

Enhanced Degradation and Mineralization of Bisphenol A by Hybrid Process Using Hydrodynamic-Acoustic Cavitation

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ТЕХТ А

A number of studies have been devoted to the degradation of BPA under the influence of cavitation (Table S 1). Torres R. A. et al. [1] a chemical compound largely used in the plastics industry, can end up in aquatic systems, which it disturbs by its endocrine disrupting effect (EDE studied the degradation of BPA under ultrasound exposure in various experimental conditions. The optimal degradation efficiency for BPA with a concentration of 118 μM , was achieved through ultrasound treatment at 300 kHz and 80 W, utilizing oxygen as the saturating gas. This resulted in the complete removal of BPA within 90 minutes. However, even after treatment for 9 hours a reduction of COD by 50 %, and TOC by 20 % has been achieved. Kitajima et al. [2] 3-dihydro-2-methylbenzofuran also studied the ultrasonic degradation of BPA (491 kHz, 120 W) in an oxygen medium and observed complete removal of the compound within 2.5 hours of treatment. They also elucidated the role of hydroxyl radicals formed by water dissociation in the oxidative process. Deggelmann M. et al. [3] performed BPA degradation under high pressure HC and achieved 50 % removal in 30 minutes of treatment, although the initial contaminant concentration was low (0.25 μM). Lu G. et al. [4] investigated the prospects of using low-pressure HC (3 bar) for BPA degradation (its concentration decreased by 27.6 % in 3 hours of treatment).

The possibility of combining cavitation with AOPs has been considered. For instance, electrochemical oxidation combined with AC reduced the concentration of BPA by 90 % in 30 minutes of treatment [5] an endocrinic disruptor, which is widely used in plastic production. Due to its endocrine disrupting effects on aquatic (micro-. Using the sono-Fenton process, 94 % of the BPA was removed in 40 minutes of treatment [6]. A study by Torres R. A. et al. [1] a chemical compound largely used in the plastics industry, can end up in aquatic systems, which it disturbs by its endocrine disrupting effect (EDE reported that complete mineralization of BPA can be achieved by combining ultrasound (300 kHz) with Fe(II) and UV (254 nm). Under these conditions, the treatment for 2 hours resulted in a reduction of COD by 96 %, and TOC by 79 %.

Currently, many studies focus on sulfate radical-based AOPs (SR-AOPs), where persulfates (PS) are used as ROS precursors. This process produces sulfate anion radicals in solution, which have a high oxidative capacity, longer lifetime in solution, and greater selectivity [7,8]. Choi J. et al. [9] in order to oxidize BPA at the water treatment, an economical treatment method is required. This study

was the first study to apply hydrodynamic cavitation/persulfate (HC/PS studied the oxidation of BPA by PS under HC conditions. At an optimum pressure of 5 bar and an elevated temperature of 50 °C, the removal efficiency of BPA reached 81.3 % in 2 hours of treatment [9] in order to oxidize BPA at the water treatment, an economical treatment method is required. This study was the first study to apply hydrodynamic cavitation/persulfate (HC/PS. Darsinou B. et al. [10] demonstrated that PS activation can be achieved using AC at 20 kHz, resulting in complete degradation of BPA in 90 minutes. After 8 hours of treatment, the reduction of TOC reached 60 %.

Table S 1. Summary of the literature on the degradation of BPA using cavitation processes

Treatment approach	Type of reactor	[BPA], μM	Optimized condition	Rate Constant	Removal/ COD/ TOC, %	Ref.
AC	Reactor with a piezo-electric disk (at the bottom)	118	V = 0.3 L, 300 kHz, 80 W, T = 20 °C, t = 9 h,		100/50/20	[1]
AC	Concave PZT transducer	219.3	V = 0.05 L, 491 kHz, 120 W. T = 20 °C, t = 2.5 h, O ₂ media	$7.3 \cdot 10^{-4} \text{ s}^{-1}$	100	[2]
HC	HC, Nozzle	0.25	V = 0.5 L, 1.7 mm nozzle, P = 25 bar, pH = 6, T = 20 °C, t = 0.5 h,		50	[3]
HC	HC, Orifice plate,	43.8	V = 20 L, P = 3 bar, Diameter of each hole 1 mm, No. of holes 61. pH = 6, T = 35 °C, t = 3 h.	2.12 s^{-1}	27.6	[4]
AC + Fenton	ULTRASONIK™ 104X bath	109.6	V = 0.25 L, 43–47 kHz, 500 W. pH = 4, T = 25 °C, t = 1 h, [Fe ²⁺]=9 μM , [H ₂ O ₂]=25 μM .		100	[6]
AC	Reactor with a piezo-electric disk (at the bottom)	118	V = 0.3 L, 300 kHz, 80 W T = 20 °C, t = 7 h, pH 3.		100/50/17	[11]
AC+Photo+Fe ²⁺	Reactor with a piezo-electric disk (at the bottom)	118	V = 0.3 L, 300 kHz, 80 W, T = 20 °C, t = 2 h, pH 3. Fe ²⁺ =100 μM . UVC 254 nm, O ₂ media		100/96/79	[11]
AC+electro-chemical treatment	Ultrasound generator with a sonotrode S 14L2D, titanium	4.38	V=0.5 L, 24 kHz, 80 W. T = 20 °C, t= 30 min. two boron doped diamond electrodes ID = 8.1 cm, [Na ₂ SO ₄] = 30 mM	$0,043 \text{ min}^{-1}$	90	[5]
AC+magnetic biochar+H ₂ O ₂	Sonicator VCX 750 with a titanium probe	100	V=0.2 L, 20 kHz, 750 W, T = 20 °C, t = 40 min. Catalyst dose = 1 g/L, [H ₂ O ₂] = 10 mM.		94	[12]
AC+UVA+TiO ₂	Fabricated stainless-steel transducer module (Fulltech, Taiwan)	4.38	V=1 L, 35 kHz, 100 W. T = 25 °C, t = 1 h. TiO ₂ =0.05 g/L UVA 350 nm.	$8.75 \times 10^{-2} \text{ min}^{-1}$	100	[13]

