Effectiveness of sonophotolysis for eliminating bisphenol A and bacteria from aqueous solution

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Abstract. This study focuses on the improvement of the effectiveness inactivation of microorganisms and degradation of micropollutants using AOPs (advanced oxidation processes) methods in deionized water. The effectiveness of sonophotolysis for degrading bisphenol A (BPA) and inactivating bacteria *Escherichia coli* and *Enterococcus faecalis* in aqueous solution was investigated using ultraviolet light-emitting diodes (UV LEDs, 365 nm) and high-frequency (1.7 MHz) ultrasound (US). The sonophotolytic system UV/US was highly efficient for inactivating *E. faecalis*, whereas no US contribution was observed for *E. coli*. A synergistic effect for sonophotolysis of BPA was found. We suggest that the obtained results are promising for developing modern sonophotochemical methods for water treatment and disinfection.

1. Introduction

To date, contamination of water by pathogenic microorganisms and organic micropollutants is one of the most challenging problem. Advanced oxidation processes, which involve the production of hydroxyl radical (OH•) as a main oxidative agent, have been successfully applied for removing organic contaminants and pathogenic microflora from water and wastewater. Among sono-based AOPs, high-frequency ultrasound (US) has attracted a considerable attention [1]. In view of environmental safety and energy efficiency, we can distinguish a sonophotolytic AOP, which is based on simultaneous or sequential irradiation of water with UV and US radiation. Since UV light is absorbed and scattered by suspended particles during UV treatment, additional US treatment is required to improve the removal efficiency [2]. It is known that the acoustic cavitation upon ultrasonication generates collapsing micro-bubbles with a formation of OH•, which enhance the oxidation processes. Simultaneous US and UV radiation is used for water treatment and disinfection, especially in sonophotocatalysis [3,4]. An increased efficiency of *E. coli* and *Streptococcal feces* inactivation under sequential US (20 kHz)/UV treatment was found [5-7]. The synergistic effect and the highest reduction of *Fecal coliform, E. coli* and *Streptococcus faecalis* after simultaneous US (28 kHz) and UV irradiation were reported [8, 9]. The decrease of *E. coli* was 5.4 logs under sequential US (40 kHz)/UV scheme, while it was reduced by 3.4 and 0.9 logs under separate UV and US irradiations, respectively.

Sonophotolytic treatment increased the inactivation *E. coli* by 1.1 logs and the photoreactivation degree was reduced [10]. It is worth noting that low-frequency US is low effective for the disintegration of bacterial cells and higher intensities and frequencies US for inactivation are needed.
The effectiveness of sonolytic, photolytic, and sonophotolytic activation of persulfate for destruction of trichloroethylene in aqueous solutions at 254 nm and 24 kHz was studied [11]. It was shown that the sonophotolytic activation of persulfate led to 96.3% removal after 20 min, while destruction under UV and US treatments resulted in 41.2 and 51.8%, respectively. These results evidenced that the combination of UV and US provided a synergistic effect with a synergistic index of 1.62. A synergistic effect with an index of 1.22 under sonophotocatalytic oxidation of antibiotic ciprofloxacin at low frequencies (20, 50 and 80 kHz) and visible light (457 nm) using TiO₂ was observed [12]. The combined use of TiO₂, UV irradiation (320–400 nm) and ultrasound (20 kHz) for destruction of diclofenac provided also a synergistic effect (>2) [13]. A synergistic effect of sonophotolysis of 2,4,6-trichlorophenol and dyes was also demonstrated [14, 15]. A low-frequency US at frequencies below 100 kHz has been used in the aforementioned research. From the point of view of radical generation, the high-frequency ultrasound at frequencies above 100 kHz is promising for application [16]. Currently, the use of high-frequency US for inactivation of microorganisms and degradation of micropollutants is poorly studied [1].

The purpose of this study was to examine the effectiveness of hybrid sonophotolytic process based on combination of high-frequency US (1.7 MHz) and UV LEDs (365 nm) for inactivation of microorganisms (E. faecalis and E. coli) and degradation of bisphenol A in model aqueous solution.

2. Materials and methods

The deionized water of Milli-Q quality (18.2 mCm·cm, Simplicity UV system, Millipore) was used as a water matrix. Bisphenol A (BPA, 99%, Aldrich) was selected as a model organic micropollutant, which is used in the production of plastics. Stock solution of a compound was prepared in deionized water.

The strains E. coli K-12 and E. faecalis B 4053 were used as representative indicator organisms of water contamination. Cells were incubated into 30 mL GRM broth and trypticase soy broth (24 h at 37°C). Afterwards, bacteria were harvested by centrifugation (4,000 rpm), washed by PBS and pellets were resuspended in PBS. The resulting cell suspension was added to deionized water for obtaining the initial number (N₀) of 10⁵ colony-forming units (CFU) per 1 mL. The degree of inactivation was calculated as a logarithmic ratio of survived and initial cell numbers (Lg (N/N₀)). UV LEDs at 365 nm (Yonton, model YT-100WUV370-0, China), and US generator of 1.7 MHz (Scoole, model SC HR UL 04 (VO), China). Irradiation of water in a steel cylinder was performed under constant magnetic stirring. UV LEDs matrix was placed above the reactor at a distance of 5 cm from the solution surface (Figure 1). The temperature of the solution was maintained at 20±2°C by the recirculation of tap water through copper tubes.

