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Degradation kinetics of 2,4-dichlorophenol by gamma ray irradiation in the presence of ozone

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Abstract Gamma ray-induced degradation of 2,4-dichlorophenol (DCP) in the presence of ozone has been investigated. The results show that ozone can remarkably increase the degradation rate of 2,4-DCP in aqueous solution. The degradation kinetics of 2,4-DCP can be described by the first-order reaction model, and the rate constant was 0.443, 0.490 and 1.247 h^{-1}, respectively, for γ-ray irradiation only, γ-ray irradiation + 13 mg/L O_3 and γ-ray irradiation + 30 mg/L O_3. High-performance liquid chromatography analysis shows that the dechlorinated products are 4-chlorophenol, 2-chlorophenol and phenol; and the oxidation products are hydroquinone, benzoquinone, maleic, fumaric, acrylic, malonic, oxalic, acetic and formic acids. The possible pathways for 2,4-DCP degradation involving all these oxidation products are tentatively proposed. Combining γ-ray irradiation with ozonation is a promising technology for removing toxic pollutants from water and wastewater.

Keywords Advanced oxidation processes · Radiolytic degradation · Chlorophenol · Decholorination · Ozonation

1 Introduction

Chlorinated phenols (CPs), which are widely used in antirust, antiseptics and herbicides [1], have also been found in disinfected water after chlorination, in flue gas of municipal waste incineration or in pulp and paper wastewater. The 2,4-dichlorophenol (2,4-DCP) is one of the most abundant CPs in aquatic environment and has caused serious ecological problems, which may cause pathological symptoms and changes to endocrine systems of human. Being among the most common organic pollutants in industrial and agricultural wastewaters, CPs have been listed as priority pollutants by the U.S. Environmental Protection Agency. Due to the toxic nature to microorganisms, the conventional wastewater treatment methods are not effective to remove them from wastewater [1–3].

Radiation technology, as a powerful advanced oxidation processes (AOPs), has received increasing attention [4–6], as a successful approach for degradation of toxic organic compounds, with high degradation rate, fast reaction rate and complete destruction of pollutants. It has been extensively investigated for degradation of toxic pollutants in aqueous solution, including chlorophenols [7–11], textile dye [12], cyclohexanebutyric acid [13], tetracyclines [14], 3-chloro-4-hydroxybenzoic acid [15], nitrophenols [16], sulfamethazine [17–19], diclofenac [20], oxytetracycline [21], cyclohexanebutyric acid [22], landfill leachate [23], and so on. On the other hand, ozone is also an effective chemical capable of removing organic pollutants from water and wastewater [24]. However, combining γ-ray

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irradiation and ozonation for degradation of toxic pollutants in aqueous solution has not received enough attention [4, 7, 10].

The objective of this study was to investigate γ-ray-induced degradation of 2,4-DCP in the presence of ozone, to examine the possibility of combining them for removal of toxic pollutants from aqueous solution.

2 Materials and methods

2.1 Chemicals

2, 4-DCP, AR grade hydrogen peroxide (H_2O_2, 30 %) and HPLC grade methanol were from Beijing Chemical Plant (China). All reagents were used without further treatment. All solutions were prepared with distilled water.

2.2 Gamma ray source

Gamma irradiations were carried out in a ^{60}Co γ-ray source of 1.33×10^{15} Bq, with a dosimetry system of the standard Fricke type, at Institute of Nuclear and New Energy Technology (INET), Tsinghua University.

2.3 Irradiation

For irradiation, 2,4-DCP solutions (100 mL) were prepared in 125-mL gas-tight Pyrex glass vials at 10, 25 and 100 mg/L of initial concentration, with the initial pH of the solution being 5.5–6.5 without adjustment. The samples were irradiated to 0.5–15 kGy. Before being analyzed, all samples were filtered through 0.45-μm syringe microfilters. All operations were performed at ambient temperature.

2.4 Analytical methods

The concentration of 2,4-DCP and its stable degradation products was analyzed using an HPLC (high-performance liquid chromatography, Agilent Technologies 1200 Series) with Eclipse XDB-C18 column (5 μm, 150 × 4.6 mm). The flow rate of the mobile phase was 1.0 mL/min and at column temperature of 25 °C. The aromatic compounds were determined by HPLC, running with mobile phase of methanol/water (v/v) at 80/20, and an UV detector was used, at the wavelength of 280 nm. The carboxylic acids were determined by the HPLC, running with mobile phase of methanol/KH_3PO_4 25/75 (v/v) at pH 2.1 adjusted with H_3PO_4, and an UV detector (210 nm) was employed. The chloride was analyzed by the DX-100 Ion Chromatograph (Dionex, USA). Total organic carbon (TOC) was measured by using Elementar High TOC analyzer (Model: Elementar Analysen-System High, Germany).

