



Design of an electro-Fenton system with a novel sandwich film cathode for wastewater treatment

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ABSTRACT

In this study, we demonstrate an electro-Fenton (E-Fenton) system constructed with a novel sandwich film cathode (SFC). For the fabrication of SFC, Fe²⁺-chitosan (Fe-CHI) was first deposited on foam nickel (Fe-CHI/Ni). Then two pieces of Fe-CHI/Ni was used to fasten one piece of activated carbon fiber (ACF) to obtain a Fe-CHI/Ni|ACF|Fe-CHI/Ni sandwich film cathode. We interestingly found that this SFC based E-Fenton system could effectively degrade rodamine B with *in situ* generating both hydrogen peroxide and iron ions. Its degradation efficiency was significantly higher than those of the E-Fenton systems constructed with composite cathodes of carbon nanotubes with Fe@Fe₂O₃ core-shell nanowires or Cu₂O nanocubes reported in our previous studies. Hydrogen peroxide electrogenerated through the reduction of O₂ adsorbed on the sandwich film cathode and the iron ions produced by the leakage from Fe²⁺-chitosan film during the E-Fenton reaction were, respectively, monitored, providing clues to understand the high efficiency of this novel SFC based E-Fenton system. More importantly, this low-cost sandwich film cathode was very stable and could be reused without catalytic activity decrease, suggesting its potential application in the wastewater treatment.

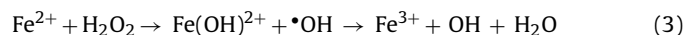
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1. Introduction

Advanced oxidation processes (AOPs), which involved *in situ* generation of highly potent chemical oxidants such as hydroxyl radicals ($\cdot\text{OH}$), have emerged as an important class of new technologies to accelerate the non-selective oxidation [1–3]. Fenton reaction is one of the most widely used AOPs for the destruction of a wide range of recalcitrant organic contaminants such as dyes that cannot be eliminated biologically in wastewater [4,5].

Although the classic Fenton reactions (Fe²⁺/H₂O₂) have been widely used for the treatment of effluents, they have two main drawbacks for large-scale application in the wastewater treatment: the high cost of H₂O₂ and the narrow working pH range (2–3) because iron ions precipitates as a hydroxide at higher pH values. Electrochemical Fenton (E-Fenton) process seems to be able to overcome these two problems because both of H₂O₂ and iron ions could be produced *in situ* in the E-Fenton system [6–10]. The generally accepted free radical chain mechanism for the cathodic E-Fenton reactions consisting of the ferrous ions and hydrogen peroxide is shown in Eqs. (1)–(6) [11,12]. The main sources of hydroxyl radicals are produced by anodic water oxidation (Eq. (1)) and con-

tinuous electrogeneration of H₂O₂ by O₂ reduction (Eq. (2)) in the presence of dissolved Fe²⁺. The combination of H₂O₂ and Fe²⁺ produces Fenton's reagent (Eq. (3)). Fe³⁺ species generated from Fenton's reaction (Eq. (3)) revert to Fe²⁺ by different reduction processes, involving H₂O₂ or organic intermediate radicals, as well as the direct reduction of Fe³⁺ on the cathode. This allows the propagation of the Fenton's reaction via a catalytic cycle. The reduction of Fe³⁺ by H₂O₂ takes place in two steps (Eqs. (4) and (5)), and also produces hydroperoxyl radicals as does the anodic oxidation of H₂O₂ (Eq. (6)). Therefore, pollutants can be destroyed by hydroxyl and hydroperoxyl radicals produced on both anode and cathode, while most of the degradation is done by the stronger oxidizing power of hydroxyl radicals.



Recently, great advances have been made in developing novel E-Fenton system for degradation of organic wastewater [13–15]. For example, mercury pool [16], reticulated vitreous carbon [17], activated carbon fiber [18] and carbon felt [19] and

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carbon-polytetrafluoroethylene (PTFE) [20,21] are used as cathode materials for the reduction of O_2 . Our group have fabricated various composite cathodes by combining carbon nanotubes with Fe@Fe₂O₃ core-shell nanowires or Cu₂O nanocubes using PTFE, to establish novel E-Fenton systems which could work effectively at neutral pH range [22,23]. Although the utilization of these nanostructured composite electrodes could significantly enhance the efficiency of E-Fenton systems, the synthesis of nanostructured materials were complicated and would increase the cost for wastewater treatment greatly. Therefore, it is still necessary to develop more cost-saving and efficient electrodes for E-Fenton process.

