

EDN: UNWMZJ

УДК 544.576

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

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Received 07.11.2023, received in revised form 12.02.2024, accepted 14.02.2024

Abstract. The present study is the first report on applying combination of low-pressure hydrodynamic cavitation and high-frequency ultrasound in the megahertz range (1.7 MHz) in a single reactor system (hydrodynamic-acoustic cavitation – HAC) in sulfate radical-based advanced oxidation processes (SR-AOPs) for degrading bisphenol A (BPA). A comparative evaluation of individual, combined and hybrid oxidation systems has been provided. The degradation efficiency of the target compound increases in the following order: AC < HC < HAC < HC/PS \approx AC/PS < HAC/PS \ll HAC/PS/Fe²⁺. The combination of two types of persulfate (PS) activation (cavitation and Fe²⁺ ions) in the hybrid oxidation system HAC/PS/Fe²⁺ shows significant synergistic effects due to faster and more efficient generation of reactive oxygen species (ROS) from PS. Only in hybrid HAC/PS/Fe²⁺ system, along with the almost complete oxidation of BPA (97 %), a quite high mineralization (up to 60 %) in terms of total organic carbon (TOC) decay has been achieved without accumulation of toxic intermediates. Radical quenching tests showed that both SO₄^{•-} and HO[•] radicals are involved in the hybrid HAC/PS/Fe²⁺ system, with HO[•] being more dominant. The effects of pH, inlet pressure, Fe²⁺ and PS concentrations were studied and discussed. The influence of natural organic matter (NOM) and coexisting inorganic anions (SO₄²⁻, Cl⁻ and HCO₃⁻) were also examined, but only Cl⁻ (10 mM) had a promoting effect on BPA degradation. This study demonstrates the great potential of hybrid HAC/PS/Fe²⁺ process for effective degradation of emerging organic contaminants with good scale-up capabilities.

Keywords: Bisphenol A, hydrodynamic-acoustic cavitation, persulfate, Fenton-like system, degradation, mineralization.

Acknowledgment. This research was financially supported by the Russian Science Foundation No. 22–29–00406, <https://rscf.ru/en/project/22–29–00406/>, using the equipment of the CCU BINM SB RAS (Ulan-Ude, Russia).

Citation: Aseev D. G., Sizykh M. R., Batoeva A. A. Enhanced degradation and mineralization of bisphenol A by hybrid process using hydrodynamic-acoustic cavitation. J. Sib. Fed. Univ. Chem., 2024, 17(1), 5–17. EDN: UNWMZJ



Кавитационная активация процессов деструкции и минерализации Бисфенола А

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Аннотация. Впервые исследованы основные закономерности процессов деструкции Бисфенола А (БФА) персульфатом (ПС) при одновременном воздействии низконапорной гидродинамической кавитации (ГК) и высокочастотного ультразвука (АК) мегагерцового диапазона (1,7 МГц) в совмещенной реакционной системе ГАК (гидродинамическая-акустическая кавитация). Дана сравнительная оценка индивидуальных, комбинированных и гибридных окислительных систем. Эффективность деструкции целевого соединения возрастает в ряду: АК < ГК < ГАК < ГК/ПС ≈ АК/ПС < ГАК/ПС << ГАК/ПС/Fe²⁺. При сочетании двух видов активации персульфата – кавитационной и ионами Fe²⁺, в гибридной окислительной системе ГАК/ПС/Fe²⁺ наблюдается значительный синергический эффект, обусловленный более быстрым и эффективным образованием активных форм кислорода из персульфата. Только в гибридной системе ГАК/ПС/Fe²⁺ наряду с практически полным окислением БФА (97 %) достигается достаточно высокая минерализация целевого соединения (до 60 %) без накопления токсичных промежуточных продуктов. С использованием ингибиторов радикальных реакций показано, что в гибридной системе ГАК/ПС/Fe²⁺ участвуют радикалы SO₄^{•-} и HO[•], причем вклад гидроксильных радикалов является доминирующим. Изучено влияние pH, давления на входе, концентраций Fe²⁺ и ПС. Кроме того, исследовано влияние природного органического вещества и сопутствующих неорганических анионов (SO₄²⁻, Cl⁻ и HCO₃⁻), установлено промотирующее влияние Cl⁻ (10 mM) на процесс дегратации БФА. Полученные результаты свидетельствуют о перспективности использования гибридной системы ГАК/ПС/Fe²⁺ для эффективного разложения биорезистентных органических загрязнителей.

