

Degradation of acid scarlet 3R with CuO/SiO₂ hollow sphere catalyst

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Abstract. Silica-supported copper catalyst materials have been synthesized via an incipient wetness impregnation. The resulting samples were characterized using X-ray diffraction (XRD) and Scanning electron microscope (SEM). The heterogeneous Fenton-like oxidation of reactive azo dye solutions by this catalyst was also investigated. The effects of various operating conditions on decolorization performance were evaluated, namely hydrogen peroxide dosage, initial pH, catalyst loading and initial dye concentration. The results indicated that by using 34 mmol/L of H₂O₂ and 6.0 g L⁻¹ of the catalyst at 60°C, pH 3.5, 97% of decolorization efficiency was achieved within 90 min. CuO/SiO₂ hollow sphere is shown a promising catalyst for degradation of azo dye aqueous solution by Fenton-like processes.

1. Introduction

In the world, more than 700,000 t of about 10,000 different types of dyes on pigments are produced every year [1]. Unfortunately about 10%~20% dyes are lost or discharged as aqueous effluents during dying and finishing processes in the textile industry. The dye wastewater has a heavy colority, which is difficult to be treated. The traditional methods of dying wastewater treatment, such as membrane separation, ion-exchange, or activated carbon adsorption, just transfer the pollutants to another phase, and the biological method is not suitable because of the high COD value of the wastewater [2].

The Fenton process is an effective method for industrial wastewater treatment. In this process, powerful oxidant hydroxyl radical ($\cdot\text{OH}$) is produced from H₂O₂ in the presence of ferrous cation, which can degrade many refractory compounds including dye [3]. However, homogeneous Fenton process suffer from some famous disadvantages such as narrow pH range of 2.5 - 3, generation of secondary pollutants and requirement of additional separation and disposal.

To overcome these disadvantages, heterogeneous Fenton catalysts have been developed. In heterogeneous Fenton process, the iron ions can be immobilized in the structure of solid supports, in which the catalysts might produce hydroxyl radicals from hydrogen peroxide and prevent the precipitation of iron hydroxide [4]. Besides iron, copper, manganese, zinc and so on, also have the effect to exciting the hydrogen peroxide and generating radicals. Results of some research show that among the transition metal oxides, iron and copper proved to be more active [5].

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On the other hand, hollow micro-/nano-structured materials have received increasing attention due to their high chemical and thermal stability, low density and high specific surface [6]. These materials have potential applications in various fields such as catalysts, chemical sensors, photonic crystals etc [7]. The main purpose of the present study was to decolorize a non-biodegradable azo dye, Acid Scarlet 3R by heterogeneous Fenton-like process using silica-supported copper catalysts. The efficiency of the heterogeneous catalyst was evaluated by color removal and COD removal. The influence of temperature, pH values, catalyst loading and H_2O_2 dosage on the oxidation process was also discussed.

2. Experimental

2.1. Materials

The reactive dye Acid Brilliant Scarlet 3R was supplied by Cangzhou Lingang Kilda Dyestuffs Co., Ltd and used without purification. H_2O_2 solution (30%) and other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. These chemicals were analytical grade and used in the same state as they were received. Deionized water was used in the whole experiment process. 0.1mol/L H_2SO_4 was used to adjust the pH value of the dye solution to examine the effect of pH value on degradation reaction.

2.2. Catalyst preparation

Carbon microspheres were synthesized through the polycondensation reaction of glucose under hydrothermal conditions according to the method reported in the literature [8].

In the process of preparing silica hollow spheres, 26 mL of $\text{C}_2\text{H}_5\text{OH}$ was firstly mixed with 14 mL of H_2O , followed by adding 0.1g of CTAB into the solution under vigorous stirring until dissolved. Subsequently, the core templates, carbon spheres were uniformly dispersed in the above solution under ultrasound irradiation. After that, a total of 4g of TEOS was added dropwise [9]. The controlled hydrolysis of TEOS around the carbon microspheres was processed under acidic conditions (pH=2.0) at 40°C for 24 h. The obtained solid product was separated by filtration and washed with water. After that, it was put in an oven and dried at 80°C for 6h. Calcination was performed at 350°C in air for 1 h (temperature increase = 1°C/min), and then at 550°C for 6 h.

