Sonophotocatalytic (1.7 MHz, 254 nm) destruction of Bisphenol-A in aqueous solutions

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Abstract. Bisphenol A (BPA) an organic compound largely used in the plastic industry as a monomer. The micropollutant BPA (43.8 µM) was employed under conditions of high-frequency ultrasound (1.7 MHz, 25 W) and ultraviolet radiation (254 nm). To enhance degradation a Fenton-like oxidation system was used, including persulfate as an oxidizing agent and ferrous iron (Fe (II)) as a catalyst. Experiments were carried out in a flow sonophotoreactor, flow rate 0.5 l/min. The progress of the treatment of Bisphenol-A solution has been monitored in terms of reduction in the concentration (HPLC) and dissolved organic carbon (DOC). A large synergistic effect (2.4) was shown in the oxidation of Bisphenol-A from the combined effect of two directed at each other sources of ultrasound. The efficacy of combined approaches was generally higher than individual treatment methods of sonolysis (87%) and photolysis (15%) in 240 min of treatment. Complete oxidation of BPA is achieved in the {UV/US/ Fe²⁺/S²O₈²⁻} system in 120 minutes, however, mineralization reaches (50%), possibly due to the lack of an oxidizing agent. The reaction rates of Bisphenol A degradation and mineralization increase in the order: {UV} <{US} <{Fe²⁺/S²O₈²⁻} <{US/Fe²⁺/S²O₈²⁻} <{UV/US/Fe²⁺/S²O₈²⁻}.

1. Introduction

Bisphenol A has an endocrine disrupting effect (EDE), inhibit the action of hormones of all organisms and microorganisms [1,2]. Bisphenol A also a xenobiotic that can enter the environment from waste [3], although it is widely used in industry as a monomer for the production of plastics. Even with micro-concentrations, Bisphenol A disrupts the behavior of organisms [4]. BPA production is one of the largest in the world. Its production volume is more than 450 million tons per year, while more than 100 tons are released into the atmosphere annually. According to numerous foreign studies, the content of BPA in surface waters, wastewater and tap water varies from 300 pg/l to 98 µg/l. The report of the International Endocrinological Society, published in 2009, contains the conclusion of 38 experts, according to which a person is currently exposed on average to a higher level of exposure to BPA than that which has a toxic effect on laboratory animals. Thus, the US Environmental Protection Agency has established a MPC for BPA of 0.05 mg/L. The European Commission recommended the maximum daily intake at the same level.

Bisphenol A practically does not oxidation using traditional removal methods, and chlorination and disinfection processes can lead to products with higher EDE and/or toxicity [5]. Advanced oxidation processes (AOP) have been successfully tested to remove organic substances, however, they can lead to the formation of secondary products more dangerous than the parent compound [6], complete...
mineralization is rarely reached and is not cost-effective [7]. AOP has a significant drawback - the high cost, which is determined by the cost of reagents and electricity (when using physical generation methods). For this reason, they are considered an alternative to wastewater treatment only when it is not possible by other methods, including biological ones.

An ultrasonic wave propagating in an aqueous medium leads to the formation of HO•, and the resulting radicals destroy organic molecules [8]. The resulting cavitation cavities are chemical microreactors. With adiabatic compression of the gas in the cavitation cavity, high temperatures and pressure are achieved [9]. Therefore, organic pollutant with high volatility will be excited and dissociate.

A hydrophilic or hydrophobic compound with low volatility cannot enter the cavity, but will be hydroxylated in the bulk solution or interfacial area as a result of reaction with HO•. These radicals generated inside the cavity result from the dissociation of H2O [10]:

\[
H_2O + US, UV \rightarrow H^+ + HO^-
\]

The speed of reactions, as well as the variety of products depend on the nature of the dissolved gases, the power and frequency of ultrasound [11]. Combining of US and UV removes limitations of mass transfer, usually associated with photocatalytic oxidation, and also increases the formation of HO•, which gives much higher degrees of conversion and mineralization. Also, the effect can be increase, for example, by injection of environmentally friendly oxidizing agents, such as hydrogen peroxide or persulfate. As well, previous studies have shown that the addition of iron ions, when combined with UV, can enhance ultrasound exposure [12]. As noted earlier, AOPs are usually based on the high oxidative ability of OH• radicals. However, sulfate anion radicals (SO₄²⁻) formed from persulfates are also considered as an alternative option for the oxidative destruction of pollutants in water.

