Chemical Engineering Journal 336 (2018) 595–601

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Degradation of carbamazepine by radiation-induced activation of peroxymonosulfate

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ARTICLE INFO

Keywords:
Peroxymonosulfate
Activation
Sulfate radicals
PPCPs
Carbamazepine
Radiation

ABSTRACT

In this study, the radiation-induced activation of peroxymonosulfate (PMS) was investigated for the degradation of carbamazepine (CBZ), and compared with single PMS system, single radiation system and Fe(II)-activated PMS system. The results showed that gamma radiation can effectively activate PMS, and the presence of PMS could decrease the absorbed dose required to completely degrade CBZ. Moreover, the removal efficiency of TOC was 38.3% in the gamma radiation-induced activation of PMS system, which was higher than that in the single PMS system, single radiation system and the Fe(II)-activated PMS system. Hydroxyl radicals played major role in the degradation of CBZ. However, the contribution of hydroxyl radicals for the CBZ degradation decreased as the absorbed dose increased from 100 Gy to 800 Gy. In addition, the sulfate radical and persulfate formed during the radiation/PMS process also contributed to CBZ degradation. The maximum decomposition efficiency was found with the molar ratio of PMS to CBZ of 20:1 at adsorbed dose of 300 Gy. Furthermore, the intermediate products were identified, and the degradation pathway of CBZ was tentatively proposed. In summary, the gamma radiation-induced activation of PMS system could be a promising technology for the removal of recalcitrant organic pollutants.

1. Introduction

Carbamazepine (CBZ) has been widely used as an anticonvulsant drug to cure depression and seizures worldwide. CBZ is poorly biodegradable as evidenced by its frequent detection in the effluents of the wastewater treatment plants [1,2]. Due to the potential toxicity to the aquatic organisms and human health, increasing attention has been paid to its removal by tertiary treatments during the wastewater treatment plants prior to discharge into the receiving water body.

Advanced oxidation processes (AOPs) based on the strong oxidation property of hydroxyl radicals have received increasing attention in recent years [3,4], which have been used for the degradation of CBZ, such as ozonation [3], Fenton oxidation [4], UV/H_2O_2 [5], and gamma-radiation [6]. AOPs have been demonstrated to be capable of decomposing CBZ completely. However, hydroxyl radicals have the non-selective property, and it can react with the non-target pollutants in the wastewater, such as natural organic matters [7], which results in the decrease of removal efficiency for the target pollutant.

In comparison to hydroxyl radicals, sulfate radicals have almost equivalent oxidation capacity, and they are more selective to the non-target pollutants [8]. For examples, the rate constants of sulfate radicals with natural organic matter ($6 \times 10^6\ M^{-1}\ s^{-1}$) were much lower than that of hydroxyl radicals ($2.2 \times 10^8\ M^{-1}\ s^{-1}$) [9]. Thus, to some extent, non-target pollutant has less effect on the oxidation of sulfate radicals to the target pollutant.

The removal of CBZ by the sulfate radicals-induced oxidation has been studied [10–14]. The removal efficiency and mineralization degree of CBZ was dependent on the activation method. The complete mineralization of CBZ was observed with persulfate through the simultaneous activation by heat energy, UV light, Fe(II) and H_2O_2 [12]. The sulfate radicals-induced oxidation can remove CBZ efficiently.

Sulfate radicals can be obtained by activation of peroxymonosulfate (PMS) using transient metals, heat energy, H_2O_2 and UV light [15]. Compared to transient metals and H_2O_2, heat energy and UV light do not require the addition of other ions into the water body. UV light can convert active PMS to form sulfate radicals [13]. The quantum yield for UV-254/PMS was 0.52, when the sink of sulfate radical into hydroxyl radicals was taken into account [16]. But the low penetration of UV light limited its application in the wastewater treatment.

Gamma irradiation as one of AOPs has stronger penetration range

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https://doi.org/10.1016/j.cej.2017.12.068
Received 20 October 2017; Received in revised form 27 November 2017; Accepted 13 December 2017
Available online 14 December 2017
1385-8947/

than UV. Moreover, many reactive species such as hydroxyl radicals and hydrated electrons can be produced simultaneously during the radiation process, which can further enhance the removal of organic pollutants [17]. It is thus expected that gamma radiation could be more efficient than UV in PMS activation. However, the activation of PMS by gamma radiation has not been investigated. Single gamma radiation process has been used for the degradation of organic pollutants, and showed good removal efficiency [6,18,19].

We have established the first industrial wastewater plant using radiation in March 2017 in Jinhua, Zhejiang Province, China. International Atomic Energy Agency (IAEA) reported it in its official website (https://www.iaea.org/newscenter/news/chinas-first-wastewater-plant-using-radiation-opens), indicating that radiation process has been put into practical application for treating real industrial wastewater. It is thus necessary to investigate how to further enhance the degradation of organic compounds by radiation process. In theory, gamma radiation can activate PMS, which will further enhance the oxidation capacity of radiation process. However, it is still unknown how PMS affect the removal of organic compounds by radiation process and the degradation mechanism.

The objective of this study was to investigate the degradation of CBZ by the gamma-induced activation of PMS; to infer the degradation mechanism; to elucidate the transformation pathways of CBZ in the gamma-induced PMS activation system.

