

The effect of different factors on degradation of disinfectant triclosan in aqueous solution under electron beam irradiation

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Abstract

The effect of different factors on degradation of disinfectant triclosan (TCS) in aqueous solution under electron beam (EB) irradiation was investigated. In this study, ethanol was used to quench hydroxyl radical ($\cdot\text{OH}$) and hydrogen radical ($\cdot\text{H}$) so that hydrated electron (e_{aq}^-) could become the primary active radical. The results showed that the higher TCS degradation rate was obtained under EB irradiation, and different factors have significant effects on TCS degradation.

1. INTRODUCTION

As a common disinfectant, triclosan (TCS; 5-chloro-2-(2,4-dichlorophenoxy)-phenol) is widely used for almost 50 years since patented in 1964. Due to its excellent properties in disinfection and sterilization, it can be commonly found in personal care products such as cosmetics, soaps, toothpaste and deodorant.

TCS is often washed down the drain and thus caused its entry to the aquatic environment, leading to ecotoxicity and human exposure, studies have found that TCS exposure to humans can cause sensitization, immunologic reaction (Savage 2012), reproductive toxicity (Dann 2011) and genotoxicity (Binelli 2009), it is also regarded as an endocrine disruptor (Daughton 1999; Bergman 2012) and the offender of antibiotic drug resistance (Yazdankhah 2006). Generally, TCS is expected to reach the wastewater treatment plants (WWTPs), where it is removed efficiently by biodegradation (Onesios 2009) and advanced oxidation technologies (AOPs) (Suarez 2007), however, it is found that during the process of biodegradation, only about 50% of TCS is biodegraded and the rest remains in the dewatered sludge (Heidler 2007). Moreover, chlorinated byproducts which is toxic to aquatic organisms is also constantly found using the technology of AOPs (Chen 2012; Yang 2011; Zhou Song 2012), so other ways remain to be developed in TCS treatment technology.

The radiation technology of EB is a promising technology for the treatment of organic pollutants during the last few decades, especially for chlorinated targets. To the best of our knowledge, the removal rate and mechanism of TCS by EB irradiation was rarely reported, Kyle N. Knust et al (2010) studied the electrochemical reduction of TCS

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and raised the possibility of its dechlorination by solvated electron (e_{solv}^-), which may significantly reduce its toxicity (Xavier 1999; Slater 2002), giving us the possibility for efficient degradation of TCS using EB irradiation, especially with the existence of e_{aq}^- .

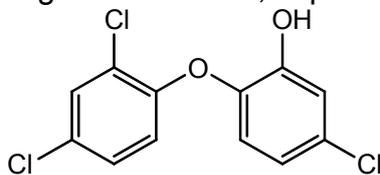


Fig. 1 Molecular structure of 5-chloro-2-(2,4-dichloro-phenoxy)- phenol

The purpose of this work is to investigate the degradation of TCS using EB radiation technology in aqueous solutions under different conditions. The effects of dissolved gas, common anions, oxidizing species were studied.

2. MATERIAL AND METHODS

2.1 Materials

Triclosan ($\geq 98\%$) was purchased from BASF (Germany) without any further purification before use. Ethanol, Na_2SO_4 , NaNO_3 , NaHCO_3 , NaCl , KCl , MgCl_2 , KI , $\text{K}_2\text{S}_2\text{O}_8$, FeCl_3 and 30% H_2O_2 were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd (China), Humic acid (HA) was purchased from Jufeng Chemical Technology Co. Ltd (Shanghai, China). Compressed nitrogen and nitrous oxide were purchased from Wugang Inc (Shanghai). The pH of the aqueous solution was adjusted with NaOH or HClO_4 . All solutions used in this study were prepared in deionized Milli-Q[®] water.

2.2 Radiolysis procedure

GJ-2-II electron accelerator (Shanghai Xianfeng electrical plant, China) was used as radiation source to provide a beam energy of 1.8 MeV and variable current (0-10 mA), the TCS samples were placed in irradiation field about 30 cm away in thin layer shape, The current of EB was changed between 0.5-2 mA to change the dose of irradiation.

TCS solutions of 100 mg L^{-1} were used as synthetic wastewater and the absorbed irradiation dose ranged from 5 to 40 kGy without adjustment of initial pH (except for the investigation of solution pH), the solutions were not aerated with any gases (except for the investigation of *dissolved gas effect*), for the effect of typical anions and oxidizing species, 50 mg L^{-1} additive were added in the TCS solutions.

