A Novel Catalyst for Treatment of Textile Wastewater by Ozonation

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Abstract
Textile industry employs large quantities of water for processing. Considering the volume and composition, textile wastewater is thought to be the most polluting wastewater among all industrial sectors. Through environmental concerns and regulations, growing pressure is being placed on textile plant to reduce the volume and improve the reuse percentage of the wastewater. Ozonation is an effective pre-treatment before the wastewater were further purified in reverse osmosis or ultrafiltration system for reuse. However, the cost for ozone is not at an acceptable level currently for the textile plants. In this paper, a novel catalyst was fabricated for ozonation of wastewater to improve the utilization rate of ozone and treatment efficiency, so as to reduce the cost incurred from ozone assumption. Commercial reactive dyestuff that frequently used in cotton dyeing was adopted in this study as the target pollutants. The performance of the catalyst in ozonation of colored wastewater was evaluated in varied conditions. Color removal and COD reduction were two main targets to assess the treatment results of the polluted water containing dyestuff. The results implied that the catalyst prepared was capable to improve the degradation percentage of dyestuff in wastewater, providing an economical solution for degradation of pollutants in effluents from textile dyeing plant for reuse.

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1. Introduction

In recent years, numerous dye sources release to wastewater, causing a danger to the environment, animals and human beings (Gosavi, Sharma, 2014). In order to afford the inexpensive and efficient technologies for the dye removal from wastewater, a series of works including chemical, electrochemical, and biological treatment were used to purify the wastewater containing dyes. However, most of them are of low efficiency and limited due to high cost in operation.

Ozone has been used for sewage purification because of its environmentally friendly property and strong oxidizing ability. However, only limited mineralization level was achieved by ozonation alone in textile effluents due to the low oxidation efficiency and selectivity. Catalytic ozonation is considered to be a promising technology for removal of organic dyes in aqueous solution. Various supported metals and metal oxides are the most common catalysts that have been tested in the ozonation of dye compounds (Martins, Quinta-Ferreira, 2014). Among the studied support materials, porous carbon materials are usually chosen as promising substrate.

We have obtained optimum results on preparation techniques and performance improvement for various carbon materials (Shang et al., 2013, Shang et al., 2009) and composite materials (Shang et al., 2009a, Shang et al., 2011, Shang et al., 2012, Yang et al., 2010, Zhang et al., 2012) in our previous study. In the present manuscript we intend to develop a novel efficient catalyst by using highly dispersed copper oxide on mesoporous carbon aerogel (MCA) for catalytic ozonation of dye wastewater. The work aimed at (a) synthesis and characterization of copper oxide/mesoporous carbon aerogel catalyst; (b) compare the degradation efficiency of C.I. Reactive Blue 19 (RB 19) in different processes; and (c) investigate the degradation efficiency of four common dyes having different chemical structures in water by catalytic ozonation.

2. Material And Methods

2.1. Dyes and Chemicals

Reactive dyes were obtained from Zhejiang Longsheng Group Co., Ltd, China and used without further purification. The dyes were dried at 378 K for 3 h before use. The experimental solutions (800 mg/L) were prepared by dissolving accurately weighed 1.600 g of different dye in 2 L volumetric flask. All Chemicals used in the catalyst preparation were of analytical grade.

2.2. Preparation of Catalyst

In the present study, resorcinol, formaldehyde, water, and surfactant were mixed according to predetermined recipes to fabricate supporting material as literature described (Wu et al., 2008). The mixture was transferred into a glass bottle and put into an oven at 85 °C for 120 h. The sample were then stored at room temperature for 2 d, and further dried at 60 ^{o}C for 24 h, followed by drying at 105 ^{o}C for 3 h and finally calcined 1173 K for 3 h under Argon gas flow. Then, the prepared sample was added into 0.2 M $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution and the mixture was loaded into the water-bath shaker at 30 ^{o}C for 24 h subsequently. After the impregnation, the sample was dried at 105 ^{o}C for 3 h and finally calcined at 450 ^{o}C for 4 h. The patter of X-ray diffraction was obtained with a diffractometer (Rigaku, SmartLab) using Cu Kα radiation. The microstructures and morphology of the prepared catalyst was investigated using TEM (JEOL Model JEM-2100F) operated at 200 kV.