Ключевые слова: Бисфенол А, гидродинамическая-акустическая кавитация, персульфат, Фентон-подобная система, дегратация, минерализация.

Благодарности. Данное исследование выполнено при финансовой поддержке Российского научного фонда № 22–29–00406, <https://rscf.ru/en/project/22–29–00406/>, с использованием оборудования ЦКП БИП СО РАН (Улан-Удэ, Россия).

Цитирование: Асеев Д. Г., Сизых М. Р., Батоева А. А. Кавитационная активация процессов деструкции и минерализации Бисфенола А. Журн. Сиб. федер. ун-та. Химия, 2024, 17(1). С. 5–17. EDN: UNWMZJ

Introduction

Research into the development of advanced oxidative methods for the treatment of persistent organic pollutants (POPs) is leading to the creation of new technologies with promising industrial applications. Although POPs are typically found in trace amounts, even these levels can have hazardous effects, such as carcinogenicity, toxicity and mutagenicity. Endocrine-disruption compounds are an important group of emerging contaminants of aquatic environment. One of the most common micropollutants is bisphenol A (BPA), which is produced in large quantities due to its wide use as a monomer in the production of polycarbonate, epoxy resins, and unsaturated polyester resins. BPA is increasingly found in both industrial wastewater and drinking water, posing a threat to humans. Even low levels of this compound have adverse effects on animals and humans [1,2].

AOPs based on in situ generation of reactive oxygen species (ROS) have been identified as the most promising to address this problem [3–5]. Hybrid treatment methods that combine cavitation with known AOPs provide lower oxidant concentrations, lower operating costs, and shorter treatment times. Enhanced oxidation of pollutants in wastewater due to cavitation effects such as localized hot spots, free radical generation, and high turbulence can also lead to more efficient use of added oxidants [6].

Acoustic Cavitation (AC) and Hydrodynamic Cavitation (HC) are two widely used methods for creating cavitation conditions [7, 8]. Thermodynamic state variables, such as pressure and temperature, along with the type of cavitation generator, reactor geometry, gas fraction, and materials to be processed, have a significant impact on bubble dynamics. The relationship between these variables is complex and not yet fully understood [9]. (A brief literature review is presented in the *Supplementary Information (SI) Text A*). Although the degradation of BPA by AOPs has been studied for many years, there are still a number of important issues that need to be investigated further.

Increased degradation of contaminants in the treatment process and greater energy efficiency can be achieved in a single hydrodynamic-acoustic cavitation (HAC) reactor system that combines the advantages of HC and AC – high bubble density and high collapse intensity [10, 11]. We propose the use of high-frequency ultrasound in the megahertz (1.7 MHz) range in combination with low-pressure HC, which has proven to be an energy-efficient method [12, 13]. Moreover, the fields of hydrodynamic and acoustic cavitation are combined, the bubbles formed in HC immediately fall into the area of sound waves and AC, thus additional bubble oscillations occur.

The combination of oxidants such as $K_2S_2O_8$ (PS) with cavitation can lead to further increase in the efficiency of the treatment process. This is because such combination increases the generation of ROS, including hydroxyl and sulfate radicals [14].

The purpose of this work is to study the degradation and mineralization of organic micropollutants (using BPA as an example) through the combined application of HC and AC (1.7 MHz) in hybrid oxidation systems HAC/PS and HAC/PS/Fe²⁺. To our knowledge, the present study is the first report

on applying combination of low-pressure HC and high-frequency ultrasound in the megahertz range in a single reactor system (HAC) in SR-AOPs for degrading BPA.

Materials and Methods

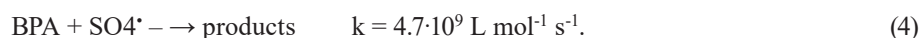
Sources of chemicals and reagents and assay methods are provided in the *Text B, SI*.

