Ultrasonics Sonochemistry 29 (2016) 156–162

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Removal of carbamazepine from aqueous solution using sono-activated persulfate process

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ARTICLE INFO

Article history:
Received 5 July 2015
Received in revised form 10 September 2015
Accepted 10 September 2015
Available online 12 September 2015

Keywords:
Ultrasound
Persulfate
Carbamazepine
Sulfate radical
Reaction kinetic

ABSTRACT

This study investigated systematically the removal of carbamazepine (CBZ) in solution using the combination of ultrasound and persulfate anions to identify the factors affecting the kinetics of the process. The effects of reaction time, initial persulfate anion concentration, initial CBZ concentration, ultrasonic power input, solution pH and temperature on CBZ removal efficiency were examined. The sulfate radical oxidation of CBZ in the presence of ultrasonic irradiation showed a significant synergistic effect on CBZ removal. It is found that up to 89.4% CBZ removal efficiency was achieved after 120 min reaction. The removal process of CBZ in solution could be described using pseudo-first-order kinetics. In this system, sulfate radicals ($SO_4^{-\cdot}$) were considered to be the mainly oxidant to remove CBZ while ultrasound power input could affect CBZ removal efficiency significantly. Changing solution pH influenced the CBZ removal efficiency and the best performance would be achieved at pH 5.0.

1. Introduction

The widely-used pharmaceuticals products would enter into ecosystems through food chains, resulting in greater pharmaceutical concentrations in aquatic environments [1]. These pollutants are treated insufficiently by the conventional treatment processes and may have harmful effects on public health and aquatic ecology [2]. In recent years, there has been an increase of public concern on these pharmaceutical pollutants [3]. As one of the most widely prescribed dibenzazepine derivatives, carbamazepine (CBZ, $C_{15}H_{12}N_2O$) has been frequently detected in aquatic environments due to their extensive use and refractory properties, and well-known of its insufficient removal efficiency (7–10%) at conventional wastewater treatment plants [4]. Due to the harmful effects of the pharmaceuticals' exposure, an effective and affordable treatment system should be under investigation. Several studies have been conducted involving the chemical oxidation of CBZ in aqueous solution using conventional advanced oxidation processes, due to the generation of strong oxidizing oxygen species, especially hydroxyl radicals (·OH), including $O_3/UV/H_2O_2$ [5], UV/H_2O_2 [6], photocatalytic [7], photo-fenton [8], ultrasonic/Fe_0/H_2O_2 [9], sonolysis [10,11] and sonophotocatalysis [12]. But the catalyst such as Fe^{2+} and TiO_2 would be external contaminant, the high cost of power and low efficiency of CBZ removal would be also the restriction reason of its application.

Persulfate anions have strong oxidation–reduction potential (2.01 V) and so appear as a potentially viable alternative for decomposing organic compounds [13]. Due to its aqueous solubility, relatively high stability and low cost, persulfate could be used as a source of an even stronger oxidant, sulfate radicals ($SO_4^{-\cdot}$, 2.6 V). Carbamazepine degradation using a Fe^{2+}-activated persulfate process [14], an UV-activated persulfate process [15] and a thermally activated persulfate process [16] have been reported. Monteagudo et al. investigated in-situ chemical oxidation of a carbamazepine solution using persulfate anions simultaneously activated by heat energy, ultrasound, UV-C light, Fe^{2+} ions, and hydrogen peroxide to analyze the mineralization reactions, and found that solution TOC removal was nearly complete (99%) within 90 min. Sulfate radicals and hydroxyl radicals would be involved in the main mineralization pathway. In addition, with excess persulfate, an unproductive $S_2O_8^{2-}$ decomposition reaction or a rapid reaction between excess sulfate radicals to produce sulfate anions could occur. Fe^{2+} could exhibit catalytic effects on H_2O_2 decomposition and persulfate activation [17]. While the activation performance of ultrasound has not been systematically discussed.

As one kind of advanced oxidation processes, ultrasonics has been investigated to degrade non-biodegradable pollutants. While in most cases degradation efficiency would be limited to low level and energy use efficiency would be very low [18]. The degradation

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http://dx.doi.org/10.1016/j.ultsonch.2015.09.008
1350-4177/

rate of organic pollutants in a conventional sonochemical process should be promoted by 10–100 times for its application in practical wastewater treatment [19]. But Sonication in aqueous solution could cause rapid formation, growth and violent collapse of cavitation bubbles, resulting in enormous local temperature and pressure rises. So ultrasound would bring about a beneficial condition because sulfate radicals ($SO_4^{-}\cdot$) would be formed from the oxidant by thermolytic cleavage of persulfate [20]. Sono-activated persulfate processes would provide a promising treatment for organic pollutant in water. Li et al. found 1,1,1-trichloroethane (TCA) removal efficiency was 20% using persulfate without activated and almost 100% when oxidizing agent persulfate was activated by sonolytic method, and demonstrated that TCA would be decomposed mainly through sulfate and hydroxyl radicals as well as ultrasonic pyrolysis [21]. Some literature investigated many kinds of pollutant degradation using sono-activated persulfate processes, such as *tert*-butyl ether (MTBE), arsenic (III) and dinitrotoluenes [20,22,23].