In this study, we demonstrate an electro-Fenton (E-Fenton) system constructed with a novel sandwich film cathode (SFC). Compared with the preparation of composite cathode with nanostructured materials, the SFC fabrication is very simple and only requires inexpensive and handy materials including FeSO₄, foam nickel, chitosan, glutaraldehyde and activated carbon fiber (ACF) (Fig. 1).

2. Experimental

2.1. Chemicals

Rodamine B, FeSO₄·7H₂O, anhydrous sodium, chitosan, glutaraldehyde, H₂SO₄ were of analytical reagent grade, and obtained from National Medicines Corporation Ltd. of China. All other reagents were of commercially available analytical grade and were used without further purification. Active carbon fiber (ACF) and foam nickel were purchased from China Southern Chemicals Import and Export Corporation. Deionized water was used throughout this study.

2.2. Fabrication of the sandwich film cathode

The Fe-CHI/Ni|ACF|Fe-CHI/Ni sandwich film cathode (SFC) was prepared as follows. First, certain amount of Fe²⁺-chitosan (Fe-CHI) aqueous solution was deposited on foam nickel (Fe-CHI/Ni) and dried, following with the immersion in 1% glutaraldehyde aqueous solution to obtain Fe-CHI/Ni film. Then, two pieces of the resulting Fe-CHI/Ni and one piece of ACF were fasten using elastic line to get the sandwich film cathode. Before fastening, the ACF was immersed in the high concentration pollutant solutions for more

than 1 day to reach saturated adsorption of pollutants on ACF. The areas of all Fe-CHI/Ni and ACF were 2 cm × 3 cm. The Fe-CHI solution was prepared by dissolving 0.5 g FeSO₄·7H₂O in 5 mL of 2% chitosan aqueous solution. Chitosan is a well-known filmogenic material, which can adsorb metal ions to prevent their fast dissolution in water [24,25]. Since the resulting Fe-CHI film on foam nickel was prone to hydrolyze and swell, especially in the acidic media, the subsequent immersion of Fe-CHI film in 1% glutaraldehyde aqueous solution was required to cross-link the chitosan film and prevent the swelling and peeling-off of the Fe-CHI film. During the immersion, glutaraldehyde was able to block amino groups and make chitosan structures more inert and resistant to acidic media.

2.3. Procedure of cathodic electro-Fenton degradation of rhodamine B

The E-Fenton experiments were performed in a single cell with a two-electrode system at room temperature, using a CHI-660B (Shanghai, China) electrochemical workstation. The as-prepared sandwich composite electrode was used as the working cathode. A Pt sheet (99.99% purity, Beijing academy of Steel Service) of 2.0 cm² in area was used as the anode. The initial concentrations of RhB was 5 mg L⁻¹. Typically, 0.05 mol L⁻¹ of Na₂SO₄ aqueous solution was used as the supporting electrolyte to increase the conductivity. Air was bubbled (0.1 m³ h⁻¹) into the solution during the E-Fenton degradation. The RhB solutions were neutral (pH 6.2) if without pH adjustment. During the degradation, the pH of the RhB solution did not change. In some cases, 0.5 mol L⁻¹ of NaOH or H₂SO₄ was used to adjust the initial pH of the RhB solution for comparison. The solution was magnetically stirred at room temperature during the whole E-Fenton reaction. Before degradation experiments, the sandwich film cathodes were contacted with 5 mg L⁻¹ RhB solution for 4 h to establish adsorption/desorption equilibrium between the solution and the electrodes. Two counterpart cathodes prepared by fastening one piece of ACF with two pieces of foam nickel without Fe-CHI coating or two pieces of foam nickel with Fe-chitosan but without ACF fastening were tested under the same conditions, which were denoted as Ni|ACF|Ni and Fe-CHI/Ni|Fe-CHI/Ni, respectively. Series of experiments with freshly prepared cathodes were performed to investigate the effect of applied current, pH, supporting electrolyte and the concentration of premonitory solution on the degradation. The concentration of RhB was monitored by colorimetry with a U-3310 UV-vis spectrometer (HITACHI) at an interval of 30 min.