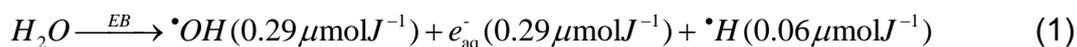
2.3 Analytical method

The TCS concentrations were detected using a high-performance liquid chromatography (HPLC) (Ultimate 3000, Dionex, USA), equipped with an XDB-C18 5 μm (4.6 mm \times 150 mm) reversed-phase column and a variable UV-Vis wavelength detector with a detection wavelength of 280 nm, The column temperature was 40 $^\circ\text{C}$; injection volume was 20 μL . The mobile phase used for HPLC analysis was a mixture of water and methanol (20/80, v/v) at a flow rate of 0.8 mL min^{-1} . Solution pH was measured using a pH meter (INESA Scientific Instrument Co. Ltd, China). The concentration of chloride ions (Cl^-) was determined by ion chromatograph (IC1010,

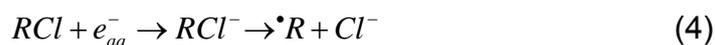
Tianmei Scientific Instrument Co. Ltd, China).

3. RESULTS AND DISCUSSION

As is known to all that when aqueous solution was irradiated with high-energy electrons, several high reactive radicals were generated (Eq. (1)) (AlSheikhly 2006):



In this study, ethanol was used as the co-solvent and the scavenger of $\cdot OH$ and $\cdot H$ (Eqs. (2) (3)), so e_{aq}^- became the main active radical. e_{aq}^- was a strong reductive radical ($E_0 = -2.9 \text{ eV}$) which could effectively react with chlorinated organic compounds and cause dechlorination (Eq. (4)).



Based on this condition, various effects were investigated in this study to make the TCS degradation pathway under EB radiation clearer.

3.1 Effect of dissolved gas

The degradation of TCS solutions with different dissolved gas using EB irradiation was investigated and the results were shown in Fig. 2.

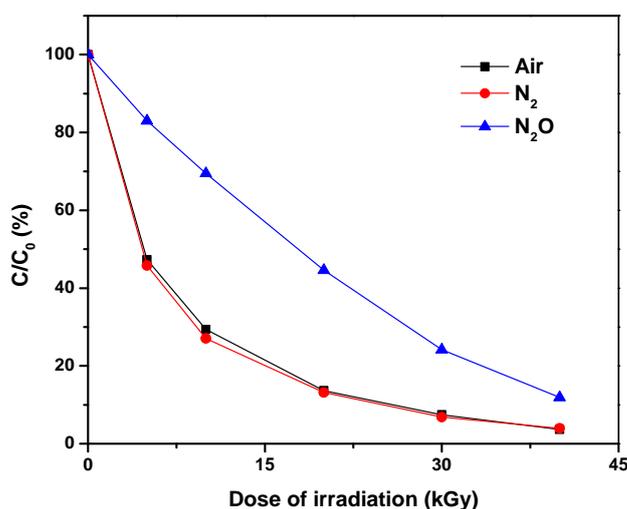
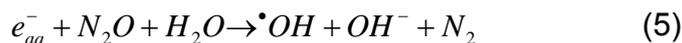


Fig. 2 Effect of dissolved gas on the degradation of TCS

As can be seen in Fig. 2, the normalized concentration of TCS dropped obviously under every condition, demonstrating that TCS could undergo efficient degradation using

g EB irradiation. For samples saturated with nitrogen and samples without any aeration, the degradation curves were almost coincided, it indicated that small amount of oxygen did not stop the abundant amount of e_{aq}^- to react with TCS. On the contrary, the existence of N_2O strongly inhibited the reaction, N_2O was used here as the scavenger of e_{aq}^- (Eq. (5)), so this result proved the great contribution of e_{aq}^- in the degradation of TCS, however, there was still apparent degradation of TCS even with saturated N_2O , it might be ascribed to topical overdose of EB irradiation which caused transient high concentration of e_{aq}^- and led to the TCS degradation.



3.2 Effect of typical anions

Anions existed everywhere in WWTPs and natural aquatic environment with considerable concentrations, so their effect on TCS degradation by EB irradiation was considered in this part.

Typical anions such as sulfate ion (SO_4^{2-}), nitrate ion (NO_3^-) and Bicarbonate ions (HCO_3^-) were studied, the obtained results were exhibited in Fig. 3.

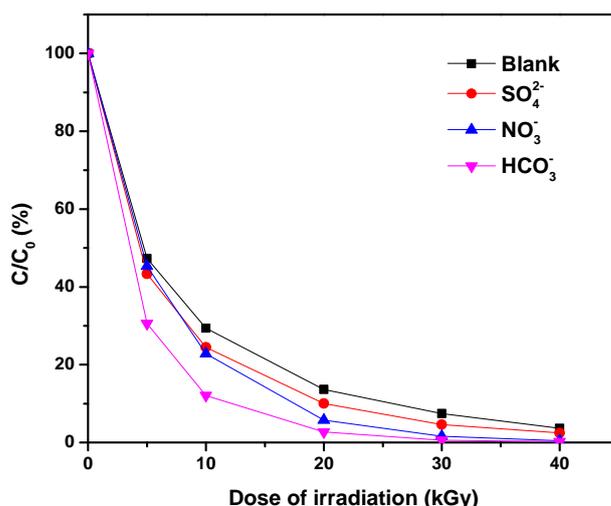


Fig. 3 Effect of dissolved gas on the degradation of TCS

It can be obviously seen in Fig. 3 that all the investigated anions accelerated the degradation of TCS, Huang et al (2007) investigated the reactivity of hydrated electron toward perfluorinated carboxylates and found that the second-order rate constant is highly dependent on the ionic strength (adding $NaClO_4$) of the medium, higher ionic strength caused better rate constant. In this study, as analyzed before, e_{aq}^- is the primary active radical, so these results correspond well with the former reports.

