



Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## Sequential helio-photo-Fenton and sonication processes for the treatment of bisphenol A

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## ARTICLE INFO

## Article history:

Received 7 January 2008

Received in revised form 14 May 2008

Accepted 19 May 2008

Available online 27 May 2008

## Keywords:

Endocrine-disrupting chemical

Bisphenol A elimination

Sonochemical degradation

Photo-Fenton

Water treatment

Advanced oxidation

## ABSTRACT

This paper demonstrates the coupling of ultrasound (300 kHz, 80 W) with Fe(II) to degrade the contaminant bisphenol A by a solar photo-assisted process carried out at natural pH ~ 5. An experimental design that allowed runs in batch (ultrasound → Fe<sup>2+</sup>/UV and Fe<sup>2+</sup>/UV → ultrasound) or in simultaneous (ultrasound/Fe<sup>2+</sup>/UV) modes was developed. To gain a better understanding of the phenomena involved in the systems, ultrasound, ultrasound/Fe<sup>2+</sup>, Fe<sup>2+</sup>/UV, and Fe<sup>2+</sup>/UV/H<sub>2</sub>O<sub>2</sub> (photo-Fenton) were also performed. After 4 h of treatment, 11%, 29%, and 70% of the initial total organic carbon had been removed by ultrasound, photo-Fenton, and ultrasound/Fe<sup>2+</sup>/UV, respectively. The synergistic effect can be explained by the complementarity of the two processes: ultrasound more effectively destroys the initial bisphenol A compound, whereas the photo-Fenton system is better able to eliminate the bisphenol A by-products. The influence of the type of saturating gas (oxygen or air) used was also investigated.

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### 1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA], a chemical compound used widely in industry as a monomer for the production of epoxy resins and polycarbonate, is an endocrine-disrupting compound that is released into the environment from bottles, packaging, landfill leachates, paper, and plastics plants [1–3]. Even at low-dose exposure, BPA induces feminization during the gonadal ontogeny of fishes, reptiles, and birds. Adult exposure to environmental concentrations of BPA is detrimental to spermatogenic endpoints and stimulates vitellogenin synthesis in model species of fish [4]. Due to its large consumption and adverse health effects on wildlife, BPA is one of the xenobiotic substances that has generated the greatest amount of interest and controversy during the past decade [4].

Advanced oxidation processes (AOPs), which are based on the production and use of the hydroxyl radical, have been tested for the elimination of BPA [5–9]. However, these procedures sometimes result in secondary products that are not eliminated significantly by the same technique or that may be more hazardous than the original compound [9,10].

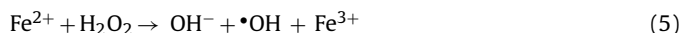
Ultrasonic treatment as an AOP is considered particularly efficient for the breakdown of volatile and nonpolar compounds. In this process, •OH radicals are generated by acoustic cavitation, which is defined as the cyclic formation, growth, and collapse of microbubbles. The fast collapse of bubbles adiabatically compresses gas and entrapped vapor, which produces small local hot spots [11]. At the final step of the bubble collapse, the temperature inside the residual bubble is thought to be >2000 K. Under these conditions, entrapped molecules of dissolved gases, vaporized water, and solutes can be brought to an excited state and dissociate. As a result, a volatile organic compound will be pyrolysed in the bubble [12,13]. A non-polar compound with low volatility will be hydroxylated at the bubble-bulk solution interface, and, to a lesser extent, a hydrophilic compound will react with •OH radicals in the bulk solution. During the sonication of water, •OH radicals are generated from water and oxygen dissociation according to the following reactions [13]:



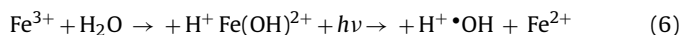
During the ultrasonic treatment a high fraction of •OH radicals that cannot reach the target compound recombine to produce hydrogen peroxide.

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The Fenton reaction is another AOP that has been used with great success to treat a wide variety of contaminants [14,15]. In this homogenous process,  $\bullet\text{OH}$  radical formation can be outlined as follows:



The photoassisted Fenton reaction (photo-Fenton) is a strongly enhanced version of the Fenton process. The positive effect of irradiation on the degradation rate is due to the photochemical regeneration of ferrous ions ( $\text{Fe}^{2+}$ ) by the photoreduction of ferric ions ( $\text{Fe}^{3+}$ ), with the production of additional  $\bullet\text{OH}$  radicals [16]:



The newly generated ferrous ion reacts with  $\text{H}_2\text{O}_2$  to produce a second  $\bullet\text{OH}$  radical (Eq. (5)), and the cycle continues. Under these conditions, iron can be considered an actual catalyst. The main advantage of the photo-Fenton process is the light sensitivity up to a wavelength of 600 nm (35% of the solar irradiation). Because photo-Fenton can be carried out with the residual  $\text{H}_2\text{O}_2$  produced by ultrasonic BPA treatment, a system that employs the two AOPs simultaneously, without  $\text{H}_2\text{O}_2$  addition, should be a worthwhile endeavor.