Previous studies have shown the high ability of SO₄²⁻ to destruction organic pollutants [13]. The main advantages of persulfates compared with hydrogen peroxide include easier activation, high stability in water, comparable standard electrode potential, wider working pH range, facilitated method of introducing a reagent, and the highest selectivity [14]. The above-mentioned advantages make sulfate radicals relatively more effective and selective for wastewater treatment. The quantum yields of the photochemical formation of SO₄²⁻ are also higher than in the case of the formation of OH• [15]. The only drawback of persulfates is the formation of residual sulfate anions and increase concentration of potassium (sodium) ions.

Some researchers have shown the possibility of complete oxidation BPA and its intermediates by the combination of US and UV in the presence of S₂O₈²⁻ or H₂O₂, using TiO₂ or Fe²⁺ as catalysts, but in the cited studies, low- and medium-frequency ultrasound (35 kHz, 300 kHz) was used [16, 17]. The objective of this study was to investigate the kinetics of BPA removal using energy-based AOPs coupled with a combination of 1.7 MHz high-frequency ultrasound, 254 nm ultraviolet radiation and using S₂O₈²⁻ oxidizing agent and an Fe²⁺ catalyst. Any research using this frequency for the destruction of BPA not found. The main advantages of using ultrasound with a frequency of 1.7 MHz is the low power consumption and chemical inertness of ceramic piezo-electric elements. Ultraviolet 254 nm a widespread and readily available source of ultraviolet radiation. On the one hand, it weakly affects BPA, but is able to activate the oxidizing agent persulfate. On the other hand, the advantage of its use is the energy consumption comparable to ultrasound 1.7 MHz.

Various AOPs was investigated, such as sonolysis using high frequency ultrasound (US 1.7 MHz), photolysis (UV 254 nm), sonophotolysis {US/UV}, sonophotocatalysis {US/UV/Fe²⁺} and Fenton-like oxidation system {US/UV/Fe²⁺/S₂O₈²⁻}.

2. Materials and methods
An aqueous solution of Bisphenol A (BPA) (≥99%, Sigma Aldrich, USA) with a concentration of 43.8 µM (10 mg/L), pH₀ = 5.5, prepared based on distilled water was used throughout the study. Reagents were also used: iron (II) sulfate FeSO₄·7H₂O (≥99.5%, Scharlab S.L., Spain), K₂S₂O₈ (99%, Khimreaktivsnab, Russia).
Experiments were performed in a flow sonophotoreactor, flow rate 0.5 l / min. The laboratory setup (Figure 1) will include a thermostatic buffer tank (V = 0.4 L, T = 25 ° C), a chemical peristaltic pump, piezo-electric disc (diameter 20 mm) powered by high-frequency ultrasound generators (1.7 MHz, 25 W) and a photoreactor containing a radiation source - a low-pressure mercury-quartz lamp with a radiation maximum at 254 nm, a cylindrical quartz reactor and a reflector. The reflector is made of aluminum sheet in the form of a shell, in the context of an ellipse. In this case, the radiation source and the reactor are located in the zones corresponding to the foci of the ellipse, because a similar shape of the reflector and the arrangement of the emitter and the reactor provide a high coefficient of utilization energy of UV radiation. The intensity of UV radiation determined by the method of atrosine dosimetry was found 0.49 mW/cm². The average thickness of the stacked film inside the quartz tube is approximately 0.4 mm.

![Figure 1. Schematic diagram of the sonophotocatalytic reactor.](image)

The BPA conversion was followed in HPLC on an Agilent 1260 Infinity liquid chromatograph with a highly sensitive fluorescence detector (λ_{excitation} = 230 nm, λ_{emission} = 315 nm). Isocratic elution chromatographic separation was carried out on a Zorbax SB-C18 analytical column with a particle size of 5 μm. A mixture of acetonitrile with 75 mM CH₃COOH in a volume ratio of 45:55, an elution rate of 0.5 ml/min, a column thermostat temperature of 35 °C, and a sample volume of 70 μl were used as the mobile phase. Sample preparation was performed by microfiltration using membrane filters FMPTFE-0.45 μm (ZAO Vladisart, Russia).

The mineralization of the organic substrate was stated by the change in the content of dissolved organic carbon (DOC), determined using a Shimadzu TOC-L CSN analyzer (detection limit of 50 μg/L).