Results and discussion

HAC/PS oxidative system

The kinetics of BPA oxidation in single AC and HC processes, combined AC/PS, HC/PS, HAC (where HC and AC occur simultaneously in the same space), and hybrid HAC/PS oxidation systems were evaluated comparatively (Fig. 1). The reaction rate of BPA oxidation in the combined HAC system ($k = 4.23 \times 10^{-4} \text{ min}^{-1}$) increased by 22 % compared to HC, while the energy input increased by only 12.5 % (from 400 W to 450 W). When an oxidant was added ($[\text{PS}]/[\text{BPA}] = 5:1$), the hybrid HAC/PS oxidation system showed a 28 % acceleration in the degradation of the targeted compound ($k = 5.4 \times 10^{-4} \text{ min}^{-1}$).

A large number of cavitating microbubbles are formed in the hybrid HAC/PS oxidation system due to the heterogeneous hydrodynamic cavitation field. Additional exposure to ultrasound (1.7 MHz) increases the number of oscillations and effective collapses of cavitating microbubbles, which ultimately leads to the formation of ROS that react with BPA at a high rate [15]:



The efficiency of the BPA oxidative degradation process increases in the following order: AC < HC < HAC < HC/PS \approx AC/PS < HAC/PS.

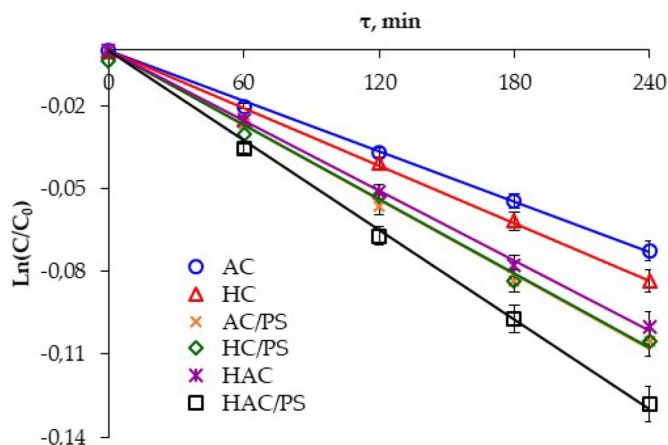


Fig. 1. Degradation of BPA in different oxidation systems. $[\text{BPA}] = 43.8 \mu\text{M}$, $[\text{PS}] = 219 \mu\text{M}$, $P = 5 \text{ bar}$, $\text{pH} = 5.6$

The results obtained suggest that the use of HAC-induced systems for cavitation activation of oxidation processes in SR-AOPs is feasible. It should be noted that under these experimental conditions the oxidation of BPA was quite slow and no decrease in TOC was observed. To enhance BPA oxidation, we next consider a hybrid HAC/PS/Fe²⁺ Fenton-like oxidation system where PS is activated by both cavitation and Fe²⁺ ions simultaneously.

HAC/PS/Fe²⁺ oxidative system

As expected, a significant increase in the rate of BPA oxidation was observed in the hybrid HAC/PS/Fe²⁺ Fenton-like oxidation system. The conversion rate reached 69 % after a 240 min treatment ([PS]/[BPA] = 5:1). Significant mineralization (46 %) of BPA degradation intermediates was observed after 240 minutes of treatment, indicating a fairly deep level of conversion (Table 1). This is a fundamental advantage of the hybrid HAC/PS/Fe²⁺ oxidation system that we are developing, which indicates the need for further detailed investigation.

The results obtained are in good agreement with the findings of other authors [16], which also confirm that the combination of several types of PS activation promotes a faster and more efficient formation of ROS.

A key factor in evaluating the overall efficiency of hybrid oxidation systems is the presence of a synergistic effect.

The high values of the synergistic indices (Table 1), both for BPA degradation ($\varphi_1 > 1$) and for mineralization in terms of TOC decay ($\varphi_2 \gg 1$), indicate that a complex radical chain mechanism of BPA degradation is taking place in a hybrid HAC/PS/Fe²⁺ oxidative system (with simultaneous activation of PS by cavitation and Fe²⁺ ions) involving the in situ generated ROS.

