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Research article

Degradation of chlorinated paraben by integrated irradiation and biological treatment process

Shizong Wang [a], Jianlong Wang [a, b, *], Yuliang Sun [a]

[a] Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China
[b] Beijing Key Laboratory of Radioactive Waste Treatment, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

Chlorinated paraben, namely, methyl 3, 5-dichloro-4-hydroxybenzoate (MDHB) is the by-product of chlorination disinfection of paraben and frequently detected in the aquatic environments, which exhibited higher persistence and toxicity than paraben itself. In this paper, the combined irradiation and biological treatment process was employed to investigate the removal of MDHB from aqueous solution. The results showed that the removal efficiency of MDHB and total organic carbon (TOC) by irradiation process increased with radiation dose no matter what the initial concentration of MDHB was. The maximum removal efficiency of MDHB was 100%, 91.1%, 93%, respectively, for the initial concentration of MDHB of 1 mg/L, 5 mg/L and 10 mg/L with the radiation dose of 800 Gy. However, the maximum removal efficiency of TOC among all the experimental groups was only 15.3% obtained with the initial concentration of 1 mg/L at dose of 800 Gy. The subsequent biological treatment enhanced the mineralization of MDHB. The suitable radiation dose for the subsequent biological treatment was determined to be 600 Gy. In this case the removal efficiency of TOC increased to about 70%. Compared to the single biological treatment, the integrated irradiation and biological treatment significantly increase the degradation and mineralization of MDHB. Moreover, the dechlorination efficiency reached 77.4% during the integrated irradiation and biological treatment process. In addition, eight intermediates were identified during the combined process and the possible degradation pathway was proposed.

1. Introduction

Parabens containing a group of alkyl esters of *p*-hydroxybenzoic acid are classified as the typical pharmaceutical and personal care products (Wang and Wang, 2016), which has been extensively used as antimicrobial agents in cosmetics, foods and pharmaceuticals (Guo and Kannan, 2013). The wide and continuous use of parabens leads to their frequent detection in aquatic environment (Jonkers et al., 2010; Renz et al., 2013). Parabens have been demonstrated to have toxic effect on the aquatic organism (Terasaki et al., 2009) and potential adverse effect on animal and human health (Tavares et al., 2009). As a result, the growing public attention has been paid to the removal of parabens.

Conventional water treatment process including chlorine oxidation can remove the parabens efficiently because the parabens can be easily transformed to chlorinated derivatives during the chlorine oxidation process (Canosa et al., 2006; Terasaki et al., 2012; Zacharias et al., 2016). However, the chlorinated by-products are difficult to be further transformed, which leads to the secondary pollution. Similar to the conventional water treatment process, wastewater treatment process has been proved to be capable of removing parabens efficiently but not the chlorinated by-products (Gonzalez-Marino et al., 2011). From the point of comprehensively environmental risk assessment of view, it is very important to know the fate of chlorinated by-products derived from the parabens.

Methyl 3,5-dichloro-4-hydroxybenzoate (MDHB) is the chlorinated by-products of the methyl paraben during the chlorine oxidation process or in the chlorinated water, which has been detected in the rivers (Terasaki et al., 2012) and swimming pools (Li et al., 2015b). Although the occurrence of MDHB has been observed in the water body, little attention has been paid to its fate in the water body due to its low concentration. However, MDHB exhibited higher toxic than methyl paraben in the water body evidenced by the hazardous concentration to the microorganisms (Li et al.,

* Corresponding author. Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China.
E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

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2015a). The hazardous concentration of methyl paraben to the microorganisms was reported as 23.8 ng/L, while 19.1 ng/L for MDHB. It is thus necessary to eliminate the potential risk caused by the MDHB in the water body. In addition, MDHB can be only partially removed during the conventional wastewater treatment process or ozone oxidation process (Li et al., 2015a), indicating that single biological treatment process or ozone cannot remove the MDHB completely. This requires improved treatment process to deal with the MDHB.

Many researches have presented the application of the combined chemical treatment and biological treatment process for the degradation of organic pollutants (Kulik et al., 2006; Oller et al., 2011). But the combined process mainly focused on the integration of ozone, Fenton and UV with the biological treatment. Few studies were concentrated on the combined gamma-irradiation and biological treatment. Gamma-irradiation as one of the advanced oxidation process has its own advantageous (Hu and Wang, 2007; Wang and Wang, 2007). For example, gamma-irradiation can simultaneously produce hydroxyl radicals, hydrated electron and hydrogen radicals (Wang and Xu, 2012). Moreover, our previous study has demonstrated that the gamma-induced irradiation can significantly improve the biodegradability of the recalcitrant compound-carbamazepine (Wang and Wang, 2016). Therefore, gamma-irradiation could be used as pre-treatment process to improve the biodegradability of MDHB.

The objective of this study was to investigate the degradation of MDHB by the combined gamma-irradiation and biological treatment, including the removal and mineralization of MDHB as well as its degradation pathway.

