

Bisphenol A Mineralization by Integrated Ultrasound-UV-Iron (II) Treatment

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Bisphenol A (BPA), an organic compound largely used in the plastic industry as a monomer for production of epoxy resins and polycarbonate, is an emerging contaminant that is released in the environment from bottles and packaging. BPA degradation ($118 \mu\text{mol L}^{-1}$) under sonochemical conditions was investigated in this study, using a 300 kHz frequency, with a 80 W electrical power. Under these conditions, BPA was eliminated by the ultrasound process (~ 90 min). However, even after long ultrasound irradiation periods (10 h), more than 50% of chemical oxygen demand (COD) and 80% of total organic carbon (TOC) remained in the solution, indicating that most BPA intermediates are recalcitrant toward ultrasonic action. Accumulation of hydrogen peroxide from $^{\circ}\text{OH}$ and $^{\circ}\text{OOH}$ radical recombination was also observed. To increase the efficiency of BPA treatment, experiments combined ultrasound with Fe^{2+} ($100 \mu\text{mol L}^{-1}$) and/or UV radiation (254 nm): Ultrasound/UV; Ultrasound/ Fe^{2+} ; Ultrasound/UV/ Fe^{2+} . Both UV and Fe^{2+} induced hydrogen peroxide dissociation, leading to additional $^{\circ}\text{OH}$ radicals and complete COD and TOC removal. Thus difficulties in obtaining mineralization of micropollutants like BPA through ultrasonic action alone, can be overcome by the Ultrasound/UV/ Fe^{2+} combination. Moreover, this technique was found to be the most cost-effective one. So, the integrated ultrasound-UV-iron(II) process was shown to be of interest for the treatment of wastewaters contaminated with BPA.

1. Introduction

Several micropollutants of water, suspected to interfere with hormone action, present endocrine disrupting effect (EDE) in aquatic organisms and micro-organisms (1–2). In addition to synthetic hormones and pesticides, several endocrine

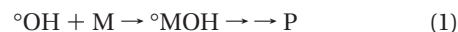
disrupting compounds (EDC) found in natural water come from industrial wastes. Bisphenol A [BPA: 2,2-bis(4-hydroxyphenyl)propane], an organic compound largely used in the plastic industry as a monomer for production of epoxy resins and polycarbonate, is a xenobiotic that can be released in the environment from bottles, packaging, landfill leachates, paper, and plastics plants (3–5). This compound disturbs the behavior of aquatic life by EDE at low level concentrations (6–7). To some extent, BPA can be eliminated through traditional physical, chemical, or biological treatments (8–11). Nevertheless, because of its estrogenic action, and the fact that chlorination disinfection processes can lead to products with higher EDE and/or toxicity (11–13), BPA should be completely removed from wastewater and water sources.

Physicochemical methods, based on the production and use of hydroxyl radical called advanced oxidation processes (AOPs) (e.g., $\text{H}_2\text{O}_2 + \text{UV}$, $\text{UV} + \text{O}_3$, $\text{H}_2\text{O}_2 + \text{O}_3$, TiO_2 photocatalysis, Fenton's reagent, photo-Fenton), have been successfully tested for elimination of aromatic compounds (14). However, the methods often conduct to secondary products that are not significantly eliminated by the same technique, or can be more hazardous than the original compound (15). Thus, a complete mineralization is rarely reached and is not cost-effective (16).

It has long been recognized that propagation of an ultrasonic wave in aqueous medium results in hydrogen peroxide formation and organic or inorganic structure oxidation (17). In 1982, it was shown that $^{\circ}\text{OH}$ radical is the oxidative reagent involved in these reactions (18). Based on these results, subsequent studies have shown the development of the technique for elimination of organic contaminants present in water (19).

Central events of the ultrasonic action are the bubbles of cavitation that can be considered as microreactors that grow, pulsate, and collapse. Compression of an ultrasonic cavitation bubble that pulsates or collapses occurs adiabatically on a microsecond time scale (20), leading to the formation of a hot nucleus with temperatures reaching thousands of degrees and pressure in hundreds of atmospheres (21–22).