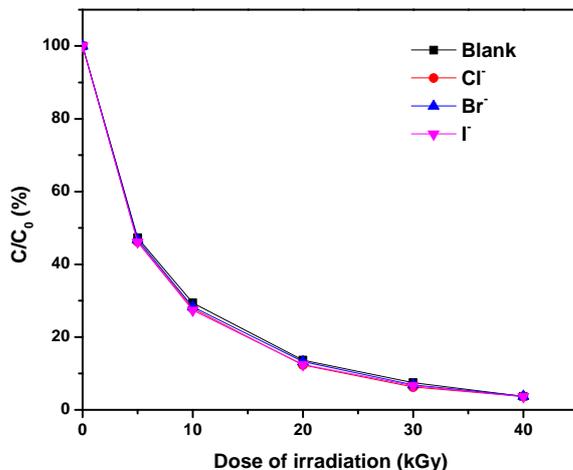


Fig. 4 Effect of halide ion on the degradation of TCS

Effect of halide ions was studied using chloridion (Cl^-), bromide ion (Br^-) and iodide ions (I^-), the results are depicted in Fig. 4, as shown in Fig. 4, all the degradation curves were almost the same as the blank control group, in which no halide ions were added, it indicates that halide ions has no effect on TCS degradation, this result is reasonable because halide ions are all electronic saturated and can not react with e_{aq}^- by any means, unfortunately, the only active radical in the solution is e_{aq}^- .

3.3 Effect of oxidizing species

During the process of e_{aq}^- reduction, the effect of oxidizing species can be of great importance, as studied in 3.1, the existence of oxygen did not make any difference on the degradation of TCS, then other oxidizing species were added and the obtained results were illustrated in Fig. 5.

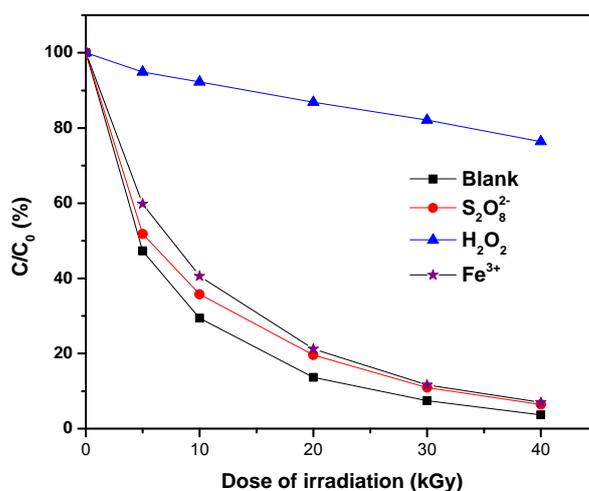


Fig. 5 Effect of oxidizing species on the degradation of TCS

As shown, all the oxidizing species inhibited the degradation procedure, especially for H_2O_2 , this result can be explained by Eq. (6), H_2O_2 could react rapidly with e_{aq}^- and form $\cdot OH$ ($k=1.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$), but $\cdot OH$ was quenched by ethanol in Eq. (2), leading to the great loss of e_{aq}^- and thus slowed down the reaction rate.



Fe (III) commonly exists in the aquatic environment, its reaction reaction equation is similar (Eq. (7)):



In this study, the solution pH was 6.4, in this condition, Fe (III) usually existed in the form of $Fe(OH)^{2+}$, $Fe(OH)_2^+$ or even precipitated (Wu 2000), so the inhibiting effect was not as strong as H_2O_2 .

In the case of $S_2O_8^{2-}$, it also react with e_{aq}^- in Eq. (8):



Alcohols that contain an α -hydrogen, such as ethanol, can react with both $SO_4^{\cdot-}$ and $\cdot OH$ (Anipsitakis 2004), so the $SO_4^{\cdot-}$ generated is supposed to be quenched by ethanol, causing the inhibition of TCS degradation rate.

4. CONCLUSIONS

The higher degradation efficiency of TCS in aqueous solution under EB irradiation was observed, the analysis of different dissolved gas proved the great contribution of e_{aq}^- in the irradiation process. The addition of different acid radical accelerated the degradation rate by increasing acid radical ion strength and then accelerating the second-order rate constant of e_{aq}^- and TCS, on the contrary, adding halide ion made no difference in the degradation process of TCS. oxidizing species could consume e_{aq}^- and thus slow down the degradation process.

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