Article

Caffeine Oxidation in Water by Fenton and Fenton-Like Processes: Effects of Inorganic Anions and Ecotoxicological Evaluation on Aquatic Organisms

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A degradação de cafeína pelo reagente de Fenton (Fe(II)/H$_2$O$_2$) e pelo reagente de Fenton modificado (Fe(III)/H$_2$O$_2$) foi investigada em água deionizada em uma concentração inicial de 5,2 µmol L^{-1} (1000 µg L^{-1}). Esses dois processos de oxidação diferentes foram comparados e foi observado que uma degradação eficiente de cafeína (95%) foi promovida pelo reagente de Fenton na razão molar de Fe(II)/H$_2$O$_2$ de 3:10 após 30 min. O efeito dos íons cloreto, sulfato e carbonato na decomposição de cafeína pelo reagente de Fenton e pelo reagente de Fenton modificado foi investigado. Também foi avaliada a toxicidade crônica dos produtos de degradação de cafeína sobre organismos aquáticos após tratamento da solução contendo inicialmente cafeína pelo reagente de Fenton usando a razão molar de Fe(II)/H$_2$O$_2$ de 3:10. Apenas quando *Ceriodaphnia dubia* foi exposta à concentração de 100% v/v dessa solução obtida após o tratamento de cafeína pelo reagente de Fenton usando uma razão molar de Fe(II)/H$_2$O$_2$ de 3:10, toxicidade crônica sobre o microcrustácio avaliado foi observada.

Caffeine degradation using Fenton's reagent (Fe(II)/H$_2$O$_2$) and the Fenton-like reagent (Fe(III)/H$_2$O$_2$) was investigated in deionized water at an initial concentration of 5.2 µmol L^{-1} (1000 µg L^{-1}). These two different oxidation processes were compared and it was observed that efficient caffeine degradation (95%) was promoted by Fenton's reagent at an Fe(II)/H$_2$O$_2$ molar ratio of 3:10 after 30 min. The effect of chloride, sulfate and carbonate ions on the decomposition of caffeine by Fenton's reagent and the Fenton-like reagent has been investigated. Also, the chronic toxicity of the caffeine degradation products was evaluated on aquatic life after treatment of a solution initially containing caffeine by Fenton's reagent using an Fe(II)/H$_2$O$_2$ ratio of 3:10. Only when *Ceriodaphnia dubia* was exposed to the concentration of 100% v/v of this solution obtained after the treatment of caffeine by Fenton's reagent using an Fe(II)/H$_2$O$_2$ ratio of 3:10, chronic toxicity over the evaluated microcrustacean was observed.

Keywords: caffeine degradation, Fenton's reagent, Fenton-like reagent, inorganic ion effects, ecotoxicological evaluation

Introduction

Pharmaceutical products have constantly been detected in the environment constituting an emerging contaminant. They are frequently found in wastewater in the ng L^{-1} to µg L^{-1} range and occasionally in ground waters.[1-3]

Caffeine, with the chemical name 1,3,7-trimethyl-xanthine, has found extensive applications in pharmacological preparations, such as analgesics, diet aids and cold/flu remedies. It is clinically used for the treatment of neurasthenia and the recovery of coma. Moreover, it can be used as an additive in many popular carbonated drinks. About 120,000 tons of caffeine are consumed worldwide annually. Pure caffeine is an odorless alkaloid with a bitter taste, which is naturally and widely found in the leaves, seeds and fruits of a large number of plants, such as cocoa beans, tea, coffee, cola and guarana. Caffeine may be consumed daily in the form of coffee, tea, cocoa, chocolate, and energy drinks, and it is also found in many painkillers and anti-migraine drugs.[4] Caffeine is, therefore, introduced continuously into the sewage system through many anthropogenic sources and is likely to persist in water because of its high solubility (21.7 g L^{-1}) and negligible volatility. The widespread occurrence of caffeine in sewage, soil and wastewaters has recently been documented.[5,6]

