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Dye wastewater treated by Fenton process with ferrous ions electrolytically generated from iron-containing sludge

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Abstract

Fenton process was employed to treat synthetic dye wastewater with supply of Fe(II) electrolytically generated from iron-containing sludge which was recycled and reused throughout the study. Treated water quality and properties of iron sludge after being repeatedly used were reported and discussed. Experimental results showed that COD was mainly removed by oxidation other than coagulation. Although, the process was quite effective for COD and color removal, conductivity of treated water was enormously high. Meanwhile, repeated use of iron-containing sludge results in accumulation of organic materials embedded in the sludge as indicated by increasing volatile suspended solid (VSS)/TSS ratio and decreasing zeta potential.

Keywords: Electrolysis; Dye; COD removal; Iron sludge; Conductivity

1. Introduction

Fenton process has been intensively investigated for oxidation of various contaminants in the past, but its practical application is limited by the huge quantity of iron-containing sludge generated by it [1,2]. Electrochemical regeneration of Fe(II) via reduction of Fe(III), denoted as Fered-Fenton process by Huang et al. [3], as EF-FeRe process by Qiang et al. [2], and as Fenton sludge recycling (FSR) process by Gnann et al. [4], was proposed to alleviate the sludge problem associated with Fenton process.

Concentration of electrolytically-generated Fe(II) depends on initial ferric concentration, pH, temperature, cathodic potential, electrolysis time, cathode area, and cathode-to-anode area ratio [2–6]. Amount of Fe(II) generated and electrolytic current efficiency increase with increasing initial ferric concentration, but are drastically decreased at pH higher than 2.5 because of $Fe(OH)_3$ precipitation [2,6]. Electrolytic pH as low as 1.0 has been recommended for operating the FSR process to effectively re-dissolve precipitated iron sludge before it can be reduced to Fe(II) [4]. Increasing concentration of Fe(II) was also observed with increasing cathodic surface area [2], and cathode-to-anode area ratio higher than 8 has been employed [3,6]. Cathodic potential ranging from −0.1 to −0.9 V has little impact on amount of Fe(II) generated, although electrolytic current efficiency decreases with decreasing cathodic potential due to electricity wasted through H_2 evolution [2].

The majority of the above-mentioned studies demonstrated electro-regeneration efficiency of Fe(II) using dissolved ferric salts (e.g., ferric sulfate or ferric nitrate) as the iron sources in batch reactors [2,3,6,7]. Although, electro-regeneration of Fe(II) using precipitated iron oxides as the iron source has been investigated by Gnann et al. [4] and Qiang et al. [2], treated water quality and properties of iron sludge after long-term repeated use had not been elaborated. Since organic materials embedded in the iron oxide precipitates might have adverse effects on the treatment efficiency after iron oxide precipitates are reused [8], and addition of acid and base for lowing pH during the electrolytic Fe(II) regeneration and for raising pH during precipitation of iron oxides will contribute to the overall treated water conductivity, it is worthwhile to investigate and address these issues in great details.

Based on the above discussion, the objectives of this study are (1) to demonstrate the treatment efficiency of dye wastewater

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using Fenton process with Fe(II) electrolytically generated using iron-containing sludge as the iron source, (2) to explore fate of Fe species in the treatment process, (3) to evaluate treated water quality, and (4) to investigate properties of iron sludge with emphasis on their dewaterability and volatile suspended solid (VSS) content.

2. Experimental

2.1. Materials

All chemicals used were of reagent grade and were diluted to predetermined concentration with deionized water (DI). A synthetic dye wastewater containing a reactive dye, R94H (I-Hwa Industrial Co. Ltd., Taiwan), with dye concentration, COD, and color of 1000 mg dm^{-3}, 3680 mg dm^{-3}, and 52460 ADMI units, respectively, was prepared to simulate high strength waste stream (denoted as wastewater A). A low strength synthetic dye wastewater (denoted as wastewater B) was prepared by 10-time dilution of wastewater A to simulate low concentration rinsing water generated from dyeing process.

The feed H_2O_2 solution with concentration of 1500 mg dm^{-3} was diluted from 30% (w/w) stock solution (Merck). Initial iron-containing sludge was obtained from neutralizing R94H containing wastewater treated with Fenton oxidation. A 10-L solution containing 1% (w/w) of R94H was treated with Fenton reaction with Fe^{2+}/H_2O_2 molar ratio of 1:3 and Fe(II) concentration of 0.27 M for one day. After pH was adjusted to around 7 to 8, solution was allowed to settle for 2 days. Then, supernatant was decanted, and precipitated iron oxide sludge was collected and repeatedly used throughout the study. Therefore, the precipitated iron-containing sludge has organic materials embedded initially. H_2SO_4 with concentration of 9.0 N and NaOH of 5.0 N were used for pH adjustment.

