# Study on the Degradation of Methyl Orange in Wastewater by the Different Forms of Iron for Photocatalytic Activation of Sodium Bisulfite

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Abstract-Methyl Orange (MO), as a kind of azo dye, is potentially harmful to water environment. Fe is the most common transition metal. In this paper, four different forms of Fe element, including FeSO4, FeCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> and NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, were researched for photocatalytic degradation of organic dye wastewater by activating the sulfite. The effects of the concentration of ferric salt and sodium bisulfite, and PH value on the catalytic degradation of methyl orange in different systems were compared. The results showed that the optimum concentration of reactants in the system of different forms of Fe element was different. According to the test and analysis results of the free radical/vacancy analysis technique - EPR, Fe has a narrow band gap and small electron escape work, which is easy to produce more photogenerated electrons and holes. HSO<sub>3</sub>- and OH- are oxidized by the photogenerated holes in the system and finally transformed into SO4<sup>•-</sup> and OH<sup>•</sup>, which are important active species in the dye degradation system. A new advanced oxidation method based on SO4. and OH has been developed for the treatment of organic dye wastewater.

*Keywords*—FeSO4, FeCl3, (NH4)2Fe(SO4)2, NH4Fe(SO4)2, NaHSO3, degradation, dye wastewater

### I. INTRODUCTION

Methyl Orange (MO), as a kind of azo dye, is widely used in dyeing clothes and making pigments. Methyl orange is one of the main components in printing and dyeing wastewater, which is weakly alkaline. If it is discharged directly into the environment without treatment, it will lead to reduced water visibility and ecological imbalance, affecting the growth of plants and animals in the water. At present, the main treatment methods of methyl orange in wastewater include physical adsorption method [1], chemical oxidation-reduction method [2], electrochemical method [3], and photocatalytic degradation method [4].

In recent years, the treatment of printing and dyeing wastewater by advanced oxidation process has become a research hotspot. It destroys the stable chemical structure of dyes by generating free radicals such as OH<sup>•</sup> and SO<sub>4</sub><sup>-•</sup> [5]. SO<sub>4</sub><sup>-•</sup> was produced by PS or PMS in dyeing wastewater and some nanomaterials were added to activate them to improve the degradation efficiency [6–7]. At present, some researchers try to add both sodium sulfite and photocatalytic activated nanomaterials in the dyeing wastewater to produce SO<sub>4</sub><sup>-•</sup> [8].

Researchers have widely pay attention to semiconductor nanocomposites for a long time, because their optical, electrical and photocatalytic properties are superior to those of single semiconductor nanomaterials. However, the preparation process of such materials may be complicated and the cost is high. It is easy to lose and difficult to recover. Besides there is secondary pollution. In this experiment, we use the different forms of iron for photocatalytic activation of sulfite to degrade the MO. It has not been reported in other literature previously. The different forms of iron and NaHSO<sub>3</sub> are easy to obtain, low cost, non-toxic and environmental protection. The study is of great significance for the treatment of dye wastewater in the environment.

### II. EXPERIMENTAL PROCEDURE

### A. Reagents and Apparatus

FeSO<sub>4</sub>, FeCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, methyl orange, sodium bisulfite, hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Company. All reagents were of analytical grade and used without further purification. All solutions were prepared with super pure water during the experiment. Photochemical reactor was purchased from Guangzhou Star Chuang Electronics Limited Company. The samples after photocatalytic degradation were analyzed by Ultraviolet and Visible Spectrophotometer of UV1200 from Shanghai Auyi Instruments Limited Company.

### B. Catalytic Degradation Experiment

Add a certain amount of catalyst to a test tube containing 50 mL of 20 ppm methyl orange solution, followed by the addition of a specific quantity of sodium bisulfite. Adjust the pH value of the mixed solution to enhance degradation efficiency by changing the conditions of the system. Subsequently, place the test tube in a photoreactor and initiate magnetic stirring to simulate solar light irradiation for experimental purposes. Extract 3 mL samples at a certain time interval, filter with a filter membrane immediately, and measure the absorbance of the supernatant at 465nm with an ultraviolet spectrophotometer. It is known that the maximum absorbance of methyl orange aqueous solution is at 465nm.

