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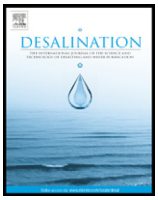

Effect of operating parameters on decolorization and COD removal of three reactive dyes by Fenton's reagent using fluidized-bed reactor

Chia-Chi Su [a], Massakul Pukdee-Asa [b], Chavalit Ratanatamskul [b], Ming-Chun Lu [a,*]

[a] *Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, Taiwan*
[b] *Department of EnvironmentalEngineering, Chulalongkorn University, Thailand*

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ABSTRACT

This investigation evaluates the effectiveness of the fluidized-bed Fenton process in treating Reactive Black 5 (RB5), Reactive Orange 16 (RO16) and Reactive Blue 2 (RB2) dyes in an aqueous medium. The Fe^{2+} as the catalyst and H_2O_2 as the oxidizing agent are added to the fluidized-bed reactor. This study also examines how operating conditions, Fenton reagent concentrations, and carriers affect the removal efficiencies of the fluidized-bed Fenton process. Experimental results indicate that excessive hydrogen peroxide had scavenging effects and decreased dye degradation. The $[H_2O_2]$:$[Fe^{2+}]$ ratio was a significant operating factor in dye decolorization. Under appropriate conditions, the highest removal rates of 99%, 99% and 96% were for the RB5, RO16 and RB2 colors, respectively. Additionally, chemical oxygen demand (COD) removal efficiencies for RB5, RO16 and RB2 were 34%, 47% and 49%, respectively. Under the same operating conditions 2 mg/L Fe^{2+}, 100 mg/L H_2O_2 and 74.07 g carrier/L, at pH 3 the removal efficiencies of color and COD had the following order: RO16>RB5>RB2.

1. Introduction

Approximately 80% of all reactive dyes are based on azo chromogen. Azo dyes are compounds containing azo groups (–N=N–) that are predominantly bound to benzene or naphtha rings; however, in some cases, they are also attached to aromatic heterocycles or enolizable aliphatic groups. Azo dyes are typically used in textile processing and paper manufacturing. A massive amount of azo dyes from textile manufacturing is discharged into natural waterways. Removal of dyes from industrial effluent is environmentally important because compounds containing benzene or naphtha rings are toxic. Different methods have been developed for dye removal, including chemical precipitation, chemical oxidation, adsorption, biological treatment and membrane-based techniques [1–7].

In recent years, advanced oxidation processes (AOPs) were used to remove toxic and persistent pollutants [8–13]. The Fenton process forms the well-known chemical AOP. In the Fenton process, the hydroxyl radical (•OH) is easily produced by the iron (II) catalyst and hydrogen peroxide (H_2O_2) as follows [14]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe{-}OOH^{2+} + H^+ \quad (2)$$

$$Fe{-}OOH^{2+} \rightarrow Fe^{2+} + \bullet O_2H \quad (3)$$

$$Fe^{3+} + \bullet O_2H \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet O_2H \quad (6)$$

$$\bullet OH + \text{organics} \rightarrow \text{products} \quad (7)$$

However, the Fenton process has a significant disadvantage in that iron sludge is produced and requires disposal. Therefore, the fluidized-bed Fenton process was developed to decrease the amount of sludge produced. This process has the following advantages: (i) homogeneous chemical oxidation (H_2O_2/Fe^{2+}) (from Eq. (1)); (ii) heterogeneous chemical oxidation (H_2O_2/iron oxide); (iii) fluidized-bed crystallization, in which iron sludge precipitates on carrier surfaces; and (iv) reductive dissolution of FeOOH [15]. The fluidized-bed Fenton process is influenced by solution pH, initial ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2) concentrations.

This study uses the fluidized-bed Fenton process (Fe^{2+}/H_2O_2/carrier) to remove Reactive Black 5 (RB5), Reactive Orange 16 (RO16) and Reactive Blue 2 (RB2) dyes, which were selected as model organic pollutants. The optimal pH value for the Fenton process was around 3.0

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* Corresponding author. Tel.: +886 6 2660489; fax: +886 6 2663411.
E-mail address: mmclu@mail.chna.edu.tw (M.-C. Lu).

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[16,17]. Experiments were performed to establish the optimal conditions for decolorization and degradation of the RB5, RO16 and RB2 dyes in an aqueous medium. Thus, the effects of carriers were investigated using silica oxide (SiO_2) and alumina (Al_2O_3) as supports.

2. Materials and methods

2.1. Materials

Hydrogen peroxide (H_2O_2, 35%; Merck), ferrous sulfate heptahydrated ($FeSO_4$•$7H_2O$; Merck), RB5 (Sigma-Aldrich), RO16 (Sigma-Aldrich) and RB2 (Sigma-Aldrich) were reagent grade and used without further purification. Fig. 1 shows the structure of the RB5, RO16 and RB2 dyes. The total surface areas of silica oxide (SiO_2) and alumina (Al_2O_3) were 0.0015 m^2/g and 314 m^2/g, respectively. The Al_2O_3 grains were obtained from Alcoa Chemicals.

2.2. Methods and reactor

A 1.35 L fluidized-bed reactor (FBR) was utilized in all experiments. The FBR is a cylindrical vessel (5.23 cm $\phi \times$ 133 cm-H) consisting of an outlet, inlet and recirculating sections. Carriers were fluidized by adjusting the internal circulation at 50% bed expansion [18]. Experiments were conducted at room temperature.

