



Degradation of Azo Dyes Wastewater Using Chlorine Dioxide and A Ternary Catalyst NiO-CuO_x-La₂O₃/Al₂O₃

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A ternary catalyst (NiO-CuO_x-La₂O₃/Al₂O₃) for chlorine dioxide (ClO₂) catalytic oxidation of azo dyes was prepared by the dipping-calcination method with activated alumina as carrier. With the simulated wastewater containing Reactive brilliant red KD-8B (RBR) as the treating object, the catalytic activity of the catalyst and the degradation features were explored. The results showed that this reaction follows apparent pseudo-first-order reaction kinetics and the reaction rate constant increased by 195 % than that of reaction without the catalyst, so the ternary catalyst can significantly reduce the time of degradation reaction and the ClO₂ dosage. The order of the degradation activity of various groups in the Reactive brilliant red KD-8B molecular structure was: azo bond > non-aromatic carbon-carbon double bond > carbon-nitrogen bond in triazine > aromatic carbon-carbon bond. It also proved that in the catalyst the active components combined with the carrier by strong chemical bonds and the catalyst was stable. So it provided a highly efficient catalyst for chlorine dioxide catalytic oxidation technology applied in treating azo dyes wastewater.

Key Words: Ternary catalyst, Chlorine dioxide, Azo dyes wastewater, Reactive brilliant red KD-8B.

INTRODUCTION

Azo dyes, a group of dyes containing azo structure (-N=N-), are the most commonly used dyes in the printing and dyeing industry, which accounts for about 50 % usage of the total dyes, so every year a large amount of wastewater containing azo dyes was produced in the process of using and producing azo dyes¹⁻³. Azo dyes wastewater is difficult to degrade, even a little bit of azo-dye in the wastewater can also cause the water transmission rate reducing, resulting in ecological destruction. So one of the difficulties in azo dyes wastewater treatment is colour removal⁴⁻⁶. Reactive brilliant red KD-8B (RBR) is a typical azo dye, so the study of its degradation characteristics has general reference value for all azo dyes degradation. Reactive Brilliant Red KD-8B, blue-ray pink powder, is mainly used for dyeing cotton or viscose fiber. Its chemical formula is C₅₂H₃₀Cl₂N₁₄O₂₀S₆Na₆ and its formula weight is 1572.12, the molecular structure of RBR is shown in Fig. 1.

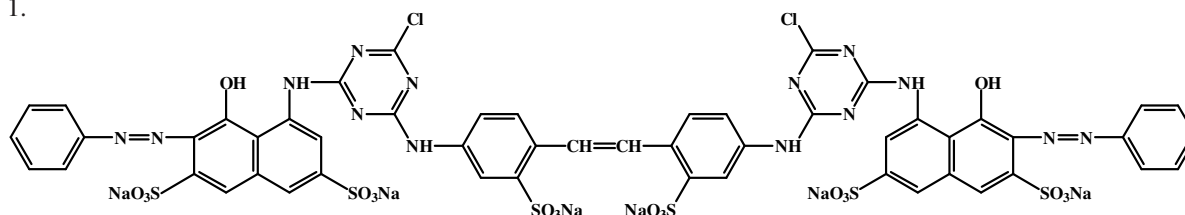


Fig. 1. Molecular structure of Reactive brilliant red KD-8B

Chlorine dioxide (ClO₂), with strong oxidizing capability produces little or none organic halides in oxidation process, has been widely used for water disinfection and paper bleaching industry⁷⁻¹⁰. 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^{11,12}. Currently, the study of ClO₂ catalytic oxidation technology is focuses on finding more efficient, stable and durable catalysts so as to shorten the reaction time and increase the applicability of this method¹³⁻¹⁵.

Through a series of extensive and careful screening experiments, a better ternary catalyst NiO-CuO_x-La₂O₃/Al₂O₃ for ClO₂ degradation of azo dye wastewater was obtained and the process of ClO₂ catalytic oxidation of RBR simulated wastewater was analyzed, which provides a highly efficient catalyst for ClO₂ advanced oxidation technology in printing and dyeing wastewater treatment.

EXPERIMENTAL

The initial concentration of ClO_2 solution is 2330 mg/L. The ClO_2 solution was stored in refrigerator at 5 °C and was standardized before using. Simulated wastewater containing RBR was prepared by dissolving 250 mg RBR in water in a 1000 mL volumetric flask. Further solutions of different concentrations were diluted using the same stock solution. All reagents used were analytical-grade.

