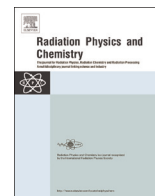




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## Radiation-induced degradation of cyclohexanebutyric acid in aqueous solutions by gamma ray irradiation

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## HIGHLIGHTS

- Gamma irradiation was efficient for removing cyclohexanebutyric acid from water.
- The degradation kinetics of cyclohexanebutyric acid followed pseudo first-order reaction.
- OH radical played a major role for oxidative degradation.
- Some possible intermediate products were identified.

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## ABSTRACT

The radiation-induced degradation of cyclohexanebutyric acid under gamma ray irradiation was investigated. Degradation experiments were performed with 100 mL sealed Pyrex glass vessels loaded with 80 mL of cyclohexanebutyric acid solutions at various initial concentrations of 10, 20, and 40 mg L<sup>-1</sup>. The absorbed doses were controlled at 0, 0.65, 1.95, 3.25, 6.5, 9.75, and 13 kGy. The results showed that gamma ray irradiation could effectively degrade cyclohexanebutyric acid in aqueous solutions. The removal rate of cyclohexanebutyric acid increased significantly with the increase of absorbed dose and the decrease of its initial concentration. At the same time, the removal of chemical oxygen demand (COD) was as effective as that of cyclohexanebutyric acid. The kinetic studies showed that the degradation of cyclohexanebutyric acid followed pseudo first-order reaction. Above all, the proposed mechanism obtained when NaNO<sub>2</sub>, NaNO<sub>3</sub> and tert-butanol were added showed that the ·OH radical played a major role in the gamma degradation process of cyclohexanebutyric acid, while ·H and e<sub>aq</sub><sup>-</sup> played a minor role in the gamma degradation process. The degradation products were identified by Fourier transform infrared spectroscopy (FTIR) and gas chromatography/mass spectrometry (GC/MS) during cyclohexanebutyric acid degradation.

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## 1. Introduction

Naphthenic acids (NAs) are carboxylic acids that include one or more saturated ring structures and are predominately monocarboxylic acids (Brient et al., 1995). Nonvolatile and chemically stable, they are natural components of crude oil at varied concentrations depending on the source of oil (Clemente and Fedorak, 2005; Headley et al., 2009). In extraction of bitumen from oil sands with caustic hot water, NAs are released to tailings ponds during oil sands extraction by hot water and eventually enter natural water systems through leaking or erosion of riverbank oil deposits

(Holowenko et al., 2002; Headley and McMartin, 2004). NAs are also found in wastewater streams from petroleum refining (Yen et al., 2004). NAs are toxic to many aquatic organisms, including microorganisms, crustaceans, and fish (McMartin et al., 2004; Frank et al., 2008). To eliminate the toxicity of NAs and prevent its damage to the ecosystem, NAs need to be removed from tailing pond and petroleum refining wastewaters.

A variety of technologies have been investigated for NAs removal, such as physical, biological and chemical methods. The biological methods must take long acclimation and retention time for microbes to decompose the NAs, and not all the microorganisms could destroy contaminants well (Herman et al., 1994; Clemente et al., 2004; Del Rio et al., 2006; Biryukova et al., 2007). The physical and chemical methods such as flocculation,

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adsorption and membrane treatment usually could not decompose the pollutants, just only transfer them from aqueous to another phase (Mohamed et al., 2008; Deriszadeh et al., 2009). Fortunately, the advanced oxidation processes (AOPs) may be applied to the treatment of cyclohexanebutyric acid. Such as, the methods were included ozone oxidation, UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process (Scott et al., 2008; Liang et al., 2011; Afzal et al., 2012).

To date only a few investigations were carried out on the degradation of cyclohexanebutyric acid by AOP. With the development of ionizing radiation technology, in particular, gamma radiation could be used as a good method to degrade organic pollutants (Wang and Wang, 2007; Xue and Wang, 2008; Homlok et al., 2011, 2012; Pálfi et al., 2011; Peng et al., 2012). As an AOP, gamma ray irradiation has been widely recommended for its effective, low-cost and environmental friendly character to remove toxic pollutants from wastewater (Getoff, 1996; Kimura et al., 2006; Zhang et al., 2008; Ito et al., 2009; Choi et al., 2010a, 2010b; Csay et al., 2012; Liu and Wang, 2013).

In the present work, cyclohexanebutyric acid was chosen as a model compound to investigate the radiolysis of NAs by gamma ray irradiation. The effects of initial cyclohexanebutyric acid concentration, absorbed doses and free radical scavenger on its degradation were investigated. In addition, the degradation kinetics was explored, and the products were identified by FTIR and GC/MS during cyclohexanebutyric acid degradation.

## 2. Materials and methods

### 2.1. Materials

Cyclohexanebutyric acid was purchased from Shanghai Chemical Co. Inc. (China). Potassium dichromate, anhydrous magnesium sulfate, silver sulfate mercury sulfate, methyl alcohol, sodium hydroxide, and sulfuric acid, all were obtained from Nanjing Chemical Reagent Co. Ltd. All chemicals were of analytical grade or the higher purity available from the supplier. Methanol, formic acid and ammonium acetate were of chromatographic purity grade. Distilled water was used in all experiments.

