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The aim of this work was to evaluate the influence of mineral and organic matrices on the sonochemical degradation of 4-isopropylphenol (4-IPP), an endocrine disrupting chemical found in water. Bicarbonate ions as mineral matrix and sucrose as organic competitor were evaluated with respect to their effect on sonochemical degradation rates. At low 4-IPP concentration, the sonolytic degradation was clearly improved in the presence of bicarbonate involving the formation of the carbonate radical resulting from the reaction of bicarbonate with hydroxyl radical. In the presence of large excess of sucrose, the sonochemical degradation of 4-IPP at low concentration was not affected.

Keywords 4-isopropylphenol; carbonate radical; endocrine disrupting chemical; sonochemical degradation; sucrose

INTRODUCTION

Water resource is strongly contaminated by organic compounds issue from human activities. Some of these xenobiotics can interfere with hormone activities resulting in an adverse effect on the aquatic ecosystem development and on human health (1,2). These compounds, named endocrine disrupting compounds (EDCs), are active at very low concentrations (n g L^{-1}), and cannot be eliminated to an inactive level in water treatment plants and can even be detected in drinking water (3–5). Most of this pollution is due to molecules bearing an aromatic ring with a special emphasis to bisphenol A (BPA) and alkylphenols (6–7).

Effective elimination of these EDCs can be realized having recourse to advanced oxidative technologies. These techniques, centered on the production and reaction of the hydroxyl radical (·OH), can conduct to the complete mineralization of the organic targets (8). Fenton reagent, photo-fenton, photocatalysis, electrochemical techniques, O_3/H_2O_2, and UV/H_2O_2 have demonstrated their efficiency towards EDCs elimination (9–14). However, a complete mineralization is required because the remaining toxicity could result from the presence of degradation intermediates (15,16). Taking one of these intermediates, as an example, this work investigates the kinetics of 4-isopropylphenol (4-IPP) elimination upon ultrasonic action in water and in the presence of two potential hydroxyl radical scavengers:

(i) the bicarbonate ion as inorganic scavenger and
(ii) sucrose as organic competitor.

4-IPP was chosen because this alkylphenol exhibiting acute and chronic toxicity has been detected as intermediate during the sonolytic and photocatalytic degradation of BPA (17–20). Additionally, this compound has been detected as a pollutant in European and United States rivers (21,22).

Ultrasonic action is linked to the formation of the bubble of cavitation that forms, grows, pulsates, and collapses under the periodic variation of the pressure wave (23). Violent contractions of the bubble filled with dissolved gases, water vapor, and volatile molecules occur adiabatically in the microsecond scale. As a consequence, the final step of the contraction is a hot and high pressure nucleus (24,25). Under these conditions, entrapped molecules of dissolved gases, vaporized water, and solutes can be brought to an excited state and dissociate. Therefore, ·OH radicals are generated from water and oxygen dissociation (26).

$$H_2O \rightarrow H^{\cdot} + {}^{\cdot}OH \quad (1)$$

$$O_2 \rightarrow 2O \quad (2)$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OOH \quad (3)$$

$$O + H_2O \rightarrow 2{}^{\cdot}OH \quad (4)$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OH + O \quad (5)$$

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The use of AOPs for aqueous organic pollutants elimination can be achieved with fair to high efficiency. However, because ·OH radicals are only slightly or not at all selective, in the case of complex matrices such as industrial wastewater, natural water and alimentary liquids, degradation rates can be tampered by the presence of organic and inorganic species that compete with the target molecule for the ·OH radicals (27). For many years, it was assumed that sonochemical oxidation reactions like other AOPs should generally be inhibited by high alkalinity usually resulting from the presence of large concentrations of radical scavengers such as bicarbonate and carbonate. It has been demonstrated that the sonochemical degradation of dyes and bisphenol A can be enhanced in the presence of bicarbonate and carbonate ions (28–30). This enhancement was attributed to the formation of carbonate radical ($CO_3^{\cdot-}$) resulting from the reaction of hydroxyl radical with bicarbaonte or carbonate. Carbonate radical, unlike the ·OH radical, can migrate towards the bulk of the solution and therefore induce the degradation of the micropollutants present in the bulk solution (28–30). In contrast to the hydroxyl radical, which reacts very rapidly with almost any organic compound, carbonate radical is very selective and the corresponding second-order rate constants cover a range of many orders of magnitude. Carbonate radical may react by electron transfer or hydrogen transfer (31). Additionally, ultrasound presents important advantages compared to other AOPs, because many researchers have indicated that in the presence of the natural environment, the rate of sonolytic degradation in a complex matrix was not affected (32,33). Additionally, ultrasonic treatment is a promising process for the destruction of malathion and chlorpyrifos in complex matrix such as apple juice (34).

