

## Catalytic ozone aqueous decomposition of methylene blue using composite metal oxides

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**Abstract.** By using the method of co-precipitation, Fe-Mn, Al-Mn, Al-Mg composite metal oxides were prepared. Using X-ray diffractometer (XRD), the phases of catalysts synthesized were observed to be  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . With the increase of the calcination temperature,  $\text{Mn}_3\text{O}_4$  was gradually transformed into  $\text{Mn}_2\text{O}_3$ . The experimental results show that: the best catalyst is the Fe-Mn composite metal oxide with the calcination temperature of  $650^\circ\text{C}$ . In this experimental condition, when the ozone amount was  $1.92\text{mg/min}$ , and the dosage of catalyst was  $0.5\text{g}$ , the removal rate of methylene blue (MB) was the best. The decolorization rate can reach to 100%. Compared with the effect of ozonation alone, the total organic carbon removal rate increased from 29.19% up to 65.78% after adding catalysts.

### 1. Introduction

Dyes are widely used in textile, printing and dyeing, photography, photochemistry and other industries. It is estimated that in the dyeing process, the textile industry has 10-15% of dye loss into the sewage discharge. Dye is not only refractory, but also has low biodegradability. These characteristics pose a great threat to human health and ecosystem.

Dye for extensive degradation products, the application of the carcinogenicity and low biodegradability, pose a great threat to human health and ecosystem [1]. Only ozone method is widely used to treatment of printing and dyeing waste water. Ozone dosage and the amount of azo groups have a great impact on the treatment results [2]. Ozone oxidation has selective degradation to organic matter and organic compounds. In order to enhance the ability of ozone oxidation of refractory organic pollutants, researchers put forward a series of advanced oxidation process to produce hydroxyl radicals [3].

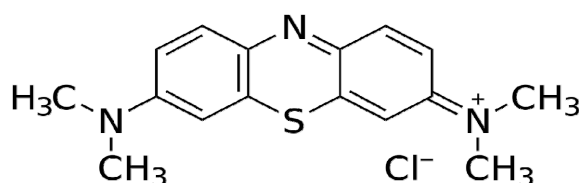
The advantage of metal oxide catalytic ozone oxidation technology is not the introduction of other energy to the process, but does not adding chemicals to the water in the complex. At the same time, the use of metal oxides in catalytic ozone oxidation technology solves the problem of the separation of the catalyst. With reasonable cost and the simple operation, the metal oxide catalytic is used in large-scale water treatment [4]. Li Xin [5-7] research group studied  $\text{CuO-MnO}_2/\text{Al}_2\text{O}_3$ ,  $\text{NiO-MnO}_2/\text{Al}_2\text{O}_3$ ,  $\text{NiO-CuO}$  composite metal catalyst was used for catalytic ozonation of Songhua River, Harbin, China.

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They achieved good experimental results, but few were reported relative to the complex oxides for catalytic ozonation dye waste water.

Azo dyes can release with aromatic amine compounds which can increase the risk of cancer [8]. Azo dyes containing azo dyes, azo dyes and human contact process, can release with aromatic amine compounds [8] cancer risk. Nevertheless, azo dyes still occupy the chief status of in the field of chemical industry [9]. Taking a typical azo dye methylene blue (MB) as the research object, its structure is shown in figure 1. The preparation method of influence on catalytic effect was through the research system. In order to find efficient catalytic ozone oxidation catalyst, the best conditions of catalytic ozonation reaction is explored, influence factors is studied, catalytic mechanism is analyzed, which provides a theoretical basis for the industrial application of catalytic ozonation. A treatment method with high efficiency, economy and design basis was proposed. This has great significance on water resource recycling, energy saving and emission reduction.



