Pulse electro-coagulation application in treating dibutyl phthalate wastewater

Tao Wang and Tianqing Liu

ABSTRACT

Pulse electro-coagulation (PEC) was applied to treat plastic factory wastewater in this study. One representative plasticizer molecule was chosen for the synthetic wastewater: dibutyl phthalate (DBP). Experiments demonstrated that PEC exhibits superior economic efficiency and removal efficiency compared to traditional electro-coagulation in wastewater treatment. Experimental data also indicated that at a given current density, compared with the aluminum electrode, the iron electrode could more efficiently remove DBP from wastewater. With an initial pH of 8–9, the required energy was 2.5 kWh m\(^{-3}\) for 75% DBP removal in the case of iron as the anode type. In general, the pollutants have been successfully reduced to environmentally acceptable levels under the following operating conditions: iron as the anode type, interelectrode distance of 10 mm, duty cycle of 0.6, pH of 8–9 and current density of 15 mA cm\(^{-2}\) for PEC time > 15 min.

Key words | DBP, pulse electro-coagulation, wastewater treatment

INTRODUCTION

Phthalate esters (PAEs) are widely used industrial chemicals, owing to their stability and low volatility, which render them highly suitable as plasticizers. They can be detected in various environmental media (Huang et al. 2014). Most mid-molecular and high-molecular weight PAEs are used in the chemical and plastics industry. The industry uses about 300 plasticizers, 20%–50% of which can be released into waterways (Jin et al. 2015). Research shows that PAEs can lead to mutagenic, carcinogenic, and teratogenic characteristics and seriously interfere with the endocrine system of humans and animals (Fisher et al. 2003; Kaneco et al. 2006; Janjua et al. 2007). Since November 2006, dibutyl phthalate (DBP) has been included in the California Proposition 65 list as a teratogen (California Environmental Protection Agency 2006). The Consumer Product Safety Improvement Act (CPSIA) of 2008 prohibits the use of more than 1,000 ppm DBP in toys and childcare (United States Congress 2008). The degradation half-lives of DBP range from 5 to 20 years (Staples et al. 1997).

Therefore, exploring the treatment of DBP in wastewater is an essential step in the study of a more effective treatment of actual industrial effluent. Electro-coagulation (EC), a reliable and economical technique used to solve numerous water pollution problems, has been widely developed in recent decades. The approach has also been successfully applied in the treatment of various industrial wastewaters, including those from catering and paper industries (Yang & McGarrahan 2005; Amos et al. 2008; Aoudj et al. 2015). However, traditional EC has to address the problem related to the reduction in treatment efficiency when power consumption is increased, which is attributed to electrode polarization and passivation. This deficiency has been overcome in recent years by advances in pulse electro-coagulation (PEC). In the pulse power supply process, the peak current is equivalent to several times that of ordinary direct current. The electrode is rapidly dissolved because of this instantaneous high current density. When current is turned off, the discharge ions near the cathode area return to the initial concentration, causing concentration polarization to disappear. Disconnecting the power period can simultaneously contribute to recrystallization and adsorption (Kalyani et al. 2009; García-García et al. 2011; Li et al. 2016a, 2016b). The underlying principle is the production of metallic hydroxide flocs within the wastewater that has to be cleaned by the dissolution of soluble anodes. Three main reactions occur in the PEC process: electrolytic reaction on the electrode surface, formation of flocs in a solution and adsorption of flocs on pollutants. According
to the literature, the following reactions occur in anode electrodes (Daneshvar et al. 2007; Heidmann & Calmano 2008; Phalakornkule et al. 2010):

\[
\begin{align*}
M^{2+} + H_2O & \leftrightarrow M(OH)^{2+} + H^+ \\
M(OH)^{2+} + H_2O & \leftrightarrow M(OH)_2^+ + H^+ \\
M(OH)_2^+ + H_2O & \leftrightarrow M(OH)_3^+ + H^+ \\
M(OH)_3^+ + H_2O & \leftrightarrow M(OH)_4^- + H^+ 
\end{align*}
\]

(1) (2) (3) (4)

In this study, the appropriate experimental parameters for removing DBP from effluent were evaluated. These parameters included electrical energy consumption, electrode type, duty cycle, electrode distance, current density, PEC time, initial pH and initial concentration.

