Advanced electro-Fenton degradation of biologically-treated coking wastewater using anthraquinone cathode and Fe-Y catalyst
Haitao Li, Yuping Li, Hongbin Cao, Xingang Li and Yi Zhang

ABSTRACT
The electrocatalytic activity of bare and 2-ethyl anthraquinone-modified graphite felt (2-EAQ/GF) toward oxygen reduction was investigated using a cyclic voltammetry technique in a neutral solution. The prepared cathodes were tested for electrogeneration of H2O2 and electro-Fenton oxidation (EFO) treatment of neutral coking wastewater (CW) after biological process, using a graphite anode and Fe-zeolite Y catalyst. The results showed that (i) H2O2 yield and current efficiency greatly depended on cathodic potential and materials; (ii) hydroxyl radicals, generated from Fe-zeolite Y-catalyzed H2O2 decomposition, played a great role in EFO treatment, while anodic direct and indirect oxidation was insignificant; (iii) chemical oxygen demand, total organic carbon (TOC) and acute toxicity of wastewater decreased by 40–50, 30–40 and 50–60%, respectively, and biodegradability increased after 1 h of EFO treatment. Due to the free-pH adjustment, EFO presents a potential engineering application for advanced treatment of CW.

Key words | anthraquinone cathode, coking wastewater, electro-Fenton, Fe-zeolite Y, hydroxyl radicals

INTRODUCTION
Electrochemical oxidation technology as one of the advanced oxidation technologies has been wildly investigated for pre/post-treatment of refractory wastewater (Zhu et al. 2009). Recently, electro-Fenton oxidation (EFO), producing a free hydroxyl radical (‘OH) from Fenton’s Reaction (1) between H2O2 in situ generated from O2 reduction Reaction (2) and ferrous ion (Fe2+) added or regenerated from cathodic reduction Reaction (3), has been used to treat various toxic and bio-refractory organics in wastewater (Gözmen et al. 2003; Brillas et al. 2004; Wang et al. 2005; Kurt et al. 2007). Cathodic materials are very important for the yield and current efficiency of electrogenerating H2O2, which affect the generation of ‘OH and EFO efficiency. Various modified quinone electrodes showed higher reactivity in a two-electron reduction reaction of O2 to H2O2 in 0.1 M KOH solution (Sarapuu et al. 2010). A polypyrrole/anthraquinone modified graphite cathode was used for the electrogeneration of H2O2, the regeneration of Fe2+ and the EFO degradation of azo dye in acidic aqueous solutions in an undivided cell (Zhang et al. 2008). However, the conventional EFO reaction only performs well in acidic medium (pH 2–4) using Fe2+/Fe3+ as catalysts and it requires additional neutralization and separation processes. Fe-zeolite Y and silica supported iron oxide performed catalytic activity for reactive azo dye and phenol removal in the presence of H2O2 under nearly neutral solution (Neamţu et al. 2004; Pham et al. 2009). To the best of our knowledge, the Fe-zeolite Y as a catalyst has seldom been used in an EFO system.

Fe2+ + H2O2 → Fe3+ + OH− + OH− (1)
O2(g) + 2H+ + 2e− → H2O2 (2)
Fe3+ + e− → Fe2+ (3)

Coking wastewater (CW) is generated from coke plants in coal coking, coke-oven gases purification and by-product recovering processes (Ning et al. 2005). It contains plenty of hazardous organic and inorganic pollutants and most of them are toxic, mutative and carcinogenic. The biological
process is the most economical method for CW treatment due to its low cost and effective removal of most organic and inorganic pollutants (Vázquez et al. 2006). However, due to the presence of biorefractory organics in CW, the chemical oxygen demand (COD) of effluent after biological processes is difficult to reduce to the level of 200 mg L$^{-1}$ (Kim et al. 2008). The effluent COD can not meet the requirement of the National Discharge Standard of China (NDSC, COD < 150 mg L$^{-1}$).

The objective of this work is to further reduce COD of CW after bio-process in a novel EFO process using Fe-zeolite Y instead of homogeneous Fe$^{2+}$ in nearly neutral media. Anthraquinone modified graphite felt was used for electrogeneration of H$_2$O$_2$, and effects of cathodic potential and the presence/absence of anthraquinone were investigated. Fe-zeolite Y was used for decomposition of H$_2$O$_2$ and the reduction of contaminants. Four different systems were compared in treating CW: (i) anodic oxidation, (ii) anodic oxidation and oxidation by cathodically generated H$_2$O$_2$, (iii) EFO, and (iv) only adsorption by Fe-zeolite Y.

