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Gamma radiolytic degradation of 3,4-dichloroaniline in aqueous solution

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ABSTRACT

Degradation of aqueous 3,4-dichloroaniline (3,4-DCA) using gamma-ray irradiation was attempted in this study. The role of e^-_{aq} during the degradation process was analyzed in detail. The results demonstrated that effective degradation of aqueous 3,4-DCA using gamma-ray irradiation was realized; when the initial concentration of 3,4-DCA was 0.050 mmol L^{-1}, and the irradiation dose was 0.4 kGy, the degradation efficiency of 3,4-DCA reached 96.2%. The degradation process of 3,4-DCA could be depicted by the pseudo first order reaction kinetics. Dechlorination was observed during the degradation process, and the concentration of detected Cl^- in the treated 3,4-DCA solution increased with increasing irradiation dose. The sequence of the contribution of free radicals to the 3,4-DCA degradation was ·OH > e^-_{aq} > ·H. The quantum efficiency ratio of ·OH, e^-_{aq} and ·H for the degradation of 3,4-DCA was 1:1:4. The degradation efficiency of 3,4-DCA was accelerated by the addition of H_2O_2, and the appropriate addition amount was 0.05% (v/v). However, HCO_3^-, NO_3^- and NO_2^- (as additives) reduced the degradation efficiency of 3,4-DCA. A gas chromatograph–mass spectrometer was employed to identify the degradation intermediates, indicating that *p*-chloroaniline was the primary degradation intermediate with the addition of 2-propanol.

1. Introduction

3,4-Dichloroaniline (3,4-DCA), a type of raw material and intermediate in chemical industries, was widely used in the manufacture of dyes, pharmaceuticals and herbicides [1,2]. This compound could pollute water bodies through agricultural runoffs and wastewaters generated from manufacturing plants. 3,4-DCA was known to accumulate at a hazardous level (around 0.68 μg L^{-1} for freshwater and 0.1 μg L^{-1} for seawater) in the environment, causing a serious health risk for mammals and fish [3,4]. As the metabolite of linuron, diuron, phenylurea, acylanilide and carbamate pesticides, 3,4-DCA was also detected during the removal process of these pesticides [5–7]. Moreover, 3,4-DCA could be converted into 3,3′,4,4′-tetra-chloroazobenzene, which was a carcinogen and potential genotoxin [1]. Squamous cell carcinoma was induced in rats treated by chronic gavage with 3,3′,4,4′-tetr a-chloroazobenzene (10–100 mg/kg) [8]. Therefore, 3,4-DCA should be removed from water before entering natural aquatic systems.

There were several processes available for the removal of aqueous 3,4-DCA, and effective degradation of 3,4-DCA by using bacteria was observed in selected studies; the fastest degradation of 3,4-DCA was observed within about 0.5 d, when the batch tests (sequence batch reactor operation) were carried out with an initial 3,4-DCA concentration of 0.25 mmol L^{-1} [1,7]. The separation of 3,4-DCA from wastewater by nanofiltration was investigated [9,10]. Advanced oxidation processes (AOPs) have been tested as effective alternatives to destroy 3,4-DCA in water [4,11]. The degradation of aqueous 3,4-DCA was investigated using photocatalysis [4] and dielectric barrier-discharge plasma [11].

As one of the AOPs, gamma-ray irradiation has been used to degrade aqueous organic pollutants because of its efficient, economical and environmentally friendly characteristics [12–14]. The majority of the studies focused on comprehending the mechanisms during the gamma-ray irradiation process, the effectiveness of which was based on radical-mediated reactions. The hydrogen radical, H·, hydrated electron, e^-_{aq} and hydroxyl radical, ·OH were the primary responsible active species for contaminant degradation by gamma-ray irradiation [15–17]. Many contaminants were degraded efficiently by the gamma-ray irradiation process [18,19]. Radiation-induced decomposition of 4-chloroaniline was studied under steady-state conditions, efficient degradation of