**EXPERIMENTAL**

**Apparatus and materials**

The PEC system used in this experiment was laboratory-scale. The PEC unit consisted of a 2,000 mL plexiglas reactor. Six electrodes are connected in a bipolar mode in the electrochemical reactor. Dimensions of electrodes were \((20 \times 12 \times 12 \text{ cm})\). Total effective areas \((S)\) of these were 480 cm\(^2\). The current was imposed by a pulsed power supply (Soyi 605M, Soyí, China). Experimental equipment schematically is illustrated in Figure 1(a). Before and after PEC, the electrode was cleaned by distilled water and immersed in HCl solution (5% v/v) for more than 10 min and then rinsed again with distilled water.

The commercial plasticizer (DBP; \(\text{C}_{16}\text{H}_{22}\text{O}_4\), CAS No. 84-74-2, MW = 78.35 g·mol\(^{-1}\)) used in this project was purchased from Sinopharm Chemical Reagent Co., Ltd (China; AR grade >99%). The chemical structure is given in Figure 1(b). The DBP wastewater was prepared by adding 30 mg·L\(^{-1}\) of DBP into distilled water (adjusting pH with NaOH or H\(_2\)SO\(_4\), conductivity with NaCl to 1.10–1.20 mS·cm\(^{-1}\)). The actual wastewater used in the experiment was obtained from a plastic factory. The wastewater was randomly sampled four times in different periods (from February 2016 to April 2016) and its characteristics are given in Table 1. Plastic factory wastewater was a mixture of wastewater from dyeing and other washing activities.

**Experimental design and analytical method**

The experiments were conducted in a batch mode with a liquid sample of 2,000 mL. The current densities of 5, 10, 15, 20 and 30 mA·cm\(^{-2}\) were studied. PEC times of 2, 5, 8, 12, 18 and 25 min were used for every current density. All the runs were performed at room temperature and stirring speed was 200 rpm. After each PEC time, the sample was left to stand at normal temperature for 20 min and then analyzed using high performance liquid chromatography.

The pH was measured by a pH meter (Testo-206, Testo, Germany). The conductivity measurement was carried out using a conductivity meter (Starter 3100C/B, Ohaus, USA). DBP concentration was measured by high performance liquid chromatography (Agilent 1200-6460 QQQ, Agilent, USA). The total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), and chemical oxygen demand (COD) were tested according to the standard methods. Inductively coupled plasma atomic emission spectroscopy (Optima 7300 DV, Perkin Elmer, USA) was used to measure the metal ion concentration. In this paper, all experiments were repeated twice. The experimental error was around 5%.

**Table 1** | Characteristics of the plastic factory wastewater

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
<th>Average value and standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.15–10.23</td>
<td>9.24 ± 0.22</td>
</tr>
<tr>
<td>Conductivity (mS·cm(^{-1}))</td>
<td>1.02–3.78</td>
<td>2.37 ± 0.31</td>
</tr>
<tr>
<td>COD (mg·dm(^{-3}))</td>
<td>435–1,328</td>
<td>816 ± 141</td>
</tr>
<tr>
<td>TS (mg·dm(^{-3}))</td>
<td>2,100–6,210</td>
<td>4,150 ± 1,260</td>
</tr>
<tr>
<td>TDS (mg·dm(^{-3}))</td>
<td>1,930–5,870</td>
<td>3,420 ± 1,320</td>
</tr>
<tr>
<td>TSS (mg·dm(^{-3}))</td>
<td>94–375</td>
<td>185 ± 89</td>
</tr>
<tr>
<td>Fe (mg·dm(^{-3}))</td>
<td>0.18–1.34</td>
<td>0.81 ± 0.35</td>
</tr>
<tr>
<td>Cu (mg·dm(^{-3}))</td>
<td>0.41–1.03</td>
<td>0.72 ± 0.26</td>
</tr>
<tr>
<td>Cr (mg·dm(^{-3}))</td>
<td>0.35–1.53</td>
<td>1.03 ± 0.42</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Effect of PEC conditions

