Effects of iron (hydr)oxides on the degradation of diethyl phthalate ester in heterogeneous (photo)-Fenton reactions

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ABSTRACT

This work studied the structural effects of hematite (α-Fe₂O₃), 2-line ferrihydrite (HFO) and goethite (α-FeOOH) on diethyl phthalate ester (DEP) degradation. The results showed that the degradation of DEP was faster under 365 nm light irradiation than in the dark in the presence of iron (hydr)oxides. The apparent kinetic rates of DEP degradation followed the order HFO > goethite ≈ hematite in the dark and HFO > hematite > goethite under 365 nm light irradiation. Two pathways governed H₂O₂ decomposition efficiency on iron (hydr)oxide surfaces: (1) forming OH on inherent surface hydroxyl groups (Fe-OH) and (2) producing O₂ and H₂O on the surface oxygen vacancies. X-ray photoelectron spectroscopy (XPS) analyses indicated that HFO not only has high Fe-OH content but also has high Vo content, resulting in its low H₂O₂ utilization efficiency (η). DEP was degraded through hydrogen abstraction and de-esterification, and the major products were (OH)₂-DEP, mono-ethyl phthalate (MEP), OH-MEP, and phthalate acid (PA). The study is important in understanding the transformation of phthalate esters in top surface soils and surface waters under ultraviolet light.

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Introduction

Heterogeneous (photo)-Fenton reactions occur commonly in soils, sediments and surface waters. They have been widely applied to remove organic pollutants in solutions, since these reactions produce much less colloidal sludge than homogenous Fenton reactions at near-neutral pH (Feng et al., 2003; Iurascu et al., 2009). Various iron (hydr)oxides, including ferrihydrite, goethite, hematite, magnetite and wustite, can be used to degrade organic pollutants (Bayat et al., 2012; Gajovic et al., 2011; Guo et al., 2017; Pereira et al., 2012) or inactivate bacteria (Ruales-Lonfat et al., 2015) due to their specific activities. Different iron (hydr)oxides with various structures exhibit substantially distinctive behaviors. For example, Huang et al. (2001) reported that the degradation of 2-chlorophenol in heterogeneous Fenton systems followed the sequence ferrihydrite > goethite > hematite (Huang et al., 2001). Du et al. (2008) reported that the degradation efficiency toward orange II in heterogeneous photo-Fenton systems followed the sequence γ-FeOOH > α-FeOOH > γ-Fe₃O₄ > α-Fe₃O₄ (Du et al., 2008).

Goethite (α-FeOOH), hematite (α-Fe₂O₃), and 2-line ferrihydrite (HFO), another name for hydrous ferric oxide: Fe₂O₃·0.5(OH)·nH₂O, 0 ≤ y ≤ 1.96, 0.82 ≤ n ≤ 1.14 (Appendix A Fig. S1) are three widely occurring Fe(III) (hydr)oxides in the environment (Gualtieri and Venturelli, 1999; Hiemstra, 2013). As shown in Appendix A Fig. S1, the (hydr)oxide core of HFO is composed of...
important roles in catalyzing H$_2$O$_2$ decomposition (Hermanek et al., 2013). Goethite has the highest stability along the [001] crystal orientation (Banfield et al., 2000), while hematite has faster conduction ability parallel to the [001] planes. The bulk structure substantially affects the surface stability of atoms (Hemstra, 2013) and hence their catalytic properties. A recent study showed that the surface abundance of exposed metal centers and hydroxyl groups can greatly affect H$_2$O$_2$ decomposition to hydroxyl radicals (·OH) based on density functional theory calculations (Lousada et al., 2012). Despite the fact that the crystal structures and crystallinity of iron (hydr)oxides play significant roles in catalyzing H$_2$O$_2$ decomposition (Hermanek et al., 2007), the relationship between their structures and (photo)-Fenton reactivity is rarely explored.