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4-chloroaniline was observed, and the probable reaction mechanisms for the degradation of 4-chloroaniline by gamma-rays and the formation of the identified products were presented [20]. Radiolytic oxidation of aniline derivatives was carried out, the reaction rates of ·OH, $O^{\cdot-}$ and $N_3^{\cdot}$ with chloro- and hydroxy-anilines were determined [21]. The individual formation, decay kinetics and the absorption characteristics of the formed primary species by ·OH attack on aqueous aniline were determined by pulse radiolysis combined with a computer optimization procedure [22]. The reactions of e_{aq}^- with halogenated aromatic compounds (fluoro-, chloro-, bromobenzene, and 2-, 3-, 4-chloro-aniline) were studied by pulse radiolysis under steady-state conditions [23].

However, the decomposition of aqueous 3,4-DCA using gamma-ray irradiation was seldom investigated, and minimal attention was paid to the role of e_{aq}^- during gamma-ray irradiation. Therefore, the purpose of this study was to investigate the degradation potential of aqueous 3,4-DCA by gamma-ray irradiation, and the role of e_{aq}^- in the degradation process was proposed. Furthermore, the factors that might affect the degradation efficiency of 3,4-DCA, i.e., the initial concentration of 3,4-DCA, irradiation dose, the addition of H_2O_2, HCO_3^-, NO_3^-, NO_2^-, 2-propanol or *tert*-butanol, were also examined.

2. Materials and methods

2.1. Chemicals

3,4-DCA (97.4%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile (Tedia, Fairfield, OH, USA) used as the eluent in the analysis was chromatography grade. The other reagents were all of analytical grade. H_2O_2 was purchased from Nanjing Chemical Reagent (Nanjing, China) and was used as received.

2.2. Experimental methods

3,4-DCA solutions of different initial concentrations (0.050, 0.075 and 0.100 mmol L^{-1}) were prepared in distilled water. $NaNO_3$, $NaNO_2$ and $NaHCO_3$ were added to the distilled water to prepare the $NaNO_3$ solution (1 mol L^{-1}), $NaNO_2$ solution (1 mol L^{-1}) and $NaHCO_3$ solution (1 mol L^{-1}), respectively. 2-propanol (5, 10 and 20 mmol L^{-1}), *tert*-butanol (5, 10 and 20 mmol L^{-1}), H_2O_2 (0.05%, 0.1%, 0.2%, 0.4% and 0.6%), $NaNO_3$ (0.12, 0.24 and 0.48 mmol L^{-1}), $NaNO_2$ (0.12, 0.24 and 0.48 mmol L^{-1}) and $NaHCO_3$ (0.12, 0.24 and 0.48 mmol L^{-1}) were added to 3,4-DCA solutions, respectively, to examine their effects on the degradation effect of 3,4-DCA, and high purity nitrogen was bubbled into these samples for 2 min before irradiation.

^{60}Co (1.85×10^{16} Bq) was used to perform the gamma-ray irradiation experiment, which was provided by the Institute of Atomic Energy, Jiangsu Academy of Agriculture Sciences, China. In the experiment, the absorbed irradiation doses of the samples were 0.05, 0.1, 0.2, 0.3 and 0.4 kGy, respectively. The samples were irradiated at a dose rate of 1 kGy h^{-1}; therefore, the irradiation times of the samples were 0.05, 0.1, 0.2, 0.3 and 0.4 h, respectively. Each experiment was repeated for three times, the standard errors of the measurements were within 5%, and the average data were reported.

2.3. Analysis methods

A UV–vis spectrophotometer (Shimadzu, UV-2450, Kyoto, Japan) was used to record the absorbance at 230–500 nm and the values of UV_{254}. The oxidation-reduction potential (ORP) and electrical conductivity of the solution were measured immediately after gamma-ray irradiation using a microcomputer pH/mV/temp meter (Shanghai, China) and a LIDA DDS-11AW microprocessor conductivity meter (Shanghai, China), respectively.