The aim of this work was to evaluate 4-IPP elimination under sonochemical conditions. It is of practical interest to examine this process in complex matrices, as various matrix components may significantly affect the sonochemical kinetics and therefore the overall treatment efficiency. Therefore, the influence of bicarbonate ion as mineral matrix and sucrose as organic competitor on the sonolytic destruction of 4-IPP at low concentrations was investigated.

EXPERIMENTAL

Chemicals

4-Isopropylphenol (molecular weight 136.19 g mol^{-1}) was obtained from Aldrich (98% purity) and was used as received. Sodium bicarbonate was obtained from Prolabo (99.5% purity) and sucrose was purchased from Merck (99.99% purity). Acetonitrile (HPLC-UV grade) was supplied by Acros organics. Pure water, obtained with activated carbon and ion exchanger resins from Fisher Bioblock Scientific (Illkirch, France), was used throughout the study for the preparation of aqueous solutions, and as a component of the mobile phase in analysis by high performance liquid chromatography (HPLC).

Reactor

Experiments were conducted in a cylindrical water-jacketed glass reactor in order to control the temperature. Ultrasonic waves (278 kHz) were emitted from the bottom of the reactor through a piezoelectric disc fixed on a Pyrex plate. The temperature of the solution was monitored using a thermocouple immersed in the reacting medium. The temperature inside the reactor was maintained at 20 ± 1°C. Acoustic power dissipated in the reactor was estimated using a standard calorimetric method (35). The reactor was periodically sampled for analysis.

Analyses

4-IPP concentration was determined by using HPLC (Waters model 515) equipped with a Supelcosil LC-18 column (ID = 4.6 mm, length = 250 mm) and UV detector (Waters model 486). Sample injections were achieved with a Rheodyne injection system equipped with a 20 µL sample loop for 4-IPP concentrations above 1 mg/L and a 200 µL loop for the lowest concentrations. The used eluent was a mixture of acetonitrile and pure water (60:40 v/v) at a flow rate of 1 mL min^{-1}.

Hydrogen peroxide concentrations were determined using the iodometric method (36). Sample aliquots taken from the reactor were added in the quartz cell of the spectrophotometer containing potassium iodide (0.1 M) and ammonium heptamolybdate (0.01 M). The mixed solutions were allowed to stand for 5 min before absorbance was measured. All experiments were carried out at least three times.

RESULTS AND DISCUSSION

4-IPP Degradation and Hydrogen Peroxide Formation

Sonochemical degradation of 4-IPP was investigated in aerated solutions for a large range of concentrations from 5 µg L^{-1} to 200 mg L^{-1} (3.67×10^{-8} to 1.47×10^{-3} M). If the time dependence elimination of the 4-IPP appears to decrease exponentially as generally reported in the literature, it is clear that degradation does not follow a first order kinetics because of the lower values of the coefficient of determination (Fig. 1). Thus, degradation kinetics cannot be characterized by a single rate constant expressed in time^{-1}. In this study, the results were presented using the initial degradation rate (µM min^{-1}) rather than a pseudo first-order kinetic constant. Initial degradation rates were computed as $\Delta C/\Delta t$ over the first minutes of sonication from the results showing the evolution of 4-IPP concentration as a function of sonication time.

