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Heterogeneous photodegradation of bisphenol A with iron oxides and oxalate in aqueous solution

F.B. Li [a,b], X.Z. Li [a,*], X.M. Li [b], T.X. Liu [b], J. Dong [b]

[a] *Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China*
[b] *Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control,*
Guangdong Institute of Eco-Environment and Soil Science, Guangzhou 510650, China

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Abstract

To understand the degradation of endocrine disrupting chemicals (EDCs) with existence of iron oxides and polycarboxylic acids in the natural environment, the photodegradation of bisphenol A (BPA) at the interface of iron oxides under UV illumination was conducted. Four iron oxides were prepared by a hydrothermal process and then sintered at different temperatures of 65, 280, 310, and 420 °C named "IO-65," "IO-280," "IO-310," and "IO-420," respectively. The prepared iron oxides were characterized by X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) methods. The XRD pattern of IO-65 showed a crystal structure of lepidocrocite (γ-FeOOH) and that of IO-420 demonstrated a crystal structure of hematite (α-Fe_2O_3), while IO-280 and IO-310 have the mixed crystal structures of maghemite (γ-Fe_2O_3) and hematite. The BET results revealed that the specific surface areas decreased with the increase of sintering temperature. The results demonstrated that the photodegradation of BPA depends strongly on the properties of iron oxides and oxalate, and pH. The properties of iron oxides influenced strongly the dependence of the BPA degradation on the oxalate concentration. The optimal initial concentrations of oxalate for BPA degradation under UV illumination were determined to be 2.0, 2.0, 2.4, and 2.0 mM for IO-65, IO-280, IO-310, and IO-420, respectively. The first-order kinetic constants k for BPA degradation under UV illumination in the presence of oxalate with the optimal initial concentration are ranked as IO-280 > IO-310 > IO-65 > IO-420. The experiments demonstrated that the optimal pH value should be in the range of 3–4. Furthermore, the dependence of BPA degradation should be also attributable to the formation of the dissolved Fe–oxalate in the solution and the adsorbed Fe–oxalate on the surface of iron oxides, and also the formation of hydrogen peroxide.

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1. Introduction

Iron oxides are a kind of natural minerals and geocatalysts, widely existing in the earth's crust and also suspending in aqueous streams, aerosol, clouds, and fogs as fine particles [1]. Major iron oxides including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [2]. The photocatalytic degradation of organic pollutants on the surface of iron oxides is very feasible and useful for removal of organic pollutants from contaminated soils and waters [3].

It is noticeable that iron oxides and polycarboxylic acids can form a photochemical system to conduct a photo-Fenton-like reaction with much higher quantum efficiency than that of the $Fe(OH)^{2+}$ photochemical process or photocatalytic reaction with iron oxides alone [4–6]. Since the polycarboxylic acids are also abundant in natural environment [7,8], this photochemical oxidation process can directly utilize natural matters such as iron oxides and polycarboxylic acids together with solar energy to decompose organic pollutants economically. It is meaningful to investigate the photochemical reaction in such an iron oxide–polycarboxylate complex system so as to better understand the natural transformation of organic pollutants. Among the fam-

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[*] Corresponding author. Fax: +852 2334 6389.
E-mail addresses: cefbli@soil.gd.cn (F.B. Li), cexzli@polyu.edu.hk (X.Z. Li).

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ily of polycarboxylic acids, oxalic acid is one of the most active members. In fact, the photochemistry of Fe(III)–oxalate complexes in natural aquatic environment, fog, precipitates, tropospheric aerosols and soil solutions have received considerable attention over the past three decades [9–13], because the iron oxide–oxalate exhibits strong ligand-to-metal charge transmitting bands in the UV and visible region. A number of investigations focused on ferrioxalate/UV and ferrioxalate/H_2O_2/UV systems for wastewater treatment [14–17]. Since they are homogeneous photochemical reactions with artificial addition of H_2O_2, these reactions do not occur in the natural environment. In fact, the photochemical reaction of iron oxide–oxalate complexes involves both mechanisms of the homogeneous reaction in aqueous solution and also the heterogeneous reaction on the surface of iron oxide [18–20], which highly relies on the characteristics of iron oxides and oxalate content.

