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Research Article

Microwave-Induced Catalytic Oxidation of High-Concentration Dye Effluent Using $CuFe_2O_4$/ACF Combined with O_3

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Abstract

Ozone-microwave catalytic oxidation system (O_3/MIOP) is a new deep composite oxidation technology based on ozone and microwave-induced catalysis. In this paper, $CuFe_2O_4$ loaded on activated carbon fiber ($CuFe_2O_4$/ACF) was prepared by sol-gel method as microwave catalyst to degrade 6 L Basic Brown (500 mg/L) and actual wastewater with O_3/MIOP technique. After the wastewater is subjected to ozone treatment for a period of time, it flows into the reactor from the water inlet through a peristaltic pump, and at the same time, a certain amount of $CuFe_2O_4$/ACF catalyst and H_2O_2 are added to the reactor. The results show that under the co-treatment of 60 min O_3 and 5 min MIOP, the decolorization rate of basic brown at 500 mg/L reached 60%, and the B/C value increased from the initial 0.18 to 0.32.As to the actual wastewater, the B/C value after degradation tends to 0.3, which is easy to the next biochemical treatment. Furthermore, •OH and O_2•$^-$ are measured to be the main active group in the process of degradation of Basic Brown under O_3/MIOP treatment. These two reactive species accelerate the degradation of the dye during the reaction, thus increasing the reaction rate. This composited oxidation technology system was proven to be suitable and of practical value in high-concentration dye effluent treatment.

Keywords

Microwave, Catalytic Oxidation, O_3, $CuFe_2O_4$ Supported on ACF, High-Concentration

1. Introduction

Traditional treatment methods of dye wastewater (such as physisorption, which mainly transfers pollutants from one phase to another) cannot easily remove aromatic compounds from dyes, resulting in a large amount of sludge and solid waste during the treatment process, resulting in higher treatment costs [1]. Advanced oxidation technologies (AOPs) include ozonation, microwave-induced catalytic oxidation (MIOP), photocatalytic degradation, etc. Although some methods can completely degrade dye wastewater into CO2 and water [2-4], However, it consumes a lot of reagent, has low energy utilization rate, and has poor effect when applied to high concentration dye and actual dye wastewater treatment.

Composite oxidation technologies such as O_3/H_2O_2, O_3/UV, UV/H_2O_2, MW/UV have gradually become research hotspots at home and abroad in recent years because of their ability to enhance the oxidation ability of pollutants and their efficient degradation of pollutants [5-7]. Ozone-microwave catalytic oxidation system (O_3/MIOP) is a new deep composite oxida-

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tion technology based on ozone and microwave-induced catalysis. Through ozone pretreatment, the reaction time of microwave can be effectively shortened and the cost can be reduced. At present, there are few researches on it in China, mainly in small-scale experiments to study the degradation of simulated wastewater, but there is no report on the actual wastewater.

Activated carbon fiber (ACF) is often used as catalyst carrier and microwave catalyst to degrade pollutants because of its large specific surface area, strong adsorption capacity, high mechanical strength and high temperature resistance [8]. In addition, as a new microwave catalyst, ferrite has become a hot research focus because of its rapid degradation of pollutants [9, 10].

In this paper, 6L high concentration alkaline brown simulated dye wastewater and high concentration dye wastewater from Jiangsu Jihua Chemical Co., Ltd. were treated as objects, and microwave catalyst was obtained by carrying copper ferrite with felt-shaped activated carbon fiber. The wastewater was pre-treated under ozone condition and then introduced into a microwave reaction system, and the biochemical indexes in the degradation process were measured and analyzed under the action of high power microwave radiation and oxidant H_2O_2.

2. Materials and Methods

2.1. Experimental Materials and Reagents

Preparing alkaline brown simulated wastewater with a mass concentration of 500 mg/L with deionized water; The actual wastewater comes from high concentration reactive azo dye wastewater from Jihua Chemical Co., Ltd., Yancheng City, Jiangsu Province, with a COD of 2680 mg/L and a dark brown color. Copper nitrate, iron nitrate alkaline brown and hydrogen peroxide are all of analytical grade, Nanjing Chemical Reagent Co., Ltd.; The viscose-based activated carbon fiber mat is a product of Jiangsu Sutong Carbon Fiber Co., Ltd., with a bulk density of 0.04 ~ 0.06 g/cm^3 and a pore size distribution of 2 ~ 5 nm.