Under such conditions molecules trapped in the bubble (water and solute vapors), can be brought to an excited-state and dissociate. Consequently, an organic pollutant with high fugacity character (high value of Henry's Law constant) will be incinerated in the bubble (23–24). A hydrophilic or hydrophobic compound with low volatility cannot enter the bubble, but will be hydroxylated in the bulk solution or interfacial area by reaction with $^{\circ}\text{OH}$ radicals (25–26):



This reactive species, generated inside the bubble, comes from H_2O and O_2 dissociation and associate reactions (24):



Ultrasonic action can be affected in several ways. Frequency, power, and nature of the dissolved gas(es) have important effects on reaction product distribution and reaction rate (27–29). Furthermore, previous studies have demonstrated that the addition of chemicals, such as iron ions or ozone,

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or combination with UV radiation, can amplify ultrasonic action (30–31).

The aim of this work was to evaluate BPA elimination and mineralization under sonochemical conditions. Additionally, the combination of ultrasound with UV irradiation and Fe(II) addition were investigated. For the combinations tested, an economical estimation as a function of total organic carbon (TOC) removal was also presented.

2. Experimental

2.1. Reagents. Bisphenol A, ferrous sulfate, potassium iodide, ammonium heptamolybdate, sodium chromate, and sodium hydroxide were obtained from Sigma-Aldrich (St. Louis, MO). Silver sulfate, potassium dichromate, and sulfuric acid were supplied by Acros Organics (New Jersey). Phosphoric acid, sodium persulphate, and potassium hydrogen phthalate were obtained from Prolabo (VWR International). Acetonitrile (HPLC gradient grade), and catalase were purchased from Fisher Scientific (Loughborough, UK), and Merck (Darmstadt, Germany), respectively. Osmotic flow modifier (OFM–OH[−]) for capillary electrophoresis was provided by Waters (St. Quentin en-Yvelines, France). All chemicals were used without any further purification. Deionized 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).

2.2. Apparatus. Experiments were performed in a cylindrical water-jacketed glass reactor with a Teflon holder. Ultrasonic waves (300 kHz, 80 W) were emitted from the bottom of the reactor through a piezo-electric disc (diameter 4 cm) fixed on a Pyrex plate (diameter 5 cm) (28). Energy dissipated in the reactor was measured by the calorimetric method (32). A low-pressure mercury lamp (Pen-Ray Lamps Group, 25 W) emitting at a predominant wavelength of 254 nm provided UV radiation. The UV photon flux entering the reactor (1.5×10^{-6} einstein s^{−1}) was determined using uranyl oxalate actinometry (33).

Experiments were performed with 300 mL of Bisphenol A $118 \mu\text{mol L}^{-1}$. This value was selected in order to use a representative concentration of industrial wastewater contaminated with BPA. A gas cylinder was used for bubbling air or oxygen through the solution at least 45 min prior to start and until completion of experiments. The reactor was sampled periodically for TOC, HPLC, HPLC coupled to mass spectrometry (HPLC/MS), capillary electrophoresis, chemical oxygen demand (COD), and hydrogen peroxide analyses.

2.3. Analyses. The BPA mineralization (TOC removal) was followed in a LABTOC analyzer using a solution of potassium phthalate as the calibration standard. Quantitative analysis of the parent compound was done by HPLC in a Waters Associates 590 instrument with a Supelcosil LC-18 column (ID = 4.6 mm, length = 250 mm) and UV detector (model 440) set at 254 nm. The mobile phase, water/acetonitrile (50/50, v/v), was run in an isocratic mode. Using this methodology, a detection limit of $0.002 \mu\text{mol L}^{-1}$ of BPA was reached. Identification of primary BPA intermediates was made by HPLC/MS through a Hewlett-Packard series 1100 MSD with electrospray ionization.

Chemical oxygen demand, COD, was carried out according to the method presented previously by Thomas and Mazas (34). In order to avoid the interference of the residual hydrogen peroxide, samples were neutralized with sodium hydroxide and treated with catalase prior to COD analysis (35).

