Phthalate degradation by glow discharge plasma enhanced with pyrite in aqueous solution
Chensi Shen, Shaoshuai Wu, Hui Chen, Sadia Rashid and Yuezhong Wen

ABSTRACT
In order to prevent health risk from potential exposures to phthalates, a glow discharge plasma (GDP) process was applied for phthalate degradation in aqueous solution. The results revealed that the phthalate derivatives 4-hydroxyphthalic acid, 4-methylphthalic acid and 4-tert-butylphthalic anhydride could be degraded efficiently in GDP process (498 V, 0.2 A) with high removal efficiencies of over 99% in 60 minutes. Additionally, pyrite as a promising heterogeneous iron source in the Fenton reaction was found to be favorable for GDP process. The phthalate degradation reaction could be significantly enhanced by the continuous formation of OH and the inhibition of the quenching reaction in the pyrite Fenton system due to the constant dissolution of Fe(II) from pyrite surface. Meanwhile, the initial pH value showed little impact on the degradation of phthalates and the energy efficiency of GDP system for phthalate degradation ranged between 0.280 × 10^{-9} and 1.210 × 10^{-9} mol/J, which is similar to the GDP system with phenol, bisphenol A and methyl tert-butyl ether as the substrates. Further, the X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectroscopy analyses indicated that the pyrite was relatively stable in GDP system and there was no obvious polymeric compound formed on the catalyst surface. Overall, this GDP process offers high removal efficiency, simple technology, considerable energy efficiency and the applicability to salt-containing phthalate wastewater.

Key words | advanced oxidation technologies, grow discharge plasma, phthalates, pyrite, wastewater treatment

INTRODUCTION
Phthalates, more precisely named phthalic acid esters (PAEs), are synthetic compounds, which are used widely as plasticizers, solvents, and additives in many consumer products (Wang et al. 2013). Several million tons of PAEs are produced worldwide every year for the production of soft polyvinyl chloride and other plastics (Guo & Kannan 2011). Among them, several PAEs have been identified and classified as endocrine disruptors possibly associated with known estrogenic and anti-androgenic activity (Farajzadeh & Mogaddam 2012). Nowadays, they have been widely dispersed and detected in waters and sediments as a result of the widespread and abundant use (Murai et al. 1998). In order to prevent the health risk from the potential exposures to phthalates, it requires simple, fast and reliable methods to remove the phthalates from industrial wastewater.

Currently, advanced oxidation processes (AOPs) constitute a promising technology for degradation of non-easily removable organic compounds, as they can effectively mineralize the contaminants or destroy them into harmless products (Andreozzi et al. 1999; Pera-Titus et al. 2004). For example, methods such as photocatalysis (Xu et al. 2009), sonophotolysis (Xu et al. 2015), Fenton process (Yang et al. 2009) and ozonation (Wen et al. 2002; de Oliveira et al. 2011) have been successfully used for the degradation of PAEs. Besides these AOP technologies, glow discharge plasma (GDP) is a unique electrical process where the glow discharge in and in contact with liquids can dissociate the water molecule into hydroxyl radical (OH) and hydrogen radical (H) (Wang et al. 2012; Wen et al. 2012). The hydroxyl radicals which diffuse in the surrounding liquid are able to oxidize organic pollutants into ‘harmless’ carbon dioxide in a non-selective way, making GDP particularly suitable for decontamination (Wen & Jiang 2001b; Wang et al. 2012). For example, GDP process has been used to destruct pentachlorophenol rapidly (Sharma et al. 2000) and degrade the methyl tert-butyl ether (MTBE).
(Tong et al. 2011) successfully. Additionally, a novel method using discharge plasma taking place at the gas–solution interface in gas atmosphere has been employed to degrade microcystin-LR in aqueous solution (Zhang et al. 2012). These successful results provide a promising insight into the application of GDP system for the degradation of PAEs.