### 2.2. Radiolysis experiments

Cyclohexanebutyric acid solutions were irradiated in 100 ml sealed Pyrex glass vessels with an initial concentration of 10, 20 and 40 mg/L at ambient temperatures. All aqueous solutions were saturated with N<sub>2</sub> prior to gamma irradiation. Samples were drawn at predetermined time intervals. The reference samples were non-irradiated samples. Both irradiated and reference samples were analyzed. The irradiated solutions were extracted with diethyl ether. The extracts were dried with anhydrous magnesium sulfate, and then were concentrated to less than 1 mL under a reduced pressure. All irradiation experiments were performed at a gamma irradiator, located at the Center of Irradiation Research, Nanjing University of Aeronautics and Astronautics (NUAA). A <sup>60</sup>Co- $\gamma$ -source with an activity of about  $1.48 \times 10^{16}$  Bq was used for irradiation. The absorbed doses were determined by means of Silver dichromate dosimeter. All experiments were carried out at normal temperature and the initial pH was adjusted to about 6.8 with 0.1 mol L<sup>-1</sup> NaOH or H<sub>2</sub>SO<sub>4</sub> solutions.

### 2.3. Analytical instruments and methods

The measurement of Cyclohexanebutyric acid concentration was carried out using a high performance liquid chromatography-mass spectrometry (HPLC-MS, AB SCIEX 3200 QTRAP). High performance liquid chromatography (Model 1200, Agilent Co.) was

equipped with a ZORBAX Eclipse XDB-C18 analytical HPLC 5- $\mu$ m (4.6 mm  $\times$  150 mm) chromatographic column. The injection volume was 3  $\mu$ L. The mobile phases were as follows: eluant A, 10 mM ammonium acetate; eluant B, methanol (0.1% formic acid). The flow rate was 200  $\mu$ L min<sup>-1</sup>, and a gradient elution program was used: 0–5 min 60% B, ramped to 70% B by 7 min, ramped to 100% B by 25 min, and held for 5 min before returning to initial conditions and equilibrating for 10 min before injection of the next sample.

The chemical oxygen demand (COD) was chosen as the parameter by which to evaluate the process of oxidation and was measured by using a COD analyzer (5B-3C, China).

For FTIR (NEXUS 670 FT-IR, Thermo Nicolet co.) analysis, the extracts were desiccated in a vacuum drying oven to wipe off the organic extractant, then were mixed with KBr powder, and finally pressed at 40 MPa to form a disk.

The irradiated sample solutions were extracted with diethyl ether. The resulting organic phases were decanted, and were then desiccated by MgSO<sub>4</sub> for one day. Portions of 0.5  $\mu$ l concentrated extracts were subjected to GC/MS (Trace DSQ, Thermo Finnigan) determination. Chromatographic measurements were performed with a capillary column (HP-5MS, Agilent). The inlet temperature was 250 °C. The carrying gas was helium and the gas flow rate was 1 ml min<sup>-1</sup>. The oven temperature was kept at 70 °C for 3 min, then increased to 250 °C at the rate of 10 °C/min, and finally kept at 250 °C for 5 min. The mass spectra were set in scan mode from 50 to 500 *m/z*.

## 3. Results and discussion

### 3.1. Radiation degradation of cyclohexanebutyric acid

The ratio of cyclohexanebutyric acid concentration before and after irradiation as a function of absorbed dose was shown in Fig. 1. The results showed that the absorbed doses determined the degradation of cyclohexanebutyric acid during  $\gamma$ -radiation. The ratio of cyclohexanebutyric acid concentration ( $C/C_0$ ) rapidly decreased with the increase of absorbed doses. The removal rate of cyclohexanebutyric acid increased with the increase of absorbed doses and decrease of initial cyclohexanebutyric acid concentration. For a dose of 9.75 kGy, the degradation efficiencies for initial aqueous cyclohexanebutyric acid concentrations of 10, 20 and 40 mg L<sup>-1</sup> were 99%, 96% and 88%, respectively.

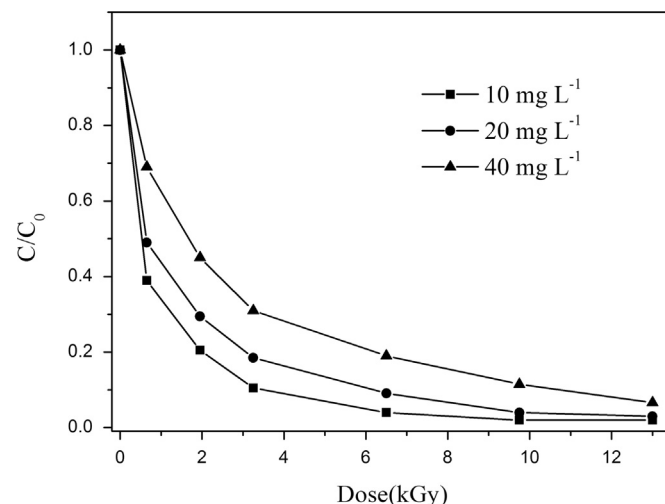


Fig. 1. Normalized cyclohexanebutyric acid concentration versus absorbed dose (initial cyclohexanebutyric acid concentration: 10, 20 and 40 mg L<sup>-1</sup>).

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