2.2. Experimental setup and methods

Fig. 1 shows the schematic experimental setup of this study, including electrolysis tank, Fenton reaction tank, neutralization tank, sedimentation tank, and acidification tank. Electrogeneration of Fe(II) was performed in the electrolysis tank which has volume of 500 cm^3 and hydraulic retention times (HRT) varying from 100 to 1111 min. The pH of the electrolysis tank was maintained at 1.0 ± 0.05 by a pH control system that consisted of a glass electrode (InLab 439, METTLER TOLEDO, Switzerland) and a pH controller (PC3200, Suntex instruments Co. Ltd., Taiwan), controlling H_2SO_4 (9 N) dosing. Both cathode and anode are made of stainless steel with area of 64 and 6.4 cm^2, respectively, corresponding to cathode-to-anode area ratio of 10. The current density was fixed at 30 A per m^2 of cathode area using a power supply (GPS-3030D, Good Will Instrument Co. Ltd., Taiwan).

Dosage of H_2O_2 was varied by adjusting flow rates of the corresponding feeding pumps. However, the feeding concentration of Fe(II) depends both on the electrogenerated concentration of Fe(II) in the electrolysis tank and flow rate of Fe(II) feeding pump. In the tests, flow rate of Fe(II) feeding pump was also adjusted to control the electrolysis time in the electrolysis tank. Table 1 shows the experimental conditions and their denoted test numbers. For example, in test number 1, the Fe(II) and H_2O_2 feeding pumps have the flow rates of 10 and 5 cm^3 min^{-1}, respectively, while the dye-containing wastewater (wastewater A) flow rate was set at 5 cm^3 min^{-1}. Under this condition the electrolysis time is 50 min, which is determined by the flow rate of Fe(II) feeding pump, and the feeding concentration of H_2O_2 is 375 mg dm^{-3}. As indicated previously, the electrogenerated concentration of Fe(II) depends on initial ferric concentration, pH, temperature, cathodic potential, electrolysis time, and the cathode-to-anode area ratio [5,6]. In this study, electrolytic

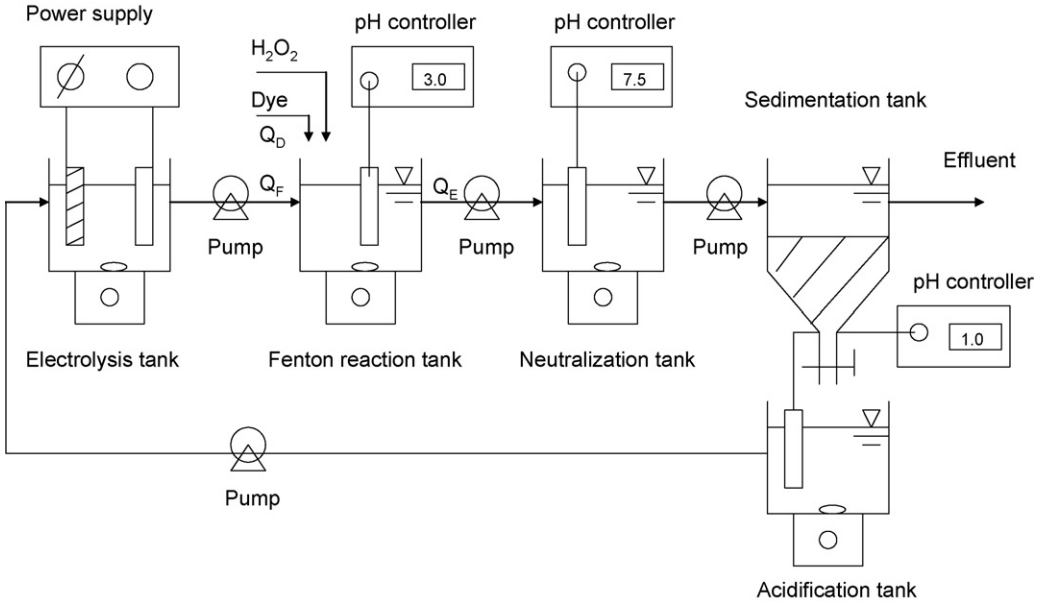

Fig. 1. The schematic experimental setup.