Effect of pH value on degradation of BPA by HAC/PS/Fe²⁺ oxidative system

The effect of pH on the degradation and mineralization of BPA in the HAC/PS/Fe²⁺ system was investigated at pH 3.5, 5.6, and 11.0 (Fig. 2). A decrease in process efficiency was observed when the pH was changed from acidic to near neutral, resulting in a slower rate of BPA degradation and mineralization. Specifically, the efficiency decreased from 69 % to 51 % for BPA degradation and from 46 % to 25 % for mineralization after 240 minutes of treatment.

In an alkaline medium, oxidation of BPA virtually stops. Two different pKa values are known for BPA: 9.6 and 10.2 [17]. Consequently, at pH 3.5 and 5.6, BPA mostly exists in a neutral molecular form, while at pH 11.0, it is completely in an ionic form. Thus, in an alkaline medium, the molecular anion of BPA is much more hydrophilic, and less likely to approach negatively charged bubbles. As a

Table 1. Degradation and mineralization of BPA in different oxidative systems (after a treatment time of 240 min): [BPA] = 43.8 μ M, [PS] = 219 μ M, pH = 3.5, P = 5 bar

Oxidative system	E, %	φ_1	M, %	φ_2
HAC/PS	12		0	
PS/Fe ²⁺	47		12	
HAC/PS/Fe ²⁺	69	1.2	46	3.8

result, the faster degradation of BPA at pH 3.5 and 5.6 (rather than pH 11.0) is explained by the more likely diffusion of the molecule at lower pH to the bubble-liquid interface, where the concentration of hydroxyl radicals is highest. A similar inhibition of BPA oxidation by sono-activated PS in alkaline medium using low frequency ultrasound (20 kHz) was reported by Darsinou et al. [18].

On the other hand, in Fenton-like systems, the reactivity of iron ions is significantly influenced by the reaction medium [19] – at pH values above 3.5 iron ions are converted to the hydroxylated form, which leads to their deactivation. Our results demonstrate that BPA degradation and mineralization in the HAC/PS/Fe²⁺ system can occur at pH 5.6, albeit with decreased efficiency (Fig. 2). The destruction of the formed iron-containing complexes and the formation of additional ROS probably occur under cavitation conditions [20]:



Effect of hydrodynamic pressure on degradation and mineralization of BPA by HAC/PS/Fe²⁺ oxidative system

In a hydrodynamic cavitation system, the inlet pressure is an important parameter that determines the intensity of the cavitation effects. An optimal inlet pressure provides the maximum cavitation effect, while too high pressure leads to a decrease in process efficiency [21, 22].

To maximize the cavitation effect (and avoid suppressed cavitation), the inlet pressure must be optimized. It has been experimentally established that the inlet pressure is a significant factor in the process of BPA degradation in the HAC/PS/Fe²⁺ oxidative system. At a pressure of 1.5 bar, the cavitation effect on the degradation efficiency of the target compound was practically negligible, however, the degree of mineralization increased significantly – by 2.4 times (Fig. 3). A further increase in inlet pressure led to an increase in the rate of BPA oxidation reactions. At the same time, the maximum efficiency of BPA degradation (69 %) and mineralization in terms of TOC decay (46 %) was achieved at 5 bar.

