Electrochemical oxidation treatment of coal tar wastewater with lead dioxide anodes
Qiang Zhao, Feng Wei, Liman Zhang, Yang Yang, Shuang Lv and Yingwu Yao

ABSTRACT
In this study, coal tar wastewater was treated by electrochemical oxidation technology using lead dioxide anodes. The influence of operating parameters, including applied current density, electrode gap and initial pH value, on the removal ratio of COD was investigated. The results demonstrated that the COD removal ratio reached 90.5% after 3.5 h electrolysis with the current density at 3 A dm\(^{-2}\) and electrode gap at 1.0 cm. Correspondingly, the COD decreased from 5,125 mg L\(^{-1}\) to 487 mg L\(^{-1}\), which fitted the wastewater discharge standards of China, and the specific energy consumption (SEC\(_{\text{COD}}\)) was 35.3 kWh kg\(_{\text{COD}}\). Not only was the COD removal ratio only 77.1% after 2 h electrolysis but the BOD\(_5\)/COD ratio of the wastewater reached 0.44, which could be biochemically treated, and the SEC\(_{\text{COD}}\) decreased by 34.3%. Moreover, the main composition of pristine wastewater before and after 2 h electrolysis was analyzed by GC-MS, and the disappearance of macromolecules (such as ethyl-2-pyrenemethanol) and the production of small molecules (such as propane-1,3-diol) could improve the biodegradability of the wastewater. Therefore, electrochemical oxidation for 2 h is a promising alternative for pretreatment of coal tar wastewater prior to biological treatment.

INTRODUCTION
Coal tar is an important product of the coking industry, which is commonly used in the production of polymer materials (such as plastics and resins), pharmaceutical reagents, pesticides and paints (Luo et al. 2016; Wang et al. 2016). With the rapid development of coal chemical and coal tar refining industries, the amount of coal tar wastewater has increased significantly, and the composition has become increasingly complex, including phenols, polycyclic aromatic hydrocarbons, and cyanide, all of which are highly toxic to most microorganisms (Ma et al. 2018). Improper disposal of coal tar wastewater results in serious environmental pollution and threats to human health. Therefore, a series of treatment methods, such as ozonation (Yang et al. 2013), biological denitrification (Lu et al. 2011), and Fenton reactions (Zhu et al. 2011), have been employed to degrade coal tar wastewater. However, these approaches have encountered many problems, such as overloading of wastewater treatment equipment, high values of COD after treatment, intensive investment and large area requirement by denitrification units, and high operation costs. Therefore, degradation techniques for coal tar with high efficiency are high in emerging demand.

Electrochemical oxidation has been proposed as an efficient and environmentally friendly approach for treating non-biodegradable organic contaminants (Kenova et al. 2018). In addition, this method has exhibited some excellent advantages, such as robustness, versatility, automation amenability, and no necessity to add other chemicals (Kaur et al. 2017). Under appropriate conditions, electrochemical oxidation can significantly remove organic compounds, ammonia nitrogen, and colors (Miyata et al. 2011; Bai et al. 2017). However, the disadvantage of the electrochemical oxidation treatment wastewater process is the high energy consumption. In that respect, anode materials play crucial roles in the electrochemical oxidation process, which strongly affect the current efficiency. In recent decades, a lot of electrode materials have been examined to improve the effectiveness of oxidation and current efficiency, such as graphite, IrO\(_2\), RuO\(_2\), PbO\(_2\) and...
BDD electrodes (Gao et al. 2017; Kaur et al. 2017; Agustina et al. 2019). Among all the materials, PbO$_2$ and BDD are the most attractive electrodes because of their high oxygen evolution overpotential. However, the high cost of BDD anodes limits their large-scale application. Therefore, PbO$_2$ electrodes have become popular due to their good electrical conductivity, high chemical inertness, and low cost, which have been widely applied to remove organic pollution in wastewater, including medical wastewater (Dai et al. 2016), textile wastewater (Aquino et al. 2014), and coking wastewater (Shen et al. 2012). These processes proved to be efficient methods in the treatment of industrial wastewater.

