



# Photocatalytic decolorization of soluble dyes by a bis-ions coexistence system of $\text{NH}_4^+$ and $\text{NO}_3^-$ with high photoreduction ability

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## ABSTRACT

In this paper, we found that the acidic and basic dyes were easily decolorized by a bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  under UV light irradiation. The coexistence of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is a necessary condition for the photocatalytic decolorization of soluble dyes. The photocatalytic decolorization of methyl orange (MO) and methylene blue (MB) follows the first order rate kinetics. The location of an absorption peak in the visible region is blue-shifted with the increase in the illumination time. It is proposed that the photocatalytic decolorization of soluble dyes in the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is a photoreduction reaction, in which the ammonium nitrate acts as a photocatalyst. The chromophore of acidic and basic dyes reacts with hydrogen and then results in their rapid decolorization.

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## 1. Introduction

Dyes are widely used in textile, painting, leather, printing, paper, cosmetic, photography, and coating industries, etc. [1,2]. They bring people a better life, but they also could cause serious environmental pollution. For example, in the textile industry, it was estimated that about 10–15% of the dyes were discharged during the manufacturing process [3]. Discharging colored effluents into the aquatic environment without adequate treatment is a major problem due to the damage caused to the environment and human health [4]. These effluents are mostly non-biodegradable and resistant to destruction by physicochemical methods. Removing color from wastewater is more meaningful than other colorless organic substances, because the trace amount of dyes can be clearly visible and can influence the water environment [5]. However, it is extremely difficult to remove the color in the dyes wastewater. Therefore, the discovery of an effective method to remove the color from the effluents is of great significance. Conventional physicochemical processes such as carbon adsorption, coagulation–flocculation, membrane filtration, ultrafiltration, electrocoagulation, sedimentation [6,7], ultrasonic irradiation, biodegradation [8], sonolysis [9], etc. were used for the treatment of such effluents. However, the

above treatments are usually not effective in removing the color. At the same time, a lot of energy and chemicals are consumed in the decoloration process. Also large amounts of sludge are produced, which requires further disposal. Adsorption and membrane filtration techniques leads to secondary waste solids or streams that need further treatment or disposal [10]. Moreover, different oxidation techniques such as catalytic ozonation,  $\text{H}_2\text{O}_2$ -based oxidation [11–13] and photocatalysis [14–17], have been developed to treat dye-contaminated wastewater effluents. Nevertheless, their applications are restricted due to some disadvantages such as excess dosage of chemicals, difficulty and high cost of operation, and ineffective removal of chrominance [18]. Thereby, it is necessary to discover a rapid and effective method for the decolorization of soluble dyes. Recently, a bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  was found to present a high capability for the photocatalytic decolorization of various soluble dyes under UV light irradiation in our laboratory. To the best of our knowledge, this is the first report of the result. The method is simple, time saving and low cost. And it may be a very promising approach to treat dye-contaminated wastewater effluents and it may provide new insights for the decolorization of dyes. Meanwhile, we found that the coexistence of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  had a high photoreduction ability, which made it possible to develop a new route for the preparation of chemicals in the field of organic synthesis.

It is known that dyes are classified into three sorts according to the chemical property: acid dyes, basic dyes and neutral dyes. Both acid dyes and basic dyes are diffuent, while neutral dyes have relatively low solubility in water. Soluble acid dyes such as

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methyl orange (MO), congo red, orange G, eosin B, xylene cyanol FF and soluble basic dyes such as methylene blue (MB), rhodamine B, pyronine G, fuchsine, victoria blue B, were used to carry out the experiment.

The objective of this study was to conduct an experimental investigation on the removal of soluble acid dyes and basic dyes using the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . The results demonstrated that both of soluble acid dyes and basic dyes could be decolorized. In this paper, we will be the first to report the results of the photocatalytic decolorization of soluble dyes by the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  under UV light irradiation. The effects of many factors, such as the structure of dyes, types of salt, reaction solvents, initial dye concentration, and illumination time, on the removal efficiency of dyes as well as the kinetics and UV-vis spectra changes were investigated. The photoreduction ability of the bis-ions coexistence of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  was proved by the photocatalytic reduction of 1,4-benzoquinone. The possible mechanisms of photocatalytic decolorization of dyes were also proposed.

