Environ Chem Lett (2011) 9:347–353
DOI 10.1007/s10311-010-0285-z

ORIGINAL PAPER

Removal of carbamazepine from urban wastewater by sulfate radical oxidation

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Received: 11 January 2010 / Accepted: 12 April 2010 / Published online: 2 June 2010

Abstract The occurrence of bioactive trace pollutants such as pharmaceuticals in natural waters is an emerging issue. Numerous pharmaceuticals are not completely removed in conventional wastewater treatment plants. Advanced oxidation processes may represent an interesting alternative to completely mineralize organic trace pollutants. In this article, we show that sulfate radicals generated from peroxymonosulfate/Co^{II} are more efficient than hydroxyl radicals generated from the Fenton's reagent (H_2O_2/Fe^{II}) for the degradation of the pharmaceutical compound, carbamazepine. The second-order rate constant for the reaction of $SO_4^{\cdot -}$ with carbamazepine is $1.92 \cdot 10^9\ M^{-1}\ s^{-1}$. In laboratory grade water and in real urban wastewater, $SO_4^{\cdot -}$ yielded a faster degradation of carbamazepine compared to $HO^{\cdot}$. Under strongly oxidizing conditions, a nearly complete mineralization of carbamazepine was achieved, while under mildly oxidizing conditions, several intermediates were identified by LC–MS. These results show for the first time in real urban wastewater that sulfate radicals are more selective than hydroxyl radicals for the oxidation of an organic pollutant and may represent an interesting alternative in advanced oxidation processes.

Keywords Peroxymonosulfate · Sulfate radical · Carbamazepine · Advanced oxidation technology · Kinetic · Second-order rate constant

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Introduction

The treatment of urban wastewater is an emerging topic related to the EU water framework directive (EC Directive 2000), particularly to achieve elimination of priority hazardous substances. To achieve viable and economical wastewater treatment plant, effective and affordable technologies are needed. It is well known that many pharmaceutical products are not completely removed in conventional waste-water treatment plants, which are mainly based on biological treatment (Ternes 1998).

One of the consequences is that pharmaceutical products or their metabolites can reach groundwater and drinking water. For example, the anticonvulsant carbamazepine has been detected in groundwater at concentrations up to 615 ng L^{-1} (Drewes et al. 2002), and clofibric acid, a lipid regulator metabolite, has been detected up to 165 ng L^{-1} in tap water in Berlin (Stan et al. 1994).

Advanced oxidation processes (Munter 2001) represent promising technologies for the remediation of polluted wastewater, particularly for eliminating refractory organic pollutants. Most advanced oxidation processes are based on the generation of the very reactive hydroxyl radical ($HO^{\cdot}$), which can oxidize almost all organics with a high second-order rate constant (10^7–10^{10} M s^{-1}). The Fenton's reagent is probably the well-known system able to generate $HO^{\cdot}$ according to the following simplified reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \quad (1)$$

The Fenton system is currently applied in advanced oxidation technologies for the treatment of industrial discharges and for soil and groundwater remediation. However, the non-selectivity of $HO^{\cdot}$ is not an advantage for oxidizing target compounds because it can be readily inactivated by the matrix. To overcome this problem, we propose here the application of the highly reactive and selective oxidant sulfate radical ($SO_4^{\cdot-}$) for the elimination of pharmaceuticals. Sulfate radicals represent an interesting alternative to hydroxyl radicals in advanced oxidation processes. Sulfate radicals are known, since the 1950s, to be involved in the mechanism of oxidation by persulfate (PS) (Tsao and Wilmarth 1959; House 1962) and more recently by peroxymonosulfate (PMS) (Warneck et al. 1994; Kim and Edwards 1995). PS and PMS are actually gaining emerging interest for their application in advanced oxidation technologies (Yang et al. 2008). One selective and efficient way to produce sulfate radicals is:

$$Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\cdot-} + HO^- \qquad (2)$$

The sulfate radical is a powerful oxidizing agent able to oxidize chloride ion into $Cl_2^{\cdot-}$ (Huie and Clifton 1990). Consequently, it has a great potential to degrade many pollutants. Similarly to hydroxyl radicals, sulfate radicals react with organics by electron transfer, hydrogen abstraction, or addition mechanisms (Zemel and Fessenden 1978; Khursan et al. 2008; Caregnato et al. 2008). However, $SO_4^{\cdot-}$ appears to be more selective than $HO^{\cdot}$ since most reactions implying $SO_4^{\cdot-}$ involve electron transfer.

