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Enhanced biodegradation of triclosan by means of gamma irradiation

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HIGHLIGHTS

- Triclosan was irradiated to improve its biodegradability.
- Irradiation at 1–5 kGy could enhance its mineralization and dechlorination.
- Triclosan was removed by combined irradiation and biodegradation process.
- The kinetics and pathway of triclosan degradation was proposed.
- Irradiation can be an alternative pretreatment for recalcitrant pollutants.

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ABSTRACT

Triclosan is an antimicrobial agent which has been frequently detected in the environment. In this paper, the biodegradation of triclosan after radiation-induced advanced oxidation was investigated. The results show that the removal efficiency of triclosan in the combined irradiation and biological treatment process ranged from 88% to 97%, depending on the absorbed dose, while it was only 54% in the single biological treatment process. The removal efficiency of total organic carbon (TOC) was in the range of 53.1%,–59.2% at dose of 1–5 kGy in the combined irradiation and biological treatment process. In comparison, the removal efficiency of TOC in the single biological treatment process was 24.5%, suggesting that irradiation can enhance the mineralization of triclosan. The dechlorination efficiency of triclosan ranged from 48.6% to 78.4% at dose of 1–5 kGy. The intermediates of triclosan degradation were tentatively identified by LC-MS analysis and the possible degradation pathway was proposed. Based on the above results, the combined irradiation and biological treatment process could be an alternative process for treating triclosan-containing wastewater.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is one of the most widely used antimicrobial agents, which is an emerging contaminant. Triclosan can block fatty acids synthesis by inhibiting enoyl reductase enzyme (McMurry et al., 1998). Recently, triclosan has been frequently detected in the environmental compartments with the concentration up to μg/L (Kasprzyk-Hordern et al., 2008; Sun et al., 2014), leading to the increasing concern on its effect on environment and human health.

Triclosan has a harmful effect on the aquatic organisms (Orvos et al., 2002; Gao et al., 2014). Thus, research on the degradation of triclosan is particularly important. Several chemical technologies such as chlorination (Canosa et al., 2005), photo-oxidation (Aranami and Readman, 2007), sono-chemical oxidation (Sanchez-Prado et al., 2008), electro-Fenton oxidation (Sirés et al., 2007) and ozone oxidation (Chen et al., 2012) have been studied to degrade triclosan. Among these technologies, chlorination, sono-chemical oxidation, electro-Fenton oxidation can achieve 100% removal of triclosan, and photo-oxidation can result in partial degradation of triclosan (>90%). The chemical technologies can achieve high removal efficiency of triclosan, but usually generate the toxic intermediate products (Wang and Wang, 2016). For instances, chlorinated products, such as chlorinated phenols were observed along with the degradation of triclosan (Canosa et al., 2005). These products are known to be carcinogenic. In addition, 2,8-dichlorodibenzo-p-dioxin was detected during the photolytic

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degradation of triclosan, which has been demonstrated to be more stable than triclosan in the seawater (Aranami and Readman, 2007).

In addition to chemical methods, biological treatments have attracted great attention. Up to now, several microorganisms, such as *Sphingomonas* sp. Rd1 (Hay et al., 2001), *Nitrosomonas europaea* (Roh et al., 2009), *Sphingopyxis* (Lee et al., 2012) and *Trametes versicolor* (Hundt et al., 2000) have been demonstrated to be capable of degrading triclosan. Among these strains, *Sphingopyxis* presented the best performance in the degradation of triclosan, which can achieve 100% removal of triclosan and complete dechlorination based on the stoichiometric release of chloride when the initial concentration of triclosan was 5 mg L^{-1}.

Activated sludge process is one of biological treatment processes, which has been widely used in wastewater treatment plants (WWTPs) for the removal of organic pollutants. It can eliminate organic pollutants via adsorption and biodegradation. Activated sludge process has been proved to be capable of removing triclosan, but the removal efficiency of triclosan was low, depending on the environmental conditions such as operational parameters (Yu et al., 2013; Blair et al., 2015; Roberts et al., 2016), which is consistent with its frequent detection in the effluent from WWTPs after treatment by activated sludge process (Bueno et al., 2012; Loos et al., 2013; Kosma et al., 2014). As mentioned above, chemical technologies can completely remove triclosan, but usually resulting in the high cost. Biological treatment has low operation cost, but it does not always provide satisfactory results. Chemical methods can transform the persistent pollutant to biodegradable intermediates (Sarria et al., 2003). It is thus expected that the combination of chemical and biological treatment can perform well in removing triclosan.