Treatment approach	Type of reactor	[BPA], μM	Optimized condition	Rate Constant	Removal/COD/TOC, %	Ref.
AC+PS	Branson 450 horn-type	21.9	V=0.12 L, 20 kHz, 450 W, T = 30 °C, t = 8 h, pH 6. PS=500 mg/L	0.11 min ⁻¹	100/-/60	[10]
HC + PS	HC, Orifice plate	43.8	V = 10 L, P = 5 bar, pH = 6, T = 50 °C, t = 2 h, PS= 0.7 mM	12.6 × 10 ⁻³ min ⁻¹	81.3/-/ 76.9	[9]

TEXT B

Materials and Methods

Chemicals and materials

Analytical grade chemicals, including BPA, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), potassium peroxydisulfate (PS, $\text{K}_2\text{S}_2\text{O}_8$, CAS: 7727–21–1), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium hydrocarbonate (NaHCO_3), methyl alcohol (MeOH), tert-butyl alcohol (TBA), were purchased from Aldrich, USA. The pH of the reaction mixtures was adjusted with 0.1 N NaOH and 0.1 N H_2SO_4 . A standard organic substance was also used (IHSS Suwannee river NOM RO Isolation 2R 101N) [14].

Experimental setup

Figure S 1 shows the scheme of the experimental setup, which included: vertical multistage centrifugal pump (Grundfos CRNE-15), AC and HC generators, manometer and thermostat. The pump (1) sets the pressure of the circulating liquid, which enters the cavitation chamber (2) through a high-pressure line. The cavitation chamber (Figure 1B) contains a titanium nozzle (outlet diameter 4 mm, internal diameter 10 mm, height 30 mm) (2.1), and ultrasonic piezoceramic transducers diameter 2 cm (2.2) connected to 1.7 MHz sound generators (3) with a distance of 10 mm between the piezoelectric elements. The thermostat (4) with external cooling maintained a constant set temperature of 25 °C.

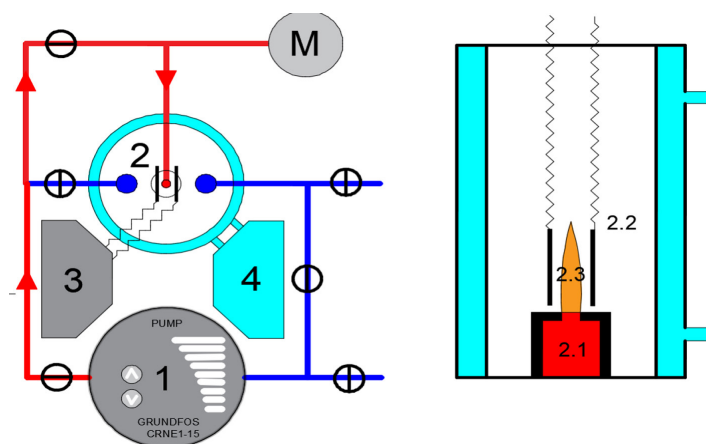


Fig. S 1. A – Laboratory bench for HC, AC and HAC generation; B – Cavitation chamber. 1 – vertical multistage pressure-controlled centrifugal pump, 2 – cavitation chamber, M – monometer, 2.1 – nozzle, 2.2 – piezo cells, 2.3 – cavitation cloud, 3 – high frequency generator 1.7 MHz, 4 – thermostat.

The total volume of the treated solution was 6.4 L. All elements of the reactor were made of stainless steel. The power consumption was 50 W for AC, and 400 W for HC (at 5 atm). The power consumption was determined using an energy monitor (Voltcraft Energie Monitor 3000, Conrad Electronic SE, Germany, with an accuracy of ± 1 %).