The CuO/SiO_2 catalyst was prepared by impregnation method. Certain amount of SiO_2 hollow sphere powder was added to 40mL of 10wt. % copper nitrate aqueous solution, depositing at r.t. for 12 h. The deposit was then dried at 80°C for 6h, followed by calcination in air at 550°C for 4 h.

2.3. Catalyst Characterization

The surface morphology and hollow structure of the samples were observed using a Hitachi S-4800 Scanning Electron Microscopy (SEM) analyzer. X-ray diffraction (XRD) patterns were recorded on a diffractometer (Philips X-Pert) with $\text{CuK}\alpha$ radiation (0.15405 nm) equipped with a graphite monochromator in 2θ ranges between 0° and 75°.

2.4. Fenton-like reactions

The catalytic properties of the material were tested via oxidation of the reactive dye Acid Scarlet 3R. The experiments were performed in a round-bottom flask fitted with a magnetic stirrer. The initial concentration of the dye is 0.4 g/L. When 50mL of dye solution in the flask attains a fixed temperature, the required amount of catalyst and 30% H_2O_2 were added. The mixture was kept under constant agitation. Afterwards, samples were withdrawn at fixed time and analyzed by a UV-Vis spectrophotometer with the maximum absorbance for the dye at 510 nm. The oxygen demand (COD) was analyzed using dichromate method.

The performance of the catalysts for the decolorization of Acid Scarlet 3R was evaluated under different conditions. The temperature, catalyst dosage and initial H_2O_2 concentration were varied between 40 and 80°C, 2-12 g L^{-1} and 27.2-40.8 mmol, respectively. At selected reaction time, aliquots

of the solution were collected. After the catalyst was separated from the reaction mixture by centrifugation, the solution was analyzed for COD removal and decolorization efficiency. In all the experiments, other parameters were kept constant and samples were withdrawn at regular time for the analysis. The decolorization efficiency of Acid Scarlet 3R was calculated using the following equation:

$$\text{Decolorization efficiency} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\%$$

where C_0 is the initial concentration of the dye and C_t the concentration at reaction time t .

3. Results and discussion

3.1. Catalyst characterization

SEM images of the hollow SiO_2 spheres are shown in figure 1. It clearly shows the hollow structure of the SiO_2 spheres.