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Some emerging contaminants like caffeine are persistent and their complete elimination by conventional water treatment is difficult.[7] Advanced oxidation processes (AOPs) are oxidation processes in which hydroxyl radicals are the main oxidants involved.[8,9] However, large amounts of oxidation-refractory compounds are usually obtained at the end of the process. This behavior is explained in terms of the reactivity of hydroxyl radicals with some simple organic intermediates formed during the oxidation of organic pollutants, such as acetic and oxalic acids, acetone or simple chloride derivatives, such as chloroform or tetrachloroethane.[10]

Among these AOPs, Fenton's reagent (Fe(II)/H_2O_2) and the Fenton-like reagent (Fe(III)/H_2O_2) have been the subject of numerous studies in order to investigate the mechanism and kinetics of the reaction or to examine the efficiency of the process for the removal of organic pollutants.[11] Fenton's oxidation appeared to be the most promising method, in terms of cost-effectiveness and ease of operation. Recently, in a comprehensive review, Neyens and Baeyens[12] indicated that Fenton's oxidation is a very effective method for the removal of many hazardous organic pollutants from wastewaters.

Inorganic anions (Cl^-, SO_4^{2-}, CO_3^{2-}, $H_2PO_4^-$/HPO_4^{2-}, etc.) present in wastewater or added as reagents ($FeSO_4$, $FeCl_3$, HCl, H_2SO_4) may also have a significant effect on the overall reaction rates in the Fenton process.[13-15] Usually, the effects of inorganic salts on the overall rates of decomposition of H_2O_2 and organic compounds are ignored.[10]

Recently, alternatives to caffeine degradation have been sought.[16-18] Since conventional treatments in municipal wastewater treatment facilities (MWTF) are not very efficient for their removal, it is necessary to look for alternatives. In this study, caffeine degradation was investigated at an initial concentration of 5.2 µmol L^{-1} (1000 µg L^{-1}) using Fenton's reagent (Fe(II)/H_2O_2) and the Fenton-like reagent (Fe(III)/H_2O_2), employing low iron and hydrogen peroxide concentrations. This work was undertaken in order to compare, under identical conditions, the effects of chloride, sulfate and carbonate in the optimized degradation conditions of caffeine. Also, the chronic toxicity on aquatic life was evaluated by exposure of *Ceriodaphnia dubia* to solutions resulting from caffeine degradation after treatment with Fenton's reagent using an Fe(II)/H_2O_2 ratio of 3:10, a condition in which higher caffeine degradation was observed in this work.

Experimental

Materials

All reagents used in this work except methanol (100%, Baker), phosphoric acid (85%, Tedia) and caffeine (100%, Synth) were purchased from Isofar and were analytical grade and used without any further purification. Ferrous sulfate heptahydrate (99%) and ferric chloride hexahydrate (97%) were used as the iron sources. Hydrogen peroxide (30% m/m) was used as the hydroxyl radical source. KCl (99%), $CaSO_4.2H_2O$ (98%) and Na_2CO_3 (99.5%) were used to adjust the total concentration of an inorganic ion. A 0.1 mol L^{-1} H_2SO_4 (99%) solution was used to adjust the pH of the solution and $Na_2S_2O_3$ (99.5%) was used for quenching H_2O_2. All solutions were prepared in Milli-Q water (Millipore).

Experimental setup

All experiments were carried out in erlenmeyer flasks open to the atmosphere. A hundred milliliters of solution containing caffeine in deionized water at an initial concentration of 5.2 µmol L^{-1} (1000 µg L^{-1}) was stirred to maintain homogeneity.