2.2. Experimental Setup and Process

The device for ozone-microwave catalytic oxidation degradation of dye wastewater is shown in Figure 1. Ozone generator (XM-T, Qingdao Xinmei Purification Equipment Co., Ltd.) Its ozone output is 3 g/h, its power is 60 w, and its air source is air source. After the wastewater is subjected to ozone treatment for a period of time, it flows into the reactor from the water inlet 2 through a peristaltic pump, and at the same time, a certain amount of $CuFe_2O_4$/ACF catalyst and H_2O_2 are added to the reactor. Close the safety door 9 and turn on the power button on the operation panel 8. Press the "microwave on" switch, the indicator light of microwave on will light up, and select to turn on 3 microwave transmitting tubes according to the experimental requirements until the required power value (up to 3 kw) is reached. After the wastewater flows out of the wastewater outlet 1, its relevant indicators are measured.

After the reaction is finished, clean water is introduced into the water outlet 1 and the water inlet 3 of the cavity to conduct ultrasonic waves through the water, and the overflow port 4 is an output port 7 that protects the water level height from submerging microwave energy. At the same time, click the [Ultrasonic] operation button on the operation panel 8, the ultrasonic indicator light will turn on, and the ultrasonic wave will start to work, and the reactor will be cleaned. After the cleaning is finished, the cavity water outlet 5 and the waste water inlet 2 are opened, and the clean water is discharged out of the reaction device.

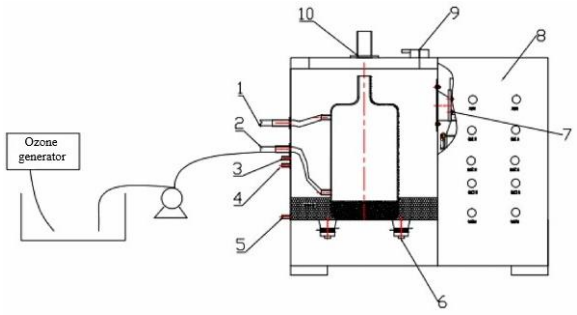

Figure 1. *Diagram of ozone-microwave catalytic device.*

2.3. Experimental Methods

2.3.1. Preparation and Characterization of Catalysts

Cut the activated carbon fiber felt into 100 mm × 100 mm squares, boil it in deionized water for 2 hours, and then dry it in a constant temperature blast drying oven at 120 ℃ for 24 hours later.

Copper nitrate and ferric nitrate with a molar ratio of 1: 2 were stirred at 60 ℃ for a period of time by sol-gel method, and then citric acid was added and stirred continuously until a sol was formed. After adding the spare activated carbon fiber felt, immersing it in the sol, and drying it at 120 ℃ for 8 hours. The dried sample was transferred into a tube furnace and calcined at 500 ℃ for 2 h. The heating rate was 3 ℃ /min, the nitrogen flow rate was 80 mL/min, and the catalyst $CuFe_2O_4$/ACF was obtained after natural cooling.

The microscopic morphology of activated carbon fibers before and after loading was observed by a scanning electron microscope type S-3400N II of Hitachi Corporation, Japan. The crystal structure of the catalyst was observed by an X-ray powder diffractometer of ARL, Switzerland.

2.3.2. Ozone-microwave Catalytic Oxidative Degradation of Dye Wastewater

The ozone generated by the ozone generator was intro-

duced into the prepared 6 L simulated wastewater alkaline brown (500 mg/L) and 6 L actual wastewater for pre-treatment, and the optimal treatment time was determined. Then, the wastewater is introduced into a reactor added with catalyst and H_2O_2, and the wastewater is degraded under microwave irradiation. The decolorization rate of alkaline brown dye wastewater was analyzed by UV-Vis (2550, Shimadzu, Japan) during the degradation process. Its maximum absorption wavelength is 461 nm, and the decolorization rate $A = (1-C/C_0) \times 100\%$, (where A is the decolorization rate, and C_0 and C are the initial and degraded concentrations, respectively) to reflect the decolorization of wastewater. At the same time, the COD value and BOD_5 value of wastewater during the degradation process were measured by HACH COD and BOD analyzer to characterize its degradation.

