

Short communication

Comparison of Fenton and sono-Fenton bisphenol A degradation

Iordache Ioan^{a,c,*}, Steven Wilson^b, Elsa Lundanes^b, Aelenei Neculai^c

^a *OLTCHIM Research Center, 1 Uzinei Street, 240050 Rm. Vâlcea, Romania*

^b *University of Oslo, Department of Chemistry, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*

^c *Technical University Gh. Asachi Iasi, Faculty of Chemical Engineering, Chemical Engineering Department, Bd. D. Mangeron, No. 71, Iasi 700050, Romania*

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Abstract

Degradation of bisphenol A (BPA) was carried out with the Fenton reagent with and without additional sonochemical treatment. The Fenton and the sono-Fenton decomposition of BPA showed that ultrasound irradiation of wastewater improved the wet oxidation process of 25 mg l⁻¹ BPA solutions.

The sonochemical degradation of BPA was monitored using UV absorption and large volume injection packed capillary LC measurements. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

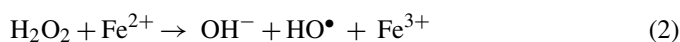
Since the beginning of the investigation on sonochemistry processes in 1927 several papers have appeared on ultrasonic treatment of wastewater. Sonication has proved to be an efficient hybrid method [1] for the pre-treatment [2] and treatment of hydrocarbon contaminated water, being successfully applied for degradation of aliphatic [3], aromatic [4–9], polycyclic aromatic [10] and halogenated hydrocarbons [11], azo dyes [12] and for some pesticides components as well [13–16].

The mechanism proposed for the sonochemical degradation of organic pollutants is usually based on the formation of short life radicals generated in violent cavitations events [17,18]:



It is known that ultrasonic irradiation of liquids causes acoustic cavitations: the formation, growth and implosive collapse of bubbles. Cavitation generates sites of locally high temperatures and pressures for short periods of time, which are responsible for unusual sonochemical effects [19,20].

In the Fenton degradation (2), hydrogen peroxide is used as oxidizing agent and iron(II) sulfate heptahydrate as catalyzing agent (Fenton reagent):



In the present study the effect of sonochemical treatment at low frequency (45–47 kHz) on the degradation of bisphenol A has been investigated in order to study the potential enhancement degradation rate of potential pollutants by ultrasound irradiation of wastewater treatment reactor. A high amount of bisphenol A (BPA) is manufactured and it is being used as a monomer for the production of, e.g. polycarbonate and epoxy resins, unsaturated polyester–styrene resins and flame retardants. It is well known that BPA has estrogenic activity and that wastewater containing BPA can be a source of contamination in the aquatic environment. Although BPA is readily degraded by microorganisms, biological degradation methods commonly require long times when the wastewater contains BPA at high concentration. Therefore, a rapid, simple and economic wastewater treatment for removal of BPA is now highly in demand [21,22].

The aim of this study was to explore the potential benefits from the combined use of ultrasound and wet catalyzed peroxide oxidation for the wastewater treatment using the estrogenic pollutant BPA as model compound.

* Corresponding author at: OLTCHIM Research Center, 1 Uzinei Street, 240050 Rm. Vâlcea, Romania. Fax: +40 250735438.
E-mail address: iordacheioan@k.ro (I. Ioan).

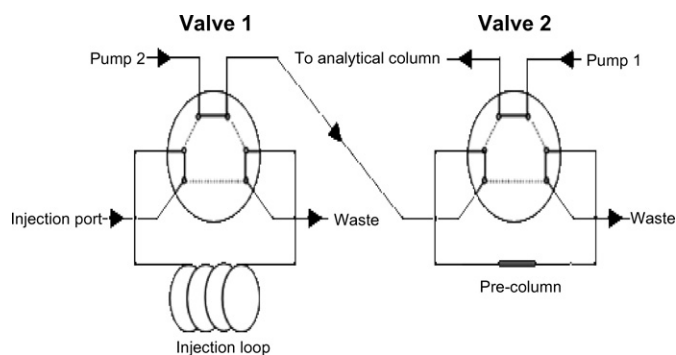


Fig. 1. Column switching system.

2. Experimental

2.1. Materials and reagents

HPLC grade acetonitrile (ACN), methanol (MeOH), carbon tetrachloride as well as analytical grade hydrochloric acid, formic acid (FA) 50% and H_2O_2 were obtained from Merck (Darmstadt, Germany). Grade 1 water used to prepare the solutions and mobile phases was obtained from a Milli-Q ultrapure water purification system (Milli-pore, Bedford, MA, USA). Nitrogen (99.99%) was purchased from AGA (Oslo, Norway). BPA and iron(II) sulfate heptahydrate were obtained from Sigma–Aldrich (Steinheim, Germany). All fused-silica capillaries were obtained from Polymicro Technologies (Phoenix, AZ, USA).