## 2. Experimental

### 2.1. Materials

Ammonium nitrate, ammonium chloride, ammonium sulphate, potassium nitrate, sodium nitrate and other chemicals used in the experiments were purchased from Shanghai and Sinopharm Chemical Reagent Ltd. All the acidic and basic dyes were purchased from Shanghai and other China Chemical Reagent Ltd. They were of analytically pure grade and used without further purification. Deionized water was used throughout this study. MO and MB were selected as models of acid dyes and basic dyes, respectively. The solution of ammonium nitrate was used as the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the experiment.

### 2.2. Photoreaction apparatus and procedure

Experiments were carried out in a photoreaction apparatus consisting of two parts [19,20]. The schematic diagram is shown in Fig. 1. The first part is an annular quartz tube with an empty chamber in which a 375 W medium pressure mercury lamp (Institute of Electric Light Source, Beijing) with a maximum emission of about 365 nm is laid. Running water passes through an inner thimble of the annular tube. Owing to continuous cooling, the temperature of the reaction solution is maintained at approximately 30 °C. The

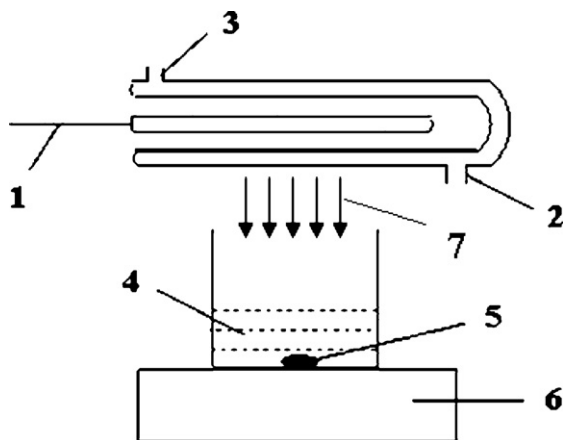


Fig. 1. Schematic diagram of photoreaction apparatus. 1, lamp; 2, water-cooling inlet; 3, water-cooling outlet; 4, reaction solution; 5, stirring rod; 6, magnetic agitator; 7, light.

second part is an unsealed beaker with a diameter of 12 cm. At the beginning of the experiment, the reaction solution (volume, 300 mL) containing reactants and ammonium nitrate was put in the unsealed beaker and stirred by a magnetic stirring device. The distance between the light source and the surface of the reaction solution is 11 cm. The UV irradiation intensity (wavelengths below 400 nm) on the reaction solution surface is about 18,300  $\mu\text{W}/\text{cm}^2$ . In the experiment, the initial pH of the reaction solution was 6.0, the initial concentrations of MO and MB were 9.5 and 2.4 mg/L, respectively, and the illumination time for each sample was 20 min, except for experiments where the initial pH and the illumination time were varied. After the illumination, the samples were analyzed. In order to determine the reproducibility of the results, duplicated runs had to be carried out in each condition for averaging the results, and the experimental error was found to be within  $\pm 4\%$ .

### 2.3. Analysis

The concentration of dyes in the solution was determined spectrophotometrically.

The photocatalytic decolorization efficiency of dyes  $\eta$  was calculated from the following expression:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial concentration of dyes before illumination and  $C_t$  is the concentration of dyes after the illumination time  $t$ .

## 3. Results and discussion

### 3.1. Effects of different structures of dyes and different bis-ions coexistence systems on the photocatalytic decolorization efficiency

It is known that acid dyes such as MO and basic dyes such as MB cannot be decolorized under UV illumination [21,22]. In our experiment, the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  was found to have high photocatalytic decolorization efficiency under UV light irradiation. Soluble acid dyes and basic dyes are easily decolorized by the system in aqueous solution. The fixed illumination time for each experiment is 20 min, and the concentration of ammonium nitrate is 2.0 g/L. The different structures of dyes, the corresponding photocatalytic decolorization efficiency ( $\eta$ ), and the initial concentration ( $C_0$ ) of dyes are listed in Table 1.

