A newly designed electric assisted micro-electrolysis filter (E-ME) was developed to investigate its degradation efficiency for coking wastewater and correlated characteristics. The performance of the E-ME system was compared with separate electrolysis (SE) and micro-electrolysis (ME) systems. The results showed a prominent synergistic effect on COD removal in E-ME systems. Gas chromatography/mass spectrometry (GC–MS) analysis confirmed that the applied electric field enhanced the degradation of phenolic compounds. Meanwhile, more biodegradable oxygen-bearing compounds were detected. SEM images of granular activated carbon (GAC) showed that inactivation and blocking were inhibited during the E-ME process. The effects of applied voltage and initial pH in E-ME systems were also studied. The best voltage value was 1 V, but synergistic effects existed even with lower applied voltage. E-ME systems exhibited some pH buffering capacity and attained the best efficiency in neutral media, which means that there is no need to adjust pH prior to or during the treatment process. Therefore, E-ME systems were confirmed as a promising technology for treatment of coking wastewater and other refractory wastewater.

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Keywords: Coking wastewater Micro-electrolysis Electrochemical COD removal
The raw wastewater used in this investigation was obtained from the outlet of a coke plant near Kunming, Yunnan, China. The main characteristics of the raw wastewater were as follows: the initial pH was in the range 6.1–6.4; the values of COD and NH$_3$-N were 5265–5865 mg/L and 684–704 mg/L, respectively.

1.2. Experimental system and procedure

The diagram of the experimental apparatus is shown in Fig. 1. A glass column was filled with a well-distributed mixture of GAC and ZVI. The mass ratio of GAC to iron filings was 2:1. In order to eliminate as much as possible the influence of adsorption from GAC on the ME process, a 0.5 hr immersion test of the GAC in a large amount of raw coking wastewater was conducted. Stainless steel net served as the cathode, and the ZVI/GAC bed as the anode, which was divided into two parts by stainless steel net and connected to a power source. The detailed structure of the ZVI/GAC bed is also shown in Fig. 1. The related parameters were designed as follows: diameter of the column 10 cm, height 30 cm, height of the solid filler 4 cm. A DC potentiostat was employed as the power supply with a voltage output up to 30 V and an air pump as the aerator. 600 mL raw coking wastewater was loaded into the experimental reactor.

1.3. Analytical methods

Samples were taken directly from the device without pH adjustment to further flocculate. The COD of the samples was analyzed by the potassium dichromate method (Gao et al., 2011). NH$_3$-N was determined according to the Chinese SEPA standard method by Nesslers reagent spectrophotometry. For the gas chromatography–mass spectrometry (GC–MS) analysis, effluent samples pretreated by trichloromethane liquid–liquid extraction were used for GC–MS analysis using the Agilent 7890 series GC system supplied with a 5975 mass selective detector. The GC program was as follows: injector temperature, 280°C; column temperature, 40–150–280°C (temperature program during run); carrier gas, helium; split ratio, 10:1; total flow rate, 1.0 mL/min. The relative content of organic compounds in the effluent was evaluated by the peak area from the results of GC–MS analysis.

2. Results and discussion

2.1. Synergetic effect within E-ME

2.1.1. Degradation performance

The performance of the coupled technique combining electrolysis (applied electric field) with micro-electrolysis (E-ME) was investigated by comparing with separate electrolysis (SE) and micro-electrolysis (ME). The removal ratios of COD and NH$_3$-N in SE, ME, and E-ME systems after 5 hr reaction at pH 6.4 are displayed in Fig. 2.