Electrical energy and anode plate consumption are important economic parameters in this study. The electrical energy consumption of removing 1 ppm of DBP ($Q$, J·ppm⁻¹/C₀) was calculated using Equation (5) (Aswathy et al. 2016; Shuman et al. 2016):

$$Q = \frac{UIt}{C_0 - C_t} \times 3600$$  \hspace{1cm} (5)

The consumption quality of the anode plate for removing 1 ppm of DBP ($S$, mg·ppm⁻¹) was calculated using Equation (6):

$$S = \frac{m_0 - m_t}{C_0 - C_t}$$  \hspace{1cm} (6)

The DBP removal efficiency ($H$) was determined according to Equation (7):

$$H = \frac{C_0 - C_t}{C_0}$$  \hspace{1cm} (7)

where $C_0$ and $C_t$ represent, respectively, the initial and the final concentrations of DBP in ppm. $U$ is average voltage in V; $I$ is current in A; $t$ is the reaction time in h, $\theta$ represents the duty cycle (when the $\theta = 1$ of the power supply by direct current). $m_0$ and $m_t$ represent initial and the final mass, respectively, of the anode plate in mg.

In the present study, the effect and the energy efficiency of the treatment were considered. As shown in Figure 2(a), the electrical energy consumption of PEC in removing DBP is markedly less than that required by traditional EC. PEC has an energy consumption of 860 J·ppm⁻¹, whereas traditional EC has an energy consumption of 1,420 J·ppm⁻¹. The consumption of the anode plate in the removal of DBP...
by PEC and traditional EC are 0.35 and 0.59 mg·ppm⁻¹, respectively. Therefore, PEC exhibits higher removal efficiency and more efficient energy consumption, compared with traditional EC.

PEC involves a series of chemical and physical mechanisms (Jiménez et al. 2012). Aluminum and iron are regarded as the most widely used anode material, and main reactions occur based on Equations (8) and (9):

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- 
\end{align*}
\]

(8) (9)

The ferrous ions (Fe²⁺) will be oxidized easily to ferric ions (Fe³⁺) in the presence of oxygen:

\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{OH}^- 
\]

(10)

At the cathode water will be hydrolyzed:

\[
\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- 
\]

(11)

Dissolution of aluminum and iron in water produces a gelatinous suspension by reaction with hydroxide ions, which can purify wastewater by either complexation or electrostatic attraction followed by coagulation. A gelatinous compound was formed in accordance with Equations (12) and (13):

\[
\begin{align*}
\text{Fe}^{3+} + 3 \text{H}_2\text{O} & = \text{Fe(OH)}_3 + 3 \text{H}^+ \\
\text{Al}^{3+} + 3 \text{H}_2\text{O} & = \text{Al(OH)}_3 + 3 \text{H}^+ 
\end{align*}
\]

(12) (13)

To determine the more effective electrode, the effects of aluminum and iron were evaluated. Figure 2(b) shows the efficiency of DBP wastewater treatment by PEC with iron. The interelectrode distance between electrodes was 10 mm. The tested current densities were 5–30 mA·cm⁻², and the removal efficiency was enhanced with increases in current density and reaction time. In addition, with current densities of 20 and 30 mA·cm⁻² and a PEC time of 10 min, DBP removal efficiency reached 73%. With a current density of 15 mA·cm⁻², a longer PEC time was needed to obtain similar experimental results. Meanwhile, at current densities of 5 and 10 mA·cm⁻², the DBP removal efficiency dropped to 54% for all PEC times tested. Figure 2(c) shows the removal efficiency of DBP wastewater by PEC with aluminum. The aluminum behaved similarly to iron. However, the treatment efficiency of aluminum was lower than that of the iron; the treatment efficiency was below 65% for all PEC times investigated.