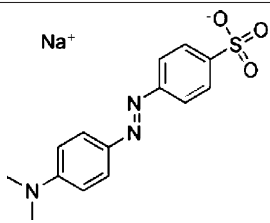
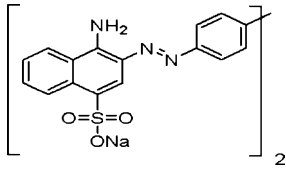
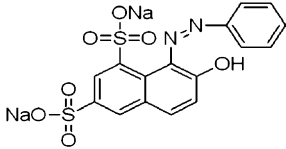
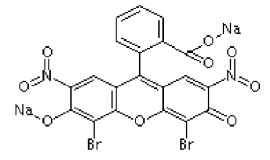
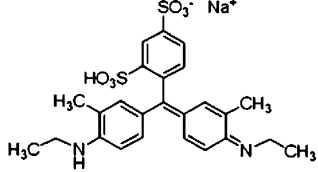
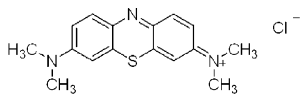
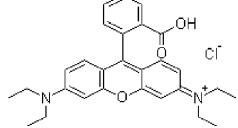
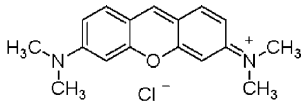
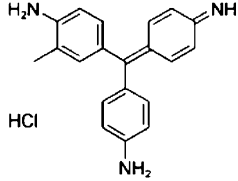
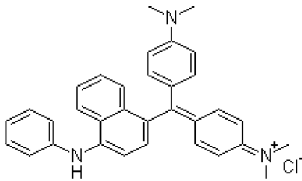
As it is shown in Table 1, soluble acidic and basic dyes are easily decolorized by the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  under UV light irradiation. Furthermore, it is noticeable that acid dyes and basic dyes can be photocatalytically decolorized not only by ammonium nitrate solution, but also by other bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , which can be formed by different ammonium salts and nitrate salts. The initial concentration of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is 2.0 g/L. The results are shown in Table 2.

From Table 2, it clearly shows that the bis-ions coexistence system is composed of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . For example, it can be formed by ammonium chloride and potassium nitrate, ammonium chloride and sodium nitrate, ammonium sulphate and potassium nitrate, ammonium sulphate and sodium nitrate, etc. The experimental results also showed that the dyes could not be decolorized only in the presence of  $\text{NH}_4^+$  or  $\text{NO}_3^-$ . Only when  $\text{NH}_4^+$  and  $\text{NO}_3^-$  existed simultaneously, could the dyes be decolorized.

### 3.2. Effect of amount of ammonium nitrate

In order to evaluate the effect of the amount of ammonium nitrate on the photocatalytic decolorization efficiency of dyes, the blank and photo-induced self-sensitized experiments were carried

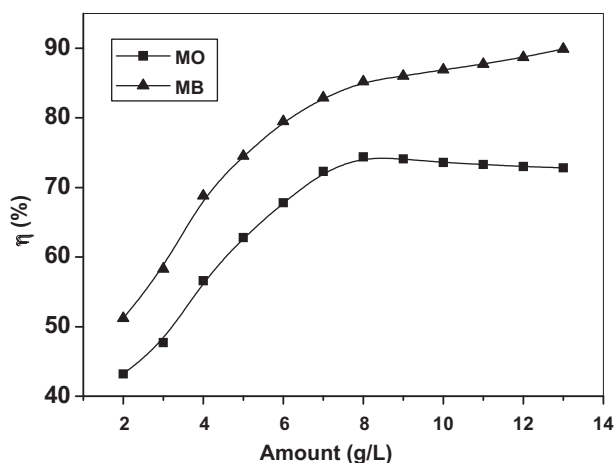
**Table 1**  
Relationship between the photocatalytic decolorization efficiency and the structure of dyes.

Entry	Dyes	C <sub>0</sub> (mg/L)	Structure of dyes	η (%)
1	Methyl orange (MO)	9.5		43.2
2	Congo red	10.7		21.1
3	Orange G	4.8		20.6
4	Eosin B	5.7		21.2
5	Xylene cyanol FF	10.9		16.0
6	Methylene blue (MB)	2.4		51.2
7	Rhodamine B	1.1		65.5
8	Pyronine G	7.5		16.1
9	Fuchsine	4.4		61.1
10	Victoria blue B	1.6		78.0

Illumination time = 20 min; concentration of ammonium nitrate = 2.0 g/L

**Table 2**  
Effect of different bis-ions coexistence systems on the photocatalytic decolorization efficiency of MO and MB.

Entry	Ammonium	Nitrate	Decolorization efficiency of MO (%)	Decolorization efficiency of MB (%)
1	NH <sub>4</sub> NO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	43.2	51.2
2	NH <sub>4</sub> Cl	KNO <sub>3</sub>	25.3	53.9
3	NH <sub>4</sub> Cl	NaNO <sub>3</sub>	24.6	54.1
4	NH <sub>4</sub> Br	KNO <sub>3</sub>	21.4	30.4
5	NH <sub>4</sub> Br	NaNO <sub>3</sub>	18.8	53.3
6	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	KNO <sub>3</sub>	19.8	55.2
7	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	22.4	51.9
8	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	KNO <sub>3</sub>	12.6	21.8
9	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	NaNO <sub>3</sub>	16.4	26.2
10	CH <sub>3</sub> COONH <sub>4</sub>	KNO <sub>3</sub>	15.0	25.7
11	CH <sub>3</sub> COONH <sub>4</sub>	NaNO <sub>3</sub>	13.8	23.4
12	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	KNO <sub>3</sub>	14.9	90.5
13	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	NaNO <sub>3</sub>	14.1	89.7
14	NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	KNO <sub>3</sub>	16.2	64.1
15	NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub>	NaNO <sub>3</sub>	15.9	63.6