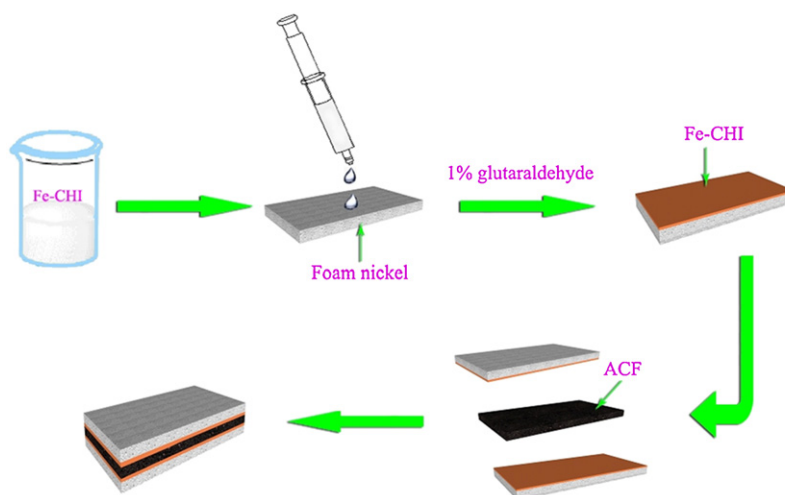


Fig. 1. Schematic illustration of preparation procedures of sandwich film cathode.

2.4. Determination of hydrogen peroxide and total iron ions concentrations

The analysis of hydrogen peroxide was carried out using the off-line sampling and UV–vis spectrum [26]. 0.75 mL of 1,2-benzenedicarboxylic acid (0.1 mol L^{-1}) was mixed with 0.75 mL of an aqueous solution containing 0.4 mol L^{-1} potassium iodide, 0.06 mol L^{-1} sodium hydroxide, and $1 \times 10^{-4} \text{ mol L}^{-1}$ ammonium-molybdate, followed by the addition of 1.5 mL of sample solution. After placed for 2 min, the resulting mixed solution was analyzed with a UV–vis spectrophotometer (U-3310, HITACHI), measuring the absorbance at 352 nm where the absorbance was linearly dependent on H_2O_2 concentration in solution. The concentration of total iron ion (Fe^{2+} and Fe^{3+}) in the solution was measured by atom absorption spectrometry (WFX-1F2, China).

3. Results and discussion

3.1. E-Fenton degradation of RhB with different cathodes at neutral pH

RhB was chosen as the model pollutants to test the efficiency of the Fe-CHI/Ni|ACF|Fe-CHI/Ni SFC based E-Fenton system in this study. For comparison, the degradation of RhB was also carried out on the two counterpart cathodes, one was a sandwich cathode without Fe-CHI coating (Ni|ACF|Ni), and the other was a double-layer cathode without ACF (Fe-CHI/Ni|Fe-CHI/Ni). SEM observation revealed that foam nickel was of network structure and CHI or Fe-CHI were covered on the network of foam nickel. The particles of Fe-CHI were obviously larger than those of CHI (Fig. S1, Supplementary Material). Before degradation experiments, the SFC electrodes were immersed in the pollutant solutions for 4 h without electricity. During the immersion, the pollutant solutions were sampled for analysis at the same interval of 30 min and found their concentrations were not changed, confirming the saturated adsorption of pollutants on the electrodes before degradation. No obvious RhB degradation was observed in the E-Fenton systems based on the Ni|ACF|Ni and Fe-CHI/Ni|Fe-CHI/Ni counterpart cathodes after 120 min of reaction (Fig. 2). Impressively, 93% of RhB was degraded in the SFC based E-Fenton system at neutral pH in 120 min, which was significantly higher than those in the E-Fenton systems based on the previous $\text{Fe}@\text{Fe}_2\text{O}_3/\text{ACF}$ (74.1%) [22] and $\text{Cu}_2\text{O}/\text{CNTs}/\text{PTFE}$