In a previous study [17], we found that mineralization of a BPA solution ( $118 \mu\text{mol L}^{-1}$ , 300 mL) could be accomplished in a simultaneous ultrasound/ $\text{Fe}^{2+}$ /UV system. However, because of the experimental conditions (initial acidic pH, UV radiation at 254 nm, and the use of oxygen as the saturating gas), the potential usefulness of this combination could not be established. To explore the practical applicability of this system, the present work investigated BPA treatment via ultrasound and photo-Fenton coupling under conditions encountered in wastewater treatment: natural pH (pH  $\sim$  5, obtained by bare BPA without the addition of any acid or basic substances) and solar radiation. The experiments were carried out in two separate systems (one irradiated with a Suntest lamp and the other subjected to ultrasound). The use of air or oxygen as the saturating gas was also investigated.

## 2. Experimental

### 2.1. Reagents

Bisphenol A (99%) and ammonium heptamolybdate (99.98%) were obtained from Aldrich. Ferrous sulfate (99.5%), potassium iodide (99%), acetic acid, and sulfuric acid were supplied by Fluka. Potassium hydrogen phthalate (99.95%) and hydrogen per-

oxide (35%) were obtained from Merck. Acetonitrile (99.99%) and methanol (99.9%) were purchased from Fisher Chemicals and Riedel-de-Haen, respectively. All chemicals were used without further purification. During all experiments, oxygen (provided by Carbagas) or air was added to the system. Milli-Q water was used for the preparation of aqueous solutions and as a component of the mobile phase in the HPLC analysis.

### 2.2. Apparatus

All experiments were carried out with 600 mL of  $118 \mu\text{mol L}^{-1}$  bisphenol A, in one of two separate systems: one irradiated with a Suntest lamp, and the other subjected to ultrasound (Fig. 1).

To maintain a constant temperature ( $22 \pm 2^\circ\text{C}$ ), a cylindrical water-jacketed glass reactor (500-mL capacity) was used as the sonochemical system. Ultrasonic waves (300 kHz and 80 W) were emitted from the bottom of the reactor through a piezoelectric disc (4-cm diameter) fixed on a Pyrex plate (5-cm diameter) [18]. The ultrasonic energy dissipated in the reactor ( $\sim$ 50% of the electrical power used) was estimated by the calorimetric method [19].

The photochemical reactor consisted of three serial Pyrex glass vessels with an illuminated volume of 50 mL. The Pyrex vessels were irradiated from the outside with a Suntest CPS solar lamp system (Atlas GmbH) with an irradiation intensity of  $830 \text{ W m}^{-2}$ . This lamp has a spectral distribution of  $\sim$ 0.5% of the emitted photons at wavelengths shorter than 300 nm and of  $\sim$ 7% at wavelengths between 300 and 400 nm. For wavelengths between 400 and 800 nm, the emission spectrum follows the solar spectrum. A peristaltic pump recirculated the solutions from the sonochemical reactor to the photochemical reactor with a flow rate of  $230 \text{ mL min}^{-1}$ . The total volume of the system (600 mL) is divided into three parts: 300 mL in the sonochemical vessel, 150 mL in the photochemical reactor, and the remaining 150 mL in the connecting tubes. This configuration allowed combinations of the two processes in simultaneous (ultrasound/ $\text{Fe}^{2+}$ /light) or batch (ultrasound followed by  $\text{Fe}^{2+}$ /light or  $\text{Fe}^{2+}$ /light followed by ultrasound) modes. Moreover, each system (ultrasound, ultrasound/ $\text{Fe}^{2+}$ ,  $\text{Fe}^{2+}$ /light, and  $\text{Fe}^{2+}$ / $\text{H}_2\text{O}_2$ /light) was tested separately. In the  $\text{Fe}^{2+}$ / $\text{H}_2\text{O}_2$ /light method,  $\text{H}_2\text{O}_2$  ( $35 \times 10^{-3} \text{ mol L}^{-1}$ ) was delivered continuously ( $2.7 \text{ mL h}^{-1}$ ) with a syringe pump. In experiments with  $\text{Fe}^{2+}$ , 0.0167 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $100 \mu\text{mol L}^{-1} \text{ Fe}^{2+}$ ) was added to the system. Reaction sets were sampled periodically for analyses. The runs were carried out at least by duplicate. The uncertainties were found lower than 2, 5 and 7% for figures reporting  $\text{H}_2\text{O}_2$ , HPLC and DOC evolution, respectively.

