High frequency ultrasound enhanced oxidation of bisphenol a by Fenton-like systems

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Abstract. High-frequency ultrasound was employed to enhance degradation of micropollutant Bisphenol A in a Fenton-like oxidative system involving persulfate as the oxidant and ferrous iron (Fe(II)) as the catalyst US/Fe2+/S2O82-. Experiments were carried out in a 400 ml glass reactor. The influence of the initial concentration of BPA, the ratio of "oxidizer-substrate", the ratio of "catalyst-substrate", temperature, on the efficiency of the oxidation of BPA was established. The reaction rates of micropollutant degradation increased in the order: \{Fe2+/ S2O82-\} < {US} < {US/Fe2+/ S2O82-}. It was shown that ultrasonic activated Fenton-like oxidative system leads to degradation of micropollutants. As a result, a method of deep degradation of toxic organic pollutants based on the ultrasonic activated – Fenton process US/Fe2+/S2O82- was suggested.

1. Introduction
Already today in some countries of the world there is a shortage of drinking water caused by pollution of the hydrosphere by numerous organic micropolutants (MP). The concentration of MP in the water is small - from 1 ng/l to 1 µg/l. Low concentration makes traditional water treatment methods unprofitable and inefficient. At the same time, many MP exhibit toxic properties, significantly affect the organoleptic properties, and are also capable of bioaccumulation, biomagnification and are often stable in the hydrosphere.

For water purification from bioresistant MP Advanced Oxidation Processes are the most promising for water purification. The principle of AOP is that high-reactive radicals - reactive oxygen species (ROS) are used as oxidizers. Both physical (photolysis, cavitation, ionizing radiation, etc.) and chemical methods (introduction of oxidizing agents and catalysts) are used to obtain radicals in an aqueous environment in situ. The resulting free radicals are particles with unpaired electrons, which makes them highly reactive [1,2]. Wastewater treatment methods using AOP are environmentally friendly, since their implementation uses non-toxic oxidizing agents (hydrogen peroxide, persulfate, etc.) and the complete mineralization of hardly oxidizable impurities is achieved without the formation of secondary pollutants [3].

Oxidation systems based on 'OH radicals are well studied, and the number of works involving radicals increases annually SO4- radicals. Investigations are shifting towards oxidative systems based on SO4- radicals (SR-AOPs). A possible reason for this is easier activation of sulfur-containing peroxo compounds (persulphates, peroxomonosulphates), a wider working pH range comparable to 'OH
radical standard electrode potential, as well as a high content of active substance (up to 99.5%) and a long shelf life (up to 3 years old) [4]. In addition, SO$_4^{\cdot-}$ radicals have a lower selectivity, for example, perfluorinated compounds that are resistant to the action of $^\cdot$OH radicals are subject to slow destruction by SO$_4^{\cdot-}$ radicals [5]. Also, studies [6,7] have shown that the presence of water matrix components enhances the effectiveness of AOPs based on SO$_4^{\cdot-}$ radicals and reduces the effectiveness of $^\cdot$OH radicals. However, the question of the influence of the water matrix components on the oxidation process is poorly understood.

Cavitation is the phenomenon of a dropping liquid breaking under the action of tensile stresses arising during a vacuum at the point of the liquid under consideration. When a dropping liquid breaks, cavities are formed — cavitation bubbles filled with steam, gas, or a mixture of them. Later on, the collapse of the bubble occurs with the release of a huge amount of energy, which leads to the formation mainly hydroxyl radicals and atomic hydrogen [8,9]. In addition, the work [10] indicates the possibility of activation of persulfate by ultrasonic cavitation. In the case of hydrophobic and volatile compounds, the destruction mainly takes place in the cavity, they are pyrolyzed at the moment of bubble explosions. Meanwhile, less volatile, hydrophilic compounds will tend to remain in solution and break down at the gas-liquid interface as a result of oxidation with reactive oxygen species [11,12].

Ultrasonic activation of persulfate proceeds through the pyrolysis of persulfate during bubble collapse:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$$

as well as through the reactions with the resulting radicals:

$$S_2O_8^{2-} + ^\cdot$OH \rightarrow SO$_4^{\cdot-}$ + HSO$_4^{\cdot} + 0.5O_2$$
$$S_2O_8^{2-} + ^\cdot$H \rightarrow SO$_4^{\cdot-}$ + H$^+$ + SO$_4^{2-}$$

The main way of chemical activation of persulfate is the use of transition metals as catalysts [13, 14]:

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + Me^{n+1}$$

However, transition transition metals are generally toxic, therefore, among the entire spectrum of metals, only iron is used as a rule (0.3 mg/l for domestic water and 0.1 mg/l for fishery water [15,16]).