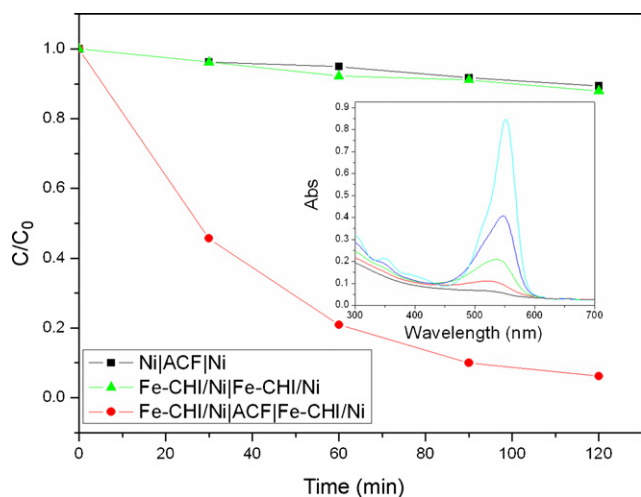


Fig. 2. Degradation of RhB in the different E-Fenton systems at neutral pH. The inset is UV–vis spectra changes of RhB during the E-Fenton degradation on the sandwich film cathode. The applied current was 10 mA, the electrolyte was $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, the initial concentration of RhB was 5 mg L^{-1} .

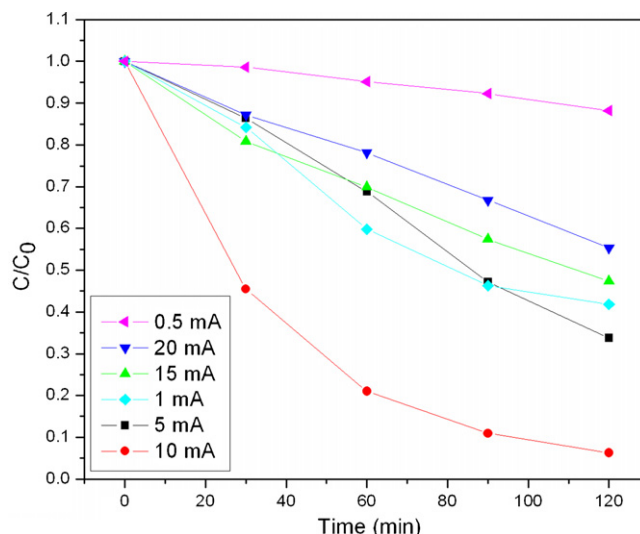


Fig. 3. Influence of applied current on the RhB degradation in the sandwich film cathode based E-Fenton system. The electrolyte was $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, the initial concentration of RhB was 5 mg L^{-1} .

(80.2%) [23]. These comparisons reveal high activity of this new E-Fenton system based on the Fe-CHI/Ni|ACF|Fe-CHI/Ni sandwich film cathode at neutral pH. UV–vis spectra change of RhB could imply the degradation mechanism in the E-Fenton system (inset of Fig. 2). The absorption spectrum of RhB solution was characterized by its maximum absorption at 555 nm in the visible region, which was attributed to the chromophore-containing azo linkage (conjugated xanthene ring) of the dye molecules. The absorption peak at 555 nm diminished with increasing E-Fenton reaction time, indicating that the rapid degradation of RhB was attributed to the decomposition of the conjugated xanthene ring in RhB. This is reasonable because the $\text{N}=\text{N}$ bond of the azo dye is the most active site attacked by $\cdot\text{OH}$ radicals.

3.2. The effect of major factors on the degradation efficiency

The influence of applied current on E-Fenton degradation of RhB with the Fe-CHI/Ni|ACF|Fe-CHI/Ni SFC at neutral pH was examined (Fig. 3). It was found that applied current significantly affect the efficiency of this novel E-Fenton system. The degradation of RhB increased with applied current increasing from 0.5 to 10 mA and then decreased steadily from 10 to 20 mA, and the voltages corresponding to different current from 0.5 to 20 mA were 1.3, 1.9, 2.1, 2.7, 3.3 and 3.8 V, respectively. This suggests 10 mA is the optimum applied current for this new E-Fenton system. The relationship between the production of $\cdot\text{OH}$ and the concentrations of Fe^{2+} and H_2O_2 can be shown in Eq. (7), where λ is the coefficient of the E-Fenton reaction, k is the apparent rate constant of the E-Fenton reaction, $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ are the concentrations of iron ions and H_2O_2 produced in the E-Fenton process, respectively:

$$[\cdot\text{OH}] = \lambda \times \left(\frac{d[\cdot\text{OH}]}{dt} \right) g = \lambda \times k \times [\text{Fe}^{2+}] \times [\text{H}_2\text{O}_2] \quad (7)$$

According to Eq. (7), higher applied current could enhance the production of electrogenerated H_2O_2 , which is the reason for the degradation efficiency enhancement with increasing applied current from 0.5 to 10 mA. However, too high absolute applied current would result in more parasitic reactions, such as electrolysis of water. These parasitic reactions would reduce the degradation efficiency. At the same time, the efficiency for currents decreased. Therefore, we chose 10 mA as the applied current.