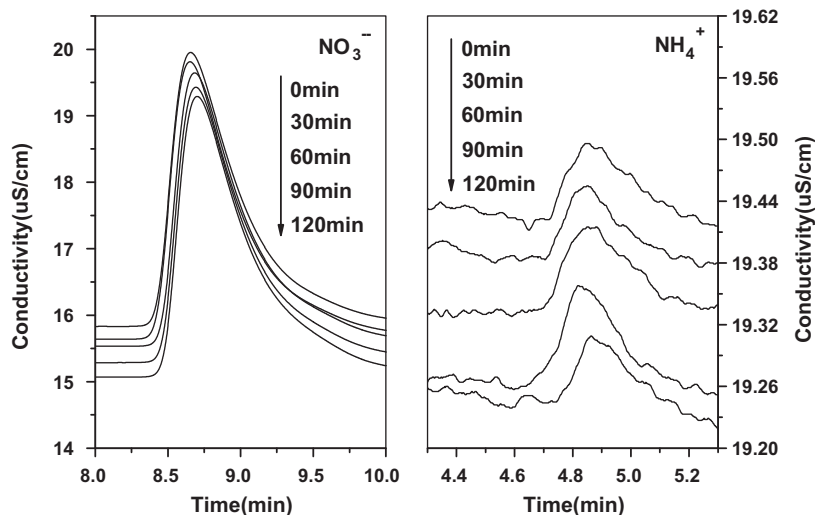
**Fig. 2.** Effect of amount of ammonium nitrate on the photocatalytic decolorization efficiency.

out. The results showed that the effect was so little that it could be neglected in the above conditions. In the experiments, the concentrations of ammonium nitrate varied from 2.0 to 13.0 g/L, and the initial concentrations of MO and MB were 9.5 and 2.4 mg/L, respectively. The effect of the amount of ammonium nitrate on the photocatalytic decolorization of dyes is shown in Fig. 2.

As it is depicted in Fig. 2, the fixed illumination time is 20 min, when the concentration of ammonium nitrate increases from 2.0 to 8.0 g/L, the decolorization efficiency of MO increases rapidly from 43.2% to 74.4% and that of MB increases remarkably from 51.2% to 83.2%. When the concentration of ammonium nitrate is higher than 8.0 g/L, the decolorization efficiency of MO decreases slightly and a small increment for the decolorization efficiency of MB can be observed. In this study, the optimum amount of ammonium nitrate is found to be 8.0 g/L for the decolorization of the MO and MB.

It is believed that the increasing number of photons absorbed conduce the enhancement of the decolorization efficiency because the amount of ammonium nitrate increases. And further increase in the concentration of ammonium nitrate beyond 8.0 g/L leads to slight difference on the decolorization efficiency between MO and MB. This may be attributed to the difference in the structures of MO and MB. It is known that MO is anionic dye and MB is cationic dye. According to Eq. (3), NO<sub>3</sub><sup>-</sup> plays an important role in the reaction. The electrostatic attraction between MB molecules and NO<sub>3</sub><sup>-</sup> is greater than that of MO molecules and NO<sub>3</sub><sup>-</sup>. MB molecules react with the ammonium nitrate more easily, resulting in further increases in the decolorization efficiency.

The amount of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the process of the photocatalytic decolorization of dyes was also measured by ion chromatogram. The changes of the amount of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the reaction processes are shown in Fig. 3. It shows that there is no obvious change for the amount of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the reaction process. An almost constant result was obtained during the whole



**Fig. 3.** Amount changes of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the process of the photocatalytic decolorization of dyes.