**MATERIALS AND METHODS**

Na-zeolite Y was purchased from Nanjing Nanda Surface and Interface Chemical Engineering and Technological Research Center Co. Ltd (China), Fe-Y was prepared with the method reported by Neamtu et al. (2004). The graphite felt (GF) with 99.5% purity and graphite plate were obtained from Beijing Carbon Sci-Tech Co. Ltd (China). 2-ethyl-9,10-anthraquinone (2-EAQ) and didodecyl dimethyl ammonium bromide (DDAB) were purchased from Johnson Matthey (UK) and Sigma (USA). 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was obtained from Shanghai Aladin-Reagent Co. Ltd (China). All solutions were prepared with Milli-Q water. The GF was dipped in 2-EAQ saturated ethanol solution in the presence of 0.1 M DDAB for 12 h at the room temperature. The 2-EAQ modified GF was washed several times with Milli-Q water and dried at 30 °C.

The COD was measured by a closed reflux spectrophotometric method using dichromate as the oxidant on a UV–Vis spectrophotometer (Labtech Co. Ltd., USA). TOC was measured on a Shimadzu TOC-V analyzer. Biochemical oxygen demand in 5 days (BOD$_5$) was analyzed by BOD self-check measurement (OxiTop IS6, WTW, Germany). H$_2$O$_2$ concentration was analyzed by spectrophotometric method using potassium titanium(IV) oxalate (Sellers 1980). Chloride ion concentration was measured by ion chromatography (ICS-1000, Dionex Corporation, USA). Organic compounds in CW were extracted by dichloromethane and determined by gas chromatography–mass spectrometry (GC-MS). The parameters of GC-MS analysis and preparation of analytical samples were the same as reported (Li et al. 2011). The acute toxicity of wastewater was assessed by a growth inhibition test using fresh water luminescent bacterium Vibrio-qinghaiensis sp. Nov.-Q67 (Ma et al. 1999). The bioluminescence inhibition ratio (r) is a ratio obtained from the formula: $r = (I_0-I)/I_0$, where $I_0$ and $I$ are the bioluminescence intensity of a blank sample and determinand. The hydroxyl radical determination was performed as follows: 0.01 g Fe-Y was added into 10 mL of 0.1 M phosphate buffer solution (PBS, pH 7.0) containing 10 mM H$_2$O$_2$ with rapidly magnetic stirring in a 20 mL glass reactor covered with silver paper at (25 ± 2) °C. Then 1 mL of 1 M DMPO solution was added into the mixture. After 5 min reaction, 2 mL of suspended solution was withdrawn, filtered and quickly inhaled into a quartz tube for electron paramagnetic resonance spectrum analysis on an E-500 X-band EPR spectrometer (Bruker, Germany) at room temperature.

**Experimental set-up**

The effluent of anoxic–aerobic–aerobic (A-O$_1$-O$_2$) biofilm system in our lab was used for electrochemical experiments and the characteristics are shown in Table 1.

The cyclic voltammetry (CV) studies of electrodes were performed with a three-electrode system using an IM6e electrochemical workstation (ZAHNER elektrik, Germany). The 2-EAQ/GF or bare GF (0.5 cm × 0.5 cm), Pt slice (1.0 cm × 1.0 cm) and saturated calomel electrode (SCE) were used as working electrode, counter electrode (CE) and reference electrode (RE), respectively. The electrogeneration of hydrogen peroxide was performed in a proton exchange membrane divided cell (Naion 115, DuPont Corp.) in constant-potential mode using a DC power supply (Weijie Electric Equipment Manufactory, China). 2-EAQ/GF or GF (40 mm × 40 mm × 5 mm) was used as the cathode with same size GF as the anode and SCE as RE. In each run, 200 mL of electrolyte (0.2 M PBS, pH 7.0) was pumped with a flowrate of 5 mL min$^{-1}$ both in cathodic and anodic departments in outside-loop mode. The cathodic electrolyte was saturated with pure O$_2$ with a dissolved oxygen concentration of ca. 40 mg L$^{-1}$. The electric quantity was calculated...
by a current integrator. H₂O₂ concentrations were analyzed when 1,080 C of electric quantity was consumed in each run.