Hydrogen peroxide concentrations were determined iodometrically (36). Nitrite and nitrate ions were measured with a Waters Capillary Ion Analyzer from Millipore, using

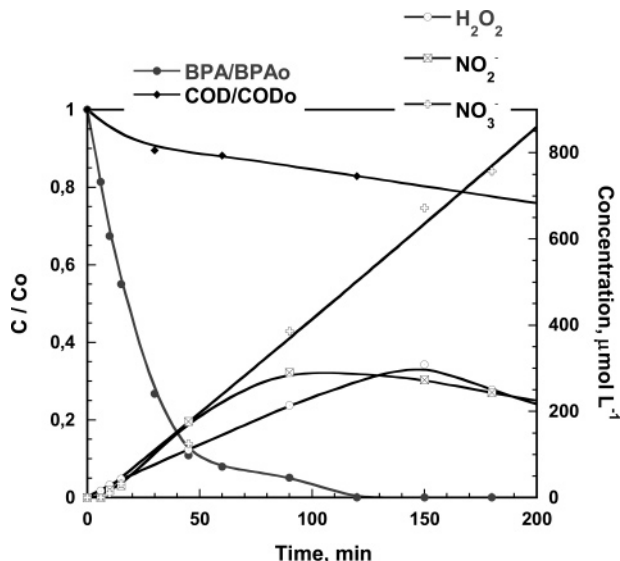


FIGURE 1. BPA ($118 \mu\text{mol L}^{-1}$) elimination, chemical oxygen demand (68 mg L^{-1}), H_2O_2 , NO_2^- , and NO_3^- evolution during ultrasonic treatment of an aerated solution. Frequency: 300 kHz; power: 80W; volume: 300 mL; natural pH; temperature: $20 \pm 1^\circ\text{C}$.

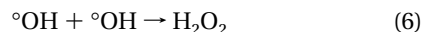
a solution of chromate and OFM–OH[−] (4.6 and 0.5 mmol L^{−1}, respectively) as electrolyte.

3. Results and Discussion

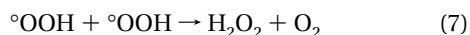
3.1. Characteristics of BPA Sonolysis. Application of 300 kHz ultrasound irradiation to 300 mL of an aerated BPA solution ($118 \mu\text{mol L}^{-1}$) resulted in the decline of the initial concentration (Figure 1). Although ultrasonic treatment eliminated BPA in less than 120 min, it conducted only to a small decrease of the oxidizable organic matter. In fact, when BPA was destroyed, only 17% of COD had been removed, and, even at the end of treatment (7 h), more than 50% of initial COD remained in solution.

As generally evidenced during aqueous sonolysis of organic compounds for aerated medium, ultrasonic treatment of BPA solution is associated with hydrogen peroxide, nitrite, and nitrate ion production (24) (Figure 1). Different sources of hydrogen peroxide include:

- Recombination of $^{\circ}\text{OH}$ radicals that do not encounter the target molecule at the interface of the bubble (28, 37):



- Perhydroxyl combination at the interface of the bubble (37):



$^{\circ}\text{OOH}$ presents a lower rate constant than $^{\circ}\text{OH}$ toward organic compounds and cannot be involved in the BPA decay. It comes from the reaction between the hydrogen atom and molecular oxygen occurring in the cooler aqueous layer of water surrounding the cavitation bubble (38), as follows:



Nitrite and nitrate ion generation under ultrasound action of aerated water has been largely investigated (39–40). NO, the primary product of the process, should be formed at high temperature inside the bubbles according to the reactions 3, 9, and 10. Reactions 11 and 12 at the interface conduct to NO_2^- releases in the medium