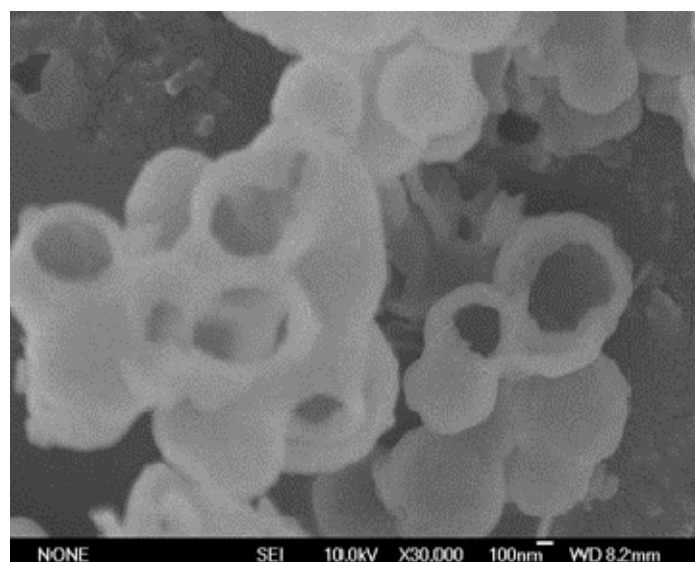
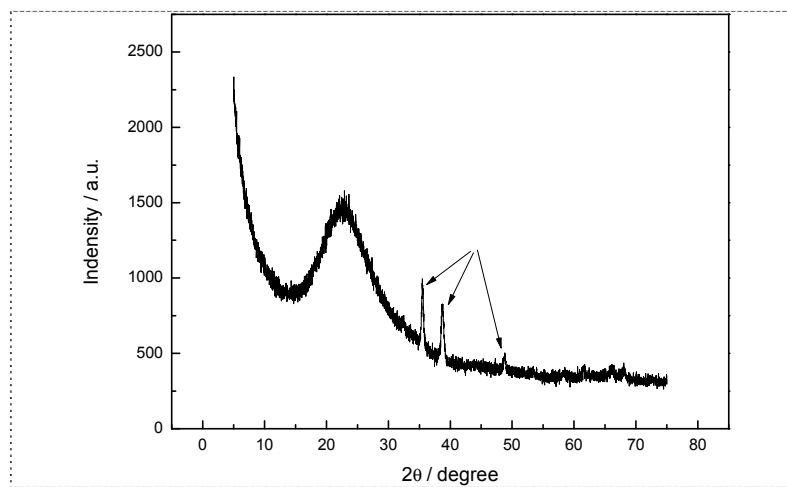
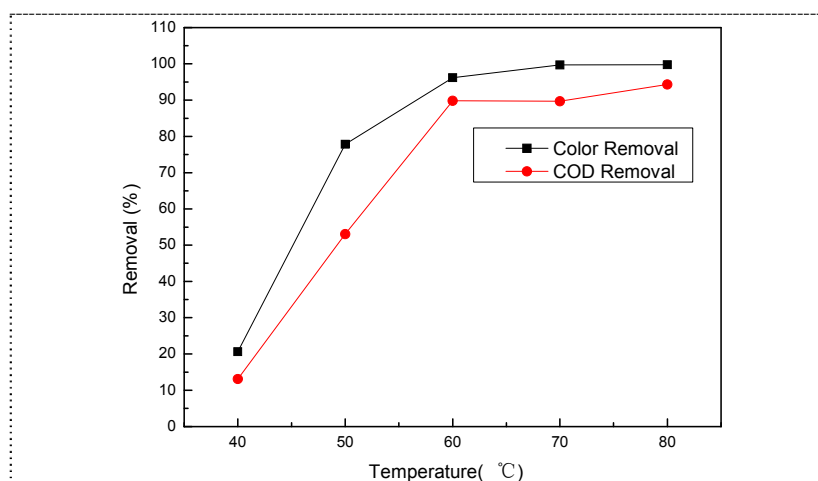
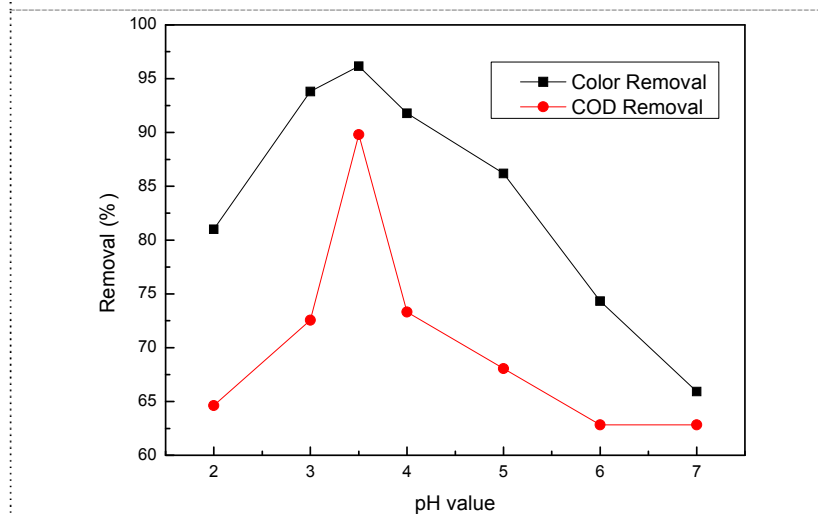


Figure 1. SEM image of SiO_2 hollow spheres.