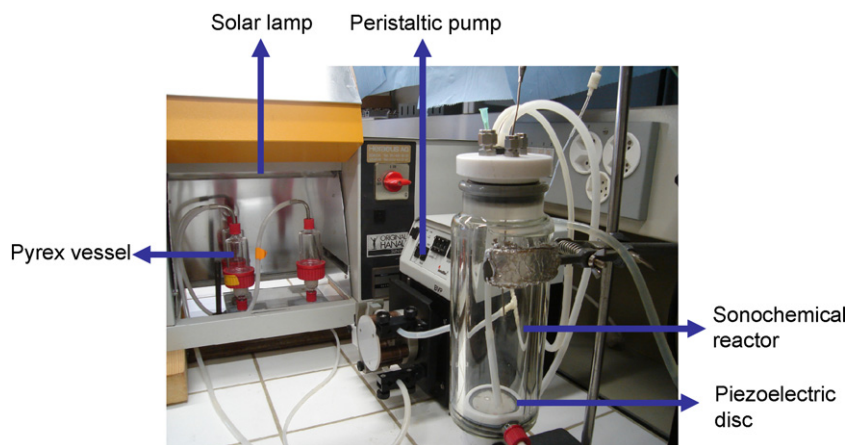


Fig. 1. Sonochemical/photocatalysis reactor used for BPA treatment.

### 2.3. Analyses

A Shimadzu TOC-Vcsm analyzer was used for total organic carbon (TOC) measurements. The instrument was equipped with an ASI automatic sample injector and a solution of potassium phthalate as the calibration standard. Acidification and stripping before analyses were always necessary to keep the solutions free of atmospheric CO<sub>2</sub>. The concentrations of pollutants and of their main degradation intermediates were determined by HPLC with a Varian 9065 instrument. A Nucleosil C-18 column (i.d. 4.6 mm, length 250 mm) and a diode array UV detector set at 273 nm were used. The mobile phase of 0.17 mol L<sup>-1</sup> acetic acid/acetonitrile was run in gradient mode: (90/10)% 0 min to (50/50)% in 15 min and 100% acetonitrile in 20 min. Using this methodology, a detection limit of 0.002 μmol L<sup>-1</sup> of BPA was reached. After preconcentration of the sample on an OASIS HLB cartridge, the first detectable BPA intermediate was identified by HPLC/MS with a Hewlett Packard series 1100 MSD device with electrospray ionization. Aliphatic acids were detected by scanning with a diode array detector.

Hydrogen peroxide concentrations were determined iodometrically [20]. Aliquots taken from the reactor were added to a quartz sample cuvette containing the reagent (0.1 M potassium iodide and 0.01 M ammonium heptamolybdate). Absorbance at 5 min was measured with a Shimadzu UV-1601 spectrophotometer.

## 3. Results and discussion

### 3.1. Ultrasound versus photo-Fenton for BPA treatment

Fig. 2A shows changes in the levels of BPA, TOC, and some BPA by-products (monohydroxylated BPA and aliphatic acids) with time under the sonochemical effect. After 105 min of treatment, the BPA concentration was below the HPLC detection limits. However, at the same time, only 9% of the TOC had been removed. Even at the end of the treatment (180 min), ~90% of the initial TOC remained in solution. Thus, the ultrasonic action transforms BPA into organic intermediates that are barely degraded by the same method.

The fragmentation of the bubbles on collapse also generates bubble nuclei, which themselves may undergo a new cavitation cycle. As indicated in recent papers [17,21,22], BPA characteristics of hydrophobicity and low volatility cause this compound to be close to the original bubble and it is also near the following bubble and therefore an enrichment of BPA at the bubble-bulk solution interface takes place. Thus, BPA is eliminated by •OH radicals principally at the bubble-bulk solution interface. Consequently, monohydroxylated BPA is formed as the first step. As shown in Fig. 2A, this compound reaches its maximal concentration after 45 min and is removed after 105 min. In contrast, the concentration of aliphatic acids in the solution increases until 120 min and then remains constant. Because of their hydrophilic character, aliphatic acids spread into the bulk solution, and the •OH radical, which has a high concentration at the interface, recombines to H<sub>2</sub>O<sub>2</sub> before it can react with them. Consequently, the aliphatic acids accumulate in solution. These results are in agreement with recent reports in the literature [17].