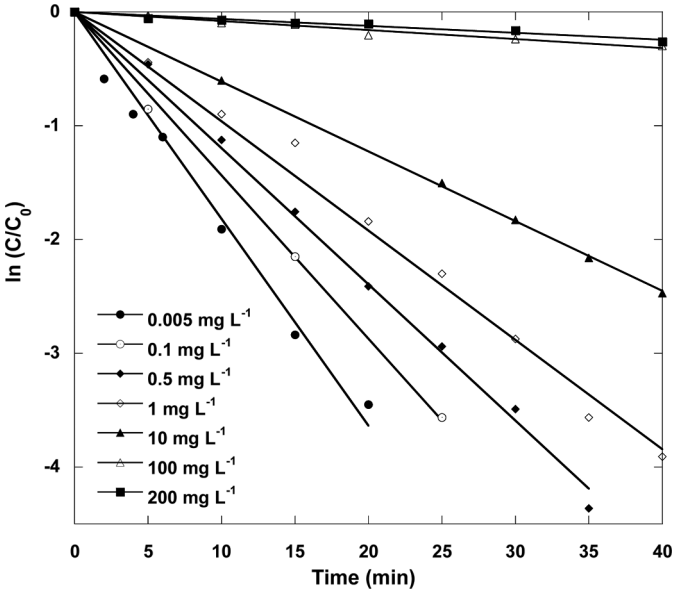

FIG. 1. Evolution of $\ln C/C_0$ versus time for the sonochemical degradation of 4-IPP (conditions—Frequency: 278 kHz; power: 80 W; volume: 300 mL; pH: natural (6.5); temperature: $20 \pm 1°C$).

The initial sonolytic destruction rate of 4-IPP versus initial substrate concentration is shown in Fig. 2. It was observed that the initial degradation rate increases with an increase in the initial concentration up to $100\,mg\,L^{-1}$ ($7.34 \times 10^{-4}\,M$), followed by almost constant sonolytic degradation rate for higher concentrations. However, a linear relationship was not observed, as expected, for a first-order kinetic law.

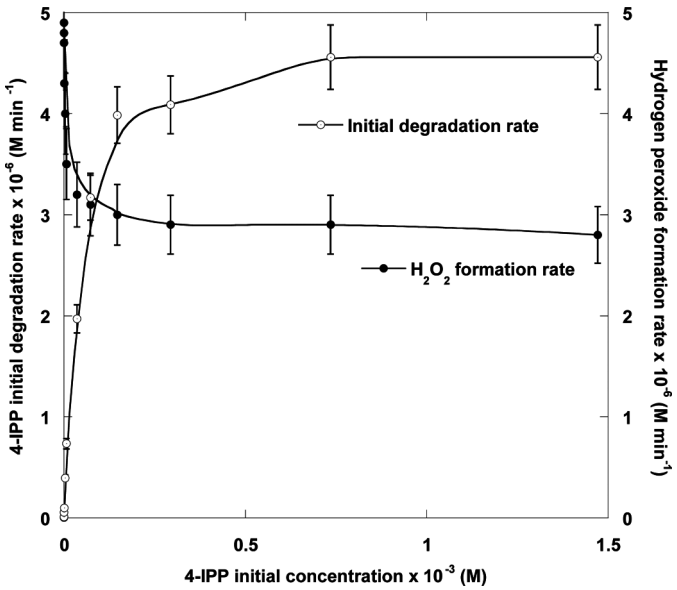

FIG. 2. Evolution of the initial rates of 4-IPP degradation and hydrogen peroxide formation versus 4-IPP intial concentration (conditions—Frequency: 278 kHz; power: 80 W; volume: 300 mL; pH: natural (6.5); temperature: $20 \pm 1°C$).

In order to evaluate the influence of hydrogen peroxide ultrasonically produced on the degradation of 4-IPP, a control experiment was conducted by adding hydrogen peroxide from an external source in a continuously stirred cell containing 4-IPP solution. The dosage of added hydrogen peroxide was the same as the amount formed with the ultrasonic reactor in pure water. The results indicate that a similar dosage of hydrogen peroxide in the absence of ultrasound did not produce any degradation of 4-IPP. Consequently, there is no direct oxidation reaction between the hydrogen peroxide and 4-IPP in solution.

4-IPP exhibit low fugacity and therefore it cannot be degraded by pyrolysis inside the cavitation bubble because of its low Henry's law constant ($1.09 \times 10^{-6}\,atm\,m^3\,mol^{-1}$). Additionally, due to its relative low solubility in water ($1.10 \times 10^3\,mg\,L^{-1}$) and relative high octanol/water partition coefficient ($\log K_{OW} = 2.9$), 4-IPP may be eliminated through reaction with hydroxyl radical at the interface of the cavitation bubble. Thus, the ·OH radicals generated by ultrasound are the main ones responsible for the degradation of 4-IPP.