In this investigation, carriers (74.07 g/L) were first added to the FBR; synthetic dye wastewater was then added. The pump was turned on to suspend the carriers and mix the solution. The solution pH was adjusted to 3.0 ± 0.2 by adding H_2SO_4 or NaOH. After the pH reading stabilized, the ferrous (Fe^{2+}) solution was added. The reaction began when the H_2O_2 solution was added. Samples extracted at selected intervals were injected immediately into tubes containing Na_2HPO_4 solution to stop the reaction, and were then filtered through 0.45 μm syringe micro-filters to separate precipitated iron from the solution. The solution was kept for 12 h before chemical oxygen demand (COD) analysis. This step was carried out to quantify the effect of the H_2O_2 concentration on COD removal.

The H_2O_2 concentration was determined using a standard iodometric method with potassium iodide and $Na_2S_2O_3$ solution as reactants [19]. The concentration of ferrous ions (Fe^{2+}) was determined by measuring light absorbance at 510 nm using an ultraviolet (UV)-vis spectrophotometer. The solution COD was determined using the standard closed-reflux titrimetric method [20]. Dye concentrations were determined by a UV-vis spectrophotometer (UV-1201; Shimadzu). Before the dye analysis operation was made, a calibration curve was plotted using standard dyes with known concentrations.

3. Results and discussion

3.1. Effect of carriers

The decolorization and degradation of 0.1 mM of the dyes in the SiO_2 and Al_2O_3 systems were evaluated under 160 mg/L H_2O_2 at pH 3. The removal efficiencies of color for the three dyes were rapid in the first 5 min in both the SiO_2 and Al_2O_3 systems (Fig. 2). At the 20 min mark during the reactions, the amount of COD remaining in the Al_2O_3 system was less than that in the SiO_2 system. The specific surface area of Al_2O_3 was higher than that of SiO_2 and, therefore, dyes were easily adsorbed on the surface of Al_2O_3. This finding likely affects the consequential degradation of dyes in the Al_2O_3 system. At reaction end, the degradation of dyes in the SiO_2 system was higher than that in the Al_2O_3 system (Table 1). The removal efficiencies for color and COD for dyes in the SiO_2 system were 98–99% and 66–91%, respectively. Roughly 82–100% and 57–66% of color and COD were removed in the Al_2O_3 system, respectively. According to these analytical results, the removal efficiencies for color and COD of dyes in the SiO_2 system were higher. Moreover, this investigation focused on decolorization and degradation of dyes not adsorption of dyes. Therefore, the SiO_2 carrier was utilized to explore the decolorization and degradation of dyes under various experimental conditions in the fluidized-bed Fenton process.

3.2. Effect of Fe^{2+} and H_2O_2 concentrations

Fig. 3 shows the effect of the Fe^{2+} concentration on the removal efficiencies of color and COD for the three dyes. The color and COD removal efficiencies in the fluidized-bed Fenton process increased as the Fe^{2+} concentration was increased. This analytical result is in agreement with Eq. (1), in that Fe^{2+} catalyzed H_2O_2 to generate •OH radicals and the dyes were then efficiently oxidized. Therefore, the amount of H_2O_2 remaining decreased as the Fe^{2+} concentration was increased (Fig. 3). Fig. 4 shows the effect of the H_2O_2 concentration on color and COD removal efficiencies. The decolorization of three dyes increased as the H_2O_2 concentration increased from 50 mg/L to 100 mg/L, and then changed insignificantly when the H_2O_2 concentration was further increased up to 200 mg/L. The COD value of dyes increased slightly in the first 5 min of the reaction (Figs. 3 and 4). The reason is that complex bonds in dyes were broken down by the Fenton reaction, increasing COD detectability.

Table 2 summarizes acquired data for each test condition. The decolorization of all dyes was >80% under a low Fe^{2+} concentration (range, 1–5 mg/L); however, the COD removal efficiency was <50%. The removal efficiencies of COD of three dyes decreased slightly when

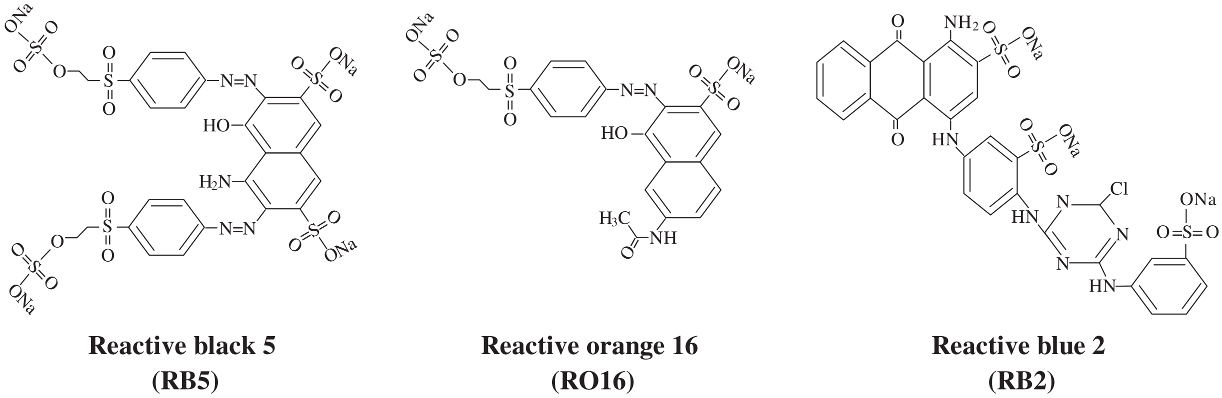

Fig. 1. Structure of dyes.