2.3. Ozonation Procedure

Ozone gas was introduced by ozone generator (Medozons BM-02, Russia) and the gas fed into a porous glass diffuser to produce fine bubbles in the bottom of the glass reactor. 400 mL dye solution was fed into the 0.5 L glass reactor in each run. The experiment was timed when the stirring and ozone gas supply were started. At predetermined time intervals, 5 mL reaction solution was carefully withdrawn from the glass reactor using a digital micropipette. The solution obtained was centrifuged at 6000 rpm for 10 min in a centrifuge (K3 Centurion Scientific Ltd, UK) to remove traces of catalyst. All treated solutions were diluted and determined by a UV-VIS Spectrophotometer (Perkin-Elmer, Lambda 18) at the maximum wavelength. The treated dye solutions were digested in COD reactor (Model DRB 200, HACH, USA) and then analyzed by COD colorimeter (Model DR 900, HACH, USA).

3. Results And Discussions

3.1. Characterization of Prepared Catalyst

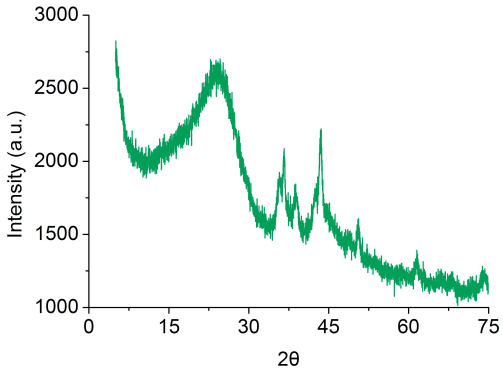

Figure 1: X-ray diffraction pattern of copper oxide/MCA

Powder x-ray diffraction pattern of copper oxide /MCA is shown in Figure 1. As it can be seen, the synthesized copper oxide /MCA catalyst are mainly exists as CuO and Cu_2O. The copper oxide /MCA catalyst only display partial peaks due to the low metal oxide concentration and small copper oxide particles in the MCA support.

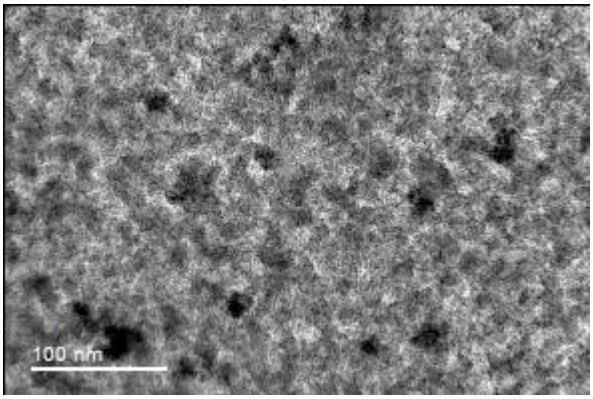

Figure 2: TEM of prepared copper oxide/MCA

TEM image was used to detect the shape and size of the copper oxide. As seen in Figure 2, the solid phase is composed of nanosized copper oxide particles (about 10 nm) and carbon nano-particles (20 to 30 nm).

3.2. Decolorization of RB 19 in the Different Processes

The color removal of ozonation alone, pure adsorption of copper oxide /MCA, and copper oxide /MCA catalytic ozonation under the same condition were compared to explore the behavior of the copper oxide /MCA in the process of dye degradation. It was clear that the decolorization of RB 19 (Figure 3) was improved with increasing the treating time in both the systems of ozonation alone and catalytic ozonation in the first 60 minutes, of which the difference was not significant. Under the same experimental conditions, the color removal rate of RB 19 only obtaintd 2.5% by the adsorption on the copper oxide/MCA catalyst surface. Therefore, the lower color removal rate can be ignored in this study. These data implied that the catalyst prepared won't adsorb dyes but has little effect on decolorisation.

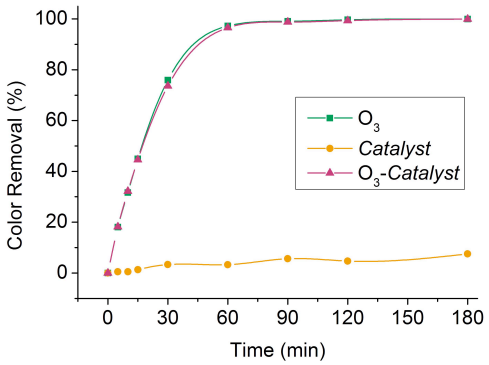

Figure 3: Comparison of the decoloration ratio of RB 19
(Temperature: 30 °C, Ozone: 4.0 mg/min, Catalyst: 1 g)

3.3 Removal of COD in the Different Processes

Dyes cannot be oxidized instantaneously to carbon dioxide and water in the degradation process and the oxidation pathway presumably proceeds via a number of intermediate species.