3. Results and Discussion

3.1. Characterization of Catalyst Properties

3.1.1. XRD Analysis of the Catalyst

Figure 2 shows the XRD pattern before and after ACF loading. From the figure, it can be seen that the characteristic diffraction peaks of $CuFe_2O_4$ appeared at 2θ = 30.16 °, 35.64 °, 57.05 ° and 62.77 ° for the prepared $CuFe_2O_4$/ACF [11, 12], At the same time, the characteristic peak of ACF also appeared at 2θ = 25.6 ° [13], which indicated that $CuFe_2O_4$ was successfully loaded on ACF. Using the XRD data of the diffraction peak at 2θ =35.64 °, the average grain size of $CuFe_2O_4$ on the catalyst was calculated by Scherrer's formula: $D = 0.89\ \lambda / \beta \cos\theta$ to be 10.06 nm. (Where λ is the wavelength of X-rays and β is the half-peak width) In addition, the characteristic diffraction peaks of elemental copper (Cu) also appear at 2θ = 50.43 ° and 74.13 ° respectively [14], which may be caused by the reduction of copper oxide to elemental copper by activated carbon fiber during calcination.

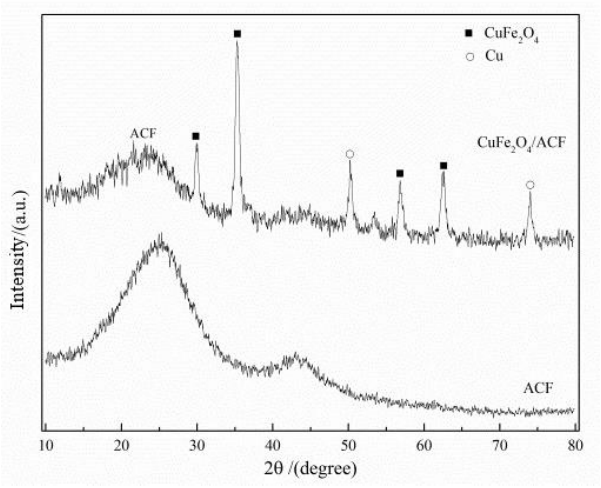

Figure 2. *XRD patterns of ACF and $CuFe_2O_4$/ACF.*

3.1.2. SEM Analysis of Catalysts

Figure 3 (a) and (b) are SEM plots of ACF versus $CuFe_2O_4$/ACF, respectively.The comparison shows that the surface of activated carbon fiber is relatively smooth when there is no loading, while after loading $CuFe_2O_4$, $CuFe_2O_4$ agglomerates and is uniformly and finely wrapped on the surface of activated carbon fiber, tightly combined with activated carbon fiber.

