



Preparation and Properties of Catalyst for Chlorine Dioxide Degrading Azo-Dye Simulated Wastewater Containing Reactive Brilliant Red KD-8B

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The preparation and properties of a new ternary catalyst for chlorine dioxide catalytic oxidation were studied. The catalyst NiO-CuO_x-La₂O₃/Al₂O₃ was prepared by the dipping-calcination method using activated alumina as a supporter. Optimum preparation conditions were as follows: the best volume ratio of Ni(NO₃)₂ and Cu(NO₃)₂ is 5:1; the optimal volume ratio of Ni(NO₃)₂ and La(NO₃)₃ is 40:9. The ternary catalyst had high catalytic activity and longer service life.

Key Words: Chlorine dioxide, Azo-dye wastewater, Ternary catalyst, Preparation.

INTRODUCTION

Azo-dyes are the most common used dyes in the printing and dyeing industry, accounts for about 50 % amounts of the whole dyes. Its wastewater is difficult to degrade because its complex composition, poor biodegradability and high colour^{1,2}. Even a small amount of dye remnants in the wastewater can also cause the reducing the water transmission rate, which resulting in ecological destruction. So the difficulties in azo-dye wastewater treatment are COD reduction and colour removal. Active Brilliant Red KD-8B (hereinafter to be referred as ABR) is a typical azo-dye, so the study of its degradation characteristics has general reference value for all azo-dyes degradation^{3,4}. The structure of ABR is shown in Fig. 1.

Chlorine dioxide, with strong oxidibility, which produces little or none organic halides in oxidation process⁵⁻⁷, has been widely used for water disinfection and paper bleaching industry^{8,9}. In recent years, novel oxidant ClO₂ has been studied

for application in the wastewater and there are reports on study of ClO₂ catalytic oxidation for printing and dyeing wastewater treatment, which has a good result in removing dye concentration and reducing COD_{Cr} value of wastewater^{10,11}. Currently, the studying focus of ClO₂ catalytic oxidation technology is to find more efficient, stable, durable catalysts so as to shorten the reaction time and increase the applicability of this method.

When transition metal oxides as catalyst, rare earth oxides which have semiconductor properties have great use to enhance their catalytic activity, improve their selectivity and increase their stability under the synergistic effect between rare earth oxides and transition metal oxides^{12,13}. This paper carried out extensive and careful screening from five carriers and seven soluble transition metal salts and compositional formulations were performed, in order to obtain better-performance ClO₂ treatment catalyst for azo wastewater, which had some reference value for industrial application of ClO₂ advanced oxidation technology in printing and dyeing wastewater treatment.

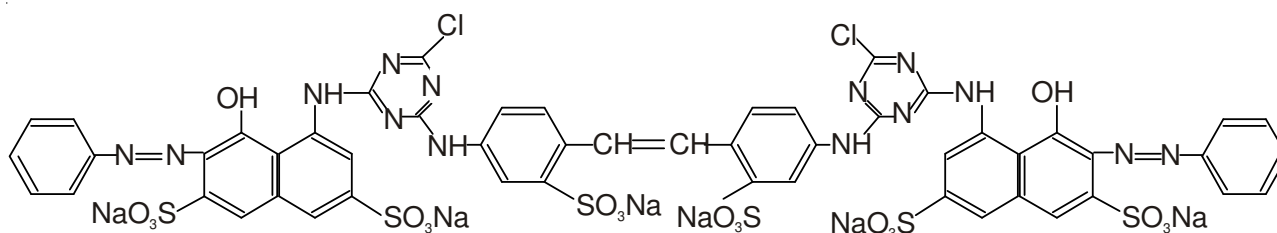


Fig. 1. Molecular structure of active brilliant red KD-8B (ABR)

EXPERIMENTAL

All the reagents used were analytical-grade. The concentration of ClO_2 solution is 2.33 g/L. Simulated wastewater containing active brilliant red KD-8B (ABR) was prepared by dissolving 5 g of ABR in water in a 1000 mL volumetric flask. The COD_{Cr} of the wastewater was 1248 mg/L. Further solutions of different concentrations were diluted using the same stock solution.