This paper presents the results of our study on Bisphenol A (model solutions) destruction by high-frequency ultrasonic (US) cavitation (1.7 MHz), Phenton-like iron persulfate system Fe$^{2+}$/S$_2$O$_8^{2-}$, and also in a combined US/Fe$^{2+}$/S$_2$O$_8^{2-}$

2. Materials and methods

Studies were carried out on model aqueous solutions of Bisphenol A (BPA) with a concentration of 1 μmol/l, 4.4 μmol/l, 8.8 μmol/l, 26.3 μmol/l and 43.9 μmol/l (pH 5.6). Distilled water with a specific electrical conductivity of <2 μS/cm was used to prepare solutions. The following reagents were used: Bisphenol A (Aldrich, USA, 99% purity), iron (II) sulfate (Scharlab S.L., Spain, 99.5% purity), potassium persulfate (99%). The experiments were carried out in a sonochemical reactor, detailed description of which can be found in the works [17,18]. The kinetics of BPA oxidation during the reaction was investigated by high performance liquid chromatography (HPLC) using an Agilent 1260 Infinity chromatograph (Agilent Technologies, USA) with a fluorimetric detector. Chromatographic separation in the isocratic elution mode was carried out on an analytical ZorbaxSB-C18 column with a particle size of 5 μm. As the mobile phase, a mixture of acetonitrile with a 75mM solution of acetic acid was used in a volume ratio of 45:55, the elution rate was 0.5 ml/min, the column thermostat temperature was 35 °C, and the volume of the injected sample was 70 μl. Detection was performed using a fluorescent-scanning detector (excitation wavelength 230 nm, emission wavelength 315 nm). A portable Multi 3410 instrument with a SenTix940 electrode (WTW) was used to measure the pH.
The oxidation efficiency was evaluated by the change in the concentration of BPA during $\tau = 180 \text{ min}$ by the formula:

$$\mathcal{E} = \frac{C_0 - C_\tau}{C_0} \times 100\%$$

where $C_0$ is the initial concentration of BPA, $\mu$mol/l; $C_\tau$ is the concentration of BPA at the time $\tau$, $\mu$mol/l.

3. Results and discussion
As the initial concentration of BPA increases, we observe that the initial rate of its oxidation also trends to increase. The study of the conversion of BPA under the influence of high-frequency ultrasound showed that in the ultrasonic field the destruction of BPA occurs slowly, which indicates the necessity of using advanced oxidation methods (Figure 1).

The temperature at which the processes occur has a greater effect on cavitation than on the kinetics of the sonochemical reactions themselves [9]. When the temperature rises, the water evaporation rate increases and the partial pressure of water inside the cavitation bubble increases, which can result from gas to steam cavitation, which, although it flows more easily, is somewhat inferior to gas in the efficiency of bubble collapse. The experimental data obtained are fully correlated with the literature data: if at $25 \ ^\circ\text{C}$ the efficiency of the oxidation of BPA (C = 1 $\mu$mol/l) was 84.2 %, then at a temperature of $35 \ ^\circ\text{C}$ it was 77 %. Nevertheless, the results of the experimental series indicate a probable nonlinear nature of the effect of temperature on cavitation processes, since at a temperature of $15 \ ^\circ\text{C}$, the efficiency was 74 %, which is probably due to the fact that with decreasing temperature, the efficiency of cavitation is leveled by the kinetic factor (Figure 2).

To assess the effect of oxidant concentration on the destruction of BPA ($C_0$ (BPA) = 1 $\mu$mol/l) in the presence of a catalyst and US, a series of experiments were carried out with different ratio of “oxidizer – substrate” $([\text{S}_2\text{O}_8^{2-}]_0:[\text{BPA}]_0)$, which showed that when the ratio $[\text{S}_2\text{O}_8^{2-}]_0:[\text{BPA}]_0 = 10:1$, the oxidation efficiency decreases (Figure 3), which is probably due to the high rate of radical recombination [19]:

$$\text{SO}_4^{2-} + \cdot\text{OH} \rightarrow \text{HSO}_5^{-} \quad k = 1.0 \times 10^{10} \text{ l mol}^{-1}\text{s}^{-1}$$
Figure 2. The destruction of BPA in high-frequency ultrasound at different temperatures $C_0$ (BPA) $1 = \mu$mol / l, pH = 5.6.

Figure 3. Sonodestruction of BPA at a different ratio of "oxidizing substrate" $C_0$ (BPA) = 1 $\mu$mol/l, $C_0$ (Fe$^{2+}$) = 1 $\mu$mol/l, $T = 25 \pm 1$ °C.

To establish the optimal ratio of “catalyst-substrate” [Fe$^{2+}$]:[BPA], a series of experiments were conducted with ratios of 0.5:1; 1:1 and 2:1. It was found that the concentration of iron has little effect on the efficiency of the oxidation of BPA, but it strongly affects the initial oxidation rates. The ratio $= [\text{Fe}^{2+}]:[\text{BPA}] = 1:1$ was chosen as optimal because the maximum value of the initial rate and efficiency of oxidation is observed (Table 1).