**Figure 1.** Schematic diagram of the MB molecular structure.

## 2. Experimental materials and methods

### 2.1. Main experimental reagent and instrument

Experimental reagents: methylene blue, Tianjin City Standard Technology Co. Ltd; manganese nitrate solution 50%, Tianjin Bodi Chemical Co. Ltd.; potassium iodide, Tianjin City Yongda Chemical Reagent Co. Ltd.; sodium thiosulfate, Tianjin City Yongda Chemical Reagent Co. Ltd.; ferric nitrate, Tianjin City Yongda Chemical Reagent Co. Ltd.; magnesium nitrate, Tianjin Bodi Chemical Limited by Share Ltd; aluminum nitrate, Tianjin City Yongda Chemical Reagent Co., Ltd; Tianjin city, sodium hydroxide, chemical reagent factory, above all is pure analysis.

Experimental instruments: SX-4-10 type muffle furnace, Tianjin Test Instrument Co. Ltd.; 101-1AB type drying oven, Tianjin city test instrument Co. Ltd.; DF-101S type heat collection type constant temperature heating stirrer, Gongyi Yuhua Instrument Co. Ltd.; UVProbe-2550 UV-VIS spectrophotometer, Japan SHIMADZU. FDX-2 type ozone generator, Dalian Beida Purifying Equipment Co. Ltd. AB204-E electronic balance Beijing international Science and Technology Co. Ltd..

Self-made experimental reactor is three neck flask (1L). The ozone reactor bottom porous cloth gas head was utilized to form small bubbles with the water solution full contact. The reaction condition for the pressure was 0.06 MPa, and generator working current was 50 mA. Emissions were exhausted by potassium iodide solution after absorption. Combined with a variety of laboratory test conditions and reaction system, the concentration of methylene blue solution was determined 100 mg/L.

### 2.2. Catalyst preparation and experimental method

#### 2.2.1. Catalyst preparation

By mixing aqueous solution of  $\text{Na}_2\text{CO}_3$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , the pH of the solution mixture was adjusted to about 10 with 1M NaOH. The mixed liquid was transferred to the autoclave with Teflon lined. The aging temperature were fixed at  $120^\circ\text{C}$  for 24 h. Finally the reaction product was collected by filtration, washed with de-ionized water, and then air-dried at  $80^\circ\text{C}$  overnight. The solid was roasted at high temperature for 3h to obtain Fe-Mn composite metal oxide samples. Changing the species, the process was repeated to obtain Al-Mg, Al-Mn composite metal oxide [10].

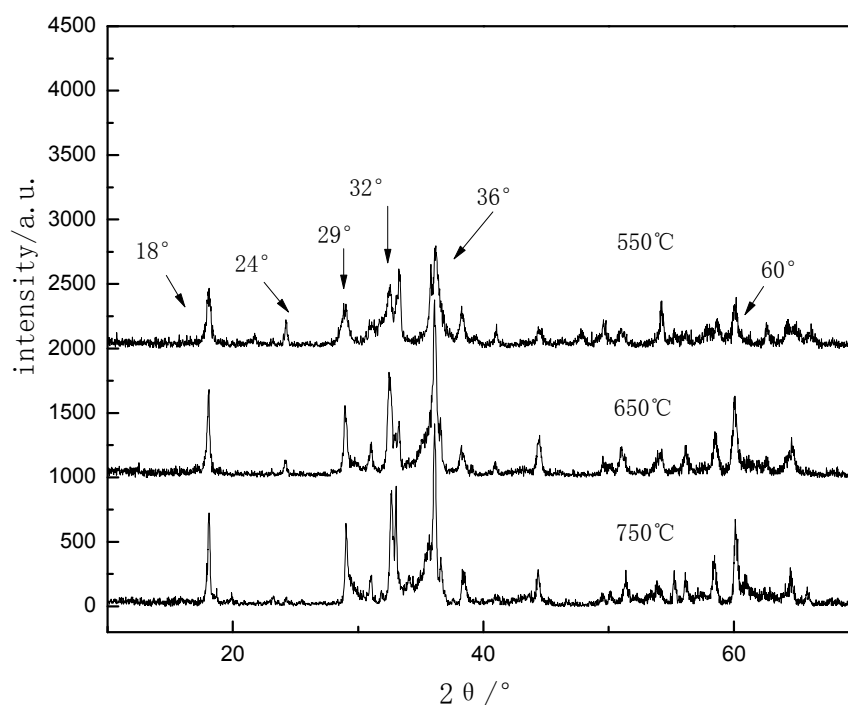
### 2.2.2. Experiments and analysis method

