



The photocatalytic dehalogenation of chlorophenols and bromophenols by cobalt doped nano TiO₂



Jing Yang^{a,b}, Shihai Cui^b, Jun-qin Qiao^a, Hong-zhen Lian^{a,*}

^a State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry & Chemical Engineering and Center of Materials Analysis, Nanjing University, 22 Hankou Road, Nanjing 210093, China

^b Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biomedical Materials, College of Chemistry and Materials Science, Nanjing Normal University, 122 Ninghai Road, Nanjing 210097, China

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ABSTRACT

Cobalt doped TiO₂ nanoparticle prepared by ultrasonic-assisted hydrothermal method was used as the photocatalyst in the degradation of chlorophenols (CPs) and bromophenols (BPs). The doping content of cobalt in this catalyst was optimized as 0.5 wt%. The degradation rates of 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4,6-tribromophenol (2,4,6-TBP), 2,4-dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), 2-bromophenol (2-BP) and 4-bromophenol (4-BP) were estimated based on the quantitative determination of the degradation products. It was found that the degradation of CPs and BPs underwent dehalogenation process with pseudo-first-order kinetics. Moreover, the photodegradation kinetics was compared between CPs and BPs. The degradation rate of BPs was more quickly than CPs due to the difference in bond energy of carbon-halogen, and the degradation rates of BPs and CPs were mainly dependent on the number and the position of substituting halogen atom respectively. In addition, 2,4,6-TCP and 2,4,6-TBP can be effectively degraded by more than 95.1% and 93.5%, respectively, within 240 and 30 min. Tri-substituted phenols were firstly photodegraded to corresponding di-substituted ones, then to mono-substituted ones, and finally to phenol by TiO₂/Co nano catalyst, although there were some differences in selectivity, rate and yield in the dehalogenation pathway of 2,4,6-TCP and 2,4,6-TBP.

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1. Introduction

Chlorophenols (CPs) and bromophenols (BPs) are widely used in chemical industry and wood industry. They are often employed as chemical intermediates, wood preservatives, herbicides, insecticides and fungicides. In addition, various BPs are largely used as flame retardants in the past decades [1–4]. Due to constant use, however, they have been detected in soils, water and environmental organisms [5–7]. CPs and BPs have adverse impacts on the ecosystem for their toxic, carcinogenic and teratogenic properties. In recent years, concerns have been raised because of their persistence and bioaccumulation both in animals and in humans [8–10]. Therefore, it is important to find innovative and effective ways to minimize the harm of halophenols in environment.

Photocatalytic degradation by semiconductor nanoparticles irradiated with UV light is a useful method for the degradation

of phenolic compounds [11,12]. TiO₂ nanoparticle has been commonly exploited as a photocatalyst for its reactivity, stability, environmental friendliness and low cost [13]. However, the application of naked TiO₂ was mainly limited due to the recombination of the generated photoholes and photoelectrons. Hence, many reformative processes such as use of transition metal [14–16], non-metal [17], binary oxide [18] and dye sensitizer [19] have been adopted as means to reduce the rate of electron-hole recombination and improve the photocatalytic effect.

Several research groups have investigated the effects of metal or metal ion doping on the photocatalytic properties of TiO₂. The incorporation of metal or metal ions into the TiO₂ crystal lattice may alter the photoreactivity. Noble metals were frequently adopted as doping metals of TiO₂. Oros-Ruiz et al. [14] studied the particle size and deposition method of Au/TiO₂ on the photodegradation of 4-chlorophenol (4-CP). Rengaraj et al. [15] found that 20 mg/L 2,4,6-trichlorophenol (2,4,6-TCP) was effectively degraded in aqueous Ag-TiO₂ suspension by more than 95% within 120 min and the degradation of 2,4,6-TCP occurred via chlorine-release pathways. Transition metals and alkaline earth metals are used as dopants

* Corresponding author. Tel.: +86 25 83686075; fax: +86 25 83325180.
E-mail address: hzlian@nju.edu.cn (H.-z. Lian).

in TiO₂ because of the comparatively high effect at much less cost than noble ones. Vijayan et al. [11] found that the photocatalytic activity of TiO₂ doped with 0.5 wt% Fe exceeded that of non-doped commercial and synthesized pure TiO₂. Venkatachalam et al. [20] concluded that the photocatalytic activity in the degradation of 4-CP is higher for Mg²⁺ and Ba²⁺ doped nano TiO₂ than those for both pure nano TiO₂ and commercial TiO₂ (DegussaP-25).

Cobalt is an abundant transition metal and it could be an attractive dopant for TiO₂. Cobalt doped TiO₂ (TiO₂/Co) has shown high activity for degradation of 2-chlorophenol (2-CP) [21], 4-CP [22], Bisphenol A [22], acetaldehyde [23–25], acetonitrile [26], methyl orange [16], methylene blue [27,28], rhodamine B [29] and azo fuchsine [30]. To the best of our knowledge, few reports have been published on TiO₂/Co nanoparticles for efficient photodegradation of BPs and other CPs. The application of TiO₂/Co to photocatalytic degradation of halophenols should be a profitable attempt. It is also interesting to explore the degradation mechanism of TiO₂/Co to halophenols. Meanwhile, the wastewaters are not only polluted by only one type of phenolic compounds but also different substituted and isomers of phenols [13], so it is of important significance to investigate the difference of various halophenols during the photocatalytic degradation process.