This study compares the oxidation kinetics of carbamazepine (CBZ) both in laboratory grade water and in real urban wastewater with sulfate or hydroxyl radicals, produced from PMS and the Fenton reagent, respectively. The major intermediates of the oxidation have been identified in the two systems.

Experimental

The chemicals peroxymonopersulfate (Oxone, $2KHSO_5$, $KHSO_4$, K_2SO_4, 95%), CBZ (99%), hydrogen peroxide (35% w/v), and methanol were purchased from Sigma–Aldrich (Saint Quentin-Fallavier, FR); Cobalt nitrate ($Co(NO_3)_2$, 6 H_2O), ($CoCl_2$, $6H_2O$), and benzene were furnished by Prolabo (Fontenay-sous-Bois, FR). *Tert*-butyl alcohol was furnished from Carlo Erba (Val de Reuil, FR) All chemicals were used as received with no further purification. All aqueous solutions were prepared with UHQ milliQ water (Millipore, Bedford, USA).

The degradation experiments of CBZ were carried out in deionised water or urban wastewater at ambient temperature in 0.5-L stirred glass reactors. CBZ was tested at the initial concentration of 50 μM except for the competition experiment where 33 μM was selected. The molar ratio $[CBZ]_0$ to $[PMS]_0$ ranged from 1 to 30. Cobalt salts, $CoCl_2$, $6H_2O$, and $Co(NO_3)_2 \cdot 6\,H_2O$ were tested to assess the role of the counterion on the transformation of CBZ. The concentration of Co^{II} was determined spectrophotometrically, and the molar ratio $[CBZ]_0$ to $[Co]_0$ was set from 0.1 to 10. A blank consisting of CBZ (50 μM) in real wastewater was performed to check the stability of CBZ at room temperature. The results show that no degradation of CBZ was observed within 24 h.

The experiments were carried out at pH 3 in order to compare the PMS/Co system with Fenton's system conditions which performs best at pH 3. pH adjustments were performed with few drops of H_2SO_4 1 M. No pH adjustment was made once the reaction had started. At different time intervals, 2-mL sample was withdrawn and quenched with 100 μL of an aqueous solution of $NaNO_2$ (10 M) before HLPC analysis. The presented results are means of three repeated experiments.

The monitoring and quantification of the transformation of CBZ and of benzene, which was used as inhibitor in the competitive kinetic investigations, was performed with HPLC–UV (Hitachi L-2200, L-2130) equipped with a L-2400 UV–Vis detector and a RP-C18 LiChrospher column (Merck, length 250 mm, diameter 4.6 mm, particle size 5 μM). Analytes were separated with a mixture of methanol and water (75:25 v/v) at a flow rate of 0.8 mL min^{-1} in isocratic mode. The peak of CBZ was detected at 286 nm, and the retention time was 5.6 ± 0.2 min.

The analysis of CBZ and its transformation intermediates were carried out by liquid chromatography multistage mass spectrometry (LC/MS^2). Positive electrospray ((+) ESP) was performed on an Esquire 6000 ion trap system (Bruker, Bremen, Germany), with a potential of 4 kV applied to the electrospray needle. Nitrogen was used as drying and nebulizing gas. The capillary temperature was held at 250°C. Full scanning analysis was performed in the range of 100–500 m/z. The relative collision energy was set at 30% of the maximum (1 V). The analytical separation was carried out with a MetaChem C-18 column (150 × 2 mm i.d., 3 μm) at a flow rate of 0.2 mL min^{-1}. The mobile phase consisted of binary mixture of solvents A (methanol) and B (0.1% formic acid in water). The gradient was operated from 5 to 100% A for 30 min and then back to initial conditions in 5 min.

