_{NW}/r_{DW} ratio was obtained during this process (DXC 0.00639 mmol L^{-1}). Previous investigations have shown that anions can be adsorbed onto the positive TiO_2 surface by attractive electrostatic forces, specifically at the holes (Chen et al., 2005; Özkan et al., 2004). Under such conditions, fewer water molecules are oxidized, hydroxyl radical formation is inhibited, and consequently, degradation efficiency is hampered. Moreover, the hydroxyl radical scavenger properties of some anions have a negative impact on DXC degradation efficiency. In natural mineral water, the bicarbonate anion is the predominant (4.9 mmol L^{-1}) being ~800 times more concentrated than the lowest tested DXC concentration (0.00639 mmol L^{-1}), while chloride and sulfate are only ~10.5 and ~6.7 times higher. Therefore, bicarbonate ions could be mainly responsible for the relatively high inhibition (~90%) observed when DXC (0.00639 mmol L^{-1}) in natural water was treated by UV/TiO_2. Similarly, the photo-Fenton system also showed a negative effect during the treatment of the lowest DXC concentration in natural water. In this case, approximately 50% inhibition was observed compared to the degradation rate in DW, confirming thus the significant scavenger effect of the anions, especially the bicarbonate ions. However, for relatively high concentrations of DXC, the photo-Fenton process remained unaffected ($r_{NW}/r_{DW} \approx 1$). For 0.213 and 0.426 mmol L^{-1} of DXC, HCO_3^- is only 23 and 11.5 times more concentrated than DXC. Thus, the results indicate that under these concentrations of both anions and substrate, the anions did not represent significant competition to the DXC molecules for the oxidative •OH radicals.

Interestingly, a remarkable enhancement of the degradation rate was observed when US was tested for the lowest DXC concentration in natural water. In fact, the degradation rate of DXC 0.00639 mmol L^{-1} in NW was ~4 times higher than that reached in DW. This is of special interest because emergent pollutants are frequently present in natural water at very low concentrations. As previously indicated, DXC sonochemical degradation at natural pH (5.8) takes place in the bulk of the solution. For low concentrations of the pollutant, hydroxyl radicals hardly attack the DXC molecules due to the large relative distance between the target molecules and the cavitation bubbles where •OH formation takes place. In natural water, new oxidative species (i.e. HCO_3•) from the reaction between the hydroxyl radicals and bicarbonate ions are produced (eqs. (8) and (9)) (Guzman-Duque et al., 2011; Pétrier et al., 2010). According to HCO_3• pKa, CO_3•$^-$ is the predominant species during all of experiments. Despite the carbonate radical being a lesser oxidative species than •OH, it has a longer half-life, so carbonate radicals can more easily make contact and degrade the DXC molecules (eq. (10)). However, as the DXC concentration increases, the pollutant molecules get closer to the cavitation bubbles due to saturation and salinity effects. Therefore, •OH can more easily participate in the degradation process. Consequently, for the most concentrated DXC solution (0.426 mmol L^{-1}), both HCO_3^- and the pollutant molecules compete for •OH. Under such conditions, and as observed in the photo-Fenton process and TiO_2 photocatalysis, the degradation rate is inhibited in NW. However, at 0.213 mmol L^{-1} (100 mg L^{-1}) the DXC degradation rate is not affected. Therefore, the results suggest that there exists a critical concentration ratio between the bicarbonate ions and DXC, where equilibrium between inhibition and enhancement takes place.

$$HCO_3^- + {\bullet}OH \rightarrow HCO_3{\bullet} + OH^-, \ k = 8.5 \times 10^6 \ M^{-1}s^{-1} \quad (8)$$

$$HCO_3{\bullet} \rightarrow CO_3{\bullet}^- + H^+, \ pKa < 0 \quad (9)$$

$$DXC + CO_3{\bullet}^- \rightarrow P_{ox} \quad (10)$$

3.2. Delineating the selection of the most suitable AOPs for isoxazolyl penicillins degradation according to the water characteristics