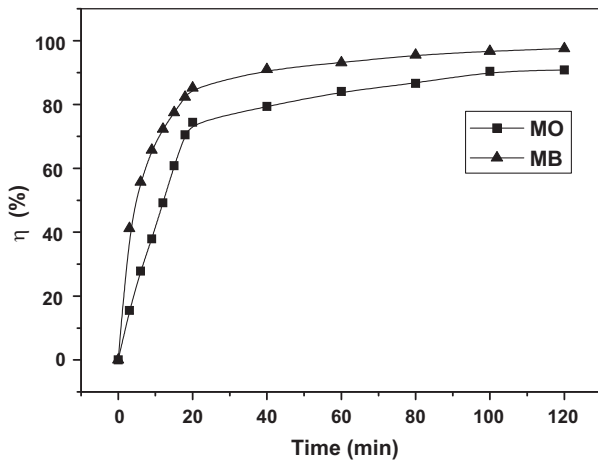


Fig. 4. Effect of illumination time on the photocatalytic decolorization efficiency of MO and MB.

reaction process, even when the dyes were completely photocatalytically decolorized.

### 3.3. Effect of illumination time

The fixed amount of ammonium nitrate was 8.0 g/L, and the initial concentrations of MO and MB were 9.5 and 2.4 mg/L, respectively. The effect of the illumination time on the decolorization efficiency of MO and MB is shown in Fig. 4.

From Fig. 4, it can be seen that the decolorization efficiencies of MO and MB increase when the illumination time increases from 0 to 20 min. However, when the illumination time is longer than 20 min, the increasing extent of the decolorization efficiencies slows down. When the illumination time is 120 min, the photocatalytic decolorization efficiency of MO and MB reaches 90.8% and 97.5%, respectively.

It is supposed that the photocatalytic decolorization of dyes may be attributed to the reaction between ammonium nitrate and dyes under UV light illumination. The longer of the illumination time being provided, the higher of the probability of reaction between ammonium nitrate and dyes have, and thus leads to the higher photocatalytic decolorization efficiency.

Table 3

Effect of the initial pH on the photocatalytic decolorization efficiency of MO and MB.

	Initial pH value					
	2.0	4.0	6.0	8.0	10.0	12.0
$\eta_1$ (%)	70.4	48.3	43.2	41.7	40.5	30.8
$\eta_2$ (%)	59.1	53.4	51.2	50.2	48.6	35.3

$\eta_1$ : photocatalytic decolorization efficiency of MO;  $\eta_2$ : photocatalytic decolorization efficiency of MB.

### 3.4. Effect of initial concentration of dye

The fixed amount of ammonium nitrate was 2.0 g/L. The fixed illumination time was 20 min. The effect of initial concentration of dye on the photocatalytic decolorization efficiency of MO and MB was studied by adopting varied initial concentration over a wide range. The result is illustrated in Fig. 5.

From Fig. 5, it can be seen that the photocatalytic decolorization efficiency of MO and MB decreases with the increase in the initial concentration. The photocatalytic decolorization efficiency of MO decreases from 43.2% to 9.8% when the initial concentration increases from 9.5 to 50 mg/L. And the photocatalytic decolorization efficiency of MB is 51.2% and 15.9% when the initial concentration is 2.4 and 10.5 mg/L, respectively. It is proposed that the acting force between the catalyst and dye is of paramount importance in controlling the photocatalytic decolorization efficiency of dye. With a fixed concentration of ammonium nitrate, the total sites available for reaction are constant. The decolorization efficiency tends to decrease with the increase in the initial dye concentration. Similar result was reported on TiO<sub>2</sub> photocatalyst [23].

### 3.5. Effect of initial pH value

The pH value is an important parameter that may influence the photocatalytic decolorization efficiency of dyes. The pH of the solutions varied from 2.0 to 12.0. The fixed amount of ammonium nitrate was 2.0 g/L. The fixed illumination time for each sample is 20 min. The effect of the initial pH on the photocatalytic decolorization of MO and MB is shown in Table 3.

From Table 3, it can be seen that when the pH increases from 2.0 to 12.0, the photocatalytic decolorization efficiency of MO decreases gradually from 70.4% to 30.8%, and the photocatalytic

