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An electro-Fenton system using magnetite coated metallic foams as cathode for dye degradation

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ABSTRACT

An electro-Fenton system with a magnetite washcoated metal foam as cathode and graphite as anode was successfully applied for the discoloration of methylene blue in aqueous. The effect of pH, applied voltage, supporting electrolyte, electrode inner space, and catalyst dosages were investigated and optimized. Using this cathode, methylene blue was removed with > 99.8% removal rate at 10 ppm after 60 min and with > 95.2% at 50 ppm after 120 min of reaction. Furthermore, those cathodes could be reused at least three times without performance degradation. Due to high degradation capability, simple recovery and high reusability, magnetite washcoated metal foams could be an effective cathode for electro-Fenton systems for removing dyes in wastewater.

1. Introduction

Dyes released from many industries such as textiles, leather, cosmetic, printing, and plastics are major problems for environment. Most of the dyes are harmful to aquatic and human life because of their toxic, carcinogenic and mutagenic properties. For these reasons, their removal from the contaminated water is of high priority. Therefore, many methods, including chemical, physical and biological treatments, have been used for the discoloration of reactive dyes from the wastewater [1,2].

Among the various methods, Fenton reaction, consisting of ferrous ion and hydrogen peroxide, has been proven to be an effective method to degrade organic pollutants in wastewater [3]. Hydroxyl radicals generated from the reaction are capable of oxidizing pollutant molecules to less polluting molecules [4]. Hydroxyl radicals have powerful oxidation potential (2.8 V) only lower than fluorine (3 V) and higher than ozone (2.07 V) [5]. Fenton reaction offers numerous advantages, such as high efficiency, non-necessity of special equipment, simple, and mild operating conditions (pressure and temperature) [6]. However, in spite of above-mentioned advantageous properties, the cost of expensive H_2O_2 and the huge amount of ferrous iron sludge after Fenton process treatment are the main obstacles for large-scale applications of the method for wastewater treatment. Recently, electro-Fenton (EF) process is drawing considerable attention as an efficient method combining electrochemical methods with Fenton's reagents, which could be a solution for the problems of the conventional Fenton reaction mentioned above [7]. This hybrid process involves the continuous generation of in situ H_2O_2 via reduction of oxygen in the water (Eqs. (1) and (2)). The catalytic reaction is propagated by Fe^{2+} regeneration (Eqs. (3) and (4)), which can take place by reduction of Fe^{3+} with H_2O_2 in the water [8]. Then the active hydroxyl radicals can attach and oxidize pollutants (RH) to less toxic compounds, even turning into non-toxic chemicals such as CO_2 and H_2O (Eqs. (5)–(7)) [9]. EF process was shown to be successful for the removal of dyes [10–12].

$$O_2 + 2H^+ + 2e\bullet \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + \cdot OH \quad (2)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \quad (3)$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

$$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO_2\bullet \quad (5)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH\bullet \quad (6)$$

$$\cdot OH + RH \rightarrow R\cdot + H_2O \quad (7)$$

Until recently, a lot of iron oxide minerals including magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and goethite (α-FeOOH) have been widely used in Fenton reaction [13–15]. Among these catalysts, magnetite

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nanoparticles have attracted most of increasing research interest. This is because those inverse spinel magnetite particles possess many advantages, such as facile preparation, high stability and the enhanced production of ·OH by Fe^{2+} in its structure [16]. Moreover, transfer of electrons between ferrous and ferric ions in the octahedral sites can avoid substantial loss of Fe [17]. In some EF systems, Fe_3O_4 nanoparticles are added in the wastewater in order to increase the efficiency of decomposition of pollutant molecules in the system [18–21]. In those cases, separating magnetite particles from the treated water is still a cumbersome process, although magnetite particles can be collected by a magnet after treatment.

In this paper, we integrated magnetite particles to the cathode of an EF system by washcoating metal foams with magnetite powder. In this novel electrode, magnetite particles were used as iron source and metal foams were employed as conducting and porous catalyst supports, maximizing the reaction efficiency by increasing the exposed surface area of the cathode and minimizing mass transport limitations. Furthermore, the foams could be easily lifted up from the treated water, leaving no sludge and no magnetite powder in the solution after wastewater treatment. Therefore, it can be suggested that the combination of magnetite particles with metal foams may offer synergistic and improved cathodes for EF systems. The EF system was applied to degrade methylene blue (MB) in water. The influence of several operating parameters, such as pH solution, voltage, catalyst loading, initial MB concentration, electrolyte on MB degradation and the reuse ability of the cathode were investigated.

2. Experimental

2.1. Chemicals and materials

The metal foams we used in the study were FeCrAl alloy foam and they were received from Alantum [22,23]. Their surface is corrugated so that washcoating oxide particles on the surface is facilitated (Fig. 1). Magnetite nanoparticles (Fe_3O_4), Na_2SO_4, Methylene Blue (MB), NaOH, H_2SO_4, acetone, and ethanol were purchased from SIGMA ALDRICH. They were used without further purification.

