Degradation of acid fuchsine by a modified electro-Fenton system with magnetic stirring as oxygen supplying

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Abstract

The current modified electro-Fenton system was designed to develop a more convenient and efficient undivided system for practical wastewater treatment. The system adopted a cathode portion that employed magnetic stirring instead of common oxygen gas diffusion or gas sparging to supply oxygen gas for the electrolyte solution. Key factors influencing the cathode fabrication and activity were investigated. The degradation of acid fuchsine with a self-made graphite-polytetrafluorethylene cathode was studied using a spectrophotometer. It was found that the cathode generated hydrogen peroxide with high current efficiency and the hydrogen peroxide yield of the cathode did not decay after 10 times reuse. With the Pt anode at a ferrous ion concentration of 0.5 mmol/L, a pH of 3, and using magnetic stirring, dye decolorization could be rapidly accomplished but the destruction of benzene rings and intermediates was fairly difficult. With a Fe anode, dye degradation was more complete.

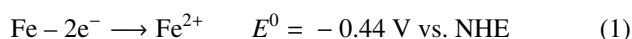## Introduction

In recent years, various treatment methods have been investigated to avoid the dangerous accumulation of the most toxic dyes in the environment. Among these cases, indirect electro-oxidation methods with electro-generated hydrogen peroxide, such as electro-Fenton (EF) and photoelectro-Fenton processes, have been developed for the treatment of toxic and refractory organic pollutants in acidic water (Boye et al., 2003; Kavitha and Palanivelu, 2005; Khataee et al., 2009). In these environment-friendly electrochemical techniques, hydrogen peroxide is generated continuously at the cathode in acidic solution from the two-electron reduction of dissolved oxygen. The oxidative power of hydrogen peroxide can be enhanced by either electro-generated ferrous ions using a sacrificial Fe anode or externally added ferrous ions using an inert anode, which allows the production of an extremely reactive hydroxyl radical ·OH ($E^0 = 2.8$ V vs. NHE) from the well-known Fenton reaction between both species with a second-order rate using the constant of 63 mol⁻¹sec⁻¹ (Sirés et al., 2007). This ·OH acts as a nonselective, strong, oxidizing agent with ability to react with organics, giving dehydrogenated or hydroxylated derivatives, and achieving their total mineralization, i.e., their conversion into carbon dioxide, water and inorganic ions. The main reactions for the generation of ·OH in an EF system are as follows (Sirés

et al., 2007; Brillas et al., 2003):

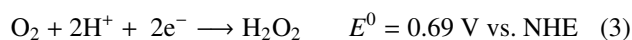Anode reaction, using Fe anode

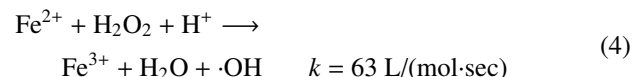$$\text{Fe} - 2e^- \longrightarrow \text{Fe}^{2+} \qquad E^0 = -0.44 \text{ V vs. NHE} \qquad (1)$$

using inert anode

$$2\text{H}_2\text{O} - 4e^- \longrightarrow 4\text{H}^+ + \text{O}_2 \qquad E^0 = 1.23 \text{ V vs. NHE} \qquad (2)$$

Cathode reaction

$$\text{O}_2 + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{O}_2 \qquad E^0 = 0.69 \text{ V vs. NHE} \qquad (3)$$

In bulk solution

$$\begin{aligned} \text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ &\longrightarrow \\ \text{Fe}^{3+} + \text{H}_2\text{O} + \cdot\text{OH} \qquad & k = 63 \text{ L/(mol·sec)} \end{aligned} \qquad (4)$$

Obviously, from the electrochemical perspective, the selection of cathode material is especially important. The materials, which are usually used in the preparation of the cathode, mainly include graphite (Panizza and Cerisola, 2001), reticulated vitreous carbon (Fockedey and Lierde, 2002), mercury (Kusvuran et al., 2004), carbon felt (Pimentel et al., 2008) and activated carbon fiber (Wang et al., 2005). Besides the selection of cathode material, the preparation procedure of the cathode also remarkably influences its electrochemical performance and stability towards the production of hydrogen peroxide. For example, Zhou et al. (2008) reported the preparation of graphite-polytetrafluorethylene cathodes using graphite powder and