2.2. LC columns

The capillary columns were slurry packed using carbon tetrachloride. The analytical columns of 0.32 mm i.d. and 0.45 mm o.d. were packed in lengths of 13 cm, and the stationary phase material was 3.5 μm Kromasil C18 (Eka Nobel, Bohus, Sweden). Valco ZU1C unions in combination with Valco FS1.4 polyimide ferrules and Valco 2SR1 steel screens served as column end fittings. The precolumn was 1 mm i.d. \times 5 mm HotSep[®] Tracy packed with 10 μm Kromasil C18 (Septech, Kolbotn, Norway).

2.3. LC-UV analysis

A Hitachi L-7110 (Merck) isocratic LC pump served as the mobile phase delivery system (pump 2 in Fig. 1), while a Shimadzu LC-10 AD LC pump provided the sample loading (pump 1). A Valco model C2 six-port-valve (Cotati, CA, USA) (valve 1) was used for manual injections of sample volumes of 0.1 ml. A Valco model C2 six-port-valve served as column-switching valve (valve 2). The mobile phase consisted of ACN/water (60/40, v/v) with 0.1% formic acid, at a flow rate of 5 $\mu\text{l min}^{-1}$, while the sample loading solution was water/ACN (97/3, v/v) with 0.1% formic acid pumped at a flow rate of 50 $\mu\text{l min}^{-1}$.

A 50 μm i.d. fused-silica capillary of 15 cm length was used to connect valves 1 and 2. The analytical column was connected to valve 2 through a 10 cm, 100 μm i.d. fused-silica capillary and

the column outlet was connected to a Spectra 100 UV detector (Spectra-Physics, Fremont, CA, USA), with a 100 μm i.d. detection capillary and detection wavelength of 224 nm. A schematic description of the column switching system is presented in Fig. 1.

Micro-LC using packed capillary columns of 0.25–0.35 mm i.d. provides increased mass sensitivity and easier coupling. Reduction in column diameter produces a higher analyte peak concentration in the detector. For the same mass of analyte injected on-column, miniaturization from a 4.6 mm i.d. analytical column to a 0.32 mm i.d. capillary column result in a theoretical concentration gain at the detector of more than two orders of magnitude. The literature has shown that large-volume injections using column-switching techniques are possible without exchange the efficiency. Therefore, the concentration limit of detection can be increased with a factor of 1500 by increasing the injection volume from the standard 0.06–100 μL [23,24].

2.4. UV analysis

The UV spectra were recorded by a Hitachi U 2000 Spectrophotometer. All the determinations were carried out in a 10 mm quartz cuvette (2 ml).

2.5. Solutions

All solutions were prepared with grade 1 water. Stock solution of BPA (100 mg l^{-1}) were prepared by dissolving the proper amount in water and stored at 4 °C. Before starting the degradation experiments, 25 mg l^{-1} solutions were prepared and pH adjustment was made using 2 M HCl solutions (see Table 1).

For the capillary LC-UV measurements, calibration curves based on 0, 5, 10, 25 and 40 mg l^{-1} solutions of the BPA were established.

2.6. Sono-Fenton and Fenton processes

Two hundred and fifty milliliters of the solutions (Table 1) were transferred to a 65 mm i.d. \times 100 mm height stainless steel vessel (laboratory made) and treated in an ULTRASONIC[™] 104X bath (NEY Dental International, CA, USA) at 43–47 kHz (ca. 500 W). The temperature of the reactions was maintained at 25 ± 5 °C. The sono-Fenton and Fenton experiments were carried out in the same vessel.

Table 1
The BPA process conditions

No.	pH	Initial BPA concentration (mg l^{-1})	H_2O_2 (mg l^{-1})	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (mg l^{-1})	Total time (min)
1	4	25	7	1.4	130
2	5	25	7	1.4	120
3	6.5	25	7	1.4	100
4	4	25	7	2.5	50