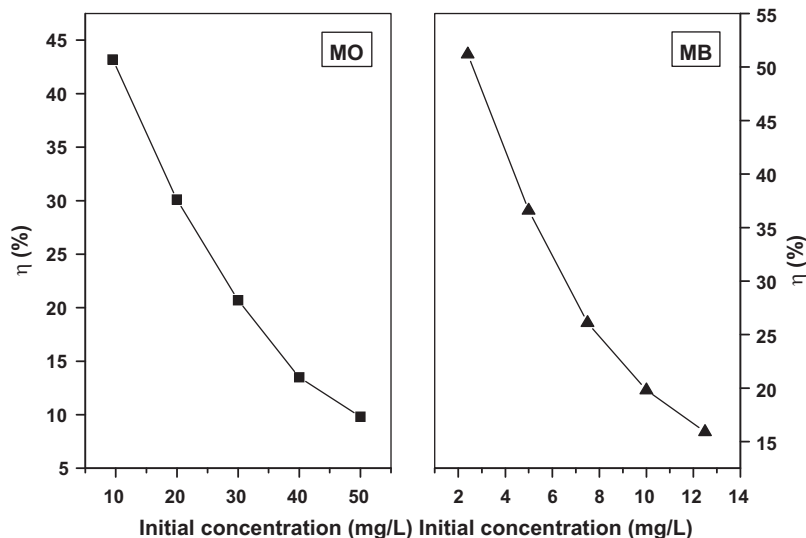


Fig. 5. Effect of initial concentration of dye on the photocatalytic decolorization efficiency of MO and MB.

decolorization efficiency of MB decreases slowly from 59.1% to 35.3%. When the pH value ranges from 4.0 to 10.0, a little change in the photocatalytic decolorization efficiency of MO and MB is observed. Ammonium nitrate in the experiment acts as photocatalyst. The assumptions are verified by the results in the Section 3.7. It is reported that electrostatic attraction or repulsion between the catalyst and the organic molecule exists, depending on the ionic form of the organic compound (anionic or cationic) and consequently enhances or inhibits the photodegradation efficiency [20]. At acidic pH, MO reacts with  $H^+$  quickly to produce a protonated complex, which displays red in the solution. It is plausible that the electrostatic attraction between dyes, molecules and  $NO_3^-$  at acidic pH is greater than that at alkaline pH. So the dye molecules are easy to react with the ammonium nitrate at acidic medium, resulting in the increase in the decolorization efficiency.

### 3.6. Kinetics studies

With the purpose of determining photocatalytic decolorization rate of MO and MB, an attempt was made to match the data for MO and MB decolorization using some common kinetic equations. The first order rate kinetics was then confirmed by making a linear plot of  $\ln(C_0/C_t)$  to time. A similar method was used to study the photocatalytic degradation of pollutants in previous report [24].

The first-order rate equation can be written as follows:

$$\ln\left(\frac{C_0}{C_t}\right) = Kt \quad \text{or} \quad \ln\frac{1}{1-\eta} = Kt \quad (2)$$

where  $C_0$ ,  $C_t$  and  $\eta$  denote the same quantities as in Eq. (1), and  $k$  is the apparent rate constant. The fixed amount of ammonium nitrate was 8.0 g/L. The plots of  $\ln(C_0/C_t)$  versus illumination time  $t$  for the photocatalytic decolorization of MO and MB are depicted in Figs. 6 and 7, respectively.

For the photocatalytic decolorization of MO, the plot of  $\ln(C_0/C)$  versus illumination time is shown in Fig. 6. From Fig. 6, it can be seen that there are two linear regions, between 0–20 min and 20–120 min, respectively. And the corresponding linear equations are  $y = 0.07185x - 0.11365$  and  $y = 0.01065x + 1.15384$ , respectively. The corresponding correlation coefficient of the plot is 0.99316 and 0.97887, respectively, which is quite good and can be used to determine the equation of the best fitting curve. The plot of  $\ln(C_0/C)$  versus illumination time follows a linear relation, which is one of the typical characteristics and it is an unique feature for the first order rate kinetics. So it comes to a conclusion that the kinetics for photocatalytic decolorization of MO can be satisfactorily described using the first-order rate equations. Fig. 7 shows the kinetics for the

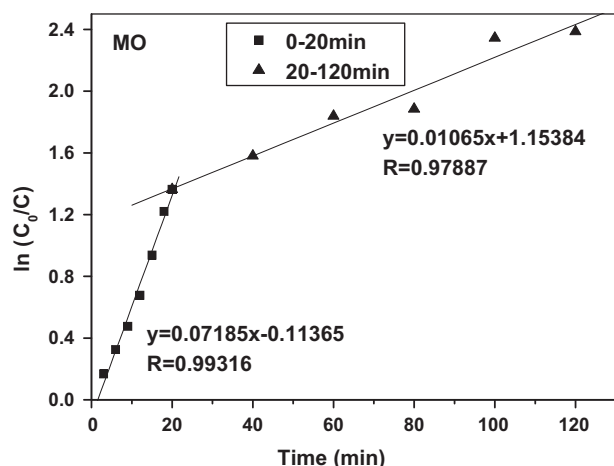


Fig. 6. Kinetics for the photocatalytic decolorization of MO.

