Design of a high efficiency electro-Fenton system with Fe⁰@Fe₃O₄/ACF composite cathode for lignin wastewater treatment

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Abstract. Lignin is a complex phenylpropanoid biopolymer conferring mechanical strength to plant cell walls. Biorefineries, along with pulp and paper industry, generate large quantities of lignin. Lignin valorization is an essential process for an advanced, sustainable, and economical biomass-based industry. In this study, for the first time nanostructured Fe⁰@Fe₃O₄ was loaded on active carbon fiber (ACF) as an oxygen diffusion cathode to be used in a heterogeneous electro-Fenton (E-Fenton) oxidation system. This novel Fe⁰@Fe₃O₄/ACF composite cathode was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), BET surface area analysis, transmission electron microscopy (TEM). On the degradation of lignin in water, this heterogeneous E-Fenton system with the Fe⁰@Fe₃O₄/ACF cathode showed much higher activity than other E-Fenton systems with commercial zero valent iron powders (Fe⁰) and Iron ions (Fe³⁺) under same condition. On the basis of experimental results, we proposed a possible pathway of lignin degradation in this heterogeneous Fe⁰@Fe₃O₄/ACF E-Fenton process. This heterogeneous E-Fenton system is very promising to remove organic pollutants in water.

1. Introduction
In nature, lignin is the second largest renewable biomass resource after cellulose[1]. According to statistics, the global annual production of about 6 X10¹⁴ t natural lignin. Due to lignin is the abundant biomass and renewable resources, lignin can be widely used as raw materials for clean energy and high value-added chemicals[2]. Lignin is a three dimensional micromolecular network aromatic polymer in plant cells[3]. It is the only non-petroleum resource in nature that can provide renewable aromatic compounds. Because lignin is not homogeneous in nature, chemical structure is complex, separation and extraction process is tedious and condensation reaction is easy to occur, which seriously restricts the development and utilization of lignin[4, 5].
In the process of paper making and pulping, hundreds of millions of tons of plant fibers are consumed each year, but a large amount of lignin by-products (about 50 million tons) are produced. These lignin by-products are directly discharged into the natural water by the form of "black liquor", and some products are concentrated and burned. Lignin utilization rate was less than 20%. Therefore, it not only causes the waste of organic resources, but also pollutes the environment seriously. At present, increasing the added value of lignin is the main focus of researchers at home and abroad. With the increasing attention to environmental pollution and non-renewable resources, people pay more and more attention to the problems of environmental pollution and non-renewable resources. Therefore, the development and utilization of lignin with high added value is a new goal of modern science and technology, and also an important subject of modern economic and social development.

Advanced oxidation technology (AOPs) was first proposed by Glaze in 1987, which refers to the chemical oxidation technology which involves a large amount of hydroxyl radicals in the reaction. The principle of AOPs is the use of catalyst, radiation, and sometimes also with the oxidant in the reaction of the active free radicals (usually hydroxyl radicals), through the free radicals and pollutants between the addition, substitution, electron transfer so that the pollutants all or close to all mineralization[6-8]. Fenton reaction is one of the most efficient AOPs. It produces •OH through various reactions between ferrous ions and hydrogen peroxide[9]. Traditional Fenton reactions with ferrous ions have been employed to efficiently treat a variety of industrial wastewater containing a range of organic compounds like phenols, pesticides, wood preservatives, plastic additives, and rubber chemicals with low cost and relatively easy operation and maintenance[10, 11]. However, despite its high efficiency, the wide application of traditional Fenton process is limited by its acidic pH requirement (pH 2–4) and the formation of iron sludge in the coagulation step as well as high cost of hydrogen peroxide[12, 13].

In this stage, we design and construct a gas diffusion electrode with good performance, which can improve the yield of cathode H₂O₂ in situ and the current efficiency of the reaction system. The activated carbon fiber (ACF) with good adsorption and stability was used in the cathode. The Fe⁰ and Fe³⁺ were loaded onto the activated carbon fiber by sol-gel process to construct the heterogeneous Fenton reaction system. In this system, not only in situ H₂O₂, but the composite cathode in the reaction process can also slowly release Fe²⁺, and the reaction of Fe³⁺ in the cathode surface reduced to Fe²⁺, to some extent to achieve Fe²⁺ and Fe³⁺ cycle. Because of the heterogeneous reaction at the same time, therefore, the recovery and reuse of the catalyst can be realized. In this experiment, the use of lignin wastewater to verify the high efficiency composite cathode. The experimental results show that the electrochemical system with high efficiency composite cathode under the same reaction conditions has better decolorization rate and degradation rate than the traditional electrochemical reaction system, and does not produce secondary pollution such as Fenton sludge.