2. Materials and methods

2.1. Chemicals

PMS (available as Oxone ($KHSO_5{\cdot}0.5kHSO_4{\cdot}0.5K_2SO_4$)) and CBZ were purchased from Aladdin Company (China) with the purity of higher than 47% and 98%, respectively. Methonal, ethanol and tert butyl alcohol (TBA), acetonitrile and formic acid were obtained from Thermo Fisher. Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥99%) was purchase from Aldrich Sigma (China). De-ionized water was provided by Wahaha Company (Hangzhou, China). The stock solution of CBZ was prepared by directly adding CBZ into the de-ionized water. Ten grams of CBZ were added into 1 L de-ionized water. The stock solution of CBZ was stirred for 48 h at 30 °C using magnetic stirrer to make CBZ completely dissolved. The pH of the stock solution of CBZ was about 7.2. Similarly, the stock solution of PMS and Fe(II) were prepared by adding the compounds directly to de-ionized water. The pH of Fe(II) was adjusted to 3 to avoid the precipitation of Fe(II). The initial pH of PMS was 3.2.

2.2. Gamma irradiation source

^{60}Co source located in the Institute of Nuclear and New Energy Technology, Tsinghua University, China were employed to produce the gamma irradiation. The radioactivity of the ^{60}Co source was 3.6×10^{14} Bq. The dose rate used in this study was 103 Gy/min.

2.3. Fe(II)-activated PMS for the degradation of CBZ

All the stocks were freshly prepared prior to the experiments. During all the experiments, the initial concentration of CBZ was 0.04 mM. This concentration was higher than that usually found in surface water or wastewater. High concentration was used aiming to investigate the transformation of CBZ. The degradation of CBZ by Fe (II)-activated PMS was conducted in a glass bottle with the volume of 100 mL. Quantified CBZ and Fe(II) stocks were added into the glass bottle. Reaction was initiated by adding quantified PMS solution. All the experiments were prepared in triplicate. During the experiments, the molar ratio of PMS to Fe(II) was fixed at 1:1 because the molar ratio has been reported to be the optimal ratio [20,21].Different concentration of PMS (0.4 mM, 0.8 mM and 1.2 mM) were used to investigate the effect of PMS concentration on the degradation of CBZ. The corresponding molar ratio of PMS to CBZ was 10:1, 20:1 and 30:1, respectively.

2.4. Gamma-induced activated PMS for the degradation of carbamzepine

During the radiation process, four doses adopted in this study were 100, 300, 600 and 800 Gy, respectively. The test tubes with the volume of 30 mL were filled with 20 mL above-mentioned stock solution of CBZ. Similarly, different molar ratio of PMS to CBZ (10:1, 20:1 and 30:1) was used.

To comprehensively understand the effect of PMS on the gamma-induced degradation of CBZ, the following experiments were conducted:

(1) The degradation of CBZ by single PMS; (2) the degradation of CBZ through the Fe^{2+}-activated PMS; (3) the degradation of CBZ by single gamma irradiation; (4) the degradation of CBZ by the gamma-induced activation of PMS.

All the experiments were conducted at 25 °C. During the experiments, the samples were taken periodically and immediately quenched with sodium thiosulfate. To determine which radical is responsible for the degradation of CBZ during the gamma-induced activation of PMS, the quenching experiments were conducted with ethanol and TBA as stated in the previous study [22]. The mole ratio of ethanol or TBA to PMS was 2000:1. The residual concentration of PMS was measured according to the ABTS colorimetric method reported in the previous study [23]. For the experiments to treat the real wastewater, the stock solution of carbamazepine was prepared using the real wastewater. The real wastewater was taken from the second secondary effluent of a wastewater treatment plant in Beijing.

All experiments were conducted in triplicate. The data presented in the paper were the average value with the standard derivation.

2.5. Analytical methods

A HPLC (Agilent 1200 Series, Agilent, USA) equipped with a C18 reversed-phase column (5 μm, 4.6 × 150 mm) was used to test the concentration of CBZ The diode array detector (DAD) set to 280 ± 10 nm. The column temperature was 20 °C, and the flow rate was maintained at 0.6 mL/min. The initial mobile phase consisted of 70% water (A) and 30% acetonitrile (B). The percentage of solvent B increased to 90% in 4 min and maintained for 2 min. Thereafter, it returned to initial settings within 4 min.

The HPLC equipped with a photo diode array (PDA) detector coupled to a Shimadzu 2010EV mass spectrometer with ESI ion was employed to identify the intermediate products. The ion mode is positive. The aforementioned measurement conditions were used.

A TOC analyzer (Multi N/C 2100, Jena, Germany) was used to determine the concentration of TOC.

The kinetics of the degradation of CBZ was studied using Radiation-chemical yield (G value), which is an index of the utilization efficiency of the reactive species in the degradation of target pollutant. The G value can be calculated using the following Eq. (2) (Spinks and Woods, 1990).

$$G_D = (R_D \times N_A)/[\ D \times 6.24 \times 10^{19}] \quad (1)$$

where R_D represents the concentration variation of targeted pollutant (mol/l); NA means Avogadro's constant (6.02×10^{23}/mol); D is the absorbed dose (kGy).

3. Results and discussion

3.1. Degradation of CBZ by Fe(II)-activated PMS

No significant degradation of CBZ was observed by single PMS. The removal efficiency of CBZ was less than 1% under all conditions,