In contrast to the NH$_3$-N removal rate of 29% in SE, more than 59% and 60% NH$_3$-N removal rate could be achieved in ME and E-ME, respectively. It is easy to see that the ZVI/GAC bed played the dominant role in the removal of NH$_3$-N and
that the applied electric field did not show an obvious enhancement effect in NH₃-N removal. Meanwhile, a maximum COD removal efficiency of 80% was observed in E-ME, followed by 31% and 41% in SE and ME, respectively. It was noted that the COD removal efficiency in the integrated technology was consistently higher than the sum of the removal efficiencies of SE and EM, which indicated that applied electric field had the ability to enhance the efficiency of the ZVI/GAC bed significantly. The underlying mechanisms responsible for COD removal enhancement could be explained as follows: (1) The excellent adsorption capacity of GAC allows the organic pollutants to concentrate on its surface. The applied electric field gives rise to electrosorption on the ZVI/GAC bed, promoting the capture of organic pollutants (Huang and Su, 2010). (2) GAC is polarized under the applied electric field, forming a series of discrete microelectrodes (Song et al., 2016), degrading the attached organic pollutants through direct and indirect oxidation (Zhu et al., 2011). (3) the ZVI/GAC bed, working as an extended anode, provided more contact area for the redox reactions of pollutants and generated more H⁺ for iron-carbon micro-electrolysis (Bayramoglu et al., 2004). (4) The applied electric field dissolved more iron in the ZVI/GAC bed, leading to more significant effects of electron donation and flocculation (Huang et al., 2013). (5) As H₂O₂ is generated with air feeding, a large number of hydroxyl radicals may be generated at the ZVI/GAC bed to enhance the degradation of organic pollutants after coupling with the applied electric field (Brillas et al., 2009; Yan et al., 2011).

The reactions of radicals involved in the E-EM system can be represented as (Oturan et al., 2000; Qiang et al., 2002):

\[
O_2 + H^+ + 2e^- \rightarrow H_2O_2 \quad E_0(O_2/H_2O_2) = 0.69 \text{ V} \tag{1}
\]

\[
H_2O_2 + Fe^{3+} + H^+ \rightarrow Fe^{3+} + H_2O + OH^- \quad E_0(Fe^{3+}/Fe^{2+}) = 0.77 \text{ V} \tag{2}
\]

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E_0(Fe^{3+}/Fe^{2+}) = 0.77 \text{ V} \tag{3}
\]
2.1.2. Organic contaminant degradation characteristics

GC-MS analysis was performed to further investigate the changes of the main organic compounds among raw coking wastewater, ME effluent and E-ME effluent. According to the results of analysis of GC-MS chromatograms, the main components were classified as phenolic compounds, nitrogen heterocycles, cycloalkanes and oxygen-bearing compounds. The sum of the relative content of each classification is shown in Fig. 3. The typical results obtained through the analysis of GC-MS are listed in Table 1.

From Fig. 3, the main compounds in raw coking wastewater were phenolic compounds and nitrogen heterocycles, which are considered toxic and refractory for biodegradation. The total relative content of phenolic compounds was 48%, with 13 kinds of compounds detected (such as, phenol, 4-methyl-phenol, 4-methyl-phenol etc.). Nitrogen heterocycles represented 34% and comprised 17 kinds of compounds (such as benzonitrile, pyrrolidinone, indole, quinoline etc.).

Compared with raw coking wastewater, the relative content of nitrogen heterocycles in ME effluent was significantly reduced. At the same time, the relative contents of cycloalkanes and oxygen-bearing compounds were nearly doubled and increased to about 15%, respectively. Cycloalkanes are considered harmful to aquatic organisms, but they can be degraded by the sludge process. The oxygen-bearing compounds are also known as degradation products that would be mineralized to carbon dioxide by further treatment. Unfortunately, there was no significant decrease for phenolic compounds. Clearly, it is hard for the ME system alone to treat coking wastewater efficiently.

E-ME and ME had similar effects against nitrogen heterocycles, with the relative content decreasing from 34% to about 14%. However, the relative content of phenolic compounds was reduced dramatically after E-ME system treatment. Clearly, an applied electric field can enhance the degradation of phenolic compounds. These results were consistent with the compared results of COD and NH3-N removal rates in E-ME and ME discussed above. From Table 1, the relative content of phenol was slightly reduced in E-ME effluent and increased in ME effluent, which may due to new phenols being generated during the degradation of quinolones and indoles. Notably, most alkyl-phenols, especially methyl-phenol and ethyl-phenol, were removed in E-ME effluent. According to the statistical results shown in Fig. 3, the relative content of cycloalkanes increased from 10% to 21% after treatment by the E-ME system, similar to ME. Nevertheless, oxygen-bearing compounds, especially organic acids and esters (Table 1), were not detected in raw coking wastewater but emerged in ME effluent and increased significantly in E-ME effluent, as shown in Fig. 3. It can be concluded that, due to the synergistic effect between the applied electric field and ME, coking wastewater was degraded more completely.