Figure 2 also shows the hydrogen peroxide production rate for each 4-IPP initial concentration and its respective value without substrate (in pure water). A higher concentration of hydrogen peroxide is reached for the lower concentration of the substrate. At low 4-IPP concentrations, the probability of reaction with ·OH radical decreases and the recombination of hydroxyl radicals occurs. At high 4-IPP concentration, the formation rate of hydrogen peroxide was low. At high substrate concentration, the recombination of ·OH radicals is low and the radicals react with 4-IPP. The degradation of 4-IPP appears to be linked to the hydrogen peroxide formation. In the absence of the substrate, ·OH radicals combine to produce hydrogen peroxide. Thus, the hydrogen peroxide measurement during acoustic cavitation is a method that can be used to estimate the ·OH radicals released by the bubble at determined sonochemical conditions.

From Fig. 2, it can be observed that there was no proportionality because hydrogen peroxide was produced from the recombination of ·OH radicals that do not encounter the target molecule at the interface of the bubble and from perhydroxyl radical (HOO·) combination at the interface of the bubble. The rate of hydrogen peroxide production in the absence of 4-IPP was $4.9 \pm 0.5\,\mu M\,min^{-1}$, but that corresponding to the plateau in Fig. 2 was $2.8 \pm 0.3\,\mu M\,min^{-1}$ corresponding to a production rate of ·OH radicals of $5.6 \pm 0.3\,\mu M\,min^{-1}$. Maximum degradation rate was obtained when all the ·OH radicals were scavenged by the substrate. At higher substrate concentrations (100 and $200\,mg\,L^{-1}$), 4-IPP initial degradation rate

($4.9 \pm 0.5\,\mu M\,min^{-1}$) was approximately similar to that of the formation of ·OH radicals ($5.6 \pm 0.3\,\mu M\,min^{-1}$).

In order to explain the local reaction zone in the interfacial region of cavitation bubbles, where 4-IPP was destroyed by high concentration of ·OH radicals, a heterogeneous kinetics model based on a Langmuir type mechanism was applied (37). This model is given by the following equation (37):

$$r = \frac{k\ K\ C_{4-IPP}}{1 + K\ C_{4-IPP}} \quad (6)$$

where r is the initial degradation rate ($M\,min^{-1}$), k is the pseudo-rate constant ($M\,min^{-1}$), K is the equilibrium constant (M^{-1}), and C_0 (M) is the 4-IPP initial concentration.

The sonolytic degradation data was analyzed by a nonlinear curve-fitting analysis method, using Microcal™ Origin® software, to fit the kinetic model. The value of the model parameters are $23.715 \pm 2.064\,mM^{-1}$ and $4.793 \pm 0.091\,\mu M\,min^{-1}$ for the equilibrium constant (K) and the pseudo-rate constant (k), respectively. An excellent description of the sonolytic destruction of 4-IPP was obtained by the used model as shown in Fig. 3. These results indicate that the sonochemical degradation of 4-IPP occurs mainly at the interfacial region of cavitation bubbles by hydroxyl radical attack.

Effect of Bicarbonate Concentration on 4-IPP Degradation

Ultrasonic degradation of 4-IPP was studied in the presence of various concentrations of bicarbonate ($30–1000\,mg\,L^{-1}$ of $NaHCO_3$). The pH of 4-IPP solutions will be imposed by bicarbonate ion that is an amphoteric substance and, in all the used concentration range, the solution pH was around 8.3. The effect of bicarbonate concentration on the sonochemical degradation of 4-IPP at various initial substrate concentrations ranging from $10\,\mu g\,L^{-1}$ to $100\,mg\,L^{-1}$ was investigated. The obtained results for three different concentrations of 4-IPP ($10\,\mu g\,L^{-1}$, 0.1 and $1\,mg\,L^{-1}$) are shown in Fig. 4. At a concentration of 4-IPP of $1\,mg\,L^{-1}$, addition of bicarbonate ion had no significant effect on the degradation rate of 4-IPP. At lower 4-IPP concentrations, the rate of 4-IPP decomposition was significantly improved by the addition of bicarbonate. For the lowest 4-IPP concentration, the initial rate of degradation in presence of $1000\,mg\,L^{-1}$ of $NaHCO_3$ is 4.4 times greater than that without bicarbonate. The improvement of 4-IPP destruction is due to the formation of the carbonate radical (reaction (7)), which may react more effectively than the ·OH radical with substrate molecules.