Results and discussion

Cobalt counter ion effect

Two sources of Co^{II} were first tested, $CoCl_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, in order to assess the effect of the counterions, chloride ion, and nitrate ion. For this purpose, a comparative degradation of CBZ (50 μM) was carried out in the presence of PMS (150 μM) and $CoCl_2 \cdot 6H_2O$ (150 μM) or $Co(NO_3)_2 \cdot 6H_2O$ (150 μM). The results are shown in Fig. 1a. The degradation of CBZ expressed as the

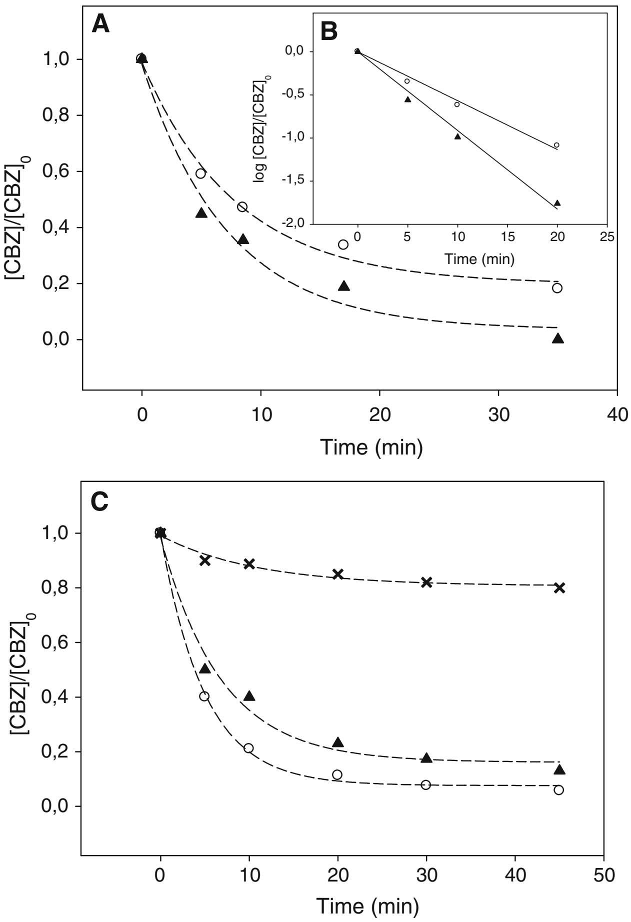


Fig. 1 **a** Time-dependent degradation curve of CBZ (50 μM) in the presence of PMS (150 μM) and (*open circle*) $CoCl_2·6H_2O$ (150 μM) and (*filled triangle*) $Co(NO_3)_2·6H_2O$ (150 μM), pH 3. **b** Plot of log $[CBZ]/[CBZ]_0$ versus time. **c** Effect of MeOH and *t*-BuOH on CBZ oxidation by PMS/Co^{II}. (*open circle*) without scavenger, (*filled triangle*) with *t*-BuOH, (*times*) with MeOH. Experimental conditions: $[CBZ]_0 = 50$ μM, $[PMS]_0 = [Co^{II}]_0 = 150$ μM, $[Alcohol] = 225$ mM, at initial pH 3

ratio of $[CBZ]/[CBZ]_0$ decreased as a function of time from 1 to 0.18 and 1 to 0 within 35 min with the catalyst $CoCl_2·6H_2O$ and $Co(NO_3)_2·6H_2O$, respectively. The curves followed a pseudo first-order decay (Fig. 1b) with a rate constant $k_{app} = (0.945 \pm 0.047)·10^{-3}\ s^{-1}$ and $k_{app} = (1.520 \pm 0.076)·10^{-3}\ s^{-1}$ for the degradation of CBZ in the presence of Cl^- and NO_3^-, respectively. This result indicated that the source of Co^{II} had an influence on the degradation rate of CBZ. In the presence of Cl^-, the transformation rate of CBZ is slower than in the presence of NO_3^-. In the case of $CoCl_2$, the slower reaction rate could be explained by the possible scavenging reaction of $SO_4^{\cdot -}$ by Cl^- at a relative high second-order rate constant ($k = 2.0·10^8\ M^{-1}\ s^{-1}$, Anipsitakis et al. 2006). The catalyst salt $Co(NO_3)_2·6H_2O$ was then chosen as source of Co^{II} in the following experiment.

