



Effects of clay minerals on diethyl phthalate degradation in Fenton reactions



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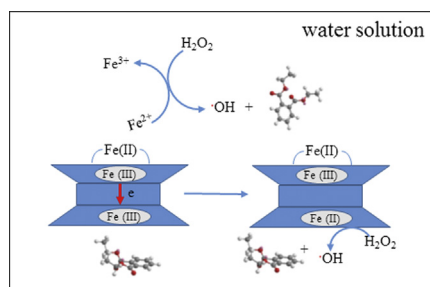
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HIGHLIGHTS

- The adsorption of DEP to clay minerals inhibited DEP degradation.
- Clay minerals with Fe content <3% quenched $\cdot\text{OH}$ radical in solution.
- Nontronite activated H_2O_2 to produce $\cdot\text{OH}$ radical and accelerate DEP degradation.
- The degradation of adsorbed DEP was increased with adsorbed concentration and Fe content in clay minerals.

GRAPHICAL ABSTRACT



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ABSTRACT

Phthalate esters are a group of plasticizers, which are commonly detected in China's soils and surface water. Fenton reactions are naturally occurring and widely applied in the degradation of contaminants. However, limited research was considered the effects of clay minerals on contaminants degradation with $\cdot\text{OH}$ oxidation. In this study, batch experiments were conducted to investigate the degradation of diethyl phthalate (DEP) in Fenton reactions in the presence of clay minerals, and the effects of clay type, Fe content in clay structure. The results showed the clay adsorption inhibited total degradation of DEP, and Fe content in clay structure played an important role in DEP degradation, including in solution and adsorbed in clay minerals. Clay minerals with less Fe content (<3%) quenched $\cdot\text{OH}$ radical, while nontronite with Fe content 19.2% improved $\cdot\text{OH}$ radical generation and accelerated DEP degradation in solution. The degradation of clay-adsorbed DEP was much slower than DEP in solution. Six main products of DEP degradation were identified, including monoethyl phthalate, phthalate acid, hydroxyl diethyl phthalate, etc. This study implied that phthalate ester's degradation would be much slower in natural water than expected in the presence of clay minerals.

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Abbreviations: Diethyl phthalate, DEP; Dimethyl phthalate, DMP; Di-*n*-butyl phthalate, DnBP; Electron paramagnetic resonance spectrometer, EPR; Gas chromatography-mass spectrometry, GC-MS; High performance liquid chromatography, HPLC; Phthalate ester, PAE.

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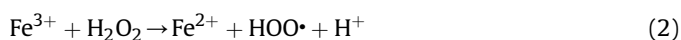
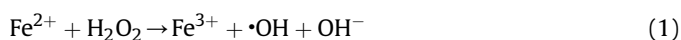
1. Introduction

Phthalate esters (PAEs) are widely used as plasticizers in plastic industry to increase plastic flexibility, transparency, durability, and longevity (Ding et al., 2008). They have been detected in surface water, sediment, agricultural soils and soils near to industrial areas (Xu et al., 2008; Chen et al., 2012). Although these compounds

could be degraded or mineralized after releasing into environments, their half-lives were varied from 1 d to several months depending on PAE structures (Ejlertsson et al., 1997; Wang et al., 1997; Amir et al., 2005).

The processes of manufacture, usage, and disposal released PAEs into the environment (Stales et al., 1997). Based on the report of the Agency for Toxic Substances and Disease Registry (ATSDR, 1995), high doses of diethyl phthalate (DEP) are added into animal feedings to promote animal weights. The PAEs pose potential risks to human health, plant growth and microorganism activities. Acute exposure to dimethyl phthalate (DMP) via inhalation would result in irritation of eyes, nose, and throat (USEPA, 2015). It has also been reported that PAEs may have xeno-estrogenic effects (Nielson and Larsen, 1996; Wolfe et al., 1980), carcinogenic and mutagenic effects (Nielson and Larsen, 1996; Huang et al., 2013; Kozumbo et al., 1982) on human. If increasing di-*n*-butyl phthalate (DnBP) concentration from 0.01 mg L⁻¹ to 1 mg L⁻¹, the ultrastructure of *Arabidopsis thaliana* in leaves could be damaged with chloroplasts disintegrating and disorganizing (Wang et al., 2005); if mixed DnBP into soil at varied concentrations from 5 to 160 mg kg⁻¹, the contents of vitamin C and capsaicin in capsicum fruit would decrease from 1.6 to 22% (Yin et al., 2003).

Fenton and Fenton-like reactions are occurring naturally in the environment. Because iron is one of the most abundant elements in the earth and the mass fraction is about 5.1%, and iron are existing in various forms in the environment (Morgan and Anders, 1980). In-situ production of hydrogen peroxide occurs naturally in water or water-soil environment, and the decomposition of hydrogen peroxide can produce •OH, which is very active and nonselective radical. The in-situ production of •OH can be performed through the presence of catalyst, ozonation, photocatalysis, electro and microbial fuel cells (Bokare and Choi, 2014; Crawford and Schneider, 2014). Fenton reactions are important in wastewater treatments, in which H₂O₂ and Fe²⁺/Fe³⁺ are added into the system (Bishop et al., 2014; Baser et al., 1990) and •OH can be generated in series of chain reactions (Equations (1) and (2) showed the two main reactions).