Table 1. BPA destruction with a different ratio of “catalyst-substrate” in ultrasonic $C_0$ (BPA) = 1 $\mu$mol/l, $C_0$ (S$_2$O$_8^{2-}$) = 5 $\mu$mol/l, $T = 25 \pm 1$ °C.

| [BPA]:[Fe$^{2+}$] | $W_0 (\mu \text{M min}^{-1})$ | Efficiency$^a$ (%) |
|------------------|-----------------|------------------|
| 1:0.5            | 0.0438          | 86.9             |
| 1:1              | 0.0556          | 91.5             |
| 1:2              | 0.0175          | 87.9             |

$^a$ after 180 min of treatment.

Among the available methods of activation of peroxocompounds, chemical activation is the most effective, since activation of persulfate by thermolysis or photolysis requires energy. The results of a series of experiments in the system Fe$^{2+}$/ S$_2$O$_8^{2-}$ (without ultrasound) show that the process of destruction of BPA in the system Fe$^{2+}$/ S$_2$O$_8^{2-}$ can be divided into the fast phase (the first 5 minutes), during which is the destruction of a most part of BPA, and the slow phase in which the reaction rate drops rapidly. The reaction rate reduction is primarily due to the rapid consumption of persulfate. At the same time, in the combined ultrasound system Fe$^{2+}$/ S$_2$O$_8^{2-}$ the oxidation of BPA proceeds a little better than in single systems (Figure 4).

The cavitation yield is resorted to assess the energy consumption for sonochemical reactions.

Cavitational yield is an integral value that indicates the amount of energy expended for the destruction of MP (at a given concentration) in the volume of polluted water. It is calculated by the formula [20]:
\[ Y = \frac{W \cdot \tau \cdot 60}{V \cdot \log \left( \frac{C_0}{C_\tau} \right)} \]

where \( C_0 \) is the initial concentration, \( \mu \text{mol/l} \); \( C_\tau \) is the concentration of the substrate after treatment, \( \mu \text{mol/l} \); \( V \) is the volume of the treated solution, l; \( W \) - power consumption, W; \( \tau \) - the duration of the process, min.

Figure 4. Comparative destruction of BPA in various oxidative systems. \( C_0 \text{(BPA)} = 1 \mu \text{mol/l} \), \( C_0 \text{(S}_2\text{O}_8^{2-}) = 5 \mu \text{mol/l} \), \( C_0 \text{(Fe}^2+) = 1 \mu \text{mol/l} \), \( T = 25 \pm 1 \degree \text{C} \).

Analyzing the obtained results and literature data, it is possible to conduct a comparative assessment of the specific energy efficiency of the processes of sonochemical oxidation BPA under the influence of high-frequency (1.7 MHz) and low-frequency (20 kHz) ultrasound [13] (Table 2).

| Frequency | W (l) | \( \tau \) (min) | T (°C) | k (min\(^{-1}\)) | Y (kJ/l) |
|-----------|-------|-----------------|--------|----------------|---------|
| This work | 1.7 MHz | 25              | 0.40   | 180            | 25      | 0.0096  | 841.2   |
| [13]      | 20 kHz | 450             | 0.12   | 60             | 30      | 0.0847  | 6,109.8 |

4. Conclusion

The influence of the initial concentration of BPA, the ratio of "oxidizer-substrate", the ratio of "catalyst-substrate", temperature, on the efficiency of the oxidation of BPA has been established. The study showed that, in terms of efficiency and energy consumption, BPA conversion is optimal in the combined US/Fe\(^{2+}/ S_2O_8^{2-}\). Same time, the oxidation efficiency increases in the order \{Fe\(^{2+}/ S_2O_8^{2-}\} < \{\text{US}\} < \{\text{US}/Fe\(^{2+}/ S_2O_8^{2-}\} \} and in 180 min and is 16; 84.3 and 91.5% respectively.

In the combined system, there is a decrease in energy consumption compared with direct sonolysis. For the initial concentration of BPA = 1 \mu \text{mol/l}, energy consumption decreases from 841.2 to 631.2 kJ/l at \( T = 25 \degree \text{C} \). Cavitation outputs for high-frequency (1.7 MHz) and low-frequency (20 kHz) ultrasound indicate a significant reduction in energy consumption (6-7 times) for the implementation of the processes of oxidative destruction of BPA under conditions of high-frequency ultrasound.

Table 2. Oxidative destruction of BPA in conditions of low-frequency and high-frequency ultrasound. \( C_0 \text{(BPA)} = 1 \mu \text{mol/l} \).
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