2.2. Surface morphologies of activated carbon

The surface morphologies of GAC before experiment, after adsorption and after the E-ME experiment are shown in Fig. 4. As shown in Fig. 4a, pristine GAC material had a micro-porous structure without deposit. Nevertheless, the pores were blocked after immersion in raw coking wastewater (Fig. 4b). This shows that GAC had significant adsorption capability for coking wastewater. From Fig. 4c, GAC particles regained a great number of micro-pores after the E-ME experiment. It could be concluded from this phenomenon that adsorption was not the only process in E-ME systems, and that oxidation and electrophoresis may occur simultaneously at the micro-pores of GAC to degrade and release the attached contaminants. Similar processes have been proposed as the mechanisms of ME, in which organic contaminants are adsorbed and then reduced by GAC (Panizza and Cerisola, 2008; Kuramitz et al., 2001; Yuan et al., 2009). In fact, particulate substance coagulation by ferrous and ferric hydroxides and absorption by GAC would gradually decrease the number of reaction sites and thereafter result in the deterioration of treatment performance (Zhang et al., 2014). But such attachments were not observed at the micro-pores of GAC particles after the E-ME experiment. This indicated that the problems of inactivation and blocking of GAC were solved to some extent when ME was coupled with an applied electric field. This means that E-ME systems may maintain stable degradation efficiency over long periods of treatment.

2.3. Effect of pH in E-ME system

It has been very clear that pH is an important factor affecting the treatment efficiency in ME systems. Thus, it is reasonable to anticipate that pH would be a key factor of COD degradation in E-ME systems. Many studies have shown that COD removal from industry wastewater in ME systems is more effective with a lower pH value (Tseng et al., 2011; Ying et al., 2012). The reason is that ME treatment generally starts with the Fe/Fe2+ half-cell reaction, and a large amount of H+ would be consumed in the very first step according to Eqs. (4)–(8) (Zhang et al., 2014).

Iron anode (oxidation):

\[
\begin{align*}
\text{Fe(s)} & \rightarrow \text{Fe}^{2+}(aq) + 2e^- & E_0(\text{Fe}^{2+}/\text{Fe}) &= 0.44 \text{ V} \\
\text{Fe}^{2+}(aq) & \rightarrow \text{Fe}^{3+}(aq) + e^- & E_0(\text{Fe}^{3+}/\text{Fe}^{2+}) &= 0.77 \text{ V}
\end{align*}
\]

---

Fig. 3 – Organic compounds in raw coking wastewater, ME effluent and E-ME effluent, with 0.75 L/min aeration, initial pH 6.4 and reaction time 4 hr.
Carbon cathode (reduction) in the presence of oxygen:

Acid:

\[ \text{O}_2(\text{g}) + 4\text{H}^+ (\text{aq}) + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O} \quad \text{E}_0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V} \]  

\[ \text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^{-} \rightarrow 2\text{H}_2\text{O}_2(\text{aq}) \quad \text{E}_0(\text{O}_2/\text{H}_2\text{O}_2) = 0.68 \text{ V} \]  

Neutral to alkaline:

\[ \text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^- (\text{aq}) \quad \text{E}_0(\text{O}_2/\text{OH}^-) = 0.40 \text{ V} \]  

On the other hand, the electrolysis process with steel electrodes generally combines with electrocoagulation (EC) and electro-oxidation (Kong et al., 2006), and pH has been established as an important parameter influencing the performance of the EC process (Mollah et al., 2004). For instance, (1) pH influences the formation of flocs and oxidation, directly influencing the COD removal rate; (2) pH influences the corrosion of the iron electrode, indirectly affecting the COD removal rate.