The primary objective of this study is to evaluate the performance of the electrochemical oxidation treatment of coal tar wastewater with PbO$_2$ anodes. The main influencing factors, such as current density, pH values, and electrode gap, on the COD removal percentage of coal tar wastewater are discussed. After that, the reaction kinetics of coal tar wastewater treatment are also established. Finally, the main components of coal tar wastewater before and after electrochemical oxidation are identified using GC-MS.

**EXPERIMENTAL**

**Coal tar wastewater**

The coal tar wastewater used in this study was obtained from the coal tar chemical company located in Hebei province, China. The factory produces on average 20 m$^3$ d$^{-1}$ of wastewater and the characteristics of the wastewater are relatively stable with different seasons. The main characteristics of the wastewater are shown in Table 1.

**Experimental procedure**

Electrochemical oxidation experiments were carried out under galvanostatic conditions in an undivided Plexiglas reactor ($10 \times 10$ cm, 10 cm of height, 1,000 mL capacity), and the working volume of the electrochemical reactor was 800 mL. The PbO$_2$ electrode ($10 \times 10$ cm, 100 cm$^2$) and a stainless-steel net ($10 \times 10$ cm, 100 cm$^2$) were respectively adopted as the anode and cathode. The pH of the wastewater was adjusted to a desirable value using NaOH and H$_2$SO$_4$ solutions. A digital DC power supply (MP1560D, China) with digital displays was used as the electric current source for all the experiments. Because the initial concentration of coal tar wastewater is certain and has high conductivity, the operating parameters we discussed in this study include the current density, initial pH, and plate spacing. During the experiments, the wastewater was mainly stirred by the H$_2$ gas bubbles generated on the cathode, the current density varied from 2 to 5 A dm$^{-2}$, initial pH value varied from 2 to 10, and the plate spacing varied from 0.5 to 2.0 cm. After that, the coal tar wastewater was treated under optimized conditions to investigate treatment performance and the variation of COD in the wastewater.

**Analytical methods**

The electrocatalytic degradation of coal tar wastewater was monitored by a COD test. The COD test was performed according to the Standard Methods for Water and Wastewater Examination of China (HJ/T399-2007). The COD removal efficiency was calculated by Equation (1) and the instantaneous current efficiency (ICE) was calculated by Equation (2):

$$\text{COD removal efficiency (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100\% \quad (1)$$

$$\text{ICE} = \frac{(\text{COD}_1 - \text{COD}_{t+\Delta t})FV}{8FMC} \times 100\% \quad (2)$$

where COD$_0$ is the initial value of the COD of wastewater (g L$^{-1}$); COD$_t$ is COD value (g L$^{-1}$) at time $t$; COD$_{t+\Delta t}$ is COD value (g L$^{-1}$) at time $t + \Delta t$; $F$ is the Faraday constant (96,487 C mol$^{-1}$); $V$ is the volume of the treated wastewater (L); and $t$ is the electrolysis time(s).

The pH and the conductivity were determined by a pH-meter (PHS-3C) and conductivity meter (DDS-11A), respectively. Biological oxygen demand (BOD$_5$) was measured by the dilution and seeding method according to HJ 505-2009. The Pb ion concentration in the solution after electrolysis reaction was detected by an atom absorption spectrometer (AAS, Thermo M6).

The specific energy consumption in terms of COD mass removed (SEC$_{\text{COD}}$, kWh kg$^{-1}$) was calculated by

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg L$^{-1}$)</td>
<td>5,125</td>
</tr>
<tr>
<td>BOD$_5$ (mg L$^{-1}$)</td>
<td>388</td>
</tr>
<tr>
<td>pH</td>
<td>3.9</td>
</tr>
<tr>
<td>Conductivity (mS cm$^{-1}$)</td>
<td>25.5</td>
</tr>
<tr>
<td>chloride ions (mg L$^{-1}$)</td>
<td>74</td>
</tr>
</tbody>
</table>
Equation (3) (Cecconet et al. 2019):

\[
\text{SEC}_{\text{COD}} = \int_0^t P(t) dt \quad \text{COD}_{\text{m}}
\]

where \( P(t) \) is the recorded power demand by the applied potential, \( t \) is time, and \( \text{COD}_{\text{m}} \) is the mass of removed COD.

