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Research Article

Electro-Fenton Degradation of Methylene Blue Using Polyacrylonitrile-Based Carbon Fiber Brush Cathode

A polyacrylonitrile-based carbon fiber brush (PAN-CFB) cathode was firstly used to decolorize and degrade methylene blue (MB) in Na_2SO_4 solution via electro-Fenton reaction between H_2O_2 from oxygen reduction and ferrous ions (Fe^{2+}) externally added. The optimal current value for H_2O_2 production was 300 mA, with a maximum H_2O_2 concentration of 185 mg L^{-1} and current efficiency of 68% after 60 min, indicating that PAN-based CF is a promising electrode material for 2 e^- oxygen reduction reaction. Additionally, the effect of different parameters, such as the initial pH of the dye solution, Fe^{2+} and initial dye concentration on the decolorization efficiency, and COD removal was thoroughly investigated in simulated wastewater containing MB. The results showed that the electro-Fenton system using the PAN-CFB cathode had a wide applicable pH range 3.00–7.00, and the optimal Fe^{2+} concentration was 0.3 mmol L^{-1} . Moreover, under the conditions of 300 mA current, pH 3.00, and $0.3 \text{ mmol L}^{-1} \text{ Fe}^{2+}$, a nearly 100% color removal after 30 min, 95.9% chemical oxygen demand (COD) removal and the low electrochemical energy consumption of $11.6 \text{ kWh kg}^{-1} \text{ COD}$ after 60 min for 100 mg L^{-1} MB solution were obtained.

Keywords: Advanced oxidation process; Cationic dyes; COD removal; Color removal; Wastewater treatment

Received: December 11, 2013; *revised:* February 26, 2014; *accepted:* March 25, 2014

DOI: 10.1002/cle.201300931

1 Introduction

Large amount of dyeing wastewater is generated in some industrial processes, such as dye production, textile, leather, paper, plastic, food, cosmetic, and rubber processing, etc. [1–5]. Dyeing wastewater is generally characterized by a high concentration of organic pollutants with complex constitution, fluctuant water quality, high chemical oxygen demand (COD) level, deep and long-lasting color, and high toxicity [6–9]. Meanwhile, many dyes and their incomplete degradation products are toxic, carcinogenic, mutagenic, and teratogenic, resulting in a huge threat to aquatic life and human health [2, 10]. Therefore, the removal of dyes from wastewater is a challenge to related industries, and is a demanding environmental issue that needs to be addressed with increasingly rigid environmental regulations.

Many treatments have been extensively used to treat dyeing wastewater, mainly physical (e.g., adsorption [5], membrane separation [2]), chemical (e.g., coagulation [11], chemical oxidation [12] or those with the assistance of light [13], electricity [14, 15], ultrasonic [16]), biological methods [17], and the combination of several methods [18–23]. Each of the methods has advantages and disadvantages. For example, the cost of adsorption and membrane separation is relatively high because of the regeneration of activated carbon absorbent and the expensive membrane module [24, 25]; chemical treatment may cause secondary pollution owing to the addition of chemical agents like flocculants, oxidizing agent [2, 25]; biological degradation is one of the most economic processes for wastewater treatment, but often shows ineffectiveness due to the toxicity and non-biodegradability of some dyes [26, 27].

Nowadays, the electrochemical method appears to be a reasonable, attractive, and promising option to solve the environmental problems caused by dye effluents discharge for its significant advantages, viz. wide application, simple equipment, easy operation, lower temperature requirements, and no sludge formation [28]. The electro-Fenton method is especially a typical electrochemical advanced oxidation process (EAOP) that combines electrochemical technique and advanced oxidation processes. In this process, the electro-generated H_2O_2 by the cathodic reduction reaction reacts with Fe^{2+} to generate oxidizing hydroxyl radicals ($\cdot\text{OH}$), which can

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Abbreviations: ACF, activated carbon fiber; AOP, advanced oxidation process; CE, current efficiency; CF, carbon fiber; COD, chemical oxygen demand; EAOP, electrochemical advanced oxidation process; EEC, electrochemical energy consumption; MB, methylene blue; NHE, normal hydrogen electrode; ORR, oxygen reduction reaction; PAN, polyacrylonitrile; PAN-CFB, polyacrylonitrile-based carbon fiber brush