A treatment line is proposed that provides the relevant information regarding water matrix effects. In this way, a specific AOP can be selected for the treatment of waters contaminated with isoxazolyl penicillin antibiotics. According to the results observed in the investigation, the solution characteristics that enhanced, or did not negatively affect, the efficiency of the AOPs during the antibiotic degradation are highlighted in Fig. 4. Enhancement effects are presented in bold letters and those that did not affect the system are presented in regular letters. The best performance of the photo-Fenton system was observed using acidic media, while a natural pH favored TiO_2 photocatalysis. However, in a wide range of pH values, US stands out as the most promising technique, since pollutant degradation occurs with a relatively high efficiency at any

Table 1
Mineral natural water characterization.

Inorganic specie	HCO_3^-	Mg^+	NO_3^-	SO_4^{2-}	K^+	Ca^{2+}	Na^+	Cl^-
mg L^{-1}	301	28.2	8.5	4.1	1.0	48.6	5.8	2.4
mmol L^{-1}	4.93	1.16	0.137	0.043	0.020	1.22	0.252	0.068

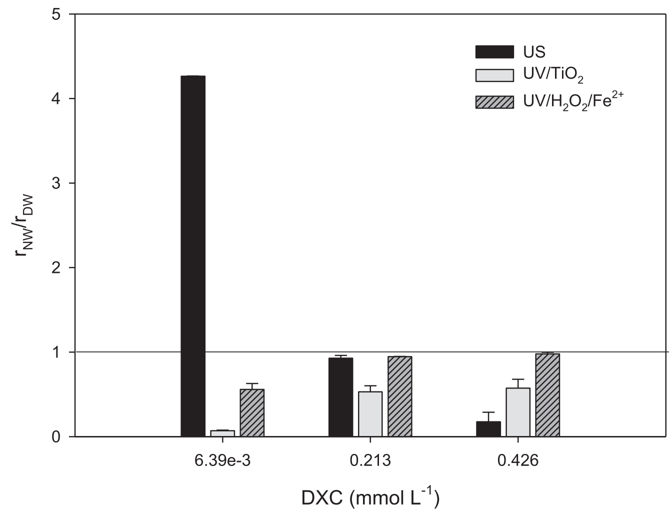

Fig. 3. Calculated ratio between DXC initial degradation rates in natural water (r_{NW}) and distilled water (r_{DW}) using US, UV/TiO_2 and UV/H_2O_2/Fe^{2+} as function of DXC initial concentration. **US**: 0.3 L, 60 W; **UV/TiO₂**: 0.1 L, 60 W and [TiO_2] = 0.05 g L^{-1}; **UV/H₂O₂/Fe²⁺**: 0.1 L, 30 W, [H_2O_2] = 10 mmol L^{-1} (180 mg L^{-1}) and [Fe^{2+}] = 0.0036 mmol L^{-1} (0.2 mg L^{-1}).

pH. In terms of water composition, significant differences are observed for organic compounds. In all cases, 2-propanol (2-prop) caused inhibition. However, a neutral hydrophilic compound such as glucose (Glu), or a relatively highly hydrophilic anionic compound like oxalic acid (OA), did not affect US process. These results indicate that, contrary to the photo-Fenton process and TiO_2 photocatalysis, sonochemical degradation can be carried out in the presence of many types of hydrophilic and non-volatile organic matter without significant effects. Interestingly, in the presence of an equimolar concentration of OA, the photo-Fenton process was significantly improved.

Inorganic species also showed interesting results. Significant differences between the AOPs tested with natural water (NW) containing a high concentration of ions, especially bicarbonate anions, depending on the [HCO_3^-]/[DXC] ratio. A high concentration ratio (~800) inhibits both photocatalytic processes, while US was remarkable enhanced. Moreover, for a concentration ratio of ~23, the US and photo-Fenton processes were not affected, whereas at the lower ratio (~11.5) only the photo-Fenton system had no interferences.

