



# Degradation of di (2-ethylhexyl) phthalate in sediment by a surfactant-enhanced Fenton-like process

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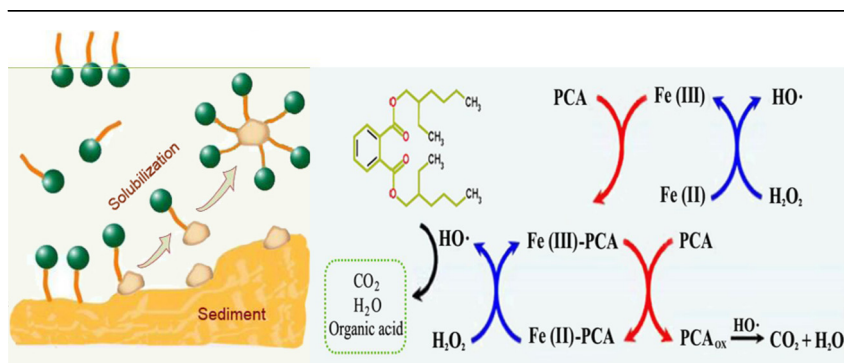
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## HIGHLIGHTS

- A surfactant-enhanced Fenton-like process was used to degrade DEHP in sediment.
- The order for desorption of DEHP was found as Tween 80 > Triton X-100 > Brij 35.
- The addition of PCA can significantly enhance DEHP removal from 48.9% to 92.5%.
- Most of the added Tween 80 and a portion of OM were co-oxidized together with DEHP.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This is the premier study reporting the remediation of di (2-ethylhexyl) phthalate (DEHP) contaminated sediment by a surfactant-enhanced Fenton-like system. Three widely used non-ionic surfactants were tested, and the order for desorption and solubilization of DEHP was determined as Tween 80 > Triton X-100 > Brij 35. The degradation of DEHP was studied at a near natural pH of 6.0 by two Fenton treatments: (i)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  and (ii)  $\text{Fe}^{3+}/\text{PCA}/\text{H}_2\text{O}_2$ . Results show that the addition of PCA can significantly enhance DEHP removal from 48.9% to 92.5%. This is consistent with observation that PCA maintained at a relative high level of iron ions, which can catalyze  $\text{H}_2\text{O}_2$  to generate the reactive hydroxyl radicals ( $\cdot\text{OH}$ ). Most of the added Tween 80 and a portion of OM were co-oxidized together with DEHP due to the non-selective nature of  $\cdot\text{OH}$ , which led to an increase in DOC content and decreases in sediment pH and total N content. The results provide an efficient and eco-friendly technique for the remediation of DEHP contaminated sediment, and also give insight to its environmental implications.

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## 1. Introduction

Phthalate acid esters (PAEs) have been widely used as polymer

additives in many industries, such as plastics, cellulose production, styrene and rubber (Bauer and Herrmann, 1997). However, PAEs can slowly migrate from the products into the hydrosphere, atmosphere and biosphere due to the fact that they are not chemically bound to the polymeric matrices (Vitali et al., 1997). Since PAEs have been found to bio-accumulate in fats and shown to be

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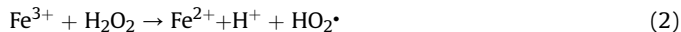
estrogenic and carcinogenic (Boonnorat et al., 2014; Cheng et al., 2016a; Xiaoyan et al., 2015), the potential risk to animals and human's health caused by these compounds has received significant attention all over the world (Wei et al., 2016).

Di (2-ethylhexyl) phthalate (DEHP) is the most highly produced PAEs and is also included in the list of priority pollutants by the U.S. Environmental Protection Agency (EPA) (Gao et al., 2016). Sediments are both sources and sinks for the distribution and bio-accumulation of PAEs in water, thus the PAEs in sediments can be present in rather high concentrations (Gao et al., 2017). For example, data acquired from 29 sites of Wuhan section of the Yangtze River shows that the maximum DEHP concentration in the sediment reaches  $323.5 \mu\text{g g}^{-1}$  (Wang et al., 2008). DEHP is hardly biodegradable, in aquatic ecosystems, the half-life of DEHP under aerobic conditions was about 390 days in acidic conditions and in neutral medium it could take more than 4 years (Liu et al., 2014; Qi et al., 2014). Therefore, it is important to develop effective methods for the decomposition of DEHP in sediments.