3. Results and discussion
In the study of the kinetics of BPA oxidation, using only the effect of high-frequency ultrasound 1.7 MHz a decrease in the concentration of BPA was observed and a synergistic effect was found. So when using two ultrasonic piezo-electric disc coaxially aligned and directed “face to face” (the distance between the piezo-electric disc is 10 mm), the BPA oxidation rate does not increase additively. The synergistic effect was found by the formula:
We already observed a similar effect when working with studies were conducted in model aqueous solutions of potassium butyl dithiocarbonate [18]. With an increase ultrasonic power, an increase the rate constant for the degradation of 2,4-dinitrophenol is possible [19]. It is also known that an increase acoustic power leads to an increase the number of active cavitation microcavities and higher reactive radicals, HO· and H·, will be generated, which will lead to better conversion and mineralization [20, 21]. However, this increase has a margin, and an excessively high power in the ultrasound can cause a large number of microcavities that stick together into an ode to a large cavity, which collapses less violently [22].

Assessment BPA photochemical activity in direct photolysis indicates a relatively low rate of its photodegradation when exposed to UV radiation (245 nm). Since the molar absorption coefficient of BPA at 254 nm is very low, weak degradation was achieved by UV treatment [23]. BPA conversion for under conditions of US and/or UV was negligible. The initial concentration of BPA for 240 min decreased by 87% during US, and only by 15% during UV, while the content of total organic carbon did not change. With US and UV radiation, hydroxylated intermediate compounds are formed which are hydrophilic character, therefore, a decrease in DOC is not effective. The removal efficiency of organic compounds in US depends directly on its hydrophobicity and hydrophilicity [24]. Hydrophobic products accumulate at the interface of the microcavities, while hydrophilic products remain in solution and the reaction with HO have a low probabilities [25].

In order to increase the BPA conversion and mineralization efficiency US and UV can be combined with Fenton-like, for example, {S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}/Fe\textsuperscript{2+}} [26]. The studies were carried out under the same experimental conditions: the pH was adjusted to 3.5 with sulfuric acid to avoid precipitation of iron in the form of iron hydroxide. To identify the kinetic BPA oxidation in the Fenton-like combined oxidizing system {UV/US/Fe\textsuperscript{2+/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} and a comparative evaluation of the effectiveness of various oxidizing systems, the experimental series were carried out with a molar ratio of BPA and oxidizing agent [S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}]/[BPA]=5:1, which is significantly lower than the stoichiometrically necessary for full mineralization:

\[
C_{15}H_{22}O_2 + 72SO_4^{2-} + 28H_2O \rightarrow 15CO_2 + 72SO_4^{2-} + 72H^+ \tag{2}
\]

The results of a comparative assessment of the efficiency the BPA conversion and mineralization in various oxidizing systems – {UV}, {US}, {Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}}, {US/Fe\textsuperscript{2+/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, {UV/US/Fe\textsuperscript{2+/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}}, indicate an increase in efficiency in Fenton-like combined system. Efficiency according to the degree of mineralization was found in the following order: {US}, {UV} < {Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} < {US/Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} < {UV/US/Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}}.

After 60 minutes, 97% of the BPA conversion was achieved in the oxidation system {UV/US/ Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}}, while 65% in the oxidation system {US/Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}}, 35% using ultrasound and only 15% with UV. Complete BPA conversion in the {UV/US/ Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} system was achieved after 90 minutes, and in the {US/Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} system after 240 minutes. (Figure 2).

The addition of Fe (II) in a catalytic amount is an increase of mineralization. As is known, Fe (II) ions interact with persulfate and hydrogen peroxide to form SO\textsubscript{4}· and HO’ in the Fenton processes {Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}}, and Fenton-like {Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}} processes [27,28]:

\[
S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} + UV, US, T \rightarrow 2SO\textsubscript{4}^{2-} \quad k = 5 \times 10^2 \text{ min}^{-1} \tag{3}
\]

\[
SO\textsubscript{4}^{2-} + H_2O \rightarrow HO' + HSO\textsubscript{4}^- \quad k = 6.5 \times 10^7 \text{ L·mol}^{-1}·\text{min}^{-1} \tag{4}
\]

\[
HO' + S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} \rightarrow SO\textsubscript{4}^{2-} + HSO\textsubscript{4}^- + 0.5O_2 \quad k = 1.2 \times 10^7 \text{ L·mol}^{-1}·\text{min}^{-1} \tag{5}
\]

\[
Fe\textsuperscript{2+} + S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} \rightarrow Fe\textsuperscript{3+} + SO\textsubscript{4}^{2-} + SO\textsubscript{4}^{2-} \quad k = 39 \text{ L·mol}^{-1}·\text{min}^{-1} \tag{6}
\]
Fe^{2+} + H_2O_2 → Fe^{3+} + HO^- + HO•  \quad k = 45-60 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (7)