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polytetrafluorethylene (PTFE), and found that under oxygen gas sparging condition the cathode with a ratio of graphite:PTFE of 2:1 (*m/m*) generated hydrogen peroxide with the highest current efficiency, and that the hydrogen peroxide yield of the cathode without calcination treatment was a little higher than that with calcination treatment at 300°C. In order to enhance cathode activity, many researchers prepare the cathodes using the carbonaceous material modified with inorganic ions or organic group. For example, Wang and Wang (2007, 2008) prepared the Pd/C gas diffusion cathode with palladium coated activated carbon powder and applied it in the electrochemical degradation of 2,4-dichlorophenol and 4-chlorophenol aqueous solutions. The results showed that the removal ratios of the contamination were higher using the Pd/C cathode than using unmodified activated carbon powder cathode. Lu et al. (2003) studied the electro-catalytic reduction of dissolved oxygen at the glassy carbon electrodes modified with four kinds of different metal-porphyrin complexes in oxygen-saturated aqueous solutions. The results revealed that all studied complexes could catalyze the two-electron reduction of dissolved oxygen. Forti et al. (2007) also studied the electrochemical synthesis of hydrogen peroxide on oxygen gas-fed graphite-PTFE cathode modified by 2-ethylanthraquinone. The results showed that hydrogen peroxide formation rate on the cathode was enhanced greatly in the presence of organic redox catalyst, and the overpotential for oxygen reduction shifted toward a more positive. Based on the above research, the results show that these electrochemical systems should generate hydrogen peroxide at a current efficiency as high as possible, and require modification to be more suitable for practical wastewater treatment and easier to scale up. Furthermore, the cathode should be also easier to fabricate and more enduring to reduce treatment costs.

In this work, the current EF system has been modified to develop a more convenient and efficient undivided electrochemical system for practical wastewater treatment. The system adopted a cathode portion employing magnetic stirring instead of common oxygen gas diffusion or gas sparging to supply oxygen gas for electrolyte solution. A series of experiments were performed to test the activity of the cathode fabricated with graphite powder and PTFE for the electrochemical generation of hydrogen peroxide. The major factors in the generation of hydrogen peroxide, such as the mass ratios of graphite:PTFE in the cathode, the calcination temperature of the cathode and oxygen gas supplying manner, have been investigated in detail. The feasibility of the EF system for organic wastewater treatment has also been investigated. Acid fuchsine (AF), a model dye with aromatic structures, is toxic and recalcitrant to biodegradation. Photocatalytic and ultrasonic degradation of AF have been investigated (Wang et al., 2007; Shi et al., 2008). However, as far as we know, there was rarely a report on the degradation of AF by the oxidation via an EF process. Therefore, the degradation of AF was investigated in an undivided EF system with Pt or Fe anode and a self-made graphite-PTFE cathode.

1 Experimental

1.1 Reagent and material

Graphite powder (200 mesh, analytical grade), PTFE (60%) and stainless steel mesh (20 mesh) were used to fabrication of the cathode. AF (analytical grade) was used to prepare dye solution. Its structure is shown in Fig. 1. All other chemicals including sulfuric acid, anhydrous sodium sulfate, sodium hydroxide, heptahydrated ferrous sulfate, potassium titanium(IV) oxalate and anhydrous ethanol were of analytical grade. Deionized water was used.
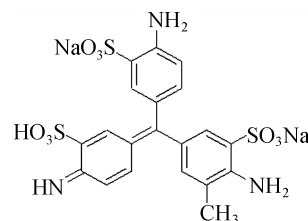

Fig. 1   Molecular structure of dye AF.

1.2 Fabrication of cathode

The graphite powder was pretreated firstly. It was boiled in deionized water for 2 hr, rinsed twice using deionized water, filtered with a filter with micropore of 0.45 μm, dried at 106°C in a thermostat desiccator, and then stored for later use. A 5-g of pretreated graphite powder was added into a 18-mL anhydrous ethanol and dissolved after in an ultrasonic bath for 10 min at room temperature, then an appropriate amount of PTFE (60%) was added to the mixture to fabricate the cathodes with different mass ratios of griphate:PTFE, and the ultrasonic dispersion was then continued for 15 min. The mixture was stirred at about 80°C until it became a wet paste. The resulting graphite-PTFE wet paste was put into a mold and formed into a rectangular sheet (6 cm × 7 cm, 1.5 mm thickness), which was then pressed into a membrane of 0.5 mm thickness by a rolling mill. A graphite-PTFE cathode was assembled in the form of membrane/stainless steel mesh/membrane and pressed at 15 MPa for 2 min. Based on requirements the fabricated graphite-PTFE cathode would be calcined in a muffle furnace at various temperatures for 1 hr.

1.3 Procedure

The experiments for the electrochemical generation of hydrogen peroxide were performed in a three-electrode undivided cell (250 mL) at room temperature and was controlled by a potentiostat/galvanostat at constant current. A graphite-PTFE cathode (12 cm^2 area) was used as working electrode, a Pt electrode (0.12 cm^2 area) as a counter electrode and a saturated calomel electrode as a reference electrode. The distance between the working electrode and the counter electrode was 3 cm. The volume of anhydrous sodium sulfate aqueous solution (0.05 mol/L) was 200 mL, and its pH was adjusted to 3 by using sulfuric acid and sodium hydroxide prior to electrolysis. Oxygen gas was supplied to the solution by either constant magnetic stirring or air bubbling at different flow rates near

the cathode. At certain time intervals, 2 mL samples were taken to measure hydrogen peroxide concentration, and the cathode potentials were recorded.