Sulfate radical identification

Metal-catalyzed activation of PMS generates sulfate radicals as the main reactive species, with hydroxyl and peroxymonosulfate radicals as secondary species (Anipsitakis and Dionysiou 2004). Quenching experiments were performed in order to identify and confirm the primary radical species produced in our system. Methanol (MeOH) and *tert*-butyl alcohol (*t*-BuOH) were selected as quenching agents since MeOH is a well-known quenching agent for both hydroxyl ($k = 9.7·10^8\ M^{-1}\ s^{-1}$) (Buxton et al. 1988) and sulfate radicals ($k = 1.1·10^7\ M^{-1}\ s^{-1}$) (Clifton and Huie 1989), while *t*-BuOH reacts at a significantly higher rate with $HO^{\cdot}$ ($k = 6.0·10^8\ M^{-1}\ s^{-1}$) (Buxton et al. 1988) than with $SO_4^{\cdot -}$ ($k = 8.4·10^5\ M^{-1}\ s^{-1}$) (Clifton and Huie 1989). Hydroxyl radicals react with MeOH approximately 90-times faster than sulfate radicals and around 700-times faster with *t*-BuOH. The reaction of alcohols and aromatics with peroxymonosulfate radicals can be neglected due to their relatively low rate constant, which is about $10^{-3}\ M^{-1}\ s^{-1}$ (Anipsitakis and Dionysiou 2004). Consequently, the presence of MeOH in the reaction mixture containing $CBZ/PMS/Co^{II}$ would inhibit much more $HO^{\cdot}$ and $SO_4^{\cdot -}$ than *t*-BuOH, which will inhibit more selectively $HO^{\cdot}$ than $SO_4^{\cdot -}$. Then, if $SO_4^{\cdot -}$ are the main reactive species, it is expected that the presence of *t*-BuOH in the reaction mixture would not affect significantly the CBZ transformation.

The results of the experiments carried out with the reaction mixture containing CBZ (50 μM), PMS (150 μM) and Co^{II} (150 μM) in the absence and in the presence of the inhibitors MeOH and *t*-BuOH are shown in Fig. 1c. The figure shows the relative transformation of normalized CBZ concentration vs. reaction time. The inhibition of CBZ decay was 74% in the presence of MeOH, while it was only 7% in the presence of *t*-BuOH, indicating that $SO_4^{\cdot -}$ was the major active free radical species. These results are in accordance with those obtained by Anipsitakis and Dionysiou (Anipsitakis and Dionysiou 2004) for the oxidation of 2,4-dichlorophenol at pH 7. However, the inhibition yields in the presence of MeOH obtained in this work were not as high as those observed by the above mentioned authors, who used $CoCl_2$ as catalyst and ethanol as the inhibitor. The supplementary quenching effect of the chlorine ions as well as the higher pH value and second-order rate constant of ethanol with $HO^{\cdot}$ ($k = 1.9·10^9\ M^{-1}\ s^{-1}$) (Buxton et al. 1988) and $SO_4^{\cdot -}$ ($k = 3.8·10^7\ M^{-1}\ s^{-1}$) (Clifton and Huie 1989) may explain the difference.

Sulfate radical second-order rate constant with CBZ

The direct rate constant measurement was determined by competitive kinetics using benzene as the reaction

