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New insights into the role of zero-valent iron surface oxidation layers in persulfate oxidation of dibutyl phthalate solutions

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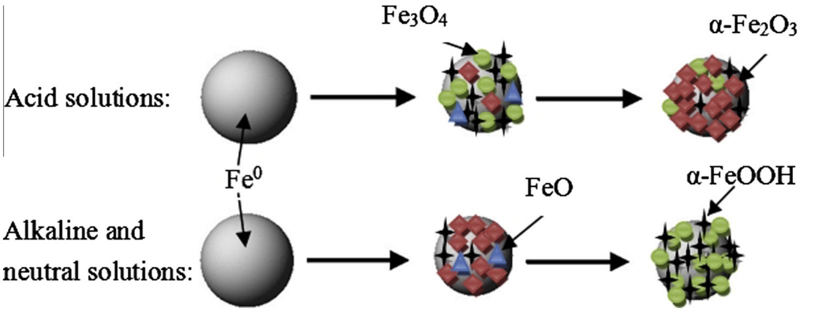
HIGHLIGHTS

- The DBP degradation at different initial pH ranked as 3 > 5 > 7 > 9 > 11.
- The iron oxide was mostly composed of α-Fe_2O_3 in acidic solution.
- The oxidation layers consisted of Fe_3O_4, α-FeOOH in alkaline and neutral solutions.
- The iron oxides exhibited an inhibitory effect on DBP degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Batch tests were conducted to investigate the effect of initial pH on the degradation of dibutyl phthalate (DBP), the formation and evolution of iron corrosion products, and the role of iron oxides on the further degradation of DBP in zero-valent iron (ZVI)–persulfate system. The study indicated that the half-lives for the oxidation of DBP by persulfate activated with ZVI were 30–176 min at pH 3.0–11.0. The constituents and the morphology of the iron corrosion coating along different initial pH and over reaction time were investigated with Raman spectroscopy, X-ray photoelectron spectroscopy and Scanning electron microscopy. The results illustrated that magnetite (Fe_3O_4), wustite (FeO), hematite (α-Fe_2O_3) and goethite (α-FeOOH) were identified as the corrosion products. In alkaline and neutral solutions, the inner layer of iron oxides was mainly composed of α-Fe_2O_3 with some α-FeOOH while the outer layer mostly consisted of Fe_3O_4 and α-FeOOH. Oppositely, the iron oxides formation in acidic solution mainly consisted of Fe_3O_4, α-FeOOH and a small amount of α-Fe_2O_3 and FeO in the inner layer, the outer layer was mostly composed of α-Fe_2O_3 and some α-FeOOH. These iron corrosion coatings exhibited an inhibitory effect on the degradation of DBP, which may be due to that the iron oxides hindered the electron transfer from ZVI core to the solid–liquid interface.

1. Introduction

Phthalic acid esters (PAEs) have received increasing attention in recent years due to their widely use as plasticizers and additives in cosmetics production. As a consequence, these toxic and recalcitrant

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compounds are ubiquitous in environments, causing a lot of harm to aquatic organisms and human health through food chain transmission and bioamplification [1,2]. Dibutyl phthalate (DBP) is one of the most widely used PAEs and it is suspected to be estrogenic disrupting compounds (EDCs) and may have reproductive development toxicity [3], mutagens and carcinogens [4]. DBP tends to be rather stable, the hydrolysis, photolysis and volatilization of DBP occur very slowly in the natural environment [5,6]. Therefore, both United States Environmental Protection Agency and China National Environmental Monitoring Center have classified DBP as a priority pollutant.

The Fenton-like reaction which is based on the activation of persulfate ion ($S_2O_8^{2-}$) to generate sulfate radicals ($SO_4^{-\cdot}$) has exhibited a great potential in destroying many refractory contaminants. Sulfate radicals can be generated from the activation of persulfate by UV, heat, microwave and transition metal ions [7,8]. However, the ZVI activation is a cost-effective, efficient and friendly technology compared with the other activation methods, and it has attracted much attention in the persulfate oxidation of contaminants processes [9–11,44]. ZVI activation not only serves as a slow-releasing source of dissolved Fe^{2+}, but also provides another way that does not involve aqueous Fe^{2+} to produce sulfate radicals. Oh et al. [11,12] hypothesized that the mechanism may be heterogeneous activation of persulfate, involving direct electron transfer from ZVI or surface-bound Fe^{2+} (Eqs. (1) and (2)).

$$Fe^0 + 2S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} + 2SO_4^{-\cdot} \quad (1)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\cdot} + SO_4^{2-} \quad (2)$$

$k = 2.0 \times 10^1\ M^{-1}\ s^{-1}$, 22 °C

Moreover, Bremner et al. [13] proposed faster recycling of ferric iron on the ZVI surface through the electron transferring to Fe^{3+}, which can keep suitable Fe^{2+} concentration in solution (Eq. (3)).