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react non-selectively with most organic pollutants until totally mineralizing (converting into CO_2 , H_2O , and inorganic ions) [29]. The key to ensure the effective electro-Fenton method is the cathode material that can generate H_2O_2 efficiently via 2e^- oxygen reduction reaction (ORR). By now, cathode materials, such as graphite [6, 30], reticulated vitreous carbon [31], mercury pool [32], activated carbon fiber (ACF) [33, 34], carbon sponge [35], and carbon nanotube [36] are typically employed, most of them are carbon materials. Wang et al. [34] used ACF felt as the cathode of electro-Fenton process and effectively mineralized Acid Red 14. $600\ \mu\text{mol L}^{-1}$ H_2O_2 was generated by the ACF cathode after 180 min, compared with $52\ \mu\text{mol L}^{-1}$ H_2O_2 by a graphite cathode. Superior performance of H_2O_2 electro-generation by the ACF cathode can be explained by the fact that it has a large specific surface area and a great number of mesoporous pores, so that O_2 might be easily electro-reduced on the surface to generate more H_2O_2 . However, in the process of ACF production, the relatively low carbonization temperature (600–800°C) leads to the low graphitized degree of ACF with high resistance, making it weakly conducive to electrochemical reaction when used as electrode.

Polyacrylonitrile (PAN)-based CF is manufactured by organic fiber precursor with higher carbonization temperature (1200–1600°C), which results in the generation of a turbostratic graphite structure with lower electrical resistivity compared with ACF [37, 38]. The electrical resistivity of PAN-based T700S CF produced by Toary, Japan, is $1.6 \times 10^{-3}\ \Omega\text{cm}$, only one tenth of ACF. Besides, cyano groups ($\text{C}\equiv\text{N}$) with strong polarity exist in the PAN precursor, some residue nitrogen content (2–6 wt.%) is still kept in the CF after carbonization at high temperature [39]. The doped-nitrogen carbon materials favoring ORR has been proved as efficient non-platinum ORR catalysts in neutral and alkaline system [40]. However, ACF (mainly from the viscose precursor) has no advantage like this. Therefore, PAN-based CF appears to be a more appropriate cathode material for the electro-Fenton process.

Commercial PAN-based CF has been widely used as electrodes in microbial fuel cells [41], energy storage electrochemical flow cells [42], and seawater batteries [43]. To our knowledge, no research on electro-Fenton using a CF cathode has been reported, so we prepared a kind of PAN-CFB for that purpose. The objective of this work is to investigate the electro-Fenton process based on this novel cathode for decolorizing and degrading a methylene blue (MB) dye solution, which is a common water pollutant in dyeing and printing textiles [44]. The generation of H_2O_2 and its CE were assessed at different applied current. The effect of different operating conditions, such as the initial pH of the dye solution, Fe^{2+} and initial dye concentration was investigated in detail.

2 Materials and methods

2.1 Chemicals

All chemicals were analytical grade (made in China) and used without further purification. Deionized water was prepared by a two-stage reverse osmosis system with conductivity $<5\ \mu\text{S cm}^{-1}$.

2.2 Electrochemical system

All electrolysis processes were conducted in an open and undivided cylindrical cell of 7 cm in diameter containing 700 mL solution, performing at 25°C in constant temperature water bath. The anode

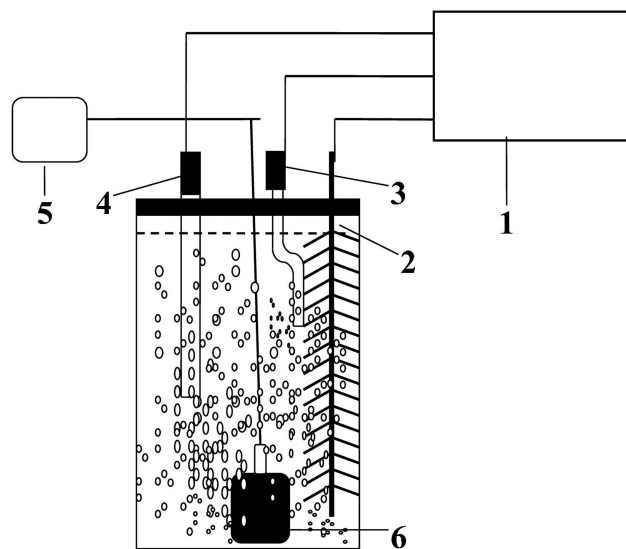


Figure 1. Schematic diagram of the electro-Fenton reactor: (1) ZF-9 potentiostat; (2) PAN-CFB cathode; (3) reference electrode: SCE; (4) $\text{Ti/IrO}_x\text{-TiO}_2/\text{IrO}_2$ mesh anode; (5) air pump; (6) aerator.