The experiments for electrochemical oxidation of AF were performed in an EF system (250 mL) with either a Pt anode (0.12 cm^2) or Fe anode (1.2 cm^2) and a self-made graphite-PTFE cathode (12 cm^2), and the procedures were similar to the cases for electrochemical generation of hydrogen peroxide.

1.4 Analytical method

Hydrogen peroxide concentration was measured by a spectrophotometer (722s, Tianjin Tuopu Instrument Co., Ltd., China) at a 400 nm wavelength, using potassium titanium(IV) oxalate as a colored indicator. The surface morphology of the cathode was observed by scanning with an electron microscope (KYKY-2800, Beijing KYKY Technology Development Ltd., China). The concentration of dissolved oxygen in electrolyte solution was measured using a dissolved oxygen meter (HI9143, Hanna, Italy). Cyclic voltammetry (CV) was employed to confirm hydrogen peroxide generation on the cathode under specific conditions. CV curves were recorded using an electrochemical workstation (CHI650C, Shanghai Chenhua Instrument Co., Ltd., China) at a scan rate of 50 mV/sec in the three-electrode cell described above. The TG-DTA curves of the cathode were recorded with TG analyzer (DTG-60A, Shimadzu, Japan). The current efficiency (CE) for the generation of hydrogen peroxide was determined using Eq. (5):

$$\text{CE} = \frac{nFC_{\text{H}_2\text{O}_2}V}{I_t} \times 100\% \tag{5}$$

where, n is the number of electrons transferred for oxygen gas reduction to hydrogen peroxide, F is the Faraday constant (96,486 C/mol), $C_{\text{H}_2\text{O}_2}$ (mol/L) is the hydrogen peroxide concentration, V (L) is the bulk volume, I (A) is the applied current, and t (sec) is time. The concentration of AF remaining in the solution was determined using a UV-visible spectrophotometer (WFZ-26A, Tianjin Tuopu Instrument Co., Ltd., China). Removal ratio (η) was calculated using Eq. (6)

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \tag{6}$$

where, C_0 and C_t are the concentrations of the dye wastewater initially and at time t, respectively.

2 Result and discussion

2.1 Electrochemical activity of cathode

2.1.1 Effect of mass ratio of graphite:PTFE

Table 1 lists the hydrogen peroxide concentration, current efficiency and cathode potential at different reaction time for the cathodes with different mass ratios of graphite:PTFE at 350°C calcination for 1 hr. As shown in Table 1, the performance of the graphite-PTFE cathode with graphite:PTFE ratio of 4:1 (*m/m*) was almost as good as that of 3:1 (*m/m*), but the performances deteriorated when the ratios were greater than 4:1 (*m/m*) or less then 3:1 (*m/m*). PTFE in the cathodes served two functions: (1) to bind high surface graphite powder into a cohesive membrane; and (2) to impart hydrophobic character to the membrane (Zhou et al., 2008). Generally, an increase in the mass ratio accompanied an increase amount in the active sites for the electrochemical generation of hydrogen peroxide, and a decrease in the hydrophobic character and the cohesive property of the membrane. As a result, the reaction opportunity of dissolved oxygen through electrochemical generating of hydrogen peroxide increased incrementally with the mass ratio, but the intensity of the membrane deteriorated. The graphite-PTFE cathode with a ratio of 2:1 (*m/m*) prepared by Zhou et al. (2008) gave the best performance in terms of both hydrogen peroxide generation and current efficiency. The reason was that the cathode was either not calcined or calcined at lower than 350°C. On account of the experimental results, the ratio of 3:1 (*m/m*) was selected for the rest of the procedures.

2.1.2 Effect of calcination temperature

Table 2 lists the hydrogen peroxide concentration, current efficiency and cathode potential for the cathodes with the ratio of 3:1 (*m/m*). As observed, both the hydrogen peroxide concentration and current efficiency of the cathodes without calcination were low. On the contrary, the concentrations and efficiencies of the cathode calcined at 350°C were the highest.

The results could be attributed to the change of surface characteristics of the cathodes. Figure 2 shows the scanning electron microscopy (SEM) pictures of cathodes. As shown, the surface of the cathode was smooth, flat and had few micropores without calcinations, and white grains could be easily identified. However, the micropores on surface increased remarkably with calcination. As a consequence, the reaction activity was enhanced.

Table 1 Hydrogen peroxide concentration ($C_{\text{H}_2\text{O}_2}$), current efficiency (CE) and cathode potential (CP) at different reaction time for the cathodes with different mass ratios of graphite:PTFE at 350°C calcination for 1 hr

