



Enhanced ultrasonic degradation of acetaminophen and naproxen in the presence of powdered activated carbon and biochar adsorbents



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ABSTRACT

This study investigated the degradation of pharmaceuticals (PhACs), acetaminophen (AAP) and naproxen (NPX), via treatment under ultrasonic (US) conditions. The most efficient frequency based on the rate of PhACs degradation and hydrogen peroxide (H₂O₂) production was found to be 580 kHz when 28, 580, and 1000 kHz frequencies were applied. Additionally, the degradation of PhACs at 580 kHz could be improved by increasing the US-power density and solution temperature. The apparent activation energy of degradation was determined via Arrhenius law to be 10.3 and 11.2 kJ mol⁻¹ for AAP and NPX, respectively, wherein the most favorable degradation pH was acidic. Density functional theory based calculations demonstrated that NPX has 8 barrierless points of reaction compared to AAP having 1 barrierless point. This molecular modeling analysis result explains the faster kinetics of NPX degradation. Additionally, a maximum rate of PhACs degradation was observed when the H₂O₂ concentration was 5 μM. The degradation of PhACs was strongly inhibited by the presence of *tert*-butanol when compared to methanol, indicating that the degradation of AAP and NPX was dependent on the presence of OH[•]. Based on the synergistic index and Langmuir–Hinshelwood model, biochar was more efficient for treating PhACs than powdered activated carbon under US irradiation, degrading PhACs mainly via a combination of adsorption onto the adsorbents and reaction with OH[•] under US irradiation with adsorbent particles providing nucleation sites. This method shows great potential in providing a viable catalyst toward degrading PhACs within catalytic industrial processes.

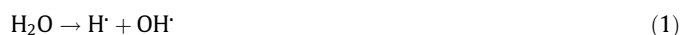
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1. Introduction

Over the past several years, polluted-water treatment technologies have significantly improved over increasing concerns about the public health risks posed by pollutants having adverse effects at low concentrations [1]. Advanced oxidation processes (AOPs) have been widely used for water and wastewater treatment; during this process, OH radicals (OH[•]) are generated, which then react with and completely degrade water contaminants. In a separate review paper of Klavarioti et al. [2], various technologies such as photocatalysis with semiconductors (32%), ozonation (30%), Fenton, photo-Fenton reactions (13%), and ultrasonic (US) processes (4%) were summarized on the basis of the number of published studies for treating pharmaceuticals (PhACs). However, US processes have

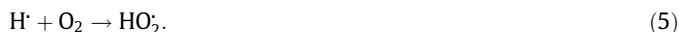
recently been recognized as a promising alternative for oxidizing a wide range of organic compounds such as PhACs [3–8], dyes [9,10], endocrine-disrupting compounds (EDCs) [11,12], chloro compounds [13,14], and organosulfa compounds [15].

The main chemical effects of US treatment originate from the development of acoustic cavitations: the formation, growth, and implosive collapse of bubbles in a liquid. During this phenomenon, high temperatures (5000 K) and pressures (1000 atm) in the created cavities are reached in a very short time [16]. Under these extreme conditions, water molecules are thermally dissociated to H[•] and OH[•]. In addition, the presence of O₂ dissolved in water leads to the formation of OH[•] and HO₂[•] during the US process. The two OH[•] can partly recombine to yield H₂O₂; brief mechanisms are given in Eqs. (1)–(6) [17,18]:



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During the US process, chemical reactions are commonly thought to occur in three reaction zones: the gaseous cavitation bubble region, the gas–liquid transition region, and the bulk liquid phase, whereby different degradation reactions occur in these different zones [19].

Recently, solid particles such as loquat seeds (LS) [10], corn-cob activated carbon (AC) [20], and granular activated carbon (GAC) [21] are typically applied during the US reaction to improve the generation of OH^\cdot via the increased presence of cavitation bubbles but also physically adsorb the pollutant onto the surface of particles. These two different reactions have not been clearly defined due to the different natures of the solid particles utilized. AC has been widely used as an adsorbent in wastewater treatment. Previous studies have shown that adsorption using powered AC (PAC) removes many organic and inorganic compounds [22,23]. In recent years, biochar has attracted increasing research interest as a new adsorbent due to its strong sorption affinity for organic pollutants in environmental media [24,25]. Biochar is produced by combusting waste source materials under low temperatures (<500 °C) in a cost-effective and eco-friendly process [26]. Additionally, according to Hale et al. [27] both AC and biochar can be successfully applied as an adsorbent toward the remediation of contaminated soil due to their high sorption capacity.

In this study, adsorbents such as PAC and biochar were employed as catalysts in the US process to degrade PhACs such as acetaminophen (AAP) and naproxen (NPX) as model compounds. These compounds have been used to reduce inflammation and relieve fever and pain by blocking enzymes and proteins associated with pain [28]. Both AAP and NPX have been frequently observed in the natural environment [29–31], partly because these compounds are not readily degraded under ambient aqueous conditions. Although these chemicals are present at nanogram per liter concentrations, the results of toxic test for PhACs have shown that these small concentrations have the potential to induce adverse effects in human cell lines [32]. However, to our knowledge little data are available regarding how such chemicals may be removed, as well as the mechanism of removing emerging contaminants using an US/adsorbent system.