Fenton and Fenton-like processes

Fenton and Fenton-like reactions were carried out at initial pH of 3.0. H_2SO_4 (0.1 mol L^{-1}) was used to adjust the pH of the solution. The concentration of hydrogen peroxide was maintained at 10.0 µmol L^{-1} in all experiments. Ten microliters of hydrogen peroxide (H_2O_2, 0.1 mol L^{-1}) were added into the caffeine solution, followed by the addition of ferrous (as ferrous sulfate heptahydrate) or ferric (as ferric chloride hexahydrate) ions at initial concentrations of 1.0, 2.0 and 3.0 µmol L^{-1}, in order to initiate the oxidation reactions. In the experiments to examine the effects of various inorganic anions, 100 mmol L^{-1} of chloride, 100 mmol L^{-1} of carbonate and 30 mmol L^{-1} of sulfate were added to the erlenmeyer flask before addition of H_2O_2 and Fe^{2+} or Fe^{3+}. The effect of counter ions derived from the different reagents used in the experiments on caffeine degradation was not studied in this work. The experiments were conducted in room light for Fenton and Fenton-like reactions.

Analytical methods

High-performance liquid chromatography (HPLC) analyses were conducted using an Agilent 1100 Series system equipped with a manual injection valve with a 20 µL sample loop, a degasser system, a quartet pump and a multiple wavelength UV detector. Data acquisition and processing were accomplished with the Agilent Chemistation LC Systems software. A ZORBAX ODS reversed-phase (RP) column (150.0 mm × 4.6 mm i.d.,

5 µm particle size) and a ZORBAX ODS pre-column (12.5 mm × 4.6 mm i.d., 5 µm particle size) were used at room temperature. The mobile phase was methanol/water (30:70), at a flow rate of 1.0 mL min^{-1} and absorbance detection of 210 nm. A solution of phosphoric acid (pH 3) was used to control the pH.

Sample aliquots were withdrawn from the aqueous solution at 0, 5, 10, 15, 20, 25 and 30 min. H$_2$O$_2$ was removed by quenching with Na$_2$S$_2$O$_3$ and the aliquots were filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter for analysis. Under the described analytical conditions, the caffeine retention time was approximately 4 min.

Ecotoxicological evaluation

Ecotoxicological tests (chronic toxicity) were performed according to NBR 13373 to determine the whole sample toxicity by exposure of *Ceriodaphnia dubia* to increasing concentrations of the resulting solution,[19] containing an initial concentration of caffeine of 1000 µg L^{-1}, after treatment with Fenton's reagent using an Fe(II)/H$_2$O$_2$ ratio of 3:10, a condition at which the higher caffeine degradation was observed in this work. To carry out these tests, surface water with specific physico-chemical conditions of pH, electrical conductivity, water hardness and dissolved oxygen was used, in order to meet the conditions required by NBR 13373. During 7 days, a control group containing only *Ceriodaphnia dubia* in a certain volume of surface water (group 1) was monitored in relation to *Ceriodaphnia dubia* in the presence of solutions with caffeine degradation products with concentrations ranging from 1 to 100% v/v (group 2). The experiments were performed at a temperature of 24 °C. Groups 1 and 2 were submitted to a period of 16 h light and 8 h dark during the experiments. The pH was maintained at 7.6 throughout the experiment. If there is a decrease in reproduction or death of *Ceriodaphnia dubia*, or both, in the different concentrations of the sample (1 to 100% v/v) over time in relation to the control group containing only *Ceriodaphnia dubia*, chronic toxicity of the sample to the evaluated organisms is observed. Chemicals added to the water for the oxidation process were removed prior to bioassay.

Results and Discussion

Fenton and Fenton-like processes

The occurrence of a great number of pharmaceutical residues in the environment has frequently been reported in recent literature, receiving increasing attention as emerging contaminants. Different classes of pharmaceuticals, such as antibiotics, hormones, anesthetics and anti-inflammatories have been encountered in the aquatic environment in the concentration range of ng L^{-1} to µg L^{-1}.[20] This way, in this study, the caffeine degradation by Fenton and Fenton-like treatments was investigated using HPLC-UV analysis. The caffeine concentration in the degradation experiments was 1000 µg L^{-1}, in an attempt to simulate low concentrations of pharmaceuticals present in the environment. Also, low iron and hydrogen peroxide concentrations were employed to promote caffeine degradation.