In this present work, TiO₂/Co nanoparticles were prepared by ultrasonic-assisted hydrothermal method. Well characterized TiO₂/Co was used as catalyst for photodegradation of CPs and BPs. The degradation rates of all the halophenols were carefully estimated based on the reliable determination of the degradation products. Moreover, the dehalogenation behaviors of 2,4,6-TCP and 2,4,6-tribromophenol (2,4,6-TBP) were compared in the process of photocatalytic degradation. In addition, the doping content of cobalt in TiO₂/Co nanoparticles were optimized for degradation of 2,4,6-TCP and 2,4,6-TBP.

2. Experimental

2.1. Materials

Tetra-*n*-butyl titanate (Ti(OBu)₄) and cobalt nitrate (Co(NO₃)₂·6H₂O) of analytical grade were purchased from Shanghai Chemical Regent Company (Shanghai, China) and used as titanium and cobalt sources, respectively, for preparation of TiO₂ and TiO₂/Co photocatalysts. Acetic acid and ammonium acetate of analytical grade from Shanghai Chemical Regent Company (Shanghai, China) were used to adjust the pH of substrate solutions. 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4,6-tribromophenol (2,4,6-TBP), 2,4-dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), 2-bromophenol (2-BP), 4-bromophenol (4-BP) and phenol were obtained from Sigma–Aldrich (St. Louis, MO, USA) with analytical grade. Purified water (Wahaha Group Ltd., Hangzhou, China) was used throughout the experiment.

2.2. Preparation of photocatalyst

TiO₂ nanoparticles were prepared by minor modification of Ref. [11] in ultrasonic-assisted hydrothermal method. Briefly, 5 mL Ti(OBu)₄ was mixed with 20 mL absolute ethanol and 40 mL water with constant and vigorous stirring for 1 h, and then the mixture was sonicated for 30 min. The resulting solution was transferred into a 100 mL Teflon-sealed autoclave and heated at 373 K for 24 h. After cooled to room temperature, the mixture was transferred into an evaporating dish and dried at room temperature. Finally, the resulting powders were calcinated at 773 K for 3 h. TiO₂/Co nanoparticles were obtained by adding about 30 mg of

Co(NO₃)₂·6H₂O in the water by stirring before hydrothermal reaction.

2.3. Apparatus

The X-ray diffraction (XRD) spectra of TiO₂/Co nanoparticles were collected on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (Shimadzu, Kyoto, Japan). UV–vis diffused reflectance spectra of the powders were recorded to measure the absorbance of the catalysts under the wavelength 200–800 nm with Shimadzu UV 2401 model ultraviolet and visible spectrophotometer (Shimadzu, Kyoto, Japan) using BaSO₄ white plate as reference. Energy dispersive X-ray spectrometry (EDX) was carried out with an EX250 spectroscope (Horiba, Kyoto, Japan) attached to an S-3400N II scanning electron microscope (SEM, Hitachi, Tokyo, Japan). Transmission electron micrographs (TEM) of the catalysts were taken by a JEM-200CX (JEOL, Tokyo, Japan) microscope operating at a 200 kV accelerating voltage. The doping concentration of Co in TiO₂/Co was measured by using an Optima 5300DV inductively coupled plasma optical-emission spectrometry (ICP-OES, Perkin-Elmer, Fremont, CA, USA). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 VersaProbe system, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW (ULVAC-PHI, Kanagawa, Japan). Fourier transform infrared (FT-IR) spectra (4000–400 cm⁻¹) in KBr were recorded on a Tensor 27 spectrometer (Bruker, Saarbrücken, Germany). The pH was controlled by a Mettler Toledo SevenMulti pH meter (Mettler-Toledo, Shanghai, China). The concentrations of CPs and BPs, as well as their photocatalytic degradation products, were quantitatively analyzed by high performance liquid chromatography (HPLC) on an Agilent 1200 equipped with a vacuum degasser, a quaternary pump, an auto-sampler, a diode array detector (DAD), and an Agilent ChemStation (Agilent, Palo Alto, CA, USA).

2.4. Photocatalytic degradation of CPs and BPs

Aqueous halophenol (400 mg/L) solution was adjusted to 5.0 by acetic acid–ammonium acetate buffer solution. Photocatalytic degradation experiments were performed in a self-made reactor. The irradiation was carried out by using an 18 W low pressure mercury lamp in the center of the reactor and CP or BP solution was placed in quartz tubes 10 cm away from the lamp. The lamp emits predominantly UV radiation at a wavelength of 254 nm. The substrate solution was first stirred for 30 min to reach adsorption–desorption equilibrium, and then illuminated for a certain time according to the substance degraded. The solutions were taken away and filtered through 0.45 μm filter membrane. The concentration of CPs or BPs and their degradation products were analyzed by HPLC, in which a C-18 column (5 μm, 150 mm × 4.6 mm i.d. Welch, Shanghai, China) was employed and a mobile phase of methanol/1.0% acetic acid aqueous solution (60:40, v/v) was used at a flow rate of 1.0 mL/min. The injection volume was 10 μL and the UV detection wavelength was 280 nm. The degradation percentage through the experiment was obtained through Eq. (1):

$$\text{Degradation percentage} = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

where, C₀ is the initial concentration of CP or BP (mg/L); C is the instant concentration of CP or BP (mg/L) when the degradation was stopped.

2.5. Determination of Co content in TiO₂/Co catalyst

About 0.10 g dried TiO₂ or TiO₂/Co catalyst was digested with HCl–HNO₃–HF (2:1:5, v/v/v) mixture. The solution from the catalyst digestion was transferred into a 25 mL volumetric flask and diluted

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