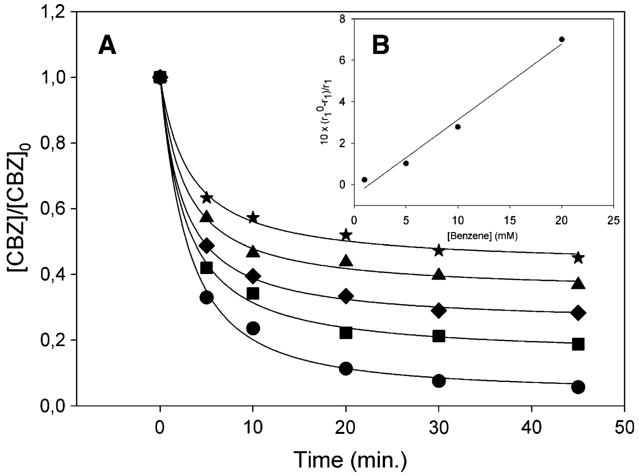


Fig. 2 Degradation kinetics of CBZ (33 μM) in the presence of PMS/Co (150 μM/150 μM) and benzene at pH 3: **a** versus reaction time (*filled circle*) [Benzene] = 0; (*filled square*) [Benzene] = $1 \cdot 10^{-3}$ M; (*filled diamond*) [Benzene] = $5 \cdot 10^{-3}$ M; (*filled triangle*) [Benzene] = $10 \cdot 10^{-3}$ M; (*filled star*) [Benzene] = $20 \cdot 10^{-3}$ M. **b** Stern–Volmer-type plot: $(r_1^0 - r_1)/r_1$ vs. [benzene]

standard. Benzene is known to react with sulfate radicals at the rate constant (k_2) of $2.4 \cdot 10^9$ M^{-1} s^{-1} (Warneck and Ziajka 1995). When benzene, in the 0–$20 \cdot 10^{-3}$ M range, was added to a solution containing the substrate CBZ (33 μM) in the presence of PMS (150 μM) and Co^{II} (150 μM), benzene was found to inhibit CBZ oxidation. For example, 20 mM of benzene caused 45% inhibition (Fig. 2a).

Since CBZ and benzene compete for the available sulfate radicals, the rate constant of CBZ in the above system can be obtained. In a typical reaction, the PMS/Co system generates $SO_4^{\cdot-}$, which in turn reacts competitively with CBZ and benzene to form oxidized CBZ derivatives and phenol, respectively. Assuming that $SO_4^{\cdot-}$ reacts as follow:

$$CBZ + SO_4^{\cdot-} \rightarrow \text{Products} \qquad r_1 = k_1[CBZ] \cdot [SO_4^{\cdot-}] \tag{3}$$

$$\text{benzene} + SO_4^{\cdot-} \rightarrow \text{Phenol} \qquad r_2 = k_2[\text{benzene}] \cdot [SO_4^{\cdot-}] \tag{4}$$

The reaction rate of sulfate radical (r) is given by:

$$r = [SO_4^{\cdot-}] \cdot (k_1[CBZ] + k_2[\text{benzene}]) \tag{5}$$

Then,

$$r_1 = r\frac{k_1[CBZ]}{k_1[CBZ] + k_2[\text{benzene}]} \tag{6}$$

In the absence of the inhibitor (benzene), the reaction rate of CBZ (r_1^0) is given by the following equation:

$$CBZ + SO_4^{\cdot-} \rightarrow \text{Products} \qquad r_1^0 = k_1[CBZ] \cdot [SO_4^{\cdot-}] \tag{7}$$

Assuming that the initial $SO_4^{\cdot-}$ radical yield is the same in both solutions, the standard competition kinetics Eq. 8 predicts that plot of $(r_1^0 - r_1)/r_1$ vs. [benzene] would give a straight line with the slope $k_2/(k_1$ [CBZ]).

$$\frac{r_1^0 - r_1}{r_1} = \frac{k_2[\text{benzene}]}{k_1[CBZ]} \tag{8}$$

The oxidation of CBZ has been performed at pH 3. The plots of $[CBZ]/[CBZ]_0$ vs. time for the different concentrations of benzene showed an exponential decay (Fig. 2a), which was fitted following the equation $y = a\,exp(-bx)$. The coefficients a and b were determined for each curve. The slope of the tangent ($y' = -ab$) to the fitting curve at the origin was determined for each curve to give r_1^0 and r_1. Then, plotting Eq. 8 as a function of [benzene] showed a simple Stern–Volmer behavior for the scavenging of $SO_4^{\cdot-}$ by benzene with a correlation coefficient of 0.985 (Fig. 2b). The ratio of $(r_1^0 - r_1)/r_1$ to [benzene] can be directly obtained from the slope of this plot (slope = $37.86 \cdot 10^3$ M^{-1}). The second-order rate constant k_1 was then deduced and found to be $(1.92 \pm 0.01) \cdot 10^9$ M^{-1} s^{-1}. This value is in good agreement with those reported by (Neta et al. 1977).