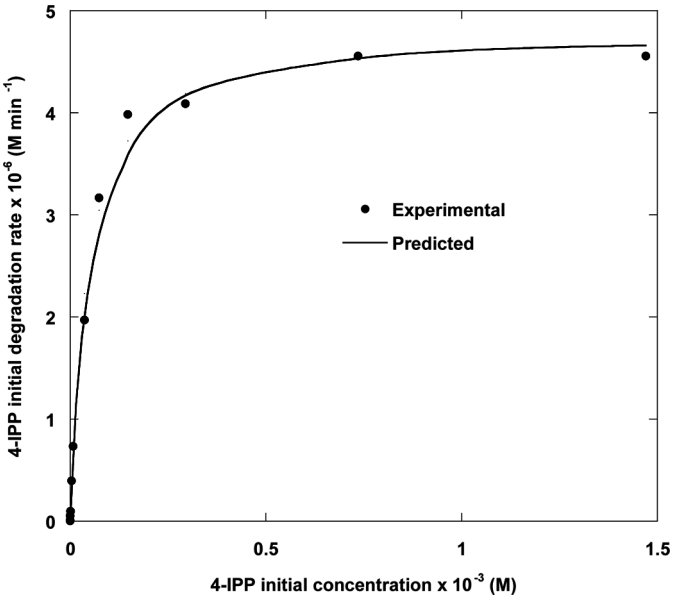

FIG. 3. Comparison of experimental and predicted initial degradation rates at various initial concentrations of 4-IPP.

Bicarbonate ions react with hydroxyl radicals with second-order rate constant of $8.5 \times 10^6\,M^{-1}\,s^{-1}$ (38). This reaction leads to the formation of the carbonate radical ($CO_3^{\cdot-}$) (reaction (7)). For many years, by analogy to the carbonate and bicarbonate anions, it was assumed that this radical normally exists as the protonated form ($HCO_3^{\cdot}$) in the neutral to basic pH range, but it is now firmly established that no protonation of $CO_3^{\cdot-}$ (reaction (8)) could be observed in the pH range of 0–10 (39), which leaves $CO_3^{\cdot-}$ as the only relevant carbonate radical species to be considered in this study. This radical is a strong one-electron oxidant (1.78 (40) and 1.59 V (41) vs. SHE at pH 7.0 and 12.5 respectively).

$$HCO_3^- + {}^{\cdot}OH \rightarrow CO_3^{\cdot-} + H_2O \qquad k_8 = 8.5 \times 10^6\,M^{-1}\,s^{-1} \quad (7)$$

$$HCO_3^{\cdot} \rightarrow CO_3^{\cdot-} + H^+ \quad pKa < 0 \quad (8)$$

From Fig. 4, it was also observed that as the concentration of 4-IPP increases, the intensification effect of bicarbonate ions decreases. Additionally, for 4-IPP concentrations higher than $1\,mg\,L^{-1}$ (figure not shown), bicarbonate ions had a slightly negative effect on the removal of 4-IPP. Thus, the enhancement of 4-IPP degradation in aqueous solutions containing bicarbonate occurs only at low 4-IPP concentrations.

The presence of salts during sonication of aqueous solutions may induce a salting out effect that pushes organic pollutants toward the bubble–bulk solution interface and, therefore, leads to a higher degradation rate. Additionally, the addition of salts may increase the hydrophobicity, the surface tension, and ionic strength of the aqueous phase and decrease the vapor pressure (30). All these factors help