Diethyl phthalate ester (DEP), which is often applied as a fragrance carrier in perfumes (Api, 2001) and additive in cosmetic products (Koo and Lee, 2004), has been frequently detected in soils, surface waters and the atmosphere (Chen et al., 2017; Fromme et al., 2004; Hu et al., 2003; Lin et al., 2014). Because phthalate esters may pose endocrine disruptive effects toward human health, they have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) (Colón et al., 2000; Wang et al., 2003). So far, a number of works have been conducted to investigate their degradation and transformation (Li et al., 2010; Roslev et al., 2007; Souza et al., 2014; Wang et al., 2004; Xu et al., 2005). In this study, we select DEP as a model compound to investigate the degradation of phthalate acid esters (PAEs) with iron (hydr)oxides.

The main objectives of this work were to investigate:

1. the structural effects of goethite, hematite and HFO on the degradation of DEP in the dark or under 365 nm ultraviolet (UV) light;
2. the catalytic efficiency of these three iron (hydr)oxides in H$_2$O$_2$ decomposition; and
3. the degradation pathways of DEP in heterogeneous (photo)-Fenton reactions with these materials. Electron paramagnetic resonance (EPR) spectroscopy was used to analyze the formation of ·OH radicals in the reactions, and X-ray photoelectron spectroscopy (XPS) was applied to analyze the surface structures of the iron (hydr)oxides.

1.1. Materials

Diethyl phthalate ester and 5,5-dimethyl-1-pyridine N-oxide (DMPO) were purchased from Sigma-Aldrich (Sigma-Aldrich Co. LLC., Darmstadt, Germany). All solutions were made with ultrapure water (>18.2 MΩ cm) from a Synergy UV ultrapure water system (Millipak-40 Filter Unit, Millipore Corporation Merck KGaA, Germany). All reagents were of analytical grade and solvents of high-performance liquid chromatography (HPLC) grade unless otherwise stated.

1.2. Iron (hydr)oxide syntheses

To synthesize HFO, 1 mol/L KOH was added into 650 mL 86 mmol/L Fe(NO$_3$)$_3$ solution at a speed of 5 mL/min until the pH reached 7.5. The suspension was left to stand for 2 hr, and the HFO precipitate at the bottom of the reaction vessel was dialyzed three times a day for 3 days to remove K$^+$ and NO$_3^-$ (Ona-Nguema et al., 2005). The obtained HFO particles were then freeze-dried, passed through a 100 mesh sieve, and stored in a glass jar at room temperature. To synthesize hematite, 200 mmol Fe(NO$_3$)$_3$ was added into 3 L boiling water, which was kept boiling for 2 hr (Madden et al., 2006). After cooling to room temperature, the hematite particles were dialyzed by the same procedures as used for HFO. Goethite was synthesized by adding 30 mL 5 mol/L KOH into 1.5 L 0.1 mmol/L Fe(NO$_3$)$_3$ solution, followed by adjusting the solution pH to 12 (Schwertmann and Cornell, 2008). The obtained suspension was heated in a water bath at 60 °C for 24 hr and the goethite particles were dialyzed by the same procedure as used for HFO and hematite.

1.3. Iron (hydr)oxide characterization

The mineral phases were identified by their powder X-ray diffraction (XRD) patterns (Rigaku’s Ultima IV system, Rigaku Corporation, Japan), using Cu-Kα radiation at a scan rate of 0.02°/min from 10° to 60° (80° for HFO). The morphology and particle size were characterized by high-resolution transmission electron microscopy (HRTEM) with a Tecnai G2F20 system (G2F20, FEI Company, USA) operating at 200 kV (point resolution r $= 0.5$ nm). Photoluminescence (PL) is an indicator for surface defects of iron (hydr)oxides, and PL spectra were obtained with a F-4500 FL spectrophotometer (F-4500 FL, Hitachi, USA) at the excitation wavelength (λ) 243 nm. The specific surface areas (SSA) of these three iron (hydr)oxides were measured following the N$_2$-Brunauer–Emmett–Teller (BET) adsorption method by using a Micromeritics ASAP2020M system (ASAP2020M, Micromeritics Instrument Corporation, USA).