Nevertheless, when hydroxyl radicals are present for pollutant abatement, the slower oxidation routes such as H₂O₂ are ‘shunted’ or even by-passed (Jiang et al. 2014). In efforts to improve the efficiency of plasma oxidations, addition of ferrous salt in plasma system is an attractive alternative arising from the fact that adding iron salts can catalytically transform formed H₂O₂ into hydroxyl radicals via Fenton reactions (Venny et al. 2012; Jiang et al. 2014). Although additional Fenton reactions offer a cost-effective source of ·OH in plasma systems, some limitations still exist, such as iron sludge formation, a narrow working pH range and the inconvenient recycling of the iron (Zhang et al. 2014). To overcome these drawbacks, not only the efficiency of GDP system needs to be investigated for PAEs removal, but also an enhanced GDP system with heterogeneous Fe-containing solid catalysts needs to be developed.

Therefore, in this study, the applicability of GDP system for PAEs removal was evaluated in view of the current–voltage (I–V) characteristics, the degradation efficiency of PAEs and the effects of pH on PAEs degradation. Meanwhile, pyrite (FeS₂), one of the most abundant natural iron sulfur minerals on the earth’s surface, has great potential to be used as a heterogeneous catalyst in the Fenton reaction to degrade organic contaminants. A few studies have indicated that pyrite can improve the oxidation ability of classic Fenton system successfully (Che et al. 2011; Bae et al. 2013; Zhang et al. 2014; Liu et al. 2015). Thus, pyrite as a promising heterogeneous iron source in the Fenton reaction was applied to enhance the degradation of PAEs in this study. The reactivity of pyrite to catalyze GDP oxidation was investigated and the reusability of pyrite was evaluated.

METHODS

Chemicals

4-hydroxyphthalic acid (4-HPA, >98%), 4-methylphthalic acid (4-MPA, >98%), and 4-tert-butylphthalic anhydride (4-BPA, >98%) were selected as the typical compounds of PAEs (Table 1), which were purchased from Tokyo Chemical Industry (Japan). The pyrite was purchased from Sinopharm Chemical Reagent Co., Ltd. It was ground and

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure formula</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
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<td>C₁₂H₁₄O₄</td>
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</table>
sieved through 150 mm mesh prior to use. The deionized distilled water was prepared from a Millipore Waters Milli-Q water purification system with a resistivity of 18.2 MΩ·cm. Other chemicals and solvents used in this study were of analytical grade or high performance liquid chromatography (HPLC) grade.

**Apparatus and experimental conditions**

The DC high-voltage power unit (variable voltage of 0–600 V and current of 0–600 mA) was supplied by Beijing Da Hua Radio Factory. The reactor contained a cylindrical vessel with an inner diameter of 40 mm (Figure 1) (Wang & Jiang 2008). The anode, from which the discharge was emitted, was a pointed platinum wire (i.d. 0.6 mm) sealed into a glass tube. The cathode was a stainless steel plate placed in another glass tube and separated from the anodic compartment by a glass frit of medium porosity. The reactor was contained within a water jacket, and the solution in the reactor was maintained at 298 ± 2 K by circulating the cell with cool water. During the reaction, the solution was gently stirred with a magnetic stirrer, and a 1 mL sample was periodically taken out to determine the PAEs concentration (Tong et al. 2011).

**Analytical method**

Quantitative analysis of PAEs was done by using an HPLC unit (Waters® 2695) equipped with a diode-array detector (Waters® 2998). An Agilent® C18 column (250 × 4.6 mm, 5 μm) was employed for separation. The isocratic mobile phase consisted of 40% acetonitrile and 60% water containing 0.5% phosphoric acid with a flow rate of 0.2 mL/min. The injection volume was 20 μL, the detection wavelength was 210 nm and the column temperature was 45 °C. For H$_2$O$_2$ consumption quantification, 100 μL samples were periodically withdrawn and filtrated through a 0.45 mm syringe filter. Aliquots of 50 μL supernatant were transferred to a 5 mL volumetric flask and diluted to 500 μL. The dilution was used for H$_2$O$_2$ measurement using a method according to Kasaka et al. (Kosaka et al. 1998; Liu et al. 2015). Total organic carbon analysis was performed using a Shimadzu TOC-V CPH (Tokyo, Japan), aliquots of 10 mL of sample were periodically withdrawn, filtrated through a 0.22 μm syringe filter and measured immediately.