As generally observed during the sonochemical treatment of organic substrates, •OH radicals that do not reach the target molecule recombine at the interface of the bubble [18,23]:



Hydrogen peroxide is also formed by perhydroxyl radical combination at the interface of the bubble [21]:

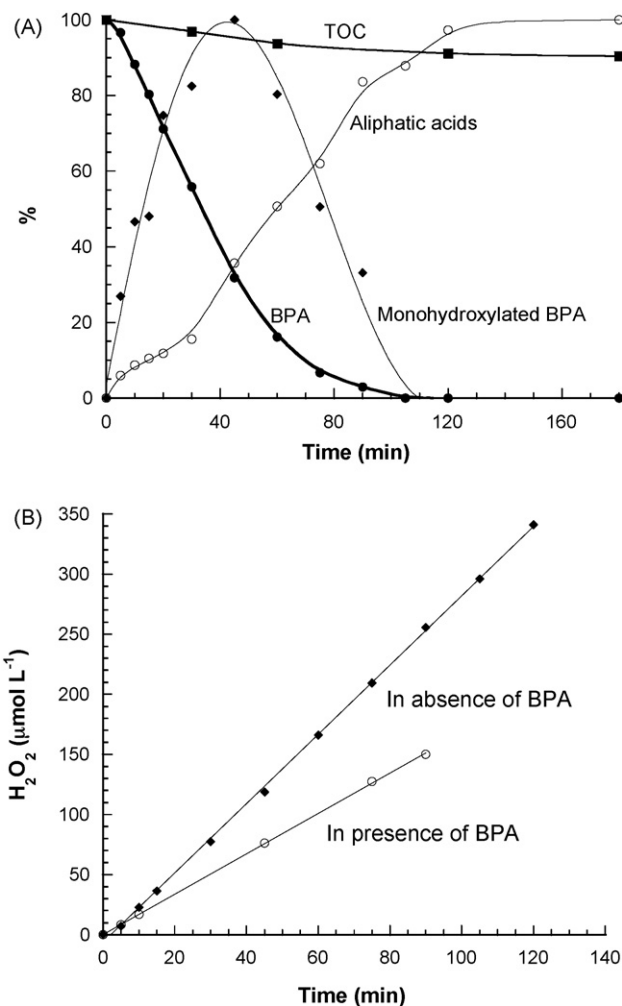


Fig. 2. Sonochemical degradation (300 kHz, 80 W) of BPA (118 μmol L<sup>-1</sup>). (A) Changes in levels of BPA, TOC, monohydroxylated BPA, and aliphatic acids with time of treatment. (B) Hydrogen peroxide formation in the presence and absence of BPA. Volume: 600 mL; pH: natural; temperature: 22 ± 2 °C; saturating gas: oxygen.

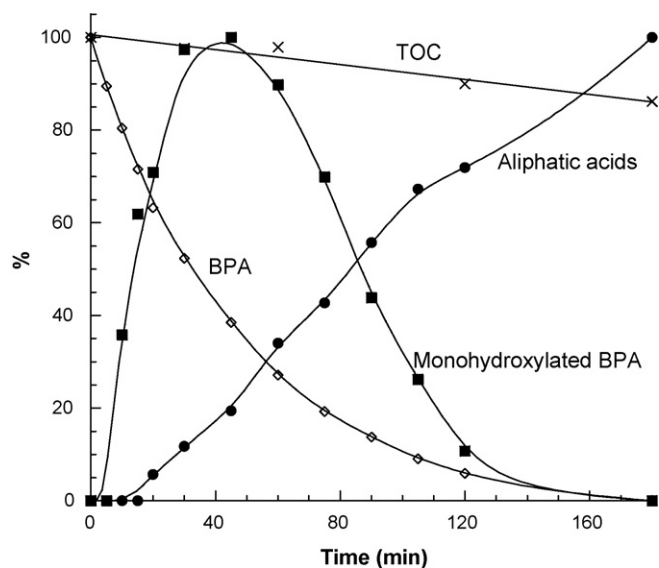
Perhydroxyl radical can be generated from the hydroxylation of organic compounds [17] or from the reaction between a hydrogen atom and molecular oxygen that occurs in the cooler aqueous layer of water surrounding the cavitation bubble [24]:



As a result, during the BPA treatment the hydrogen peroxide concentration increases linearly with a formation rate of 117 μmol h<sup>-1</sup> L<sup>-1</sup>, a lower rate than in oxygenated water in the absence of substrate (160 μmol h<sup>-1</sup> L<sup>-1</sup>) (Fig. 2B).

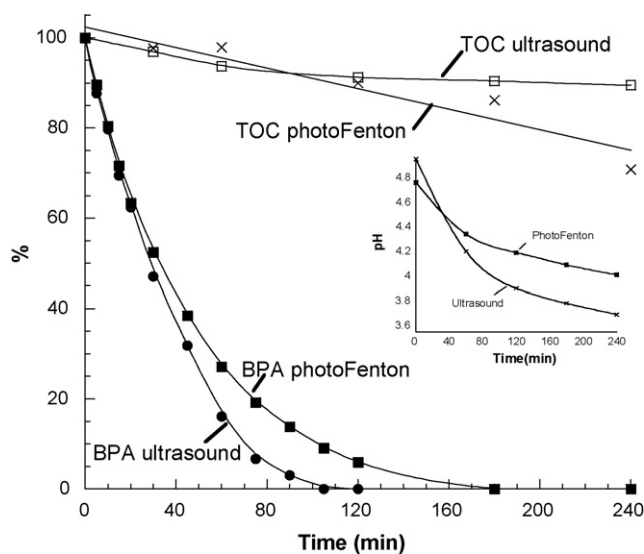
Fig. 3 shows the effects of the photo-Fenton reaction on the levels of BPA, TOC, and BPA by-products. The Fe(II) concentration was 100 μmol L<sup>-1</sup>, and H<sub>2</sub>O<sub>2</sub> was introduced at the same rate (96 μmol h<sup>-1</sup>) as it was generated during oxygenated water sonication in the absence of BPA (Fig. 2B). At 180 min of treatment, BPA was eliminated, whereas the initial value of TOC had decreased by 14%. The monohydroxylated BPA by-product reached a maximum at ~45 min and was eliminated by 180 min, whereas the aliphatic acid concentration increased during the entire period of photo-Fenton treatment.