Because high pH would induce Fe²⁺/Fe³⁺ precipitation and then be removed from the system, the reactions were often conducted in an acidic condition (around pH 3) (Bokare and Choi, 2014; Sedlak and Andren, 1991).

Phthalate esters could be degraded in Fenton reactions (Bajt et al., 2001; Tay et al., 2011). The previous researches of Tay et al. (2011) and An et al. (2014) focused on degradation mechanisms and products of phthalate esters in reactions with •OH, which would attack aromatic ring or aliphatic chains of PAE. Photon irradiation could promote the degradations of PAEs in the Fe²⁺/Fe³⁺ and H₂O₂ system through promoting •OH production (An et al., 2014; Xu et al., 2007), and the major primary products were hydroxy, dihydroxy and carboxylic derivatives.

Clay minerals are natural components of soils and always appearing in surface waters, which play important roles in the transport of PAEs in the environment. The research of Wu et al. (2015) found that montmorillonite clay had much higher adsorption of DEP than kaolinite clay and the interlayer *d*₀₀₁ spacings of K⁺ saturated montmorillonite were important adsorption sites for DEP, while DnBP was limited to intercalate into the interlayers due to bigger stereo structure. In the study of Hofstetter et al. (2003; 2005), nitroaromatic compounds would be degraded to anilines with Fe(II) species associated with clay minerals, including

structural Fe(II) in nontronite and Fe(II) complexed by clay surface hydroxyl groups. The results of Schultz and Grundl (2000) showed that montmorillonite clay minerals could adsorb more surface bound Fe(II) and FeOH⁺ ion when increasing pH from 6.0 to 8.0, and the system of Fe(II)/montmorillonite had higher reactivity in reducing 4-Cl-Nitrobenzene than the system with only Fe²⁺ in solution.

The objective of this study was to investigate effects of clay minerals on PAE's degradation in Fenton reactions, including clay types, iron contents in clay minerals, and PAEs statuses (adsorbed to clay minerals or free in solution). We also proposed the most possible structures of products in DEP degradation in this study. The properties of DMP, DEP and DnBP can be found in Table 1. Clay minerals, including kaolinite, smectite montmorillonite with low Fe content and nontronite NAu-2, were chosen in the study (Table 2).

2. Materials and methods

2.1. Chemicals and clay mineral preparation

The chemicals used, suppliers and purities are described in the Supplementary Material (Text S1).

In order to examine the degradation of adsorbed PAEs to clay minerals, K⁺ saturated clay instead of pristine clay was selected in this study. In previous studies of Wu et al. (2015) and Rana et al. (2009), less hydration of K⁺ caused interlayers of K-montmorillonite more hydrophobic area than those of Na⁺ and Ca²⁺ saturated montmorillonite clays, so much more adsorption of DEP to K-montmorillonite was observed than that to Na- or Ca-montmorillonite. The clay minerals were pretreated to obtain K⁺ saturated particles with 0.5–2.0 μm diameters, following the method of Rana et al. (2009). Detail steps of clay preparation could also be found in the Supplementary Material (Text S2).

2.2. Fenton reactions

The Fenton reactions were conducted in 50 mL brown glass bottles with continue stirring in dark at 22 °C. Nitrogen purging was applied at least 30 min before and during reactions to make an oxygen-free condition. At the time of 0, 0.5, 1.0, 1.5, 2.0, or 3.0 min, 0.5 mL solution was withdrawn and added into a 2 mL HPLC vial, in which 0.5 mL methanol was pre-added to quench reactions, and the quenched solution was stored at 4 °C till analysis. Duplicated reactions were conducted at each condition. The control experiments without H₂O₂ addition were also carried out in parallel. Based on the preliminary experiments (see the Supplementary Material Figs. S1 and S2), the optimum reaction condition was at the initial concentrations [Fe²⁺]₀ 300 μM, [H₂O₂]₀ 2.2 mM and [DEP]₀ 100 μM at pH 3.0. For comparison, the degradations of DMP and DnBP were also conducted in the same optimum condition.

2.3. Fenton reactions in presence of clay minerals

In order to investigate effects of clay minerals on PAEs degradation, a certain amount of pretreated K⁺ saturated clay mineral was added into PAE solution (the initial concentration of DEP/DMP was 100, 450, or 900 μM) at the ratio of 1:150 (clay: solution) in a 20 mL centrifugation tube. Phosphate buffer (37.1 mM) was used to control solution pH. The preliminary experiments showed phosphate buffer had no significantly influence on DEP degradation from 8.8 mM to 78.8 mM. The suspensions were kept shaking at 22 °C for 5 days in an oscillation incubator to arrive adsorption equilibrium (Wu et al., 2015). Four parallel adsorption tubes were setup at the same condition. After adsorption equilibrium, two tubes were centrifuged at 4000g for 15 min, and 14 mL

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