Degradation of carbamazepine in the presence of PMS/Co compared to the Fenton reagent

The oxidation of CBZ (50 μM) was performed in Milli-Q water and in wastewater (Major chemical parameters are reported in Table 1) in the presence of PMS (250 μM) and Co^{II} (250 μM) at pH 3, and compared with the degradation of CBZ in the same conditions in the presence of H_2O_2/Fe^{II}. The results are shown in Fig. 3. Under our experimental conditions, the curves indicated that no evolution was observed after 30 min. If we compare the capacity PMS/Co^{II} and H_2O_2/Fe^{II}, it clearly appeared that these two oxidation systems had different efficiencies to convert CBZ in both milli-Q water and urban wastewater. In milli-Q water, the transformation of CBZ reached 100% in 20 min in the presence of PMS/Co^{II} while it only reached 83% after 60 min in the presence of H_2O_2/Fe^{II}. The apparent first-order kinetics of CBZ degradation were determined to

Table 1 Major ions present in the wastewater sample

Ion	Concentration (mg L^{-1})
TOC	16.1
Chloride ion (Cl^-)	71
Nitrite ion (NO_2^-)	0.506
Nitrate ion (NO_3^-)	7.25
Sulfate ion (SO_4^{2-})	35
Carbonate ion (HCO_3^-)	24.2
Phosphate (PO_4^{3-})	0.488
Ferrous iron (Fe^{2+})	n.d.

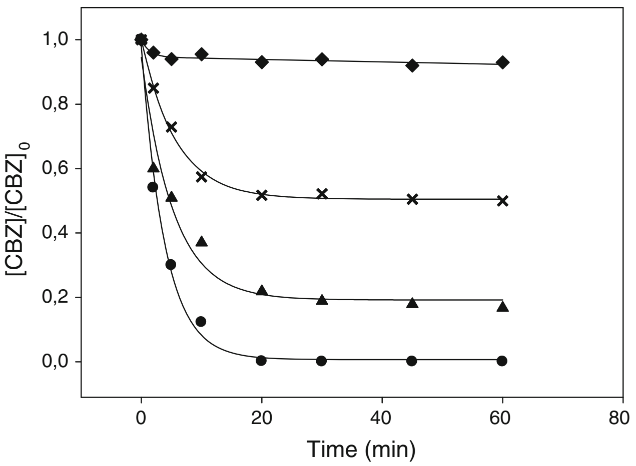


Fig. 3 Comparative degradation of CBZ in PMS/Co^{II} and H_2O_2/Fe^{II} systems, in milliQ (mQ) water and in wastewater (WW). (*filled circle*) PMS/Co in mQ, (*times*) PMS/Co in WW, (*filled triangle*) Fenton in mQ, (*filled square*) Fenton in WW. Exp. conditions: $[CBZ]_0 = 50\ \mu M$, $[PMS]_0 = [H_2O_2]_0 = 250\ \mu M$, $[Co^{II}]_0 = [Fe^{II}]_0 = 250\ \mu M$, initial pH 3.0

be $4.13 \cdot 10^{-3}\ s^{-1}$ and $3.15 \cdot 10^{-3}\ s^{-1}$ for PMS/Co and H_2O_2/Fe systems, respectively. The difference of CBZ degradation kinetics for the two oxidative systems may be explained by the probable difference of the initial radical concentration, which is assumed to be higher in the case of $SO_4^{\cdot -}$ ($2.15 \cdot 10^{-12}$ M) than $HO^{\cdot}$ ($1.64 \cdot 10^{-12}$ M). The radical concentration was estimated as follow: [radical] = k_{1st}/k_{2nd} where k_{1st} is the apparent first-order constant, and k_{2nd} is the second-order rate constant of sulfate and hydroxyl with CBZ ($1.92 \cdot 10^{9}\ M^{-1}\ s^{-1}$ (this work) and $8.8 \cdot 10^{9}\ M^{-1}\ s^{-1}$ (Huber et al. 2003), respectively). The figure also shows that the wastewater had an important inhibition effect on the oxidation of CBZ for the two oxidation systems. In the presence of PMS/Co, 50% of CBZ conversion was inhibited in urban wastewater, while in the presence of H_2O_2/Fe, only 7% of CBZ was transformed. The better lability of dissolved Cobalt than Iron in the presence of organic matter (Warnken et al. 2008) could explain the observed difference and consequently the probable higher initial [$SO_4^{\cdot -}$] than [$HO^{\cdot}$].