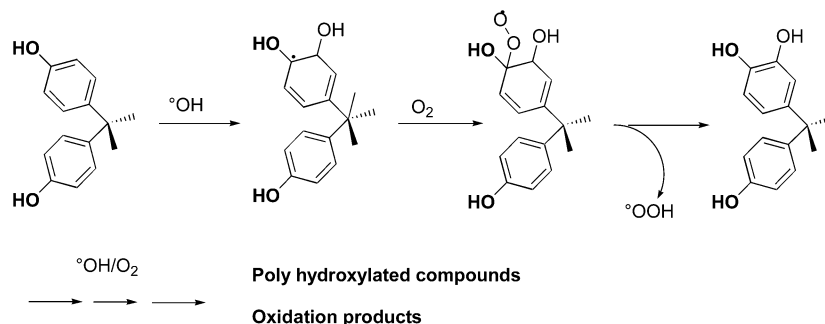


FIGURE 2. Monohydroxylated BPA formation and perhydroxyl generation from BPA reaction with °OH radical in oxygenated medium.

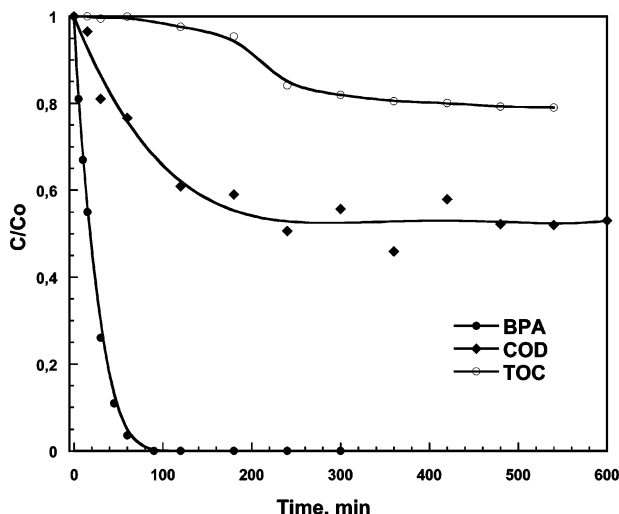
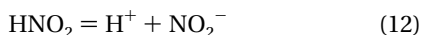
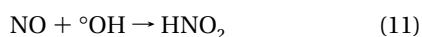
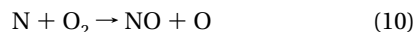
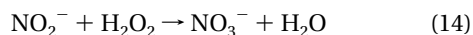


FIGURE 3. BPA ($118 \mu\text{mol L}^{-1}$) elimination, chemical oxygen demand (68 mg L^{-1}), and total organic carbon (21.2 mg L^{-1}) evolution during ultrasonic treatment of a solution saturated with oxygen. Frequency: 300 kHz ; power: 80W ; volume: 300 mL ; pH: 3 ; temperature: $20 \pm 1 \text{ }^\circ\text{C}$.



As shown in Figure 1, both nitrite ion and hydrogen peroxide concentrations increased, reaching a maximum at 90 and 150 min, respectively. The simultaneous concentration decrease can be attributed to the oxidation of nitrites by hydrogen peroxide (41):



As a result, nitrate ions accumulated in the reactor reached a concentration of approximately $760 \mu\text{mol L}^{-1}$ after 180 min, and pH values decreased from 6.6 to 3 after 120 min. The pK_a value of BPA being given between 9.6 and 10.2 (42), the compound is present in its neutral form during the whole course of the treatment.

Analysis of the reaction products and reaction pathways was out of the scope of this study, but a short HPLC/MS investigation resulted in the identification of several hydroxylated products—monohydroxylated BPA [2-(4-hydroxyphenyl)-2-(3',4'-dihydroxyphenyl)propane] and dihydroxylated BPA [2-(4-hydroxyphenyl)-2-(3',4',5'-trihydroxyphenyl)propane]—as primary products of the reaction. The formation of these products is in accordance with