Preparation of catalysts

Choice of carrier: The catalysts were prepared by the dipping-calcination method. First, the carriers (including aluminum silicate, activated alumina, activated carbon, 4A zeolite, titanium dioxide) were weighed 10 g respectively, then immersed into 50 mL 0.1 mol/L $\text{Fe}(\text{NO}_3)_3$ aqueous solution for 24 h at room temperature, filtered, dried at 110 °C for 4 h and calcined at 450 °C for 4 h. The formed Fe_2O_3 was loaded on the surface of carriers.

Choice of active component: Seven active component solutions with the concentration of 0.1 mol/L including $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ were tested as discussed earlier and two nitrates of its metal oxide with high catalytic activity were screened out. By using one metal oxide as the main active component, at the same time, recombining the second active component and electron promoter, ternary catalyst was obtained.

Decolourization experiments: A certain volume of ABR simulated wastewater of a certain concentration was added in a 250 mL flask. Some amounts of the catalysts and ClO_2 solution were added. The treatment was carried out at room temperature under the condition of stirring. 2 mL samples of the examined solution were withdrawn from the reactor at every 2 min, then analyzed the remaining dyes using 8453 UV-VIS spectrophotometer (Agilent Technologies Co. Ltd., USA). The simulated wastewater containing ABR, the effluent by chemical oxidation and the effluent by catalytic oxidation were diluted by some times before determination if necessary. The decolourization rate as an key indicators for evaluating the oxidative effects. Considering the volume of oxidant, calculated as follows¹⁴:

$$X(\%) = \frac{C_0 V_{\text{wastewater}} - C_t (V_{\text{wastewater}} + V_{\text{ClO}_2})}{C_0 V_{\text{wastewater}}} \times 100\% \quad (1)$$

where, X is the decolourization rate (%); C_0 and C_t are the initial and final concentration of ABR, respectively (mg/L); $V_{\text{wastewater}}$, V_{ClO_2} are the volumes of wastewater, ClO_2 solutions, respectively (L).

RESULTS AND DISCUSSION

Determination of carrier: 50 mL simulated wastewater containing 200 mg/L ABR was added to 250 mL conical flask, following addition of 6 mL ClO_2 solutions (40 mg/L). Catalyst dosage was 1.5 g. Absorbance of wastewater was measured after reaction for 2 min in order to examine the effect of different carriers on the catalytic activity, the results were shown in Fig. 2.

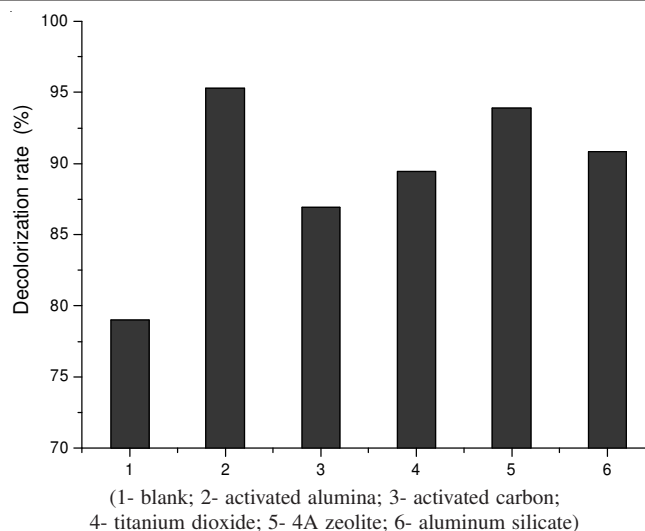


Fig. 2. Decolourization effect of catalysts with different carriers

After loaded active component Fe oxide on any carrier, the decolourization rate has been improved to a degree than that without catalyst, among the five carriers, when using activated alumina as the carrier, it has the strongest catalytic capacity for ClO_2 oxidation (Fig. 2). Therefore, activated alumina was chosen as the best catalyst carrier.