### III. RESULTS AND DISCUSSION

# A. Effect of Different Photocatalysts on the Degradation of MO

We compared the degradation effects of different catalysts on MO under optimal experimental condition, and the result was showed in Fig. 1. When NaHSO<sub>3</sub> alone, FeSO<sub>4</sub> alone, and FeSO<sub>4</sub>/NaHSO<sub>3</sub> were used as catalysts, the degradation rates of MO were 0.81%, 3.44% and 79.50%, respectively. When NaHSO<sub>3</sub> alone, FeCl<sub>3</sub> alone, and FeCl<sub>3</sub>/NaHSO<sub>3</sub> were used as catalysts, the degradation rates of MO were 0.81%, 11.64% and 83.82%, respectively. When NaHSO<sub>3</sub> alone, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> alone, and (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> were used as catalysts, the degradation rates of MO were 0.81%, 1.54% and 85.72%, respectively. When NaHSO<sub>3</sub> alone, NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> alone, and NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> were used as catalysts, the degradation rates of MO were 0.81%, 4.98% and 88.07%, respectively. It can be seen that the catalytic degradation effect of different forms of iron activated NaHSO<sub>3</sub> on MO is significantly higher than that of different forms of iron or NaHSO<sub>3</sub> alone. Therefore, the following experiments mainly discuss the factors, which affected the degradation of MO solution with different forms of iron activated NaHSO<sub>3</sub> under the visible light.



Fig. 1. The degradation effects of MO with the different catalysts under the optimized experimental conditions (a) NaHSO<sub>3</sub> alone, FeSO<sub>4</sub> alone and FeSO<sub>4</sub>/NaHSO<sub>3</sub>; (b) NaHSO<sub>3</sub> alone, FeCl<sub>3</sub> alone and FeCl<sub>3</sub>/NaHSO<sub>3</sub>; (c) NaHSO<sub>3</sub> alone,  $(NH_4)_2Fe(SO_4)_2$  alone and  $(NH_4)_2Fe(SO_4)_2/NaHSO_3$ ; (d) NaHSO<sub>3</sub> alone,  $NH_4Fe(SO_4)_2$  alone and  $NH_4Fe(SO_4)_2/NaHSO_3$ .

### B. Effect of PH Value on the Degradation of MO

We discussed the influence of pH value on the catalytic degradation of MO by FeSO<sub>4</sub>/NaHSO<sub>3</sub>, FeCl<sub>3</sub>/NaHSO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> and NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> systems, respectively. The pH value of the reaction system was adjusted by adding 1mol/L HCl and 1mol/L NaOH solution, and the results were shown in Fig. 2. In the FeSO<sub>4</sub>/NaHSO<sub>3</sub> reaction system at PH=3, PH=7 and PH=11, the degradation rates of MO were 85.51%, 59.22% and 32.06%, respectively. In the FeCl<sub>3</sub>/NaHSO<sub>3</sub> reaction system at PH=3, PH=7 and PH=11, the degradation rates of MO were 87.92%, 82.36% and 89.82%, respectively. In the (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> reaction system at PH=3, PH=7 and PH=11, the degradation rates of MO were 88.80%, 5.12% and 19.91%, respectively. In the NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>/NaHSO<sub>3</sub> reaction system at PH=3, PH=7 and PH=11, the degradation rates of MO were 87.34%, 85.58% and 15.30%, respectively. The results showed that different Fe/ NaHSO3 forms were different in the most suitable acidbase conditions, but they all showed high photocatalytic degradation activity under acidic conditions. It may be due to the fact that the different forms of iron activated NaHSO3 are more likely to produce sulfate free radicals under acidic conditions. Sulfate free radicals are very good decolorizing active substances and react quickly with MO in solution to achieve the purpose of degrading MO.





