Removal of organic micropollutants from water by sonophotolytic-activated persulfate process

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Abstract. The present study focuses on the improvement of the efficiency of water treatment by coupling irradiation with ultraviolet (UV) light-emitting diodes and high-frequency ultrasound (US) for activation of persulfate (PS). Organic micropollutants (atrazine, bisphenol A and carbamazepine) were sequentially treated in aqueous solution at non-adjusted pH and initial concentration of 20 μM in a batch sonophotoreactor. The hybrid oxidation system (UV/US/PS) showed the highest efficiency (≥90%) for removing bisphenol A and carbamazepine within 40 min of treatment, whereas atrazine was degraded with comparable rates under UV/PS and UV/US/PS processes. In terms of removal efficiency, the applied systems for bisphenol A and carbamazepine can be arranged as follows: UV/US/PS > UV/PS > US/PS > UV/US ≈ UV ≈ US. Overall, the hybrid sonophotolytic method using high-frequency US appears to be a promising technique to activate PS for eliminating organic micropollutants from aqueous media.

1. Introduction
Municipal wastewater effluents contain large number of organic micropollutants, which cannot be easily degraded by conventional biological treatment. Residual amounts of such compounds and their metabolites, continuously discharging into natural waters, represent a severe problem for aquatic organisms and exposure even at low doses may result in adverse effects and pose a risk to human health. Advanced oxidation processes (AOPs) have proven to be effective for degrading biologically recalcitrant organic micropollutants in aqueous media via oxidative reactions with generated reactive oxygen species, such as hydroxyl radical (OH•) and sulfate radical anion (SO₄•⁻). During last decade, sulfate radical-based AOPs (SR-AOPs) have received great attention for the application in water and wastewater treatment [1]. In particular, SO₄•⁻ can be produced in water through activation of persulfate (PS) by ultraviolet (UV) or ultrasonic (US) radiation (1, 2); OH• are formed under reaction of sulphate radicals with water and hydroxyl ions (3, 4) [2]:

\[
\begin{align*}
S_2O_8^{2-} & \rightarrow 2SO_4^{•-} \quad (1) \\
S_2O_8^{2-} & \rightarrow 2SO_4^{•-} \quad (2) \\
SO_4^{•-} + H_2O & \rightarrow OH^{•-} + SO_4^{2-} + H^+ \quad k = 12M^{-1}s^{-1} \quad (3) \\
SO_4^{•-} + OH^{•-} & \rightarrow OH^{•-} + SO_4^{2-} \quad k = 7.0 \times 10^7M^{-1}s^{-1} \quad (4)
\end{align*}
\]
Individual irradiation with UV or US has been extensively used for the activation of PS or peroxomonosulfate (PMS), whereas simultaneous US and UV treatment has been applied more rarely in SR-AOPs. In recent years, UV/US-based hybrid systems, with the emphasis on the sonophotocatalysis, has been considered as a promising environmental-friendly technology for the enhanced degradation of recalcitrant organic contaminants [3,4]. Particularly, the sonophotolytic-activated persulfate system (UV/US/PS) showed the highest efficiency and the synergistic effect for degrading trichloroethylene [5] and a dye Azorubine [6]. The combined sonophotooxidation (US/UV/PMS/PS) also exhibited the synergistic effect for the mineralization of simulated dyehouse effluent [7]. More recently, similar results were obtained for decolorization of Direct Orange 26 by simultaneously employed UV and US to activate PMS [8]. Importantly, the application of the above hybrid system was also successful in treating real textile wastewater, and it also increased biodegradability.

However, it should be emphasized that the low-frequency US, emitting lower than 100 kHz (20-40 kHz), was applied in the above studies and also in most research, which is focused on the use of US for degradation purpose. Meanwhile, it is known that the high-frequency US (>100 KHz and MHz range) produces significantly higher OH• levels in aqueous solutions than the low-frequency US. Specifically, the production of OH• was reported to be most significant at frequencies of 585 and 1040 kHz [9] and, therefore, high-frequency US appears to be an attractive alternative to the commonly used low-frequency US.

