

A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters

R.A. Torres^{a,c}, F. Abdelmalek^{b,c}, E. Combet^c, C. Pétrier^{c,*}, C. Pulgarin^d

^a Grupo de Electroquímica, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, A.A. 1226, Medellín, Colombia

^b Laboratoire des sciences et techniques de l'environnement et de la valorisation (STEVA), faculté des sciences de l'ingénieur, université de Mostaganem, 27000 Mostaganem, Algeria

^c Université de Savoie, 73376 Le Bourget-du-Lac, France

^d Groupe de génie électrochimique, institut des sciences et ingénierie chimique, EPFL, CH-1015 Lausanne, Switzerland

Available online 20 April 2007

Abstract

Bisphenol A (BPA), a xenobiotic that exhibits endocrine disrupting action can be found in surface water. Its complete elimination can be obtained by advanced oxidation processes, notably upon the application of ultrasonic waves. In order to evaluate the feature of ultrasound relevance and the involvement of the hydroxyl radical in the BPA sonochemical degradation, ultrasound action was compared to Fenton's reaction in the cases of deionised acidic water (pH 3) and natural water (pH 7.6, main ions concentration: $\text{Ca}^{2+} = 486 \text{ mg L}^{-1}$, $\text{Na}^+ = 9.1 \text{ mg L}^{-1}$, $\text{Cl}^- = 10 \text{ mg L}^{-1}$, $\text{SO}_4^{2-} = 1187 \text{ mg L}^{-1}$, $\text{HCO}_3^- = 402 \text{ mg L}^{-1}$). Ultrasound was performed at 300 kHz and 80 W. Fenton's process was operated using ferrous sulphate ($100 \mu\text{mol L}^{-1}$) and continuous H_2O_2 addition at the rate as it is produced when sonication is applied in water in absence of substrate. Experiments carried out in deionised water show that both processes exhibit identical BPA elimination rate and identical primary intermediates. Main chemical pathways involve reactions with $\bullet\text{OH}$ radical. Chemical oxygen demand (COD) and total organic carbon (TOC) analyses show that the Fenton's process is slightly more efficient than ultrasonic treatment for the removal of BPA by-products in the case of deionised water. Experiments conducted in natural water evidenced the inhibition of the Fenton process while the ultrasound action was not hampered.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Endocrine disrupting chemical; Bisphenol A elimination; Sonochemical degradation; Fenton's reagent; Water treatment; Advanced oxidation

1. Introduction

Advanced oxidation processes (AOPs) have been proposed as an attractive alternative method for the treatment of polluted waters. These processes are known to generate $\bullet\text{OH}$ radical which is able to oxidise almost all toxic and non-biodegradable pollutants present in the water matrix [1,2].

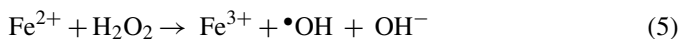
Ultrasonic treatment is considered as an AOP that generates $\bullet\text{OH}$ radicals through the acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles. Fast collapse of the bubbles compresses adiabatically gas and vapour entrapped, which conducts to short and local hot spots [3]. At the final step of the collapse, temperature inside the residual bubble is thought to be above 2000 K. Under these conditions, entrapped molecules of dissolved gases, vaporised water and solutes can be brought to an excited state

and dissociate. Therefore, $\bullet\text{OH}$ radicals are generated from water and oxygen dissociation [4].

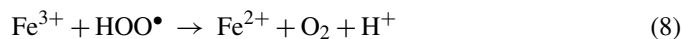
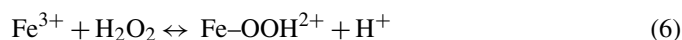


In absence of any organic compound, $\bullet\text{OH}$ radicals combine to produce H_2O_2 . Thus, H_2O_2 measurement during acoustic cavitation, is a method that can be used to estimate the $\bullet\text{OH}$ radicals release by the bubble at determined sonochemical conditions.

Because of its simplicity and high oxidising power, the Fenton's process is an AOP frequently used for oxidation and degradation of organic substances [2,5,6]. In this case, hydroxyl radical is formed through hydrogen peroxide and Fe^{2+} reaction.