High performance liquid chromatography (HPLC) (Agilent 1200, Santa Clara, CA, USA) was used to determine the concentrations of 3,4-DCA, *m*-chloroaniline and *p*-chloroaniline. The chromatographic column was a Hypersil ODS HPLC column (250 mm × 4.6 mm i.d., 5 μm, Agilent, Santa Clara, CA, USA). The eluent was a mixture of acetonitrile and ultrapure water (70/30, v/v) at a flow rate of 1.0 mL min^{-1}. The determination wavelength and the column temperature were set at 243 nm and 30 °C, respectively.

The degradation efficiency of 3,4-DCA was calculated by Eq. (1):

$$\eta = (C_0 - C_D)/C_0 \times 100\% \quad (1)$$

where η is the degradation efficiency of 3,4-DCA (%); C_D is the concentration of the treated 3,4-DCA solution (mmol L^{-1}); and C_0 is the initial concentration of 3,4-DCA (mmol L^{-1}).

The concentration of Cl^- was determined by ion chromatography (IC) (ICS-1000, anions column ASII-HC, 250 mm, Waltham, MA, USA). The eluent was 30 mmol L^{-1} NaOH at a flow rate of 1.0 mL min^{-1}, and the column temperature was set to 30 °C.

The analysis of the degradation intermediates of 3,4-DCA was conducted with a gas chromatography-mass spectrometry (GC–MS) system (Trace DSQ II, Thermo, Waltham, MA, USA). The treated 3,4-DCA samples (20 mL) were extracted with an equal volume of dichloromethane before analysis, and the separated organic fraction was concentrated to approximately 1 mL. In total, 1.0 μL of the treated sample was automatically injected into a GC column (DB-5 capillary column, 30 m × 0.25 mm i.d., 0.25 μm, Agilent, Santa Clara, CA, USA) using the splitless mode. Helium (⩾99.999%) was used as the carrier gas at a flow of 1.0 mL min^{-1}. The oven temperature started at 60 °C for 5 min, then increased at a rate of 4 °C min^{-1} to 160 °C, and then increased at a rate of 10 °C min^{-1} to 250 °C and was finally held for 1 min.

3. Results and discussion

3.1. Effect of the initial concentration and irradiation dose on the degradation of 3,4-DCA

The initial concentration and irradiation dose were two important parameters that influenced the degradation efficiency of 3,4-DCA. As shown in Fig. 1, when the initial concentration of 3,4-DCA was 0.050 mmol L^{-1}, the degradation efficiency of 3,4-DCA was 96.2% at the irradiation dose of 0.4 kGy. However, when the initial concentrations of 3,4-DCA were 0.075 and 0.100 mmol L^{-1}, and the identical irradiation dose was selected,

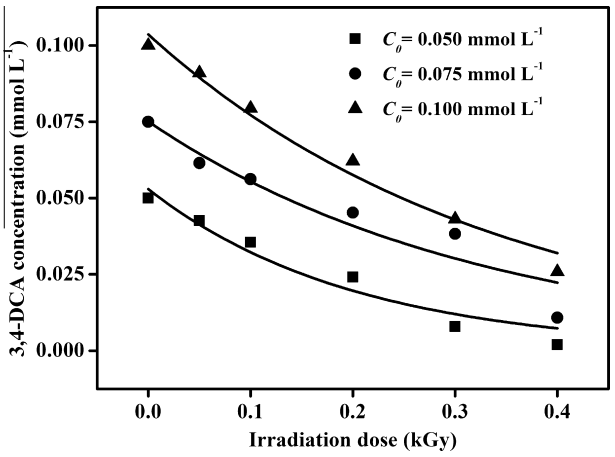

Fig. 1. Concentration changes of the 3,4-DCA by gamma-ray irradiation.