Experimental and analytic methods

For a typical degradation experiment, 6.4 L BPA aqueous solution with a concentration 43.8 μM was prepared. In the HC experiments, the inlet pressure varied from 1.5 to 5 bar. In the AC only experiments, the solution was passed through an additional circuit bypassing the HC nozzle. In SR-AOPs experiments, reagents were added to the cavitation chamber. The concentration of $\text{K}_2\text{S}_2\text{O}_8$ was set in the range of 219–657 μM , and Fe^{2+} in the range of 17.8–133.5 μM . Samples were taken from the cavitation chamber before the reaction (0 min, initial concentration), and after 5, 10, 20, 40, 60, 120, 180, 240 min reaction time. All experiments were performed in duplicates.

BPA was quantitatively analyzed by HPLC using an Agilent 1260 Infinity with Zorbax SB-C 18 4.6 \times 150 mm column. Samples were filtered on FMPTFE-0.45 μm membrane filters prior to analysis.

The degree of organic substrate mineralization was assessed by measuring the change in TOC, using a Shimadzu TOC–L CSN analyzer with a detection limit of 50 $\mu\text{g/L}$. Calibration of the analyzer was carried out using standard samples of potassium hydrophthalate and sodium hydrocarbonate.

The Multi 3410 Pocket Meter with SenTix®940 electrode (WTW, Germany) was used to measure pH values.

The toxicity assessment method used was based on bioluminescence inhibition of the recombinant strain of *E. coli* K12 TG1 carrying lux operons of the luminescent *Photobacterium leiognathi* [15]. The toxicity was tested before and after treatment for 240 min.

The degradation (E) and mineralization (M) of BPA were calculated by measuring the changes in BPA and TOC concentrations in the treated solution at time τ using the formulas:

$$E(\%) = \left(1 - \frac{C_\tau}{C_0}\right) \times 100, \quad (1)$$

$$M(\%) = \left(1 - \frac{TOC_\tau}{TOC_0}\right) \times 100. \quad (2)$$

In our study, the synergy of HAC/PS/ Fe^{2+} system was quantified by calculating synergistic indices φ_1 and φ_2 ($\varphi > 1$ indicates a synergistic effect). The synergistic indices for the efficiency of BPA degradation (φ_1) and mineralization (φ_2) were calculated according to the formulas:

$$\varphi_1 = \frac{E_{\text{HAC/PS/Fe}^{2+}}}{E_{\text{HAC/PS}} + E_{\text{PS/Fe}^{2+}}} \quad (3)$$

$$\varphi_2 = \frac{M_{\text{HAC/PS/Fe}^{2+}}}{M_{\text{HAC/PS}} + M_{\text{PS/Fe}^{2+}}}, \quad (4)$$

where E is the BPA degradation efficiency, M is the mineralization efficiency (in terms of TOC decay). A similar calculation of synergistic indices was adopted analogously from the work of the authors A. Delavaran Shiraz et al. [16].

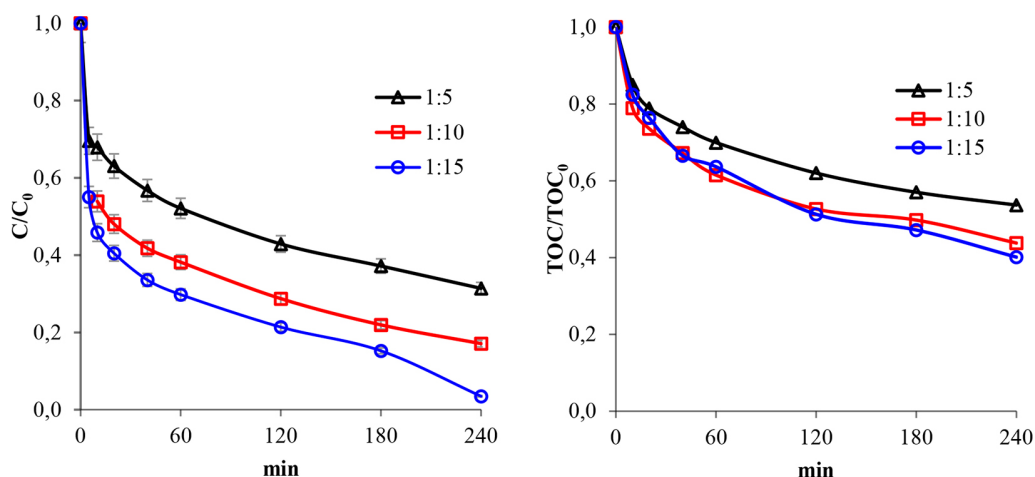


Fig. S 2. The kinetics of destruction and mineralization of BPA in hybrid HAC/PS/Fe²⁺ system at different molar ratio [BPA]:[PS]. $C_0(\text{BPA}) = 43.8 \mu\text{M}$, $C_0(\text{Fe}^{2+}) = 89 \mu\text{M}$, $C_0(\text{PS}) = 219, 438 \text{ и } 657 \mu\text{M}$, $T = 25 \pm 1^\circ\text{C}$, $\text{pH} = 3.5$, $P = 5 \text{ atm}$.

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