Hydroxyl radical formation in batch and continuous flow ultrasonic systems

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ABSTRACT

The creation of free radicals by ultrasonic cavitation is the main mechanism that leads to chemical degradation of target pollutants and the process is considered an alternative advanced oxidation technology. The goal of this study was to compare the effects of batch and continuous flow ultrasonic systems on the formation of hydroxyl radicals. Ultrasonic batch experiments were conducted in two reactors (small and large) using a standard 20 kHz catenoidal titanium horn at varying amplitudes and sonication times. The effect of saturating gas was also investigated by introducing helium and air at $1 \, L \, min^{-1}$ into the larger 100 mL reactor. In the continuous flow system, the experiments were conducted with a 20 kHz, 3.3 kW ultrasonic systems using a titanium "donut" horn at varying volumetric flow rates and amplitudes. Formation of hydroxyl radicals was determined using terephthalic acid dosimetry measurements. At the same energy densities, higher hydroxyl radical concentrations were formed in the batch system than in the continuous flow system. Sonication time appeared to be the main factor that influenced the results in batch and continuous flow systems. The two gases (helium and air) did not increase the hydroxyl radical formation at any amplitude or sonication time tested.

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1. Introduction

Advanced oxidation processes involve the production of hydroxyl radicals (·OH) and are used for the oxidation of pollutants in water and wastewater [1]. Hydroxyl radicals react with pollutants by addition to the double bonds, hydrogen abstraction, or, electron transfer [2,4]. These highly reactive ·OH typically react with organic compounds with reaction rate constants in the order of 10^8–$10^{10} \, M^{-1} \, s^{-1}$ [2,3]. Hydroxyl radicals are effective primarily because they are strong oxidants, they are non-selective in nature, and are capable of converting recalcitrant compounds into biodegradable forms [4].

Hydroxyl radicals can be produced using various methods, such as electrolysis, ozonation, ultraviolet radiation, microwave, ultrasonication, or as a combination of two of these processes.

Here, we investigated ultrasonication as a promising alternative technology when considering advanced oxidation processes (AOPs). Ultrasound is sound waves at frequencies beyond the normal human hearing range (15–20 kHz) [5,6]. During ultrasonication, hydroxyl radicals are generated as a result of thermal decomposition of water [7]. As sound waves pass through a liquid, during the expansion half-cycle of the waves, microbubbles will be formed if sufficiently large negative pressure is applied to overcome the tensile strength of the liquid. Most liquids are contaminated by the presence of gas molecules and particulate matter creating weak sites serving as cavitation nuclei, which lower the tensile strength. The tension generated by ultrasound waves is responsible for the formation of cavitation bubbles at these sites. Once produced, these small bubbles will expand and contract in accordance with the energy absorbed from alternating rarefaction and compression cycles of the acoustic waves. The fate of these bubbles in the acoustic region depends on many factors, including the intensity of the applied ultrasound. For low-intensity ultrasound, the size of the bubble oscillates about some equilibrium size

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for many acoustic cycles and these stable bubbles may grow by a process called rectified diffusion [8]. As the bubble grows, it may be transformed into a transient bubble (normally produced by applying high-intensity ultrasound) that collapses violently, giving rise to very intense localized heating (5000 K) [9] and pressure spikes (1000 atm) [10] that lead to the pyrolysis of water, producing $\cdot$OH [7]. During thermal decomposition of water, other reactive species can also form, e.g., oxidizing hydrogen peroxide (H_2O_2) and oxygen radical ($O\cdot$) and the reducing hydrogen atom ($H\cdot$) [4].

There are a growing number of studies in water and wastewater treatment involving AOPs [1,2,11–14]. Several of these studies have shown the potential of ultrasonication in water and wastewater treatment [15–17] for enhanced pollution degradation. Hoffmann et al. [17] showed the successful degradation of several chemical contaminants, such as chlorinated hydrocarbons, pesticides, and phenols. They also found that the chemical degradation by ultrasonication followed three pathways: oxidation by $\cdot$OH, pyrolytic decomposition, and supercritical water oxidation. Méndez-Arriaga et al. [18] utilized ultrasound to treat water contaminated with ibuprofen, a pollutant that is typically not removed in municipal treatment systems [19]. Ultrasonics destroyed 98% of ibuprofen ($21\ mg\ L^{-1}$ initial ibuprofen concentration) after 30 min of treatment at a frequency of 300 kHz and 80 W of applied power. In addition, Pengphol et al. [20] has effectively combined ozone and ultrasonication treatment of chlorpyrifos, an organophosphate pesticide sometimes found in shrimp. Their results showed a reduction of chlorpyrifos toxicity to brine shrimp after this combined treatment.