A comparison between the two AOPs is shown in Fig. 4. Under our conditions, photo-Fenton and ultrasonic processes had simi-



**Fig. 3.** Changes in levels of BPA, TOC, monohydroxylated BPA, and aliphatic acids during the BPA ( $118 \mu\text{mol L}^{-1}$ ) degradation by photo-Fenton. Volume: 600 mL; pH: natural; temperature:  $22 \pm 2^\circ\text{C}$ ; saturating gas: oxygen. UV irradiation: solar simulator;  $[\text{Fe(II)}]_0$ :  $100 \mu\text{mol L}^{-1}$ ;  $\text{H}_2\text{O}_2$ :  $96 \mu\text{mol h}^{-1}$ .

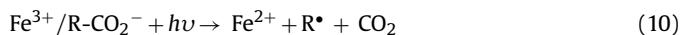
lar BPA degradation rates until 30 min of treatment. However, after this time the ultrasound treatment was clearly superior. Thus, BPA was eliminated after 105 min and 180 min of ultrasound and photo-Fenton treatment, respectively. Contrary to the result observed for BPA elimination, the photo-Fenton process showed better performance for BPA mineralization (TOC removal). After 240 min, 30% and 10% of TOC had been removed with photo-Fenton and ultrasound, respectively. Although ultrasound was more effective at eliminating the initial substrate, photo-Fenton more efficiently degraded BPA intermediates. This result can be explained by the fact that at the beginning of the treatment, BPA is the only organic compound present in the solution. After 30 min, ~50% of the initial pollutant has been transformed into BPA by-products (Fig. 4). As we reported previously [22], both techniques lead to BPA by-products



**Fig. 4.** Ultrasound (300 kHz, 80 W) versus photo-Fenton (solar simulator,  $100 \mu\text{mol L}^{-1} \text{Fe}^{2+}$ ,  $96 \mu\text{mol h}^{-1} \text{H}_2\text{O}_2$ ) for BPA degradation. Inset shows pH changes as a function of time of treatment. Volume: 600 mL; pH: natural; temperature:  $22 \pm 2^\circ\text{C}$ ; saturating gas: oxygen.

with more hydrophilic character than BPA itself. Therefore, during the ultrasonic treatment BPA is closer to the bubble than are its intermediates, and BPA is degraded selectively. Conversely, in the homogeneous photo-Fenton process, all organic compounds are present in solution and, depending on their concentrations and degradation rates, have opportunities to react with  $\cdot\text{OH}$  radicals and thereby compete with BPA removal.

Photolysis of Fe(III) complexes with organic ligands is another important factor responsible for the superior performance of photo-Fenton in TOC elimination. Some aliphatic acids found during BPA treatment by the Fenton reaction [22] may complex with Fe(III) ions [25]:



The regenerated  $\text{Fe}^{2+}$  reacts with  $\text{H}_2\text{O}_2$ , and the organic radical decomposes to give carbon dioxide.

The inset of Fig. 4 shows the pH decrease during the ultrasound and photo-Fenton processes. The pH reduction is more substantial for the ultrasonic process than for the photo-Fenton system, probably due to the fact that during the ultrasonic process there is a higher accumulation of aliphatic acids.

These results indicate that the ultrasonic process has higher selectivity toward hydrophobic compounds than the photo-Fenton. However, the lower selectivity of the photo-Fenton leads to better mineralization. The complementarity of these two processes suggests that a system combining them could be effective for the treatment of water contaminated with BPA. A particular advantage of this combination is that the  $\text{H}_2\text{O}_2$  required for the photo-Fenton system could be provided by the sonochemical process.

### 3.2. BPA degradation by ultrasound, $\text{Fe}^{2+}$ , and solar lamp coupling

Tests were conducted under similar experimental conditions with the same reactor (600 mL), oxygen-saturated solutions, and natural pH. The ultrasound system was operated under the same conditions (80 W, 300 kHz). For the combined techniques, a solar lamp and/or  $100 \mu\text{mol L}^{-1} \text{FeSO}_4$  was used.