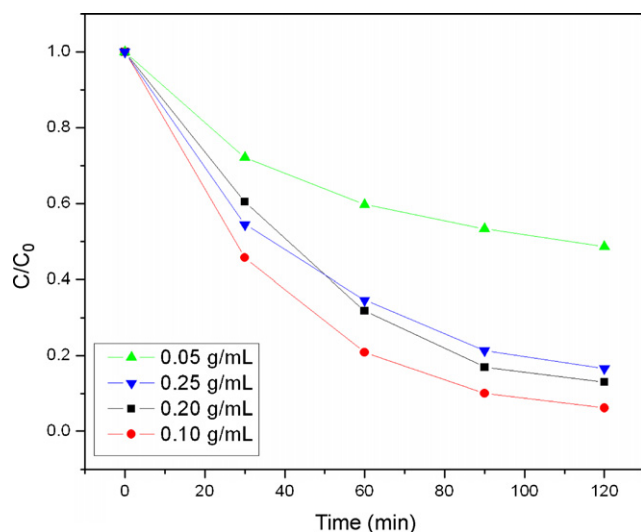


Fig. 4. Influence of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration in the chitosan solution on the degradation of RhB in the sandwich film cathode based E-Fenton system. The applied current was 10 mA, the electrolyte was 0.05 mol L^{-1} of Na_2SO_4 , the initial concentration of RhB was 5 mg L^{-1} .

The concentration of iron reagent plays an important role in the E-Fenton system because iron ions can catalyze the decomposition of H_2O_2 to form $\cdot\text{OH}$ in the Fenton oxidation process [27–29]. In order to investigate the influence of iron reagent concentration, we performed E-Fenton degradation experiments with a series of SFCs fabricated with the chitosan solutions containing different concentrations (from 50 to 250 g L^{-1}) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. As showed in Fig. 4, the degradation was 51%, 93%, 87%, and 83% when the concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in chitosan solutions were 50, 100, 200 and 250 g L^{-1} , respectively. Obviously, when the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in chitosan solution was 50 g L^{-1} , the amount of Fe^{2+} in the RhB aqueous solution were too few, resulting in low degradation efficiency of the E-Fenton system. More $\cdot\text{OH}$ would form from Fenton's reaction in case of higher concentrations of Fe^{2+} in the sandwich film cathode. The degradation efficiency reached maximum when the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was 100 g L^{-1} in the chitosan aqueous solution. When the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the chitosan solution was too high (in case of 200 and 250 g L^{-1}), excess Fe^{2+} would produce in the RhB solution by the leakage of Fe-CHI and convert to plenty of Fe^{3+} through Fenton's reaction (Eq. (3)). At this time, if the amount of electrogenerated H_2O_2 could not sufficiently supply for the reduction of Fe^{3+} (Eq. (4)), the conversion of Fe^{2+} species generated from Fenton's reaction to Fe^{2+} would be inhibited (Eq. (5)), which decreased the formation of $\cdot\text{OH}$ finally [27,30]. This can account for the low degradation efficiency in case of 200 and 250 g L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the chitosan solution. Therefore, the optimum $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration in chitosan aqueous solution was found to be 100 g L^{-1} .

The pH of solution plays an important role in Fenton system. It is known that the optimum pH for Fe^{2+} to catalyze the decomposition of hydrogen peroxide is 2–3. However, the optimum condition for the electrochemical generation of hydrogen peroxide in the E-Fenton system is in basic pH range, especially at pH 10–11 [31]. Therefore, most of E-Fenton systems cannot exhibit desirable degradation efficiency at neutral pH. Actually, E-Fenton reactions are generally performed in acidic conditions with pH between 2 and 4 [32], their oxidative ability will become weak if $\text{pH} > 4$ [33–36]. In this study, we investigated the influence of the initial pH on the degradation efficiency of this SFC based E-Fenton system (Fig. 5). It was found that this new E-Fenton system could effectively work under pH ranging from 2.5 to 7.5.