The concentration of iron and hydrogen peroxide are important parameters in the oxidation process. An excess or lack of these additives can significantly reduce the efficiency of the degradation process. Some studies have reported that H$_2$O$_2$/Fe ratios higher than 10 can result in excess peroxide in solution and consequently in the scavenging of hydroxyl radicals, hindering the efficiency of degradation, according to equation 1.[20]

$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet HO_2 \qquad (1)$$

pH has a significant role in determining the efficiency of Fenton oxidation. Maximum degradation carried out by H$_2$O$_2$/Fe using Fenton reagent is expected at pH between 2 and 4. At pH < 2.5, (FeOH)$^{2+}$ is formed, which reacts more slowly with hydrogen peroxide and therefore reduces the degradation efficiency. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at very low pH. At pH > 4, degradation rates decrease due to the formation of Fe(II) complexes and the precipitation of ferric oxyhydroxides. Furthermore, the oxidation potential of hydroxyl radicals is known to decrease with an increase in the pH.[21]

Thus, Fenton and Fenton-like reactions were carried out at pH 3.0, at hydrogen peroxide concentration of 10 µmol L^{-1}. Ferrous and ferric ions at concentrations of 1, 2 and 3 µmol L^{-1} were used, which resulted in a molar ratio of 1:10, 2:10 and 3:10 Fe/H$_2$O$_2$, respectively, producing H$_2$O$_2$/Fe ratios of 10, 5 and almost 3. The degradation of caffeine increased with increasing initial Fe(II) and Fe(III) concentration (see Figure 1), and was faster with Fenton reaction as compared to Fenton-like reaction.

As shown in Figure 1, the larger the added amount of ferrous and ferric ions, the higher the elimination of caffeine. Thus, the degradation of caffeine was promoted with increasing ferrous and ferric concentrations from 1 to 3 µmol L^{-1}, by both Fenton and Fenton-like reactions. However, when 1 and 2 µmol L^{-1} of ferrous and ferric ions were used, a similar degradation of caffeine was observed. The removal of caffeine by Fenton reaction increased from
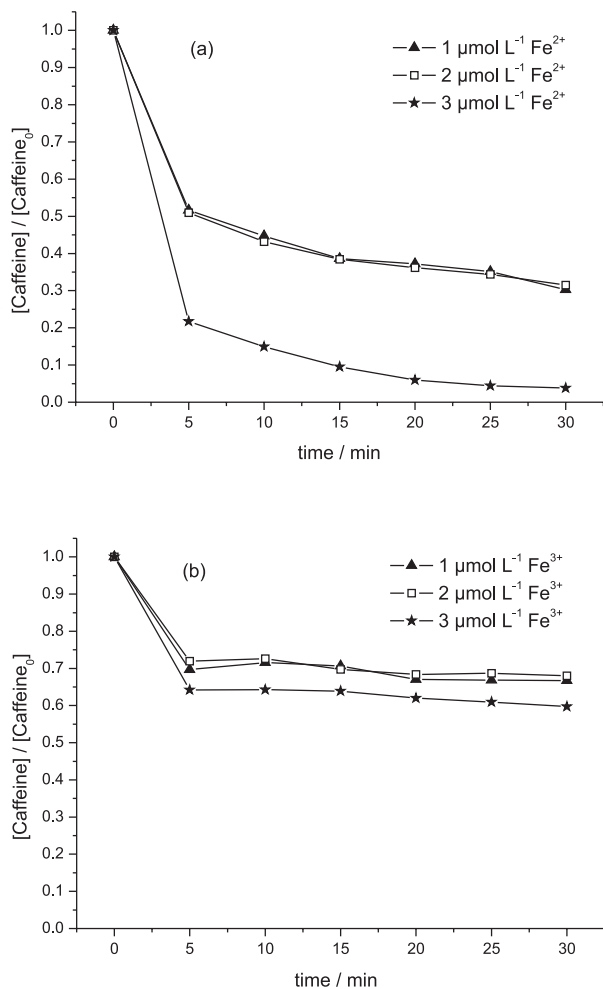
Figure 1. Caffeine degradation by Fenton reagent (a) and Fenton-like reagent (b) treatment using different iron concentrations. Caffeine: 5.2 µmol L^{-1}; H$_2$O$_2$: 10 µmol L^{-1}; pH: 3.0.