was a $\text{Ti/IrO}_x\text{-TiO}_2/\text{IrO}_2$ mesh electrode prepared according to our previous study [45]. The cathode was a PAN-CFB electrode constructed as described by Logan et al. [46], which had a two-wire Ti core that served as a current collector and about 2 g of PAN-based CF wires (T300–12 K, Yancheng Xiangsheng carbon fiber plant, China) twisted between the two titanium wires (TA2, $\Phi 1\text{ mm}$). The brush was 30 mm in diameter and 180 mm in length. The inter-electrode distance was 20 mm. During electrolysis, air was sparged near the cathode at a flow rate of 3 L min^{-1} by an air pump. Electrolysis was performed at constant current controlled by ZF-9 potentiostat/galvanostat (Shanghai Zhengfang Electric Appliance).

The electro-generation of H_2O_2 was carried out in a three-electrode system illustrated in Fig. 1. The brush cathode was used as working electrode, the titanium mesh anode as counter electrode, and a saturated calomel electrode as reference electrode. A 0.4 mol L^{-1} Na_2SO_4 solution was used as electrolyte.

The experiments to decolorize and degrade MB were performed in a two-electrode system (the same experimental apparatus as illustrated in Fig. 1 but without the reference electrode) in 0.4 mol L^{-1} Na_2SO_4 solution containing MB with different concentrations. The brush cathode was pre-saturated with 100 mg L^{-1} MB solution for 12 h to preclude the influence of color and COD removal due to MB adsorption on CF.

2.3 Apparatus and analytical procedures

2.3.1 H_2O_2 determination and CE

The concentration of accumulated H_2O_2 was determined spectrophotometrically by the titanium potassium oxalate ($\text{C}_4\text{K}_2\text{O}_9\text{Ti}$) method using UV-Vis spectrophotometry (Shimadzu UV 2450, Japan) at 400 nm [47]. The CE for H_2O_2 generation is defined as follows:

$$\text{CE}(\%) = \frac{zF\text{C}_{\text{H}_2\text{O}_2}V}{M_{\text{H}_2\text{O}_2}It} \times 100 \quad (1)$$

where $c_{\text{H}_2\text{O}_2}$ is the concentration of H_2O_2 (mg L^{-1}), F is the Faraday constant (96485 C mol^{-1}), z is the number of electron transferred for oxygen reduction to H_2O_2 , V is the bulk volume (L), $M_{\text{H}_2\text{O}_2}$ is the molar mass of H_2O_2 (34.01 g mol^{-1}), I is the applied current (A), and t is the electrolysis time (s).

2.3.2 Absorption spectra and color removal

Samples at different electrolysis times were taken from the solution and then filtered through $0.45 \mu\text{m}$ polyethersulphone membranes (Germany Membrane) for analysis. The absorption spectra of the filtrate were recorded by UV-Vis spectrophotometry equipped with 10 mm quartz cuvettes. The decolorization of MB solution was obtained by measuring the absorbance of the samples at λ_{max} (664 nm) in the visible region. The pH was measured with a Delta-320 pH-meter (Mettler Toledo) and the required pH values were adjusted by $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ or $0.5 \text{ mol L}^{-1} \text{ NaOH}$. The percentage of color removal was calculated from Eq. (2):

$$\text{Color removal (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

where A_0 and A_t are the absorbance at initial time and time t at the corresponding λ_{max} , respectively.

2.3.3 COD removal

The COD was measured according to Standard Methods for the Examination of Water and Wastewater [48] using the colorimetric method at 420 nm (Shimadzu, UV 2450). The percentage of COD removal was calculated using Eq. (3):

$$\text{COD removal (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (3)$$

where COD_0 and COD_t are the COD value (g L^{-1}) at initial time and given time t , respectively.

2.3.4 Electrochemical energy consumption (EEC)

EEC ($\text{kWh kg}^{-1} \text{ COD}$) was calculated according to Eq. (4) [49]:

$$\text{EEC} = \frac{IU t}{(\text{COD}_0 - \text{COD}_t)V} \quad (4)$$

where U is the applied voltage (V), t is the electrolysis time (h) and other parameters are the same as stated above.