Catalytic ozonation reaction of MB was carried out in a 1000 mL glass flask. In a typical catalytic reaction, a certain amount of the catalyst and 500 mL of MB solution with a concentration of 100 mg/L were stirred in the water bath ( $30 \pm 0.2^\circ\text{C}$ ) with a magnetic stir, while  $\text{O}_3$  is added. And 5 ml sample solution was collected at different time during the catalytic reactions. The degradation of MB was determined from the absorption intensity at its maximum visible absorption wavelength (664 nm) by UV-vis spectrophotometer. The mineralization degree of sample solutions was analyzed using a total organic carbon analysis system.

## 3. Results and discussion

### 3.1. Characterization of XRD

The XRD images of Fe-Mn composite metal oxide calcined in different temperature were shown in figure 2. Diffraction peaks corresponding to the Fe-Mn composite metal oxide ( $550^\circ\text{C}$ ) were observed at  $18^\circ$ ,  $24^\circ$ ,  $19^\circ$ ,  $32^\circ$ ,  $36^\circ$  and  $60^\circ$  in the XRD. Compared with the standard card, the formed complexes were shown as  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . When the calcination temperature was increasing, the characteristic diffraction peak at  $24^\circ$  became weakened, while the others were enhanced. It shows that  $\text{Mn}_3\text{O}_4$  was gradually transformed into  $\text{Mn}_2\text{O}_3$  with the increase of calcination temperature.



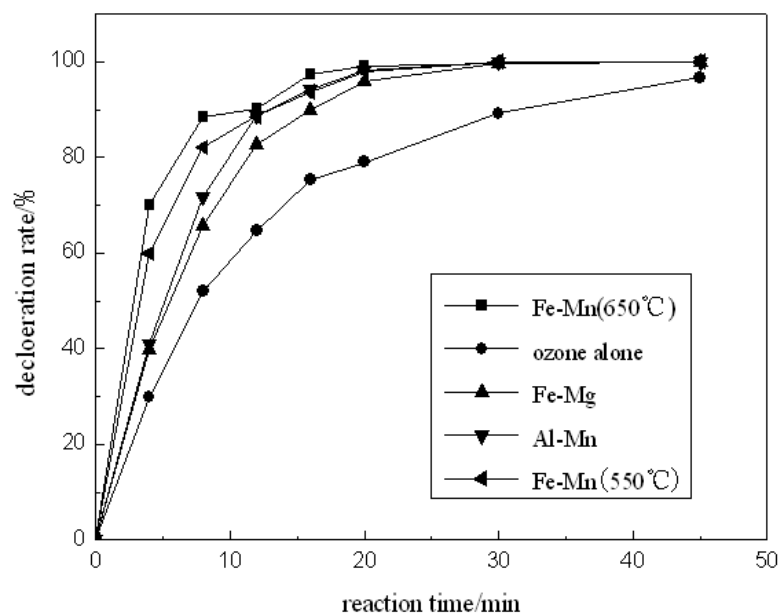
**Figure 2.** XRD images of the Fe-Mn composite metal oxide.

### 3.2. Effect of different catalytics on MB removal

Respectively, Fe-Mn, Al-Mg, Al-Mn composite metal oxides ( $550^\circ\text{C}$ ) and Fe-Mn composite metal oxide ( $650^\circ\text{C}$ ) were for the degradation of MB. Ozone flux is 1.92 mg/min, the dosage of catalyst is 0.5 g, and its catalytic effect can be investigated. Figure 3 showed the MB removal efficiency about the different systems.

Figure 3 shows that, with the increase of the calcination temperature of Fe-Mn composite metal oxide, the catalytic crystal form was changed, which would influence the removal of MB. Fe-Mn composite metal oxide showed a good catalytic performance. It is known that the  $\text{Mn}_3\text{O}_4$  was produced at  $550^\circ\text{C}$  calcination temperature. It was the important active composition in this reaction system.