The pristine coal tar wastewater and wastewater solution after 2 h electrolysis were extracted by isopyknic dichloromethane (DCM), respectively, and were then injected into the GC-MS (Agilent GC 6890 coupled with Agilent 5973 mass spectrometer) for content analysis. The injected volume was 20 \( \mu \)L. Helium was used as the carrier gas with a flow rate of 3 mL min \(^{-1} \). The injector temperature was set at 300 °C. The column temperature was held at 50 °C for 5 min, and then heated at 20 °C min \(^{-1} \) to 280 °C, and maintained at this temperature for 10 min.

**RESULTS AND DISCUSSION**

**Effect of current density**

Figure 1(a) shows the influence of current density on the electrocatalytic degradation efficiency of coal tar wastewater. When the current density increased from 2 to 3 A dm \(^{-2} \) after reaction for 3.5 h, the COD removal ratio increased from 75.0% to 88.9%, which is ascribed to more hydroxyl radicals generated at higher current density. However, when the current density increased from 3 to 5 A dm \(^{-2} \), the COD removal ratio increased only by 3.5% after 3.5 h, probably due to the fact that the oxidation was controlled by the rate at which organic molecules were transferred from the bulk solution to the electrode surface rather than the generation rate of hydroxyl radicals (Muazu et al. 2015). In addition, the removal of COD was faster at the beginning of the experiment, but gradually slowed down with the extension of degradation time. The possible reason is that the content of aromatic organic matter in the wastewater was higher at the beginning, which decreased after a period of degradation time to produce a large number of byproducts, and the degradation rate of byproducts by the electrode was lower than that of the aromatic organic matter (Hurwitz et al. 2014). Therefore, the removal curve of COD became gradually more gentle with the extension of time.

Figure 1(b) presents the COD degradation kinetics of coal tar wastewater with different current densities. The values of \( R^2 \) (correlation coefficient) and \( k_1 \) (rate constant) are summarized in Table 2. A considerable increase of the rate constant with the increasing current density could be observed. For an applied current density of 2 A dm \(^{-2} \), the rate constant was only 0.3910 h \(^{-1} \), while it was 0.6336 h \(^{-1} \).
under the current density of 3 A dm\(^{-2}\). The latter was about 1.6 times higher than the former. The results indicated that the driving force of the electron transfer in the electrode reactions became greater with the increase of current density, and higher current density contributed to a higher rate of hydroxyl radical generation responsible for the coal tar waste-water oxidation processes (Muazu et al. 2015). In addition, the increased anodic current density amplified the oxygen evolution reaction, and then the formation and detachment of oxygen bubbles facilitated the diffusion of organic matter in solution (Duan et al. 2012). For an applied current density of 4 A dm\(^{-2}\), the rate constant was 0.7079 h\(^{-1}\), while it was 0.7665 h\(^{-1}\) under the current density of 5 A dm\(^{-2}\).

Figure 1(c) shows the variation of ICE with time for the degradation assays performed at 2 A dm\(^{-2}\), 3 A dm\(^{-2}\), 4 A dm\(^{-2}\) and 5 A dm\(^{-2}\), respectively. The higher applied current intensity gave higher loss in the current efficiency, revealing that the electrolysis mainly operated under mass transport control. The loss of current efficiency was due to the side reactions, such as oxygen evolution and electrolyte decomposition (Fajardo et al. 2017). These side reactions were enhanced at higher applied current density.

The applied current depends on the enterprise’s requirements for wastewater discharge and the treatment cost of wastewater. In the process of electrolysis, a further increase of current density up to 5 A dm\(^{-2}\) did not produce significant improvements on COD removal, but gave higher loss current efficiency. In order to obtain the best results, both in COD removal and in electrolytic efficiency, the optimum value for the current density in this study was 3 A dm\(^{-2}\).