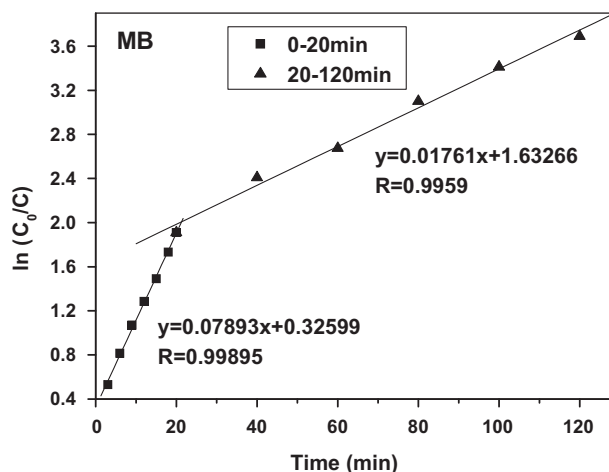


Fig. 7. Kinetics for the photocatalytic decolorization of MB.

photocatalytic decolorization of MB. Similar results were obtained in the experiment. It was found that the first order rate kinetics was confirmed by making plot from the linearity of the plots of  $\ln(C_0/C)$  against time. The kinetics equation for photocatalytic decolorization of MB is  $y = 0.07893x + 0.32599$  when the illumination time changes from 0 to 20 min, and it is  $y = 0.01761x + 1.63266$  when the illumination time changes from 20 to 120 min. The corresponding correlation coefficient of the plot is 0.99895 and 0.9959, respectively. Thus it is concluded that the kinetics for photocatalytic decolorization of MB can also be satisfactorily described using the first-order rate equations. Figs. 6 and 7 also show that within the first 20 min, the apparent rate constants for photocatalytic decolorization of MB and MO are determined to be  $0.07893 \text{ min}^{-1}$  and  $0.07185 \text{ min}^{-1}$ , respectively. For illumination time beyond 20 min, the apparent rate constants for photocatalytic decolorization of MB and MO are  $0.01761 \text{ min}^{-1}$  and  $0.01065 \text{ min}^{-1}$ , respectively.

### 3.7. Reason for photocatalytic decolorization of dyes

In order to determine the effect of  $H_2O$  on the photocatalytic decolorization of dyes, several solvents were used in the experiment. The result demonstrated that  $H_2O$  had a significant influence on the photocatalytic decolorization efficiency of MO and MB. An important conclusion was obtained: only in aqueous solution, could dyes be decolorized. If dyes were dissolved in nonaqueous solvents, such as absolute ethanol, propyl alcohol etc., no photocatalytic decolorization of dyes were observed. This indicated that  $H_2O$  was indispensable to the photocatalytic decolorization of dyes and it participated in the photocatalytic reaction system.

In order to determine the reason for the photocatalytic decolorization of dyes, electron paramagnetic resonance (EPR) spectra measurements of  $OH$  and  $O_2$  were carried out. The amount of ammonium nitrate was fixed at 8.0 g/L, and the initial concentrations of MO and MB were 9.5 and 2.4 mg/L, respectively. The mixture was stirred and then put into a quartz tube. In situ irradiation by a laser (365 nm) was used in this experiment. The results are shown in Fig. 8. From Fig. 8(a), it can be seen that there is no obvious difference in EPR spectra of ammonium nitrate solution in the dark and under UV light irradiation. It means that no  $\bullet OH$  is generated from ammonium nitrate solution under illumination. As it is shown in Fig. 8(b) and (c), after adding MO into ammonium nitrate solution, the EPR analysis demonstrates that no signal of  $\bullet OH$  and  $\bullet O_2^-$  is detected during the photoreaction. Consequently, it is concluded that the photocatalytic decolorization of dyes is not a photooxidation reaction. At the same time, the TOC and COD experiments of the reaction solution were conducted. If the dyes



