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Reaction pathways of dimethyl phthalate degradation in TiO_2–UV–O_2 and TiO_2–UV–Fe(VI) systems

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Abstract

The photocatalytic degradation of dimethyl phthalate (DMP) in aqueous TiO_2 suspension under UV illumination has been investigated using oxygen (O_2) and ferrate (Fe(VI)) as electron acceptors. The experiments demonstrated that Fe(VI) was a more effective electron acceptor than O_2 for scavenging the conduction band electrons from the surface of the catalyst. Some major intermediate products from DMP degradation were identified by HPLC and GC/MS analyses. The analytical results identified dimethyl 3-hydroxyphthalate and dimethyl 2-hydroxyphthalate as the two main intermediate products from the DMP degradation in the TiO_2–UV–O_2 system, while in contrast phthalic acid was found to be the main intermediate product in the TiO_2–UV–Fe(VI) system. These findings indicate that DMP degradation in the TiO_2–UV–O_2 and TiO_2–UV–Fe(VI) systems followed different reaction pathways. An electron spin resonance analysis confirmed that hydroxyl radicals existed in the TiO_2–UV–O_2 reaction system and an unknown radical species (most likely an iron–oxo species) is suspected to exist in the TiO_2–UV–Fe(VI) reaction system. Two pathway schemes of DMP degradation in the TiO_2–UV–O_2 and TiO_2–UV–Fe(VI) reaction systems are proposed. It is believed that the radicals formed in the TiO_2–UV–O_2 reaction system preferably attack the aromatic ring of the DMP, while in contrast the radicals formed in the TiO_2–UV–Fe(VI) reaction systems attack the alkyl chain of DMP.

Keywords: Dimethyl phthalate; DMP; Electron acceptor; Ferrate; Fe(VI); Photocatalysis

1. Introduction

Phthalate esters represent a large family of chemicals which are widely used as plasticizers, primarily in the production of polyvinyl chloride resins (Bemis et al., 1978). Dimethyl phthalate (DMP) is a short-chained ester with two carboxyl groups on the aromatic ring. It is typically used in cellulose-ester-based plastics, such as cellulose acetate and butyrate (Staples et al., 1997), and it is a component of paints, adhesives, printing inks and coatings. Due to its wide applications in industry and large quantities of use, DMP has been recognized as a significant environmental contaminant and is commonly detected in natural ecosystems. Health and environmental concerns about this phthalate ester have been recognized for many years, particularly in regard to its physiological and biochemical effects on organisms (Zhao et al., 2004; Wang et al., 2004). It is known as an endocrine-disrupting chemical which may promote chromosome injuries in human leucocytes and interfere with the reproductive system and normal development of animals and humans (Jobling et al., 1995; Allsopp et al., 1997).

DMP is a relatively stable compound in the natural environment. The hydrolysis half-life is estimated to be about 20 yr (Staples et al., 1997). Studies of its biodegradation in fresh water, marine water, sediment, wastewater

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and sludge, have revealed a low degradation rate in the range of several days to a few months (Staples et al., 1997). Only a few results concerning DMP photolysis are available since phthalic acid dialkyl esters have been reported to be relatively photoresistant; for example, quantum yields of decomposition of phthalate <0.03 (Hizal et al., 1993). In view of this, it is necessary to identify a satisfactory treatment process for the effective destruction of this compound from contaminated waters and wastewaters.

In recent years, a great deal of attention has been paid to the photocatalytic degradation of alkyl phthalate esters using titanium dioxide either immobilized on films or dispersed in aqueous suspension (Taborda et al., 2001; Rahman et al., 2003). In the photocatalytic process, one strategy to enhance oxidative efficiency is to inhibit the e^-/h^+ recombination by adding other (irreversible) electron acceptors to the reaction (Malato et al., 1998; Wong and Chu, 2003). Oxygen has been widely chosen as a good electron acceptor for such a purpose, although its role is more than just electron scavenging such as partial charge transfer from the surface adsorption site to the oxygen molecule to form O_2^- (Linsebigler et al., 1995).