XPS was used to determine the surface features of the iron (hydr)oxides. Film samples were prepared on (0.7 mm × 5 mm × 5 mm) indium tin oxide (ITO) plates, and high-resolution Fe$_{2p}$ spectra were recorded using the ESCALAB 250XI system (ESCALAB 250XI, Thermo Fisher Scientific, USA).

To quantify the produced oxygen from the surface iron (hydr)oxides from the decomposition of H$_2$O$_2$, experiments were conducted as follows: 1 mL 10 g/L HFO, goethite or hematite was added into 40 mL bottles containing 1 mL 30% H$_2$O$_2$, and the bottles were sealed quickly with an oxygen probe inside (Seven2Go pro, Mettler Toledo, Switzerland). The changes in the oxygen concentration in the headspace of the bottles were measured after 5 min.

1.4. Reaction setup

The heterogeneous (photo)-Fenton reactions were conducted in 45 mL 10 mmol/L acetate buffer at pH 4.5. The reaction solutions were placed in 60 mL quartz tubes, which were put in an XPA-7 photoreactor system (XPA-7, Xujiang Machinery and Electric Co., China) with a monochromatic low-pressure mercury lamp (365 nm, 0.6 mW/cm$^2$) located in the middle. The reactors were kept moving around the lamp for 3 hr with
continuous stirring. The initial concentrations of DEP and H$_2$O$_2$ were 0.089 and 10 mmol/L, respectively. The amount of iron (hydr)oxide ($\alpha$-FeOOH, HFO or $\alpha$-Fe$_2$O$_3$) added was 1 g/L. At predetermined time intervals, 0.5 mL samples of suspensions or solutions were withdrawn and well mixed with 0.5 mL ethanol. Preliminary experiments showed that added ethanol can quench the Fenton reactions and thoroughly desorb the adsorbed DEP from the iron (hydr)oxides (data not shown). After filtration, the concentrations of DEP in filtrates were analyzed by using an HPLC 1260 system (HPLC 1260, Agilent Technologies, Fig. 1 – High-resolution transmission electron microscopy (HRTEM) images of (a–c) 2-line ferrihydrite (hydrous ferric oxide: HFO), (d–f) goethite, and (g–i) hematite at resolutions of 200, 20, and 5 nm respectively.

Table 1 – Physicochemical properties of the three iron (hydr)oxides in this study.

<table>
<thead>
<tr>
<th>Iron (hydr)oxide</th>
<th>SSA (m$^2$/g)</th>
<th>Particle size (nm)</th>
<th>$\text{pH}_{\text{pzc}}$</th>
<th>Zeta potential (mV)</th>
<th>PL spectrum peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO</td>
<td>302</td>
<td>100 (5)</td>
<td>7.9</td>
<td>34.5 $\pm$ 1.9</td>
<td>22,805</td>
</tr>
<tr>
<td>Goethite</td>
<td>66.9</td>
<td>25</td>
<td>7.9</td>
<td>26.6 $\pm$ 1.8</td>
<td>17,276</td>
</tr>
<tr>
<td>Hematite</td>
<td>157</td>
<td>50</td>
<td>8.2</td>
<td>20.6 $\pm$ 0.5</td>
<td>18,674</td>
</tr>
</tbody>
</table>

SSA: specific surface area; PL: photoluminescence; $\text{pH}_{\text{pzc}}$: pH of the point of zero charge; HFO: hydrous ferric oxide. Particle size: average size based on TEM image; zeta potential: measured at pH 4.5; PL spectrum peak area: measured at excitation light of 243 nm.
Inc., USA). An isocratic mobile phase with 65% methanol and 35% water was used throughout the detection and the flow rate was 1 mL/min. The concentration of H$_2$O$_2$ was detected according to the optimized titanium sulfate spectrophotometric method (Pobiner, 1961).