Time (min)	Graphite:PTFE (5:1, *m/m*)			Graphite:PTFE (4:1, *m/m*)			Graphite-PTFE (3:1, *m/m*)			Graphite-PTFE (2:1, *m/m*)		
	$C_{\text{H}_2\text{O}_2}$ (mg/L)	CE (%)	CP (V)	$C_{\text{H}_2\text{O}_2}$ (mg/L)	CE (%)	CP (V)	$C_{\text{H}_2\text{O}_2}$ (mg/L)	CE (%)	CP (V)	$C_{\text{H}_2\text{O}_2}$ (mg/L)	CE (%)	CP (V)
30	26.5	46.4	0.79	24.6	43.2	0.68	28.3	49.6	0.78	23.2	40.7	0.90
60	50.6	44.3	0.80	50.6	44.3	0.68	45.7	40.0	0.77	45.9	40.2	0.88
90	67.4	39.3	0.79	73.5	42.9	0.68	70.2	41.0	0.73	61.6	36.0	0.89
120	82.1	35.9	0.79	94.4	41.3	0.66	97.2	42.6	0.73	78.6	34.4	0.89
150	99.5	34.8	0.79	112.8	39.5	0.66	113.8	39.9	0.73	88.4	31.1	0.88

Table 2 Hydrogen peroxide concentration, current efficiency and cathode potential for the cathodes with graphite:PTFE ratio of 3:1 (*m/m*) via calcination at different temperatures

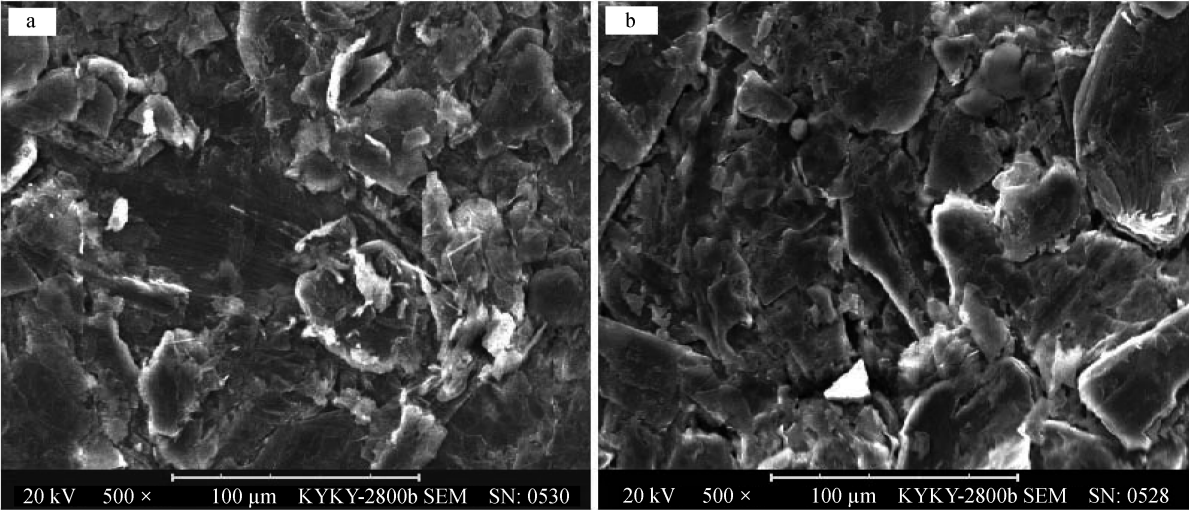| Time (min)	No calcination			300°C			350°C			400°C		
	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)
30	9.9	17.4	0.95	23.2	40.7	0.84	28.3	49.6	0.78	15.0	26.3	0.83
60	12.4	10.8	0.93	38.9	34.1	0.81	45.7	40.0	0.77	30.8	27.0	0.83
90	16.7	9.7	0.92	63.1	36.8	0.80	70.2	41.0	0.73	50.4	29.4	0.82
120	17.9	7.8	0.90	81.5	35.7	0.80	97.2	42.6	0.73	63.3	27.7	0.80
150	18.1	6.3	0.89	91.7	32.1	0.79	113.8	39.9	0.73	65.7	23.0	0.78

Fig. 2 SEM pictures of cathodes without (a) and with calcination (b).

This conclusion was also supported by TG-DTA analysis and a cyclic voltammetry study of the cathodes. Figure 3a, b shows the TG-DTA curves of a cathode. As indicated in Fig. 3b, an endothermic peak, which was a phase transformation point of PTFE appeared at about 343°C (Fig. 3b). Figure 4 shows the cyclic voltammograms of the cathodes calcined at various temperatures. It was also observed, the peak current of the cathode which was calcined at 350°C was the highest. Without calcination, the graphite in the cathode was covered by a thin PTFE membrane. After calcinating at 350°C, phase transforma-

tion and shrinkage both occurred for PTFE in the cathode, and the nude graphite also appeared, which suggests that the activity of the cathode was enhanced. Therefore, in the succeeding experiments all the cathodes were calcined at 350°C.