The presence of chloride ions in wastewater (Table 1) may contribute to the inhibition of the oxidation reaction as chloride ion reacts with $SO_4^{\cdot -}$ and $HO^{\cdot}$ with a relatively elevated second-order rate constant ($2.6 \cdot 10^{8}$ and $3.0 \cdot 10^{8}$ $M^{-1}\ s^{-1}$, respectively) (Grigor'ev et al. 1987; Padmaja et al. 1993). The oxidation of CBZ (50 μM) was performed in the presence of sodium chloride (100 mg L^{-1}), and the results (not shown) indicated that the apparent degradation kinetic decreased by a factor 1.8 compared to the blank, similarly to the curves shown in Fig. 1a, supporting that chloride ions in wastewater act as a quencher of the oxidation.

Considering our acidic experimental condition and the relatively low second-order rate constant for the reaction of $SO_4^{\cdot -}$ with bicarbonate, HCO_3^{-} may certainly not be considered as a quenching ion. Additionally, nitrate ions may not influence the oxidation reaction either because of the low second-order rate constant with $SO_4^{\cdot -}$ ($5 \cdot 10^{4}$ $M^{-1}\ s^{-1}$) (Logager et al. 1993).

By-products identification

Various similar intermediates were identified at pH 3 by HPLC–MS^{n} in both oxidation systems (PMS/Co^{II} and