### *C.* Effect of the Concentration of Catalyst on the Degradation of MO

We discussed the effect of the input of the catalyst on the degradation of MO in different forms of iron activated NaHSO<sub>3</sub> system, as shown in Fig. 3. When the initial dosage of FeSO4 was 0.01g/L, 0.05g/L, 0.10g/L, 0.20g/L, 0.50g/L and 1.0g/L, the degradation rates of MO were 16.47% 20.90%, 33.74%, 45.21%, 41.41% and 13.68%, respectively. When the initial dosage of FeCl<sub>3</sub> was 0.01g/L, 0.05g/L, 0.1g/L, 0.2g/L, 0.4g/L, 0.8g/L, 1.2g/L, 1.6g/L, and 2.0g/L, the degradation rates of MO were 21.30%, 60.25%, 83.97%, 84.63%, 79.72%, 79.72%, 80.01%, 79.94% and 78.92%, respectively. When the initial dosage of  $(NH_4)_2Fe(SO_4)_2$  was 0.01g/L, 0.05g/L, 0.10g/L, 0.20g/L, 0.50g/L, and 1.0g/L, the degradation rates of MO were 43.85%, 59.59%, 72.18%, 81.92%, 81.04% and 80.53%, respectively. When the initial dosage of NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> was 0.01g/L, 0.05g/L, 0.1g/L, 0.2g/L, 0.4g/L, 0.8g/L, 1.2g/L, 1.6g/L and 2.0g/L, the degradation rates of MO were 35.12%, 61.71%, 70.13%, 83.89%, 84.26%, 81.63%, 79.65%, 78.40%, and 80.31%, respectively. According to the experimental results, the most suitable inputs of FeSO<sub>4</sub>, FeCl<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> and NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> were 0.20g/L, 0.2g/L, 0.20g/L and 0.4g/L, respectively. When the concentration of different forms of iron is less than 0.2g/L, the degradation rate of MO increases with the increase of the concentration of catalyst. When the concentration of different forms of iron was 0.2g/L-0.4g/L, the degradation effect of MO was the best. When the concentration of different forms of iron continued to increase, the degradation effect of MO became worse. It is inferred that when the concentration of catalyst is low, too little active substance is produced. With the increasing of catalyst concentration, the required active substance gradually reaches saturation. When the catalyst concentration is too large, the side reaction increases, resulting in the deterioration of the degradation effect of MO.





Fig. 3. The effect of the initial concentrations of the different forms of iron on the degradation rate of MO in 0.1mol/L NaHSO<sub>3</sub> solution.

## D. Effect of the Concentration of NaHSO<sub>3</sub> on the Degradation of MO

We discussed the effect of the initial concentration of NaHSO<sub>3</sub> on the catalytic degradation of MO by different forms of iron activated NaHSO<sub>3</sub>, and the experimental results were shown in Fig. 4. With FeSO<sub>4</sub> as catalyst, when the initial concentration of NaHSO3 was 0.01g/L, 0.02/L, 0.04g/L, 0.05g/L, 0.06g/L, 0.08g/L, 0.10g/L, 0.20g/L, 0.50g/L, 1.0g/L, the degradation rates of MO were 10.61%, 15.37%, 41.73%, 49.49%, 50.95%, 52.12%, 59.15%, 62.30%, 68.37% and 70.79%, respectively. With FeCl<sub>3</sub> as catalyst, when the initial concentrations of NaHSO3 was 0.005g/L, 0.01g/L, 0.05/L, 0.1g/L, 0.2g/L, 0.3g/L, 0.4g/L, 0.5g/L, 1.0g/L, the degradation rates of MO were 36.02%, 41.29%, 53.44%, 58.45%, 68.04%, 76.64%, 76.94%, 77.67% and 78.92%, respectively. With (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> as catalyst, when the initial concentrations of NaHSO3 was 0.02g/L, 0.04g/L, 0.06g/L, 0.08g/L, 0.1g/L, 0.2g/L, 0.5g/L and 1g/L, the degradation rates of MO were 27.31%, 44.51%, 57.69%, 66.52%, 73.06%, 77.60%, 79.14%, 76.65%, respectively. With NH<sub>4</sub>Fe(SO4)2 as catalyst, when the initial concentration of NaHSO3 was 0.005g/L, 0.01g/L, 0.05/L, 0.1g/L, 0.2g/L, 0.3g/L, 0.4g/L, 0.5g/L, 1.0g/L, the degradation rates of MO were 58.13%, 59.22%, 59.44%, 77.45%, 81.70%, 84.41%, 84.63%, 85.65%, 86.31%, respectively. The experimental results showed that the degradation rate of MO increased rapidly with the increase of the initial concentration of NaHSO<sub>3</sub>. With FeSO<sub>4</sub> or FeCl<sub>3</sub> as catalyst, the degradation rate of MO is about 50% when the initial concentration of NaHSO<sub>3</sub> is 0.1g/L. With  $(NH_4)_2Fe(SO_4)_2$  or  $NH_4Fe(SO_4)_2$  as catalyst, the degradation rate of MO reached about 70% when the initial concentration of NaHSO<sub>3</sub> was 0.1mol/L. It can be seen that the catalytic effect of iron coordination ions is significantly higher than that of iron ions alone, possibly because the dissociation equilibrium between the iron coordination ions and the iron ions made the generated sulfate radical (SO<sub>4</sub><sup>•</sup>) more stable in the solution.