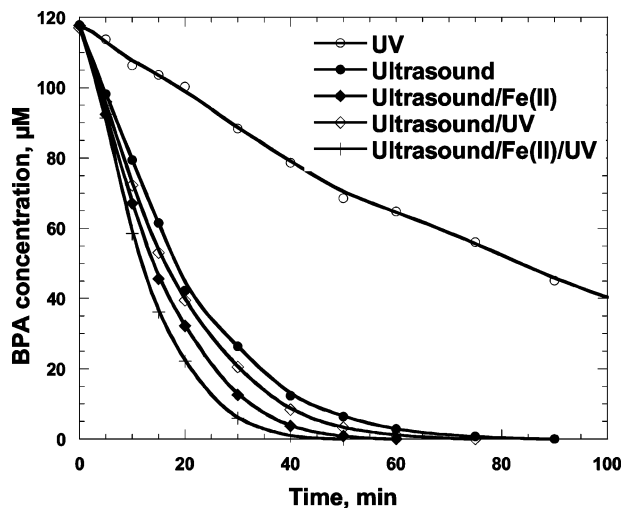


FIGURE 4. BPA ($118 \mu\text{mol L}^{-1}$) elimination by different AOPs applied to solutions saturated with oxygen. Volume: 300 mL ; pH: 3 ; temperature: $20 \pm 1 \text{ }^\circ\text{C}$. Ultrasound: $300 \text{ kHz}/80\text{W}$; UV irradiation: 254 nm ; $[\text{Fe(II)}]_0$: $100 \mu\text{mol L}^{-1}$.

previous studies establishing the hydroxylation of nonvolatile organic compounds subjected to an ultrasonic irradiation (25–26). Presence of these hydroxylated compounds, that are also generated in the treatment of BPA by the Fenton's reagent (42) suggests a competition between reactions 1 and 6 at the interface of the bubble. Figure 2, shows the initial step of the Bisphenol A degradation during the sonochemical action. As can be seen, perhydroxyl radicals can be also formed (42, 43) which, as indicated in reaction 7, recombine to produce additional H_2O_2 .

3.2. BPA Degradation in Water Saturated with Oxygen.

Although BPA degradation in aerated solution appears efficient, the oxidation of organic matter is relatively slow. Such observations are in accordance with previous studies, and point to the low efficiency of ultrasonic treatment for mineralization of organic matter.

In the high-frequency range, it has been shown that oxygen appears to give better results than air for organic compound elimination (44). Enhancement from the substitution of oxygen for air has been tested for TOC and COD removal. Oxygen use in sonochemical treatment is justified not only for best performance concerning BPA elimination, but also because this gas precludes the formation of the undesirable NO_x^- species.

Substitution of oxygen for air results in faster BPA elimination. With oxygen, the BPA detection limit is reached in less than 90 min, instead of 120 min obtained in the case of the aerated medium (Figure 3). COD evolution follows decrease of BPA concentration, with a plateau: $\text{COD}/\text{COD}_0 = 0.5$ at 200 min. TOC reduction is low and proceeds in two steps: 5% abatement is obtained at 180 min, and is followed

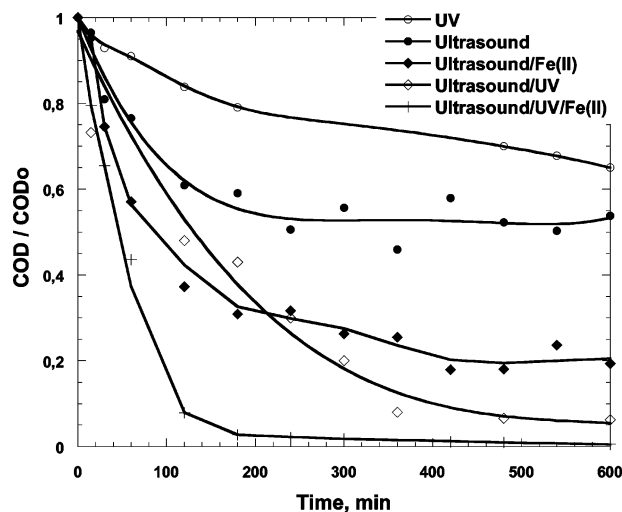


FIGURE 5. Chemical oxygen demand (68 mg L^{-1}) abatement by different AOPs applied to solutions saturated with oxygen. $[\text{BPA}]_0$: $118 \mu\text{mol L}^{-1}$; volume: 300 mL ; pH: 3; temperature: $20 \pm 1 \text{ }^\circ\text{C}$. Ultrasound: $300 \text{ kHz}/80\text{W}$; UV irradiation: 254 nm ; $[\text{Fe(II)}]_0$: $100 \mu\text{mol L}^{-1}$.

by a sharper decrease to reach a plateau (85% TOC remaining) at 300 min.