3.3. Evaluation of antimicrobial activity, mineralization and level of biodegradability of the treatment solutions

Previous investigations have revealed that the degradation of recalcitrant compounds may lead to the creation of harmful solutions (Bernabeu et al., 2012; Pereira et al., 2014; Wu et al., 2009). To evaluate the extent of degradation during the UV/H_2O_2/Fe^{2+}, UV/TiO_2 and US processes, the evolution of DXC and dissolved organic carbon (DOC) was determined (Fig. 5). As can be observed, total elimination of DXC was reached for the three AOPs tested, indicating that the proposed systems are viable alternatives for the antibiotic elimination. However, significant differences were observed with respect to DOC. Interestingly, the best performance was obtained during the UV/TiO_2 process, where more than 95% of DOC was removed after the treatment. In contrast, US showed zero mineralization despite total removal of DXC, suggesting that the pollutant transformed into stable by-products during sonochemical action (Torres et al., 2008). During the application of the sonochemical system, a pH reduction from 5.8 to 2.9 was observed as

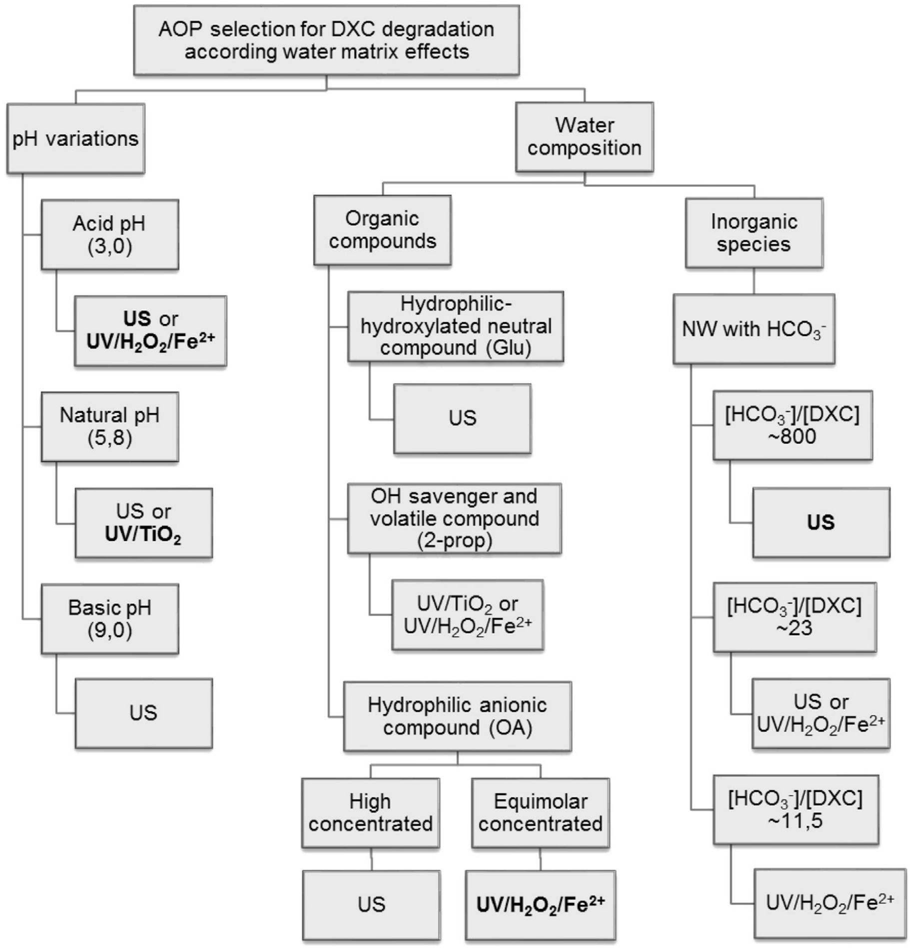

Fig. 4. Favored and non-affected AOP under different water matrix characteristics during the degradation of the antibiotic DXC. Glu stands for glucose; 2-prop represents 2-propanol, OA oxalic acid and NW natural water. Blond letter represents enhanced process.