3 Results and discussion

3.1 Effect of dose

The 2,4-DCP solutions of 100 mg/L initial concentration were irradiated to different doses. Figure 1 shows the 2,4-DCP and TOC concentrations of the samples irradiated to 0–15 kGy and the release of chloride ion (Cl^-) during the radiation degradation process of 2,4-DCP. It can be seen that the radiation-induced degradation of 2,4-DCP resulted in the reduction of TOC and the release of ring-bound chlorine to the solution in the form of chloride ions. The concentration of 2,4-DCP decreased with increasing dose. At 6 kGy, the removal efficiency of 2,4-DCP was over 95.0 %. Under irradiation, the Cl^- was released, and the dechlorination efficiency increased with the dose, reaching over 70.0 % at 6 kGy. However, only 85 % Cl^- was released at 10 kGy, indicating that the intermediates of 2,4-DCP degradation included chlorine-containing organic compounds.

3.2 Effect of initial 2,4-DCP concentration

The 2,4-DCP solutions of 10, 25 and 100 mg/L in initial concentration were irradiated to different doses, and their 2,4-DCP removal efficiencies are shown in Fig. 2. At 0.5 kGy, the removal efficiencies of 2,4-DCP were 85, 62 and 28 % for initial concentrations of 10, 25 and

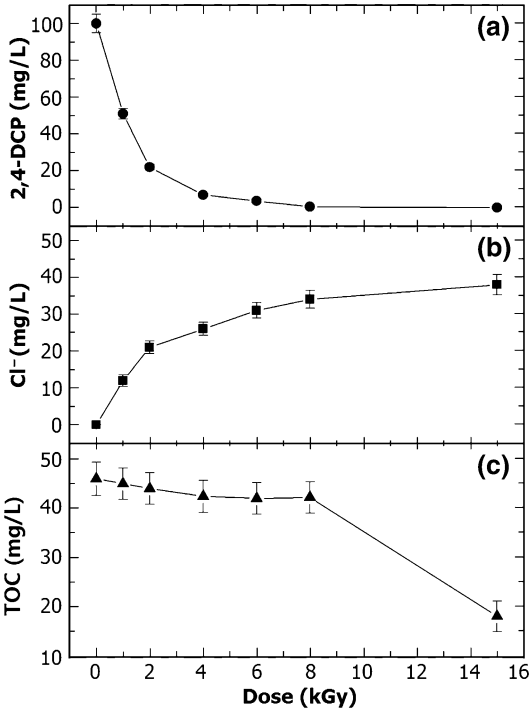

Fig. 1 Effect of absorbed dose on 2, 4-DCP degradation

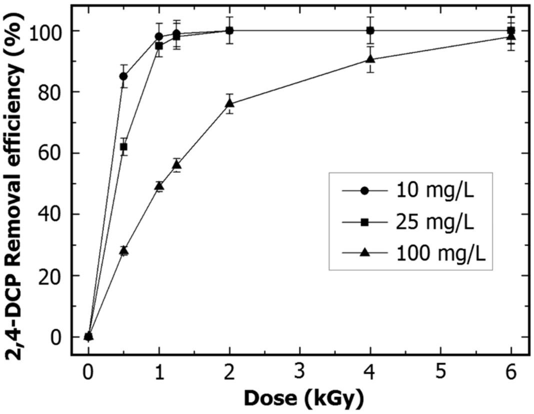

Fig. 2 Removal efficiency of 2,4-DCP at different initial concentrations as a function of absorbed dose

100 mg/L, respectively; while at 1 kGy they increased to 98, 95 and 49 %, respectively.