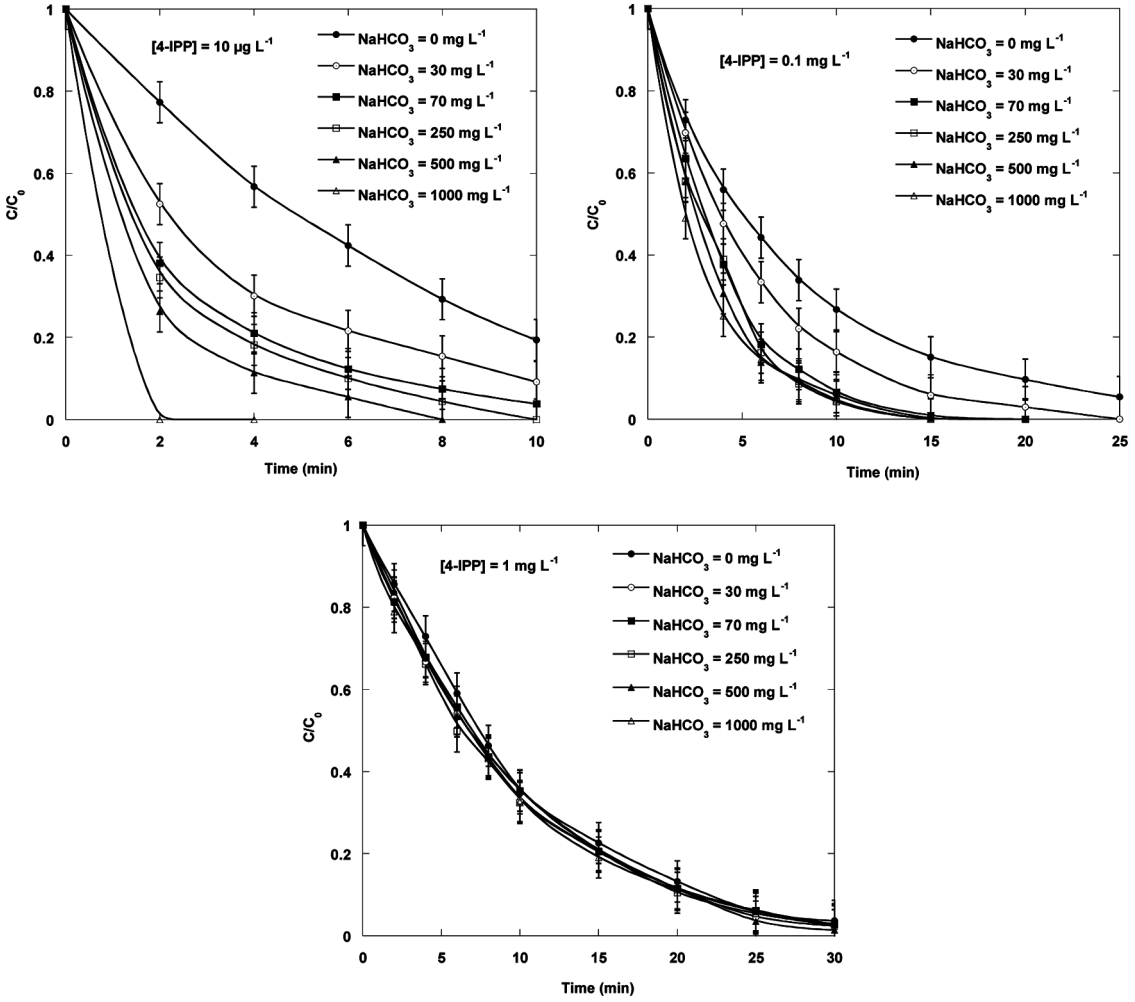

FIG. 4. Effect of bicarbonate concentration on the sonochemical degradation of 4-IPP at various initial concentrations (conditions—Frequency: 278 kHz; power: 80 W; volume: 300 mL; pH: 8.3; temperature: $20 \pm 1^{\circ}C$).

in collapsing of the bubbles more violently, resulting in high degradation of the substrate for all the tested 4-IPP concentrations. This was not true in the present work because the addition of bicarbonate had a negative effect on the destruction rate for higher 4-IPP concentrations. Moreover, the addition of sodium sulfate in the same concentration range (30–1000 mg L^{-1}) had no significant impact on the degradation rate that excludes salting effect.

The enhancement of the degradation rates observed for the lower concentrations of 4-IPP should involve the presence of the carbonate radical ($CO_3^{\cdot-}$) coming from the reaction of bicarbonate ion with ·OH diffused from the cavitation bubble. For a lower concentration of 4-IPP, the combination of ·OH radical (reaction (9), $k_{10} = 5.5 \times 10^9\ M^{-1}\ s^{-1}$) is dominant, but in the presence of bicarbonate, the formation of $CO_3^{\cdot-}$ radical that is less reactive than ·OH radical, minimizing the combination of $CO_3^{\cdot-}$ that decays by reacting with itself according to reaction (10) or (11) ($k_{10,11} = 2 \times 10^7\ M^{-1}\ s^{-1}$). The substitution of ·OH with $CO_3^{\cdot-}$ could enhance degradation if the latter, although less reactive than ·OH, undergoes radical-radical recombination at a lesser extent than the hydroxyl radical. The combination of ·OH is known to be 275 times higher than that of the reaction of $CO_3^{\cdot-}$ with itself.