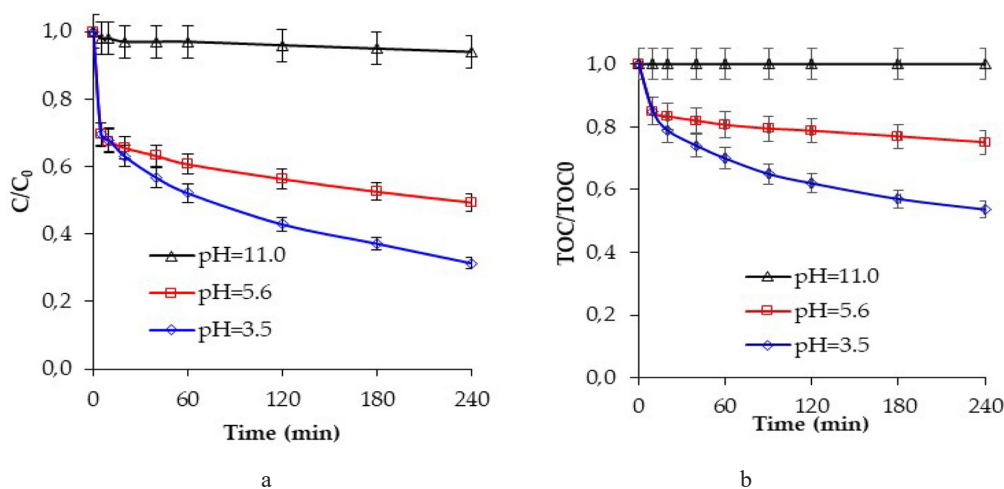


Fig. 2. Degradation (a) and mineralization (b) of BPA in the HAC/PS/Fe²⁺ system at different pH. [BPA] = 43.8 μM, [PS] = 219 μM, [Fe²⁺] = 89 μM, P = 5 bar

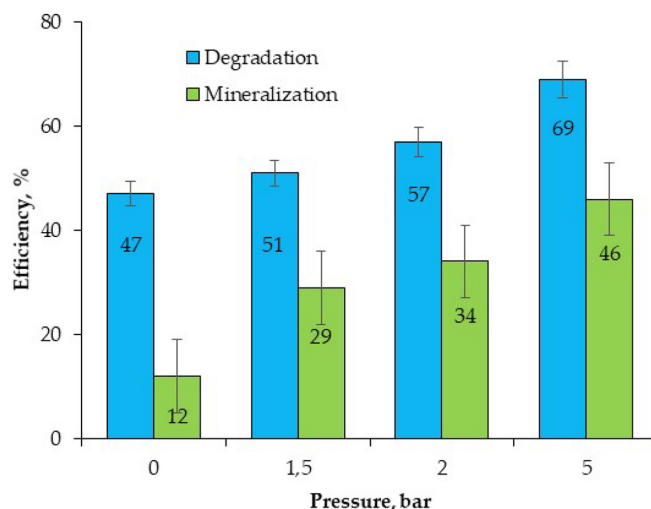


Fig. 3. Effect of inlet pressure on degradation and mineralization of BPA by HAC/PS/Fe²⁺ oxidative system (after 240 min of the process). [BPA] = 43.8 μM, [PS] = 219 μM, [Fe²⁺] = 89 μM, pH=3.5. Pressure equal to 0 means that the liquid is moving along the path bypassing the hydrodynamic cavitation

Effect of Fe²⁺ concentration on degradation and mineralization of BPA by HAC/PS/Fe²⁺ oxidative system

Fe²⁺ concentration has a significant influence in Fenton-like oxidation processes. Hydroxyl and sulfate radicals are formed during the catalytic decomposition of H₂O₂ and PS, so the amount of iron ions has a significant impact on performance and operating costs. Optimizing the concentration of Fe²⁺ is extremely important because an excess of iron can reduce the efficiency of destruction due to non-target reactions of radicals [23]. It should be noted that many of the studies [24, 25] use high concentrations of iron, which is not acceptable in the development of eco-friendly technologies.

The Fe²⁺ concentration was experimentally found to have a significant effect on the degree of degradation and mineralization of BPA in the HAC/PS/Fe²⁺ system (Fig. 4). By increasing the Fe²⁺ concentration from 17.8 μM to 89 μM, the degradation efficiency increased from 30 % to 57 %, and the degree of mineralization of dissolved organic carbon increased from 26 % to 34 % after 4 h of treatment. Further increase in the concentration of iron ions up to 133.5 μM had no significant effect on the rate and efficiency of the oxidative process, so in our subsequent studies we used a concentration of 89 μM (5 mg/L).