1.5. EPR studies

The EPR signals of the .OH adduct of DMPO (DMPO-OH) were recorded with a Bruker EMX 10/12 spectrometer (EMX 10/12, Bruker, Germany). The resonance frequency was set at 9.77 GHz, microwave power was 20.02 mW, modulation frequency was 100 kHz and modulation amplitude was 1.0 G. The sweep width was 100 G and the time constant was 40.96 msec.

1.6. Degradation products of DEP

The reaction solution was filtered and analyzed by Shimadzu LC/MS 8050 system (LC/MS 8050, Shimadzu Co., Japan). The detection method followed the method of Sun et al. (2015) with some modification. In brief, the mobile phase A was 0.001% formic acid dissolved in 5% methanol water solution; B was acetonitrile. A gradient effluent mobile phase was set combining different ratios of A with B. The injection volume was 5 μL. The capillary voltage was set at 3.2 kV, and cone voltage was 30 eV.

2. Results and discussions

2.1. Iron (hydr)oxide characterization

The HRTEM images (Fig. 1a–c) demonstrated that HFO consisted of agglomerations of cotton-like nano-sized particles (~5 nm) to form 100 nm particles, which contributed to its high SSA (302.00 m$^2$/g) (Table 1). The synthesized goethite had an accicular morphology (Fig. 1d) containing edge-sharing ferric octahedra, which is stable along the (001) crystal orientation compared to other crystal directions (Alexandrov and Rosso, 2015). The diameter of the goethite needles was about 25 nm (Fig. 1e) with SSA of 66.87 m$^2$/g (Table 1). The synthesized hematite had a rice-shaped morphology (Fig. 1g) with a particle size of about 50 nm and SSA of 156.63 m$^2$/g.

The XRD patterns (Fig. 2) indicated that the HFO synthesized in this study was poorly crystallized 2-line ferrihydride with two rather broad peaks observed; while goethite and hematite had obvious sharp peaks, and their patterns were comparable to the standard PDF cards for these phases. The XRD patterns were in good accordance with the HRTEM images at 5 nm scale, in which hematite and goethite had obvious lattice lines, while none were observed for HFO. The PL signal peak areas (Table 1) demonstrate that the synthesized hematite had the most surface defects (including oxygen vacancies) among the three iron (hydr)oxides, and goethite had the least (Liqiang et al., 2006).

2.2. Heterogeneous (photo)-Fenton reactions for DEP degradation

All the reactions were considered heterogeneous since no dissolved iron was detected in any of our experiments (Lin et al., 2014). Both DEP degradation and H$_2$O$_2$ decomposition in the (photo)-Fenton systems were fitted with Eq. (1). The apparent initial reaction rates ($k_{ij}$/hr) of DEP and H$_2$O$_2$ degradations were calculated based on the first 3 hr of sampling points, and the values are presented in Table 2.

\[ \frac{dC_i}{dt} = -k_{ij} \times t + a \]

where $C_i$ (mmol/L) and $C_{i,0}$ (mmol/L) are concentrations of $i$ (DEP or H$_2$O$_2$) at time $t$ (hr) and 0 (hr), $j$ is the reaction type (in the dark (d) and under 365 nm irradiation (p)), and $a$ is the intercept of the fitted line.

The degradation of DEP under UV irradiation was 2.19–6.49 times faster than that in the dark. Fig. 3a shows the kinetics of DEP degradation in the dark, and the values of $k_{DEP,d}$ follow the sequence HFO > hematite > goethite (Table 2), as shown in Fig. 3c and d, respectively. The sequence of $k_{DEP,f}$ values for the three iron (hydr)oxides was found to decrease in the order HFO > hematite > goethite (Table 2), while the sequence for the decomposition of H$_2$O$_2$ was HFO > hematite > goethite (Table 2), as shown in Fig. 3c and d, respectively. The sequence of $k_{H2O2}$ values for the three iron (hydr)oxides was not in the same order as that of the $k_{DEP}$ values (Table 2).