The following configurations were tested:

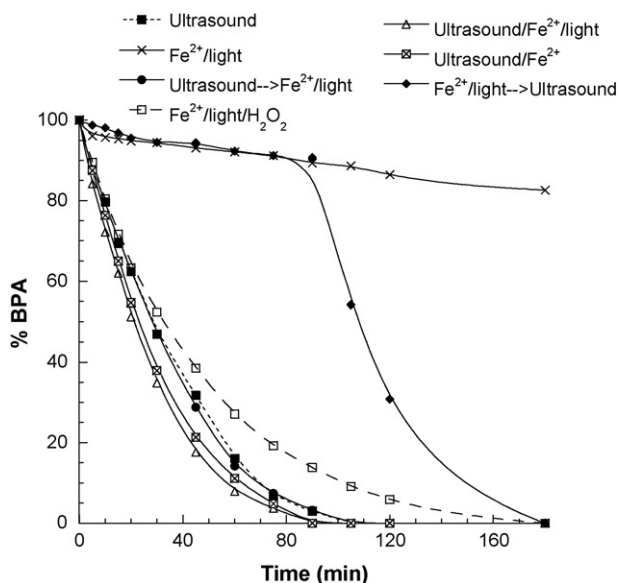
- Simultaneous modes: ultrasound, ultrasound/ $\text{Fe}^{2+}$ , ultrasound/ $\text{Fe}^{2+}$ /light,  $\text{Fe}^{2+}$ /light, and  $\text{Fe}^{2+}$ /light/ $\text{H}_2\text{O}_2$  (photo-Fenton)
- Sequential batch modes: ultrasound followed by  $\text{Fe}^{2+}$ /light (ultrasound  $\rightarrow$   $\text{Fe}^{2+}$ /light) and  $\text{Fe}^{2+}$ /light followed by ultrasound ( $\text{Fe}^{2+}$ /light  $\rightarrow$  ultrasound).

In batch experiments, the first system (ultrasound or  $\text{Fe}^{2+}$ /light) was operated for 90 min and then stopped, and the second system was turned on.

Fig. 5 shows the BPA decay for all of the tested experiments. The efficiency of BPA degradation followed the order  $\text{Fe}^{2+}$ /light  $\leq$   $\text{Fe}^{2+}$ /light  $\rightarrow$  ultrasound  $<$   $\text{Fe}^{2+}$ /light/ $\text{H}_2\text{O}_2$   $<$  ultrasound = ultrasound  $\rightarrow$   $\text{Fe}^{2+}$ /light  $<$  ultrasound/ $\text{Fe}^{2+}$   $<$  ultrasound/ $\text{Fe}^{2+}$ /light (Table 1). Although the combined ultrasound/ $\text{Fe}^{2+}$ /light system

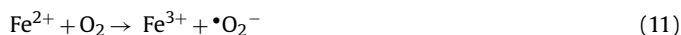
**Table 1**  
BPA elimination and mineralization by different AOPs

Process	Elimination of BPA after 60 min (%)	Elimination of TOC after 240 min (%)
Ultrasound/ $\text{Fe}^{2+}$ /light	92	70
Ultrasound/ $\text{Fe}^{2+}$	89	29
Ultrasound	85	11
Ultrasound $\rightarrow$ $\text{Fe}^{2+}$ /light	85	18
$\text{Fe}^{2+}$ /light/ $\text{H}_2\text{O}_2$	73	22
$\text{Fe}^{2+}$ /light $\rightarrow$ Ultrasound	8	11
$\text{Fe}^{2+}$ /light	8	4



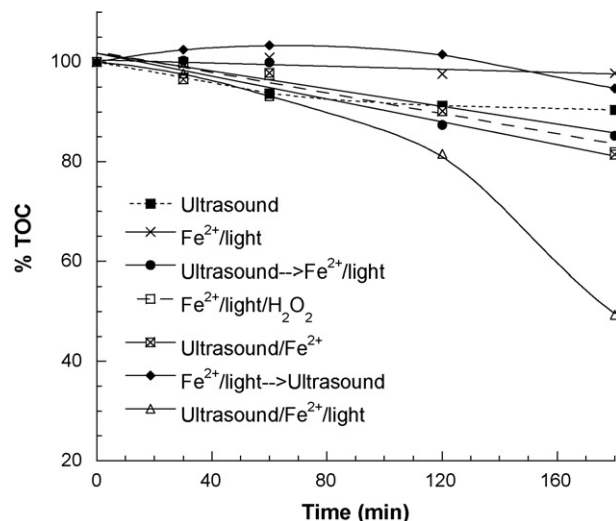
**Fig. 5.** BPA ( $118 \mu\text{mol L}^{-1}$ ) elimination by different AOPs applied to solutions saturated with oxygen. Volume: 600 mL; pH: natural; temperature:  $22 \pm 2^\circ\text{C}$ . Ultrasound: 300 kHz/80 W; UV irradiation: solar simulator;  $[\text{Fe(II)}]_0$ :  $100 \mu\text{mol L}^{-1}$ ;  $\text{H}_2\text{O}_2$ :  $96 \mu\text{mol L}^{-1}$ .