To date, in comparison with low-frequency US, the potential of high-frequency US remains less investigated. The latter was previously applied in combination with TiO2 [3, 10], Fe2+ and H2O2 [11], UV [12], solar photo-Fenton [13], ozone [14], Fe2+, photo-Fenton and photo-Fenton/H2C2O4 [15]. Meanwhile, only few studies have used PS for sonochemical degradation [16-18] and, to the best of our knowledge, no study has been published on the PS-enhanced sonophotolytic degradation (UV/US/PS) using high-frequency US in the absence of any catalyst. Hence, the objective of this study was to evaluate the efficiency of catalyst-free UV/US/PS oxidation system toward removal of organic micropollutants from aqueous solution using US at 0.88 and 2.64 MHz and UV light-emitting diodes (LEDs), emitting at 365 nm. In a current study, we have applied UV LEDs as a modern mercury-free source, supporting the Minamata Convention on Mercury [19].

2. Materials and methods

2.1. Reagents

Atrazine (ATZ, 99.1%), bisphenol A (BPA, 99%) and carbamazepine (CBZ, ≥99%), purchased from Sigma-Aldrich, were selected as model organic micropollutants for degradation experiments (Table 1).

| Molecular formula | Structure | $k_{OH•}$, M$^{-1}$ s$^{-1}$ | $k_{SO4•}$, M$^{-1}$ s$^{-1}$ | Application |
|-------------------|-----------|-------------------------|-------------------------|-------------|
| Atrazine C8H14ClN5 | ![Atrazine Structure](image) | $3.0 \times 10^9$ [20] | $3 \times 10^9$ [21] | A selective triazine herbicide. |
| Bisphenol A C15H16O2 | ![Bisphenol A Structure](image) | $6.9 \times 10^9$ [22] | $1.37 \times 10^9$ [23] | A monomer in the polycarbonate plastic, polyester and epoxy resins, an endocrine disruptor compound. |
| Carbamazepine C15H12N2O | ![Carbamazepine Structure](image) | $8.8 \times 10^9$ [24] | $1.92 \times 10^9$ [25] | A first-choice antiepileptic drug. |

*Apparent second-order rate constants of target micropollutants with OH• and SO4•*.
Stock solutions of compounds and working solutions for experiments were prepared in deionized water (18.2 mΩ·cm) produced by a Simplicity®UV system from Millipore. Potassium persulfate (Vekton, Russia) was used as received. HPLC-grade acetonitrile and acetic acid were purchased from Cryochrom (Russia) and Khimreaktivsnab (Russia), respectively.

2.2. Sonophotoreactor
Experiments were performed in a cylindrical sonophotoreactor made of stainless steel (AISI 304) with a volume of 200 mL and equipped with a magnetic stirrer (IKA®color squid white, Germany) (Figure 1). Ultrasound at a frequency of 0.88 or 2.64 MHz was applied from the sidewall of the reactor via a fixed US transducer, which operated with a double-frequency ultrasonic amplifier (UZT-1.3.01F, “MedTeko”, Russia). UV LEDs array (Yonton, model YT-100WUV370-0, 100 W, China), emitting at 365 nm, was placed above the reactor at a distance of 7 cm from the surface of the solution. The temperature of the irradiated solution was maintained at 20±2°C by circulating cooling water through the close-coiled copper tubes. Due to relatively high power, UV LEDs array was also thermostated by a water jacket. The incident irradiance, measured with a calibrated radiometer (TKA-PKM-06, TKA Scientific Instruments, Russia), was 0.15 W/cm² across the UVA spectrum.

![Figure 1. Schematic diagram of the used sonophotoreactor.](image)

2.3. Experimental procedure
In a typical experiment, 100 mL of each micropollutant solution with an initial concentration of 20 μM was treated at non-adjusted pH of 6.3±0.2 under irradiation by solely UV, US, UV or US in the presence of PS (UV/PS, US/PS), simultaneously UV and US (UV/US), UV and US in the presence of PS (UV/US/PS). The initial concentration of PS was 312.5 μM, as selected in our previous study [26]. The solutions were sequentially treated in the above-described sonophotoreactor under magnetic stirring. During each experiment, the samples were withdrawn at desired treatment times and analysed by HPLC for residual concentrations.