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (3)$$

Kusic et al. [14] reported that at the determined optimal condition, the $Fe^0/S_2O_8^{2-}$ process yielded 53.36% mineralization, whereas only 34.89% mineralization was achieved by the $Fe^{2+}/S_2O_8^{2-}$ process.

While a various contaminants could be removed effectively by activation of persulfate with ZVI under certain conditions (e.g., the acidic condition), the resulting iron corrosion product(s) (e.g., iron oxides, oxide hydroxides) may significantly affect reaction under environmental conditions [15,16]. Liang and Lai [17] demonstrated that acicular aggregate and coarse aggregate were observed with SEM images in the absence and presence of TCE, respectively, and the XRD spectrum revealed the formation of magnetite over the surface of ZVI after contact with persulfate. However, it has been found that the ZVI reactivity differs in part depending on the resulting iron oxides. Oxides such as magnetite or green rusts may promote the reactivity of ZVI, while others such as maghemite may demote the reactivity of ZVI [18–20]. According to the Stumm's research [21], the formation of inner-sphere complexation of Fe^{2+} to metal oxides can create a strong reductant at pH $\geqslant 7.0$. Hydrolysis of Fe^{2+} to $FeOH^+$ can also increase reducing power. Therefore, the formation of iron products would affect the performance of persulfate on generating sulfate radicals during the persulfate oxidation. Unfortunately, the information about the effect of iron corrosion layers of ZVI on the ZVI reactivity and contaminants degradation in ZVI–persulfate system is limited. Studies are still needed to elucidate the formation, structure, and function of iron oxides coatings on ZVI surface in the ZVI–persulfate processes.

In the context of the recent progresses, it would be interested to know (1) the effect of initial pH on the formation of iron corrosion products; (2) the relationship between the corrosion products and contaminants degradation; (3) the impact of ZVI surface oxidation layers on the reactivity of ZVI activation of persulfate.

The objective of the present study focused on ZVI corrosion products and their transformations with changing environments, the reactivity of ZVI in the presence of various iron corrosion coatings, and the unique role involved in aqueous Fe^{2+}. Specifically, we focused on the formation and transformations of iron corrosion products, and their impact on the reactivity of degradation of DBP in ZVI–persulfate systems.

2. Materials and methods

2.1. Materials

Unless otherwise indicated, all chemicals used in this study were reagent grade. Ultrapure water was produced by a Millipore milli-Qsystem. The ZVI (purity >99%) was obtained from Aladdin chemistry Co., Ltd (Shanghai, China). The iron particles were approximately 0.15 μm in diameter, with a smooth surface and a Brunauer–Emmett–Teller (BET) surface area of 0.389 m^2/g. DBP ($C_{16}H_{22}O_4$, MW = 278), with high quality (purity >99.5% (GC)) was purchased from Aladdin chemistry Co., Ltd (Shanghai, China) and used without any further purification. All other chemicals used were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China).

2.2. Experimental procedure

Batch experiments were conducted in 250 mL serum bottles capped with rubber stoppers using a total volume of 100 mL under a rotary shaker (ZHWY-20102C, Shanghai, China) at 180 rpm and 25 ± 0.2 °C. The vessel was wrapped with the tinfoil in order to avoid any photochemical effects. Stock solution of DBP was prepared at an initial approximate concentration of 5 mg/L (0.018 mM) and a fixed persulfate/DBP molar ratio of 10/1 was employed in all tests. In order to ensure complete dissolution of DBP, the suspension of DBP was mixed for over 24 h in the dark at 20 °C in a constant temperature chamber. The initial pH values of all solutions were adjusted with 1 M sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). All reactions were initiated by adding an amount of persulfate stock solution and 0.03 g ZVI. All samples were withdrawn in the predetermined time intervals by ethanol (1.0 mL of ethanol for each 1.0 mL sample), a well-known quenching agent for sulfate radicals [22], and the residual ZVI was separated by centrifugation for 5 min at 10,000 rpm in 2 mL polypropylene microcentrifuge tubes, then the supernatant was filtered through a 0.45-μm membrane filter and analyzed for DBP, $Na_2S_2O_8$, dissolved Fe^{2+} and total dissolved iron.

After different time from 15 min to 120 min, the precipitated iron oxide and non-dissolved ZVI were filtrated by 0.45-μm membrane filter, and then rinsed with N_2-sparged ultrapure water and ethanol for several times and dried at 35 °C inside a vacuum drying oven. This low temperature was chosen to avoid the changing of the ZVI surface oxidation layers during drying. The ZVI surface composition was studied by Scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The ultrapure water was deoxygenated by purging with N_2 gas for 30 min before use. All reagents were prepared using deoxygenated ultrapure water.

2.3. Analytical methods

2.3.1. HPLC analysis

DBP was analyzed using a high performance liquid chromatography (HPLC) (Agilent 1100, USA) equipped with a variable