Electrolytic experiments were carried out in an undivided organic glass cell (60 mm × 60 mm × 60 mm) placed in a water bath at (23 ± 2) °C using a DC power supply. As shown in Figure 1, a graphite anode (40 mm × 50 mm × 5 mm) was placed between two 2-EAQ/GF cathodes (40 mm × 50 mm × 5 mm) in the electrolytic cell. The distance between electrodes was 2.0 cm. Air or nitrogen gas (99.9%) was bubbled from the bottom of the cathodes through porous ceramic pipes. Before electrolysis, 50 g of the catalyst was dipped in CW several times to eliminate the effect of adsorption. Then the catalyst and 50 mL of fresh CW were added into the reactor for electrolysis.

The first experiment was to investigate the effect of electrolysis time on COD removal and current efficiency, sampling at 20, 40, 60, 80, 100, 120, 180, 240 min, respectively, and constant-potential mode at cathodic potential of −0.7 V was employed. The second experiment was to compare four systems in CW treatment, the current density applied was 10 A m⁻² and the electrolysis time was 1 h. The COD, TOC and current efficiency were analyzed for each experiment. All the experiments were conducted in duplicate and the mean values (R.S.D. <10%) as final results were reported.

Defining CE(H₂O₂) and CE(COD) for current efficiencies of H₂O₂ and COD removal as Equation (4) and Equation (5) and COD removal rate (COD%) as Equation (6), where COD₀ (mg L⁻¹) is the initial COD, CODₜ (mg L⁻¹) the COD at given time t (s), V (L) the volume of the electrolyte solution, C (mol L⁻¹) H₂O₂ concentration, F (96,480 C mol⁻¹) the Faraday constant and I (A) is the current intensity.

\[
\text{CE(H}_2\text{O}_2) = \frac{2CVF}{Iadt} \times 100\% \quad (4)
\]

\[
\text{CE(COD)} = \frac{V(COD_0 - COD_t)F}{8Iadt} \times 100\% \quad (5)
\]

\[
\text{COD\%} = \frac{COD_0 - COD_t}{COD_0} \times 100\% \quad (6)
\]

RESULTS AND DISCUSSION

To investigate the electrochemical behavior of O₂ on bare GF and 2-EAQ/GF electrodes, the CV measurements were carried out in N₂ or O₂ saturated 0.2 M PBS as shown in Figure 2. On bare GF electrode, there was no notable reduction peak between 0 and −1.2 V in N₂ saturated PBS (Figure 2, curve (c)), while in O₂ saturated PBS (Figure 2, curve (a)).
buffer (Figure 2(b)), a reduction peak at −0.502 V was attributed to the reaction (2) of O₂ to H₂O₂. Qiang et al. (2002) reported the reduction of O₂ to H₂O₂ at −0.5 V on graphite. The CV curve of 2-EAQ/GF in N₂ saturated buffer is shown in Figure 2 (curve c). Two redox peaks with current values of −0.106 mA (Ipc) and 0.095 mA (Ipa) appeared at −0.554 V (peak c1) and −0.476 V (peak c2), which were attributed to the reduction peak of 2-EAQ and oxidation peak of reduced 2-EAQ (2-EAQ²⁻) by Reactions (7, 8) (Sarapuu et al. 2010). The results revealed that 2-EAQ/2-EAQ²⁻ were a pair of quasi-reversible redox catalysts on the GF electrode. As shown in Figure 2, curve (d) in the O₂ saturated buffer, the amplitude of Ipc of O₂ increased from 35.1 µA (peak b1) on the bare GF electrode to 72.7 µA (peak d1) on the 2-EAQ/GF electrode. The increase of peak amplitude indicated that 2-EAQ/GF promoted the activity of O₂ reduction by Reactions (7, 9). The oxidation peak current (Ipa, peak d4) of 42.43 µA of 2-EAQ²⁻ in the O₂ saturated buffer decreased compared with that (peak c2) in the N₂ saturated buffer, which may be due to oxidation of part 2-EAQ²⁻ to 2-EAQ by Reaction (9). The peak d3 at −0.937 V may be attributed to the reduction Reaction (10) of H₂O₂ to H₂O (Wang et al. 2005; Kurt et al. 2007).