Catalytic effect of single-component catalysts: For testing catalytic results of single-component catalyst for ClO_2 oxidation, 40 mg/L ClO_2 with dosage of 3 mL was put into 25 mL solution containing 175 mg/L ABR, each catalyst dosage was 1 g and the reaction time of catalytic oxidation was 2 min. The results were shown in Fig. 3.

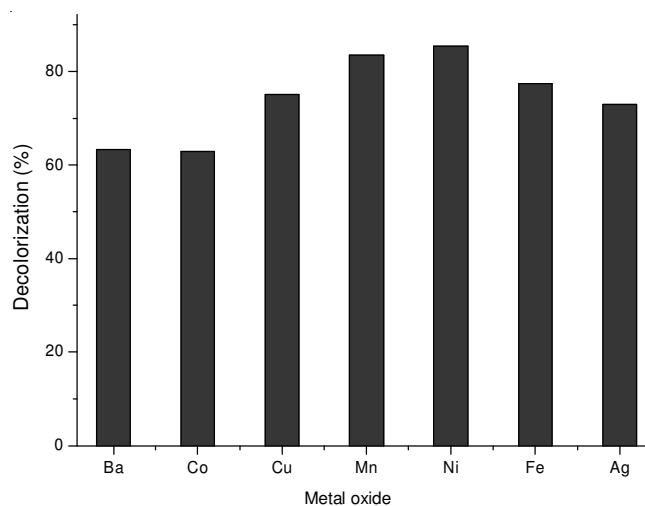


Fig. 3. Decolourization effect of single component catalysts

When the dosage of ClO_2 was the same, the order of decolourization rate of each catalyst on catalyzing ClO_2 oxidation was $\text{Ni} > \text{Mn} > \text{Fe} > \text{Cu} > \text{Ag} > \text{Ba} > \text{Co}$. Both oxides of Mn and Ni showed strong catalytic effect, so oxides of Mn and Ni were chosen for further study as the main active component.

Catalytic effect of composite catalysts: Oxides of Mn and Ni had high catalytic activity in ClO_2 oxidation, so using $\text{Mn}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ as materials of main catalyst,

$\text{Cu}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ as materials of assistant catalyst and the proportion of main catalyst and assistant catalyst dosages was 10:1, which were loaded on Al_2O_3 carrier to prepare composite catalysts. For testing catalytic results of binary catalysts for ClO_2 oxidation, 40 mg/L ClO_2 with dosage of 6 mL was put into 200 mg/L ABR solution of 50 mL, each catalyst dosage was 1 g and the reaction time of catalytic oxidation was 2 min. Catalytic results were shown in Fig. 4.