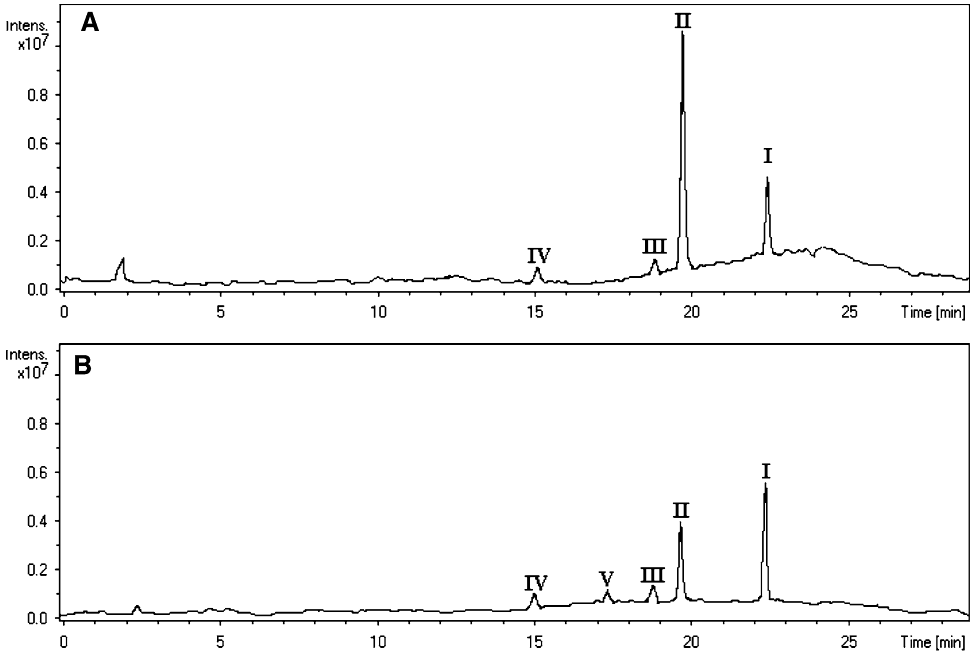


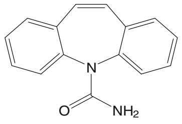
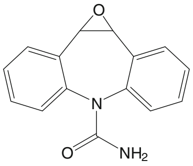
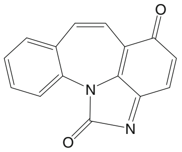
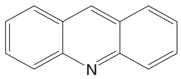
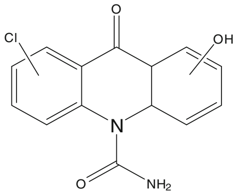
Fig. 4 LC/MS chromatograms under positive electrospray ionization mode (full scan), obtained after 5-min oxidation of CBZ in: **a** Fenton system, **b** PMS/Co system. Conditions: $[CBZ]_0 = 50\ \mu M$, $[PMS]_0 = 150\ \mu M$, $[Co^{II}]_0 = 150\ \mu M$, initial pH 3

H_2O_2/Fe^{II}). Intermediates were identified by comparing their MS data with those previously reported in the literature. Figure 4 reports the Total Ion Chromatograms concerning CBZ degradation upon the two oxidation systems. Table 2 reports molecular ions and fragment ions used for the identification of CBZ by-products in LC-ESI(+) MS^2. Four common compounds were identified in both oxidation systems (I–IV), and an additional compound (V) was detected in the H_2O_2/Fe^{II} system only. The presence of the initial CBZ (I) indicated that its degradation was incomplete, due to the use of low concentration of PMS or H_2O_2 in the experimental setup (ratio CBZ/oxidant = 1/3). The major identified by-product structure was 10,11-dihydro-10,11-epoxycarbamazepine (II), known as a metabolite of CBZ and also identified in a sewage treatment plant (Miao and Metcalfe 2003). The compounds III, IV, and V were identified as quinone derivatives, acridine, and chloro-hydroxy acridone, which were also identified during the photodegradation of CBZ into estuarine waters (Chiron et al. 2006). When high concentration of PMS (1.5 mM) was used, HPLC and HPLC–MS analyses (not shown here) demonstrated that the by-products further mineralized into more polar compounds.

Conclusion

The oxidation system consisting of PMS/Co^{II} to generate sulfate radicals has been demonstrated to be a more effective oxidant reagent to degrade CBZ both in laboratory grade water and wastewater, in acidic conditions, compared to the Fenton's reagent system generating hydroxyl radical. The second-order rate constant of $SO_4^{\cdot -}$ with CBZ has been determined ($1.92 \cdot 10^9$ M^{-1} s^{-1}) on the basis of competitive kinetic in the presence of benzene. The wastewater matrix seemed to play an important role on the inhibition of both oxidation PMS/Co^{II} and H_2O_2/Fe^{II} systems. It has been demonstrated that chloride ions were involved in the inhibition effect, and it is also suggested that organic matter could have the preponderant effect on the oxidation kinetic decrease. Concerning the different apparent degradation kinetics of CBZ induced by either the PMS/Co^{II} or the H_2O_2/Fe^{II} oxidation system in laboratory grade water, it was suggested that metal complex exchange kinetics may be responsible of the better lability of Cobalt in solution than Iron, inducing a better initial production of $SO_4^{\cdot -}$. The identification of the same intermediates in the two different oxidation systems support that the reactivity of $SO_4^{\cdot -}$ and $HO^{\cdot}$ could be similar and that the efficiency

Table 2 Molecular weight of carbamazepine by-products, molecular ions detected in ESI(+) MS, and fragmentation ions detected in MS^2

Product	I	II	III	IV	V
Name	Carbamazepine (CBZ)	10,11-dihydro-10,11-epoxycarbamazepine	Quinone derivate	Acridine	Quinone derivate
Chemical structure					
Molecular weight (g/mol)	236	252	250	180	292
ESI (+) m/z	237 [M+H]$^+$ 259 [M+Na]$^+$	253 [M+H]$^+$	251 [M+H]$^+$	181 [M+H]$^+$	291 [M+H]$^+$
ESI (+) MS^2 m/z	**237**>220, 194	**253**>236,210,180	**251**>223,195	180	**291**>273>257>223>180
R_T (min)	22.3	19.7	18.8	15	17.4

The precursor ions used in MS^2 are highlighted in bold. Roman numbers of by-products are those given Figure of a system would only depend on initial concentration of free reactive radicals.

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