3 Results and discussion

3.1 Influence of applied current on H_2O_2 production and current efficiency

The performance of wastewater treatment by electro-Fenton is deemed to be related with the production of hydrogen peroxide, which determines the amount of hydroxyl radical [35, 50]. Besides its catalytic activity to ORR from inherent doped nitrogen, the brush cathode with a fiber wire structure is beneficial to non-linear diffusion as well [51]. When enough dissolved oxygen from continuously pumping-in air diffuses to the cathode surface, a 2 e^- or 4 e^- ORR may take place (Eq. (5) [30] or Eq. (6) [52]).



In Na_2SO_4 solution, the reactions given in Eqs. (7) and (8) might take place on the anode, i.e. $\cdot\text{OH}$ is formed by the oxidation of water and H_2O_2 is formed by the combination of two $\cdot\text{OH}$ radicals [53]. Therefore, the electro-generation of H_2O_2 by a $\text{Ti}/\text{IrO}_x\text{-TiO}_2/\text{IrO}_2$ mesh anode was investigated firstly. Here, when using a $\text{Ti}/\text{IrO}_x\text{-TiO}_2/\text{IrO}_2$ mesh electrode as anode, a stainless steel electrode as cathode, no H_2O_2 was detected after electrolysis time of 60 min, which indicated that a $\text{Ti}/\text{IrO}_x\text{-TiO}_2/\text{IrO}_2$ mesh anode could not generate reactive oxygen species as e.g. $\cdot\text{OH}$, H_2O_2 under such conditions. Therefore, in the subsequent study, H_2O_2 was completely ascribed to the cathodic reduction reaction.



The catalytic performance of PAN-based CF to generate H_2O_2 via 2 e^- ORR was investigated at different current and the results are shown in Fig. 2. In Fig. 2a, the yield of H_2O_2 increased with the increasing applied current in the range of 100–300 mA. The concentration of H_2O_2 reached a maximum of 185 mg L^{-1} after 1 h at 300 mA, significantly higher than that from Wang et al. [34] who obtained a H_2O_2 generation rate of ca. $6.8 \text{ mg L}^{-1} \text{ h}^{-1}$ at 360 mA using an ACF felt cathode. This confirmed that PAN-based CF has obvious advantages over ACF as a cathode for the electro-Fenton system.

However, the concentration of H_2O_2 decreased when the applied current increased to 400 mA. It can be ascribed to the following two reasons: (1) the rate of side reactions on the cathode simultaneously

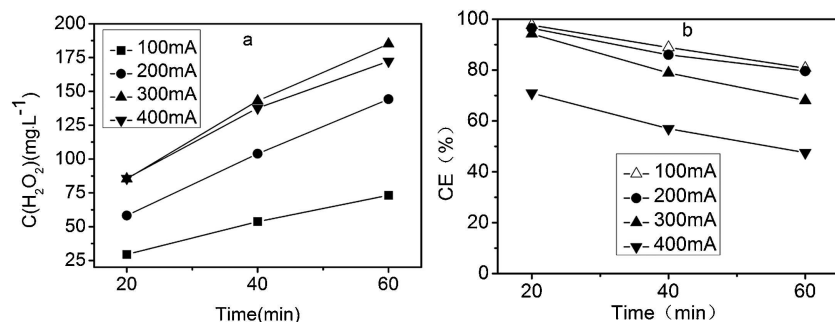


Figure 2. Production of H_2O_2 at different current: (a) H_2O_2 concentration vs. time and (b) current efficiency (CE) vs. time.