Preparation of the catalyst: The ternary catalyst was prepared by the dipping-calcination method. The best preparation technology is: the carrier Al_2O_3 weighed 20 g was calcined at 500 °C for 4 h; then immersed into 50 mL solution containing 0.25 mol/L mixed metal nitrate in which $V_{\text{Ni}(\text{NO}_3)_2}:V_{\text{Cu}(\text{NO}_3)_2}:V_{\text{La}(\text{NO}_3)_3} = 5:1:1$ for 12 h at room temperature, filtered, dried at 110 °C for 2 h and calcined at 450 °C for 3 h, then the ternary catalyst $\text{NiO-CuO}_x\text{-La}_2\text{O}_3/\text{Al}_2\text{O}_3$ was obtained.

Reactive brilliant red degradation experiments:

Experiments were performed at the room temperature (25 °C) with ClO_2 alone, carrier and ClO_2 and the different combined ClO_2 /catalyst systems, respectively, to investigate the degradation efficiency of RBR simulated wastewater of the same concentration. 50 mL simulated wastewater containing 125 mg/L RBR was added to 250 mL conical flask, following addition of 60 mg/L ClO_2 solutions at the speed of 2 mL/min. Catalyst dosage was 1.5 g. 2 mL samples of the examined solution were withdrawn from the reactor at every 2 min and analyzed the remaining dyes using 8453 UV-VIS spectrophotometer (Agilent Technologies Co., Ltd, USA). The degradation efficiency was the key indicator for evaluating the oxidative effect. Considering the volume of oxidant, calculated as follows :

$$X(\%) = \frac{C_0 V_{\text{wastewater}} - C_1 (V_{\text{wastewater}} + V_{\text{ClO}_2})}{C_0 V_{\text{wastewater}}} \times 100\% \quad (1)$$

where, X is the degradation efficiency (%); C_0 and C_1 are the initial and final concentration of RBR (mg/L); $V_{\text{wastewater}}$, V_{ClO_2} are the volumes of wastewater, ClO_2 solutions, respectively (L).

Testing methods of catalyst : BX 95038 FT-IR spectrometer (Perkin Elmer Co., Ltd, USA) was used for determining the chemical composition of the catalyst. S-3400N scanning electron microscopy (Hitachi Group, Japan) and PV-8200 X-ray energy dispersive analyzer (EDAX Inc., USA) were used for determining the surface physical morphology and elements of the catalyst.

RESULTS AND DISCUSSION

Degradation effect of RBR dye: The degradation results were shown in Fig. 2. When treating 125 mg/L RBR simulated wastewater by ClO_2 and the ternary catalyst, the degradation efficiency was up to 90.2 % in 2 min and 100 % in 3 min. Obviously, the degradation efficiency of RBR by using ClO_2 and the ternary catalyst is much more than that of using ClO_2 alone and ClO_2 with other catalysts. So the catalytic activity of $\text{NiO-CuO}_x\text{-La}_2\text{O}_3/\text{Al}_2\text{O}_3$ is higher than that of Al_2O_3 and other three catalysts $\text{NiO}/\text{Al}_2\text{O}_3$, $\text{CuO}_x/\text{Al}_2\text{O}_3$, $\text{NiO-CuO}_x/\text{Al}_2\text{O}_3$. It also proved that in the presence of transition metals the

addition of rare earth oxides (La_2O_3) can enhance the catalytic activity.