These results underline the fact that degradation products of BPA are recalcitrant toward sonochemical treatment. The formation of hydroxylated intermediates with higher hydrophilic character (Figure 2) explains the low efficiency of the ultrasonic action for COD and TOC removal. Several works have clearly evidenced that, in water sonochemistry, the efficiency of the $^\circ\text{OH}$ radical scavenging of an organic compound is related to its hydrophobicity (37, 45–46). In other words, hydrophobic organic compounds accumulate at the interface of the bubble. Thus, the low abatement of COD and TOC in the ultrasonic treatment of BPA could be explained by formation of hydrophilic products, which stay in the bulk solution and do not accumulate at the interface (47). These products have very low probabilities of making contact with $^\circ\text{OH}$ radicals, which react mainly at the interface of the bubble (reactions 1 and 6). Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency toward TOC and COD abatement.

In order to increase the efficiency of oxidation and mineralization, ultrasound action can be combined with different oxidation processes: ozone, TiO_2 photocatalysis, UV radiation, H_2O_2 , and Fe^{2+} (30–31, 48). As hydrogen peroxide is found to accumulate during BPA elimination, improvement of the mineralization was evaluated under ultrasound action combined with Fe^{2+} and/or UV irradiation.

3.3. Ultrasonic Degradation of BPA Coupled to UV Radiation and/or Fe(II). Comparisons were conducted under similar experimental conditions: O_2 saturated solutions and pH adjusted to 3 with sulfuric acid, in order to avoid iron precipitation as iron hydroxide. Ultrasonic treatment was operated with the same conditions (80 W and 300 kHz). For the combined techniques, a low-pressure mercury lamp (254 nm) and/or $100 \mu\text{mol L}^{-1}$ FeSO_4 were used.

Figure 4 shows BPA decay under ultrasound or UV irradiation and by the combination of the processes. Efficiency was found to follow the order: $\text{UV} \ll \text{Ultrasound} < \text{Ultrasound}/\text{UV} < \text{Ultrasound}/\text{Fe}^{2+} < \text{Ultrasound}/\text{UV}/\text{Fe}^{2+}$. After 30 min, 95% of BPA was degraded using the Ultrasound/UV/Fe(II) system, whereas 89% was eliminated with Ultrasound/Fe(II), 82% with Ultrasound/UV, 77% with Ultrasound, and only 25% with UV. For all processes after 75 min approximately 100% of BPA was eliminated, except for UV