Under the circumstance of persulfate combined with ultrasound, many kinds of radicals and oxidants would be generated, such as $SO_4^{-}\cdot$, $\cdot OH$, $SO_5^{-}\cdot$ and HSO_5^{-}. It is generally believed that a typical sonochemical oxidation of pollutants in the persulfate anion reaction should involve two key reactions: (1) the generation of radicals from persulfate anions and water decomposed into sulfate and hydroxyl radicals; (2) the degradation of organic substance by the radicals and oxidants. In the meantime, some reversed reactions and side reactions coexist along with the key reactions as summarized below [24–28]:

$$S_2O_8^{2-} +))) \rightarrow 2SO_4^{-}\cdot \quad (1)$$

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-}\cdot \quad (2)$$

$$H_2O +))) \rightarrow \cdot OH + \cdot H \quad (3)$$

$$H_2O + 2SO_4^{-}\cdot \rightarrow H^+ + 2SO_4^{2-} + \cdot OH \quad k = 6.5 \times 10^7\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (4)$$

$$SO_4^{-}\cdot + SO_4^{-}\cdot \rightarrow S_2O_8^{2-} \quad k = 3.1 \times 10^8\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (5)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad k = 5.5 \times 10^9\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (6)$$

$$\cdot OH + SO_4^{-}\cdot \rightarrow HSO_5^{-} \quad k = 1 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (7)$$

$$SO_4^{-}\cdot + HSO_5^{-} \rightarrow HSO_4^{-} + SO_5^{-}\cdot \quad k = 1 \times 10^5\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (8)$$

$$\cdot OH + HSO_5^{-} \rightarrow SO_5^{-}\cdot + H_2O \quad k = 1.7 \times 10^7\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (9)$$

$$2SO_5^{-}\cdot \rightarrow S_2O_8^{2-} + O_2 \quad k = 1 \times 10^8\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (10)$$

$$S_2O_8^{2-} + SO_4^{-}\cdot \rightarrow SO_4^{2-} + S_2O_8^{-}\cdot \quad k = 6.1 \times 10^5\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (11)$$

$$S_2O_8^{2-} + \cdot OH \rightarrow OH^- + S_2O_8^{-}\cdot \quad k = 1.2 \times 10^7\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (12)$$

All these radicals and oxidants could react with CBZ in varying degrees, leading to the complex CBZ reaction kinetics.

In present work, the sono-activated persulfate oxidation of CBZ was systematically studied at fixed frequency of 40 kHz. The batch experiments were carried out to examine the critical parameters of reaction time, initial persulfate anion concentration, initial CBZ concentration, ultrasonic power input, solution pH and temperature on the CBZ degradation. Additionally, this work also investigated the reaction kinetics and the possible radical contributions.

2. Materials and methods

2.1. Materials

Carbamazepine used in the research, $C_{15}H_{12}N_2O$ (purity 99%) was obtained from Acros, Belgium. Analytical grade potassium persulfate ($K_2S_2O_8$), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Shanghai Chemical Reagents Co. Ltd., China and were used as received. All other chemicals and solvents were analytical grade and used without further purification.

2.2. Experimental setup

Experiment reactor was a 200 mL beaker, which was placed at certain position in ultrasonic bath. Two kinds of ultrasonics bath, from Kunshan Ultrasonic Instruments Co. Ltd, China, with fixed ultrasonic frequency of 40 kHz were used in the series of experiments. The power input of KQ5200DB ultrasonics bath could be adjusted continuously from 80 to 200 W. The power input of KQ50DE ultrasonics bath could be fixed at 50 W. A sample of 100 ml was sonicated in the covered beaker. The water level inside the ultrasonic bath was maintained by continuous circulation of cooling water, and subsequently the temperature was maintained constantly at intended temperature. The pH of initial solution was adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH before reaction.

2.3. Procedure

The stock solution of CBZ were prepared in glass beakers containing 1.0 L of demineralized water. CBZ was solubilized using a magnetic stirrer (300 rpm) at an ambient temperature (20 °C) for 24 h. The resulting mixtures constituted the CBZ solutions (final concentrations in the range of 2.5 mmol L^{-1}). All CBZ degradation experiments were performed with a volume of 100 mL. It was diluted with deionized water to desirable experimental initial concentrations when necessary, and adjusted to the required pH with H_2SO_4 or NaOH. The pH was measured by a model pHs-25 pH meter.

After adding persulfate, the beaker was quickly sealed with the film (PTFE) and bundled with a rubber band, and then the sample was sonicated at the predetermined power intensity. At selected time interval, aliquot of 2 mL reaction mixture were taken and immediately cooled down to room temperature. All experiments were repeated at least three times. Data were reported as averages.

2.4. Analytical methods

CBZ concentration was determined using high-performance liquid chromatography with UV detection (Shimadzu, LC20A) in the isocratic mode immediately after sampling. An Eclipse XDB-C18 column (5 μm, 4.6 × 250 mm) was used, and a 60:40 (v/v) acetonitrile/water mixture was used as the mobile phase (detection wavelength = 286 nm; flow rate of 1.0 mL min^{-1}).

3. Results and discussion

3.1. The synergistic effect of ultrasound and persulfate process on CBZ removal

Fig. 1 showed the time dependence of CBZ removal efficiency of different combinations such as single ultrasound system, single persulfate system and the binary system of persulfate combined with ultrasound. The results mirror that CBZ removal efficiency of persulfate combined with ultrasound is the highest compared to single ultrasound irradiation or single persulfate. Here, the