The investigation of the effect of initial pH on E-ME performance was carried out with 6 V voltage and 0.75 L/min aeration, and the COD removal ratios after 2 hr for different initial pH are shown in Fig. 5. The highest COD removal efficiency was obtained when initial pH was 7 (65%), followed by 51%, 47%, 34% and 24% when the initial pH was 5, 3, 9 and 11, respectively. It should be noted that the E-ME system was more efficient in the neutral medium. Therefore, there is no need to adjust pH with a large amount of acid, which decreases the treatment cost compared with the ME process.

---

### Table 1 – Changes of main organic compounds for raw coking wastewater, SME effluent and E-ME effluent.

<table>
<thead>
<tr>
<th>Retention time</th>
<th>Main compound</th>
<th>Raw coking wastewater</th>
<th>SME effluent</th>
<th>E-ME effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.984</td>
<td>Pentanoic acid</td>
<td>–</td>
<td>–</td>
<td>1.55</td>
</tr>
<tr>
<td>10.463</td>
<td>3-Methyl-2-Cyclopenten-1-one</td>
<td>3.67</td>
<td>8.90</td>
<td>11.60</td>
</tr>
<tr>
<td>10.873</td>
<td>Phenol</td>
<td>10.50</td>
<td>16.77</td>
<td>8.45</td>
</tr>
<tr>
<td>11.034</td>
<td>Hexanoic acid</td>
<td>–</td>
<td>2.01</td>
<td>4.21</td>
</tr>
<tr>
<td>12.277</td>
<td>2-Methyl-phenol</td>
<td>5.02</td>
<td>3.02</td>
<td>1.19</td>
</tr>
<tr>
<td>12.628</td>
<td>Hexanoic acid, trimethylsilyl ester</td>
<td>–</td>
<td>–</td>
<td>1.53</td>
</tr>
<tr>
<td>12.639</td>
<td>4-Methyl-phenol</td>
<td>11.28</td>
<td>17.61</td>
<td>5.39</td>
</tr>
<tr>
<td>12.739</td>
<td>Heptanoic acid</td>
<td>–</td>
<td>–</td>
<td>5.19</td>
</tr>
<tr>
<td>12.954</td>
<td>1,5-Dimethyl-2-pyrrrolidone</td>
<td>2.45</td>
<td>2.75</td>
<td>3.18</td>
</tr>
<tr>
<td>13.873</td>
<td>3,5-Dimethyl-phenol</td>
<td>5.14</td>
<td>4.02</td>
<td>2.45</td>
</tr>
<tr>
<td>14.163</td>
<td>4-Ethyl-phenol</td>
<td>2.17</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14.201</td>
<td>3-Ethyl-phenol</td>
<td>5.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14.211</td>
<td>Heptanoic acid, trimethylsilyl ester</td>
<td>–</td>
<td>5.39</td>
<td>6.51</td>
</tr>
<tr>
<td>14.282</td>
<td>1-(3-Aminophenyl)-ethanone</td>
<td>3.01</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14.302</td>
<td>Octanoic acid</td>
<td>–</td>
<td>5.53</td>
<td>9.00</td>
</tr>
<tr>
<td>14.587</td>
<td>3,4-Dimethyl-phenol</td>
<td>2.52</td>
<td>2.33</td>
<td>1.57</td>
</tr>
<tr>
<td>15.358</td>
<td>Quinoline</td>
<td>5.01</td>
<td>1.18</td>
<td>1.00</td>
</tr>
<tr>
<td>15.439</td>
<td>3-Hydroxy-4-methoxy-benzonitrile</td>
<td>2.02</td>
<td>1.85</td>
<td>1.84</td>
</tr>
<tr>
<td>15.642</td>
<td>Octanoic acid, trimethylsilyl ester</td>
<td>–</td>
<td>1.00</td>
<td>2.11</td>
</tr>
<tr>
<td>15.693</td>
<td>Nonanoic acid</td>
<td>–</td>
<td>1.26</td>
<td>2.04</td>
</tr>
<tr>
<td>15.973</td>
<td>2,3-Dihydro-1H-Inden-1-one</td>
<td>1.70</td>
<td>0.89</td>
<td>–</td>
</tr>
<tr>
<td>16.139</td>
<td>Indole</td>
<td>5.56</td>
<td>2.30</td>
<td>–</td>
</tr>
</tbody>
</table>