### Effect of pH

Figure 2 shows the COD removal ratio of coal tar wastewater versus time under different pH values. It can be seen that the COD removal ratio decreased with increasing pH, and the highest value was observed at pH = 2 after 3.5 h degradation. Figure 2(a) shows that along with the pH of coal tar wastewater increasing from 2 to 10, the COD removal percentage decreased from 91.0% to 72.1% after 3.5 h. Figure 2(b) shows the first-order reaction kinetics fitting plots for different pH. The values of \(R^2\) and \(k_1\) are shown in Table 2. These results indicated that the coal tar degradation for different pH was in agreement with

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**Table 2: Kinetics parameters of electrochemical degradation of coal tar wastewater by lead dioxide electrode with different operational parameters**

<table>
<thead>
<tr>
<th>Current density (A dm(^{-2}))</th>
<th>Electrode gap (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(k_1) (h(^{-1}))</td>
<td>0.3910</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9961</td>
</tr>
<tr>
<td>Removal ratio (%)</td>
<td>75.0</td>
</tr>
<tr>
<td>Initial pH value</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>(k_1) (h(^{-1}))</td>
<td>0.7050</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9932</td>
</tr>
<tr>
<td>Removal ratio (%)</td>
<td>91.0</td>
</tr>
</tbody>
</table>

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**Figure 2**: The effect of pH, i.e. \(pH = 2\), \(pH = 4\), \(pH = 7\), \(pH = 10\), on (a) the removal of COD with time, (b) \(\ln(COD_0/COD_t)\) with time.
pseudo-first-order reaction kinetics. There was a decrease in $k_1$ with the increase of initial pH, which might be because the electrocatalytic oxidation reaction always competes with the anodic oxygen evolution reaction in the electrochemical degradation process for coal tar wastewater. In an alkaline environment, the oxygen evolution potential is relative low, and an oxygen evolution side reaction easily occurs to compete with the electrocatalytic oxidation of wastewater. However, under acidic conditions, the oxygen evolution potential of the electrode is high, and the oxygen evolution reaction will be suppressed (Wang et al. 2011). Moreover, some researchers have found that active hydroxyl radicals are of stronger oxidative capability toward organic molecules under acidic conditions, further improving the degradation effect of coal tar wastewater (Li et al. 2018).

However, the low initial pH exhibits a corrosive effect on the electrode, which will decrease the catalytic activity of the electrode and increase the cost. Although the maximum COD removal ratio was 91.0% obtained at pH = 2.0, we chose pH = 4.0 as the optimal pH value because of the similar COD removal (88.9%) at the more implementable subacidic condition, which means the pH adjustment is not required and thus treatment costs will be reduced in practical applications.

**Effect of electrode gap**

Figure 3 shows the influence of electrode gap on the electrocatalytic degradation efficiency of coal tar wastewater. As shown in Figure 3(a), the electrode gap has a slight effect on the COD degradation of coal tar wastewater. When the electrode distance was less than 1.0 cm, the COD removal ratio of coal tar wastewater was no different under different electrode gaps. However, when the distance was greater than 1.0 cm, the COD removal ratio gradually decreased as the electrode distance increased. For example, when the electrode gap increased from 1.0 cm to 2.0 cm, the removal ratio decreased from 90.5% to 84.6%, and the $k_1$ value also decreased from 0.6867 h$^{-1}$ to 0.5480 h$^{-1}$. This is because larger electrode distance will bring on the vanishing and quenching of highly active hydroxyl radicals generated on the surface of the electrode.