Chemical oxidation by Fenton reaction is a viable method for the remediation of organic compounds contaminated soils and sediments (Cheng et al., 2016b). Fenton reaction is mainly based on the generation of highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ) through Eqs (1) and (2) (Hoigné and Bader, 1983; Zepp et al., 1992). However, ferric ions are quickly accumulated during the conventional Fenton reactions, because the reaction rate of Eq (2) is much slower than that of Eq (1). As a consequence, acidic conditions ( $\text{pH} \leq 3.0$ ) are required to prevent  $\text{Fe}^{3+}$  from precipitating as iron hydroxides.



$$K_1 = 70 \text{ M}^{-1} \text{ s}^{-1}$$



$$K_2 = 0.001\text{--}0.1 \text{ M}^{-1} \text{ s}^{-1}$$

To overcome this limitation, organic ligands, such as polycarboxylates and carboxylic acid, are used to complex iron and maintain it in solution (Cheng et al., 2017b). Among them, Ethylenediaminetetraacetic acid (EDTA) has been the most widely used chelating agent for Fenton ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  or  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) systems (Liu et al., 2017; Wang et al., 2017; Zhou et al., 2008). EDTA is able to prevent iron precipitation for more efficient Fenton oxidation of organic pollutants even at neutral pH. However, the wide application of EDTA may cause some adverse environmental consequences because of its poor biodegradability and strong heavy metal chelating ability (Evangelou et al., 2007). On the other hand, Qin et al. (2015) demonstrated the use of a new and strong chelating agent protocatechuic acid (PCA) in the homogeneous Fenton process. They found that the performance of alachlor oxidation can be dramatically enhanced by PCA, and this system could also work well at near natural pH. More importantly, the added PCA could be effectively decomposed in this Fenton system, suggesting the environmental benignity of  $\text{Fe}^{3+}/\text{PCA}/\text{H}_2\text{O}_2$  Fenton-like system. However, they have concentrated solely on this technology employed in treating water pollution, and to date, the evaluation of  $\text{Fe}^{3+}/\text{PCA}/\text{H}_2\text{O}_2$  Fenton-like system for sediments or soils remediation has not been reported.

Owing to its highly hydrophobic and low solubility, DEHP tends to be absorbed on the organic fraction of sediments (Cheng et al., 2017c; Zhao et al., 2016). This is another challenge for the mineralization of DEHP in the sediments with Fenton process, because the generated  $\cdot\text{OH}$  is only effective in the aqueous phase (Sedlak

and Andren, 1994). In practical applications, surfactants were often used as solubilizing agents to desorb the hydrophobic contaminants from sediments, which facilitates the following oxidation (Edwards et al., 1991; Zhang and Somasundaran, 2006). And according the published articles, nonionic surfactants are more desirable than cationic and anionic surfactants for soil remediation, since cationic surfactants would be easily sorbed onto soil particles, while anionic surfactants can be precipitated with the cations in soil (Cheng et al., 2017a; Luo et al., 2010; Qin et al., 2007).

According to the literature, researchers have mainly focused on the bioremediation of DEHP contaminated sediment (Chang et al., 2005; Otton et al., 2008; Yuan et al., 2010). To date, no study on the surfactant-aided Fenton oxidation of DEHP in the sediment has been reported. The purpose of this study is to develop a highly efficient Fenton oxidation system for the treatment of DEHP contaminated sediments. Three nonionic surfactants Triton X-100, Tween 80, Brij 35, were examined for the desorption of DEHP from sediments. We investigated the effects of PCA on the DEHP oxidation performance of surfactant/ $\text{Fe}^{3+}/\text{PCA}/\text{H}_2\text{O}_2$  Fenton-like system. The impacts of Fenton oxidation on the sediment were also studied.

## 2. Experimental section

### 2.1. Chemicals

Di (2-ethylhexyl) phthalate (DEHP), protocatechuic acid (PCA),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30% w/w in water), the utilized nonionic surfactants, hydroxylamine hydrochloride, sodium acetate (NaAc), isopropyl alc-OH, 1,10-phenanthroline,  $\text{H}_2\text{SO}_4$  and NaOH were all of analytical grade and purchased from Sino-pharm Chemical Reagent Co., Ltd. China. Stock solutions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  with concentrations of 2 mmol/L were prepared by dissolving  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in Milli-Q water.

### 2.2. Preparation of contaminated sediment

The sediment was collected (0–20 cm) from in the Pearl River, Guangzhou, China. The main physicochemical properties of the sediment are included in Table 1. After collection, the sediment was immediately transferred into glass bottles, and stored in a refrigerator ( $-20^\circ\text{C}$ ) until they were used. Around 1 kg of sediments were homogenized by a tumbling mixer and then air dried and sieved at 2 mm. The sediment was artificially polluted by DEHP solution (200 mg/L), mixed well and kept at room temperature for 2 months. The final DEHP concentration in the sediment was 187.3 mg/kg dw.

### 2.3. Desorption of DEHP from sediments by surfactants

In this study Tween 80, Brij 35, and Triton X-100 (characteristics of the surfactants are indicated in Table 2), three of the most commonly used synthetic nonionic surfactants were selected for the desorption of DEHP from the sediments (Cheng et al., 2017a; Wang et al., 2008). In the batch experiments, 250 mL of surfactant solutions (0–2 mmol/L) were added to a series of 1 L flasks, each containing 50 g of DEHP polluted sediment. The flasks were sealed and mechanically shaken (120 rpm) in a water bath shaker. After 4 h, the sediment suspensions were centrifuged for 5 min at 4000g, and then the supernatant was used for the measurement of desorbed DEHP. All batch experiments were performed in duplicates. Error bars in the Figures represent the standard deviations of triplicate experiments.

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