2.1.3 Effect of oxygen gas supplying manner

Oxygen gas must be supplied to the cathode for the electrochemical generation of hydrogen peroxide as shown in Reaction (3). A variety of oxygen gas supplying manners, such as oxygen gas diffusion, air bubbling or gas sparging, were adopted. These manners were confined
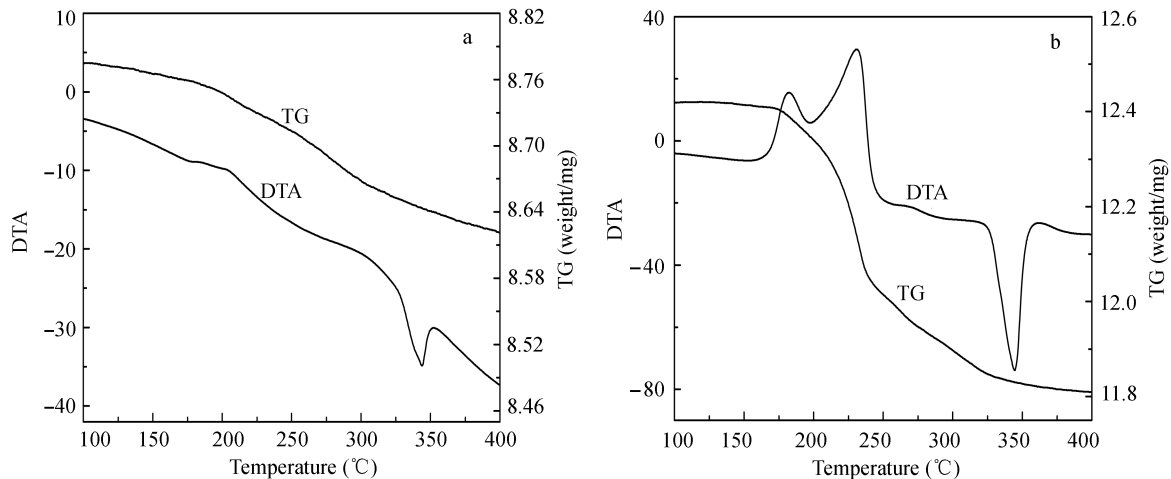

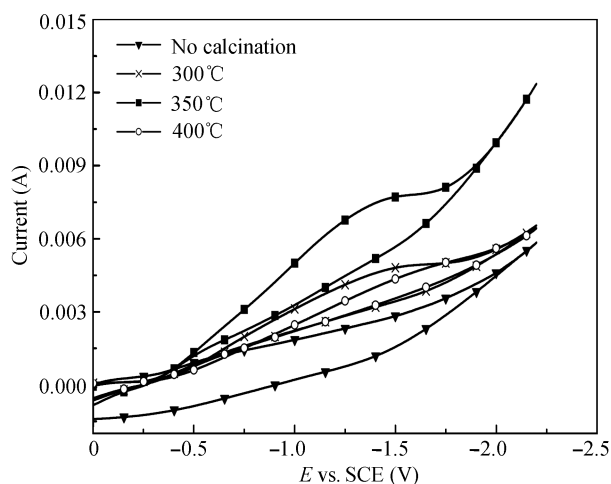**Fig. 3** TG-DTA curves of self-made graphite-PTFE cathode (a) and PTFE (b).

Fig. 4 Cyclic voltammograms of oxygen gas reduction on the cathodes calcined at different temperatures. Experimental conditions: sodium sulfate 0.05 mol/L; pH 3; scanning rate of 50 mV/sec.

Fig. 5 Effect of pH on hydrogen peroxide accumulation. Experimental conditions: Pt anode 0.12 cm^2; self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; sodium sulfate 0.05 mol/L; magnetic stirring.

to have a gas supplying system, which complicated the electrochemical system and increased operation costs. In this study, the current EF system was modified to develop a more convenient and efficient undivided EF system for practical wastewater treatment. The system had a cathode portion, which employed magnetic stirring instead of common oxygen gas diffusion or gas sparging to supply dissolved oxygen to the electrolyte solution. Table 3 lists hydrogen peroxide concentration, current efficiency and cathode potential under different oxygen gas supplying methods. As indicated, the performance of the cathode was the best while oxygen gas was supplied only by magnetic stirring. The concentration of dissolved oxygen in the electrolyte solution was measured throughout the course of experiments. The results showed that when oxygen gas was supplied only by magnetic stirring, the concentration of dissolved oxygen was the highest, with an average value of 18.5 mg/L. By comparison, when oxygen gas was solely supplied by air bubbling, the average value was only 8.85 mg/L. This difference was ascribed to the different utilization ratios of oxygen gas under different oxygen gas supplying manners. With magnetic stirring, small oxygen gas bubbles generated at Pt anode surface were dragged to rotate in whirlpools, which then dispersed into the bulk solution, leading to an increase in the concentration of dissolved oxygen. However, with air bubbling, the small oxygen gas bubbles were dragged upwards and incorporated into bigger air bubbles, leading to a decrease in the concentration of dissolved oxygen.
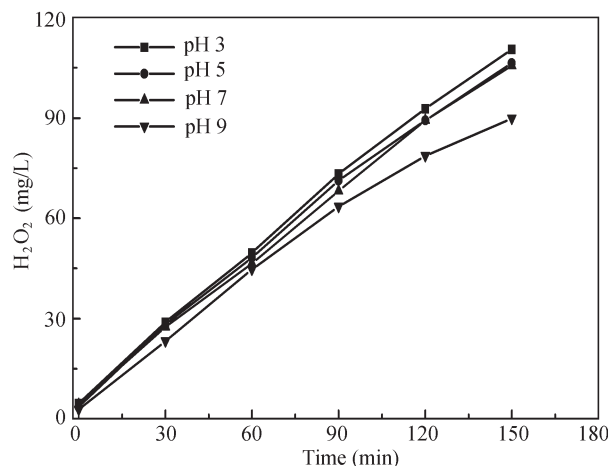
2.1.4 Effect of pH