Fe^{3+} + S_2O_8^{2-} → Fe^{2+} + 2SO_4^-  \quad k = 22 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (8)

Fe^{3+} + H_2O_2 → Fe^{2+} + HOO^- + H^+  \quad k = 0.6 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (9)

Fe^{2+} + SO_4^{2-} → Fe^{3+} + SO_4^{2-}  \quad k = 9.9×10^8 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (10)

Fe^{2+} + OH^\cdot → Fe^{3+} + OH^-  \quad k = (3.0-4.8)×10^8 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (11)

2SO_4^- → S_2O_8^{2-}  \quad k = 8.1×10^7 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (12)

BPA + HO^\cdot → \text{product}  \quad k = 6.9×10^9 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (13)

BPA + SO_4^{2-} → \text{product}  \quad k = 1.37×10^9 \text{ L·mol}^{-1}·\text{min}^{-1}  \quad (14)

The reduction of Fe (III) to Fe (II) with persulfate (8) and hydrogen peroxide (9) occurs at a lower rate compared to reactions (6) and (7). Hydrogen peroxide in small quantities was formed under ultrasound conditions.

At the same time, competing reactions 10 and 11 proceed rather quickly; therefore, the concentrations of Fe^{2+} and the oxidizing agent determine the efficiency of the process of destruction of organic compounds.

The degree of conversion and mineralization is higher than that observed in the case of only US or UV, but the oxidation process does not end. The increase in the degree of conversion and mineralization is also explained by S_2O_8^{2-} and H_2O_2 photodecomposition, as well as by the photolysis of Fe (III) or the hydroxide complex Fe(OH)^{2+}, producing additional HO^- radicals or photolysis complexes of {Fe (III) -organic ligand} [29]. These photochemical reactions regenerate Fe(II):

\[ \text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{HO}^- \]  \quad (15)

\[ \text{Fe}^{2+} - \text{RO}^- + h\nu \rightarrow \text{Fe}^{3+} + \text{RO}^- \]  \quad (16)

Regenerated Fe (II) re-reacts with S_2O_8^{2-} and H_2O_2 (reaction 9, 10), as a result, almost all of the small amount of hydrogen peroxide formed by treatment in ultrasound and UV is consumed.

4. Conclusion
The present work reports an important investigation of using a combination of High-frequency ultrasound (1.7 MHz, 25W) and ultraviolet radiation (254 nm) oxidation for the treatment of micropollutant Bisphenol-A in a Fenton-like oxidation system involving persulfate as an oxidant and
ferrous iron (Fe(II)) as a catalyst. Experiments were carried out in a flow sonophotoreactor, flow rate 0.5 l/min. A large synergistic effect (2.4) was shown in the oxidation of Bisphenol-A from the combined effect of two directed at each other sources of ultrasound. It was clearly demonstrated that conversion and mineralization was enhanced by the use of {UV/US/Fe^{2+}/S_{2}O_{8}^{2-}} oxidation system.

The reaction rates of Bisphenol-A degradation and mineralization increase in the order: {UV} < {US} < {Fe^{2+}/S_{2}O_{8}^{2-}} < {US/Fe^{2+}/S_{2}O_{8}^{2-}} < {UV/US/Fe^{2+}/S_{2}O_{8}^{2-}}. Fenton-like oxidation system enhanced by ultrasonic and ultraviolet activation leads to complete degradation of Bisphenol-A. After 60 minutes, 97% of the BPA conversion was achieved in the oxidation system {UV/US/Fe^{2+}/S_{2}O_{8}^{2-}}, while 65% in the oxidation system {US/Fe^{2+}/S_{2}O_{8}^{2-}}, 35% using ultrasound and only 15% with UV. Complete BPA conversion in the {UV/US/Fe^{2+}/S_{2}O_{8}^{2-}} system was achieved after 90 minutes, and in the {US/Fe^{2+}/S_{2}O_{8}^{2-}} system after 240 minutes. Based on the obtained data, a method for the degradation of toxic organic pollutants based on Fenton-like oxidation system enhanced by high-frequency ultrasound (1.7 MHz) and ultraviolet (254 nm) was suggested. These physical methods consume a small amount of energy and are economically feasible.

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Acknowledgements
This work was conducted under the Program of Basic Research of BINM SB RAS.