| Table 2 – Apparent kinetic rate constants of the degradation of DEP ($k_{DEP}$) and decomposition of H$_2$O$_2$ ($k_{H2O2}$) with the three iron (hydr)oxides in different reactions. |
|-------------|-------------|-------------|-------------|
| Iron (hydr)oxide | $k_{DEP}$ (×10$^{-2}$/hr) | $k_{H2O2}$ (×10$^{-2}$/hr) |
| Dark | Hematite | 1.30 ± 0.36 | 8.40 ± 0.75 |
| | HFO | 4.53 ± 0.69 | 10.75 ± 0.91 |
| | Goethite | 1.60 ± 0.23 | 0.35 ± 0.57 |
| UV (365 nm) | Hematite | 8.43 ± 0.52 | 14.37 ± 0.76 |
| | HFO | 9.91 ± 1.66 | 18.72 ± 1.27 |
| | Goethite | 3.56 ± 0.07 | 4.148 ± 0.79 |

UV: ultraviolet light; DEP: diethyl phthalate ester; HFO: hydrous ferric oxide.
Fig. 3 – a, b: Diethyl phthalate ester (DEP) concentration ratio of time $t$ (hr) to time 0 (hr) (denoted as $C_t/C_0$ of DEP); c, d: $H_2O_2$ concentration ratio of time $t$ (hr) to time 0 (hr) in the reaction systems with the three iron (hydr)oxides (denoted as $C_t/C_0$ of $H_2O_2$).
In the dark: a and c; under ultraviolet (UV) 365 nm light irradiation: b and d.
Reaction conditions: initial concentration of DEP 0.089 mmol/L, 10 mmol/L $H_2O_2$, 1 g/L iron hydroxide, and solution pH 4.5.

Fig. 4 – Electron paramagnetic resonance (EPR) spectra of dimethyl pyridine N-oxide trapped hydroxyl radical (DMPO-OH) in different reaction systems of the three iron (hydr)oxides (a) in the dark and (b) under UV (365 nm) irradiation.
Reaction conditions: initial solution pH 4.5 and 1 g/L iron (hydr)oxides. UV: ultraviolet light.
After normalizing the $k$ values with the SSA of these three iron (hydr)oxides (Appendix A Table S1), the sequences of $k_{\text{DEP}}$/SSA and $k_{\text{H}_2\text{O}_2}$/SSA were not inconsistent. In the reaction systems, DEP was degraded by the formed .OH. However, some $\text{H}_2\text{O}_2$ molecules can decompose to $\text{O}_2$ and $\text{H}_2\text{O}$ on the surface of iron (hydr)oxides (Huang and Huang, 2008), which lowers the $\text{H}_2\text{O}_2$ utilization efficiency for DEP degradation. The generation of .OH can be detected in each reaction by EPR technology. Fig. 4a and b shows the first derivative EPR spectrum of DMPO-OH, featured by a 1:2:2:1 pattern of peaks, in the heterogeneous (photo)-Fenton reaction systems and control systems. In the control experiment without iron (hydr)oxide under 365 nm UV irradiation, the formation of .OH was rather low compared to the system with iron (hydr)oxide. The results show that the formation of .OH was higher under UV irradiation than in the dark, which is in accordance with the DEP degradation.

To further quantify the utilization of $\text{H}_2\text{O}_2$ for DEP degradation, the utilization efficiency ($\eta$) of $\text{H}_2\text{O}_2$ was calculated according to Eq. (2):

$$\eta = \frac{\Delta C_{\text{DEP}}}{\Delta C_{\text{H}_2\text{O}_2}}$$

(2)

---

**Fig. 5** – $\text{H}_2\text{O}_2$ utilization efficiencies ($\eta$) with three iron (hydr)oxides in heterogeneous Fenton reactions in the dark or under UV irradiation. Same letters presented above the bars indicate no significant differences within or between groups at the 95% confidence level. UV: ultraviolet light.