*— No corresponding substance was observed or detected.*

---

Fig. 4 – Physical characterization of granular activated carbon (GAC) particles: (a) before experiment; (b) immersed in raw coking wastewater 1 hr; (c) after E-ME experiment, with initial pH 6.4, 6 V voltage, 0.75 L/min aeration, and reaction time 5 hr.
In contrast with alkaline medium, COD removal efficiency was higher in acidic medium. It is clear that the ME system was more effective under acidic conditions. The main reason is the following, (1) Large amounts of H⁺ need be consumed at the very first step of the half-cell reactions. (2) The standard reduction electrode potential of the cathode in the presence of acid is higher than that in the neutral system. Therefore, it is easy to explain the better efficiency when initial pH was 3 compared with alkaline conditions. It should be noted that the COD removal rate increased as pH increased from 3 to 7. H₂O₂, as mentioned above, is generated in more alkaline solutions (Wang et al., 2009; Zhang et al., 2013). In addition, the increase in the pH value decreased the hydroxyl radicals’ reduction potential (Xie et al., 2016). Thus, more hydroxyl radicals will be generated because the energy barrier for this reaction decreases. The efficiency of COD removal decreased rapidly after adjusting pH to alkaline conditions. The reason is that the ZVI/GAC ME process (Ruan et al., 2010), electrocoagulation process (Sengil and Ozacar, 2006) and electrochemical oxidation process (Moreno-Casillas et al., 2007) taking place in E-ME systems all showed poorer degradation efficiency.

Fig. 6 illustrates the variation of pH in E-ME systems after 2 hr. As can be observed in Fig. 6, the final pH was higher than the initial pH when initial pH below 7, and above this point the final pH was lower. These results suggest that E-ME systems exhibit some pH buffering capacity. According to Eqs. (6)–(8), large amounts of H⁺ would be consumed at the very beginning of the ME reaction. In addition, in acid medium, the iron corrosion reaction occurs rapidly to remove H⁺ via H₂ evolution. Thus, this reaction led to the increase of pH. In comparison, under alkaline conditions, the applied electric field dissolved more iron in the ZVI/GAC bed, consuming a large amount of hydroxide ions, leading to a decrease in pH.

2.4. Effect of voltage in the E-ME system

The influence of applied voltage on COD removal in the E-ME system is shown in Fig. 7. As seen from the Fig. 7, COD removal increased from 33% to 70% as voltage was raised from 0 to 1 V. Interestingly, COD removal slightly decreased with continued increase in voltage to 6 V, but was still higher than at 0.1 V and 0.5 V. Obviously, the applied electric field had the ability to enhance ME processes. The reason could be: (1) the applied electric field accelerated the dissolution of iron. This then enhanced a series of reactions, including redox,
electromigration, coagulation, adsorption, etc. (2) As the voltage increased, the increased current accelerated the transport rate of electrons and therefore promoted the degradation reaction on the GAC/ZVI bed. We observed poor COD removal when the voltage was 12 V, even lower than in the ME process. Considering that the applied voltage was much higher than the potentials of GAC/ZVI cells, the strengthened electrostatic repulsion force among filler materials probably weakened the flocculation and electrophoresis processes. Moreover, excessive ferrous and ferric hydroxides generated due to overpotential may attach to GAC particles and therefore inactivate and block the micro-pores.

3. Conclusions

A newly designed electric-assisted micro-electrolysis filter (E-ME) was developed to investigate its degradation efficiency for coking wastewater and correlated characteristics. It could be concluded that, (1) E-ME showed a prominent synergistic effect on COD removal compared with SE and ME systems; (2) GC-MS analysis indicated that the degradation of phenolic compounds was reinforced after an applied electric field was coupled with ME. Meanwhile, more biodegradable oxygen-bearing compounds were detected; (3) inactivation and blocking of GAC were inhibited during the E-ME process; (4) the optimal voltage value is 1 V, but a synergistic effect existed even with a lower applied voltage; (5) E-ME systems exhibited some pH buffering capacity and attained the best efficiency in neutral medium, which means there is no need to adjust pH prior or during the treatment process. Therefore, E-ME systems were confirmed as a promising technology for treatment of coking wastewater and other refractory wastewater.

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