well as an accumulation of by-products that have a very short retention time in the HPLC chromatogram (data not shown), suggesting that carboxylic acids are formed as degradation by-products. These hydrophilic intermediates move away from the cavitation bubbles where few hydroxyl radicals can arrive. The formation of carboxylic acids during •OH attack on DXC also explains the high mineralization level achieved using the UV/TiO_2 system given that these can be easily adsorbed onto the catalyst and undergo direct oxidation, as seen for OA in section 3.2.

On the other hand, even if the DXC was efficiently eliminated by $UV/H_2O_2/Fe^{2+}$, only ~10% of mineralization was attained at the end of the treatment (480 min). Interestingly, an almost constant H_2O_2 concentration (~6 mM) was observed after 120 min of treatment, suggesting that after this time the Fenton reaction stops. These findings suggest the formation of a stable iron-byproduct complex. Hence, the mineralization can be described by the following sequence: $UV/TiO_2 \gg UV/H_2O_2/Fe^{2+} > US$.

The incomplete mineralization during the ultrasound and photo-Fenton processes indicates the presence of organic matter that might represent environmental risks. A previous investigation has reported the by-products identification of this family of antibiotics upon ultrasound and photo-Fenton systems (Serna-Galvis et al., 2016). The authors found that the main possible pathways of isoxazolyl penicillin compounds when submitted to ultrasound are associated to the opening of the β-lactam ring, oxidation of the thioether moiety and breakdown of the central secondary amide; while the photo-Fenton action induces all the mentioned pathways, in addition to the hydroxylation of the aromatic ring. These structural transformations have been also reported by other authors for β-lactam antibiotics and organic compounds (Dail and Mezyk, 2010; Pignatello et al., 2006; Song et al., 2008). Despite the possible transformations, the HPLC analyses suggests that both photo-Fenton and ultrasound systems are able to lead DXC and its primary degradation by-products into carboxylic acids. Then, even if no mineralization is achieved by neither of the systems, the results suggest that the final by-products do not represent an environmental risk. In order to provide further information about the possible environmental risk of the treated solutions, the antimicrobial activity (AA) and biodegradability were determined along the processes (Fig. 6). As can be observed, both the processes were able to achieve total elimination of the antimicrobial activity with significant differences. During the photo-Fenton process, AA was quickly eliminated during the first stage (0–120 min) of the treatment followed by a slight plateau (from 120 min to 360 min). This behavior can be associated to the formation of the previously mentioned stable intermediate which is rapidly obtained at the beginning of the process. In contrast, there was a slow elimination of AA at the beginning of the US process (0–120 min) followed by a fast decrease ending with total AA removal. Even though the analysis of DXC by-products is not within the scope of this paper,

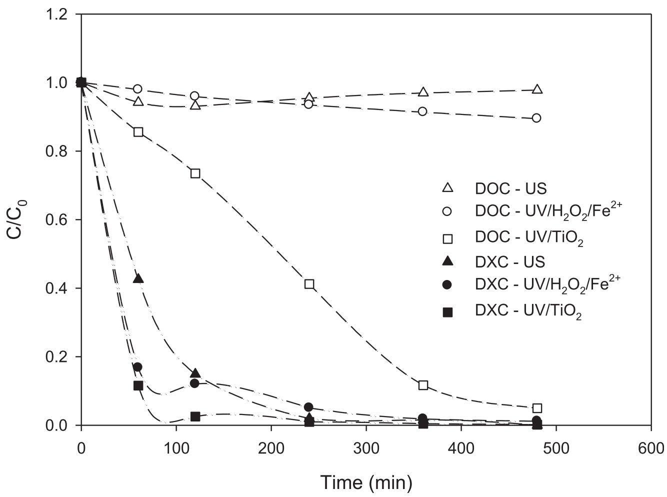

Fig. 5. DXC and DOC evolution during US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$ treatments. $[DXC]_{inital}$ = 0.213 mmol L^{-1}, natural pH (5.6). **US**: 0.3 L, 60 W; **UV/TiO_2**: 0.1 L, 150 W and $[TiO_2]$ = 0.05 g L^{-1}; **$UV/H_2O_2/Fe^{2+}$**: 0.1 L, 30W $[H_2O_2]$ = 10 mmol L^{-1} and $[Fe^{2+}]$ = 0.0036 mmol L^{-1}.