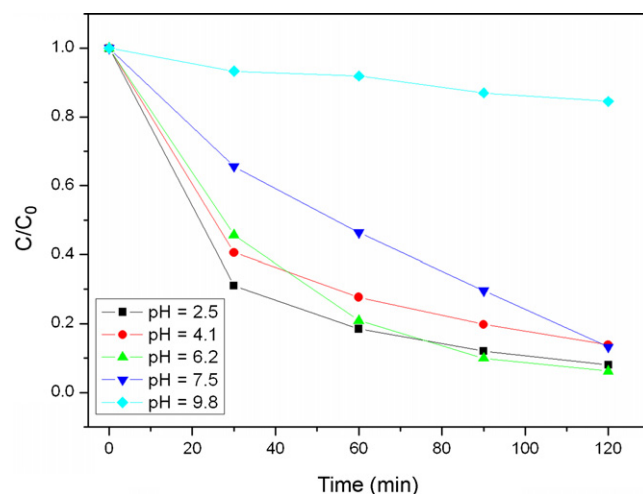


Fig. 5. Influence of solution pH on the RhB degradation in the sandwich film cathode based E-Fenton system. The applied current was 10 mA, the electrolyte was 0.05 mol L^{-1} Na_2SO_4 , the initial concentration of RhB was 5 mg L^{-1} .

The degradation of RhB at neutral pH of 6.2 could impressively reach up to 92%. The degradation efficiency decreased with further increase of pH value to 7.5–9.8. This is because the free iron species in the solution decrease due to the formation of Fe^{2+} complexes and the precipitation of ferric oxyhydroxides at a basic pH [37,38].

In order to investigate the effect of supporting electrolyte on the degradation of RhB, the solution of different sodium salts (nitrate, carbonate and sulfate) were used as supporting electrolyte under the same conditions (Fig. 6). The selection of sodium chloride was ruled out, because Cl_2 would be produced as a result of chlorine oxidation during the electrolysis process in the presence of sodium chloride, resulting in secondary pollution. The degradation efficiencies were 93.8%, 62.8%, and 20.6% for sodium sulfate, sodium nitrate and sodium carbonate supporting electrolytes, respectively. Sodium carbonate system can consume hydroxyl radicals, because CO_3^{2-} gave an electron to hydroxyl radical making it to be OH^- , and decreased the oxidation of hydroxyl radicals. Actually, the reactions of SO_4^{2-} and NO_3^- with $\cdot\text{OH}$ are slow to the degree of being ignored. In this E-Fenton system, the performance of sodium sulfate supporting electrolyte is better than that of sodium nitrate. Therefore,

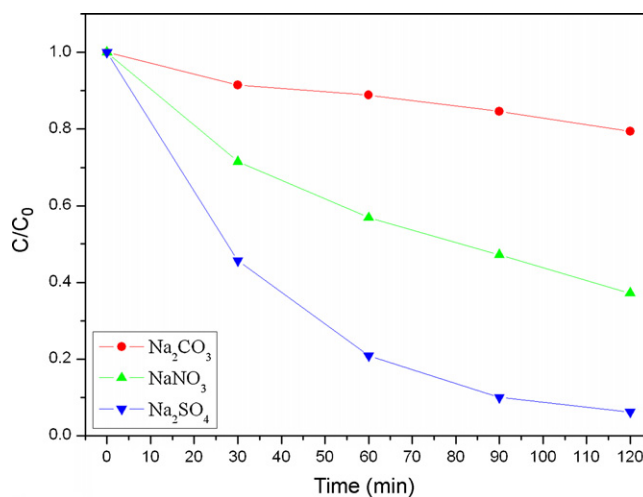


Fig. 6. Influence of supporting electrolyte on the degradation of RhB in the sandwich film cathode based E-Fenton system at neutral pH. The applied current was 10 mA, the initial concentration of RhB was 5 mg L^{-1} .