2. Materials and methods

2.1. Chemicals

Methyl 3,5-dichloro-4-hydrogenbenzoate (MDHB) was purchased from Aladdin Company (China). The purity is higher than 98%. All other chemicals and solvents used in this study were reagent grades.

2.2. Degradation of MDHB by gamma irradiation

The initial concentration of MDHB stock solution was prepared by adding the MDHB directly to the deionized water reaching 10 mg/L. The initial pH of MDHB stock solution was 7.03. The irradiation experiment was conducted in a 250 mL serum bottle with 200 mL MDHB solution using a $^{60}C_o$ source located in the institute of nuclear and new energy technology, Tsinghua University. Four radiation doses (100 Gy, 300 Gy, 600 Gy and 800 Gy) were used. In order to investigate the effect of initial concentration of MDHB on its mineralization by gamma-irradiation, different initial concentrations (1 mg/L, 5 mg/L and 10 mg/L) were employed. At the end of the irradiation process, 20 mL solution was taken for determining the concentrations of the MDHB, the chlorine atom and the total organic carbon (TOC).

2.3. Biodegradation of the irradiated MDHB solution

To enable the detection of the intermediates of MDHB during the biological treatment process, the irradiated solution from the MDHB initial concentration of 10 mg/L was adopted because the concentration of MDHB was the highest among the three initial concentrations at the end of the irradiation process. Biodegradation experiments were conducted with the aerobic activated sludge obtained from a wastewater treatment plant in Beijing. The mixed liquor suspended solids (MLSS) of the aerobic activated sludge were 3.73 g/L. The aerobic activated sludge was aerated for one day without adding any substrate to remove the residual compounds and then washed three times by phosphate buffer (7.0) prior to the experiment. The biodegradation experiments were carried out in a 250 ml serum bottle at 200 rpm with the room temperature (25 °C). Each bottle contained 180 mL irradiated solution. The initial MLSS was adjusted to 3 g/L. During the biodegradation process, aerobic condition was maintained by blowing air. To prevent from the photo-degradation of MDHB, the serum bottle was fully covered by the aluminum foil. Quantified samples (5 mL) were taken at regular interval time to determine the aforementioned parameters. To determine the concentration of MDHB in the activated sludge, the samples were centrifuged at 10,000 rpm for 15 min. The sludge was extracted by 5 mL of ethyl acetate, and then sonicated for 15 min (40 kHz). Thereafter, the solvent was evaporated under a gentle nitrogen stream. Finally, the extracts were resolved in 1 mL of methanol and kept at 4 °C for further analysis. In addition, a control experiment was conducted with single biological treatment process to investigate the effect of irradiation process on the removal of MDHB. All the experiments were performed in duplicate.

2.4. Analytical methods

The HPLC equipped with a C18 reversed-phase column (5 μm, 4.6 × 150 mm) and photo diode array (PDA) detector coupled to a Shimadzu 2010EV mass spectrometer with ESI ion source (LC-MS) was used to determine the concentration of MDHB and to identify its intermediates. The wavelength was set to 214 nm. The temperature of the column was kept at 35 °C, and the flow rate was constantly 1 mL/min. The initial mobile phase consisted of 80% water (A) and 20% acetonitrile (B). The level of solvent B was increased to 90% within 5 min and maintained for 2 min, and then returned to initial settings in 4 min. The retention time for carbamazepine is 4.2 min. The injected volume is 50 μL. This method achieves detection limits to 20 μg/L.

The concentration of chlorine ion was determined by an Ion Chromatography (Dionex ICS-2100) equipped with Dionex RFICTM IonPac AS 11 analytical column (4 × 250 mm). The flow rate is 4.0 ml/min, and the eluent was 20 mM KOH. The injected volume was 25 μL. The detection limit is 100 μg/L.

The pH of the initial and irradiated solution was measured by the pH meter (Thermo Scientific Orion Star A211). The total organic carbon (TOC) was measured by a TOC analyzer (Multi N/C 2100, Jena, Germany) with the detection limit 500 μg/L. The injected volume is 25 μL.

3. Results and discussion

3.1. Degradation of MDHB by irradiation process

Fig. 1 shows the removal efficiency of MDHB under different conditions. The removal efficiency of MDHB increased with the increase of radiation dose. When the initial concentration of MDHB was 1 mg/L, the removal efficiency of MDHB was 36.7%, 51%, 100% and 100%, respectively, with the radiation dose of 100 Gy, 300 Gy, 600 Gy and 800 Gy at the end of the irradiation process. When the initial concentration of MDHB was increased to 5 mg/L, the removal efficiency of MDHB was 70%, 75%, 86% and 91.1%, respectively, correspondingly, the radiation dose was 100 Gy, 300 Gy, 600 Gy and 800 Gy. When the initial concentration was 10 mg/L, at the end of the irradiation process, the removal efficiency of MDHB was 57%, 67.3%, 86.1% and 93%, respectively, for the radiation dose of 100 Gy, 300 Gy, 600 Gy and 800 Gy. When the initial concentration of MDHB was 1 mg/L, the removal efficiency was lower than that obtained with 5 mg/L and 10 mg/L of MDHB when the radiation