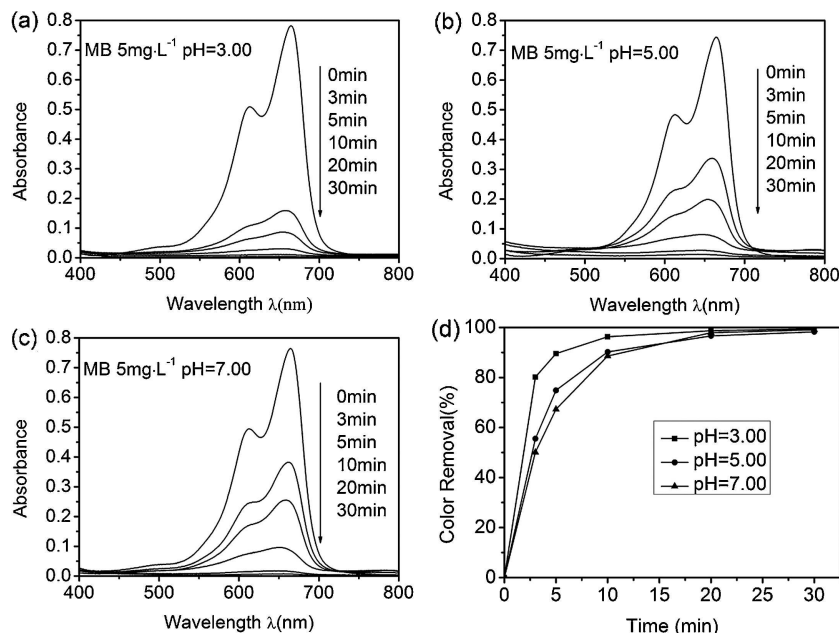


Figure 3. MB absorption spectra changes at different initial pH: (a) pH 3, (b) pH 5, (c) pH 7 and (d) color removal percentage with the electrolysis time. [MB] = 5 mg L⁻¹, [Fe²⁺] = 1 mmol L⁻¹, *I* = 300 mA.

increased with the applied current. The possible side reactions involved 4e⁻ ORR (Eq. (6)), hydrogen evolution reaction (Eq. (9)), and further reduction of H₂O₂ (Eq. (10) [54]); (2) the higher anode potential accelerated the decomposition of H₂O₂ on the anode (Eqs. (11) and (12) [55]).



In Fig. 2b, all current efficiencies approached 100% in the current range of 100–300 mA after 20 min, indicating a high catalytic activity to 2e⁻ ORR for the PAN-CFB cathode. Then, the current efficiency decreased with the proceeding of electrolysis, which may be caused by side reactions as mentioned above. But they still maintained >68% (the value at 300 mA) after 1 h, indicating that 2e⁻ ORR plays a dominant role and the PAN-CFB cathode possesses a high selectivity to 2e⁻ ORR. Therefore, considering both H₂O₂ yield and current efficiency, the electrolysis current of 300 mA was applied thereafter.

3.2 Influence of initial solution pH on color removal

The electro-generated H₂O₂ diffuses into the bulk solution and reacts with Fe²⁺, generating the strong oxidant [•]OH (Eq. (13)), and Fe²⁺ can be partially regenerated on the cathode via the reduction reaction of Fe³⁺ (Eq. (14)) [30].

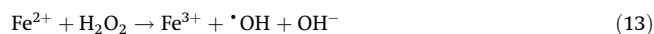


Figure 3 shows the decolorization performance of MB via the electro-Fenton process at different initial pH values. In general, absorption spectra of high MB concentrations shows two absorption peaks at 610 and 664 nm, respectively, whereas only one absorption peak at 664 nm can be observed for low MB concentrations. So the characteristic absorption peak at 664 nm is usually ascribed to the MB monomer (this strong absorbance is relevant to the blue color of MB in aqueous solution), and that at 610 nm is ascribed to the MB dimer [56]. In Fig. 3a, the variations of MB absorption spectra with time at initial pH 3 showed the best decolorization performance, with the MB absorption peaks plummeting most rapidly. In only 10 min, the peaks at 610 and 664 nm disappeared, indicating the breakdown of the MB dimer and the destruction of chromophore groups. This result is consistent with the optimal pH range of 2.8–3.5 reported by other authors [49]. Within this range, [•]OH has the most oxidizing power (the oxidation potential of [•]OH decreases with increasing pH and reaches the maximum value 2.65–2.80 V (vs. normal hydrogen electrode (NHE)) at pH 3, while only 1.9 V (vs. NHE) when pH increases to 7) and the catalytic activity of Fe²⁺/Fe³⁺ redox couple can be kept [57, 58]. Besides, less [•]OH generation at a very high pH also contributes to a little worse decolorization performance compared with that at pH 3. For instance, at pH > 5, Fe²⁺ is oxidized and hydrolysis occurs generating precipitates like Fe(OH)₃, resulting in insufficient Fe²⁺ to react with H₂O₂.

