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Ultrasonic degradation of acetaminophen and naproxen in the presence of single-walled carbon nanotubes

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HIGHLIGHTS

- Sonodegradation of acetaminophen and naproxen was performed.
- Degradation was enhanced with the dispersion of SWNTs under US irradiation.
- Synergistic effect on the degradation PhACs was observed in US/SWNT process.
- Significant removal of dissolved organic carbon was achieved.

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ABSTRACT

Ultrasonic (US) and single-walled carbon nanotube (SWNT)-catalyzed ultrasonic (US/SWNT) degradation of a pharmaceutical (PhAC) mixture of acetaminophen (AAP) and naproxen (NPX) used as analgesics was carried out in water. In the absence of SWNTs, maximum degradations of AAP and NPX occurred at a high frequency (1000 kHz) and under acidic conditions (pH 3) and different solution temperatures (25 °C at 28 kHz and 35 °C at 1000 kHz) during US reactions. Rapid degradation of PhACs occurred within 10 min at 28 kHz (44.5% for AAP; 90.3% for NPX) and 1000 kHz (39.2% for AAP; 74.8% for NPX) at a SWNT concentration of 45 mg L^{-1} under US/SWNT process, compared with 28 kHz (5.2% for AAP; 10.6% for NPX) and 1000 kHz (29.1% for AAP; 46.2% for NPX) under US process. Degradation was associated with the dispersion of SWNTs; small particles acted as nuclei during US reactions, enhancing the H_2O_2 production yield. NPX removal was greater than AAP removal under all US-induced reaction and SWNT adsorption conditions, which is governed by the chemical properties of PhACs. Based on the results, the optimal treatment performance was observed at 28 kHz with 45 mg L^{-1} SWNTs (US/SWNT) within 10 min.

1. Introduction

Acetaminophen (AAP) and naproxen (NPX) are evidence-based pharmaceuticals (PhACs) used for pain relief and fever reduction, especially in patients with symptomatic osteoarthritis [1]. Recently, great interest has grown in identifying water contaminants, including PhACs, and treatment methods for protecting water resources [2,3]. AAP and NPX have frequently been detected in sewage treatment plant effluent [4], surface water [5,6], rivers [4], drinking water [7], and groundwater [5] worldwide due to the excretion of PhACs via urine [8] and improper disposal [9], creating a demand for novel wastewater treatment technologies.

Data from ecotoxicity tests show that PhACs cause adverse effects in *Daphnia magna*, *Desmodesmus subspicatus*, and *Litaneutria minor*, including immobilization and growth inhibition, at very low concentrations [10,11]. Many reports have suggested treatment methods for AAP and NPX using adsorption [12,13], biotreatment [14,15], membranes [15,16], and advanced oxidation processes (AOPs) such as photo-induced [17,18], ozone-induced [19,20], Fenton-induced [21,22], and ultrasonic (US)-induced oxidation [23]. Among them, AOPs have been widely used to remove recalcitrant organic compounds, including PhACs and endocrine-disrupting chemicals.

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US treatment has been recognized as an attractive advanced technology for the removal of contaminants. In US reactions, three reaction regions have different temperatures and concentrations of reactive free radicals (i.e., $OH^\bullet$, $HO_2{}^\bullet$, and $O^\bullet$): a gaseous region, a gas–liquid interface region, and a bulk liquid region that forms by rapid growth and implosive collapse of bubbles during cavitation [24]. Thus, US processes can induce destruction and oxidation of a variety of contaminants having different physicochemical properties (e.g., pK_a, octanol-water partition coefficient (K_{OW}), and S_H values based on Henry's law) [25].

To accelerate the degradation rate, supporting materials (solid particles) are used as heterogeneous catalysts in US processes to enhance the production rate of cavitation bubbles by acting as additional nuclei that increase the pyrolysis of water molecules and the formation of $OH^\bullet$ [25–27]. Recent studies have focused on carbon nanotubes (CNTs) as promising adsorbents for effective adsorption of organic and inorganic compounds due to their unique properties, including electrical conductivity, optical activity, and mechanical strength [28]. Adsorption is governed by interactions between organic chemicals and CNTs, such as hydrophobic interactions, π—π bonds, electrostatic interactions, and hydrogen bonds [29]. However, these adsorption mechanisms depend on the nature of the organic chemicals. Various methods of preparing and dispersing CNTs have been reported to enhance the properties of CNTs, including the use of surfactants and US processes, resulting in synergistic effects for pollutant removal [30,31]. However, to our knowledge, no study has investigated CNTs as catalysts in US processes or proposed adsorption and oxidation mechanisms. In this study, the degradation kinetics and efficiencies of mixtures of two PhACs (AAP and NPX) were investigated, and the production rate of hydrogen peroxide (H_2O_2) during US reactions was studied as a function of solution pH (3, 6, and 10.5), and temperature (15 °C, 25 °C, 35 °C, and 55 °C) at two different US-frequencies (28 kHz and 1000 kHz). Furthermore, the role of single-walled carbon nanotubes (SWNTs) in US processes was evaluated based on mineralization and H_2O_2 formation during degradation reactions of PhACs. Finally, a possible mechanism for US and US/SWNT processes is proposed.