The powder diffraction pattern of the catalyst is depicted in figure 2. It is seen that the spectrum of the catalyst shows the characteristic peaks of bulk CuO at $2\theta = 35.5^\circ$, 38.7° and 48.8° . The wide diffraction peak around 23° , was characterized as amorphous silica, which proved the hollow silica spheres were amorphous silica.

3.2. Effect of reaction temperature

The influence of reaction temperature on the decolorization and COD removal efficiency of Acid Scarlet 3R was studied by changing temperature from 40°C to 80°C . It can be seen (figure 3) that raising the temperature has a positive impact on the decolorization of Acid Scarlet 3R. The COD removal increased from 13% to 90% as the temperature increased from 40 to 60°C . That's because the elevated temperature can increase the reaction rate of hydrogen peroxide and catalysts, thereby increasing the production rate of hydroxyl radicals or high-valence copper species [10]. Furthermore, increasing temperature makes the reactant molecules have more energy to overcome the activation energy of the reaction [11]. While raising temperature up to 60°C does not show significant improvement in COD removals maybe because too high temperature will promote the decomposition of hydrogen peroxide to oxygen and water [12].

**Figure 2.** XRD patterns of CuO/SiO₂ heterogeneous catalyst.**Figure 3.** Effect of temperature on catalytic activity, (●) COD and (■) colority. Reactions conditions: [dye]₀ = 400 mg/L, catalyst = 6.0 g/L, [H₂O₂]₀ = 34 mmol/L, pH = 3.5.**Figure 4.** Effect of pH on catalytic activity, (●) COD and (■) colority. Reactions conditions: [dye]₀ = 400 mg/L, catalyst = 6.0 g/L, [H₂O₂]₀ = 34mmol/L, temperature = 60°C.

3.3. Effect of initial pH values on dye degradation

pH value is one of the most important parameters that influence the catalytic degradation. The effects of pH from 2 to 7 (adjusted by H_2SO_4 , the initial pH was 9.18) on the catalytic decolorization are shown in figure 4. The figure shows that adjusting pH value of the dye solution from 2 to 3.5 increased the decolorization, but thereafter the decolorization decreased. At low pH ($\text{pH} < 3.0$), more H_2O_2 molecules will be solvated by reaction with H^+ to form oxonium ion (H_3O_2^+), which results in their lower activity, or recombination of hydroxyl radicals becomes prominent resulting in inhibition of the catalytic reaction [13]. COD removal coincided with the color removal, but the curve of COD removal was below down the curve of color removal. That's because the hydroxyl radicals ($\cdot\text{OH}$) mainly attacked the chromophores first, thus the colority of the solution slowed down fast.

3.4. Effect of H_2O_2 dosage

The results of COD and color removal for 400 mg/L of Acid scarlet 3R for determination of optimum H_2O_2 dosage are illustrated in figure 5. It can be seen that color removal efficiency increased by increasing H_2O_2 dosage from 68% to 110% of stoichiometric amount (34 mmol/L). 110% of stoichiometric amount of H_2O_2 can be considered as the optimum dosage, which will produce 86% color removal and 67% COD removals. When the dosage of H_2O_2 increased to 125% of stoichiometric amount, COD removal didn't increase any more, but dropped to 65%. This is probably because hydroxyl radicals were produced from H_2O_2 with catalyst promoting and lower H_2O_2 dosage was not adequate to produce enough hydroxyl radicals. Furthermore, higher H_2O_2 concentration make hydroxyl radicals have more chance to react with each other, thereby reducing the concentration of them [14].

3.5. Effect of catalyst dosage

Figure 6 shows the influence of catalyst dosage on Acid scarlet 3R decolorization and COD removal. The results indicated that higher catalyst amount was associated with increased decolorization, and it was found that 99% decolorization efficiency was achieved with catalyst dosage of 10 g/L. Increased catalyst amount would lead to the formation of more copper sites on the catalyst surface, which would accelerate the decomposition of H_2O_2 to produce more $\cdot\text{OH}$. However, at low catalyst dosage, the color removal can also reach a high value if given adequate time. So the catalyst dosage can accelerate the reaction rate.