**RESULTS AND DISCUSSION**

**I-V curve characteristic**

An I-V curve is a typical characteristic during the onset of discharge (Wen & Jiang 2001a). Figure 2 shows the typical I-V curve during the onset of GDP. All the I-V curves of GDP systems with or without the PAEs are almost the same, suggesting that the existence of PAEs pollutant had little impact on the onset of GDP. At the first stage (0 < V < 180 V), the current increased linearly with the increase of the applied voltage, while the conventional electrolysis of water could be observed with small bubbles around the
When the applied voltage ranged from 180 to 440 V, the current first decreased rapidly then oscillated due to the formation and collapse of vapor sheath around the anode. Finally, glow discharge occurred when the applied voltage was higher than 500 V, and the current increased steadily.

During the GDP process, various chemically active species and their combination products are formed in the solution due to the bombardment of energetic H_2O^+ ions from the plasma according to Reactions (1) to (6) (Liu & Jiang 2005).

\[
\begin{align*}
H_2O^+ + nH_2O & \rightarrow nH_2O^{++} + H_2O^+ \quad (R1) \\
H_2O^+ & \rightarrow OH^+ + H^+ \quad (R2) \\
e^{++} + nH_2O & \rightarrow m*OH + mH^+ + e^- \quad (R3) \\
OH^+ + *OH & \rightarrow H_2O_2 \quad (R4)
\end{align*}
\]

The degradation of PAEs

In GDP, 500 V was employed for PAEs degradation because the platinum anode would melt at a higher voltage. Figure 3(a) shows the efficiency of 4-HPA, 4-MPA and 4-BPA degradation when 50 mL of solution containing 100 mg/L PAEs was subjected to the discharge treatment. It can be observed that 97.95%, 98.13% and 97.66% of 4-HPA, 4-MPA and 4-BPA could be removed by GDP in 60 minutes. In GDP process, PAEs could be degraded in both the plasma zone and bulk zone. The description of the kinetic mechanism can be simplified as Equation (1):

\[
\frac{dC}{dt} = -k_1 C - k_0
\]

where \( k_0 \) is the zero-order rate constant due to degradation in the plasma zone, \( k_1 \) is the first-order rate constant due to oxidation degradation in the bulk zone and \( C \) is the concentration of PAEs.

As shown in Figure 3(b) for the three kinds of PAEs, straight lines with linear relationships between ln C and the treatment time were achieved for each dataset. All three degradation lines were approximately the same, suggesting that the GDP process of all three PAEs followed first-order kinetic under experimental conditions. These results imply that the zero-order rate constant in Equation (1), associated with degradation in the plasma zone, is
negligible. Because the plasma zone is very small, the PAEs degradation in this zone is negligible in comparison with that in the bulk zone.

**Effects of pH on PAEs degradation**

The pH variation during the discharge process with or without PAEs is shown in Table 2. In the absence of PAEs, the pH of GDP system was almost unchanged before and after the discharge, whereas in the presence of PAEs, the pH value of the solution dropped appreciably from 9.96, 9.92 and 10.05 to 4.43, 5.18, and 4.96 for 4-HPA, 4-MPA and 4-BPA, respectively. According to the published studies, formic acid, oxalic acid, pyruvic acid or other low-molecular-weight organic acids were the major intermediate byproducts during the process of PAEs degradation by AOPs (Du et al. 2015). Meanwhile, the decline of the system pH has been widely observed in GDP process for the degradation of organic pollutant, which can be attributed to the generation of organic acid during the discharge treatment (Liu et al. 2016). Thus, it could be deduced that some low-molecular-weight organic acids such as formic acid, oxalic acid or other organic acid were generated during the PAEs degradation by GDP process.

Meanwhile, the effect of initial pH on the PAEs degradation is shown in Figure 4. The removal efficiency of 4-HPA, 4-MPA and 4-BPA by GDP process achieved above 96.0% in 60 minutes when the initial pH value increased from 5 to 11, indicating that the degradation of these three kinds of PAEs was almost independent of pH during the GDP process. This advantage of pH-independence could be attributed to the pH change of the GDP reaction system, because the oxidative ability of the oxygen-containing radical is fairly strong under acidic conditions (*OH + H+ + e− → H2O) (Liu & Jiang 2005).