* Corresponding author. Tel.: +33 4 79 75 88 04; fax: +33 4 79 75 87 72.
E-mail address: Christian.petrier@univ-savoie.fr (C. Pétrier).



Most of the time, the use of AOPs for aqueous organic pollutants elimination can be achieved with fair to high efficiency. However, in the case of industrial wastewater and natural water, degradation rates can be tampered by the presence of inorganic species that compete with the target molecule for the $\bullet\text{OH}$ radicals [7].

Bisphenol A (BPA), an organic compound largely used in plastic industry as a monomer for production of epoxy resins and polycarbonate [8] disturbs the behaviour of the aquatic life by its endocrine disrupting effect at low concentration [9,10]. BPA can contaminate aquatic environment owing to its release from industrial waste water. It has been evidenced that BPA cannot be completely eliminated by conventional treatment in drinking-water supplies and in some case, can conduct to by-products with higher endocrine disrupting action [11–13].

AOPs can be applied for the elimination of BPA present in water resource or in industrial wastewater [14–18]. Ultrasonic treatment has been found efficient in BPA decomposition [19,20], the combination of ultrasonic action with UV irradiation and iron(II) leading to the complete mineralization of the pollutant [21].

Taking BPA as the target molecule, the first object of this work intends to compare intermediates of degradation obtained in Fenton's process and upon ultrasound to evaluate the part of hydroxyl radical attack involved in BPA sonochemical degradation.

As elimination of BPA with AOPs is generally inhibited by the presence of inorganic ions [22,23], the second object is to compare the degradation yields obtained with each of the processes in the case of deionised water or for a typical natural water that contains high concentrations of inorganic species.

In order to compare ultrasonic action with the Fenton process, hydrogen peroxide for the Fenton process experiments was introduced continuously at the rate it is generated when ultrasonic irradiation is applied.

2. Experimental

2.1. Apparatus

To keep a constant temperature ($20 \pm 1^\circ\text{C}$), the experiments were performed in water-jacketed cylindrical glass reactors (300 mL). Ultrasonic waves (300 kHz and 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) [24]. Ultrasonic energy dissipated in the reactor ($\sim 50\%$ of the electrical power used) was estimated by the calorimetric method [25].

Fenton process was carried out using FeSO_4 (from Aldrich) $100 \mu\text{mol L}^{-1}$. H_2O_2 ($35 \times 10^{-3} \text{ mol L}^{-1}$) was delivered continuously using a syringe pump: 119 μmoles per hour for experiments conducted in deionised water and oxygen as sat-

urating gas; 110 μmoles per hour in the case of experiments conducted in natural water and air as saturating gas. Reaction sets were sampled periodically for analyses.

2.2. Analyses

TOC removal was followed in a LABTOC analyser using a solution of potassium phthalate (from Prolabo) as the calibration standard. Quantitative analysis of bisphenol A (from Aldrich) was done by HPLC in a Waters Associates 590 instrument with a Supelcosil LC-18 column ($5 \mu\text{m}$; I.D = 4.6 mm, length = 250 mm). Detection was achieved with an UV detector (model 486) set at 254 nm. With a 200 μL sampling loop, the detection limit for BPA was $0.002 \mu\text{mol L}^{-1}$. The mobile phase, water/acetonitrile (50/50, v/v), was run in an isocratic mode. Identification of primary BPA intermediates was made by HPLC/MS analysis through a Hewlett Packard series 1100 MSD with electrospray ionization (positive and negative mode). Final by-products were identified by HPLC using a Sarasep CAR-H column and a sulphuric acid solution (4.8 mmol L^{-1}) as mobile phase. Deionised water, obtained with activated carbon and ion exchanger resins from Fisher Bioblock Scientific, was used throughout for the preparation of aqueous solutions and as a component of the mobile phase in HPLC analysis.

Chemical oxygen demand (COD), was carried out according to the method presented by Thomas and Mazas [26], using a dichromate solution (from Aldrich) as the oxidiser in a strong acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150°C for 2 h. The optical density for the change of colour of dichromate solution was determined at 445 nm with a Spectroquant NOVA 30 spectrophotometer. In order to avoid the interference of the residual hydrogen peroxide, samples were neutralised with sodium hydroxide (provided by Aldrich) and treated with catalase (supplied by Merck) previous to COD analysis [27].

