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

F Xie¹, ², ³, J Zhong¹, L Wang¹, K Wang² and D X Hua²

¹School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, China
²College of Science, China University of Petroleum (East China), Qingdao, China

E-mail: xiefei2013@foxmail.com

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 dyeing 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 (·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].

³ Address for correspondence: F Xie, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, China. E-mail: xiefei2013@foxmail.com.
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 H₂O₂ 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. H₂O₂ 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 H₂SO₄ 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 C₂H₅OH was firstly mixed with 14 mL of H₂O, 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/SiO₂ catalyst was prepared by impregnation method. Certain amount of SiO₂ 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 CuKα 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% H₂O₂ 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 H₂O₂ 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:

\[
\text{Decolorization efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

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.

![SEM image of SiO\(_2\) hollow spheres.](image)

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 \(\theta = 35.5^\circ, 38.7^\circ\) and \(48.8^\circ\). The widen diffraction peak around \(23^\circ\), 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/SiO$_2$ heterogeneous catalyst.

Figure 3. Effect of temperature on catalytic activity, (●) COD and (■) colority. Reactions conditions: [dye]$_o$ = 400 mg/L, catalyst = 6.0 g/L, [H$_2$O$_2$]$_o$ = 34 mmol/L, pH = 3.5.

Figure 4. Effect of pH on catalytic activity, (●) COD and (■) colority. Reactions conditions: [dye]$_o$ = 400 mg/L, catalyst = 6.0 g/L, [H$_2$O$_2$]$_o$ = 34 mmol/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 H₂SO₄, 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 (pH<3.0), more H₂O₂ molecules will be solvated by reaction with H⁺ to form oxonium ion (H₃O₂⁺), 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 (·OH) mainly attacked the chromophores first, thus the colority of the solution slowed down fast.

3.4. Effect of H₂O₂ dosage

The results of COD and color removal for 400 mg/L of Acid scarlet 3R for determination of optimum H₂O₂ dosage are illustrated in figure 5. It can be seen that color removal efficiency increased by increasing H₂O₂ dosage from 68% to 110% of stoichiometric amount (34 mmol/L). 110% of stoichiometric amount of H₂O₂ can be considered as the optimum dosage, which will produce 86% color removal and 67% COD removals. When the dosage of H₂O₂ 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 H₂O₂ with catalyst promoting and lower H₂O₂ dosage was not adequate to produce enough hydroxyl radicals. Furthermore, higher H₂O₂ 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 H₂O₂ to produce more ·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](image)

Figure 5. Effect of H₂O₂ concentration on catalytic activity, (●) COD and (■) colority. Reactions conditions: [dye]₀ = 400 mg/L, catalyst = 6.0 g/L, pH = 3.5, temperature = 60°C.
4. Conclusions
This study investigated the oxidation of azo dye using the heterogeneous catalyst and H$_2$O$_2$ under mild conditions. When temperature is 60°C, the dosage of H$_2$O$_2$ 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.

References
[1] Papic S, Vujevic D, Koprivanac N and Sinko D 2009 Decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes J. Hazard. Mater. 164 1137-45
[2] Han F, Kambala V S R, Srinivasan M, Rajarathnam D and Naidu R 2009 Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review Appl. Catal. A. 359 25-40
[3] Dükkanç II, Gündüz G, Yılmaz S and Prihod'ko R V 2010 Heterogeneous Fenton-like degradation of rhodamine 6G in water using CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis J. Hazard. Mater. 181 343-50
[4] Hassan H and Hameed B H 2011 Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of reactive blue 4 Chem. Eng. J. 171 912-18
[5] Xu X R, Li H B, Wang W H and Gu J D 2004 Degradation of dyes in aqueous solutions by the Fenton process Chemosphere 57 595-600
[6] Yu J, Liu S and Yu H 2007 Microstructures and photoactivity of mesoporous anatase hollow microspheres fabricated by fluoride-mediated self-transformation J. Catal. 249 59-66
[7] Wang C H, Chu X F and Wu M M 2007 Highly sensitive gas sensors based on hollow SnO$_2$ spheres prepared by carbon sphere template method Sens Actuators B 120 508-13
[8] Sun X and Li Y 2004 Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles Angew. Chem. Int. Edit. 43 597-601
[9] Shen W, Zhu Y, Dong X, Gu J and Shi J 2005 A new strategy to synthesize TiO$_2$ hollow spheres using carbon spheres as template Chem. Lett. 34 840-41
[10] Sun J H, Sun S P, Wang G L and Qiao L P 2007 Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process Dyes Pigments 74 647-52
[11] Xu H-y, Prasad M and Liu Y 2009 Schorl: A novel catalyst in mineral-catalyzed Fenton-like system for dyeing wastewater discoloration J. Hazard. Mater. 165 1186-92
[12] Benitez F J, Acero J L, Real F J, Rubio F J and Leal A I 2001 The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions Water Res. 35 1338-43
[13] Chang M C, Shu H Y and Yu H H 2006 An integrated technique using zero-valent iron and UV/H₂O₂ sequential process for complete decolorization and mineralization of CI Acid Black 24 wastewater J. Hazard. Mater. 138 574-81
[14] Tekbaş M, Yatmaz H C and Bektaş N 2008 Heterogeneous photo-Fenton oxidation of reactive azo dye solutions using iron exchanged zeolite as a catalyst Micropor. Mesopor. Mat. 115 594-602