Ferrate (Fe(VI)) as a strong oxidizing reagent has been used to trap the electrons produced during the photocatalytic process and enhance the photocatalytic degradation of organic compounds (Sharma and Chenay, 2005; Yuan et al., 2006). Coincidentally, the chemical reduction of the ferrate in this photocatalytic process is believed to produce highly reactive Fe(V) species with a more powerful ability to oxidize less reactive substrates such as ammonia. A combination of the oxidant Fe(VI) and the photocatalyst TiO_2 therefore has potential in environmentally friendly syntheses and remediation processes (Sharma et al., 2001).

In our previous studies, it has been found that the ferrate enhanced photocatalytic degradation of alkyl phthalate ester is strongly influenced by different parameters such as, the mass ratio of ferrate to TiO_2, the pH of reaction solution and so on, but the mechanism and the reaction pathway of DMP degradation by photocatalysis alone and synergetic photocatalysis with ferrate are still not clear. Therefore, this paper presents a further investigation of DMP degradation in an attempt to gain more insight into the underlying reaction mechanisms by photocatalysis alone and synergetic photocatalysis with ferrate, respectively. This study has been particularly focused on the analysis of the intermediate products and the determination of free radicals formed during the photocatalytic reaction.

2. Methodology

2.1. Chemicals

DMP chemical was purchased from Aldrich (98.7% purity) and used as a model pollutant. Potassium ferrate (K_2FeO_4) with high purity (>90%) was synthesized in our laboratory according to an improved method (Li et al., 2005) and used as an oxidizing reagent. TiO_2 (Degussa P-25) was used as a photocatalyst in this study.

2.2. Experimental

Aqueous DMP solution with an initial concentration of 7–10 mg l^{-1} was prepared at pH 9.0, containing 1 mM sodium borate ($Na_2B_4O_7 \cdot 10H_2O$)/5 mM sodium phosphate dibasic (Na_2HPO_4). At this pH, ferrate (as deprotonated FeO_4^{2-}) is stable and its spontaneous decomposition can be ignored. In the above solution, phosphate serves as a complexing agent for Fe(III) to eliminate its interference in the ferrate analysis by spectrophotometry. The TiO_2 catalyst (40 mg l^{-1}) and ferrate were applied at different concentrations for the different experiments. All experiments were carried out in a quartz bottle and a UV lamp (Philips 8W) with its main emission at 365 nm was used as an external UVA light source. The light intensity on to the reaction solution was determined to be 0.40 mW cm^{-2} by a radiometer (Lutron UVA-365). During each experiment, a gas flow of either O_2 or N_2 was applied (bubbled) to the reaction solution continuously, to either oxygenate or de-oxygenate the solution, respectively, and which also maintained a well-mixed solution and a fully suspended TiO_2 catalyst. Samples taken at different time intervals were immediately quenched with sodium sulphite to stop any further reaction and then filtered through a Millipore (0.22 μm) membrane using a syringe prior to the analysis.

2.3. Analytical methods

DMP was analyzed by HPLC, using a high pressure pump (Spectra system HPLC P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). In the HPLC analysis, a Pinnacle II C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.) was employed with a mobile phase of acetonitrile/water (80:20, v/v) at a flow rate of 0.8 ml min^{-1}. An injection volume of 20 μl was used and the concentration of DMP was determined by the UV detector at 227 nm.

To determine the intermediate products from the DMP degradation reaction, a solid phase extraction (SPE) method was applied to concentrate the compounds from the reaction solution using a Sulpeco C18 100 mg solid phase extraction cartridge, which was primed with methanol (10 ml) first and then distilled water (15 ml) as pretreatment. A solution sample was first filtered through a Millpore filter and its pH was adjusted to 1–2 with 0.1 M hydrochloric acid. The solution sample was then passed through the pretreated Sulpeco C_{18} 100 mg solid phase extraction cartridge at a flow rate of 10 ml min^{-1} using vacuum suction. The cartridge was subsequently washed thoroughly with distilled water (10 ml), 10% methanol (10 ml) and 20% methanol (5 ml) in sequence and then dried by air blowing for 2 min. After this, the dried cartridge was