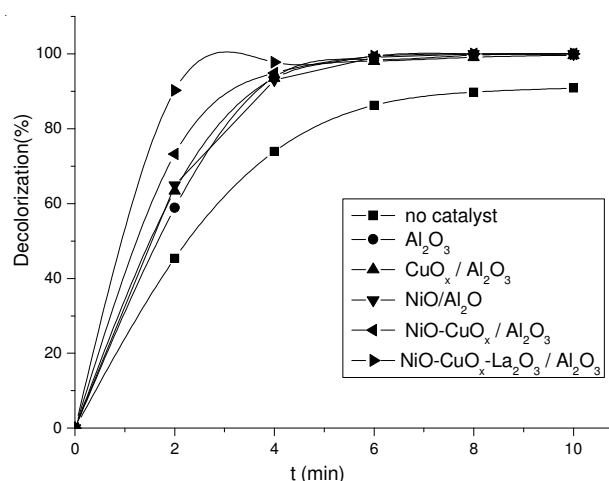


Fig. 2. Comparison of degradation efficiency of RBR

The data were processed by origin 8.0 software and the degradation efficiency of RBR simulated wastewater with/without the ternary catalyst follows apparent pseudo-first-order reaction kinetics (Fig. 3). The apparent pseudo-first-order rate constant $k_2 = 0.8873 \text{ min}^{-1}$ in the combined ClO_2 /ternary catalyst system, which improved 0.5861 min^{-1} than $k_1 = 0.3012 \text{ min}^{-1}$ achieved in ClO_2 alone system. The ternary catalyst can play an enhanced role in promoting the oxidation efficiency of ClO_2 and the reaction rate constant increased by 195 %, so that it can significantly reduce the degradation time and the ClO_2 dosage.

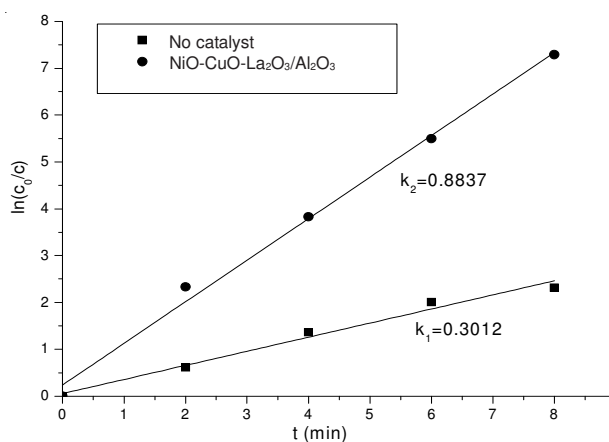


Fig. 3. Comparison of reaction rate constant

UV-VIS spectra changes of RBR in treating process:

As can be observed from Fig. 4, before the oxidation, the absorption spectrum of RBR in water was characterized by one main band in the visible region, with its maximum absorption peak at 535 nm, which was originated from an extended chromo-phore and by three other bands in the ultra-violet region located at 341, 286 and 256 nm. The extended chromophore comprises a aromatic ring and a naphthalene ring, which are connected through an azo bond. The peak at 341 nm was associated with a large conjugated system formed by two benzene rings through a carbon-carbon double bond. The peak at 286 nm was caused by a conjugated system of

s-triazine. The peak at 256 nm was associated with benzene structure in the molecule.

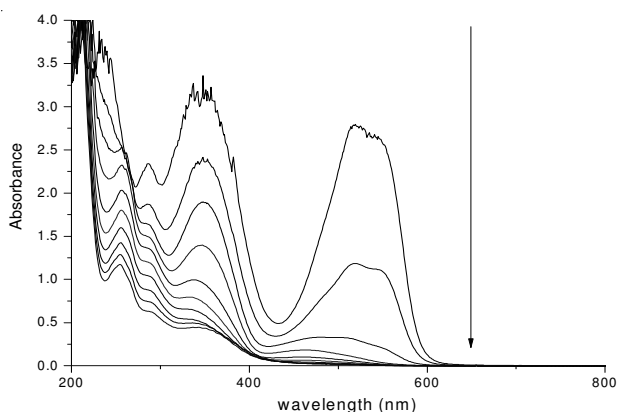


Fig. 4. UV-VIS spectra changes in treating process

With the reaction proceeding, the disappearance of the visible band was due to the fragmentation of the azo links by direct ClO_2 attack. Meanwhile, the decay of the absorptions at 341, 286 and 239 nm was considered as evidence of carbon-carbon double bond, heterocyclic and aromatic fragment in the dye molecule and its intermediates. And there was a very strong absorption peak at *ca.* 217 nm, due to $\log \epsilon > 4$ (ϵ is absorbance), the absorption peak could not be fully shown in Fig. 4, which indicated the formation of many conjugated diolefines systems during decomposition of benzene and naphthalene rings and the conjugated diolefines system would be eventually oxidized to carbon dioxide. The rate of abatement of the four absorption bands were shown in Fig. 5, which all followed apparent pseudo-first-order kinetics, the rate constants k were 0.4631, 0.1138, 0.0684 and 0.0501 min^{-1} , respectively (Fig. 5). Therefore, the order of the reaction activity of various groups in the RBR molecular structure was as follows: azo bond > non-aromatic carbon-carbon double bond > carbon-nitrogen bond in triazine > aromatic carbon-carbon bond. Absorption peaks of chromophoric groups significantly lowered, the colour of dye noticeably lightened, all the facts fully illustrated that ClO_2 combined the ternary catalyst can be effectively degrade the RBR dye in a very short time, so the catalyst is an ideal accelerator for ClO_2 degradation of azo-dyes.