Hydrogen peroxide concentrations were determined iodometrically [28]: aliquots taken from the reactor were added in the sample quartz cuvette of the spectrophotometer (Shimadzu, UV-2101 PC) containing the reagent (potassium iodide, 0.1 M and ammonium heptamolybdate, 0.01 M). Absorbance was recorded at 5 min.

3. Results and discussion

3.1. Bisphenol A treatment in deionised water

When water solutions, in equilibrium with air, are treated by ultrasound, nitrogen induces formation of NO_2^- , which reacts with H_2O_2 to produce NO_3^- [21,29]. In order to avoid analytical problems in the determination of hydrogen peroxide concentrations, experiments were conducted in solutions saturated with oxygen.

In a preliminary experiment, hydrogen peroxide generation upon ultrasonic irradiation of deionised water saturated with oxygen, in absence of organic target was determined. At the frequency of 300 kHz, for a power input of 80 W the rate was found to be $119 \mu\text{mol h}^{-1}$. This value was then taken as the

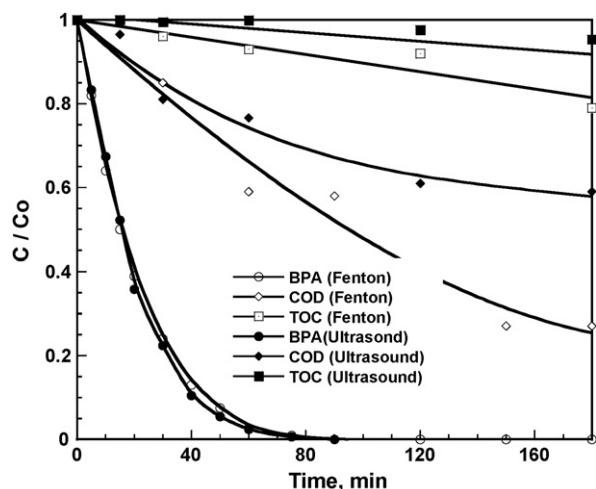


Fig. 1. BPA ($118 \mu\text{mol L}^{-1}$) elimination, chemical oxygen demand (68 mg L^{-1}), total organic carbon (21.2 mg L^{-1}) evolution during the sonochemical and Fenton treatments of a BPA solution saturated with oxygen. Volume: 300 mL; pH 3; temperature: $20 \pm 1^\circ\text{C}$. Ultrasound conditions: 300 kHz, 80W. Fenton conditions: FeSO_4 $100 \mu\text{mol L}^{-1}$ and continuous H_2O_2 addition: $119 \mu\text{mol h}^{-1}$.

feeding rate used for hydrogen peroxide addition in the Fenton experiments. Reactions were conducted at pH 3 to avoid iron hydroxide precipitation.

Fig. 1 shows TOC, COD and BPA decays during the treatment by acoustic cavitation or Fenton's process of BPA solutions at

$118 \mu\text{mol L}^{-1}$ initial concentration. In the two cases, BPA concentration is under the detection limit after 90 min. COD and TOC evolutions indicate that both techniques conducted to the formation of more oxidised intermediates (significant decrease of COD) which are hardly mineralised (low decrease of TOC). Fenton process show better performances in the mineralisation of BPA, as evidenced by the lower TOC value than in the ultrasonic experiment. After 180 min, 75% of COD and 20% of TOC have been removed with the Fenton process whereas, at the same time, only 40% of COD and 5% of TOC have been eliminated using ultrasound.

3.2. Analyses of by-products formed in Fenton and ultrasound treatments of BPA

As TOC was not completely removed in our experiments, and because we cannot exclude the possibility to generate compounds more hazardous than the initial one, the identification of main BPA by-products formed during the ultrasound and Fenton treatments was carried out. The study of the main BPA intermediates was achieved in HPLC/MS experiments that were run in both positive and negative electrospray modes ($M+H$ and $M-H$ detection).

