Computer Assisted Design of Electro-Fenton Reactor to Improve the Pollutants Degradation Ability

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Abstract. The traditional electro-Fenton catalysis is performed in batch reactors or flow-by reactors. In these types of reactors, electro-Fenton reaction suffers low current efficiency and high energy consumption caused by limited electrode/solution catalytic interface and negative electrostatic repulsion effect. In this work, a flow-through type electro-Fenton reactor was designed by implanting the biomass derived self-supporting cathode and cheap titanium mesh. The flow-through reactor has three advantages: Flow-through three-dimensional electrodes can lower the energy consumption and operating costs; Short distance between cathode and anode is conducive to electron transfer; High-porosity electrode materials can improve mass transfer of pollutants. The effects of electrode assembly pattern and flow direction on pollutants removal efficiency were investigated to optimize the electro-Fenton performance of the flow-through type reactor.

Keywords: Novel flow-through reactor, Heterogenous electro-Fenton, phenol degradation

1. Introduction
The development of cost-effective and environmentally friendly water pollution remediation technologies is of great significance to alleviate current water pollution, and protect the ecological environment and human health [1]. The electro-Fenton (EF) method uses clean and efficient electrons to catalyze O2 and H2O for generating strong oxidizing free radicals, which can degrade organic pollutants non-selectively [2]. Electro-Fenton has several outstanding advantage: One is that it can reduce O2 to in situ generate H2O2 by two electrons reaction, avoiding long-distance transportation and storage of H2O2; Another is that the cathode can simultaneously regenerate Fe2+; Moreover, the catalyst can be recycled [3].

Electro-Fenton is divided into homogeneous electro-Fenton (homo-EF) and heterogeneous electro-Fenton (hetero-EF). Homo-EF has been intensively studied, but Fe2+ exists in the form of dissolved state in the system, thus strong acid condition is required to prevent iron precipitation. Moreover, the treated effluent needs to be neutralized, which will produce a large amount of iron-containing sludge and limit its large-scale use [4]. The hetero-EF method develops heterogeneous catalyst using solid iron to substitute the dissolved Fe2+, such as Fe0 and iron oxide [5, 6], which overcomes the drawbacks of homo-
EF. At present, the heterogeneous catalysts are often coated on zeolite, clay and porous carbonaceous supports to prepare catalytic electrodes. However, such heterogeneous loading method leads to uneven distribution of active materials, agglomeration and easy falling off [7]. Preparation of integrated electrode provides a feasible solution to solve this problem.

The reaction modes of electro-Fenton have also been extensively studied, including static and flow-by modes. In static reactors and flow-by reactors, since the electro-Fenton reactions occur at the cathode/solution interface, the electrostatic repulsion will prevent organic molecules from migrating to the active sites on the cathode, leading to low current efficiency and high processing energy consumption [8]. Notably, the flow-through reactor has developed and is successfully applied to enhance anodic oxidation efficiency and homogeneous electro-Fenton performance. The flow-through reactor has three advantages: Flow-through three-dimensional electrodes can lower the energy consumption and operating costs; Short distance between cathode and anode is conducive to reactants transfer; High-porosity electrode materials can improve mass transfer of pollutants [9]. For example, the flow-through pack-bed reactor system was reported to enhance the mass-transfer of organic pollutants in low concentration, which is proved to be effective at low current density during the process of decontamination.

In this work, a flow-through type electro-Fenton reactor was designed by implanting the biomass derived self-supporting bulk cathode, cheap titanium mesh anode and non-woven membrane layer. The cathode is prepared by loading iron in biomass absorbent cotton based carbon. The effects of electrode assembly pattern and flow direction on pollutants removal efficiency were investigated to optimize the electro-Fenton performance of the flow-through type reactor. This work presents the flow-through type reactor design for hetero-EF catalysis, which provides technical support for enhancing heterogeneous-EF efficiency of pollutants degradation.

2. Experimental Section

2.1. Experimental chemicals
Sodium sulfate and sulfuric acid were offered by Xilong Chemical Reagent Co., Ltd; Ferric chloride Tianjin Damao Chemical Reagent Co., Ltd; Phenol Aladdin Co. Ltd., China. All chemicals are analytically pure.

