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Sonochemical degradation of ciprofloxacin and ibuprofen in the presence of matrix organic compounds

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ABSTRACT

Ciprofloxacin (CIPRO) and ibuprofen (IBU), a hydrophilic and a hydrophobic compound, respectively, were degraded by ultrasound at the frequencies of 20 and 620 kHz in aqueous solution containing matrix organic compounds. Compared to in its absence, in the presence of terephthalate (TA), a commonly used ·OH scavenger, CIPRO degradation was inhibited by a factor of 40–1500 depending on the frequency and initial concentration. However, the degradation rates of IBU were only reduced between 30% and 80% with TA present compared to in its absence. Similar to TA, the presence of Suwannee River Fulvic Acid (SRFA) inhibited CIPRO degradation to a greater extent than that of IBU but overall inhibition by SRFA was dramatically less than by TA. Although both TA and SRFA inhibited the degradation of CIPRO and IBU, the mechanisms of inhibition are different. TA reacts with ·OH in bulk solution and our evidence also indicates that it accumulates on or interacts with cavitation bubbles. On the other hand, SRFA stays in bulk solution, quenching ·OH and/or associating with the target compounds.

1. Introduction

Numerous studies have reported measuring pharmaceuticals at parts-per-trillion to parts-per-billion concentrations in aquatic systems [1–3]. Since these microconstituents are present in much lower concentrations than conventional contaminants, it is difficult to remove them in the presence of organic and inorganic matrices that are a thousand to a million fold more abundant. Although the toxicity of continual low-level exposure to these compounds by humans is uncertain and these emerging pollutants are unregulated, studies have shown adverse effects to aquatic microorganisms [4] and fish [5]. To date, an effective strategy to mitigate these unforeseen microconstituents from the aquatic environment does not exist.

Advanced oxidation processes (AOPs) have the potential to substantially reduce contaminants from water and wastewater [6,7]. Ultrasonic irradiation is an emerging AOP with advantages over other AOPs due to its ease of use, lack of chemical addition, and unique degradation mechanisms. Sonochemical techniques involve the use of ultrasonic waves to produce cavitation bubbles in solution. During the collapse of cavitation bubbles, localized hot spots are formed [8], reaching average bubble temperatures of roughly 5000 K and pressures of approximately 500 atm [9].

Considering these cavitation bubbles as microreactors, three different reaction zones have been postulated: (i) the gaseous interiors of collapsing cavities resulting in the dissociation of volatile compounds including water through thermolysis; (ii) the interfacial liquid surrounding cavitation bubbles where high temperature (ca. 1000–2000 K) and high concentrations of ·OH (4 mM) exist [10]; and (iii) bulk solution (at ambient temperature) where small amounts of ·OH diffusing from bubble interfaces may contribute to contaminant destruction reactions [9,11]. The degradation pathway of a particular organic compound depends on its physicochemical properties, surface activity, and hydroxyl radical reactivity. Thus, sonochemistry is a complex phenomenon with two primary mechanisms: thermolysis and radical species reactions.

Recently, sonication of aqueous solutions has been shown to be effective for the destruction of IBU and CIPRO. Mendez-Arriaga et al. concluded that ultrasound may be used to eliminate IBU in aqueous solution and demonstrated that applied sonication power, dissolved gas, pH and initial concentration played roles during the process [12]. De Bel et al., observed that pH affected the ultrasonic degradation rate, biodegradability, and ecotoxicity of aqueous CIPRO solution [13,14]. These studies investigated the sonolysis of IBU and CIPRO in the absence of matrix constituents.

When AOPs are investigated in water treatment, the water matrix containing inorganic and organic components significantly slows the degradation of the target contaminants [7,15–17]. How

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the matrix of organic components affect the sonochemical degradation of contaminants appears to be complex based on limited previous studies [18–21]. On one hand, the presence of an organic matrix reduces the sonochemical degradation of target contaminants [18,19,22]. NOM is reported to react rapidly with ·OH with a second-order rate constant $k_{OH\text{-}SRFA} = 2.7 \times 10^4$ $(mgC/L)^{-1}\ s^{-1}$ [23], potentially hindering target contaminant degradation. Lu and Weavers observed that humic acid (HA) decreased the sonochemical degradation rate of 4-chlorobiphenyl (4-CB) and the effect was more pronounced with an increase in HA concentration [18]. Additionally, the sonication of polycyclic aromatic hydrocarbons (PAHs) with fulvic acid (FA) dramatically reduced the degradation rate of PAHs [22]. On the other hand, the presence of organic matter did not affect the sonochemical degradation of methyl tert-butyl ether (MTBE) [24], perfluorooctane sulfonate (PFOS), and perfluorooctanoate (PFOA) [20].

Terephthalate (TA), a typical ·OH scavenger and dissolved Suwannee River FA (SRFA), a model natural organic matter (NOM), were used as a bulk ·OH scavenger and as a model matrix organic compound, respectively. The very low concentrations of CIPRO and IBU observed in water and wastewater compared to matrix organics indicates the need to understand the role of matrix organics on pharmaceutical compound degradation. IBU and CIPRO were chosen because they are, respectively, relatively hydrophobic (true log $K_{ow} = 3.97$) and hydrophilic (log $K_{ow} = 0.28$) examples within these classes of compounds.