However, in this study, the effect of initial pH on decolorization performance was not as obvious as in many studies [49]. In Fig. 3b and c, though the MB absorption peaks did not decrease so rapidly as those at initial pH 3, no obvious absorption can be observed in the whole visible region after 30 min as well. Furthermore, by monitoring the MB absorption peak at 664 nm and calculating by Eq. (2), color removal percentages of the solution with initial pH at 3, 5, and 7 reached 99.5, 98.3, and 99.1%, respectively, as shown in Fig. 3d, and the final absorbance was 0.004, 0.013, and 0.007, respectively. The final weak absorption was ascribed to a tiny amount of Fe²⁺ and Fe³⁺, which made the final solution unstable

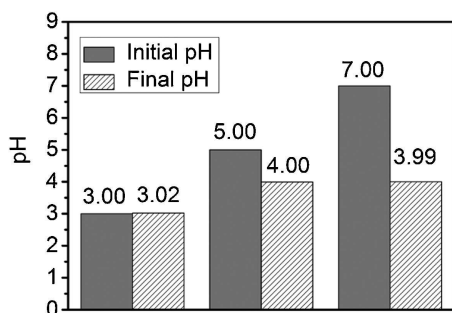


Figure 4. pH variation of MB solutions with different initial pH afore and after 60 min of electrolysis. [MB] = 5 mg L⁻¹, [Fe²⁺] = 1 mmol L⁻¹, *I* = 300 mA.

and slightly fluctuant color removal percentage (<100%). In summary, the electro-Fenton system using a PAN-CFB cathode has a wide applicable pH range (3–7), which is cost-effective for wastewater treatment since no pH adjustment is necessary, and relieves the corrosion of equipments under strong acidic condition. The wide applicable pH range of the decolorization process might be explained as follows:

Firstly, it is related to the pH variation of the solution. The pH values before and after electrolysis were tested and are shown in Fig. 4. After 60 min, the initial solution pH 3 is more or less unchanged, while the other two solutions dramatically dropped from 5 and 7 to 3.99 and 4, respectively. The drop of pH is favorable to the Fenton reaction and leads to good decolorization results at initial pH 5 and 7 as well. The acidification of the solution during the electrolysis can be ascribed to hydrolytic precipitation of the iron (Eq. (15)), anodic oxygen evolution reaction (Eq. (16)), and the generated short-chain carboxylic acids in the step preceding CO₂ evolution. The pK_a value of these acids is predominant in the pH range 3–4, which corresponds to final pH values of the solution [59].



Secondly, it might be related to the amount of H₂O₂ generated on the cathode. In the study, the initial solution pH did not dramatically affect the H₂O₂ yield in the Na₂SO₄ solution. The electrochemical formation of H₂O₂ was almost equal with a high concentration of 168.6, 151.2, 155.1 mg L⁻¹ in 1 h, respectively, at initial pH 3, 5, and 7, which differed from the study with high H₂O₂ production only in a narrow range of pH [60].

Besides, the color removal at initial pH 7 can be partially ascribed to coagulation, which was verified by chemical coagulation experiments using FeCl₃ as flocculant with the same concentration as the added FeSO₄ in the electro-Fenton process. The coagulation treatment revealed that after 30 min, the absorbance of MB solution decreased from 0.7681 to 0.7125 and the color removal was only 7.2%. Further decolorization was not observed with the increasing treatment time. In the electro-Fenton process, FeSO₄ was added as a Fe²⁺ source and it was partially converted into Fe³⁺ via the Fenton reaction and played the role of the flocculant. So, color removal caused by coagulation was quite limited and was <7.2% in the electro-Fenton process.

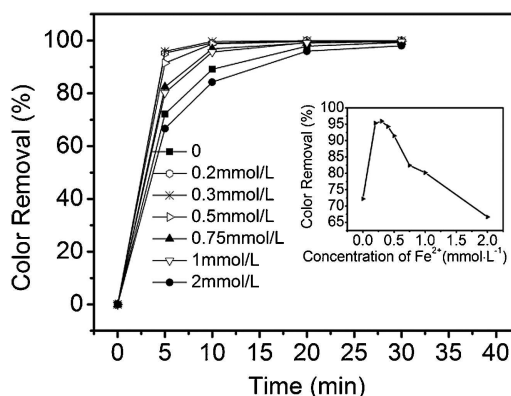


Figure 5. Effect of Fe²⁺ concentration on color removal of MB with the electrolysis time. [MB] = 5 mg L⁻¹, *I* = 300 mA, initial pH 3. The inset shows the color removal percentage after 5 min of electrolysis as a function of Fe²⁺ concentration.