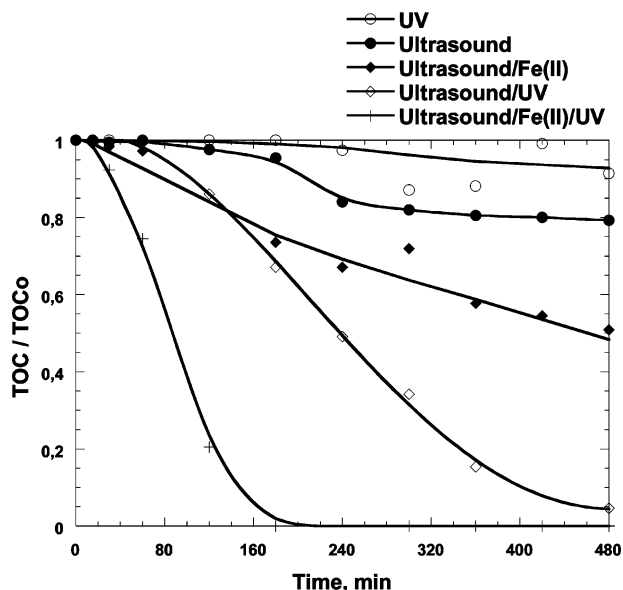


FIGURE 6. Total organic carbon (21.2 mg L^{-1}) abatement by different AOPs applied to solutions saturated with oxygen. $[\text{BPA}]_0$: $118 \mu\text{mol L}^{-1}$; volume: 300 mL ; pH: 3; temperature: $20 \pm 1 \text{ }^\circ\text{C}$. Ultrasound: $300 \text{ kHz}/80\text{W}$; UV irradiation: 254 nm ; $[\text{Fe(II)}]_0$: $100 \mu\text{mol L}^{-1}$.

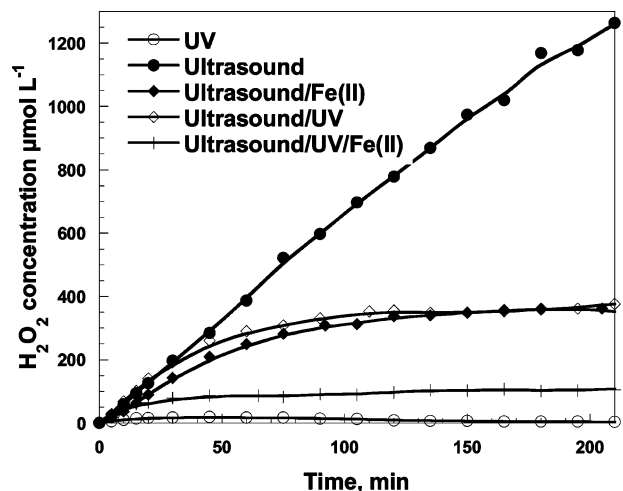
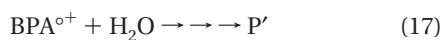
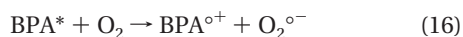


FIGURE 7. Evolution of hydrogen peroxide generated by different AOPs applied to water saturated with oxygen. Volume: 300 mL ; pH: 3; temperature: $20 \pm 1 \text{ }^\circ\text{C}$. Ultrasound: $300 \text{ kHz}/80\text{W}$; UV irradiation: 254 nm ; $[\text{Fe(II)}]_0$: $100 \mu\text{mol L}^{-1}$.

treatment where approximately 50% remained in solution. In the latter case, 240 min are necessary to obtain almost complete elimination of the initial molecule (data not shown). The poor degradation attained by UV treatment was not unexpected, because of the low BPA molar absorption coefficient at 254 nm (49). Combinations exhibit considerable enhancement in oxidation and mineralization of organic matter. COD and TOC can be completely removed from the medium when ultrasound is combined with UV and Fe^{2+} (Figures 5 and 6).

The control experiment, conducted under the sole UV irradiation in a well-stirred reactor, displays a low effect on the amount of organic carbon dissolved in the medium. The combination of the same light source with ultrasound initiates a complete elimination of the COD and TOC that cannot result from the simple addition of the two processes. UV irradiation can induce BPA degradation through photodecomposition or photooxidation (reactions 15–17) (50)



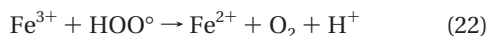
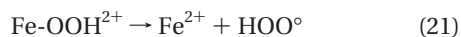
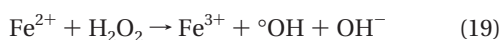


Under the conditions in the study, this process showed limited elimination of COD and TOC. However, complete mineralization was observed when ultrasonic treatment was combined with UV irradiation. This may result from the photodecomposition, at 254 nm, of hydrogen peroxide produced by ultrasound. At this wavelength, H_2O_2 absorbs radiation with a molar absorption coefficient of $18.6 \text{ L mol}^{-1} \text{ cm}^{-1}$. It decomposes with a quantum yield of 0.98, generating $^{\circ}\text{OH}$ radical (eq 18) (50)



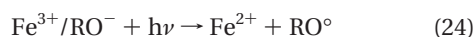
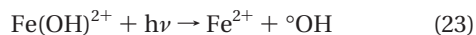
Indeed, adding UV irradiation to ultrasound action maintains the hydrogen peroxide at a low level (Figure 7). The extra $^{\circ}\text{OH}$ radicals photochemically formed in bulk react mainly with the products of ultrasonic and photochemical action (more hydrophilic or with lower absorption coefficient than BPA), resulting in complete mineralization of the organic matter.

