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Gamma radiolytic degradation of naphthalene in aqueous solution

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HIGHLIGHTS

- Gamma irradiation led to complete removal of naphthalene and partial mineralization.
- Degradation rate was higher at higher initial conc., lower dose rate and neutral pH.
- Addition of H₂O₂ and TiO₂ exhibited synergetic effect on naphthalene degradation.
- TiO₂ was favorable due to higher TOC removal and low cost in practical application.

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ABSTRACT

The decomposition of naphthalene in aqueous solution was studied using gamma irradiation combined with both H₂O₂ and TiO₂ nanoparticles. Gamma irradiation led to a complete degradation of naphthalene and a partial mineralization. With initial concentration of 5–32 mg/L, more than 98% of naphthalene was removed and TOC reduction reached 28–31% at an absorbed dose of 3.0 kGy. The degradation of naphthalene was faster at neutral pH and the initial degradation rate increased with increasing the initial concentration of naphthalene. Addition of H₂O₂ and TiO₂ nanoparticles all enhanced the degradation and mineralization of naphthalene. TOC removal efficiency increased from 28% (irradiation alone) to 35% with addition of H₂O₂ (40 mg/L), and to 48% with addition of TiO₂ (0.8 g/L). The degradation of naphthalene in aqueous solution by gamma irradiation was mainly through the oxidation by •OH radicals. The intermediate naphthol and carboxylic acids such as formic acid and oxalic acid were identified by LC–MS and IC.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), consisting of two or more fused benzene rings, are well-known persistent organic pollutants owing to their chemical stability and biodegradation resistance. They are produced mostly from the petroleum refining processes, coke making industry and incomplete combustion of carbonaceous materials (Butt and Qureshi, 2008). PAHs have recently attracted increasingly attention because they are suspected carcinogens and mutagens and have both acute and chronic effects on human health. Many of them have been identified as the priority persistent organic pollutants by the U.S. Environmental Protection Agency. The World Health Organization sets the maximum admissible concentration limit of 10 ng/L for the highly toxic benzo(a)pyrene and 200 ng/L for the remaining PAHs on drinking

waters (Wang and Campiglia, 2008).

Biological, physical and chemical methods have been used to removal PAHs from aqueous solution (Ania et al., 2007; Goel et al., 2003; Zheng et al., 2007). Because many of PAHs are biorecalcitrant, the biological treatment processes commonly used for water treatment are not successful in degrading PAHs (Manoli and Samara, 2008) and their removal efficiency depended markedly on seasonal variations (Tian et al., 2012). The advanced oxidation processes (AOP), involving O₃/UV, UV/H₂O₂, Fenton and Fenton-like oxidation etc., were proved to be effective to decompose PAHs (Rubio-Clemente et al., 2014). Among them, the ionizing radiation process (gamma irradiation or electron beam accelerator) has demonstrated as a promising alternative for degrading PAHs in aqueous solution and is drawing increasingly attention in many countries. The primary reactive species generated in water radiolysis mainly are hydroxyl radicals, hydrated electrons, and hydrogen atoms, which play the primary role in decomposition of the organic pollutants (Wang and Wang, 2007; Hu and Wang, 2007). Cooper et al. (2002) documented that a complete removal of naphthalene in distilled water was achieved using gamma

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irradiation with absorbed doses of 3–10 kGy, initial concentrations of 10–30 mg/L and pH 9.0. An efficient degradation of fluorene (Popov and Getoff, 2004), fluoranthene (Popov and Getoff, 2005) and benzo(a)pyrene (Butt et al., 2005) by gamma irradiation has been reported.

Ionizing radiation is often combined with other techniques to enhance the degradation efficacy and reduce the cost. It has been reported that in the presence of hydrogen peroxide, at an appropriate concentration, the removal of metronidazole (Sanchez-Polo et al., 2009), ibuprofen (Zheng et al., 2011), sulfadiazine (Guo et al., 2012), diclofenac (Homlok et al., 2011; He et al., 2014), sulfamethazine (Liu and Wang, 2013) and pharmaceutical residues chloramphenicol (Csay et al., 2012) in aqueous solution was increased by accelerating the production of hydroxyl radicals during gamma irradiation. Our previous study showed that the removal efficiency of sulfamethazine in the sewage sludge mixture increased from 65% to 76% and the inactivity of culturable bacteria increased by around 3% by addition of H₂O₂ at an absorbed dose of 1.0 kGy. Literature review has shown that the presence of Fenton or Fe²⁺ additives (Guo et al., 2012; Liu et al., 2014), oxygen or air (Chu et al., 2010; Homlok et al., 2012), and ozone (Drzewicz et al., 2004; Kubesch et al., 2005; Torun et al., 2011) could accelerate the production of oxidizing species hydroxyl radicals during gamma irradiation and promote the degradation of organic pollutants. TiO₂ is a well-known semiconductor and commonly used in the photocatalytic reaction. The nanoparticles of TiO₂ with large surface area could increase the gamma irradiation-induced degradation of EDTA (Krapfenbauer and Getoff, 1999), p-nitrophenol (Yu et al., 2010) and phenol (Chitose et al., 2003) in aqueous solution due to accumulating and concentrating pollutants on their surface.