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad k_9 = 5.5 \times 10^9\ M^{-1}\ s^{-1} \tag{9}$$

$$CO_3^{\cdot-} + CO_3^{\cdot-} \leftrightarrow C_2O_6^{2-} \rightarrow CO_4^{2-} + CO_2 \qquad k_{10} = 2 \times 10^7\ M^{-1}\ s^{-1} \tag{10}$$

$$CO_3^{\cdot-} + CO_3^{\cdot-} \xrightarrow{H_2O} 2CO_2 + HO_2^- + OH^- \qquad k_{11} = 2 \times 10^7\ M^{-1}\ s^{-1} \tag{11}$$

At higher 4-IPP concentrations, the slight negative effect of bicarbonate ions on the rate of substrate destruction may be due to the much slower formation of carbonate radical, because of the differences of the reaction rate. In this case, the ·OH radicals generated in the bubble, which can diffuse into the bulk solution are intercepted by 4-IPP molecules. However, the presence of inorganic salts could have a minor detrimental effect on the phenomenon of cavitation. Taking into account the results of the present work, it can be concluded that the addition of bicarbonate had a significant concentration dependant effect on the rate of degradation at lower 4-IPP concentrations. The lower the concentration of 4-IPP is, the higher the positive effect of bicarbonate ions on the destruction rate is.

4-IPP Degradation in Sucrose Solution

Influence of sucrose on the sonolytic degradation of 4-IPP solution at $10\,\mu g\,L^{-1}$ was studied. Addition of sucrose as an organic matrix, in the range 100–1000 $mg\,L^{-1}$, for an identical pH (6.5) had no significant effect on the degradation rate of 4-IPP (Fig. 5). This behavior is due to the very low Henry's law constant (4.47×10^{-22} atm $m^3\,mol^{-1}$) of sucrose compared to that of 4-IPP (1.09×10^{-6} atm $m^3\,mol^{-1}$). Additionally, sucrose has a very high solubility in water ($2.12 \times 10^6\,mg\,L^{-1}$) and extremely low octanol/water partition coefficient (log $K_{OW} = -3.7$) in comparison with those of 4-IPP (water solubility $= 1.10 \times 10^3\,mg\,L^{-1}$, log $K_{OW} = 2.9$). Therefore, because the degradation of 4-IPP takes place at the interface of the cavitation bubbles by ·OH radicals generated by ultrasound, the destruction of 4-IPP was not influenced by sucrose that cannot be accumulated in the bubble-liquid bulk interface. These results confirmed the significance of interfacial reactions in the destruction pathway of 4-IPP by hydroxyl radicals.

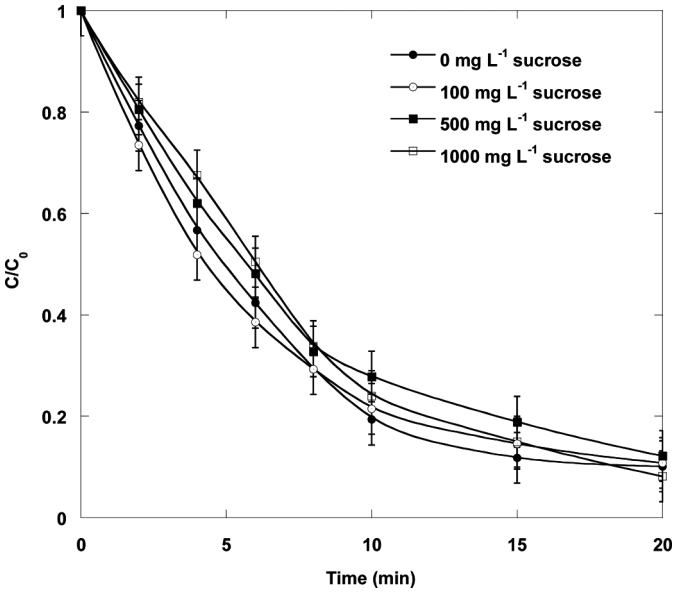

FIG. 5. Effect of sucrose on the sonochemical degradation of 4-IPP at $10\,\mu g\,L^{-1}$ (conditions—Frequency: 278 kHz; power: 80 W; volume: 300 mL; pH: natural (6.5); temperature: $20 \pm 1°C$).