The formation of hydroxyl radicals during batch ultrasonication has been explored extensively. However, as with other technologies, the scale-up of the process can be challenging. Therefore, the goal of this study was to compare the $\cdot$OH generation efficiency in batch and continuous flow ultrasonic systems, where the continuous flow ultrasonic system corresponds to a scaled-up design. It should be noted that the continuous flow system contained the same "donut" horn technology typically used in a commercial scale ultrasonic system used to treat waste activated sludge for enhanced anaerobic digestion [21].

2. Materials and methods

Typically, the transient characteristics of hydroxyl radicals require an in-situ scavenger compound to quantify them [22]. In this study, terephthalic acid (TA) was used to scavenge hydroxyl radicals and the fluorescence properties of the product, 2-hydroxyterephthalate (2-HTA) used to measure the yield of 2-HTA, representing an estimate of steady-state concentration of $\cdot$OH radicals.

2.1. Materials and equipment

Synthesized standard 2-hydroxyterephthalate (2-HTA) solution and 2 mM terephthalic acid (TA) solution were prepared using the method described by Mason et al. [22]. All chemicals used were reagent grade and obtained from Sigma Aldrich. The synthesis of 2-HTA yielded 2.975 g, and its purity of 95.7% was determined by high performance liquid chromatography (HPLC); its melting point was 304 °C as determined by differential scanning calorimetry (DSC).

2.2. Ultrasonic batch experiments

The ultrasonic batch experiments were conducted in two reactors, 50 mL polypropylene conical centrifuge tubes (small batch) and an aluminum alloy chamber (large batch) (see Fig. 1). The small and large batch studies used working volumes of 35 mL and 100 mL, respectively. Aqueous TA solution (2 mM) was prepared and sonicated using a Branson 2000 Series bench-scale ultrasonic unit (Branson Ultrasonics, Danbury, CT) at varying amplitudes (9.6, 14.4, 19.2, 28.8, 38.4 and 48 $\mu m_{peak-to-peak(pp)}$) and sonication times (1, 1.5, 2, 3, 4, 5, 8, 10 min). The ultrasonic system was capable of operating at a maximum power output of 2.2 kW and a constant frequency of 20 kHz. The horn was a standard, 20 kHz catenoidal titanium horn with a flat 13 mm diameter face (gain = 8). The same horn was used in both batch experiments. Ultrasonication was assumed to be 70% efficient. This conservative assumption was based on another study where the same ultrasonic "donut" horn was used [23].

2.3. Ultrasonic experiments with gas addition

To determine the effects of dissolved gases on the formation of hydroxyl radicals during ultrasonication, solutions of TA were saturated with helium or air. One hundred milliliters (100 mL) of aqueous TA solution (2 mM) was saturated with air or helium for 10 min before the sample was sonicated. To insure that solutions were saturated during sonication, gases were continuously introduced into the reactor at flow rate of 1 L min^{-1}.

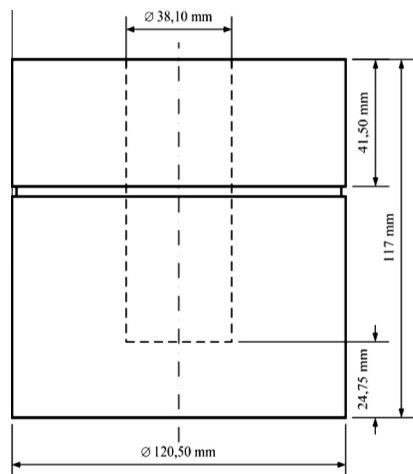Fig. 1. Ultrasonic large batch reactor experimental set-up.