\[ \begin{align*}
2{-}\text{EAQ} + 2e^- & \rightarrow 2{-}\text{EAQ}^{2-} \quad (7) \\
2{-}\text{EAQ}^{2-} - 2e^- & \rightarrow 2{-}\text{EAQ} \quad (8) \\
2{-}\text{EAQ}^{2-} + 2\text{H}^+ + \text{O}_2 & \rightarrow 2{-}\text{EAQ} + \text{H}_2\text{O}_2 \quad (9) \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O} \quad (10)
\end{align*} \]

The effects of cathodic potentials and cathodic materials on the electrogeneration of H₂O₂ were investigated. As shown in Table 2, for the 2-EAQ/GF electrode, H₂O₂ concentration and current efficiency decreased slightly with the decrease of cathodic potential from −0.5 to −0.7 V. The current efficiency and H₂O₂ concentration decreased sharply at the cathodic potential of −0.9 V, which may be attributed to reaction (10) of H₂O₂ as shown in Figure 2 (d3). For the bare GF electrode, H₂O₂ concentration and current efficiency were much lower at cathodic potential of −0.7 V. The results indicated that 2-EAQ/GF greatly promoted the generation of H₂O₂ and current efficiency through 2-EAQ/2-EAQ²⁻ catalytic Reactions (7, 9) in neutral pH solution (Zhang et al. 2008).

In order to achieve the application of real CW treatment, Fe-Y was used for decomposing H₂O₂ in a heterogeneous Fenton reaction at neutral pH and room temperature. As reported by Pham et al. (2009) and Rey et al. (2010), the H₂O₂ decomposition may follow two mechanisms: (i) Haber-Weiss mechanism (production of hydroxyl radicals and superoxide radicals); (ii) non-radical mechanism (production of oxygen and water). The hydroxyl radical was detected by ESR spectrum analysis using DMPO as a spin trap. As shown in Figure 3, a typical DMPO-OH adduct signal with an intensity ratio of 1:2:2:1 was detected by EPR spectra, which indicated that the ‘OH radical was generated in the Fe-Y/H₂O₂ system.

The above results revealed that, at neutral pH, the 2-EAQ/GF cathode showed good performance for electrogeneration of H₂O₂ and the Fe-Y could decompose H₂O₂ for hydroxyl radical generation. For practical application, the advanced treatment of CW were carried out in an EFO reactor without pH control. The COD removal rate and current efficiency with electrolysis time are shown in Figure 4. In the first hour, the COD removal rate and current efficiency showed a rapid increase to 49.7% and 46.9%. By prolonging time to 4 h, the COD removal rate increased slightly to 69.3% while the current efficiency obviously decreased to 16.5%. The

<table>
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<th>Electrodes</th>
<th>E_{r} (V versus SCE)</th>
<th>[H_{2}O_{2}] mM</th>
<th>CE(H_{2}O_{2}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-EAQ/GF</td>
<td>−0.5</td>
<td>15.0</td>
<td>53.4</td>
</tr>
<tr>
<td></td>
<td>−0.7</td>
<td>13.5</td>
<td>48.2</td>
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<tr>
<td></td>
<td>−0.9</td>
<td>5.4</td>
<td>19.3</td>
</tr>
<tr>
<td>GF</td>
<td>−0.7</td>
<td>6.5</td>
<td>23.1</td>
</tr>
</tbody>
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Figure 3 | EPR spectra for hydroxyl radical with 10 mM H₂O₂ and 0.1 M DMPO over 10 g L⁻¹ of Fe-Y catalyst at 25°C and pH 7.

Table 2 | Effects of various parameters on hydrogen peroxide accumulation and current efficiency in O₂-saturated 0.2 M PBS in a membrane cell, pH = 7, Q = 1,080 C
UV-Vis spectra of the wastewater with electrolysis time are shown in Figure 4 (inset). The absorbency from 300 to 600 nm almost completely disappeared after 1 h reaction, which indicated some organic pollutants were removed. Meanwhile, the CW was almost decolored, which indicated some chromophore groups of organic pollutants were broken. The present absorbency between 200 and 250 nm after 2 h electrolysis indicated that some pollutants might still exist in wastewater.