When Reaction (3) takes place in acidic medium, lower pH values lead to a higher H_2O_2 yield, which was also confirmed in this work. Figure 5 shows hydrogen peroxide accumulation with reaction time at pH 3, 5, 7 and 9, respectively. As indicated, hydrogen peroxide concentration was the highest at pH 3, and when pH rose up from 3 to 9, hydrogen peroxide concentration gradually decreased by 18.7%.

2.1.5 Effect of current density

Figure 6 shows that at the current density of 3 mA/cm^2, H_2O_2 concentration was the highest after 150 min. These results could be attributed to the variation of cathode potential. When the current density was 1, 3, 5 and 7 mA/cm^2, the corresponding cathode potential was -0.45, -0.81, -1.2 and -1.5 V, respectively. Once the cathode potential was higher than -1.2 V, the possibility of side reactions increased and hydrogen peroxide yield decreased.

2.2 Stability for electrogeneration of hydrogen peroxide

The cathode stability for the electrogeneration of hydrogen peroxide was examined. As shown in Fig. 7, in the early 6 times reuse, H_2O_2 concentration slightly increased, which could be attributed to the decrement of the charge transfer resistance and increment of double layer capacity with reaction time (Alcaide et al., 2002). In addition, H_2O_2 concentration did not decrease after 10 times reuse. This result indicates that the present of cathode might be

Table 3 Hydrogen peroxide concentration, current efficiency and cathode potential for the cathodes with a ratio of graphite:PTFE of 3:1 (*m/m*) at 350°C calcination for 1 hr using different O$_2$ supplying methods

| Time	Blowing air bubble (1 L/min)			Blowing air bubble (2 L/min)			Magnetic stirring			Magnetic stirring plus blowing air bubble (2 L/min)		
(min)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)	$C_{H_2O_2}$ (mg/L)	CE (%)	CP (V)
30	24.6	43.2	0.76	38.5	67.5	0.67	28.3	49.6	0.78	31.4	55.0	0.78
60	42.2	37.0	0.78	53.1	46.5	0.86	45.7	40.0	0.77	50.8	44.5	0.88
90	51.0	29.8	0.93	58.0	33.8	1.07	70.2	41.0	0.73	66.5	38.9	0.90
120	54.7	24.0	0.95	59.4	26.0	1.08	97.2	42.6	0.73	69.4	30.4	0.97
150	53.9	18.9	1.03	53.7	18.8	1.10	113.8	39.9	0.73	67.6	23.7	1.07
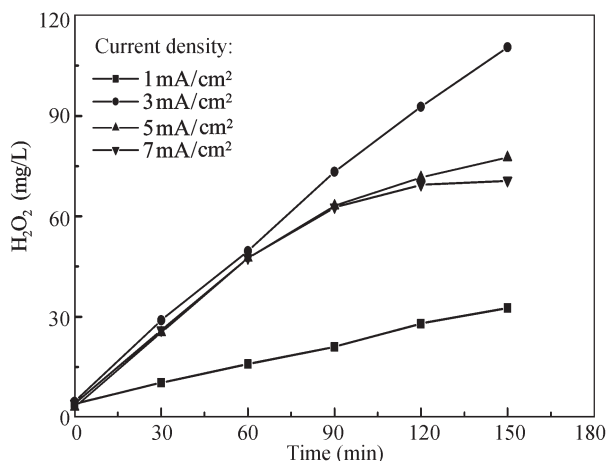
Fig. 6 Effect of current density on hydrogen peroxide accumulation. Experimental conditions: Pt anode (0.12 cm^2); self-made graphite-PTFE cathode (12 cm^2); sodium sulfate 0.05 mol/L; magnetic stirring; pH 3.
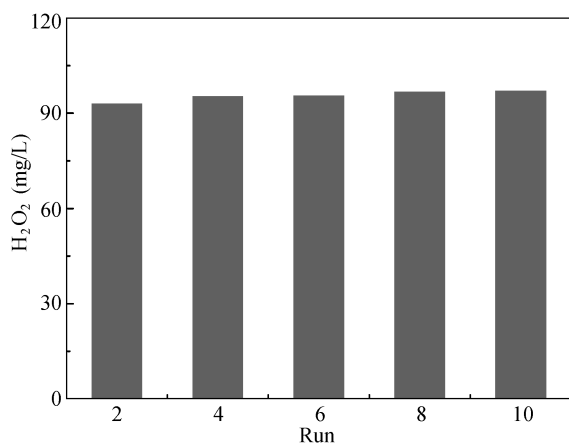

Fig. 7 Stability of the cathode. Experimental conditions: Pt anode 0.12 cm^2; self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; sodium sulfate 0.05 mol/L; pH 3; magnetic stirring.

useful for practical wastewater treatment, and thus it could be applied to dye wastewater treatment in the following section.