Figure 2(d) compares the power consumption of the iron and aluminum electrodes. As shown in Figure 2(d), the iron anode consumes less electrical energy, i.e., 0.35–3.10 kWh per cubic metre of synthetic wastewater.

The conclusion can be drawn from Figure 2(b)–2(d) that the removal efficiency varied between the iron electrode and the aluminum electrode. This difference can be explained by the following points. (1) In the solution containing aluminum hydroxide, ion transfer could be more difficult, resulting in increased resistance and power consumption (Asaithambi et al. 2012; Li et al. 2016a, 2016b). (2) Aluminum exhibits a greater inclination than iron toward passivation, resulting in the termination of anodic dissolution. This occurrence reduces the current efficiency and treatment efficiency. Thus, iron acts as an anode in treating DBP wastewater, which was in accordance with our results.

Duty cycle is a key parameter that distinguishes between PEC and traditional EC. This factor can influence sewage purification economics and PEC floc size, production rate of bubbles, and coagulant dosage (Franz et al. 2002; Bayramoglu et al. 2007; Essadki et al. 2008). Figure 3(a) presents the removal efficiency of the DBP as a function of duty cycle and PEC time. Figure 3(b) shows power consumption as a function of duty cycle and PEC time in the removal of DBP wastewater. When the duty cycle was 0.6, the power consumption was lower than the duty cycle, i.e., 0.3 and 0.9.

The interelectrode distance is another key parameter affecting PEC. Figure 3(c) shows the treatment efficiency of DBP as a function of interelectrode distance and PEC time. Figure 3(d) presents the power consumption of synthetic wastewater treatment as a function of interelectrode distance and PEC time. Figure 3(c) and 3(d) indicate that the lowest power consumption was obtained when the interelectrode distance was 10 mm; meanwhile, power consumption increased when the interelectrode distance was 15 and 5 mm. When the interelectrode distance was small (<5 mm), the produced ions could be hardly diffused and could not be effectively combined with DBP molecules, resulting in a relatively low treatment effect. When distance increased (10–15 mm), the transfer of produced ions was slower, thereby increasing the opportunity for pollutant adsorption (Daneshvar et al. 2004). Moreover, increased production of flocs indicates an enhanced treatment effect. However, Figure 3(c) reveals that removal efficiency was reduced when the interelectrode distance exceeded 15 mm. This result can be explained as follows. When distance increased, the production rate of bubbles weakened. Thus, the flotation effect was also reduced, leading to a
decline in treatment effect. Simultaneously, when the inter-electrode distance increased, the energy consumption of electrolysis was also increased.

**Effect of environmental factors**

These experimental conditions remained valid when these factors were changed: (1) pH and (2) DBP concentration. The typical pH of the actual plastic factory wastewater was altered. Consequently, DBP solutions with different initial pH values (3.0, 8.5, 12.0) were studied. Figure 4(a) shows the effect of pH on the efficiency of DBP treatment by PEC.

The treatment efficiency significantly decreased with decreasing or increasing initial pH. At pH of 3 or 12, PEC time had to be increased to obtain improved treatment results. This result can be explained as follows. (1) In an acidic environment, more hydroxide ions are neutralized by hydrogen ions, and an insufficient amount of flocs is produced, leading to a decrease in removal efficiency (Daneshrav et al. 2006; Liang et al. 2016; Wei et al. 2016). (2) In an alkaline environment, a dominant position is occupied by the Fe(OH)$_4$$^-$, which impedes the formation of flocs (Yilmaz et al. 2005).