3.3 Effect of ozone concentration

To investigate the synergistic effect of combined γ-ray irradiation with ozonation, 2,4-DCP solutions were treated by γ-ray irradiation only or irradiation in the presence of O_3. The results are shown in Fig. 3. Obviously, the presence of ozone could enhance the 2,4-DCP degradation, in other words, the combination of radiation with ozonation led to higher 2,4-DCP degradation efficiency, which increased quickly with the O_3 concentration, being 79, 86 and 97 % at O_3 concentration of 0, 13 and 30 mg/L, respectively, at 2 kGy. When 2,4-DCP was irradiated in the presence of ozone, the O_3 could stimulate the formation of ·OH, a powerful oxidant with a reaction rate being 100–1000 times higher than that of ozone itself. As a result of the synergistic effect, a very high irradiation degradation yield was achieved and the degradation of organic pollutant was improved [7].

The ozone enhancement of radiation degradation can be explained by the following chemical reactions:

$$O_3 + \cdot H \rightarrow HO_3^{\cdot} \tag{1}$$

$$HO_3^{\cdot} \leftrightarrow O_3^{\cdot -} + H^+ \tag{2}$$

$$HO_3^{\cdot} \rightarrow O_2 + \cdot OH \tag{3}$$

$$O_3^{\cdot -} + H^+ \rightarrow O_2 + \cdot OH \tag{4}$$

$$e_{aq} + O_3 \rightarrow O_3^{\cdot -} \tag{5}$$

$$O_3 + \cdot OH \rightarrow HO_2^{\cdot} + O_2 \tag{6}$$

$$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2 \tag{7}$$

$$O_3 + HO_2^{-} \rightarrow O_2^{-\cdot} + O_2 + \cdot OH \tag{8}$$

$$\begin{aligned} &DCP + \cdot OH \rightarrow \text{intermediates, intermediates} \\ &\quad + O_2 \rightarrow IOO\cdot \rightarrow CO_2 + H_2O + Cl^- \end{aligned} \tag{9}$$

3.4 Kinetic analysis of 2,4-DCP degradation

The degradation kinetics of 2,4-DCP was analyzed under different conditions, including γ-ray irradiation only, and γ-ray irradiation in the presence of O_3 of 13 and 30 mg/L in concentration. The results of 100 mg/L initial concentration of 2,4-DCP, irradiated to 8 kGy, are shown in Fig. 4. The plots of ln C_0/C versus time are linear, which demonstrates that the degradation of 2,4-DCP followed a first-order kinetics model. The rate constants determined from the slopes, together with the linear equations, are given in Table 1. Their correlation coefficients are better than 0.99 in all cases.

The rate constants of 2,4-DCP degradation in different processes are in the following order:

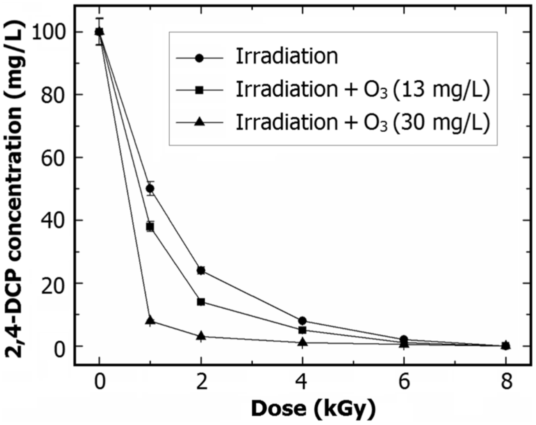

Fig. 3 Effect of ozone dosage on 2.4-DCP degradation

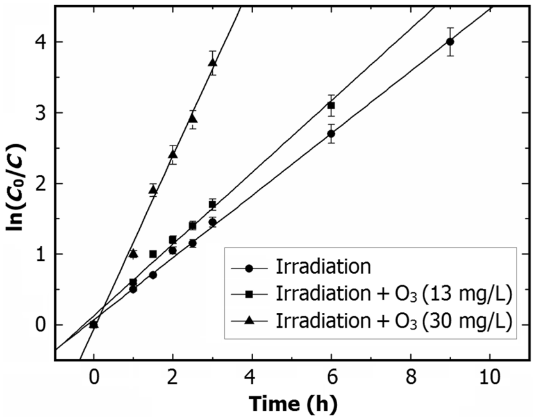

Fig. 4 Relationship of ln (C_0/C) and radiation time

Table 1 Kinetic equations and rate constants of 2,4-DCP degradation

Processes	Equations	Rate constants (h^{-1})	R^2
γ-ray irradiation	$\ln(C_0/C) = 0.443\,t + 0.056$	0.443	0.998
γ-ray irradiation +13 mg/L O_3	$\ln(C_0/C) = 0.490\,t + 0.175$	0.490	0.994
γ-ray irradiation +30 mg/L O_3	$\ln(C_0/C) = 1.247\,t + 0.013$	1.247	0.999