2.2. Preparation of the electrode
The absorbent cotton-derived carbon fiber electrode (ACCE) was synthesized by simple impregnation method. The clean absorbent cotton sheets were immersed in FeCl₃ solution with certain concentration followed by uniform mixing. After 1 hour of ultrasound, the mixture was placed in an oven at 90 °C for 10 hours. The iron oxide nanoparticles-loaded carbon fiber electrode are obtained by carbonization at 800 °C under Ar for 5 hours.

2.3. Design of the flow-through reactor and pollutants degradation experiment
In this work, a flow-through type electro-Fenton reactor was fabricated using the prepared cathode, cheap titanium mesh anode and non-woven membrane layer. The main components of the reactor included water inlet and outlet, rubber ring, titanium wire, titanium mesh anode, non-woven isolation layer, cathode, etc, as shown in Figure 1. The cathode and anode were separated with a non-woven fabric with a distance of about 0.1 cm. The titanium wire was used to collect and distribute current on electrode surface. The rubber ring is served as a seal to prevent the electrolyte solution from passing through the surrounding voids. Pollutant degradation experiments were conducted in this home-made reactor. The reaction solution was pumped into the reactor through a peristaltic pump at a rate of 0.15 mL/min. The voltage was set to 3.0 V, and the pH of the solution was adjusted to 5. At regular intervals, a liquid phase vial was used to connect about 1 mL of the effluent and filtered with a 0.22 um filter membrane to analyze the concentration.

The main functions of the reactor are presented as follows:
1. High-efficiency in-situ generation of H$_2$O$_2$ is achieved by exposing oxygen to the reaction liquid.
2. The flow-through reaction structure and greatly shortened electrode spacing that can enhance the mass transfer and electrode utilization efficiency largely in the reaction process.

Figure 1. (a) The schematic diagram of the reactor (b) Digital photograph of the reactor

3. Results and discussion

3.1. The effect of the electrode assembly pattern

The electrode assembly pattern has a great influence on the stable operation of the vertical flow system, especially for the sealed system with a small reaction volume in this experiment. To explore the influence of the relative positions of electrodes on phenol removal, two positions are used: cathode above (CA) and anode above (AA). The results are shown in Figure 2. It can be seen from Figure 2(a) that under the same operating conditions, a much better phenol removal (93%) is achieved at CA mode, compared with the other mode (80%). The main reason is that a much higher current can be obtained in the CA mode, as shown in Figure 2 (b). The high current will increase the production of H$_2$O$_2$ and electro-Fenton reaction rate, promoting the phenol removal [10].

Figure 2. (a) The effect of relative position of electrodes on phenol removal (b) The current during the degradation process. (Conditions: The solution flows from top to bottom, voltage 3.0 V, flow rate 0.15 mL/min, pH 5, phenol 20 ppm)
3.2. The effect of solution flow directions

The effect of solution flow directions (From top to bottom: TB, from bottom to top: BT) on phenol removal is explored. Notably, the flow rate is increased to 0.75 mL/min from 0.15 mL/min to improve the treatment rate of this reactor. The phenol removal efficiencies with different solution flow directions are shown in Figure 3. It can be seen that the removal efficiency is about 62% at TB mode, which has no obvious difference compared to the other mode (59%). The little performance difference between two reaction modes indicates that the flow direction has little effect on the phenol removal. However, the follow-up experiments choose the TB mode, in consideration of the power consumption from water gravity overcoming, which would lead to a higher current efficiency and much lower electricity consumption.

4. Conclusions

In this paper, a flow-through type electro-Fenton reactor was designed, where the bulk cathode, cheap titanium mesh anode and non-woven membrane layer were used fabricate the reactor. The effects of electrode assembly pattern and flow direction on the pollutant degradation efficiency were investigated. CA mode achieved much higher phenol removal efficiency, and TB mode is favorable to obtain low electricity consumption. This paper explored the flow-through reactor for hetero-EF reaction for effective and stable organic pollutants treatment, which provides technical support for improving heterogeneous-EF efficiency.

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