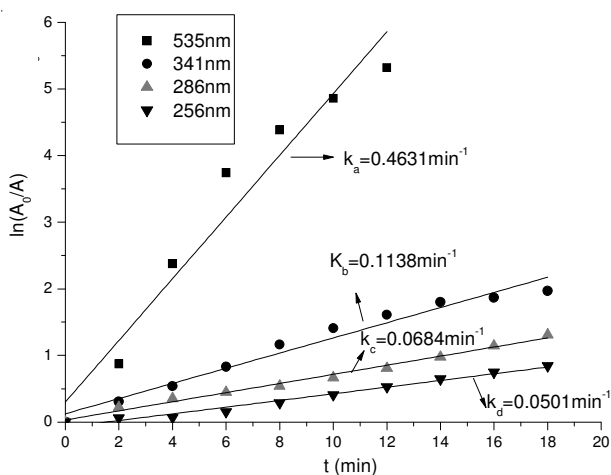
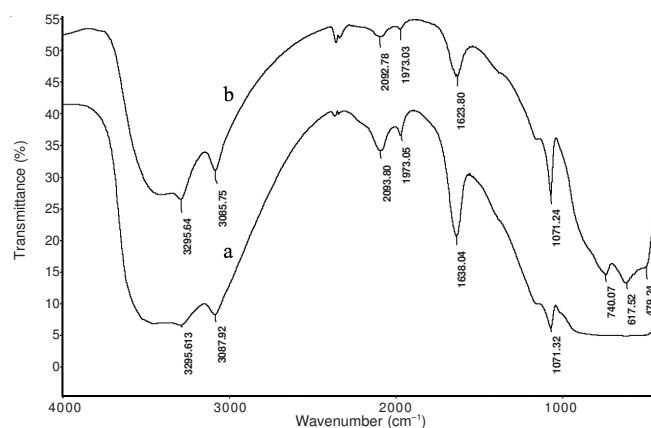


Fig. 5. Evolution of absorbance at each absorption peak

FT-IR analysis of the ternary catalyst: The FT-IR spectra differences of carrier Al_2O_3 and $\text{NiO-CuO}_x\text{-La}_2\text{O}_3/\text{Al}_2\text{O}_3$ were seen in Fig. 6. At functional group region absorption peak 1638.04 cm^{-1} was characteristic absorption peak of O-H bending vibration of water adsorbed on Al_2O_3 surface, while absorption peak of O-H bending vibration in the catalyst was at 1623.80 cm^{-1} which reduced 14.24 cm^{-1} compared to 1623.80 cm^{-1} , it was caused by the interaction between -OH and metal oxides MO (including NiO, CuO_x , La_2O_3) that results in the formation of M-O-H structure, so it indicated that carrier Al_2O_3 is not simply mechanically mixing with metal oxides, but connecting together by strong chemical bonds. At fingerprint area 740.07 cm^{-1} and 479.24 cm^{-1} were bending vibration absorption peaks of both Cu-O and Ni-O and 617.52 cm^{-1} was bending vibration absorption peak of La-O, which proved the presence of NiO, CuO_x and La_2O_3 .



(a- Al_2O_3 ; b- $\text{NiO-CuO}_x\text{-La}_2\text{O}_3/\text{Al}_2\text{O}_3$)
Fig. 6. FT-IR spectra of carrier and catalyst

Surface analysis of the ternary catalyst: The catalyst changes of surface topography and elements before and after loading were analyzed by SEM-EDX analyzer. The surface of activated alumina was relatively smooth before loading, only Al, O elements were detected (Fig. 7); after loading the surface of the catalyst appeared many protruding and hollow cavities, so that the specific surface area has improved significantly, Ni, Cu, La elements were detected on the catalyst surface (Fig. 8).