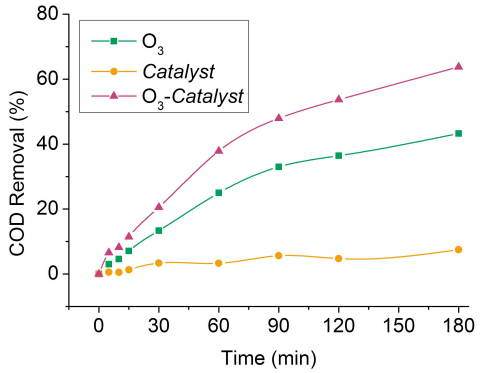

Figure 4: Comparison of the COD removal of RB 19
(Temperature: 30 °C, Initial COD: 625, Ozone: 4.0 mg/min, Catalyst: 1 g)

Thus COD removal of the three different processes including ozonation alone, adsorption of copper oxide/MCA catalyst and catalytic ozonation were also investigated. The results are shown in Figure 4. It was suggested that the degradation degree of RB 19 was drastically enhanced by copper oxide /MCA catalyst. It also can be seen that the COD removal rate was much less than color removal rate at the same conditions by comparing Figure 3 and Figure 4.

3.4. Catalytic Ozonation of Various Dyes

In order to examined the feasibility of the novel catalyst in treatment of some synthetic dyes having different chemical structures, we attempted to choose four dyes that belonging to the most representative classes such as RB 5 (C.I. Reactive Black 5), RB 19 (C.I. Reactive Blue 19), RR 239 (C.I. Reactive Red 239) and RY 176 (C.I. Reactive Yellow 176) as degradation targets.

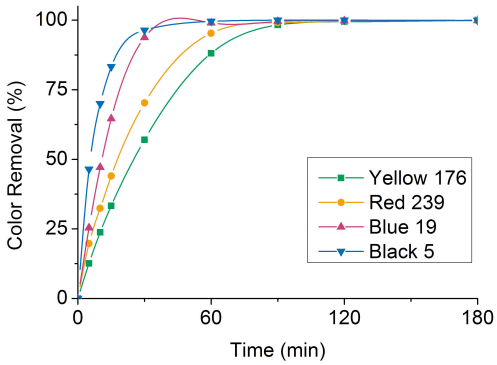

Figure 5: Comparison of the decoloration ratio of different dyes
(Temperature: 30 ^{o}C, Ozone: 4.0 mg/min, Catalyst: 1 g)

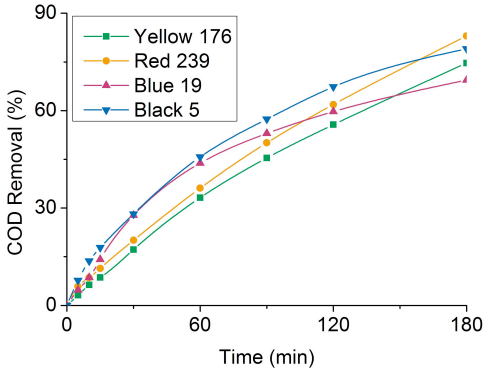

Figure 6: Comparison of the COD removal of different dyes
(Temperature: 30 ^{o}C, Initial COD: 625 (RB 19), 720 (RB 19), 396 (RY 176), 420 (RR 239), Ozone: 4.0 mg/min, Catalyst: 1 g)

All selected syhthtic dyes are commonly used in dyeing processes of cotton and cellulose substrates. The results are shown in Figure 5 and Figure 6. It can be observed that the catalytic ozonation is effective for decolorization of all dyes, with color removal rates reaching 99% after 90 min treatment under the selected conditions. The COD removal rate of four dyes could reach 69%~83% at 180 min. The novel copper oxide/MCA catalyst has a good prospects of application in treatment of dye pollutants in wastewater.

4. Conclusion

The novel copper oxide/MCA catalyst has been successfully prepared and characterized by XRD and TEM. The results demonstrated that the copper oxide nano-particles were well-dispersed in the mesoporous carbon support. This research also showed that the prepared catalyst was a good candidate for catalytic ozonation of dye and the degradation degree of the dye solution notably enhanced by the combination of copper oxide/MCA with ozone. This investigation opens new perspectives in ozonation of textile wastewater with high efficiency for wastewater purification.

Acknowledgment

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