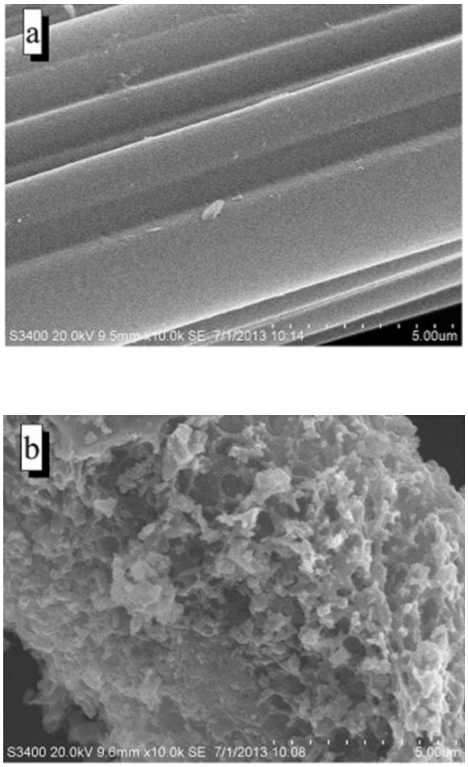

Figure 3. *SEM images of ACF (a) and $CuFe_2O_4$/ACF (b).*

3.2. Ozone-microwave Catalytic Oxidation Degradation of Alkaline Brown Dye Wastewater

3.2.1. Degradation of Basic Brown Dye Wastewater by O_3 and MIOP

The degradation experiments of 6 L of basic brown dye wastewater with a mass concentration of 500 mg/L were carried out by O_3 alone and microwave alone. Among them, in the microwave catalytic oxidation degradation, the dosage of $CuFe_2O_4$/ACF catalyst is 3 g/L, the concentration of H_2O_2 is 1 mL/L, and the microwave power is 2 kw. It can be seen from Figure 4 that under the condition of O_3 alone, the decolorization rate of the dye continues to increase with time until it reaches 30% at 60 minutes. However, when the O_3 treatment time reached 80 min, the decolorization rate did not increase significantly. This may be due to the fact that excess O_3 is less easily dissolved in wastewater and reacts with • OH in water

to produce • HO_2 with relatively weak oxidation capacity, which makes the decolorization rate not obvious [15]. Therefore, the optimal reaction time of O_3 treatment is 60 min.

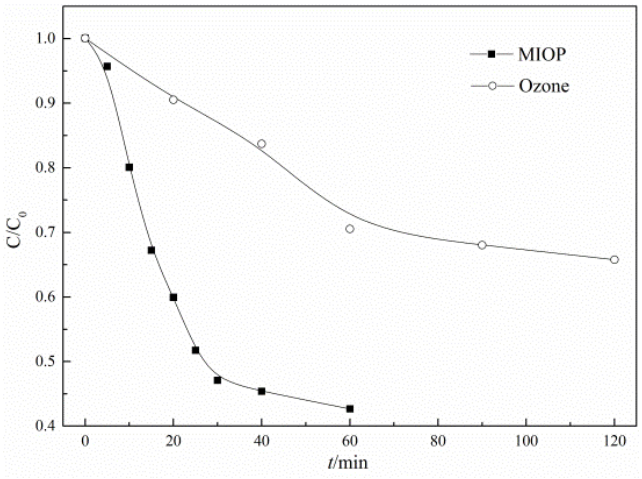

Figure 4. *Degradation curves of Basic Brown by ozone and MIOP.*

Correspondingly, it can be seen from Figure 4 that under microwave catalytic oxidation degradation alone, the decolorization rate also increases with the increase of microwave irradiation time. After 30 minutes of reaction, the decolorization rate reaches 53%, further increasing the microwave reaction time, the decolorization rate does not increase significantly. However, such a long radiation time not only increases the cost of wastewater treatment, but also causes the waste of energy. Therefore, it is necessary to carry out pretreatment before microwave treatment.

3.2.2. O_3/MIOP Synergistic Treatment of Alkaline Brown Dye Wastewater

6 L of basic brown dye wastewater with a mass concentration of 500 mg/L was first treated with O3 for 60 min and then subjected to microwave catalytic oxidation degradation. The experimental results are shown in Figure 5 (a) and (b).