results of AA evolution suggest that some of the intermediates produced during the $UV/H_2O_2/Fe^{2+}$ and US processes may be different.

Concerning the biodegradability of the treated solutions, the BOD_5/COD ratio was calculated as a reasonable approximation considering biodegradable when the BOD_5/COD ratio is above 0.4 (Marco et al., 1997). In spite of the fact that in both the US and $UV/H_2O_2/Fe^{2+}$ systems the BOD_5/COD ratio increased, associated to the formation of more oxidized and biodegradable compounds, significant differences were found. Interestingly, an almost linear increment was observed during the US process (Fig. 6). In turn, the photo-Fenton process showed the exact opposite tendency for AA elimination, suggesting a close relationship between these two parameters during this process. Despite these differences, results suggest that both processes (US and $UV/H_2O_2/Fe^{2+}$) can produce biodegradable solutions after the treatments.

4. Conclusion

This study contributes to the proper selection of an advanced oxidation process (US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$) to degrade

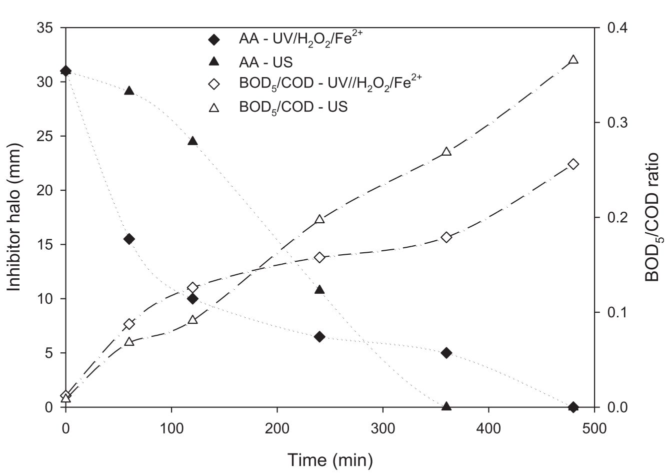

Fig. 6. Antimicrobial activity (AA) and biodegradability (BOD_5/COD) evolution during US, UV/TiO_2 and $UV/H_2O_2/Fe^{2+}$ process. $[DXC]_{inital}$ = 0.213 mmol L^{-1}, natural pH (5.6). **US**: 0.3 L; **UV/TiO_2**: 0.1 L and $[TiO_2]$ = 0.05 g L^{-1}; **$UV/H_2O_2/Fe^{2+}$**: 0.1 L, $[H_2O_2]$ = 10 mmol L^{-1} and $[Fe^{2+}]$ = 0.0036 mmol L^{-1}.

isoxazolyl penicillin antibiotics, based on the effect of several water matrix characteristics. Variations on pH showed inhibition or enhancement according to the submitted process and the pollutant structural modifications. UV/TiO_2 is not the best AOP for natural waters containing significant concentrations of anionic and organic species. US is the most promising technique for contaminated waters containing low concentrations of the pollutant, while the photo-Fenton system is recommended for waters highly contaminated with the antibiotic as residual pharmaceutical wastewaters.

AOPs shown to be efficient techniques for this type of antibiotic elimination and the treated solutions can be considered environmental friendly according to the mineralization and AA elimination, indicating that the application of these techniques for water treatment is viable. However, the selection of the most suitable AOP should depend on water matrix effects, which must be considered in order to achieve the best compromise between pollutant elimination and extent of degradation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.12.056.

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