Fig. 4. The effect of the initial concentration of  $NaHSO_3$  on the degradation rate of MO in 0.1g/L different forms of iron solution.

### *E. Degradation Mechanism and Degradation Products of the Degradation of MO*

Under optimal experimental conditions, the test and analysis results of the free radical/vacancy analysis technique -EPR were shown in Table 1. It can be inferred that  $HSO_3^-$  was oxidized into  $SO_3^{\bullet-}$  free radicals by the photogenerated holes in the system, and  $OH^-$  was oxidized into  $OH^\bullet$  free radicals by the photogenerated holes in the system at the same time.  $SO_3^{\bullet-}$  can react with  $OH^\bullet$  to form  $HSO_4^-$ , and  $HSO_4^-$  is oxidized into  $SO_4^{\bullet-}$  free radicals by photogenic holes in the system. All free radicals of  $SO_3^{\bullet-}$ ,  $SO_4^{\bullet-}$  and  $OH^\bullet$  are important active species in dye degradation system. The different forms of iron activated NaHSO<sub>3</sub> is helpful to produce more photogenerated electrons and holes under the visible light, and further increases the active species in the degradation system.

Combined with previous reports [9–10] we supposed that in the acid system with the catalyst of the different forms of iron activated NaHSO<sub>3</sub>, the MO tends to be degraded to the smaller molecular weight of benzene compounds (e.g., m/z = 156), and a small account of small molecules such as CH<sub>3</sub>COO<sup>-</sup>,  $HCOO^{-}$ ,  $NO_{3}^{-}$ ,  $SO_{4}^{2-}$ . However, the removal rate of the Total Organic Carbon (TOC) is very low, and the dye is difficult to mineralize in this system. In the experiment, the degradation process is divided into two steps. In the first step, the carbonnitrogen bond of MO is easily broken, and the MO is degraded into benzene compounds with smaller molecular weight, which causes the degradation products to become colorless. But the benzene ring is difficult to be destroyed. In the second step, a small account of the benzene compounds are oxidized by SO3<sup>•-</sup>, SO4<sup>•-</sup> and OH<sup>•</sup> into small organic acids and inorganic ions. More detailed degradation mechanisms are needed for further study. The findings of this study provide a promising advanced oxidation method for the degradation of organic pollutants through sulfite activation.

Free Radical	gFactor	A <sub>N</sub> (G)	A <sub>Hβ</sub> (G)	spins/mL	M(mol/L)	Spins (Number of unpaired electrons)
SO₄•-	2.0	14	16	3.7e+13	6.1e-05	1.17e+15
OH•-	2.0	14	14	8.7e+12	1.4e-05	2.75e+14

Table 1. The test results of free radical/vacancy analysis technique-EPR under optimal experimental conditions for 5min of visible light

### IV. CONCLUSION

The photocatalytic degradation of MO by different catalysts in different systems was studied. The experimental study found that the photocatalytic degradation effect of the different forms of Fe / NaHSO<sub>3</sub> was higher than that of NaHSO<sub>3</sub> or the different forms of Fe alone. We supposed that it may be due to the narrow band gap of Fe, small electron escape work, and easy to produce more photogenerated electrons and holes. HSO<sub>3</sub><sup>-</sup> is oxidized by photogenic holes in the system and eventually converted to SO<sub>4</sub><sup>•-</sup> free radicals. SO<sub>4</sub><sup>•-</sup> is an important active species in dye degradation system. In addition, we used the different forms of Fe as catalyst to study the effects of pH value, catalyst input and initial concentration of NaHSO<sub>3</sub> on the degradation rate of MO. Under optimal experimental conditions, the instantaneous degradation rate reached more than 80%. MO exists widely in organic dye wastewater, and the work in this experiment is of great significance to guide workers to treat organic dye wastewater.

### CONFLICT OF INTEREST

The authors declare no conflict of interest.

### AUTHOR CONTRIBUTIONS

Jinai Ma was responsible to design the research, analyzed the experimental data and wrote the manuscript; Zhenhua Yu, Xiangyuan Yu, and Yang Hu performed the research; Junhao You was concentrated on the analytical test with Ultraviolet and Visible Spectrophotometer of UV1200 from Shanghai Auyi Instruments Limited Company; all authors had approved the final version.

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