2.2. Fabrication of magnetite washcoated metal foam

For washcoating magnetite particles on metal foams, we followed basically the same procedure we applied for washcoating γ-alumina particles on FeCrAl foams [22]. Magnetite slurry was made by vigorous stirring of the suspension in distilled water for 30 min. Desired solid content in the slurry was monitored by controlling the ratio of the amount of magnetite to that of distilled water. The cleaned metallic supports were washcoated with magnetite particles by dipping the supports into the slurry for 30 s and pulling out. After pulling out, they were dried by air blowing to remove residual slurry. The washcoated supports were then dried thoroughly in an oven in argon environment for 1 h at 120 °C [23].

2.3. Electro-Fenton experiment

A diagram of the experimental set up is presented in Fig. 2. Batch electrolytic experiments for 10 mg/l of methylene blue (MB) (10 ppm) solution were carried out in a 100 ml cylindrical beaker. 100 ml of the solution was chosen as the working volume for the electrolysis experiments. The pH of solution was controlled by using 0.2 M H_2SO_4 and 0.1 M NaOH. Graphite plate with effective area of 3 × 4 cm was used as anode. When carbonaceous materials are used as anode in electrochemical setups, there is a possibility of anodic decomposition of the material. Actually, nanostructured carbons such as carbon nanofibers are very unstable and oxidized in a short time when used as anode. Therefore, in such an electrochemical setup, dimensionally stable anodes (DSA) made of precious metals and metal oxide are typically used as anode for their stability. However, for practical applications, DSAs are too expensive. Carbonaceous materials can be stable as anode depending on their structures. For example, Boron-doped-diamond (BDD) is an excellent anode. Still, BDD is also expensive. Graphite is in the middle in terms of price and stability. Therefore, for practical applications, regular change of graphite anode is more practical. As our study is aiming practical applications of our electro Fenton system, we chose graphite as anode. Fe_3O_4 washcoated FeCrAl foam with 2 × 2 cm in size was used as cathode. The electrodes were placed inside the beaker vertically and adjusted to required inner electrode spacing. The solution was stirred thoroughly by using a magnetic bar at 240 rpm. Na_2SO_4 was used as the supporting electrolyte in the initial stage of

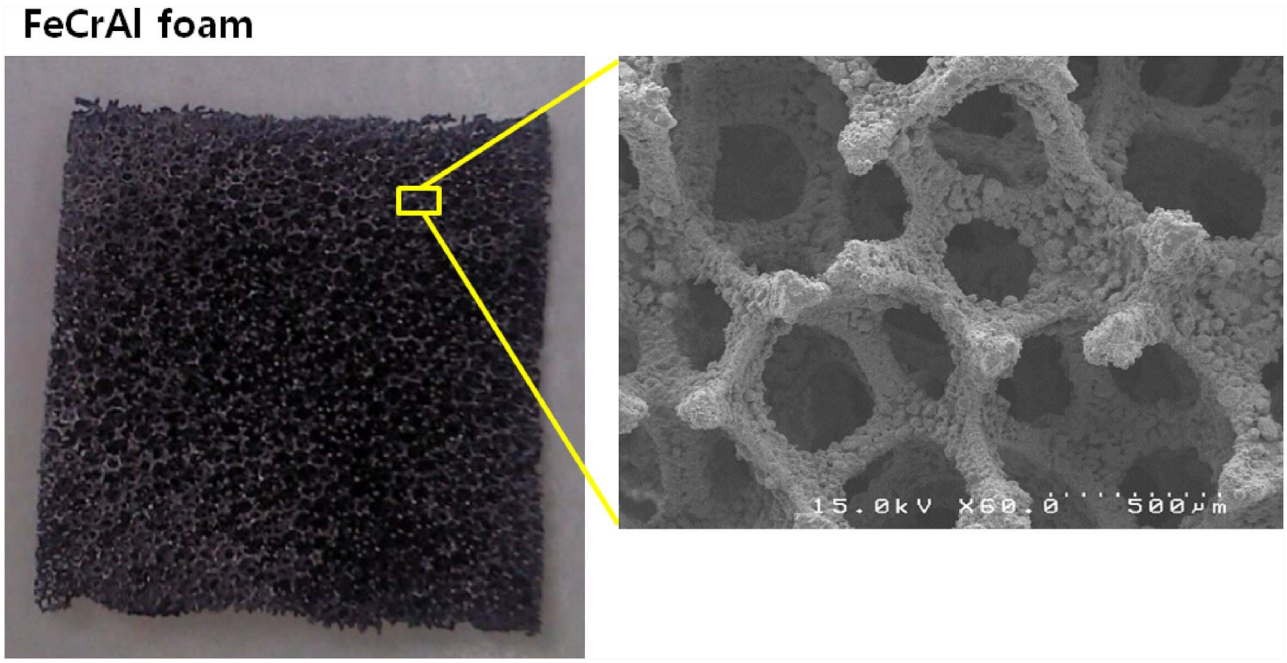

Fig. 1. Optical microscope (left) and SEM (right) images of FeCrAl foam.