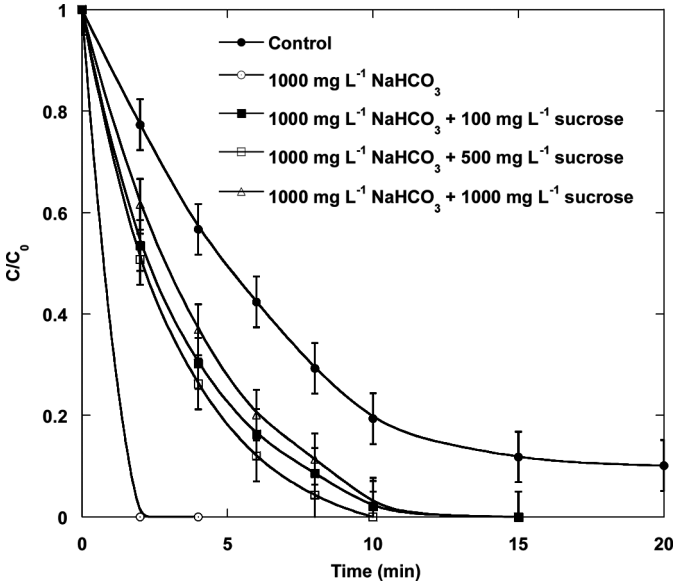

FIG. 6. Effect of sucrose on the sonochemical degradation of 4-IPP at $10\,\mu g\,L^{-1}$ in the presence of $1000\,mg\,L^{-1}$ of $NaHCO_3$ (conditions—Frequency: 278 kHz; power: 80 W; volume: 300 mL; pH: 8.3; temperature: $20 \pm 1°C$).

The sonolytic degradation of 4-IPP solution containing bicarbonate ions was investigated in the presence of sucrose (Fig. 6). It was observed that the enhancement effect of bicarbonate on the sonolytic degradation of the substrate was diminished in the presence of sucrose, but it is faster than that obtained in the absence of bicarbonate (control). Thus, the degradation by carbonate radical occurring in the solution bulk is slowed down in the presence of sucrose by scavenging carbonate radicals in the liquid bulk. Finally, the degree of scavenging of sucrose was much larger in the presence of carbonate radical than hydroxyl radical, showing the significance of interfacial reactions in the destruction pathway of 4-IPP by hydroxyl radical, while the degradation by carbonate radical occurs in the liquid bulk.

CONCLUSION

This work demonstrates the potential of ultrasonic irradiation for the removal of endocrine disrupting pollutant 4-IPP, even in complex matrices: bicarbonate ion as inorganic matrix and sucrose as organic competitor.

The initial concentrations of 4-IPP were varied from $5\,\mu g\,L^{-1}$ to $200\,mg\,L^{-1}$ to analyze the reaction kinetics. The degradation rate increases with increasing initial

4-IPP concentration up to a plateau at $100\,mg\,L^{-1}$. These results were reasonably well explained with a Langmuir type mechanism.

At low 4-IPP concentration, the destruction of the pollutant in the presence of bicarbonate ions is drastically intensified because of the formation of carbonate radical resulting from the reaction of ultrasonically generated hydroxyl radical with bicarbonate ion. Degradation improvement occurs because carbonate radicals sonochemically formed on the surface of the collapsing cavitation bubbles undergo radical-radical recombination at a lesser extent than hydroxyl radicals. The generated carbonate radicals are likely able to migrate from the cavitation bubbles towards the bulk of the solution to degrade the pollutant.

In the presence of a large excess of sucrose as organic competitor, the sonochemical degradation of 4-IPP at low concentration, occurring mainly through reactions with hydroxyl radicals, was not affected. In the presence of bicarbonate, the degradation by carbonate radical taking place in the solution bulk was slowed down in the presence of sucrose by scavenging carbonate radicals in the liquid bulk. The degree of scavenging of sucrose was much larger in the presence of the carbonate radical than hydroxyl radical. Therefore, ultrasonic treatment represents a very interesting AOP for the removal of 4-IPP in complex matrices.

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