Figure 4(b) shows the effect of DBP concentration on the efficiency of DBP wastewater treatment by PEC. Figure 4(b) shows that the initial concentration is inversely proportional to removal efficiency. This result can be explained by Faraday’s law (Equation (14)). At the same current density and time for all DBP concentrations, a constant amount of Fe$^{2+}$ is dissolved into the solution, which suggests that the same amount of flocs is formed in the solution. The result directly shows that the flocs cannot sufficiently adsorb all of the DBP molecules (Bagga et al. 2008; Sun et al. 2015; Yu et al. 2015).

$$\Delta M = \frac{MIT}{nF}$$

(14)
where $\Delta M$ is the amount of iron dissolution (g); $M$ is the molecular weight of iron (g·mol\(^{-1}\)); $t$ is the time of pulse of electro-coagulation; $F$ is the Faraday constant ($F = 96,487$ C·mol\(^{-1}\)).

### Treatment of actual plastic factory wastewater

Figure 4(c) shows the treatment of actual plastic factory wastewater samples by applying optimal PEC conditions.

### Table 2 | Characteristics of the plastic factory effluent before and after treatment

<table>
<thead>
<tr>
<th>Property</th>
<th>Expt. 1 Before/after</th>
<th>Expt. 2 Before/after</th>
<th>Expt. 3 Before/after</th>
<th>Expt. 4 Before/after</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBP removal rate (%)</td>
<td>70.1</td>
<td>69.5</td>
<td>68.7</td>
<td>70.3</td>
</tr>
<tr>
<td>Conductivity (mS·cm(^{-1}))</td>
<td>1.7/1.7</td>
<td>2.5/2.4</td>
<td>1.9/2.0</td>
<td>3.2/3.1</td>
</tr>
<tr>
<td>COD (mg·dm(^{-3}))</td>
<td>529/57</td>
<td>936/79</td>
<td>728/156</td>
<td>769/134</td>
</tr>
<tr>
<td>TS (mg·dm(^{-3}))</td>
<td>NA</td>
<td>2,860/2,150</td>
<td>4,630/1,870</td>
<td>5,140/1,920</td>
</tr>
<tr>
<td>TDS (mg·dm(^{-3}))</td>
<td>2,790/2,210</td>
<td>5,260/2,180</td>
<td>3,160/1,590</td>
<td>3,680/2,460</td>
</tr>
<tr>
<td>TSS (mg·dm(^{-3}))</td>
<td>120/21</td>
<td>210/19</td>
<td>NA</td>
<td>310/18</td>
</tr>
<tr>
<td>Fe (mg·dm(^{-3}))</td>
<td>0.45/0.47</td>
<td>0.52/0.50</td>
<td>1.17/1.02</td>
<td>0.62/0.63</td>
</tr>
<tr>
<td>Cu (mg·dm(^{-3}))</td>
<td>0.32/0.28</td>
<td>NA</td>
<td>NA</td>
<td>0.23/0.21</td>
</tr>
<tr>
<td>Cr (mg·dm(^{-3}))</td>
<td>NA</td>
<td>0.78/0.65</td>
<td>NA</td>
<td>0.86/0.73</td>
</tr>
</tbody>
</table>

NA: not available.
described in the previous section. Table 2 compares the properties of the plastic factory effluent before and after PEC. Figure 4(c) and Table 2 present the result. The treatment effect was satisfactory. However, a deficiency was also observed. Further study has to be conducted to improve the effects of PEC.

CONCLUSIONS

To achieve a more effective treatment of plastic factory effluent, conducting a study on the treatment of DBP wastewater is a necessary step. We investigated the efficiency of DBP wastewater treatment by PEC. The experimental data indicated that under similar conditions, the iron was preferable to aluminum in terms of treatment efficiency and power consumption. We also identified the initial pH and initial DBP concentration as influencing factors. The current density of 15 mA cm⁻² could also be used. However, a longer PEC time was required. The overall data also suggested that the interelectrode distance of 10 mm and duty cycle of 0.6 were suitable for this study. Overall, the PEC method can treat the plastic factory effluent, thereby reducing pollution caused by this industrial wastewater.

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