With the increase of calcination temperature,  $\text{Mn}_3\text{O}_4$  began to transform gradually to  $\text{Mn}_2\text{O}_3$ , and catalytic performance was also gradually reduced as well.

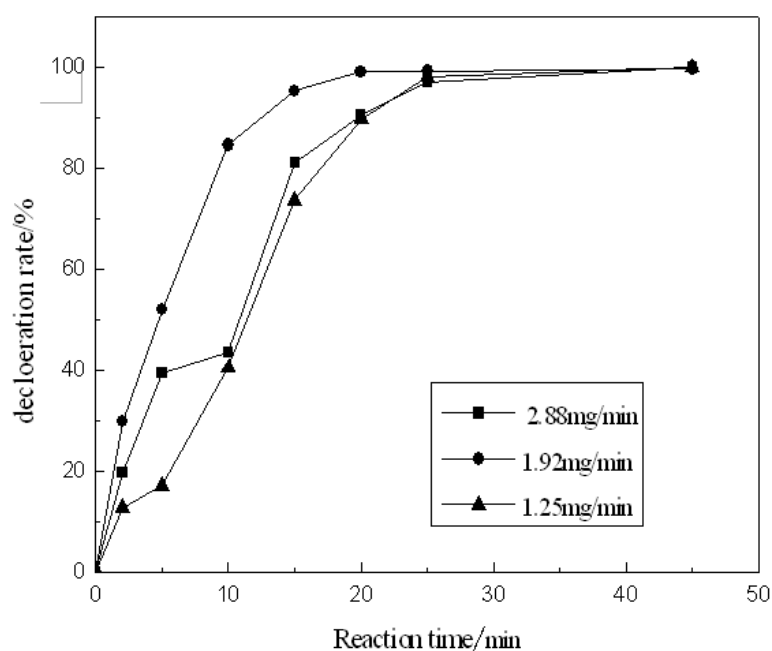


**Figure 3.** The effect of different catalysts on MB.

### 3.3. Influence of ozone flow on MB removal

Catalytic ozonation in water is three-phase reaction, including gas liquid and solid. The amount of catalyst is 0.5 g. The ozone flux is changed to research the effect on MB degradation.

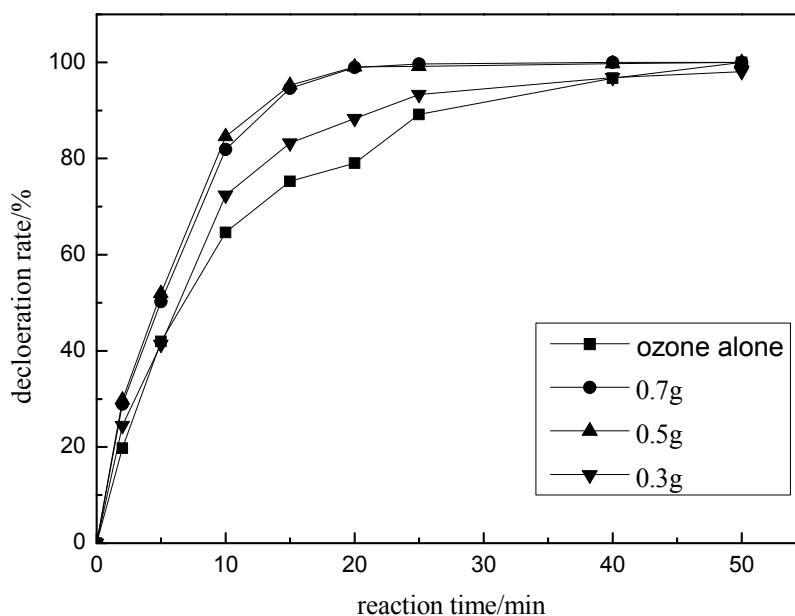
Figure 4 showed that, with the increasing of ozone flux, the effect of the removal of MB has improved obviously. Because in the presence of the catalyst, hydroxyl radical increased with the increase of the concentration of ozone, which accelerated the degradation of MB [11]. But when the ozone flux kept increasing (2.88 mg/min), the removal of MB became decreased obviously. This is because the utilization rate of ozone was decreased, and ozone flux wasn't the main factor affecting the removal rate of MB.