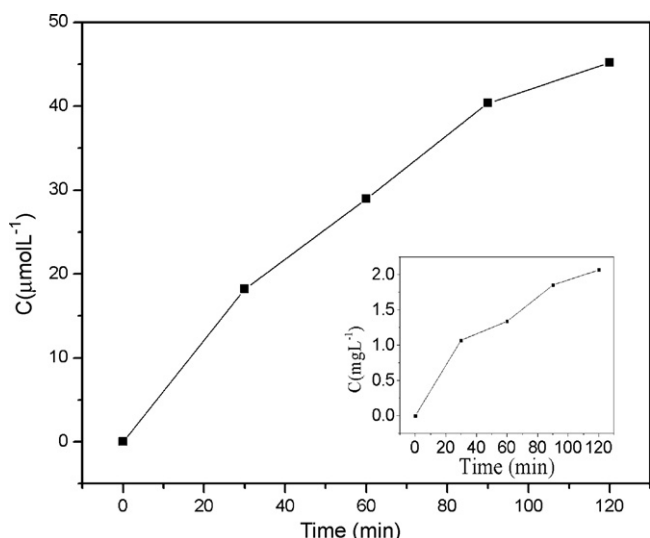


Fig. 7. Time-course of H₂O₂ concentrations and iron concentrations (inset) during the E-Fenton degradation of RhB based on the SFC at neutral pH with a two-electrode system.

sodium sulfate was finally chosen as the supporting electrolyte in this study.

3.3. The analysis of H₂O₂ and iron ions in the reaction solution

To understand the high degradation efficiency of this Fe-CHI/Ni|ACF|Fe-CHI/Ni SFC based E-Fenton system at neutral pH, we measured the concentrations of H₂O₂ and iron ions *in situ* produced during the degradation process (Fig. 7). The formation of H₂O₂ is crucial to produce •OH during Fenton reactions. The RhB aqueous solutions were sampled at an interval of 30 min to measure the concentrations of electrogenerated hydrogen peroxide (Fig. 7). It could be observed that the generation of hydrogen peroxide almost increased linearly with the reaction proceeds at the first stage, then reached a balance after 90 min. The concentration of H₂O₂ was $45.17 \times 10^{-6} \text{ mol L}^{-1}$ at 120 min of E-Fenton reaction, indicating that the SFC is a suitable cathode for the electrogeneration of H₂O₂. Meanwhile, the concentrations of iron ions at different reaction time during the E-Fenton process were detected by atom absorption spectrometry (inset of Fig. 7). It was found that the concentration of iron ions went up steadily from zero to 2.068 mg L^{-1} at 120 min. Therefore, after 120 min, the concentration of iron reagent

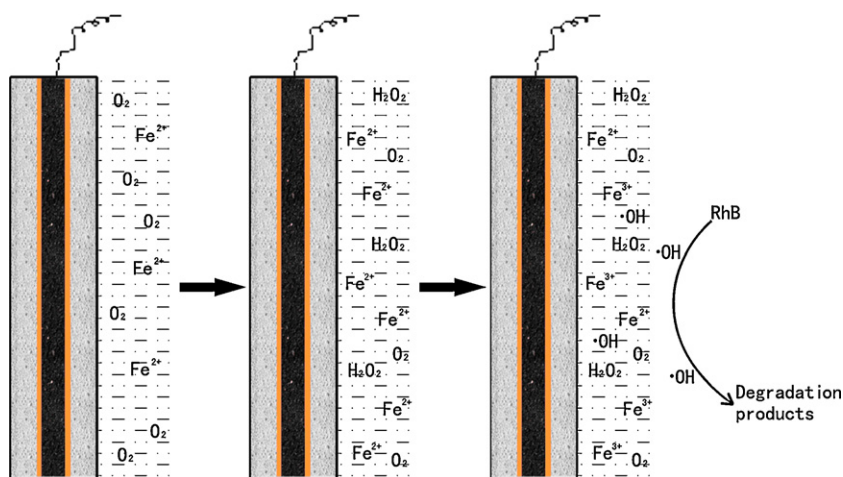
and H₂O₂ were 36.9 and $45.17 \mu\text{M}$ in this E-Fenton system, respectively. This nature of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ less than 1 would favor the Fenton reactions [39]. These free iron ions in the solution would react with electrogenerated H₂O₂ to generate plenty of hydroxyl radicals to degrade organic pollutants (Eqs. (4) and (5)). These results confirm that this Fe-CHI/Ni|ACF|Fe-CHI/Ni sandwich film cathode is a promising cathode for both H₂O₂ electro-generation and iron reagent production at neutral pH.