Effect of PS concentration on degradation and mineralization of BPA in HAC/PS/Fe²⁺ oxidative system

Oxidant concentration has a significant effect on the rate and efficiency of oxidation of bioresistant micropollutants in AOPs. Experimental observations showed that by increasing the PS concentration from 219 μM to 657 μM (oxidant-substrate molar ratio from 5:1 to 15:1), the initial rate of the BPA oxidation reaction in the HAC/PS/Fe²⁺ system increased 1.7-fold and the destruction efficiency increased by 28 % (Table 2, Fig. S2, S1). The molar ratio of [PS]:[BPA]=15:1 corresponds to 42 % of the stoichiometrically required amount of oxidant calculated from the hypothetical reaction equation of complete BPA oxidation

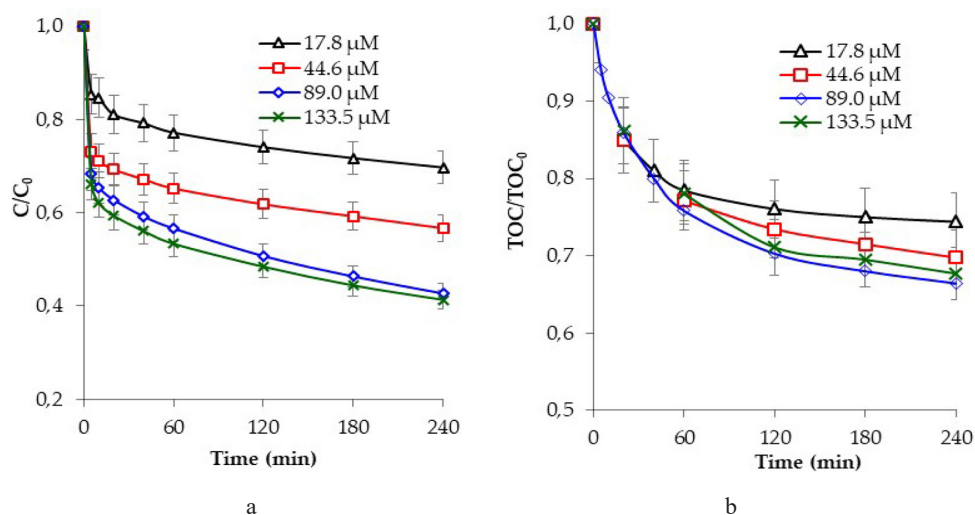
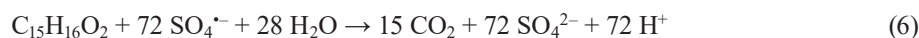


Fig. 4. Degradation (a) and mineralization (b) of BPA in the HAC/PS/Fe²⁺ at different iron concentrations. [BPA] = 43.8 μM, [PS] = 219 μM, pH = 3.5, P = 2 bar

Table 2. Degradation and mineralization of BPA in the hybrid HAC/PS/Fe²⁺ system at different concentrations of oxidant. [BPA] = 43.8 μM, [Fe²⁺] = 89 μM, pH = 3.5, P = 5 bar, τ = 240 min

[PS], μM	[PS]/[BPA]	Degradation BPA		Mineralization TOC	
		W ₀ , μM·min ⁻¹	E, %	W ₀ , mgC·min ⁻¹	M, %
219	5	1.41	69	0.13	46
438	10	2.02	83	0.18	56
657	15	2.37	97	0.15	60

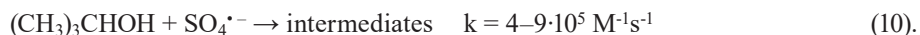
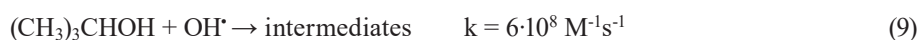
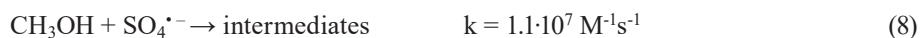
(reaction 6). However, at this ratio, there was almost complete conversion of the target compound (97 %), and oxidation of intermediate products with their subsequent mineralization (60 %).