As shown in Figure 3(b), as the distance between anode and cathode increased, the energy consumption also increased. Similarly, the increase on energy consumption was not obvious when the electrode distance was less than 1.0 cm. But when the electrode gap was greater than 1.0 cm, the energy consumption was significantly enhanced. For example, when the COD removal ratio of coal tar wastewater was 80%, the energy consumption was 19.6, 20.1, 28.7 and 35.3 kW h kg$^{-1}$C_0 if the electrode gaps were 0.5 cm, 1.0 cm, 1.5 cm and 2.0 cm, respectively. Short circuits can be made in the smaller electrode gap, and wastewater treatment costs increased with the larger electrode gap (He et al. 2011). After considering the COD removal ratio and energy consumption, the 1.0 cm distance was selected as the most suitable electrode gap.

**Energy consumption and biochemical study**

As shown in Figure 4(a), after electrochemical oxidation with current density at 3 A dm$^{-2}$, pH = 4 and electrode gap at 1.0 cm for 3.5 h, the COD decreased from 5,125 mg L$^{-1}$ to 487 mg L$^{-1}$, and the COD removal reached 90.5%. The remaining COD was 487 mg L$^{-1}$, which was lower than the industrial wastewater third-class discharge standard of China at 1,000 mg L$^{-1}$. The effective removal of coal tar wastewater by other oxidation methods, such as the ozonation and Fenton processes, have reported by previous literature.

Table 3 presents the removal percentages of COD in the same coal tar wastewater with different methods. The COD removal efficiency of electrochemical oxidation was compared with the ozonation and Fenton processes. As
can be seen, under the best conditions, the highest COD removal was obtained by electrochemical oxidation, followed by Fenton and ozonation. These results indicate that three methods were feasible for the removal of COD from wastewater. However, as proposed previously, due to insufficient hydroxyl radical generation by ozone in the oxidation process and high investment, the chemical oxidation approach requires costly strong oxidizers. Therefore, anodic oxidation with PbO2 electrodes is an effective method to degrade coal tar wastewater and has promising application prospects in wastewater treatment.

For industry application, it is very important to estimate the cost of the electrochemical oxidation treatment of wastewater. As shown in Figure 4(a), the initial BOD5 value of coal tar wastewater was below 390 mg L⁻¹, and the initial COD value was 5,125 mg L⁻¹. Hence the BOD5/COD ratio was only 0.08, which revealed that the coal tar wastewater was non-biodegradable and microbiologically toxic. According to the reported literature, when the BOD5/COD ratio exceeds 0.35, the solution is regarded as biodegradable (Tan et al. 2016). When the electrocatalytic time reached 2 h, the BOD5/COD ratio of the coal tar wastewater reached 0.44, which could be biochemically treated. At this time, the SECOD was 25.7 kWh kg⁻¹. The results revealed that combined treatment of electrochemical oxidation for 2 h and then a biological process was less expensive in comparison with a single stage of electrochemical oxidation for 3.5 h. It has been reported in previous literature that biological methods (such as aerobic and anaerobic) can effectively degrade coal tar wastewater. Lu et al. (2011) treated coal tar wastewater by the aerobic biological method, and the efficiencies of COD and NH4⁺-N removal reached 92.8%–96.0% and 71.3%–100%. Park et al. (2012) treated coal tar wastewater using a membrane-less tubular microbial fuel cell (MFC); the MFC achieved a high level of COD removal (88%) and the electrical voltage reached as high as 543 mV (10 kΩ) on day 7, and the MFC system was effective for removing coal tar compounds. However, the large amounts of activated sludge that are produced during aerobic processes require further treatment and disposal. Thus, considering the cost of treatment and the environmental compatibility of biological treatment, a two-stage electrochemical oxidation/anaerobic biological treatment could be an effective treatment approach for coal tar wastewater degradation.