The combined chemical and biological treatment process has been reported to remove the recalcitrant pollutants, such as tetracycline (Gómez-Pacheco et al., 2011) and carbamazepine (Keen et al., 2012). During the combined process, chemical treatment can fully decompose the recalcitrant pollutants but with low mineralization. The subsequent biological treatment can increase the mineralization significantly. Consequently, the combined chemical and biological treatment has shown good performance in removing and mineralizing the tetracycline and carbamazepine. Gamma-ray induced irradiation is one of chemical technologies (Wang and Wang, 2007; Wang and Xu, 2012; Wang and Chu, 2016). Studies have demonstrated that gamma-induced irradiation can decompose the organic pollutants, such as chlorophenols (Hu and Wang, 2007), nitrophenol (Yu et al., 2010) and sulfamethazine (Liu and Wang, 2013). However, no study has been conducted to investigate the performance of the combined irradiation and biological treatment process in removing triclosan.

The objective of this study was to investigate the removal of triclosan by the combined irradiation and biological treatment process.

2. Material and methods

2.1. Chemicals

Triclosan (97% purity) was purchased from Aladdin Industrial Corporation (Shanghai, China). Dichloromethane (99.9% purity) was obtained from Coleman Chemicals (Villepinte, France). Acetonitrile and de-ionized water for high performance liquid chromatography-mass spectrometry (HPLC-MS) measurements were provided by Wahaha Company (Hangzhou, China). Unless otherwise specified, all other chemicals used were of reagent grade.

2.2. Irradiation

Gamma irradiation was conducted with a ^{60}Co source in the Institute of Nuclear and New Energy Technology, Tsinghua University. The radioactivity of the ^{60}Co source was 3.6×10^{14} Bq, and the dose rate was 103 Gy min^{-1}. The solubility of triclosan in water is about 10 mg L^{-1} at 20 °C according to the database published by the National Center for Biotechnology Information (https://pubchem.ncbi.nlm.nih.gov/compound/). Thus, the stock solution of triclosan was prepared by directly adding into de-ionized water to achieve the initial concentration of 10 mg L^{-1}. The initial pH of triclosan solution was 7.4. The experiments were carried out in a 250-mL glass tube with 200 mL stock solution of triclosam. In order to investigate the effect of dose on the removal of triclosan, different doses (1 kGy, 2 kGy, 3 kGy, 4 kGy and 5 kGy) were adopted. Duplicate were established for each dose. After irradiation, 1 mL of sample was injected into HPLC-MS for analyzing the concentrations of triclosan and its intermediates, and 10 mL of sample was used to determine the concentrations of TOC and chloride in the water.

2.3. Biodegradation of triclosan and its intermediates

The activated sludge taken from a wastewater treatment plant located in Beijing was used as inoculum for biodegradation. The characteristics of the activated sludge were as follows: mixed liquor suspended solids (MLSS) of 3.73 g L^{-1} and volatile suspended solids (VSS) of 2.25 g L^{-1}. The activated sludge was aerated for one day to remove the residual compounds and then washed three times by phosphate buffer (7.0) prior to the experiment.

Biodegradation experiments were conducted in 250-mL glass bottles (Reeko Company, China). Each bottle contained 160 mL of the irradiated solution of triclosan without the adjustment of pH. Quantified activated sludge was added to the bottles to set the initial concentration of MLSS to be 3 g L^{-1}. During the experiment, the bottles were put into an orbital shaker at 200 rpm and 25 °C. In addition, to avoid the photo-degradation, each bottle was completely covered by aluminium foil. Two milliliter of sample was taken at the regular interval time. Thereafter, the samples were centrifuged at 14,000 rpm for 15 min, and the supernatant was taken for analysis. The residual activated sludge from the sample was extracted by 5 mL of dichloromethane, and then sonicated for 15 min (40 kHz). 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. All the experiments were performed in duplicate. In addition, the single biological treatment (without irradiation process) was conducted as the control experiment to look into the effect of irradiation on the removal of triclosan in the biodegradation.

2.4. Analytical methods

Triclosan was determined by high performance liquid chromatography (Agilent 1200 Series, Agilent, USA) equipped with a C18 reverse phase column (5 μm, 4.6 × 150 mm). The detector is a diode array detector (DAD) set to 200 ± 10 nm. The temperature of the column was kept at 30 °C. The flow rate was maintained at 1 mL min^{-1}. The initial solvent ratio was 70% water (A) and 30% acetonitrile (B). The level of solvent B was increased to 90% within 3 min and maintained for 4 min, and then returned to initial settings in 3 min. The retention time for triclosan is 6.0 min. The injected volume was 50 μL.

The intermediates of triclosan were identified using HPLC-MS equipped with the above-mentioned column coupled to a Shimadzu 2010EV mass spectrometer with ESI ion source (LC-MS 2010, Columbia, USA), which is equipped with a photo diode array (PDA) detector, and operated in a negative mode. The aforementioned solvent conditions were used for the analysis of the intermediates. The injected volume was 30 μL.