**Figure 4.** The effect of MB removal.

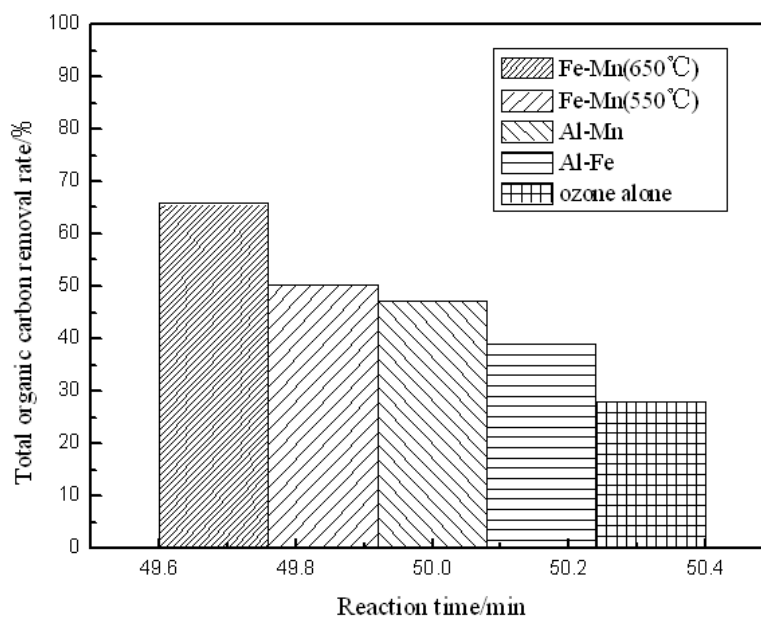
### 3.4. Influence of the dosage of catalyst on MB removal

Figure 5 showed that MB removal rate increased with the increasing catalyst dosage. The higher the dosage of catalyst, the larger for catalytic ozonation apparent rate [12]. The decomposition of ozone was accelerated under the high dose of catalysts. Catalytic reaction produced more hydroxyl radicals. They accelerated the degradation of MB. Although the low dose of catalyst resulted in a low removal rate, the degradation efficiency was higher than that using ozonation alone.

**Figure 5.** Effects of different catalyst dosage on removal of MB.

### 3.5. Mineralization degree of MB

The MB decoloration was investigated by UV-Visual, but MB degradation degree cannot be completely reflected. Therefore, the mineralization degree of MB (illustrated by TOC removal) was explored in this study. After the reaction, through the comparison of removal rate of total organic carbon (TOC) of MB, the catalytic performance of different catalysts was investigated.



**Figure 6.** The mineralization degree of MB.

Figure 6 showed that the TOC removal rate is 65.8% in the presence of the Fe-Mn composite metal oxide (650°C), while it is only 31.2% in the single O<sub>3</sub> system at 50 min. Therefore, it can be concluded that Fe-Mn composite metal oxide added contribute a lot to higher TOC removal percentages. The decomposition of organic matter is more thorough than the single O<sub>3</sub> system.

#### 4. Conclusion

In this paper, the high activity catalyst Fe-Mn composite metal oxide is successfully prepared with catalytic oxidation MB dye solution in the presence of O<sub>3</sub>. The study reveals that the O<sub>3</sub>/Fe-Mn composite metal oxide system has an obvious degradation effect on MB solution. The results show that catalyst calcination temperature, the dosage of catalyst and ozone flux are important influence factors of MB degradation in a certain flux of O<sub>3</sub>. And the mineralization degree of MB is much higher (65.8%) than the pure ozone system (31.2%). Fe-Mn composite metal oxide, as promising water treatment materials, has a good application prospect.

#### Acknowledgments

This work was supported by the National Nature Science Foundation of China (No. 21276183) and the Natural Science Foundation of Hebei Province (No. B2012208086).

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