100 mg/L initial concentration of 2,4-DCP, irradiated to 8 kGy

$$\gamma + 30\,\mathrm{mg/L}\ O_3(1.247\,\mathrm{h}^{-1}) > \gamma + 13\,\mathrm{mg/L}\ O_3\ (0.490\,\mathrm{h}^{-1}) > \gamma\,\mathrm{radiation}\,(0.443\,\mathrm{h}^{-1}).$$

3.5 Possible pathway of 2,4-DCP degradation

The radiation-induced oxidation products were identified as 4-chlorophenol (4-CP), 2-chlorophenol (2-CP) and phenol. As the absorbed dose increased, they were further oxidized to hydroquinone and benzoquinone, and even further oxidized to form aliphatic carboxylic acids (maleic, fumaric, acrylic, malonic, oxalic, acetic and formic acids). Finally, most of the aliphatic carboxylic acids were transformed into carbon dioxide and water. These indicate that all aromatic intermediates were transformed into carboxylic acids, because they reacted rapidly with larger amount of HO· formed during irradiation. Further analyses show that the concentration of dechlorination products (4-chlorophenol and 2-chlorophenol) increased at first and then decreased until their complete removal. It was interesting to find that 2-chlorophenol concentration was higher than that of 4-chlorphenol in the irradiated solution throughout the experiment, suggesting that Cl at 4-position of 2,4-dichlorophenol was easier to be removed by γ-ray irradiation than Cl at 2-position. The reason may be due to the steric hindrance caused by the neighboring functional groups. Furthermore, reductive cleavage of C–Cl bond at 4-position of the phenyl ring proceeded faster than that at 2-position.

The possible pathways for 2,4-chlorophenol degradation by γ-ray irradiation are tentatively proposed, as shown in Fig. 5. The degradation pathways can be described briefly as follows: firstly, 2,4-dichlorophenol is dechlorinated to 4-chlorophenol and 2-chlorophenol, which are further dechlorinated to form phenol. Hydroxylation on the C(4)-position of phenol leads to hydroquinone, which is subsequently dehydrogenated to benzoquinone. Then, benzoquinone is further oxidized to form aliphatic carboxylic acids, such as maleic acid and fumaric acid, which are degraded to acrylic acid, and malonic acid. The final products are CO_2 and H_2O.

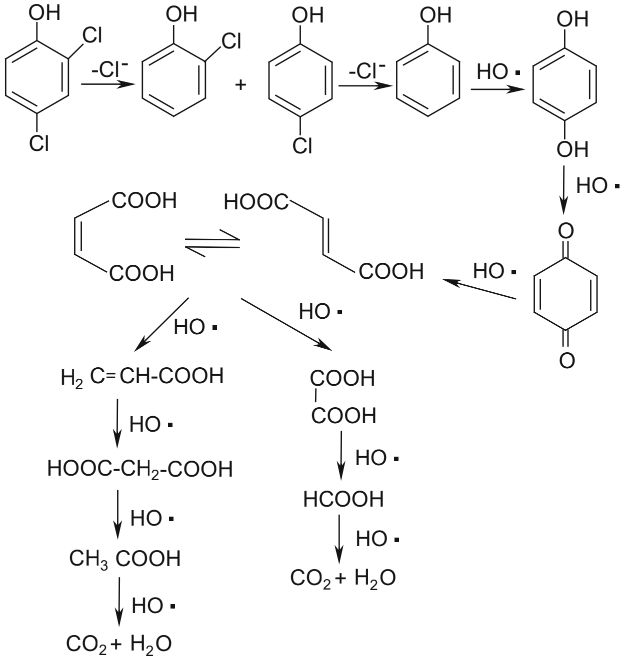

Fig. 5 Possible degradation pathways of 2,4-dichlorophenol by γ-ray irradiation

4 Conclusion

The presence of O_3 can significantly enhance the degradation rate of 2,4-DCP by γ-ray irradiation. The degradation of 2,4-DCP follows the first-order kinetics model, and the rate constant increases with ozone dosage. The main oxidized products of 2,4-dichlorophenol degradation by γ-ray irradiation have been determined, and the possible degradation pathways of 2,4-dichlorophenol is tentatively proposed. The combined process of γ-ray irradiation with ozonation is a promising technology for removal of toxic pollutants from water and wastewater.

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