In this study, AAP and NPX were selected as model PhACs and treated via US to investigate the effects of factors such as US frequency, US-power density, solution pH, solution temperature, OH^\cdot promoter concentration [in this case, hydrogen peroxide (H_2O_2)] and scavenger concentration (here, methanol (MeOH) and *tert*-butanol (*t*-BuOH)). Molecular modeling was performed using density functional theory to evaluate the mechanisms of AAP and NPX removal using OH^\cdot . Furthermore, the feasibility of adsorbents (PAC and biochar) as catalysts in the US process was evaluated and a possible mechanism for the US/adsorbents process proposed.

2. Materials and methods

2.1. Materials

AAP ($\text{C}_8\text{H}_9\text{NO}_2$, 98%) and NPX ($\text{C}_{14}\text{H}_{14}\text{O}_3$, 98%) were purchased in neat form (Sigma–Aldrich, St. Louis, MO, USA) and dissolved in nanopure deionized (DI) water ($R = 18.2 \text{ M}\Omega \text{ cm}^{-1}$, Barnstead; Thermo Scientific, Newton, NH, USA) to yield a stock solution

with a concentration of $50 \mu\text{M L}^{-1}$. The physical characteristics of PhACs are summarized in Table S1. Potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$, 99.95%), potassium iodide (KI, 99%), ammonium molybdate tetrahydrate ($\text{H}_{24}\text{Mo}_7\text{N}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$), and H_2O_2 (30% w/v) obtained from Sigma–Aldrich were used to measure H_2O_2 production. Hydrochloric acid (HCl, 99%) and sodium hydroxide (NaOH, 98%) were used to adjust the initial pH of solutions. OH^\cdot scavenging effects were investigated using MeOH (CH_3OH , 99.9%) and *t*-BuOH ($\text{C}_4\text{H}_{10}\text{O}$, 99.9%) (Table S2). All chemicals were utilized as received without further purification.

The coal-based virgin, high-performance PAC (WPM, PAC form of F400) employed as the adsorbent in this study was supplied by the Calgon Carbon Corp (Pittsburgh, PA, USA) and biochar was prepared using loblolly pine, an abundant and commercially important tree species in USA. A bench-scale slow pyrolyzer was used to convert loblolly pine into biochar by raising the temperature to 300 °C for 15 min under N_2 . The biochar was then milled and sieved using a 200 mesh (74 μm). The physical characteristics of PAC and biochar are given in Table S3.

2.2. Apparatus

US irradiation was performed at 28, 580, and 1000 kHz with a power of $180 \pm 3 \text{ W}$ in the absence and presence of PAC and biochar adsorbents at 1, 5, 10, and 15 mg L^{-1} under ambient air conditions. US and US/adsorbent systems composed of double-jacketed stainless steel reservoirs (L:W:H, 15:10:20 cm) with a water-cooled (Fisher Scientific Inc., Pittsburgh, PA, USA) US generator (Ultech, Dalseo, Daegu, South Korea) were used to maintain the given temperature (Fig. S1).

Batch adsorption experiments were performed to evaluate the PAC and biochar adsorption capacities without US irradiation. The adsorbents were hydrated for 24 h in DI water prior to use and the desired dosage (1, 5, 10, and 15 mg L^{-1}) was added to the reactor beaker; they were then covered with aluminum foil and mixed for 1 h on a benchtop magnetic stirrer at 300 rpm. Both US/adsorbent and adsorption experiments carried out using 1000 mL of this initial solution. Samples were taken periodically and immediately filtered with 0.22- μm glass microfiber filters (Whatman, Little Chalfont, Buckinghamshire, UK) for further analysis.

2.3. Analysis

Quantification of AAP and NPX was carried out via high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Santa Clara, CA, USA) consisting of a high-pressure pump (G1312A, Agilent Technologies), a photodiode array detector (G1315D, Agilent Technologies), and a C18 column (LiChrosorb RP-18, 4.6 mm \times 100 mm i.d., 5- μm particles, Atlantis; Waters, Milford, MA, USA). The mobile phase was a mixture of 40/60 (water/MeOH, v/v) for AAP and 40/60 (water/acetonitrile, v/v) for NPX at a flow rate of 1.0 mL min^{-1} . The detection wavelength was 243 nm for AAP and 227 nm for NPX.

The H_2O_2 concentration was measured by KI dosimetry using a 0.1 M potassium hydrogen phthalate and KI reagent consisting of 0.4 M KI, 0.06 M NaOH, and 1×10^{-4} M ammonium molybdate [33]. The absorbance at 350 nm was determined using an ultraviolet–visible spectrophotometer (G1103A, Agilent Technologies).

A visually indirect measurement of OH^\cdot was made via a sonchemiluminescence (SCL) image captured using a luminal method with a digital camera (T3, EOS, Canon). In this process, OH^\cdot produced by US reactions will oxidize luminal in the bulk solution to form aminophthalate anions, which emit blue light [34]. The luminal solution contained 100 mM NaOH and 2 mM luminal (3-aminophthalhydrazide).

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