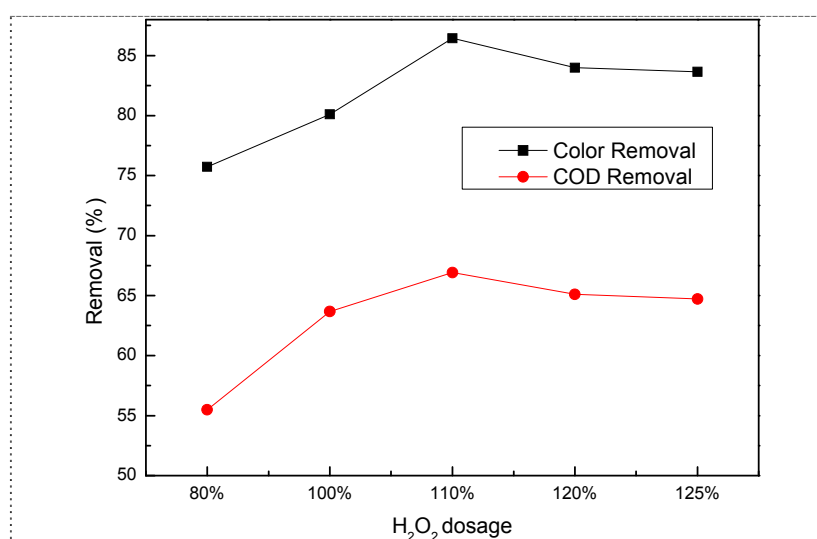


Figure 5. Effect of H_2O_2 concentration on catalytic activity, (●) COD and (■) colority. Reactions conditions: $[\text{dye}]_0 = 400 \text{ mg/L}$, catalyst = 6.0 g/L, pH = 3.5, temperature = 60°C.

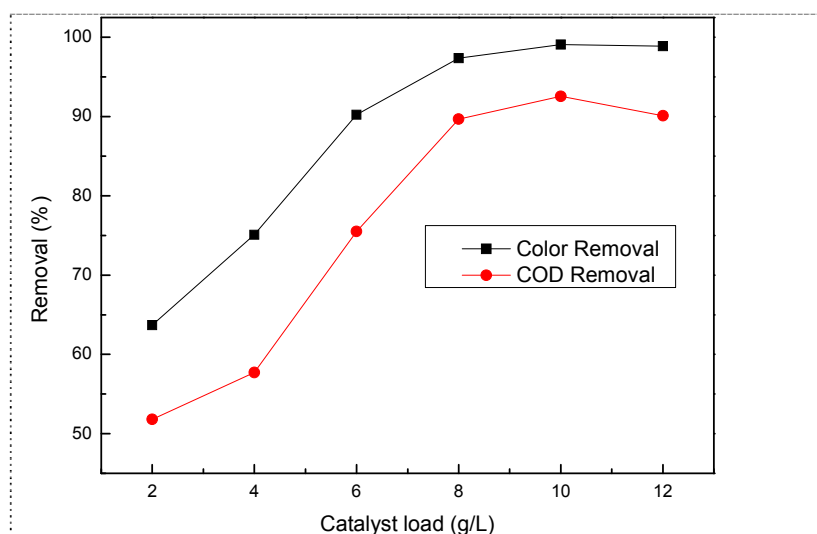


Figure 6. Effect of catalyst concentration on catalytic activity, (●) COD and (■) colority. Reactions conditions: $[H_2O_2]_0 = 34$ mmol/L, pH = 3.5, temperature = 60°C, reaction time = 90 min.

4. Conclusions

This study investigated the oxidation of azo dye using the heterogeneous catalyst and H_2O_2 under mild conditions. When temperature is 60°C, the dosage of H_2O_2 is 34 mmol L⁻¹, initial dye concentration is 400 mg L⁻¹ and pH value of reaction solution is 3.5, the decolorization efficiency of Acid Scarlet 3R reached 97% within 90 min.

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