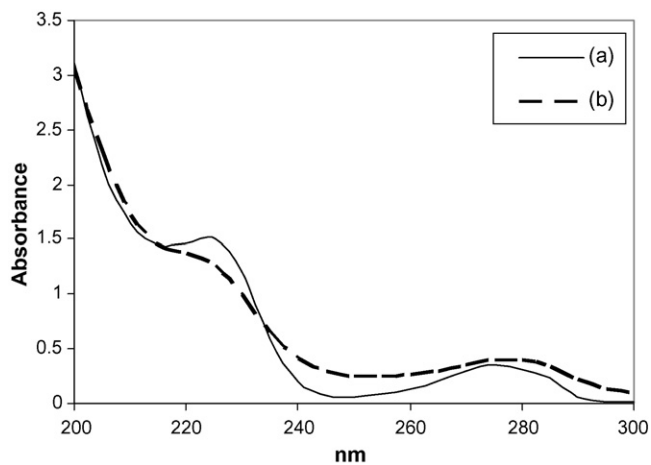


Fig. 2. UV absorption spectra of BPA before and after the sono-Fenton treatment, $1.4 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$, $7 \text{ mg l}^{-1} \text{ H}_2\text{O}_2$ and pH 4: (a) before reaction; (b) after 100 min.

3. Results and discussion

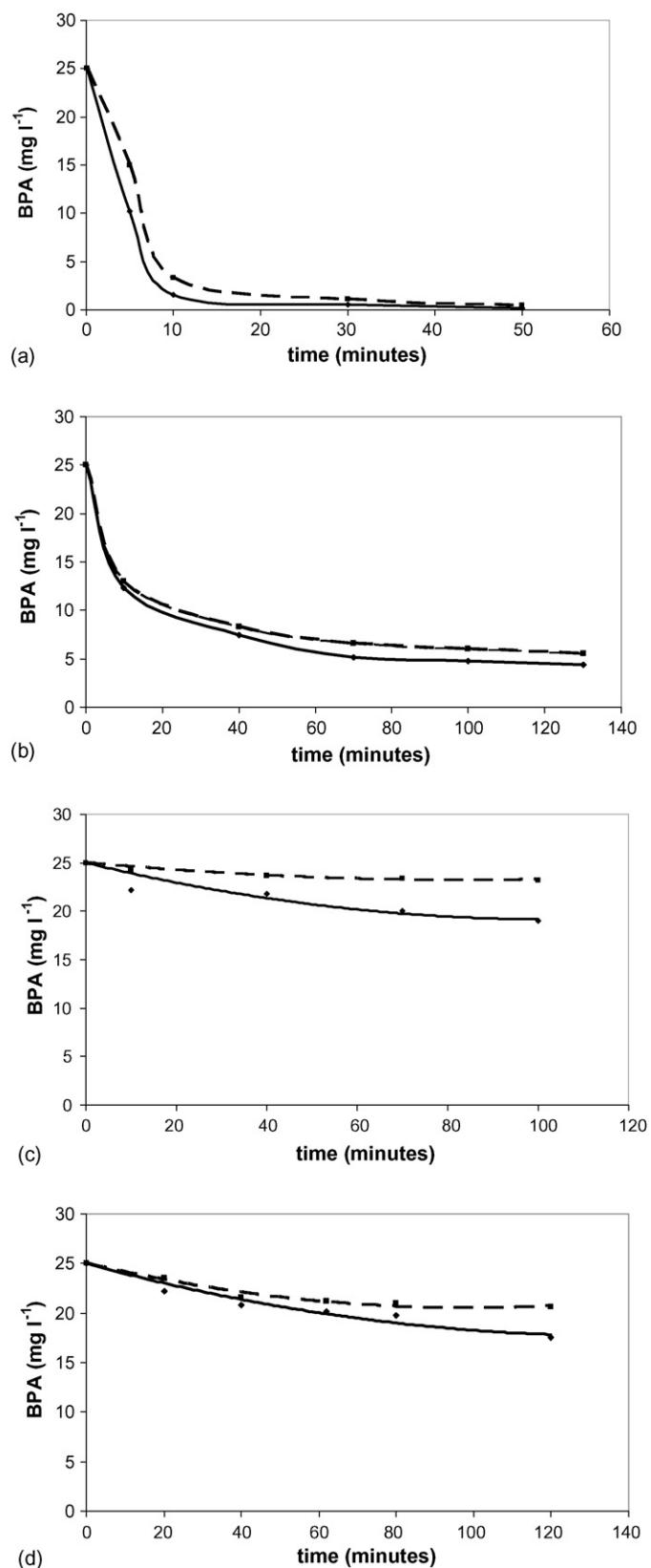
In this study the degradation of BPA by the Fenton process with (sono-Fenton) and without (Fenton) ultrasound has been studied using UV absorption and capillary LC-UV analyses. The BPA concentration in the degradation experiments was as low as 25 mg l^{-1} due to its low water solubility [21]. Because of the low concentration of BPA in the initial and especially the treated solutions, a method providing low detection limits was needed. Hence, capillary LC-UV with large volume injection was used [23].