Similar products were found to form in both AOPs tested (Table 1) (Fig. 2): monohydroxylated-4-isopropenylphenol (A), 4-isopropenyl phenol (B), 4-hydroxyacetophenone (C), dihydroxylated bisphenol A (D), quinone of dihydroxylated

Table 1
Main BPA intermediates resulting from ultrasonic and Fenton's treatment identified in HPLC/MS experiment

	Structure	Retention time (min)	ES positive $M+H$	ES negative $M-H$	Molecular weight (M)
A		3.30	151	149	150
B		4.84	135		134
C		6.98		135	136
D		12.10		259	260
E		12.10	259	257	258
F		13.22		243	244
G		13.22	243	241	242
BPA		14.76		227	228

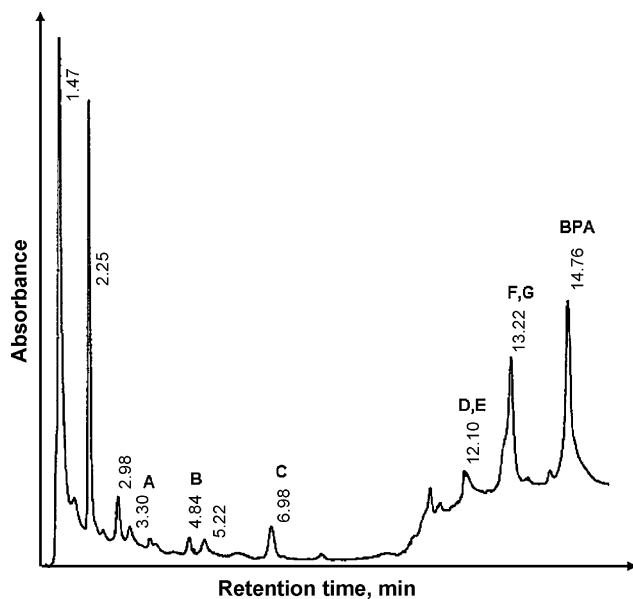


Fig. 2. Typical HPLC analysis, at 30 min, for sonochemical and Fenton's process degradation of BPA. monohydroxylated-4-isopropenylphenol (A), 4-isopropenyl phenol (B), 4-hydroxyacetophenone (C), dihydroxylated bisphenol A (D), quinone of dihydroxylated bisphenol A (E), monohydroxylated bisphenol A (F), quinone of monohydroxylated bisphenol A (G).

bisphenol A (E), monohydroxylated bisphenol A (F), quinone of monohydroxylated bisphenol A (G). The compounds labelled C and 4-isopropylphenol have the same molecular weight ($M=136$). The use of standards for both substances confirmed that only C (4-hydroxyacetophenone) is formed in our experiments. The BPA by-products identified, except compound A, were reported by authors that have investigated the Fenton's process [30] and TiO_2 photocatalysis [31,32]. It is then evidenced that both techniques follow similar reaction pathways involving $\bullet\text{OH}$ radicals. The seven main by-products found exhibit retention times shorter than BPA, which agrees with the fact that they are more hydrophilic than the parent compound. Although some of them can have an endocrine disrupting effect, in all of cases, these aromatic intermediates were eliminated after 120 min of treatments.

At 180 min, some aliphatic acids that remain in solution: oxalic, formic and acetic acids were detected but were not quantified. These compounds were found recalcitrant toward the ultrasonic action leading to poor TOC and COD removal. This is mainly due to their high hydrophilic character. These compounds with high solubility do not accumulate at the interface of the cavitation bubble and remain in the bulk solution. Then most of $\bullet\text{OH}$ radicals, which have a very short life time, combine to form hydrogen peroxide before reactions with the organic targets [33]. These end compounds are biodegradable and then can be eliminated in a subsequent economical biological treatment.

3.3. Bisphenol A treatment in natural waters

In order to assess the applicability of these AOPs to a real water treatment, BPA was dissolved in a natural mineral water. Degradation was achieved substituting air for oxygen as satu-

Table 2
Characteristics of the natural water

pH	Cl^- (mg L^{-1})	Ca^{2+} (mg L^{-1})	Na^+ (mg L^{-1})	SO_4^{2-} (mg L^{-1})	HCO_3^- (mg L^{-1})
7.6	10	486	9.1	1187	402