2.4. Analysis
The target micropollutants were determined using an Agilent 1260 Infinity HPLC system with an UV and a fluorescence detector equipped with a Zorbax SB-C18 column (4.6 × 150 mm, 5 μm). The eluent was a mixture of acetonitrile and 75 mM acetic acid at a flow rate of 0.5 mL/min. UV detection was at 222 and 285 nm for ATZ and CBZ, respectively. Fluorescence detection was for BPA with excitation at 230 nm and emission at 315 nm. The pH of the solutions was measured using a Metrohm 827 pH meter (Metrohm, Switzerland).
3. Results and Discussion

A comparative study of micropollutants removal was conducted via photolysis (UV), sonolysis (US) and hybrid process (UV/US) in the absence and presence of PS. Figure 2 illustrates the kinetics of degradation in the above systems at a frequency of 0.88 MHz. It can be observed, that the individual irradiation with UV or US, as well as simultaneous UV/US treatment, was ineffective for degrading target compounds.

![Graphs showing degradation of Carbamazepine, Bisphenol A, and Atrazine under different processes](image)

**Figure 2.** Degradation of target micropollutants under different processes using UV LEDs (365 nm) and high-frequency US (0.88 MHz) in the absence and presence of persulfate. [Micropollutant]₀ = 20 μM, [PS]₀ = 312.5 μM.

Addition of PS activated the oxidation processes and resulted in 42% (CBZ), 18% (ATZ) and 13% (BPA) removal after 40 min US/PS treatment. Much higher removal (≥ 90%) was observed for all selected micropollutants in the hybrid system UV/US/PS (Figures 2 and 3), indicating the efficient generation of SO₄•⁻ and OH•. The highest performance of hybrid system was also reported in previous studies for other organic contaminants using low-frequency US at 24 [5], 40 [6], 35 [7] and 20 kHz [8]. However, the rates of ATZ degradation under both UV/PS and UV/US/PS processes were comparable, whereas the hybrid treatment was more efficient than the UV/PS for BPA and CBZ. Assuming the higher SO₄•⁻ exposure in the UV/PS system, this observation may be attributed to the lower reactivity of BPA and CBZ towards SO₄•⁻ as compared to ATZ (Table 1). In turn, OH• can be yielded in a greater degree upon UV/US/PS exposure due to simultaneous application of UV and US activators. Additionally, sonolysis of water could also contribute to generating more OH• (5) [7]:

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**Figure 2**.
Degradation of target micropollutants under different processes using UV LEDs (365 nm) and high-frequency US (0.88 MHz) in the absence and presence of persulfate. [Micropollutant]₀ = 20 μM, [PS]₀ = 312.5 μM.
Therefore, BPA and CBZ, fast-reacting compounds with OH•, were degraded more rapidly than under UV/PS treatment. Note, the reaction rates of ATZ with OH• and SO₄•⁻ are similar (Table 1). In terms of removal efficiency, no difference between 0.88 and 2.64 MHz (data not shown) was observed, presumably, due to low operating ultrasonic intensity (1 W/cm²).

We have evaluated the synergistic effect of UV/US/PS system at 0.88 MHz by calculating the synergy index values for BPA and CBZ degradation after 40 min treatment (6):

\[
\text{Synergy index} = \frac{\text{Removal (UV/US/PS)}}{\text{Removal (UV/PS) + Removal (UV/US) + Removal (US/PS)}}
\]

The obtained synergy indexes for CBZ and BPA were 0.8 and 1.1, respectively. It is known, that the synergy index greater than 1.0 indicates a synergistic effect, otherwise one can conclude about the antagonistic or additive effect. Although the synergy of hybrid treatment was not achieved for CBZ under the experimental conditions used, the simultaneous application of UV, US and PS can synergistically degrade BPA in aqueous solution.

4. Conclusion
The hybrid sonophotolytic treatment in the presence of perulfate (UV/US/PS) enhanced the degradation of bisphenol A and carbamazepine. The efficiency of the applied systems decreased in the order: UV/US/PS > UV/PS > US/PS > UV/US ≈ UV ≈ US. The obtained results demonstrated the applicability of sonophotolytic-activated persulfate method using high-frequency US at 0.88/2.64 MHz for degrading organic micropollutants in pure aqueous solution, but its performance for treatment of real water matrices and the associated synergistic effect need further research.
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