The oxidizing experiments were carried out in the 43–47 kHz batch reactor using hydrogen peroxide as oxidizing agent and iron(II) sulfate heptahydrate as catalyzing agent (Fenton reagent) at $25 \pm 5 \text{ }^\circ\text{C}$ (Table 1).

The UV absorption spectra of BPA solution are presented in Fig. 2. Decreasing of the 220–230 nm absorption bands was observed with increasing degradation time. In the same time the absorbance spectra, after 100 min, was not only for BPA, it was for all the reaction products and the chromophore species that can interfere with the spectra of BPA. However, the absorbance at 240–260 nm increased with increasing degradation time. None of the reagents Fe(II, III), H_2O_2 and HCl, had absorption in this wavelength range. Therefore, the increase of absorbance might be due to the presence of intermediate products, similar to those observed by Katsumata et al., using photo-Fenton degradation of BPA [21].

Fig. 3. (a) Reduction of the concentration of BPA with treatment time: (---) Fenton and (—) sono-Fenton process, $2.5 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH 4. The concentration of BPA was measured using capillary LC-UV. (b) Reduction of the concentration of BPA with treatment time: (---) Fenton and (—) sono-Fenton process, $1.4 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH 4. The concentration of BPA was measured using capillary LC-UV. (c) Reduction of the concentration of BPA with treatment time: (---) Fenton and (—) sono-Fenton process, $1.4 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH 6.5. The concentration of BPA was measured using capillary LC-UV. (d) Reduction of the concentration of BPA with treatment time: (---) Fenton and (—) sono-Fenton process, $1.4 \text{ mg l}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH 5. The concentration of BPA was measured using capillary LC-UV.

Both BPA and its intermediate products might react with iron species followed by the formation of iron complexes and assist the catalytic cycles of iron in the Fenton or sono-Fenton system. Therefore, according with literature and ours experiments,



the degradation efficiency of BPA is the highest at pH 4. The degradation rate of BPA increased with increasing initial Fe(II) concentration and with decreasing initial pH (see Fig. 3), and was faster with sono-Fenton as compared to Fenton.

The ultrasound effect can be replaced by exchanged of the pH, see Fig. 3a and b, or by adding a double amount of H₂O₂, 14 mg l⁻¹, step-by-step and not all amount at the beginning of the experiment.

The Fenton reaction has been widely studied, but the optimal ratio of [H₂O₂]/[Fe(II)] differs. Katsumata et al. have reported the use of different ratios of these two reactants, using a H₂O₂/Fe(II) ratio from 1:4 (chlorobiphenyl) to 100:1 (chlorophenol) and 400:1 for wastewater [21]. In the present study we used a ratio of 2.8:1.

The faster degradation of BPA with sono-Fenton as compared to Fenton is believed to be due to the higher efficiency for the production of OH• radicals (reaction (2)) as well as to the ultrasonic physical (bubble collapse and mixing effects) and chemical (OH radicals) processes [1,2]. In the present work a 500 W ultrasonic bath was used.

In our experiments, at low frequency and for this type of compound, we observed, in accord with the literature [1], that the irradiation with ultrasound had improved the chemical velocity of reaction. The OH radicals generated by ultrasounds at 43–47 kHz and intensity less than 1 W cm⁻¹, was not enough to destroy the BPA in 120 min without adding H₂O₂. The same situation was observed when was added the iron(II) sulfate heptahydrate without H₂O₂. For a large amount of iron(II) sulfate heptahydrate, 100 mg l⁻¹, the disappearance of BPA was caused by physical adsorption at the surface of iron salt.

Guo et al. have shown that the degradation rate of organic compounds increases with increasing output intensities. Thus, a larger difference between the sono-Fenton and Fenton degradation of BPA can be expected if higher output intensity is used [20].

4. Conclusions

The degradation rate of BPA in aqueous solution was investigated by the Fenton and sono-Fenton treatment. The degradation rate was strongly affected by the pH value and the initial concentrations of Fe(II). Complete degradation of BPA was achieved after 60 min under both sono-Fenton and Fenton conditions; however, the sono-Fenton enhanced the degradation rate as compared to Fenton only. In our experiments was used two ratios of H₂O₂/Fe(II)/BPA, 2.8:1:10 and 5:1:18, the former ratio was better than the latter one.

The study demonstrates that ultrasonically treatment can be a suitable method to improve the Fenton degradation of BPA as an environmental pollutant.

Therefore, the combination of ultrasonic treatment and Fenton reagent represents a promising new technique in the field of environmental engineering. We have also found that capillary LC-UV with large volume injection is a suitable method for investigation of degradation of organic compounds present at low concentration in water.

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