3.3 Influence of Fe²⁺ concentration on color removal

It is important to establish the suitable amount of Fe²⁺ needed for the electrolysis to achieve higher efficiency. Figure 5 plots the influence of the Fe²⁺ concentration on color removal. The percentage of the color removal reached nearly 100% after 30 min of electrolysis in the range of 0–2 mmol L⁻¹ Fe²⁺. The MB decolorization performed better when the Fe²⁺ concentration was between 0.2 and 1 mmol L⁻¹ compared to 0 or 2 mmol L⁻¹. The color removal percentage after 5 min versus Fe²⁺ concentration was illustrated in the inset, and a gradual increase of the color removal from 72.2 to 96.0% can be observed when the Fe²⁺ concentration increased from 0 to 0.3 mmol L⁻¹. However, a further increase of Fe²⁺ concentration from 0.4 to 2 mmol L⁻¹ caused a gradual decrease of the color removal from 94.3 to 66.7%.

When the Fe²⁺ concentration is low, insufficient Fe²⁺ can catalyze the conversion of H₂O₂ into [•]OH via reaction (9) leading to a reduction in the [•]OH generation rate and accumulation of H₂O₂. The excessive H₂O₂ would react with [•]OH via Eq. (17). This side reaction leads to the consumption of both H₂O₂ and [•]OH and the production of hydroperoxyl (HO₂[•]), a much weaker oxidizing species compared with [•]OH [61]. When the Fe²⁺ concentration is high, excessive Fe²⁺ also consumes [•]OH via Eq. (18) [62], which leads to the decrease of the Fenton reaction efficiency. Consequently, both insufficient and excessive Fe²⁺ weakened the decolorization performance.



3.4 The decolorization/degradation performance under different concentration of MB

3.4.1 UV-Vis spectra

Figure 6 reveals the UV-Vis absorption spectra of MB solutions changing with time. The UV-Vis spectra presents two characteristic peaks in the Vis region at 610 and 664 nm, and two characteristic

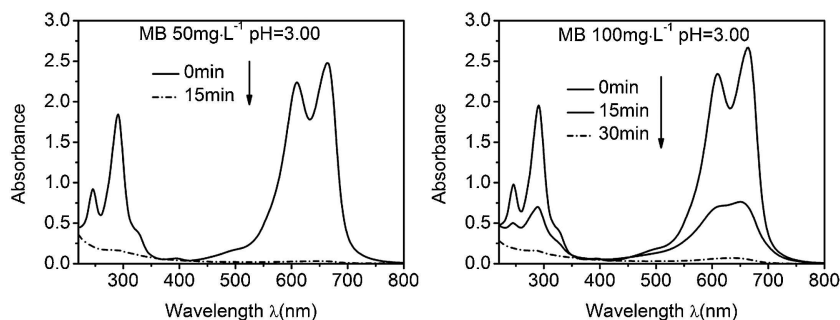


Figure 6. Changes in the UV–Vis spectra of 50 and 100 mg L^{−1} MB with the electrolysis time. [Fe²⁺] = 0.3 mmol L^{−1}, *I* = 300 mA, initial pH 3. The samples were diluted for onefold and fourfold, respectively, for 50 and 100 mg L^{−1} of MB solution before monitoring.

peaks in the UV region at 245 and 292 nm. In 50 mg L^{−1} MB solution, all four characteristic peaks disappeared after 15 min, while they significantly decreased after 15 min and almost disappeared after 30 min in 100 mg L^{−1} MB solution. It is worth mentioning that the slight absorption in the UV region might be ascribed to the small molecules generated by MB degradation; what's more, there is strong absorption of H₂O₂ in the range of 185–300 nm [63], which also contributes to the absorption in the UV region to some extent. The bands at 245 and 292 nm decreased significantly within 30 min and no new bands appeared. This implies that a full oxidative decomposition of phenothiazine species has occurred and no intermediates containing the phenothiazine moiety were formed [64].