The role of ROS and effect of coexisting inorganic anions and NOM on degradation and mineralization of BPA in HAC/PS/Fe²⁺ oxidative system

As BPA is a low volatile and moderately soluble compound (vapor pressure at 25 °C C = 4.0·10⁻⁸ mmHg; solubility = 120 mg/L [26], K_{ow} = 10^{3.40} [27]), its main degradation pathway is expected to be oxidation by radicals in the solution volume. Experiments were conducted to investigate the influence of hydroxyl and sulfate radicals in the hybrid HAC/PS/Fe²⁺ oxidative system. For this purpose, inhibitors of radical reactions, namely methyl and tert-butyl alcohols, were added (Fig. 5). The contribution of ROS to the oxidative process can be identified based on the different rates of interaction of free radicals with alcohols (reactions 7–10), which act as “traps” [28].





Analyzing the rate constants of radicals with alcohols, it can be concluded that methanol CH_3OH interacts with both $\cdot\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals, whereas tert-butanol $(\text{CH}_3)_3\text{CHOH}$ primarily interacts with OH^{\bullet} . Considering the rate constants of radicals with BPA (reactions 3, 4), it is necessary to utilize an excess of alcohols.

Experiments have shown that the addition of radical “traps” significantly slowed the process of BPA degradation (Fig. 5) and reduced its efficiency. After 240 minutes of treatment, the efficiency of BPA degradation decreased by 43 % with the addition of methanol, and by 33 % with tert-butanol. The experimental results have convincingly demonstrated that in the considered hybrid HAC/PS/ Fe^{2+} system, both $\cdot\text{OH}$, так и $\text{SO}_4^{\bullet-}$ radicals participate in the oxidative degradation, with the contribution of hydroxyl radicals being dominant.

The interaction of inorganic anions with ROS can lead to changes in the type and concentration of radicals, which in turn can significantly affect the effectiveness of organic contaminant removal. The influence of inorganic anions on the effectiveness of AOPs is complex and depends on the types and concentrations of the anions, the oxidant, and the nature of the target organic pollutants [29].

It was found experimentally that the addition of hydrocarbonates virtually stopped the degradation of BPA in HAC/PS/ Fe^{2+} system: the degradation efficiency did not exceed 10 % after 240 minutes of treatment. When hydrocarbonates were added, the pH of the solution became slightly alkaline (pH about 8), which led to hydrolysis of iron, its precipitation and removal from the reaction medium. In addition, hydrocarbonates react with ROS at a high rate ($k_{\cdot\text{OH}} = 8.5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{SO}_4^{\bullet-}} = 1.6 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [29, 30]) and can compete with the target compound.

The addition of sulfates or NOM slowed down the BPA oxidation process (Fig. 6), and the degradation efficiency was reduced by 13 % and 10 %, respectively. A similar effect of sulfates and

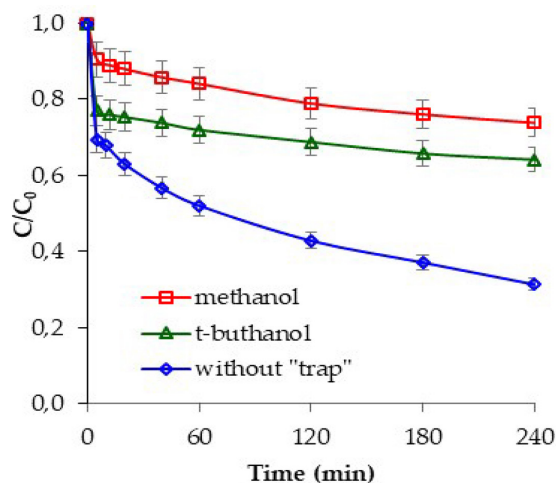


Fig. 5. Radical scavenging in the hybrid HAC/ Fe^{2+} /PS system. $[\text{BPA}] = 43.8 \mu\text{M}$, $[\text{PS}] = 219 \mu\text{M}$, $[\text{Fe}^{2+}] = 89 \mu\text{M}$, $[\text{ROH}] = 109.5 \text{ mM}$, $\text{pH} = 3.5$, $P = 5 \text{ bar}$