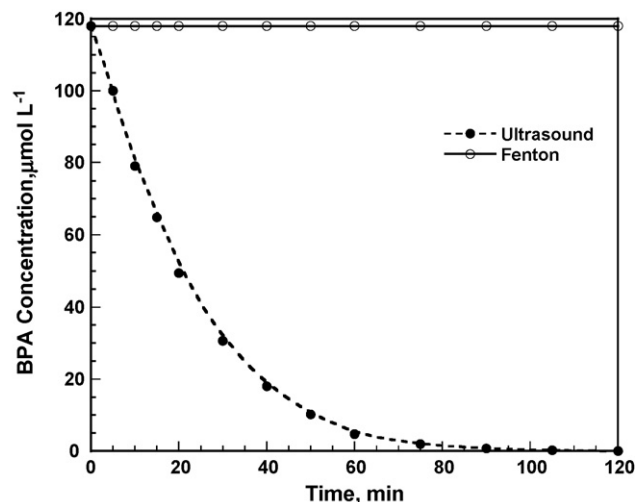


Fig. 3. Ultrasound vs. Fenton process for elimination of BPA ($118 \mu\text{mol L}^{-1}$) dissolved in a natural water. Volume: 300 mL; pH 7.6; temperature: $20 \pm 1^\circ\text{C}$. Ultrasound conditions: 300 kHz, 80W. Fenton process: FeSO_4 $100 \mu\text{mol L}^{-1}$ and continuous H_2O_2 addition: $110 \mu\text{mol h}^{-1}$.

rating gas. The natural water characteristics are summarised in Table 2.

Fig. 3 evidenced the consequences of sonochemical or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ effect on the behaviour of BPA in the natural water. As expected, Fenton's reagent action is completely inhibited in this medium because of the low solubility of iron hydroxide at pH 7.6. Moreover the anionic species (especially HCO_3^-) act as scavengers towards $\bullet\text{OH}$ radicals. Figs. 3 and 4 show that unlike from the Fenton process, the ultrasonic treatment of BPA is not

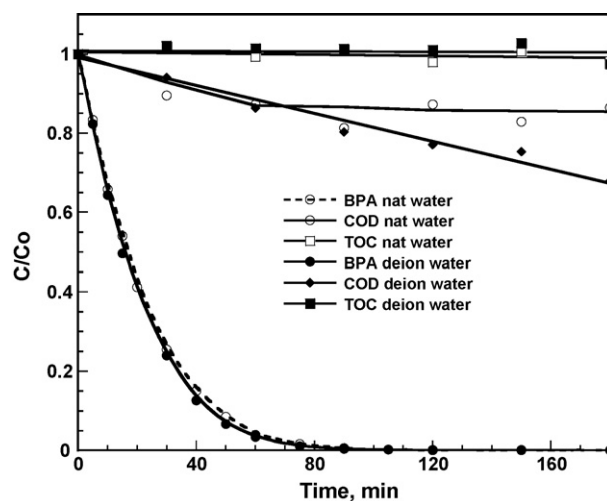


Fig. 4. Evolution of initial compound, TOC and COD during the ultrasonic treatment (300 kHz, 80 W, 300 mL) of BPA $118 \mu\text{mol L}^{-1}$ at pH 7.6 in air saturated natural water (nat water) at pH 7.6 and deionised water (deion water) at pH 3.

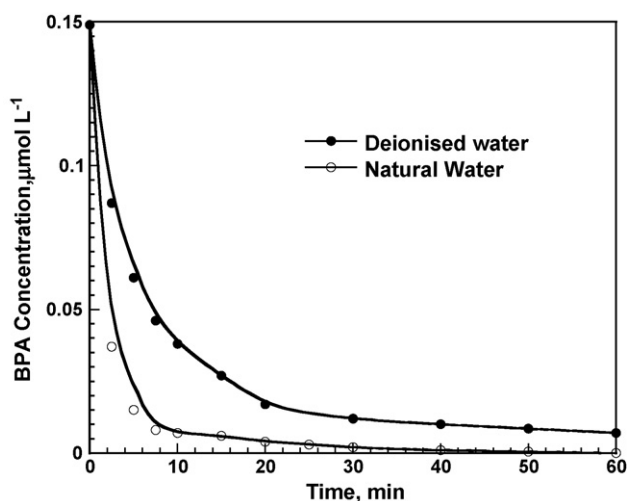


Fig. 5. BPA ($0.15 \mu\text{mol L}^{-1}$) sonochemical elimination in air saturated natural and deionised water. 300 kHz, 80 W, 300 mL and pH 7.6.

affected by pH and ionic species present in the natural water: identical results are found for BPA, COD and TOC removal (Fig. 4).