2.3 Degradation of AF

2.3.1 Change of UV-visible absorption bands

In order to clarify the changes of molecular and structural characteristics of AF as a result of oxidation at different conditions in the EF system, UV-visible spectra were measured and some representative changes of AF aqueous solution were observed in the course of oxidation as shown in Fig. 8. As seen from these spectra, before oxidation, the absorption spectrum of AF was characterized by one main band in the visible region with the absorption peak at 540 nm (peak 1) and two other bands in the ultraviolet region with absorption peaks at 283 (peak 2) and 208 nm (peak 3), respectively. The peak at 540 nm might originate from the three chromogenic ethylene double bonds in the molecule and the peaks at 283 and 208 nm were associated with benzene rings. As seen in Fig. 8a, with Pt anode at a ferrous ion of 0.5 mmol/L, pH 3 and under magnetic stirring condition, the peak absorbance of AF (0.08 mmol/L) at 540 nm quickly decreased by 92.5% after 30 min. At the same time the peaks at 283 and 208
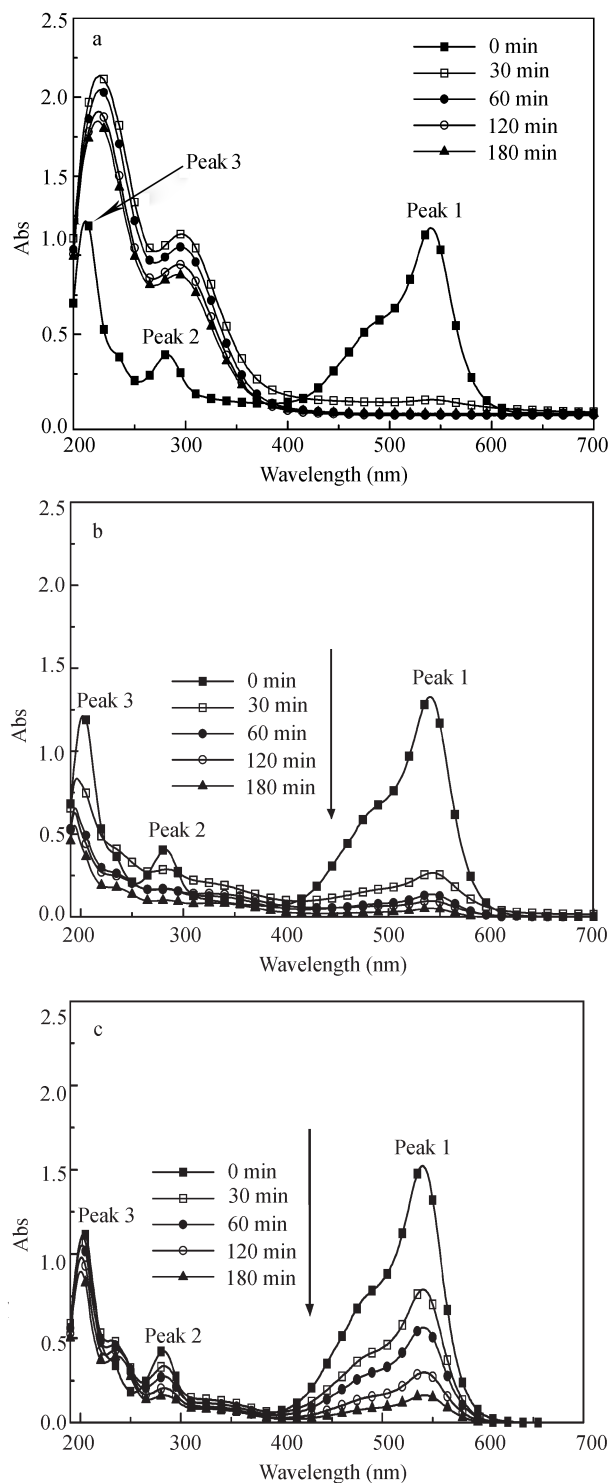

Fig. 8 UV-visible spectral changes with electrolysis time for 200 mL AF solution of 0.08 mmol/L in 0.05 mol/L sodium sulfate of pH 3. Experimental conditions: (a) Pt anode 0.12 cm^2 and self-made graphite-PTFE cathode 12 cm^2; ferrous ion 0.5 mmol/L; current density 3 mA/cm^2; magnetic stirring; (b) Fe anode 1.2 cm^2 and self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; magnetic stirring; (c) Fe anode 1.2 cm^2 and self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; and air bubbling.