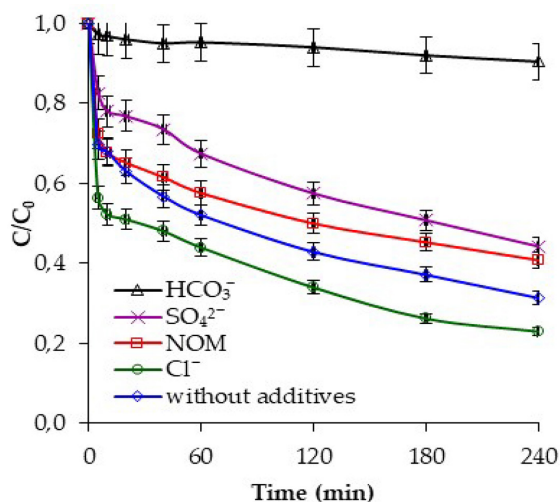
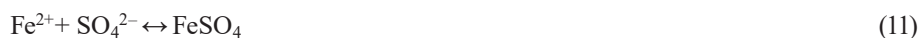


Fig. 6. Effect of co-existing inorganic anions and NOM in the hybrid HAC/Fe²⁺/PS system. [BPA] = 43.8 μM, [PS] = 219 μM, [Fe²⁺] = 89 μM, [Cl⁻] = 10 mM, [SO₄²⁻] = 10 mM, [HCO₃⁻] = 10 mM, C₀(NOM) = 2 mg/L, pH = 3.5, P = 5 bar.

NOM on the oxidation of BPA by activated PS has been reported in other studies [18, 31]. It is assumed that sulfates can form aqua complexes with Fe²⁺ and Fe³⁺, reducing the concentration of free iron ions capable of activating PS [32]:



NOM reacts with ROS at a high rate ($k_{\text{OH}} = 3 \cdot 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_{\text{SO}_4^{\cdot-}} = 2.4 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ [33]) and can compete with the target compound.

The addition of chlorides to the solution resulted in an increase in the rate of BPA oxidation reaction and increased the degradation efficiency by 8 %. Chlorides reacted with ROS at a high rate ($k_{\text{OH}} = 4.3 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_{\text{SO}_4^{\cdot-}} = 3.1 \cdot 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$), resulting in the formation of chlorine-containing radicals (Cl[•], Cl₂[•], ClO[•], etc.) in solution. These radicals react with organic compounds having electron donor groups (including BPA) by stripping hydrogen atoms and forming radical products [34], thereby stimulating the degradation of organic pollutants [35].

Conclusions

In this paper, we investigated the degradation and mineralization of BPA in SR-AOPs using HAC – the combined effect of low-pressure hydrodynamic cavitation and high-frequency ultrasound in the megahertz (1.7 MHz) range. A comparative evaluation of the discussed oxidative systems has been provided. The degradation efficiency of the target compound increases in the following order: AC < HC < HAC < HC/PS ≈ AC/PS < HAC/PS << HAC/PS/ Fe²⁺. Our findings indicate the feasibility of using HAC-induced systems for cavitation activation of oxidative processes in SR-AOPs.

The combination of two types of PS activation (cavitation and Fe²⁺ ions) in the hybrid oxidation system HAC/PS/Fe²⁺ showed significant synergistic effects due to faster and more efficient generation

of ROS from PS. The high values of the synergistic indices, both for BPA degradation ($\phi_1 > 1$) and for mineralization in terms of TOC decay ($\phi_2 \gg 1$), indicate that a complex radical chain mechanism of organic matter degradation is taking place in a hybrid HAC/PS/Fe²⁺ oxidative system involving the *in situ* generated ROS.

In hybrid HAC/PS/Fe²⁺ system, along with the almost complete oxidation of BPA (97 %), a quite high mineralization (up to 60 %) of dissolved organic matter has been achieved without accumulation of toxic intermediates. Radical quenching tests showed that both SO₄^{•-} and HO[•] radicals are involved in the hybrid HAC/PS/Fe²⁺ system, with HO[•] being more dominant. The effects of pH, inlet pressure, Fe²⁺ and PS concentrations were studied and discussed. The influence of NOM and coexisting inorganic anions (SO₄²⁻, Cl⁻ and HCO₃⁻) was also examined, but only Cl⁻ (10 mM) had a promoting effect on BPA degradation. This study demonstrates the great potential of hybrid the HAC/PS/Fe²⁺ process for effective degradation of emerging organic microcontaminants with good scale-up capabilities.

Supplementary Information



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