Results of HPLC/MS show the formation of the same intermediates as in deionised water, indicating that the characteristics of natural water do not change the mechanism of the ultrasonic degradation of BPA.

Since BPA presents an endocrine disrupting effect at low levels, and because, in several cases, BPA has been found in natural waters at low concentrations, the study of the elimination of low BPA level in natural water containing high concentrations of scavenger has to be investigated. Results presented in Fig. 5 show that even at very low BPA concentrations, the high quantity of salt does not reduce the efficiency of the ultrasonic process. Surprisingly, BPA removal is more efficient in the natural water than in the deionised one.

4. Conclusion

This work evidences that even in complex media containing significant amounts of inorganic $\bullet\text{OH}$ radicals scavengers and having neutral pH, where the efficiency of the Fenton process is totally inhibited, ultrasonic process transforms BPA in biodegradable aliphatic acids that could be eliminated in a subsequent biological treatment. Therefore, ultrasound systems represent a very interesting AOP for the treatment of water contaminated with BPA.

Unexpected enhancement of the salts effects observed for natural water is under evaluation.

Acknowledgements

The authors wish to express their gratitude to the “Corporation para los estudios en Francia” of French Embassy in Colombia, to the Cooperation@EPFL in the framework of the Colombo-Swiss action and the Rhône-Alpes region for financial support to Mr. Torres, and to the “agence universitaire de francophonie” for the postdoctoral fellowship to Miss Abdel-

maleck. They greatly appreciate the assistance of Mrs. Marion Carrier (LACE, université Claude-Bernard Lyon I) for aliphatic acids analyses, and Mr. Baudot and Mr. Païssé (service central d’analyses, CNRS) for HPLC/MS analyses.

References

- [1] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods, *Adv. Environ. Res.* 8 (2004) 553–597.
- [2] S.A. Parsons, A. Byrne, Water treatment applications, in: S. Parson (Ed.), *Advanced Oxidation Processes for Water and Wastewater treatment*, IWA Publishing, London, 2004, pp. 329–346.
- [3] L.A. Crum, Comments on the evolving field of sonochemistry by a cavitation physicist, *Ultrason. Sonochem.* 2 (1995) S147–S152.
- [4] T.J. Mason, C. Pétrier, Ultrasound processes, in: S. Parson (Ed.), *Advanced Oxidation Processes for Water and Wastewater treatment*, IWA Publishing, London, 2004, pp. 185–208.
- [5] C. Walling, Fenton’s reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [6] E. Neyens, J. Baeyens, A review of classic Fenton’s peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* B98 (2003) 33–50.
- [7] E. Lipczynska-Kochany, G. Sprah, S. Harmas, Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction, *Chemosphere* 30 (1995) 9–20.
- [8] M. Ash, I. Ash, *Handbook of Plastic and Rubber Additives*, Gower, Hampshire, 1995.
- [9] N. Ben-Jonathan, R. Steinmetz, Xenoestrogens: The emerging story of bisphenol A, *Trends Endocrinol. Metab.* 9 (1998) 124–128.
- [10] G. Levy, I. Lutz, A. Krüger, W. Kloas, Bisphenol A induces feminization in *Xenopus laevis* tadpoles, *Environ. Res.* 94 (2004) 102–111.
- [11] R. Kuruto-Niwa, Y. Terao, R. Nozawa, Identification of estrogenic activity of chlorinated bisphenol A using a GFP expression system, *Environ. Toxicol. Phar.* 12 (2002) 27–35.
- [12] P.E. Stackelberg, E.T. Furlong, M.T. Meyer, S.D. Zaugg, A.K. Henderson, D.B. Reisman, Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water treatment plant, *Sci. Total Environ.* 329 (2004) 99–113.
- [13] G.V. Korshin, J. Kim, L. Gan, Comparative study of reactions of endocrine disruptors bisphenol A and diethylstilbestrol in electrochemical treatment and chlorination, *Water Res.* 40 (2006) 1070–1078.
- [14] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Photocatalytic degradation and mineralization of bisphenol A by TiO_2 and platinumized TiO_2 , *Appl. Catal., A* 261 (2004) 225–237.
- [15] S. Kaneco, M.A. Rahman, T. Suzuki, H. Katsumata, K. Ohta, Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide, *J. Photochem. Photobiol., A* 163 (2004) 419–424.
- [16] H. Katsumata, S. Kawabe, S. Kaneco, T. Suzuki, K. Ohta, Degradation of bisphenol A in water by the photo-Fenton reaction, *J. Photochem. Photobiol., A* 162 (2004) 297–305.
- [17] S. Irmak, O. Erbatur, A. Akgerman, Degradation of 17β -estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques, *J. Hazard. Mater.* B 126 (2005) 54–62.
- [18] S. Horikoshi, A. Tokunaga, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV illumination method. VII. Thermal/non-thermal effects in the microwave assisted photocatalyzed mineralization of bisphenol-A, *J. Photochem. Photobiol., A* 162 (2004) 33–40.
- [19] I. Ioan, S. Wilson, E. Lundanes, A. Neculai, Comparison of Fenton and sono-Fenton bisphenol A degradation, *J. Hazard. Mater.* 142 (2007) 559–563.
- [20] M. Kitajima, S. Hatanaka, S. Hayashi, Mechanism of O_2 -mediated sonolysis of bisphenol A, *Ultrasonics* 44 (2006) e371–e373.
- [21] R.A. Torres, C. Pétrier, E. Combet, F. Moullet, C. Pulgarin, Bisphenol A mineralization by integrated ultrasound-UV-ion(II) treatment, *Environ. Sci. Technol.* 41 (2007) 297–302.