2. Experimental

2.1 Chemicals
Sodium sulfate anhydrous, ferric chloride, sodium borohydride, sulfuric acid, reduced iron powder and other chemical reagents were all of analytical grade and purchased from Shanghai Chemical Reagents Company. All chemicals were used as received without further purification. Active carbon fiber (ACF) and titanium mesh were purchased from China Southern Chemicals Import and Export Corporation. Doubly distilled water was used in all experiments.

2.2 Preparation of the Fe⁰@Fe₃O₄/ACF composite cathode
The activated carbon fibers were cut at 10.0 cm X 3.0 cm, ultrasonically cleaned in deionized water, and dried in a 50 °C blast oven. In a 100 mL beaker, 9.66 g FeCl₃·6H₂O was weighed into 50 mL of the solution (anhydrous ethanol: deionized water = 4: 1). The above-mentioned pre-treated activated carbon fibers were immersed in a ferric chloride solution for 1 hour and then taken out on a clean petri dish. 3.54 g NaBH₄ was preliminarily weighed and dissolved in 100 mL of deionized water. The NaBH₄ solution was dropwise added dropwise to the activated carbon fibers placed in the surface pan using a dropper.
The dropping speed was 0.5 mL/s. The entire operation is done at room temperature without vacuum. In the process of dropping, there will be a large number of bubbles generated, and in the activated carbon fiber, a black fluffy material is produced. After the completion of the dropwise addition for 1 hour, the activated carbon fiber was taken out, and NaBH4 on the surface of the activated carbon fiber was rinsed with deionized water and ethanol, and then dried with an infrared lamp under argon gas to obtain a highly efficient composite cathode.

2.3 Characterization of the Fe0@Fe3O4/ACF electrode

The method of X-ray diffraction (XRD) was used to investigate the material structure of iron nano particles. The XRD analysis was conducted with a Philips XRD 3100 diffractometer (Philips electronic Co., Eindhoven, Netherlands) at 45 kV and 30 mA. The BET isotherm is the basis for determining the extent of nitrogen adsorption on a given surface. A Micromeritics ASAP 2010 Chemisorption Surface Area Analyzer (Micromeritics Instrument Corp., Norcross, GA) was used in this work. Scanning electron microscopy (SEM, JSM-5600LV) with an accelerating voltage of 20 kV. The analysis was conducted with a Scienta ESCA-300 high-resolution X-ray photoelectron spectrometer (HR-XPS). A Kα X-ray beam at 3.8 kW was generated from an Al rotating anode. The X-ray beam is monochromatized using seven crystals mounted on three Rowland circles. The kinetic energy was analyzed using a high-resolution 300-mm mean radius hemispherical electrostatic analyzer and detected by a multi-channel plate-CCD camera.

2.4 Degradation of lignin wastewater

E-Fenton degradation of lignin was preformed in a divided thermostatic cell with a two-electrode system that has been reported in our previous work, by using a CHI-660B (Shanghai, China) electrochemical workstation. The orthogonal experiment was used to determine the influencing factors and levels (as shown in Table 1).

| Table 1 Treatment of lignin by orthogonal experiment with electro Fenton method |
|---------------------------------|-----------------|-------------|-----------|-----------|
| 1 | A: Voltage/V | B: Current/A | C: time/min | D: pH     |
| 2 | 10           | 0.3          | 10          | 2.0       |
| 3 | 12           | 0.5          | 20          | 2.5       |
|     | 14           | 0.7          | 30          | 3.0       |

2.5 Determination of hydrogen peroxide

The analysis of hydrogen peroxide produced the solution was carried out with triiodide method using the UV-vis spectrum and off-line sampling.