**Fig. 6** – $\text{Fe}_{2p}$ X-ray photoelectron spectra (XPS) of the three iron (hydr)oxides and the production of $\text{O}_2$ in the systems of $\text{H}_2\text{O}_2$ and iron (hydr)oxides. $\Delta C_{\text{O}_2}$: $\text{O}_2$ concentration changes before and after $\text{H}_2\text{O}_2$ reacted with iron (hydr)oxides; $V_0$: surface oxygen vacancy.
where, $\Delta C_{\text{DEP}}$ (mmol/L) and $\Delta C_{\text{H}_2\text{O}_2}$ (mmol/L) are defined as the concentration changes of DEP and H$_2$O$_2$ in the heterogeneous (photo)-Fenton reactions, and $i$ is one of the three iron (hydr)oxides.

Fig. 5 schematically shows that goethite had significantly higher H$_2$O$_2$ utilization efficiency than HFO in the dark, followed by hematite. The values of $\eta_i$ did not have significant differences for the three iron (hydr)oxides under 365 nm light irradiation. Besides, the $\eta_i$ values for goethite and HFO under UV irradiation did not increase compared with the values in the dark. However, the kinetic rate constants for the degradation of DEP and the decomposition of H$_2$O$_2$ for all three iron (hydr)oxides were higher under UV irradiation than in the dark (Fig. 3). These results indicated that UV irradiation could produce more $\cdot$OH radicals, which were created, however, at the expense of much more H$_2$O$_2$ decomposition, resulting in lower $\eta_i$ for goethite and HFO. The situation for hematite was the opposite, which might be attributed to the lower bandgap energy of hematite (Eggleston et al., 2009). The 365 nm UV irradiation could produce surface holes ($h^+$) and electrons ($e^-$), which facilitated H$_2$O$_2$ decomposition into $\cdot$OH.

$\equiv$Fe$^{II}$IOH$^+$ $+$ H$_2$O$_2$ $\rightarrow$ $\equiv$Fe$^{III}$OH$^+$ $+$ H$^+$ $+$ HO$_2^-$ $\quad (3)$

$\equiv$Fe$^{II}$OH $+$ H$_2$O$_2$ $\rightarrow$ $\equiv$Fe$^{III}$OH $+$ OH$^-$ $+$ OH$^-\quad (4)$

$\equiv$Fe$^{III}$O (oxygen vacancies) $+$ H$_2$O$_2$ $\rightarrow$ $\equiv$Fe $+$ H$_2$O $+$ O$_2\quad (5)$

To better characterize the surface Fe-OH groups and Vo, XPS spectra of the three iron (hydr)oxides were obtained (Fig. 6). Studies have shown that Fe$^{2p_{3/2}}$ of Fe-OH has a binding energy of 725 eV (Sharan et al., 2015) and Fe$^{2p_{3/2}}$ of Vo is positioned at a binding energy of 712.8 eV (Meng et al., 2017). The Fe-OH and Vo in this study were identified in the XPS spectra of the three iron (hydr)oxides in Fig. 6 and the peak areas are listed in Table 3; the peak area ratios of Fe-OH to Vo were also calculated and listed in Table 3. As is shown in Table 3, the peak areas of Fe-OH for HFO, goethite and hematite were 77,993.78, 45,042.27 and 43,752.61 respectively;