3.4. E-Fenton RhB degradation mechanism with the novel SFC cathode

On the basis of the above results, we proposed a possible pathway for the degradation of RhB in this novel SFC based E-Fenton system at neutral pH (Scheme 1). First, oxygen was adsorbed on the surface of the SFC and part of iron ions were leached into the RhB solution. H₂O₂ was then produced by the electrochemical reduction of oxygen adsorbed on the SFC electrode and subsequently decomposed into hydroxyl radicals via the catalysis of leached iron ions. This degradation pathway is similar with the Fe@Fe₂O₃/ACF electro-Fenton system with slight differences [26]. We measured the degradation of RhB with Ni|ACF|Ni in the presence of ferrous ions, which was similar to that of the Fe-CHI/Ni|ACF|Fe-CHI/Ni (Fig. S2, Supplementary Material). This comparison suggests that in the SFC based E-Fenton system the functions of Fe-CHI and ACF are to provide Fe source and reduce O₂ to H₂O₂, respectively. The variations of H₂O₂ and Fe²⁺ during the degradation of RhB with Ni|ACF|Ni in the presence of ferrous ions were also similar to those in the SFC based E-Fenton system (Fig. S3, Supplementary Material), further confirming the functions of Fe-CHI and ACF. Therefore, this SFC based E-Fenton system could realize the controllable supply of H₂O₂ and ferrous ions at a relatively feasible proportion. Fe-CHI was used as the iron reagent which could release Fe²⁺ more quickly and realize the recycle of iron (Fe²⁺ → Fe³⁺ → Fe²⁺), more attractive than Fe@Fe₂O₃ with a different recycle pathway of iron (Fe⁰ → Feⁿ⁺ → Fe₂O₃).

3.5. Stability of the SFC

The stability of electrodes is a key issue for their practical application. The stability of the sandwich film cathode was investigated (Fig. 8). We cleaned the used SFC with deionized water and then reused it for E-Fenton degradation of RhB under the same conditions. It was interesting to find that there was no obvious decrease in degradation efficiency after seven recycles, suggesting that the electrode is very stable and reusable to same degree. However,



Scheme 1. The illustration of E-Fenton degradation of RhB on the novel sandwich film cathode.

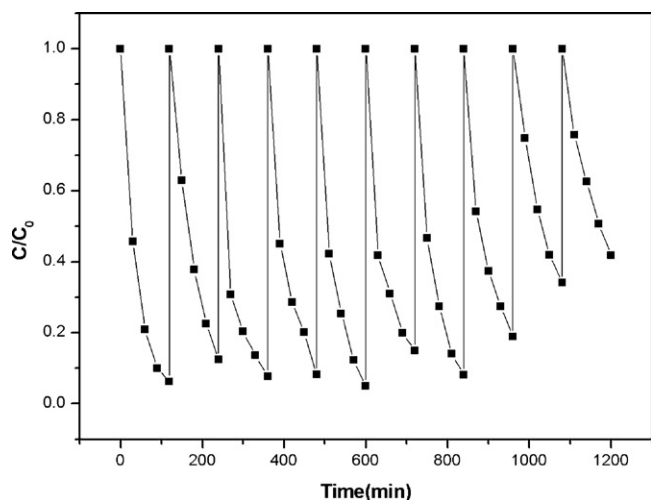


Fig. 8. Stability of the sandwich film cathode during E-Fenton degradation of RhB at neutral pH. The applied current was 10 mA, the electrolyte was 0.05 mol L⁻¹ of Na₂SO₄, the initial concentration of RhB was 5 mg L⁻¹.

when we performed the degradation with more cycles, we found the efficiency declined with the continuous release of ferrous iron. During each cycle the loss of iron was about 0.2 mg. After 10 cycles, the degradation efficiency declined to 56%. This degradation efficiency decline could be stopped by adding iron ions to the sandwich film cathode. The reusability of the Fe-CHI/Ni/ACF/Fe-CHI/Ni sandwich film cathode makes it promising for the practical wastewater treatment.

4. Conclusions

In summary, we have demonstrated a novel E-Fenton system constructed with a sandwich film cathode. The SFC fabrication is very simple and only requires inexpensive and handy materials including FeSO₄, foam nickel, chitosan, glutaraldehyde and activated carbon fiber. This SFC based E-Fenton system exhibited significant high catalytic activity on the degradation of RhB at neutral pH. The SFC was very stable and reusable on the degradation of organic pollutants without losing activity after long-term run. The high efficiency and stability of this system makes it very promising for wastewater treatment.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.11.085.

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