**The production of H2O2 and the catalytic effect of pyrite**

It has been demonstrated that glow discharge in water leads to the formation of a large quantity of H2O2 in bulk solution (Reaction (4)). It was confirmed in this study and the results are shown in Figure 5(a). The concentration of H2O2 in the solution increased with the treatment time in the presence or in the absence of PAEs and achieved 20 mmol/L in 60 minutes. Meanwhile, the presence of PAEs had almost no effect on the accumulation of H2O2 in GDP process. However, this accumulated H2O2 would be ‘shunted’ or even by-passed when ·OH is present for pollutant abatement.

Pyrite (FeS2) is one of the most abundant metal sulfide minerals on earth, which can act as a heterogeneous catalyst
in the Fenton reaction to degrade organic contaminations. A few studies have indicated that pyrite is a potential and promising source of ferrous ion activators (Che et al. 2011; Bae et al. 2013; Zhang et al. 2014; Liu et al. 2015). Thus, in order to take advantage of the excessive H$_2$O$_2$, pyrite was applied as a promising heterogeneous iron source in the Fenton reaction to enhance the efficiency of GDP process for the PAEs degradation. The catalytic activity of pyrite is shown in Figure 5(b) and the results show that the pyrite had obvious catalytic effects on PAEs removal. In the presence of pyrite, more than 99% of 4-HPA, 4-MPA and 4-BPA were removed by GDP process after 20 minutes reaction, while about 60% of 4-HPA, 4-MPA and 4-BPA were removed in the absence of pyrite. According to the published reports, the reactions in the pyrite Fenton system are shown in Reactions (7) to (10) (Mckibben & Barnes 1986; Lipczynskakochany 1991).

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (R7)$$

$$2\text{FeS}_2 + 15\text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 2\text{H}^+ + 14\text{H}_2\text{O} \quad (R8)$$

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (R9)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (R10)$$

In this study, the total amount of Fe ions in bulk solution was 0.104 mmol/L after the GDP reaction for 20 minutes, which was quite a bit lower than that in the published GDP/Fe(II)/Fe(III) homogeneous system (ranged from 6.7 to 14.3 mmol/L) (Gao et al. 2003; Wang & Jiang 2009; Liu et al. 2010). Further, the Fe$^{2+}$/GDP system with the same concentration of Fe ions in bulk solution was used for the degradation of PAEs. Figure 5(b) shows that less than 85% of 4-HPA, 4-MPA and 4-BPA were removed by Fe$^{2+}$/GDP process after 20 minutes reaction, lower than pyrite/GDP system. It has been reported that Fe(II) was mostly in aqueous phase in the classic Fenton system, easily leading to a scavenging reaction with $\cdot\text{OH}$, which may significantly inhibit the organic pollutant degradation. However, in the pyrite Fenton system, the continuous dissolution of Fe(II) from the pyrite surface seems to be a key factor to complete the degradation of organic matters by continuously producing $\cdot\text{OH}$ and inhibiting the quenching reactions (Zhang et al. 2014).

### The characterization of pyrite

Figure 6 shows the X-ray diffraction (XRD) patterns of the initial pyrite and the used pyrite. The diffraction peaks of all the pyrite minerals can be indexed to pyrite (JCPDS file, No. 71-1680, labelled as ‘◆’), silicon (JCPDS file, No. 65-1060, ...)
labelled as ‘★’), and FeOOH (JCPDS file, No. 34-1266, labelled as ‘▴’. The identical XRD pattern of FeSO₄·H₂O (JCPDS file, No 34-1266, labelled as ‘●’) was shown in the initial pyrite, but disappeared after the GDP process, while the identical XRD patterns of FeOOH and silicon were enhanced. These results indicate that the pyrite mineral would be partially consumed, while the main structure could be maintained.

The morphology of the initial and used pyrite was examined by transmission electron microscopy (TEM) (Figure 7). Based on images A1, B1 and C1, both the initial and GDP-treated pyrite samples were irregularly shaped. Changes in the external morphology were evaluated by comparing images in A2, B2 and C2. After the GDP treatment, lots of dark particles at nano-scale occurred at the edge of pyrite powders. Also, in the presence of 4-MPA (Figure 7(C2)), the dark particles were more intensive than those in the absence of 4-MPA (Figure 7(B2)). It is known that plasma is a very reactive environment in which several different interactions between it and a surface are possible (Wen et al. 2012). Additionally, some polymeric compounds might be formed and adsorbed on the surface of the catalyst due to the catalytic oxidation of organic compounds. Thus, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was used to investigate this.