3.4.2 Color and COD removal

As shown in Fig. 7, in 50 mg L^{−1} MB solution, the color removal percentage reached 98.8% while only 60.6% COD was removed after 15 min. Similarly, in 100 mg L^{−1} MB solution, the color removal percentage reached 98.0% after 30 min, with only 58.8% COD removed. This indicates that the COD removal lags behind the color removal, and the complete color removal does not mean the whole degradation of organics but mere destruction of the chromophore, indicating that MB was oxidized firstly to colorless intermediates. Eventually, prolonging the electrolysis time to 60 min, the COD removal of these two MB solutions reached 84.0 and 95.9%, respectively, indicating that MB was almost completely degraded. The COD removal for 50 mg L^{−1} MB is less than that of 100 mg L^{−1} MB. This phenomenon is probably related to bad mass transfer performance of [•]OH. The mean lifetime of [•]OH is estimated to be only a few nanoseconds in water [49]. For high MB concentration solutions, the reaction probability between [•]OH and MB molecules is high, so is the COD removal percentage. While in low MB concentration solutions, a substantial portion of [•]OH quenches

before it reacts with MB, leading to lower COD removal percentage. Zhao et al. [65] studied the MB (5 mg L^{−1}) degradation by the electro-Fenton process and its decolorization efficiency reached 95% after 90 min treatment under the optimum condition. In contrast, the time to completely decolorize MB (100 mg L^{−1}) here is significantly shorter (only 30 min). There is no literature related to electro-Fenton degradation of MB that shows comparable COD data, so we just compared the COD removal with the related literature [66, 67] using other electrochemical methods, and the COD removal efficiency is also significantly higher in the same treatment time. Meanwhile, the electrochemical energy consumption for degrading 100 mg L^{−1} MB solution for 1 h was calculated to be 11.6 kWh kg^{−1} COD by Eq. (4), which is lower and the process time is shorter compared with the related literature [50, 68]. Therefore, the electro-Fenton system using a PAN-CFB cathode to degrade organic contaminants is quite promising.

4 Conclusions

The PAN-CFB cathode has good conductivity and excellent oxygen-transfer performance, and H₂O₂ could be effectively generated for its high catalytic performance to 2 e[−] ORR. Under the condition of applied current 300 mA, the H₂O₂ concentration could reach a maximum of 185 mg L^{−1} in 1 h.

The decolorization process performed best at initial pH 3 with a color removal percentage of nearly 100% in short time. However, the effect of initial pH on decolorization performance of MB via the electro-Fenton process using the PAN-CFB cathode was not so obvious, namely the process possessed a wide applicable pH range from 3–7. The optimum concentration of Fe²⁺ for the process was 0.3 mmol L^{−1}.

Regarding the 100 mg L^{−1} MB solution, the complete color removal could be obtained in 30 min, and the COD removal reached 95.9% in 1 h under the following condition: applied current 300 mA,

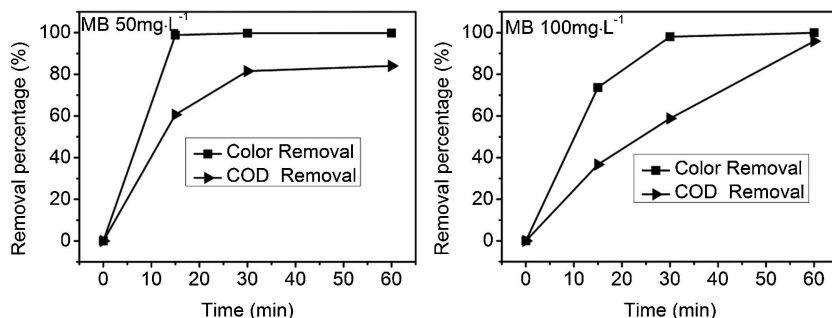


Figure 7. Color removal and COD removal percentages of 50 and 100 mg L^{−1} MB solution with the electrolysis time. [Fe²⁺] = 0.3 mmol L^{−1}, *I* = 300 mA, initial pH 3.

initial pH 3, Fe^{2+} concentration 0.3 mmol L^{-1} ; the EEC was 11.6 kWh kg^{-1} COD.

Consequently, the PAN-CFB electrode is a promising cathode for the electro-Fenton process because of the high selectivity to 2 e^- ORR with high H_2O_2 production, the wide applicable pH range, the short process time, low energy consumption, and high color and COD removal percentage.

Acknowledgement

The authors thank the National High Technology Research and Development Programme for Advanced Materials of China (No. 2012AA03A602), Award Foundation for Outstanding Middle-aged and Young Scientist of Shandong Province (No. BS2011NJ019), Science-Technology Program for Basic Research Project of Qingdao (No. 12-1-4-1-(28)-jch).

The authors have declared no conflict of interest.

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