3. Results and discussion

3.1 Characterizations of the resulting Fe0@Fe3O4/ACF electrode
Fig. 1 Composite cathode X-ray diffraction pattern. A: ACF; B: Fe$^0$@Fe$_3$O$_4$/ACF; C: after use the Fe$^0$@Fe$_3$O$_4$/ACF

XRD pattern reveals the existence of cubic Fe (JCPDS, file No. 06-0696) in the as-prepared electrode (Fig. 1). The broad peak reveals the existence of an amorphous phase of iron. Apparent peaks at the 2θ of 44.9° and 35.8° indicate the presence of both zero-valent iron ($\alpha$-Fe) and iron oxide (FeO) crystalline phases. This was further confirmed by the XPS response (Fig. 2). Fig. 2a shows a full survey of the surface composition. For the survey of Fe 2p core levels (Fig. 2b), the photoelectron peaks at 710.9 eV, 711.9 eV, 722.5 eV, 712.8 eV, 725.4 eV and 723.3 eV represent the binding energies of Fe(2p3/2), shake-up satellite 2p3/2 and 2p1/2, respectively. The three main feature peaks suggest that the surface of iron nanoparticles consist mainly of a layer of iron oxides, likely in the form of FeO. Furthermore, a small shoulder at around 706.01 eV can also be observed, suggesting the 2p3/2 peaks of zero-valent iron (Fe$^0$).

Fig. 2a Sample full survey of the surface composition.
The morphologies of the ACF and as-synthesized composite electrode were investigated by SEM. The morphologies of the ACF and as-synthesized composite electrode were investigated by SEM. The original ACFs are about 15-20μm diameter and several tens to hundreds micrometers in length (Fig. 3). Fig. 3 shows that nanostructured iron was successfully loaded on ACF.

Figure 4 for the composite electrode sample N₂ adsorption-desorption isotherm. According to the IUPAC, the adsorption-desorption isotherms of the three samples are type III with a hysteresis loop, which is a typical pore. Mesoporous adsorption-desorption isotherm. Preparation of the pre-activated carbon fiber felt, composite cathode after the completion of the preparation and the use of the specific surface area were 783.2 m² g⁻¹, 921.7 m² g⁻¹ and 879.9 m² g⁻¹. Obviously, the specific surface area of the composite cathode is much larger than the specific surface area of the activated carbon fiber felt before the preparation of the composite cathode, which indicates that a compact Fe⁰ or Fe³⁺ is loaded on the surface of the active carbon fiber felt. The specific surface area of the composite electrode after use is decreased compared with the specific surface area of the sample after preparation. It shows that Fe⁰ or Fe³⁺ supported on the surface of the composite electrode enters the solution during the degradation process and participates in the Fenton reaction. After using the composite electrode surface area is still higher than that of activated carbon fiber felt preparation before the specific surface area of the composite electrode preparation finish has better stability and sustained response, there may be a certain degree in the process of iron cycle.
3.2. The E-Fenton degradation of lignin wastewater

As shown in Fig. 5, the degradation rate of methyl orange was 99.95% when the voltage was 14 V, the current was 0.3 A, the degradation time was 30 min and the pH value was 2.5, and the decolorization was the best. By comparing the composite cathode electro-Fenton and the traditional Fenton process, the composite electrode electro-Fenton method does not produce reddish-brown precipitates in the degradation of lignin wastewater, and does not need to add H2O2 and ferrous ions, so the operation cost is lower.
3.3. The analysis of \( \text{H}_2\text{O}_2 \) in the reaction solution

As shown in Fig. 6, the \( \text{H}_2\text{O}_2 \) content in the composite cathode electro-Fenton reaction system continued to grow with the increase of reaction time under different operating conditions. However, the traditional electrochemical reaction system, \( \text{H}_2\text{O}_2 \) content of the trend showed a first increase and then reduce the phenomenon. The main reason may be that as the reaction progresses, a large amount of Fe(OH)\(_3\) precipitates in the solution, blocking the transfer of the electrolyte in the solution, resulting in a decrease in electrical efficiency.

4. Conclusion

It can be seen from the experimental results that it is an effective measure to improve the performance of Fenton by loading zero-valent iron and iron oxide on the activated carbon fiber mat. When the applied current is 0.3 A, the initial concentration of lignin was 10 mg/L, the concentration of \( \text{Na}_2\text{SO}_4 \) was 0.05 mol/L, the initial pH of the wastewater is 2.5, the operation of the electric Fenton process after 30 min, Congo red degradation rate was 99.95%. Therefore, this novel Fe@Fe\(_2\text{O}_3\)/ACF E-Fenton system showed good performance on the degradation of lignin at low pH. The application of this promising E-Fenton process to degrade other pollutants at neutral pH is in progress.

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