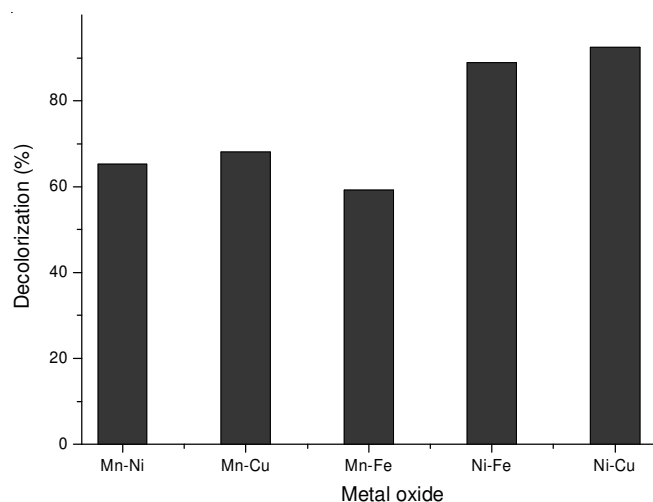


Fig. 4. Decolourization effect of binary catalysts

In all the binary catalysts, Ni-Cu oxides had the highest catalytic activity (Fig. 4). So adding the second active component in the catalyst, it can play a role of synergetic effect. The effect of different dosages of the main and assistant active components on ClO_2 catalyzing oxidation was examined, it showed that a certain dosage of Cu oxide had enhancement effect on the catalytic activity of Ni oxide (Fig. 5). However, when the volume ratio of active component solutions of $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ was more than 1.5:1, not only the catalytic effect hadn't been improved, but also decolourization rate was even less than that used Ni oxide alone, which indicated that the best volume ratio of $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ was 5:1 (Fig. 5).

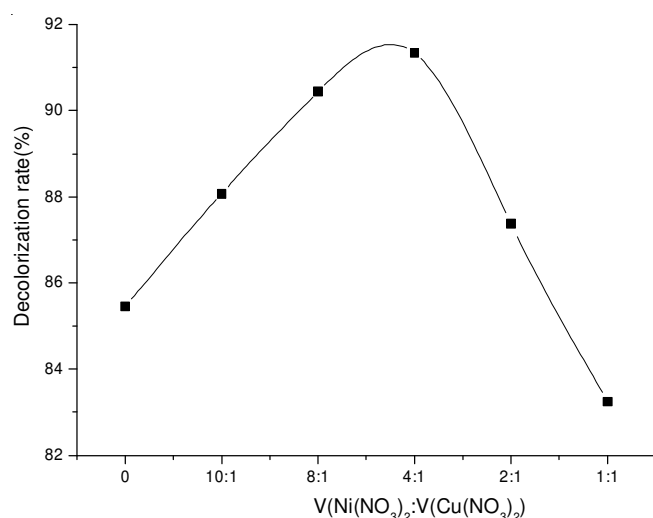


Fig. 5. Decolourization effect of different dosage of the two active components

Catalytic effect of doping electron promoter: Proper electron promoter can let grain size of composite catalyst become smaller, so that there are more active micro-crystals in the catalyst¹⁵. When $V[\text{Ni}(\text{NO}_3)_2]:V[\text{Cu}(\text{NO}_3)_2] = 5:1$, $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ were chosen as electron promoters to prepare ternary composite catalyst, catalytic effects of them on ClO_2 oxidation were examined under the same conditions.

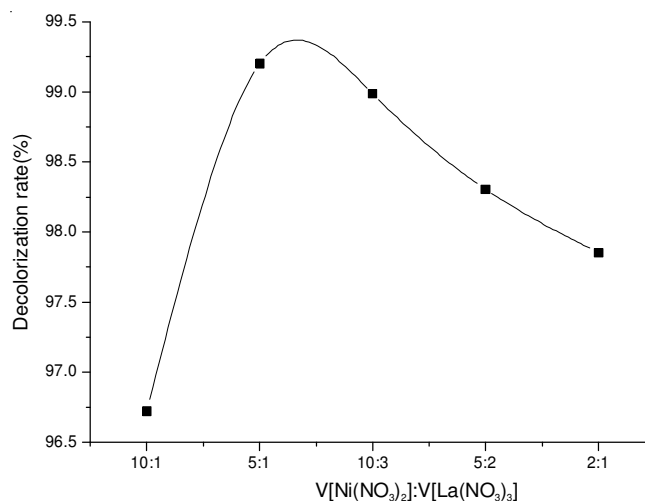


Fig. 6. Decolourization effect of different dosage of lanthanum nitrate

At the same experimental conditions, the decolourization effect of La element is better than that of Ce (data not shown). Therefore, La was used as the electron promoter in composite catalyst. When there was larger dosage of La element, the catalytic effect would be lower, due to a great deal of La causing the loss of Ni and Cu in the catalyst, which results in lower catalytic effect. Therefore, the optimal volume ratio of $\text{Ni}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ should be 40:9 (Fig. 6).

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