was the most efficient for BPA removal, a synergistic effect not was observed. In Fig. 5, it can be seen that for all processes starting with ultrasound,  $\sim 100\%$  of the BPA was eliminated after 105 min. With the  $\text{Fe}^{2+}/\text{light}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}/\text{light} \rightarrow \text{ultrasound}$  systems, BPA was below the HPLC detection limit at 180 min, while at the same time with the  $\text{Fe}^{2+}/\text{light}$  system, more than 80% of the initial BPA remained in solution. The poor performance of the latter system can be explained by the fact that a complex between BPA and  $\text{Fe}^{2+}$  does not form and by the very low BPA absorption in the UV region emitted by the Suntest lamp (data not shown). Thus, the small fraction of BPA degraded by the  $\text{Fe}^{2+}/\text{light}$  process can be attributed to  $\cdot\text{OH}$  radicals coming from the photo-activated  $\text{Fe}^{3+}$  aqua complex (Eq. (6)), obtained via a previous transformation of  $\text{Fe}^{2+}$  in  $\text{Fe}^{3+}$  by dissolved oxygen:



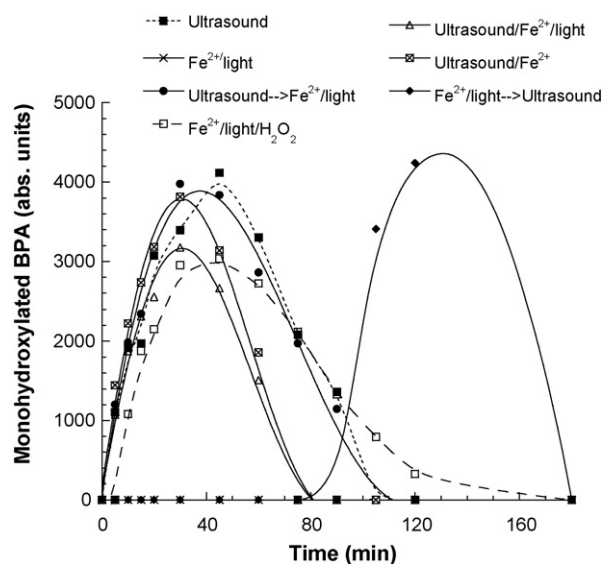
The levels of TOC for all of the tested processes are shown in Fig. 6. TOC removal increased in the following order:  $\text{Fe}^{2+}/\text{light} < \text{Fe}^{2+}/\text{light} \rightarrow \text{ultrasound} = \text{ultrasound} < \text{ultrasound} \rightarrow \text{Fe}^{2+}/\text{light} < \text{Fe}^{2+}/\text{light}/\text{H}_2\text{O}_2 = \text{ultrasound}/\text{Fe}^{2+} < \text{ultrasound}/\text{Fe}^{2+}/\text{light}$ . From Fig. 6, it is possible to note that for the more efficient process (the combined ultrasound/ $\text{Fe}^{2+}/\text{light}$  system), the TOC removal is carried out in two stages. In the first one, until 120 min, a low mineralization degree is achieved. This indicates that during this period of time the target compound is predominantly transformed in BPA by-products. In the second step, after 120 min, a steeper slope is observed, indicating a rapid transformation of BPA intermediates in  $\text{CO}_2$ . Results after 4 h of treatment are presented in Table 1. These results show that the ultrasound/ $\text{Fe}^{2+}/\text{light}$  system affords a higher degree of mineralization (70%) than the simple addition of ultrasound (11%) and photo-Fenton (22%) processes acting separately. Thus, a synergistic effect is observed for BPA mineralization with the ultrasound/ $\text{Fe}^{2+}/\text{light}$  coupling.

Fig. 7 shows the progress of monohydroxylated BPA evolution during treatment of the target compound with each of



**Fig. 6.** TOC ( $21.2 \text{mg L}^{-1}$ ) elimination by different AOPs applied to solutions saturated with oxygen. Volume: 600 mL; pH: natural; temperature:  $22 \pm 2^\circ\text{C}$ . Ultrasound: 300 kHz/80 W; UV irradiation: solar simulator;  $[\text{Fe(II)}]_0$ :  $100 \mu\text{mol L}^{-1}$ ;  $\text{H}_2\text{O}_2$ :  $96 \mu\text{mol L}^{-1}$ .

the evaluated processes. The study of monohydroxylated BPA is important because this compound is the first BPA by-product that is detectable by HPLC during both ultrasound and Fenton treatments [22]. From Fig. 7, it can be seen that for the combined systems ultrasound/ $\text{Fe}^{2+}/\text{light}$  and ultrasound/ $\text{Fe}^{2+}$  the maximum of monohydroxylated BPA was reached earlier (30 min) than for the other processes. Furthermore, using these systems or the photo-Fenton process, the accumulation of this intermediate is lower than when the others process are used. On the other hand, even if the use of ultrasound alone is also effective to eliminate the monohydroxylated BPA, this system produces the highest concentrations of this intermediate. These findings are important because the chemical structures of monohydroxylated BPA and BPA are very similar; thus, the former compound could also have an endocrine-disrupting effect.