![Figure 1. A scheme of experimental set-up.](image-url)
During the experiment, the deionized water (100 mL) containing bisphenol A (~4 mg/L) and microorganisms (10^5 CFU/mL) were irradiated in the reactor. A series of separate experiments on degradation and inactivation were performed under the following conditions:

1. Direct photolysis – UV;
2. Direct sonolysis – US;
3. Sonophotolysis – UV/US.

Samples were withdrawn at set time intervals. To determine the residual concentration of BPA, HPLC method (Agilent 1260 Infinity system) was used. Acetonitrile and acetic acid 45:55 (v/v) was used as the mobile phase at a flow rate of 0.5 mL/min. The efficiency of degradation was assessed by changes of concentration of BPA during treatment.

3. Results and discussion

3.1. Inactivation of bacteria

Figure 2 shows the experimental survival curves for E. faecalis and E. coli after UV, US treatments and simultaneous exposure to UV/US.

As shown in Figure 2, E. faecalis by US was not inactivated. Probably, OH• were generated in insufficient amounts due to low-intensity US. Complete inactivation of E. faecalis was achieved after 20 min UV treatment. The sonophotolytic system was more efficient for E. faecalis, reducing the duration for total inactivation to 15 min (Figure 2). This suggests the higher OH• exposure during sonophotolysis [17]. Inactivation of E. coli (Figure 3) was more intensive in contrast to E. faecalis. Complete inactivation in UV and UV/US systems was achieved after 10 min. These systems were equally effective for E. coli. Evidently, US did not contribute to this process. Apparently, this is due to the high-intensity UV radiation, which mitigated the contribution of low-intensity US.

Gram-positive E. faecalis is more resistant to ROS due to a thicker peptidoglycan layer of the cell membrane. The gram-negative E. coli is more sensitive to UV due to thinner cell wall and other composition [18].

A "shoulder" on the E. faecalis and E. coli survival curves was observed during the first 5 min treatment for UV/US and UV systems. It can be explained by screening effect. Thus, a hybrid sonophotolytic system was the most effective for inactivating E. faecalis, whereas no US contribution was observed for E. coli.
Figure 3. Survival curves of *E. coli* obtained after irradiation by UV LEDs (365 nm) and high-frequency US (1.7 MHz). \([N_0] = 10^5 \text{ CFU/mL}\).

3.2. Degradation of bisphenol A

BPA was resistant to direct photolysis (Figure 4). This is due to the fact that the maximum absorbance bands of BPA (225, 276 nm) are far from the emission wavelength of UV LEDs (365 nm). The degradation degree of sonolysis of BPA was minimal. Figure 4 shows that the sonophotolysis significantly improved BPA degradation (24.4% in 40 min) compared to the removal observed for sole US (5% in 40 min) or sole UV (8.2% in 40 min) treatments.

Figure 4. Removal efficiency of BPA by UV LEDs (365 nm) and high-frequency US (1.7 MHz). \([\text{BPA}]_0 = 20 \mu\text{M}, \text{treatment time} = 40 \text{ min}\).

To evaluate the synergistic effect in hybrid UV/US treatment synergistic index \((\phi)\) was calculated for BPA degradation after 40 min treatment according to the formula (1) [19]:

\[
\phi = \frac{\text{Removal(UV / US)}}{\text{Removal(UV)} + \text{Removal(US)}}
\]  

(1)

It is known, that the value \(\phi > 1\) indicates a synergistic effect, otherwise \((\phi \leq 1)\) an antagonistic or additive effect is observed. The obtained synergistic index was 1.8, which indicates a synergism between UV and US in this hybrid process.

The efficiency of sonophotolysis has been also shown in previous studies. For example, in a study of sonophotolytic degradation of dimethyl phthalate a synergistic effect was shown [20]. In another study, a synergistic effect in sonophotolytic degradation of 4-n-nonylphenol using high frequency US was observed [21]. Majority of previous studies were conducted using photocatalysts for UV/US...
degradation of organic pollutants. For example, removal and mineralization of diethyl phthalate under US/UV treatment in the presence of TiO$_2$ was observed [22]. Sonophotocatalysis of paracetamol in the presence of Fe$^{3+}$ and TiO$_2$ using US was studied [23]. A synergistic effect in the sonophotocatalytic oxidation of reactive black 5 in the presence of Fe$^{3+}$ was found [24]. The results obtained for sonophotolytic treatment of BPA using high-frequency US are comparable with those reported earlier, while sonophotocatalysis was more effective in terms of removal efficiency and mineralization.

4. Conclusions
Sonophotolysis was the most effective for inactivating E. faecalis, while it was ineffective for E. coli (a UV-sensitive bacterium). The latter is due to high-intensity UV radiation, which covered the contribution of US. The sonophotolytic system was low-effective for degrading bisphenol A; however, it exhibited a synergistic effect. Sonophotochemical AOPs, involving oxidizers and/or catalysts, should be applied to improve the micropollutants degradation and microbial inactivation.

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