- [22] J. Sajiki, T. Masumizu, Inhibition of BPA degradation by serum as a hydroxyl radical scavenger and an Fe trapping agent in Fenton process, *Chemosphere* 57 (2004) 241–252.
- [23] J. Sajiki, J. Yonekubo, Inhibition of seawater on bisphenol A (BPA) degradation by Fenton reagent, *Environ. Int.* 30 (2004) 145–150.
- [24] C. Pétrier, M.F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, N. Gondrexon, Sonochemical degradation of phenol in dilute aqueous solutions: comparison of the degradation rates at 20 and 487 kHz, *J. Phys. Chem.* 98 (1994) 10514–10520.
- [25] T.J. Mason, J.P. Lorimer, D.M. Bates, Quantifying sonochemistry: casting some light on a 'black art', *Ultrasonics* 30 (1992) 40–42.
- [26] O. Thomas, N. Mazas, La mesure de la demande chimique en oxygène dans les milieux faiblement pollués, *Analisis* 14 (1986) 300–302.
- [27] W. Liu, S.A. Andrews, M.I. Stefan, J.R. Bolton, Optimal methods for quenching H₂O₂ residuals prior to UFC testing, *Water Res.* 37 (2003) 3697–3703.
- [28] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Photocatalytic production of H₂O₂ and organic peroxides in aqueous suspensions of TiO₂, ZnO, and desert sand, *Environ. Sci. Technol.* 22 (1988) 798–806.
- [29] C. Pétrier, D. Casadonte, The sonochemical degradation of aromatic and chloroaromatic contaminants, *Adv. Sonochem.* 6 (2001) 91–109.
- [30] B. Gözmen, M.A. Oturan, N. Oturan, O. Erbatur, Indirect electrochemical treatment of bisphenol A in water via electrochemically generated Fenton's reagent, *Environ. Sci. Technol.* 37 (2003) 3716–3723.
- [31] Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, Degradation of Bisphenol A in water by TiO₂ photocatalyst, *Environ. Sci. Technol.* 35 (2001) 2365–2368.
- [32] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, Capturing of Bisphenol A photodecomposition intermediates by composite TiO₂-zeolite sheets, *Appl. Catal., B* 46 (2003) 453–462.
- [33] A. Henglein, Sonochemistry: historical developments and modern aspects, *Ultrasonics* 25 (1987) 6–16.