2. Materials and methods

2.1. Chemicals and ultrasonic system

AAP ($C_8H_9NO_2$, 98%), NPX ($C_{14}H_{14}O_3$, 98%), potassium hydrogen phthalate ($C_8H_5KO_4$, 99.95%), potassium iodide (KI, 99%), ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}\cdot 4H_2O$), and H_2O_2 (30%, w/v) were purchased from Sigma–Aldrich (St. Louis, MO, USA). SWNTs (>90%) with a length of 5–30 μm and an outer diameter of 1–2 nm were obtained from Cheap Tubes, Inc. (Brattleboro, VT, USA). Synthetic feed solution containing a mixture of AAP and NPX was prepared in nanopure deionized water ($R = 18.2\ M\Omega\ cm^{-1}$, Barnstead; Thermo Scientific, Newington, NH, USA). The SWNTs were also prepared via hydration for 24 h in deionized water prior to use, and the desired dosage of SWNTs was added to the reactor, which was covered by aluminum foil to minimize experimental error (i.e., dust and/or atmospheric gases). All chemicals were used as received without further purification. Fig. S1 shows the US and US/SWNT system consisting of a stainless steel reservoir (length × width × height, 15 cm × 10 cm × 20 cm) with a water jacket, cooler (Fisher Scientific Inc., Pittsburgh, PA, USA), and US generator (frequencies of 28 and 1000 kHz, power of 180 ± 3 W; UlTech, Dalseo, Daegu, Korea). Solutions were sonicated (1000 mL) in a mixture of 5 μM AAP and 5 μM NPX, and pH was adjusted using 1 N H_2SO_4 and 1 N NaOH.

2.2. Analysis

The AAP and NPX concentrations were determined by high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Santa Clara, CA, USA). All samples from sonocatalysis reactions were filtered through 0.22-μm glass microfiber filters (Whatman, Little Chalfont, Buckinghamshire, UK) to remove the catalyst prior to analysis. The mobile phase consisted of a mixture of 40% water and 60% methanol. Separation was achieved with a LiChrosorb RP-18 analytical column (4.6 mm × 100 mm i.d., 5-μm particles, Atlantis; Waters, Milford, MA, USA) with a 100-μL sample loop at a flow rate of $1.0\ mL\ min^{-1}$. The detection wavelength was 227 nm for NPX and 243 nm for AAP. Total organic carbon (TOC) measurements were obtained with a TOC-V CNS with an ASI-V autosampler (Shimadzu, Kyoto, Japan). A pH meter (Orion 3-Star; Thermo Scientific Co., Singapore) was used to determine the pH of the solution during reactions.

The H_2O_2 concentration was determined by the KI dosimetry method [32] using an ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Technologies) at 350 nm during US reactions. To visually observe the presence of $OH^\bullet$, luminal fluorescence was performed, and the sonochemiluminescence (SCL) image was captured using a digital camera. A 3-L solution containing 100 mM NaOH and 2 mM luminal (3-aminophthalhydrazide) was prepared in the US reactor. $OH^\bullet$ produced during US degradation reacts with luminal, releasing aminophthalate anions and blue fluorescence as intense US waves propagate through the luminal solution [33]; i.e., the luminal exhibits SCL.

3. Results and discussion

3.1. Effects of frequency on H_2O_2 formation and PhACs degradation

The effect of frequency on AAP (5 μM) and NPX (5 μM) degradation in the mixture was monitored using 5 μM of each pollutant at 28 and 1000 kHz with an US power of 180 ± 3 W at a solution temperature of 25 ± 0.5 °C. As shown in Fig. 1a–c, the efficiencies of AAP and NPX degradation at 1000 kHz (86.1% for AAP and >99% for NPX) were significantly higher than those at 28 kHz (27.1% for AAP and 52.5% for NPX). The degradation efficiencies of both PhACs increased from 28 to 1000 kHz. In general, the relatively low frequency (<1000 kHz) increased the number of cavitational events, ejecting a greater fraction of $OH^\bullet$ into the bulk liquid [34]. However, for relatively high frequency (≥1000 kHz) a large number of oscillations might still be attributed to a larger fraction of $OH^\bullet$ ejection to the bulk liquid [35].

These results were confirmed by the photographs of SCL and production of H_2O_2. Fig. 2 shows photographs of SCL at different frequencies, indicating the presence of $OH^\bullet$ in the blue region. Generally, the US mechanism in water is initiated by $OH^\bullet$ and $H^\bullet$ generation from water dissociation (Eq. (1)). Next, $HO_2{}^\bullet$ is generated by the reaction of $H^\bullet$ with O_2 (Eq. (2)). Finally, H_2O_2 is formed by recombination of two $OH^\bullet$ and $HO_2{}^\bullet$, releasing O_2 (Eqs. (3) and (4)); however, $OH^\bullet$ production is primarily attributable to the production of H_2O_2 based on the k values ($k_4 \gg k_3$) in Eqs. (3) and (4) [36].

$$H_2O \rightarrow H^\bullet + OH^\bullet \quad k_1 = \text{unknown} \tag{1}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \quad k_2 = 2.1 \times 10^{10} \quad M^{-1} \quad s^{-1} \tag{2}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad k_3 = 8.3 \times 10^5 \quad M^{-1} \quad s^{-1} \tag{3}$$

$$2OH^\bullet \rightarrow H_2O_2 \quad k_4 = 5.5 \times 10^9 \quad M^{-1} \quad s^{-1} \tag{4}$$