nm significantly increased and thereafter decreased slowly within 180 min. This indicated that the chromophore groups were destroyed quickly and some intermediates were generated and were difficult to decompose. With Fe anode at pH 3 and under magnetic stirring condition, all the
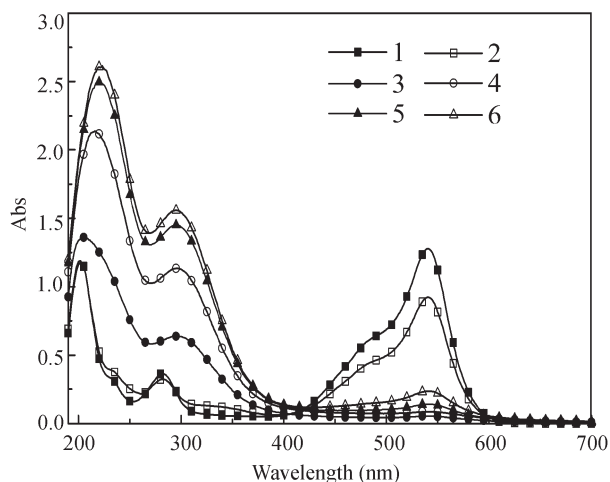
Fig. 9 Effect of the concentration of ferrous ion on AF degradation. 1: before oxidation; 2–6: after oxidation of 30 min at the concentrations of 0.0, 0.2, 0.5, 0.8, 1.0 mmol/L, respectively. Experimental conditions: Pt anode 0.12 cm^2; self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; magnetic stirring.

Fig. 10 Effect of the initial AF on degradation. Experimental conditions: Fe anode 1.2 cm^2; self-made graphite-PTFE cathode 12 cm^2; current density 3 mA/cm^2; magnetic stirring.

peak absorbance at 540, 283 and 208 nm decreased gradually and simultaneously, and the corresponding removal ratios were 96.1%, 75.2% and 54.5% within 180 min, respectively. The present results indicate that the benzene rings and the intermediates were also destructed gradually, as shown in Fig. 8b. In the case with Fe anode and under air bubbling condition, the decreasing rates of all the peak absorbance were slower than that with Fe anode and under magnetic stirring condition, as seen in Fig. 8c.

2.3.2 Effect of ferrous ion concentration

Figure 9 shows the effect of ferrous ion concentration on the dye degradation after oxidation of 30 min with Pt anode at an initial dye concentration of 0.08 mmol/L. It can also be seen that the addition of ferrous ion remarkably enhanced the color removal ratio. The removal ratio reaches the highest value at the concentration of 0.2 mmol/L. With ferrous ion concentration increasing, the absorbance in violet region rose up remarkably.

2.3.3 Effect of initial dye concentration

Figure 10 shows the effect of initial dye concentration from 0.04 to 0.12 mmol/L on the removal ratios of all the peak absorbance with Fe anode after oxidation of 180 min. The removal ratio of peak 1 decreased from 94% to 86% with the dye concentration increasing. The removal ratio of peak 2 increased from 58% to 75% with the change of the dye concentration from 0.04 to 0.08 mmol/L and then decreased from 75% to 60% with further increase in the dye concentration from 0.08 to 0.12 mmol/L. The removal ratio of peak 3 reaches the highest value (54%) at 0.1 mmol/L dye concentration.

3 Conclusions

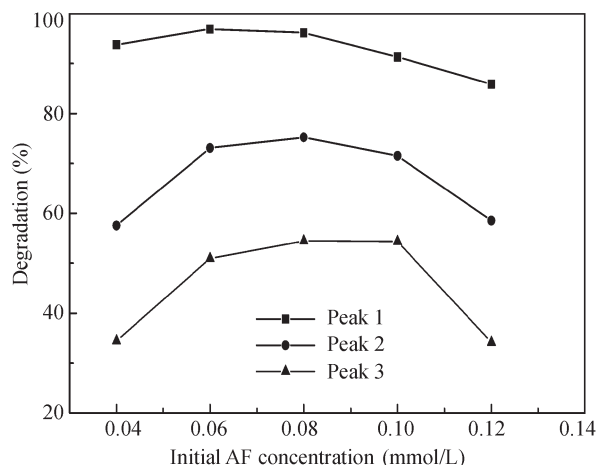An undivided EF system with the cathode portion, which employed the magnetic stirring method for supplying oxygen gas to electrolyte solution, could be more readily scaled up. Moreover, the required equipment was simpler and hydrogen peroxide yield was higher than that for the cathode employing air bubbling method. Calcination temperature remarkably influenced the performance of the self-made graphite-PTFE cathode. Hydrogen peroxide yield was the highest with the cathode with graphite:PTFE ratio of 4:1 (*m/m*) or of 3:1 (*m/m*) and calcinated at 350°C for 1 hr. In addition, in the EF system with Pt or Fe anode, the spectra of AF has shown different characteristics. With Pt anode the dye decolorization could be rapidly accomplished, but the destruction of benzene rings and intermediates was fairly difficult. In comparison, with the Fe anode the dye degradation was more complete. These results suggest that the present system may offer a bright prospect to dye removal.

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