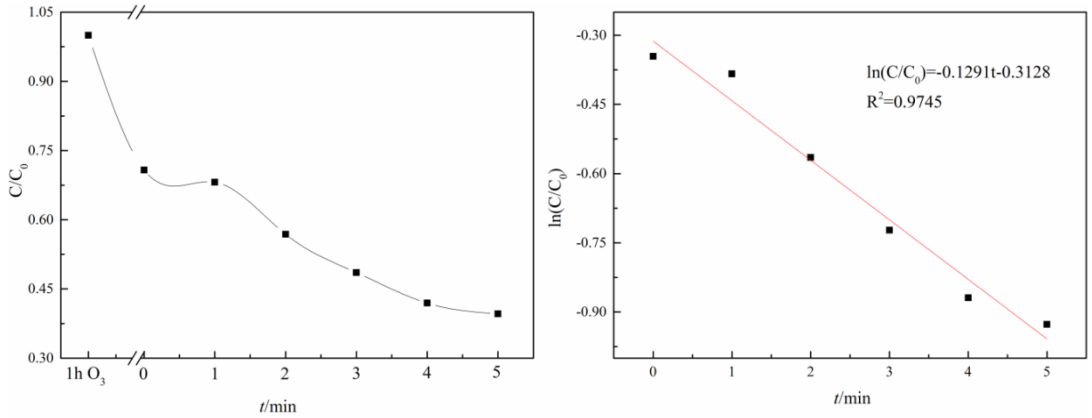

Figure 5. *Degradation curve of Basic Brown by ozone/MIOP (a) and the kinetic curves of Basic Brown degradation (b).*

It can be seen from the figure that after the pretreatment of O_3, the dye wastewater only reacted in the microwave for 5 minutes, the decolorization rate reached 60%, and the reaction rate reached 0.13 min-1, following the pseudo-first-order kinetics. The reason for this may be that •OH generated in the pretreatment of O_3 accelerates the oxidation of dyes under the irradiation of microwaves, which greatly improves the degradation efficiency and reduces the cost [16, 17]. Therefore, the O_3/MIOP synergy is particularly pronounced relative to O_3 and MIOP alone.

3.2.3. Analysis of Biochemical Indexes in O_3/MIOP Synergistic Processing

During the O_3/MIOP co-treatment process, the COD value and BOD_5 value of alkaline brown simulated wastewater were measured, and the results are shown in Figure 6.

After 6 L wastewater was first treated with ozone for 60 min, the COD value increased from 270 mg/L to 290 mg/L. After 5 minutes of microwave catalytic oxidation degradation, the COD value still increased to a certain value and then decreased to 205 mg/L. This may be due to the production of some small molecules that are difficult to degrade during the reaction process, which leads to the increase of COD value [18], and then these small molecules are gradually degraded, so the COD value decreases to 205 mg/L. Furthermore, after co-treatment, the BOD_5/COD value (B/C) of the wastewater rose from the initial 0.18 to 0.32, exceeding 0.3.This shows that the biodegradability of alkaline brown simulated wastewater has been significantly improved after O_3/MIOP degradation [19].

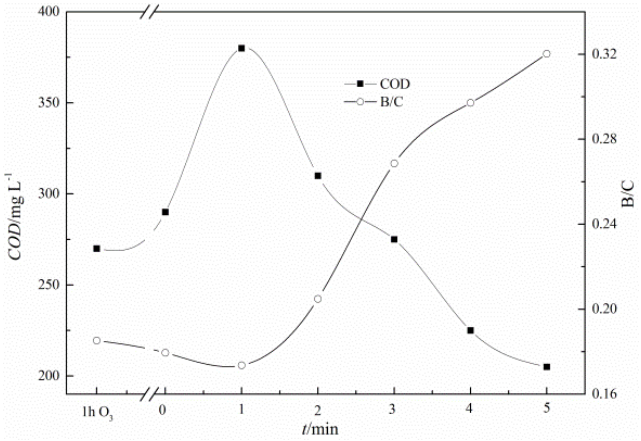

Figure 6. *Variations of COD and B/C on degradation of Basic Brown.*

3.3. Synergistic Degradation of Actual Dye Wastewater by O_3/MIOP

O_3/MIOP synergistic degradation of high concentration azo dye wastewater from Jiangsu Jihua Chemical Co., Ltd. was carried out. The results are shown in Figure 7.

As can be seen from the figure, after O_3/MIOP co-treatment of actual wastewater, the COD value of the wastewater decreased from the original 2680 mg/L to 1660 mg/L, and the BOD_5/COD value (B/C) increased to 0.27, which shows that the BOD_5 value increased during the degradation process, significantly improving the biodegradability of wastewater and facilitating subsequent treatment.