Enhancement of mineralization can also be realized by Fe(II) addition in a catalytic amount. This combination results in H_2O_2 decomposition and $^{\circ}\text{OH}$ generation in the Fenton {Fe(II)/ H_2O_2 } (15), and Fenton-like {Fe(III)/ H_2O_2 } processes (reactions 19–22) (51–52)



If reaction 19 proceeds at a high rate, reduction of Fe(III) to Fe(II) by hydrogen peroxide occurs at a lower rate. Then, levels of oxidation and mineralization are higher than the levels observed in the case of ultrasound alone, but elimination does not come to completion.

Efficiency of the overall process can be improved by UV irradiation in a photoassisted Fenton reaction. This enhancement is explained by H_2O_2 photodecomposition, as mentioned above, but also by photolysis of the Fe(III) hydroxide complex $\text{Fe}(\text{OH})^{2+}$, producing additional $^{\circ}\text{OH}$ radicals, or photolysis of complexes {Fe(III)-organic ligand}. The organic ligand can be an intermediate of degradation such as an organic acid (reactions 23, 24) (53–55). These photochemical reactions regenerate Fe(II),



The Fe(II) regenerated reacts with H_2O_2 (reaction 19). As a result, almost all H_2O_2 formed by sonication is consumed (Figure 7). Like hydrogen peroxide photodissociation, Fenton and photoFenton reactions take place in the bulk of the solution, causing the mineralization of products that are resistant to ultrasound action.

3.4. Economical Evaluation of Processes. To assess an economical comparison of AOP employed, Bolton (56) proposed a figure-of-merit, the electric energy per order of pollutant removal (EE/O). EE/O is the electric energy in kilowatt-hours (kWh) required to invoke the degradation of a contaminant C by 1 order of magnitude in 1 m^3 (1000 L) of contaminated water, which can be calculated using

TABLE 1. Electric energy cost estimates for Bisphenol A degradation by various AOPs

process	BPA ($\mu\text{mol L}^{-1}$)	power (W)	volume (mL)	time (min)	% TOC removed	EE/O (kWh m^{-3})
UV	118	25	300	600	less than 60%	
ultrasound	118	80	300	600	less than 60%	
ultrasound/Fe(II)	118	80	300	600	64	6010
ultrasound/UV	118	105	300	300	66	3735
ultrasound/UV/Fe(II)	118	105	300	120	79	1033

$$\text{EE/O} = [P \times t \times 1000] / [V \times 60 \times \log(C_i/C_f)]$$

where P is the rated power (kW) of the AOP system, V is the volume (L) of water treated in the time t (min), and C_i and C_f are the initial and final concentrations of C, respectively.

The EE/O values for BPA mineralization with the different conditions are presented in Table 1. The following assumptions were made: (i) only energy cost was estimated, not the investment cost for chemicals, apparatus, or buildings, and (ii) only processes with more than 60% of TOC removal were considered. The EE/O value for the Ultrasound/UV/Fe(II) system, 1033 kWh m^{-3} , is four and six times lower than the Ultrasound/UV and the Ultrasound/Fe(II) treatment, respectively. Therefore, among all different processes tested in this study, the Ultrasound/UV/Fe(II) system presents the best cost-effective ratio for mineralization of BPA.

Acknowledgments

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Note Added after ASAP Publication. Due to a production error, the version published ASAP on November 17 contained an error in Table 1. The correct version was published ASAP on November 27, 2006.

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