68% at a molar ratio of 1:10 Fe(II)/H$_2$O$_2$ to 95% at a molar ratio of 3:10 Fe(II)/H$_2$O$_2$, within a 30 min reaction time; by Fenton-like reaction, the removal of caffeine increased from 33% at a molar ratio of 1:10 Fe(III)/H$_2$O$_2$ to 40% at a molar ratio of 3:10 Fe(III)/H$_2$O$_2$ in the same reaction time.

Figure 2 presents typical experiments conducted by Fenton (FR) and Fenton-like reactions (FLR) comparing the caffeine degradation with increasing Fe(II) and Fe(III) concentrations of 3 and 4 µmol L^{-1}. As can be seen in the case of caffeine degradation by Fenton reagent, a slight increase in caffeine removal occurred. However, caffeine degradation was suppressed with increasing Fe(III) concentration. Therefore, an increasing concentration of Fe(III) produces a controversial effect on the oxidation reactions studied.

In the Fenton mechanism, the continuous formation of •OH occurs via the reaction between hydrogen peroxide and ferrous iron, and side reactions in which Fe(II) is regenerated (reduced) from ferric Fe(III) (equations 2 and 3). The
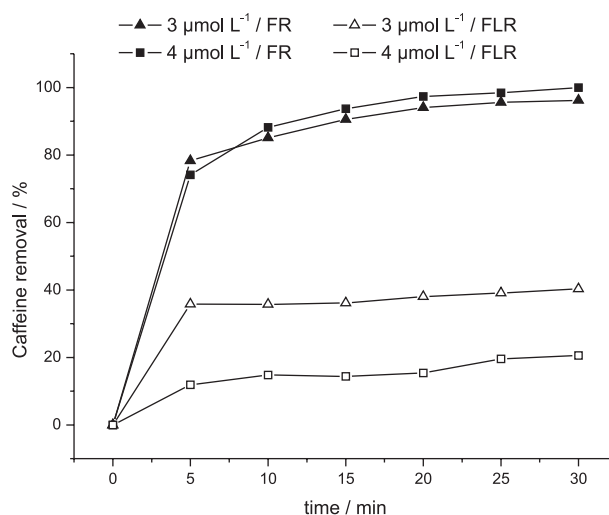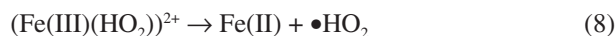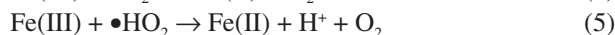

Figure 2. Caffeine degradation by Fenton reagent (FR) and Fenton-like reagent (FLR) treatment using the Fe/H$_2$O$_2$ molar ratios 3:10 and 4:10. Caffeine: 5.2 µmol L^{-1}; H$_2$O$_2$: 10 µmol L^{-1}; pH: 3.0.

superoxide radical (•O$_2^-$) (equation 4) is the non-protonated form of •HO$_2$ (pKa = 4.8) and is a strong reductant, whereas •HO$_2$ (equation 5) is not.[22,23] In homogeneous Fenton-like systems, the spontaneous reaction of H$_2$O$_2$ and Fe(III) leads to the formation of two ferro-peroxy complexes, (Fe(III)(HO$_2$))$^{2+}$, (Fe(III)(OH)(HO$_2$))$^+$, as shown in equations 6 and 7.[13] Once formed, these Fe(III)-peroxy complexes are assumed to decompose to yield Fe(II) (equations 8 and 9). Fe(III) reduction is a critical step in the Fenton-like mechanism due to the formation of Fe(II), the rate-limiting constituent in most Fenton systems.[15]

$$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \bullet\text{OH} + \text{OH}^- \qquad (2)$$
$$\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \bullet\text{O}_2^- + 2\text{H}^+ \qquad (3)$$