As shown in Table 1, 1923 mg L\(^{-1}\) chloride ion in CW can be oxidized on the graphite anode to produce active chlorine (\(\text{Cl}_2\), \(\text{HClO}\) and \(\text{ClO}^{-}\)), which was in favor of decoloring of dye in wastewater (Wang et al. 2005). Unfortunately, active chlorine could react with some aromatic organics in the electrophilic substitution reaction. This would lead to the formation of more toxic chlorinated by-products. Therefore, the organics in CW before and after the EFO process were detected by the GC-MS technique. The results are shown in Table 3. Most of the organic contaminants detected in CW were polycyclic hydrocarbons containing nitrogen and oxygen and the alkanes with 13–21 carbon atoms. After 1 h electrolysis, the chlorinated by-products were not detected in the wastewater. The fact that these products were not detected by the technique employed does not imply that they were not generated, and this was likely due to the limitation of the technique. Some additional experiments were supplied to evaluate acute toxicity and biodegradability of wastewater. The results were shown in Table 4, inhibition ratios of luminescence decreased from 0.33–0.38 to 0.13–0.16, which revealed the acute toxicity of wastewater decreased by 50–60%. The ratios of BOD\(_5\)/COD increased from 0.044 to 0.12–0.15, which suggested the biodegradability increased. It was proposed that the quantity of the formed chlorinated by-products was very tiny and their presence showed little effect on the toxicity and biodegradability of wastewater.

In order to investigate the effects of the anode, cathode and catalyst in the EFO system, four parallel experiments were conducted. A: anodic oxidation (0.5 L min\(^{-1}\) nitrogen gas bubbling and 10 A m\(^{-2}\) current density); A + C: anodic oxidation and cathodic indirect oxidation (0.5 L min\(^{-1}\) air bubbling and 10 A m\(^{-2}\) current density); A + C + Fe-Y: EFO process (addition of Fe-Y in A + C); Fe-Y: only

![Figure 4](https://iwaponline.com/wst/article-pdf/64/1/63/444002/63.pdf)
adsorption by Fe-Y (0.5 L min⁻¹ nitrogen gas bubbling and Fe-Y without electric current). The results are shown in Figure 5, and the COD removal efficiencies of the above four conditions were 11, 23, 49 and 9.4%, respectively. This indicated that 11% and 12% of COD removal were attributed to anodic oxidation and indirect cathodic oxidation by H₂O₂, respectively. With addition of Fe-Y in electrochemical systems, COD removal efficiency increased to 49% due to the 'OH generation from decomposition of H₂O₂, which was confirmed by the EPR spectra. The catalyst adsorption was not the major contributor to COD removal. TOC removal and current efficiency showed the similar tendency as: A + C + Fe-Y > A + C > A > Fe-Y. This indicated the EFO reaction for organic removal in wastewater may follow the mechanism: (i) hydrogen peroxide is generated from reduction of dissolved oxygen with 2-EAQ/2-EAQ²⁻ as catalysts on cathode; (ii) hydroxyl radicals are generated from decomposition of hydrogen peroxide on the Fe-Y catalyst surface; (iii) the adsorbed organics are degraded mainly by hydroxy radicals and partly by H₂O₂; (iv) there is little direct oxidation of organics on the anode or indirect oxidation by active chlorine (HClO, ClO⁻, Cl₂).

CONCLUSION

An EFO reactor with 2-EAQ/GF cathode and Fe-Y catalyst was used for the treatment of neutral CW after biological process. The 2-EAQ/GF electrode performed higher catalytic activity for generation of H₂O₂ than bare GF electrode, producing 15 mM H₂O₂ at -0.5 V in a membrane cell in neutral solution. The removal efficiencies of COD, TOC, acute toxicity and colority were 40–50, 30–40, 50–60% and approximately 100%, respectively, after 1 h electrolysis. Hydroxyl radicals generated from H₂O₂ decomposition on the surface of Fe-zeolite Y played an important role on the decay of organic compounds, while anodic direct and indirect oxidation was little. Due to the free-pH adjustment, the EFO presents a potential engineering application for advanced treatment of CW.

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