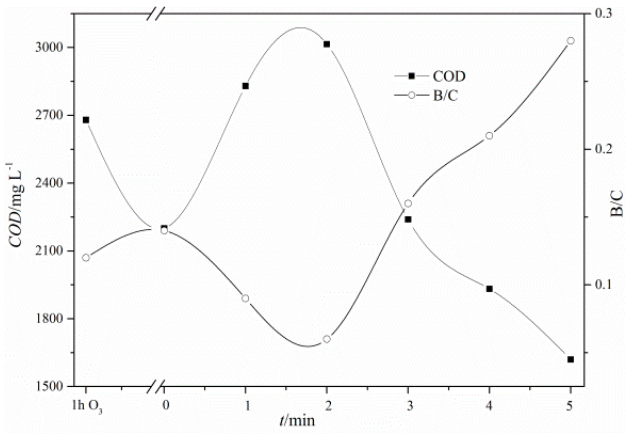

Figure 7. *Degradation of actual wastewater by O_3/MIOP.*

3.4. Mechanism of Synergistic Degradation of Dye Wastewater by O_3/MIOP

In order to study the active species that play a role in the degradation of basic brown dye wastewater by ozone and microwave, tert-butanol, sodium azide and benzoquinone were selected as hydroxyl radical quencher, hole quencher and O_2•-quencher respectively [20-22], and the results are shown in Figure 8.

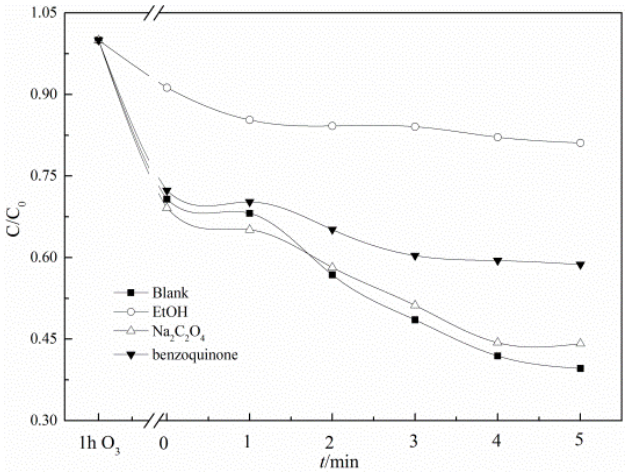

Figure 8. *The effects of various additives on decomposing Basic Brown by ozone and MIOP.*

It can be seen from the figure that during the O_3 pretreatment process, compared with the addition of sodium azide and benzoquinone, the degradation of basic brown after the addition of tert-butanol was greatly inhibited, indicating that it is mainly •OH rather than h + and O_2•-that plays a role in the O_3 pretreatment process. Similarly, it can also be seen from the figure that •OH and O_2•-play the main roles in the microwave-catalyzed oxidative degradation process. This is because ACF absorbs microwave energy under the irradiation of microwaves, thus generating many hot spots on its surface, which promotes the decomposition of H_2O_2 to produce •OH [23, 24]. In addition, lattice oxygen on $CuFe_2O_4$ also generates electrophilic oxygen ions (O_2•-) under microwave irradiation [10, 25]. These •OH (including those produced in the O_3 stage) and O_2•-accelerated the removal of pollutants under the stimulation of microwave energy, allowing the degradation efficiency to be greatly improved.

4. Conclusion

(1) The efficient and stable $CuFe_2O_4$/ACF microwave catalyst prepared by sol-gel method can effectively degrade a large amount of high-concentration wastewater by ozone pretreatment in the designed reactor and is suitable for industrial application.

(2) Under the co-treatment of 60 min O_3 and 5 min MIOP, the decolorization rate of basic brown at 500 mg/L reached 60%, and the B/C value increased from the initial 0.18 to 0.32. In addition, it also shows a very good degradation effect on actual wastewater. The COD removal rate is 38%, and the B/C value is increased to 0.27, which is conducive to subsequent biochemical treatment.

(3) In the process of synergistic degradation of dye wastewater by O_3/MIOP, •OH and O_2•-play a role. These two reactive species accelerate the degradation of the dye during the reaction, thus increasing the reaction rate.

Author Contributions

Xiao Jun is the sole author. The author read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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