$$\text{Fe(III)} + \bullet\text{O}_2^- \rightarrow \text{Fe(II)} + \text{O}_2 \qquad (4)$$
$$\text{Fe(III)} + \bullet\text{HO}_2 \rightarrow \text{Fe(II)} + \text{H}^+ + \text{O}_2 \qquad (5)$$

$$\text{Fe(III)} + \text{H}_2\text{O}_2 \leftrightarrow (\text{Fe(III)(HO}_2))^{2+} + \text{H}^+ \qquad (6)$$
$$\text{FeOH}^{2+} + \text{H}_2\text{O}_2 \leftrightarrow (\text{Fe(III)(OH)(HO}_2))^+ + \text{H}^+ \qquad (7)$$

$$(\text{Fe(III)(HO}_2))^{2+} \rightarrow \text{Fe(II)} + \bullet\text{HO}_2 \qquad (8)$$
$$(\text{Fe(III)(OH)(HO}_2))^+ \rightarrow \text{Fe(II)} + \bullet\text{HO}_2 + \text{OH}^- \qquad (9)$$

The effect of inorganic ions on caffeine degradation

The effect of some anions on the degradation of caffeine was examined in the optimized degradation conditions to try to simulate an effluent containing caffeine at an initial concentration of 5.2 µmol L^{-1} (1000 µg L^{-1}) in the presence of high concentrations of chloride, sulfate and carbonate. Therefore, all experiments to evaluate the influence of inorganic ions under caffeine degradation were realized

using Fenton reaction and Fenton-like reaction in a Fe/H_2O_2 ratio of 3:10. Thus, we intend to evaluate the degradation of caffeine using the proposed oxidation methods in environments containing high concentrations of selected inorganic ions, since large quantities of anions are often present in wastewater, and its influence on the Fenton and Fenton-like reactions is little studied. The studied sulfate concentration was less than that for carbonate and chloride concentrations because undissolved $CaSO_4.2H_2O$ was observed at concentrations above 30 mmol L^{-1}.

Fenton reaction is extremely sensitive to anions that remain in the solution.[24] In this study, the effects of chloride, sulfate and carbonate on the oxidation processes applied were investigated. The role of these anions could include complexation reactions with Fe(II) or Fe(III), which affect the distribution and reactivity of the Fe species, precipitation reactions affecting the availability of Fe and radical scavenging reactions with $\bullet OH$.[11] Inorganic anions may react with the Fe(III)-peroxy complex and interfere with the formation of $\bullet O_2^-/\bullet HO_2$ (equations 8 and 9).[13] Lower concentrations of $\bullet O_2^-$ result in a decline in the production of Fe(II), and consequently, the overall production of $\bullet OH$.[15]

Figures 3a and 3b show the effect of the evaluated ions on the caffeine oxidation by Fenton and Fenton-like reactions, respectively. In the conditions of the Fenton reaction, anions suppress the decomposition of caffeine in the following sequence: $CO_3^{2-} > SO_4^{2-} > Cl^-$. In the case of caffeine degradation under Fenton-like reaction, the sequence of anions suppression was: $SO_4^{2-} > Cl^- > CO_3^{2-}$. It can be seen that the suppression of caffeine degradation by the studied ions was higher when the Fenton reaction was employed in relation to caffeine degradation by the Fenton-like reaction.