2.3. Proposed mechanisms of $\cdot$OH production

The crystal structures of iron (hydr)oxides can affect H$_2$O$_2$ decomposition in heterogeneous (photo)-Fenton reactions (Hermanek et al., 2007), which can further affect DEP degradation. It has been hypothesized that H$_2$O$_2$ is adsorbed on iron (hydr)oxide surfaces through a bond between $\cdot$OH of H$_2$O$_2$ and Fe centers on the (hydr)oxide surfaces, based on density functional theory (DFT) calculations (Lousada et al., 2013). In this study, the inherent $\cdot$OH groups on iron (hydr)oxide surfaces (Fe-OH) may provide proper sites for H$_2$O$_2$ to form H-bonds and facilitate the cleavage of O-O to produce surface $\cdot$OH radicals (Eqs. (3) and (4)), which contribute to DEP degradation. However, there is another pathway (Eq. (5)) of H$_2$O$_2$ decomposition on surface oxygen vacancies (Vo), which is a type of surface point defect (Al-Mashta et al., 1982; Hiemstra, 2013). If more H$_2$O$_2$ decomposed through this pathway, the utilization efficiency of H$_2$O$_2$ was decreased.

Table 3 – Fe$^{2p}$ XPS peak areas and atomic percentages of surface hydroxyl group (Fe-OH) and oxygen vacancy (Vo).

<table>
<thead>
<tr>
<th>Iron (hydr)oxide</th>
<th>Fe$^{2p}$ binding energy (eV)</th>
<th>Peak area</th>
<th>Atomic percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>725.00</td>
<td>45,042.27</td>
<td>85.98</td>
</tr>
<tr>
<td></td>
<td>712.82</td>
<td>7368.43</td>
<td>14.02</td>
</tr>
<tr>
<td>Hematite</td>
<td>725.03</td>
<td>30,074.62</td>
<td>40.11</td>
</tr>
<tr>
<td></td>
<td>712.80</td>
<td>43,752.61</td>
<td>59.19</td>
</tr>
<tr>
<td>HFO</td>
<td>725.00</td>
<td>77,993.78</td>
<td>48.67</td>
</tr>
<tr>
<td></td>
<td>712.80</td>
<td>82,501.55</td>
<td>51.33</td>
</tr>
</tbody>
</table>

HFO: hydrous ferric oxide.

![Fig. 7 – Proposed degradation pathways of DEP. DEP: diethyl phthalate ester.](image-url)
the value sequence is in the same order as \( k_{\text{DEP,d}} \) for the three iron (hydr)oxides (Table 2). Furthermore, the amount of \( O_2 \) produced by HFO and hematite (Fig. 6) was much higher than that by goethite. This result not only explained the lower \( H_2O_2 \) decomposition efficiency of HFO and hematite (Fig. 5), but also was consistent with their higher \( Vo \) peak areas compared to goethite (Table 3).

2.4. DEP degradation and reaction scheme

Based on liquid chromatography–mass spectrometry (LCMS) analyses (Appendix A Fig. S2), the major products from DEP degradation in the heterogeneous (photo)-Fenton systems were (OH)_2-DEP, mono-ethyl phthalate (MEP), OH-MEP and phthalate acid (PA). Fig. 7 shows two possible pathways of DEP degradation. DEP could be degraded through stepwise hydrogen abstraction on the α carbons of esters, resulting in highly unstable –OH substituted molecules (Bajt et al., 2001), and MEP, which are finally transformed into PA. This hypothesis is supported by the previous work of Chen et al. (2016) and An et al. (2014). The second pathway involved the addition of two OH radicals onto both the benzene ring and the end of the sidechain carbon atom, forming 2OH-DEP, which was also detected by Chen et al. (2016) using gas chromatography–mass spectrometry (GCMS).

3. Conclusions

Heterogeneous (photo)-Fenton reactions naturally occur in surface waters and the top layer of soils. Our work is the first to illustrate the effects of the surface structures of iron (hydr)oxides on their heterogeneous (photo)-Fenton reactions for contaminant degradation. The results indicate that surface hydroxyl groups are important in decomposing \( H_2O_2 \) to \(-OH\), while oxygen vacancies can produce \( O_2 \) and \( H_2O \). HFO had high DEP degradation ability both in the dark and under 365 nm light irradiation, but the higher \( O_2 \) production yield was conserved with higher \( Vo \) peak areas compared to goethite (Table 3).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.06.015.

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