**Fig. 7.** Monohydroxylated BPA evolution during treatment of BPA solutions saturated with oxygen with different AOPs. Volume: 600 mL; pH: natural; temperature:  $22 \pm 2^\circ\text{C}$ . Ultrasound: 300 kHz/80 W; UV irradiation: solar simulator;  $[\text{Fe(II)}]_0$ :  $100 \mu\text{mol L}^{-1}$ ;  $\text{H}_2\text{O}_2$ :  $96 \mu\text{mol L}^{-1}$ .



- photolysis of Fe(III)-aliphatic acid complexes (Eq. (10)). The regenerated  $\text{Fe}^{2+}$  reacts with  $\text{H}_2\text{O}_2$  to produce additional  $\bullet\text{OH}$  radicals.

### 3.3. Effect of the saturating gas during BPA treatment

The previous results indicate that a simultaneous ultrasound/ $\text{Fe}^{2+}$ /light system operating at natural pH, with solar radiation as the light source and oxygen as the saturating gas, could be very efficient for BPA mineralization. During the sonochemical degradation of BPA, the gaseous atmosphere inside the cavitation bubble is mainly composed of the saturating gas and water vapor. For economical reasons, the use of air as the saturating gas instead of oxygen was evaluated. Fig. 9 compares the effects of air and oxygen on both the elimination and mineralization of BPA by ultrasound and ultrasound/ $\text{Fe}^{2+}$ /light systems. Under our conditions, the use of air instead of oxygen did not influence the BPA degradation rate. Thus, BPA evolution is not dependent on the saturating gas. On the contrary, the use of oxygen favored the mineralization of the pollutant. After 7 h of treatment with the ultrasound system alone, 18% and 7% of the initial TOC was removed using  $\text{O}_2$  and air, respectively. The positive effect of  $\text{O}_2$  was more substantial for the coupled process (ultrasound/ $\text{Fe}^{2+}$ /light). After 4 h, 72% and 39% of the initial TOC had been eliminated, and at the end of treatment (7 h), 82% and 61% of the initial TOC had been removed using  $\text{O}_2$  and air, respectively. With oxygen as the saturating gas, Eqs. (2)–(4) occur to a higher extent and more  $\bullet\text{OH}$  radicals are formed. Because of their high reactivity, most of the  $\bullet\text{OH}$  radicals recombine to  $\text{H}_2\text{O}_2$ . The higher quantity of hydrogen peroxide attained with oxygen-saturated solutions enhances the Fenton processes, which, as already shown, are mainly responsible for BPA mineralization.

Despite the superior performance for mineralization of oxygen as the saturating gas, the use of air in the combined system showed a mineralization degree that could be of interest in some applications. However, several authors have evidenced the formation of nitrite and nitrate ions when air is used as the saturating gas during sonochemical treatment [17,26,27]. Consequently, if air is used in a photo-Fenton/sonication coupling for the mineralization of organic pollutants, the concentrations of nitrite and nitrate ions at the end of treatment must be considered.

The relationships among reactions induced by ultrasound and photo-Fenton processes at natural pH, with a solar simulator as the radiation supply, are summarized in Scheme 1. In this schema is possible to note that  $\bullet\text{OH}$  radicals generated into the bubbles oxidize BPA to more hydrophilic intermediates at the interface bubble-solution. The hydrophilic BPA by-products are degraded mainly in the solution bulk by  $\bullet\text{OH}$  radicals coming from the photo-Fenton reaction ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ). This reaction is possible thanks to the residual  $\text{H}_2\text{O}_2$  coming from the ultrasonic system.  $\text{Fe}^{3+}$  can form complex with aliphatic acids, which suffer a rapid decarboxylation in presence of light. In this reaction  $\text{Fe}^{2+}$ , used for the photo-Fenton process is regenerated.  $\text{Fe}^{2+}$  can also be regenerated by light action, with the concomitant formation of additional  $\bullet\text{OH}$  radicals.

## 4. Conclusions

This study has shown that, thanks to the synergy between ultrasound and photo-Fenton, a system that uses both of them, even at natural pH and using solar light, can be effectively used for the

mineralization of BPA. In this system, the  $\text{H}_2\text{O}_2$  necessary for the photo-Fenton process can be provided by water sonication.

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