As shown in Figure 3a, in the case of carbonate, sulfate and chloride anions, a larger suppression of caffeine degradation was observed in relation to reactions realized in the absence of these ions. This was probably due to complexation reactions of SO_4^{2-} and Cl^- with Fe(II) and the reaction of hydroxyl radicals with SO_4^{2-} and Cl^- to generate inorganic radicals with activity that is lower than that of the hydroxyl radical. In the case of Figure 3b, the addition of inorganic anions exhibited different inhibiting behaviors in Fenton-like treatment. The effect of the addition of SO_4^{2-} and Cl^- could be attributed to a decrease of the rate of generation of hydroxyl radicals because the formation of chloro- and sulfato-Fe(III) complexes decreases the rates of the generation of Fe(II) and leads to the formation of inorganic radicals ($Cl_2\bullet^-$ and $SO_4\bullet^-$) which are less reactive than $\bullet OH$.[11] Some of these reactions are shown from equations 10 to 15. Carbonate anions cause the suppression of caffeine degradation
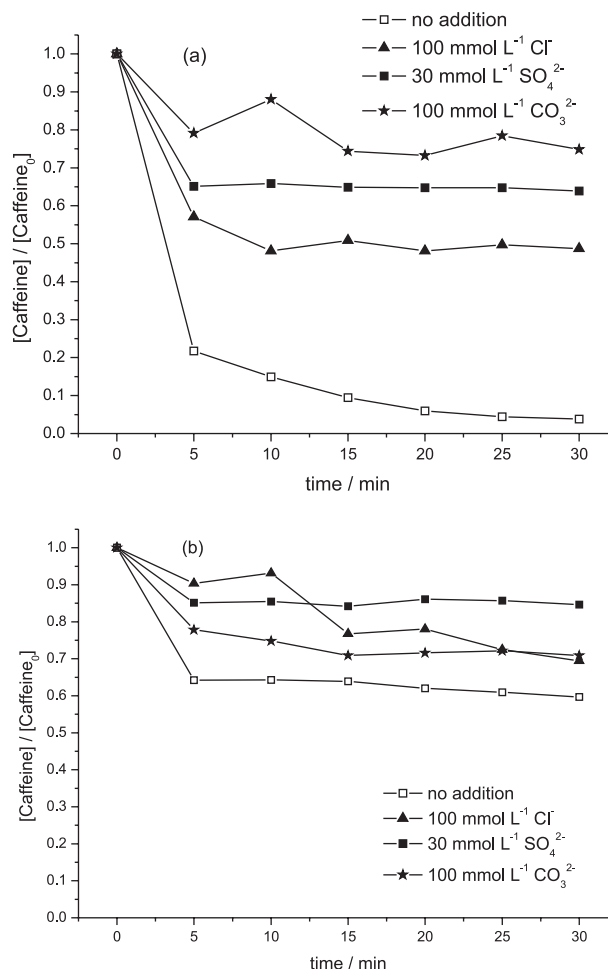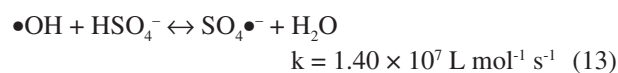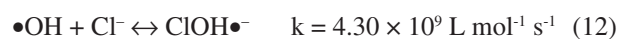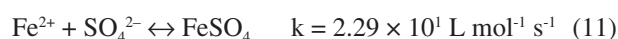

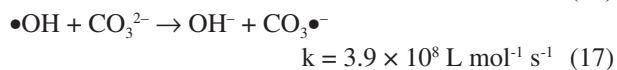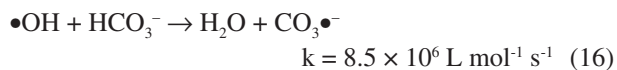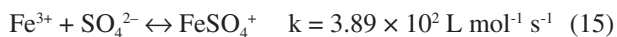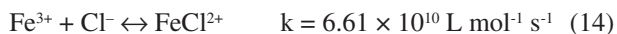**Figure 3.** Caffeine degradation by Fenton (a) and Fenton-like (b) reactions in the absence and presence of Cl^-, CO_3^{2-} (100 mmol L^{-1}) and SO_4^{2-} (30 mmol L^{-1}) ions. Caffeine: 5.2 µmol L^{-1}; H_2O_2: 10 µmol L^{-1}; Fe: 3 µmol L^{-1}; pH: 3.0.