The objectives of this study were to investigate the catalytic degradation of naphthalene in aqueous solution using gamma-ray irradiation combined with H₂O₂ and TiO₂ nanoparticles, respectively. Factors that affect naphthalene degradation, such as the initial concentrations, pH values, dose rate, etc. were explored. The mechanism of irradiation-induced degradation of naphthalene was proposed by analyzing the intermediates and carboxylic acids formed after irradiation treatment. These findings could provide useful information for understanding the mechanism of irradiation-induced degradation of PAHs and determining the favorable catalytic irradiation process.

2. Materials and methods

2.1. Reagents

The chemical reagents used in the study (naphthalene, hydrogen peroxide, hydrogen chloride and sodium hydroxide for pH adjustment) were high-purity analytical grade and purchased from Beijing Chemical Plant (China). TiO₂ nanoparticles with a mean diameter of 30 nm and a specific surface area of 50 m²/g were supplied by Degussa (Germany).

2.2. Irradiation experiments

Irradiation experiments were carried out using a ⁶⁰Co gamma irradiation facility at the Institute of Nuclear and New Energy Technology in Tsinghua University. The radioactivity is 3.6 × 10¹⁴ Bq. Irradiations were performed on 125 mL gastight Pyrex glass vials with a solution volume of 100 mL. The sample vials were placed near the central source with a dose rate of 225 Gy/min. The desired series of absorbed doses were regulated by adjusting the irradiation time. For the experiments of studying the effect of dose rate, the samples were placed at a certain distance from the source to obtain a dose rate of 7.15 Gy/min. All the

irradiation experiments were performed at least in duplicate at ambient temperature of 24–28 °C and the representative results were shown here.

The naphthalene-containing solution was prepared by dissolving solid crystal in deionized water which was then shaken to make mixing completely. pH adjustment was made by adding hydrogen chloride or sodium hydroxide before irradiation. To evaluate the enhancement of gamma irradiation-induced catalytic degradation, a certain amount of H₂O₂ and TiO₂ nanoparticles were added to the naphthalene-contaminated solution and stirred, respectively prior to irradiation. All the samples were filtered using 0.45 μm filters before analysis.

The radiation chemical yield (*G*-value) refers to the number of species formed or decomposed in solution when one Joule energy is absorbed. It is calculated by the following equation (Kongmany et al., 2014):

$$G = (C_0 - C)/D \times 1.0 \times 10^6 \quad (1)$$

where *C*₀ (mol/L) is the initial naphthalene concentration; *C* (mol/L) is the naphthalene concentration at an absorbed dose of *D* (Gy); *G*-value is expressed in μmol/J.

2.3. Analytical methods

The concentration of naphthalene before and after irradiation was analyzed using high-performance liquid chromatography (HPLC, Agilent 1200 Series, USA) with a reversed-phase column (ZORBAX Eclipse XDB-C18, 5 μm, 4.6 × 150 mm). A mixture of methanol and water at a ratio of 80:20 was used as mobile phase with a flow rate of 1.0 mL/min. Sample injections were held at 20 μL using a fixed volume injection loop. Detection was performed with a UV-vis diode array detector at the wavelength of 219 nm. The retention time of naphthalene was 4.4 min.

The intermediates formed from naphthalene degradation were identified by a LC-MS (2010EV, Shimadzu, Japan) equipped with a photo diode array (PDA) and an MS detector with an atmospheric pressure chemical ionization (APCI) source. The scanning wavelength of PDA was set at 190–800 nm, applying a bandwidth of 1.2 nm. The column was the same as that used in HPLC and high-purity nitrogen (99.999%) was used as carrier gas. The mobile phase was CH₃OH/H₂O (30/70, v/v) with a flow rate of 0.5 mL/min.

Carboxylic acids such as formic acid and oxalic acid produced from naphthalene decomposition following gamma irradiation were evaluated by an ion chromatograph (DX-100, Dionex, Germany) equipped with an analytical column (Dionex RFICTM IonPac AS14, 4 × 250 mm), a guard column (IonPac AG14, 4 × 50 mm) and a conductivity detector. The mobile phase was 3.5 mM Na₂CO₃/1.0 mM NaHCO₃ with a flow rate of 1.0 mL/min. The sample loop volume was 25 μL. The retention time of formic acid and oxalic acid was 3.5 min and 12.1 min, respectively.

TOC was determined using a TOC analyzer (Shimadzu TOC-V_{CPH}, Japan). pH was evaluated by a HI 223, HANNA pH meter (Italy). UV-vis spectrum of samples after irradiation treatment was analyzed using a Lambda 25, PerkinElmer UV-vis spectrophotometer (USA).

3. Results and discussion

3.1. Radiolytic degradation of naphthalene and kinetics

3.1.1. Effect of operational parameters

Fig. 1 shows the effect of initial concentrations, dose rate and initial pH values on naphthalene removal following gamma irradiation. The concentration of naphthalene decreased with increasing the

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