The composition analysis of coal tar wastewater and its degradation byproducts

Next, we employed GC-MS to analyze the composition of the DCM extracting solution from coal tar wastewater before and after electrolysis for 2 h. As shown in Figure S1 (Supplement), after extraction of DCM from pristine coal tar wastewater, the GC spectrum exhibited multiple strong signals corresponding to the series of organic contents in the wastewater. By analyzing the mass spectra relating to the GC peak signals with different retention times...
(Figure S2-S8, Supplement), the component and molecular structure could be confirmed and are summarized in Table 4. The strong peak at the retention time of 1.032 min belongs to the solvent DCM. As shown in Table 4, from a retention time of 1.593 min to 10.46 min, the GC signal is relatively low and composed of small molecules with low concentration, such as ethylene, ethanol, acetaldehyde, propionic acid, N,N-dimethylformamide, 1-butylene, valeric acid, diethyl sulfide, and aniline. These molecules are easily biodegraded. After that, the multiple peaks with strong intensity from 13.279 min to 17.841 min should be the main content of coal tar wastewater, which are mainly polycyclic aromatic compounds, including derivatives of naphthalene, quinoline, anthracene, pyrene, and coronene. These aromatic molecules are chemically structurally stable and non-biodegradable.
After electrolysis for 2 h by PbO₂ electrodes, as shown in Figure S9 (Supplement), the intensity of GC signals decreased sharply, especially peaks in the small molecular zone from 6.229 min to 8.222 min, and the polycyclic aromatic peaks from 13 min to 18 min could hardly be detected. As shown in Table 5, after 2 h electrolysis, ethylene, ethanol, propionic acid, 1-butylene, diethyl sulfide, and aniline could still exist in solution, but the concentration decreased dramatically. Different from pristine coal tar wastewater, the polycyclic aromatic compounds could not be found after treatment by electrochemical degradation, and might have been decomposed to small linear or aromatic molecules, such as acetic acid, propane-1,3-diol, N,N-dimethyl ethanol amine, benzene, monomethylaniline, xylenes, and phenylacetylene. All these byproducts are more biodegradable than polycyclic aromatic compounds. Therefore, electrochemical treatment of coal tar wastewater using PbO₂ electrodes for 2 h could promote the biodegradability and the BOD₅/COD ratio of the solution, which is in accordance with the experimental results we discussed above.

### The reusability and safety of lead dioxide electrodes

Figure 5 shows the removal efficiency of COD by PbO₂ electrodes after 3.5 h for 20 successive reactions. Although a slight decrease in COD removals can be observed, the degradation efficiency was still up to 86.15% after 20 cycles. The results demonstrate that PbO₂ electrodes possess excellent reusability in organic pollutant degradation. The main drawback of PbO₂ electrodes is the possible release of Pb ions in the electrolysis process, which would present a potential risk for industrial applications of electrochemical technology. To evaluate the safety of PbO₂ electrodes, the Pb ion concentration in the electrolyte after 3.5 h of electrolysis was analyzed by AAS as 0.020 mg L⁻¹, which was below the integrated wastewater discharge standard of China (GB 8978-1996, 1 mg L⁻¹). Even after ten cycles of usage,
results indicate that PbO2 electrodes have excellent safety and reusability in degrading coal tar wastewater.

**CONCLUSION**

Electrochemical oxidation technology was adopted for the treatment of coal tar wastewater. The COD removal ratio reached 90.5%, and the COD decreased from 5,125 mg L⁻¹ to 487 mg L⁻¹ after electrolysis for 3.5 h by PbO2 anodes with current density at 3 A dm⁻² and electrode gap at 1.0 cm, which met the discharge standard of industrial wastewater of China (GB 8978-1996), and the SEC COD was 35.3 kWh kg⁻¹COD. The electrochemical oxidation process followed the pseudo-first-order kinetics model. The results revealed that the electrochemical oxidation method could effectively treat coal tar wastewater, but the energy consumption was relatively high. It was noteworthy that the COD removal ratio of coal tar wastewater reached 77.1% and the BOD₅/COD ratio reached 0.44 after 2 h electrolysis, which could be biochemically treated, and the SEC COD was only 23.7 kWh kg⁻¹COD. The composition analysis of coal tar wastewater by GC-MS proved that 2 h electrolysis could promote the BOD₅/COD ratio and biodegradability of the solution.

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**NOTES**

The authors declare no competing financial interest.

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