under Fenton and Fenton-like reaction (Figures 3a and 3b) probably because of radical scavenging reaction with $\bullet OH$. Radical scavengers such as carbonate species (CO_3^{2-} and HCO_3^-) especially compete with organic contaminants for hydroxyl radicals and significantly decrease the degradation efficiencies of organics through equations 16 and 17.[25] Thus, the radical scavenging reaction with $\bullet OH$ by CO_3^{2-} predominates when caffeine degradation is promoted by Fenton reagent but is not the predominant effect when the Fenton-like reaction was employed.

$$Fe^{2+} + Cl^- \leftrightarrow FeCl^+ \qquad k = 2.88 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \quad (10)$$

$$Fe^{2+} + SO_4^{2-} \leftrightarrow FeSO_4 \qquad k = 2.29 \times 10^{1} \text{ L mol}^{-1} \text{ s}^{-1} \quad (11)$$

$$\bullet OH + Cl^- \leftrightarrow ClOH\bullet^- \qquad k = 4.30 \times 10^{9} \text{ L mol}^{-1} \text{ s}^{-1} \quad (12)$$

$$\bullet OH + HSO_4^- \leftrightarrow SO_4\bullet^- + H_2O$$
$$k = 1.40 \times 10^{7} \text{ L mol}^{-1} \text{ s}^{-1} \quad (13)$$

$$Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+} \qquad k = 6.61 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \quad (14)$$

$$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+ \quad k = 3.89 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1} \quad (15)$$

$$\bullet OH + HCO_3^- \rightarrow H_2O + CO_3\bullet^-$$
$$k = 8.5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \quad (16)$$
$$\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3\bullet^-$$
$$k = 3.9 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad (17)$$
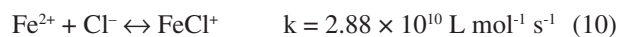
Ecotoxicological evaluation

After exposure of *Ceriodaphnia dubia* to even higher concentrations (1 to 100% v/v) of the resulting solution obtained from the treatment of caffeine by Fenton reagent using an Fe(II)/H$_2$O$_2$ ratio of 3:10, it was shown that exposure of *Ceriodaphnia dubia* to concentrations up to 75% v/v of this solution chronic toxicity was not observed. Only when *Ceriodaphnia dubia* was exposed to the concentration of 100% v/v of the resulting solution cited above, chronic toxicity was observed. Determining the toxicity has been chosen here because toxicity assays are standardized and reliable.

Conclusions

The experiments showed that caffeine at a concentration of 1000 μg L^{-1} can be degraded using low iron and H$_2$O$_2$ concentrations. However, efficient caffeine degradation (95%) was promoted by Fenton reagent at a Fe/H$_2$O$_2$ molar ratio of 3:10 after 30 min. The present work has shown that the efficiency of the Fe(II)/H$_2$O$_2$ and Fe(III)/H$_2$O$_2$ oxidation processes can be decreased in the presence of chloride, sulfate and carbonate. In the case of Fenton reagent, these effects have been attributed to complexation reactions of SO$_4^{2-}$ and Cl$^-$ with Fe(II) and the reaction of hydroxyl radicals with SO$_4^{2-}$ and Cl$^-$ to generate inorganic radicals whose activity is lower than that of the hydroxyl radical. In the oxidation of caffeine by Fenton-like reagent, the effect of SO$_4^{2-}$ and Cl$^-$ addition could be attributed to a decrease of the rate of hydroxyl radical generation because the formation of chloro- and sulfato-Fe(III) complexes decreases the rates of generation of Fe(II) and leads to the formation of inorganic radicals Cl$_2\bullet^-$ and SO$_4\bullet^-$. Carbonate anions suppress caffeine degradation under Fenton and Fenton-like reactions probably because of the radical scavenging reaction with $\bullet$OH and this suppression was higher when the Fenton reaction was employed. After exposure of *Ceriodaphnia dubia* to different concentrations of the resulting solution of caffeine degradation after the treatment of caffeine by Fenton reagent using an Fe(II)/H$_2$O$_2$ ratio of 3:10, chronic toxicity was only observed when *Ceriodaphnia dubia* was exposed to the concentration of 100% v/v of this solution.

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