Figure 8 shows the SEM morphologies and the EDS mapping of the pyrite before and after GDP process. The pristine pyrite has a rock-like morphology with a homogeneous covering of tiny particles. After the GDP degradation of PAEs, the pyrites were partially cracked and the tiny particles disappeared. Figure 8(C) and 8(D) show the EDS mapping data of pyrites. Both the pyrites before and after GDP process show the homogeneous mixing of iron and sulfur which was caused by intermetallic compound of FeS₂. For the initial pyrite, the carbon was uniformly aggregated on the surface, which might be caused by the carbon impurities of pyrite minerals. After the GDP process, the carbon distribution shows a characteristic similar to the initial pyrite, which means there was little adsorption of polymeric compounds on the surface of pyrite after the PAEs degradation by GDP process. However, the nano-particles at the edge of the pyrite powder which were observed in TEM graphs could not be found in SEM results. This might be brought about by the electrochemical corrosion and further research still needs to be conducted to study the surface modification of pyrite in GDP system.

The reuse of pyrite

The reuse and stability are two major concerns for a catalyst to be used in practical applications (Liu et al. 2015). In the durability test, the same pyrites were repeatedly applied...
for PAEs removal in GDP system. After reuse for three consecutive times, a slight decline of removal efficiency occurred (Figure 9). For example, the removal efficiency of all three PAEs was over 99% for the initial reaction, but it dropped to about 90% for the third reaction. This decline might be due to the loss of pyrite powders during the recovery procedures and the release of Fe$^{2+}$ ions from pyrite.

**Energy efficiency**

Energy efficiency is an important parameter for industrial-scale application. In this study, the energy efficiency of PAEs removal by GDP process ($J_{PAEs}$) was calculated
using the Equation (2):

$$J_{\text{PAEs}} = \frac{(1/2)C_0 V}{U I t_{1/2}}$$  \hspace{1cm} (E2)

where $C_0$ is the initial PAEs concentration in mol/L, $V$ is the liquid volume in L, $U$ is the applied voltage in V, $I$ is the current in A and $t_{1/2}$ is the reaction time required for decomposing half of the initial PAEs molecules. Different energy efficiencies for PAEs are shown in Table 3.

The results indicate that the energy efficiency increased obviously with the adding of pyrite, which increased from $0.398 \times 10^{-9}$, $0.403 \times 10^{-9}$ and $0.280 \times 10^{-9}$ mol/L to $1.195 \times 10^{-9}$, $1.210 \times 10^{-9}$ and $0.784 \times 10^{-9}$ mol/L for 4-HPA, 4-MPA and 4-BPA, respectively. It is noted that the application of pyrite as a heterogeneous Fenton catalyst was of great importance in GDP system. Table 3 also shows the energy efficiency of GDP with other organic pollutants as substrates. With phenol, bisphenol A (BPA) and MTBE as substrates, all the values of energy efficiency are in the magnitude of $10^{-9}$ mol/L, which is similar to the $J_{\text{PAEs}}$ in this work.

With further design improvements and reactor optimization, GDP system may become a competitive wastewater treatment technology for PAEs removal.

**CONCLUSIONS**

The phthalate derivatives 4-HPA, 4-MPA and 4-BPA could be degraded efficiently in GDP process (498 V, 0.2 A) with high removal efficiencies of over 99% in 60 minutes. Meanwhile, the initial pH value shows little impact on the degradation of phthalates, which might be attributed to the pH change of GDP reaction system. Furthermore, pyrite as a promising heterogeneous iron source was explored for synergistic removal of phthalates by combined GDP and catalysis, and the energy efficiency of GDP system for PAEs degradation ranged from $0.280 \times 10^{-9}$ to $1210 \times 10^{-9}$ mol/J. Overall, this GDP process offered high removal efficiency, simple technology, considerable energy efficiency and the applicability to salt-containing phthalate wastewater.

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