2. Materials and methods

2.1. Materials

IBU (99%, Acros) and CIPRO (BioChemika, ⩾98%) were purchased from Aldrich and used as target compounds without further purification. Table 1 lists relevant data for both pharmaceuticals. Water used to prepare solutions was from a Millipore system ($R = 18.2$ M-cm). Terephthalic acid (99%) was purchased from Fluka. SRFA reference material was obtained from the International Humic Substances Society and used without further purification.

2.2. Sonochemical experiments

Two ultrasonic units, a 20 kHz ultrasonic probe system (Sonic Dismembrator 550, Fisher Scientific) with an irradiating area of 1.27 cm^2 and a 620 kHz transducer system (ELAC Nautik, Inc., Kiel, Germany) with a 23 cm^2 transducer were applied to irradiate CIPRO and IBU in water. In both systems, the sonochemical power density input into the reactor was adjusted and measured by calorimetry to be approximately 400 W/L. Water-jacketed glass reactors containing either 50 mL (for 20 kHz) or 125 mL (for 620 kHz) of reaction solution were controlled at 20 °C by a cooling bath (Fisher Scientific, 1006S). The sonication time was selected based on the initial concentrations (for 1 μM, 12 min; for 10 and 100 μM, 60 min). Although the power densities used were the same, the cavitation fields between the two sonication systems were different due to different frequencies, geometries, and irradiating surface areas.

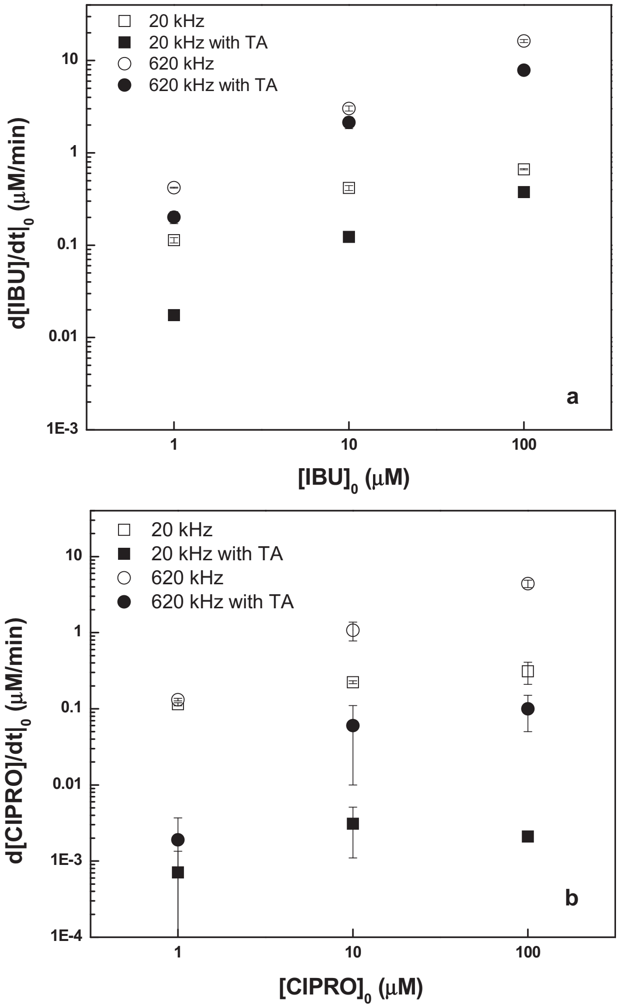
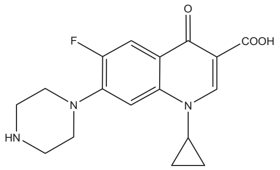
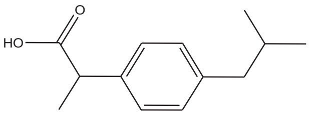


Fig. 1. Sonochemical degradation rates at different concentrations of IBU (a) and CIPRO (b) with 2 mM terephthalate (TA) (pH 8.5, 20 °C and sonication power density at 400 W/L).

Table 1
Physicochemical properties of CIPRO and IBU.

Compounds	Ciprofloxacin (CIPRO)	Ibuprofen (IBU)
Structure		
Use class	Antibiotic	Painkiller
Solubility ($mg\ L^{-1}$)	3×10^4 [51]	21 [52]
Log Henry's law constant at 25 °C ($atm\text{-}m^3\ mol^{-1}$)	−18.30 [53]	−6.82 [53]
True log K_{ow}	0.28 [54]	3.97 [55]
Apparent log K_{ow}	−1.52 (pH = 8.5) [56]	0.24 (pH = 8.5) [55]
pK_a	3.64, 5.05, 6.95, 8.95 [13]	4.90 [57]
Second-order ·OH rate constant ($M^{-1}\ s^{-1}$)	$4.1 \pm 0.3 \times 10^9$ (pH = 7.0) [58]	$6.5 \pm 0.2 \times 10^9$ (pH = 7.0) [59]