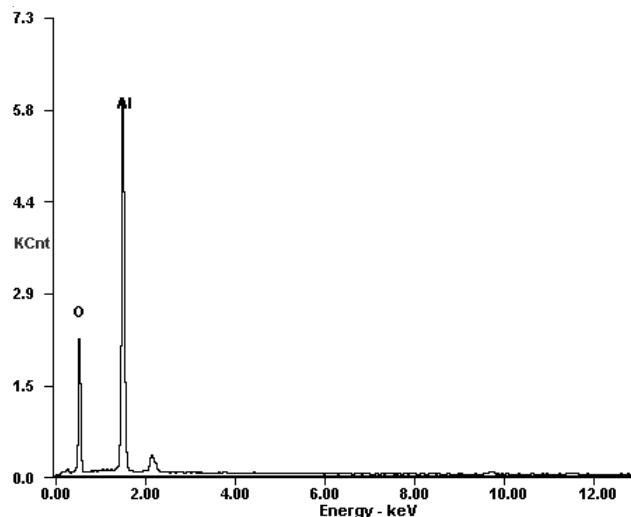


Fig. 7. EDX of carrier Al_2O_3

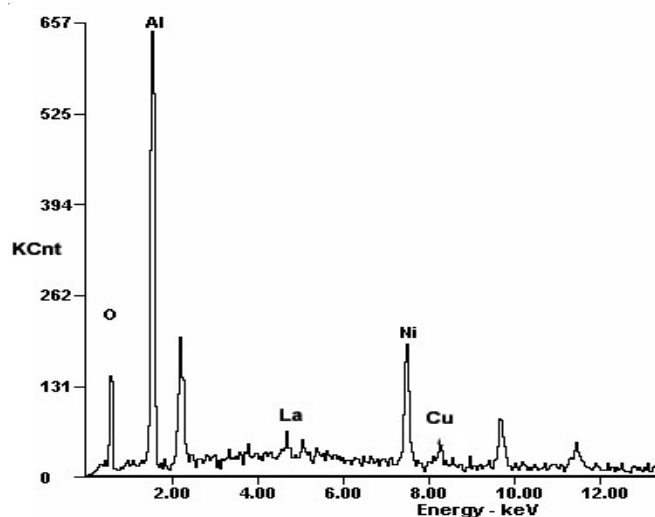


Fig. 8. EDX of the ternary catalyst

Stability of the ternary catalyst: To examine the loss and recycling effect of the catalyst, 5 g catalyst was used to carry out repeated experiments. After completion of a catalytic experiment of degrading RBR simulated wastewater, the catalyst was filtered and dried for 8 h at 120 °C for repeated use. After using the catalyst for 4 times, the structure of the catalyst was detected by FT-IR spectrometer (Fig. 9).

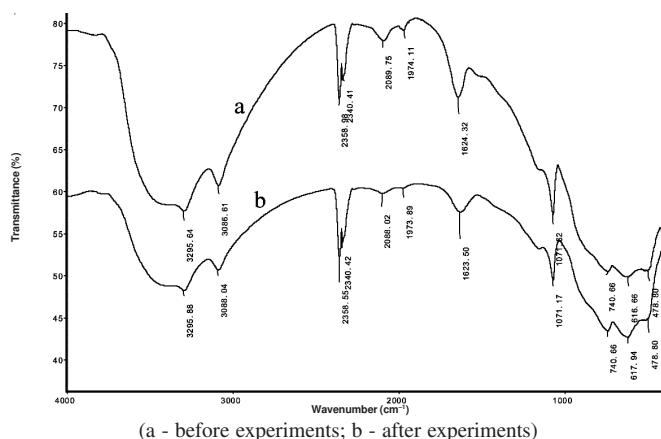


Fig. 9. FT-IR spectra changes of catalyst after using four times

Before and after the catalytic reactions, the FT-IR spectra of the catalyst hadn't changed significantly, which indicated that the ternary catalyst only played a catalytic role in the reaction, itself hadn't involved in the reaction, thus it proved that the catalyst was stable.

Conclusion

Chlorine dioxide (ClO₂) catalytic oxidation of RBR simulated wastewater follows apparent pseudo-first-order reaction kinetics and using the ternary catalyst the reaction rate constant increased by 195 % than that achieved without the catalyst. So the catalyst can significantly reduce the degradation time and the ClO₂ dosage. The abatement rate of the four absorption bands in UV-VIS spectrum were all followed apparent pseudo-first-order kinetics. The order of the reaction activity of various groups in the RBR molecular structure was: azo bond > non-aromatic carbon-carbon double bond > carbon-nitrogen bond in triazine > aromatic carbon-carbon bond. Through the FT-IR spectrum of the catalyst and the analysis of the catalyst's surface by SEM-EDX, it proved that in the catalyst the metal oxides combined with the carrier by strong chemical bonds and the catalyst is stable. Above all, it provided a highly efficient catalyst for chlorine dioxide catalytic oxidation technology applied in treating azo dyes wastewater.

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