Bisphenol A (BPA) as the raw materials of epoxy and polycarbonate resins has been extensively used in softeners, fungicides, and similar products at about 1700 tons annually all over the world [21]. BPA can be released into the natural environment as well as surface water during manufacturing, processing and application. Since it was detected in aquatic environment, air and soil from ppb to ppm levels [21], BPA as one of endocrine disrupting chemicals has been paid great attention to its removal and degradation. Even though many literatures had reported the photocatalytic degradation of BPA by using TiO_2, TiO_2-zeolite, TiO_2 pillared montmorillonite [22–24] for wastewater treatment, to the best of our knowledge, the photocatalytic degradation of BPA in an iron oxide–oxalate complex system has been only investigated up to a limited extent. This study was aimed at investigating the photocatalytic reaction of BPA with iron oxides and oxalate under UV illumination in order to determine the key factors affecting such a heterogeneous reaction.

2. Experimental

2.1. Preparation of iron oxides

Lepidocrocite (γ-FeOOH) samples were first prepared using ferrous chloride ($FeCl_2{\cdot}4H_2O$), sodium nitrite ($NaNO_2$) and hexamethylenetetramine ($(CH_2)_6N_4$) with the following procedure [25]: 20 g of $FeCl_2{\cdot}4H_2O$, 28 g of $(CH_2)_6N_4$, and 7 g of $NaNO_2$ were dissolved in 400, 80, and 80 mL of distilled water, respectively; the three solutions were well mixed to form a bluish green precipitate; the precipitate was remained in the solution and aged at 65 °C for 3 h, then centrifuged and washed three times with 95% alcohol and other three times with distilled water to remove anions and organic impurities; after dried at 65 °C for 48 h, the precipitate became dehydrated gel and was ground as γ-FeOOH; then the γ-FeOOH sample was sintered at 3 different temperatures of 280, 310, and 420 °C for 2 h, respectively. Eventually, one non-sintered iron oxide (IO-65) and three sintered iron oxides (IO-280, IO-310, and IO-420) were obtained.

2.2. Characterization of iron oxides

To determine the crystal phase composition of iron oxides samples, X-ray diffraction (XRD) measurement was carried out using a Rigaku D/MAX-IIIA diffractometer with CuK_α radiation ($\lambda = 0.15418$ nm). The accelerating voltage of 35 kV and an emission current of 30 mA were applied. The specific surface area, micropore surface area, and total pore volume were measured by the Brunauer–Emmett–Teller (BET) method [26,27], in which the N_2 adsorption at $-196\,^\circ$C was applied and a Carlo Erba Sorptometer was used.

2.3. Experimental setup and procedures

A Pyrex cylindrical photoreactor with an effective volume of 250 mL was used to conduct all photocatalytic reaction experiments, in which an 8-W UV lamp (Luzchem Research, Inc.) with the main emission at 365 nm is positioned at the center of the vessel as a UV light source. Light intensity ($I = 1.2\ \text{mW}\,\text{cm}^{-2}$) was determined using a black-ray ultraviolet meter (Model No. J221). This cylindrical photoreactor is surrounded by a circulating water jacket to control temperature at $25 \pm 2\,^\circ$C during the reaction, and is covered with aluminum foil to keep away from any indoor light irradiation. The BPA chemical was purchased from Aldrich. The reaction suspension was prepared by adding 0.25 g of iron oxide powder into 250 mL of BPA solution or a mixture solution of BPA and oxalic acid. Prior to photoreaction, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium status. During the photoreaction, the aqueous suspension was irradiated by UV light with constant aeration. During each experiment, several analytical samples were taken from the suspension at the given time intervals for analyses after centrifuged for 20 min and filtered through a 0.45 μm Millipore filter to remove the particles.

2.4. Analytical methods

The BPA concentration was determined by liquid chromatography (Finnigan LCQ DUO) with a UV detector. While a Pinnacle II C18 column (5 μm beads, 250 × 4.6 mm ID) and a mobile phase (70% HCN:30% water) at a flow rate of $0.8\ \text{mL}\,\text{min}^{-1}$ were used for BPA separation, a maximum absorption wavelength at 278 nm was used for BPA determination. The oxalic acid concentration was determined by ion chromatography (Dionex DX-120), in which an ion column (IONPAC ASII-AC) together with a guard column (AGII-HC 4 mm) was used and a mobile phase consisting of 15 mM KOH solution was operated at a flow rate of $1.5\ \text{mL}\,\text{min}^{-1}$. Total Fe concentration was analyzed by atomic absorption spectrometry and ferrous ion (Fe^{2+}) concentration was analyzed by the ferrozine method. In this study, the adsorbed $Fe^{3+/2+}$ species and Fe^{2+} species on the surface of iron oxides were extracted by using 0.1 M HCl solution under 30 min stirring prior to the above analyses. The H_2O_2 concentration in the solution was determined using a H_2O_2-photometer (Lovibond ET-8600 Germany) at LED 528 nm with a detection limit of $0.03\ \text{mg}\,\text{L}^{-1}$.

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