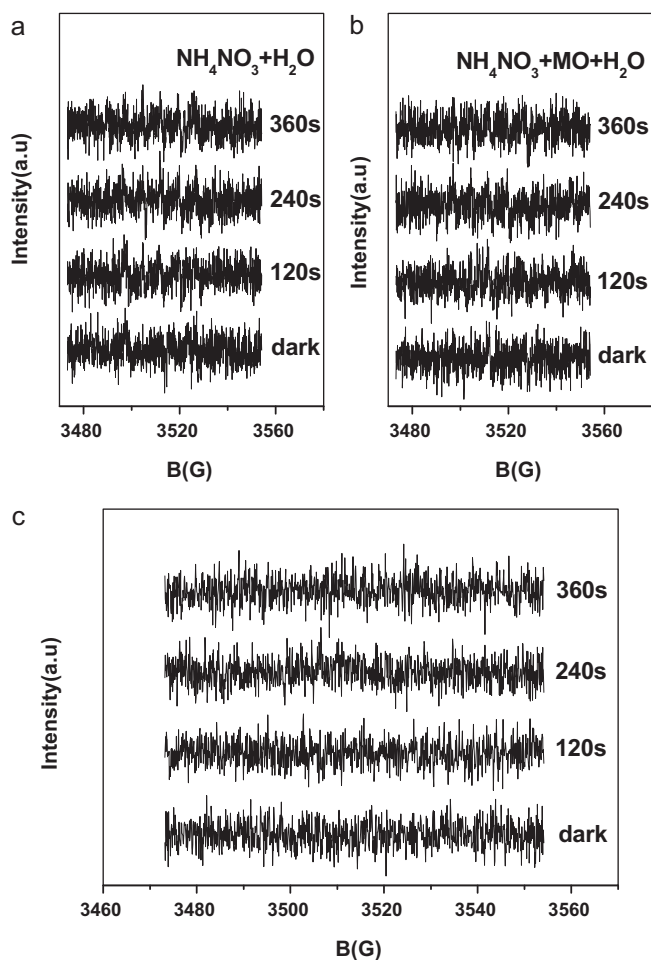


Fig. 8. The EPR spectra of  $\bullet\text{OH}$  (a and b) and  $\bullet\text{O}_2^-$  (c).

are decolorized from oxidative degradation, the TOC and COD of the reaction solution should be lower than that of original solution. However, the result showed that after the illumination for 120 min, the TOC was constant and the COD was not lower. Meanwhile, thin layer chromatogram analysis demonstrated that only one product was observed in the course of the photocatalytic decolorization of MO and MB. It means that MO and MB are not decomposed in the photocatalytic decolorization. Based on the above result, it is proposed that the photocatalytic decolorization of dyes may be a photoreduction reaction.

In order to determine the photoreduction ability of the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , the experiments for the photocatalytic reduction of 1,4-benzoquinone by ammonium nitrate under UV light illumination were conducted. The concentration of ammonium nitrate and 1,4-benzoquinone are 8.0 g/L and 10 mg/L, respectively. It is known that 1,4-benzoquinone and hydroquinone are colorless, and quinhydrone displays reddish brown when it is observed towards light or dissolved in hot water. The solution also turns yellow after quinhydrone is dissolved in ethanol or ether, and it turns green when it is dissolved in ammonia. These are the characteristics of generated quinhydrone color reaction, and they can be used as the identification of the formation of quinhydrone. At the same time, we also know that 1,4-benzoquinone can be reduced into hydroquinone, and that 1,4-benzoquinone combines with hydroquinone to generate quickly a molecular complex, quinhydrone. The chemical reaction processes are shown in Fig. 9.

The result showed that under the protection of nitrogen and after the illumination for 5 h, the reaction solution displayed

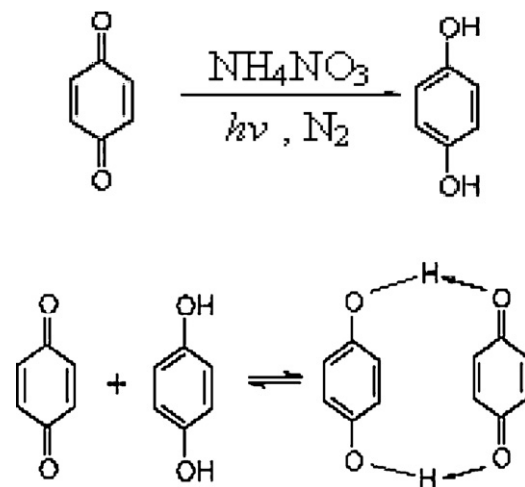


Fig. 9. Formation of quinhydrone product.

reddish brown, and other color reactions were accord with the characteristics color reactions of quinhydrone. It is concluded that quinhydrone is formed in the reaction process. However, quinhydrone was not identified in the absence of ammonium nitrate under the same experimental conditions. Namely, the bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  has high photocatalytic reduction ability.

In a word, the acidic and basic dyes were easily decolorized by a bis-ions coexistence system of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  under UV light irradiation. Furthermore, the chemical property and the concentration of ammonium nitrate was kept constant before and after the reaction, which indicates a typical characteristic of the catalyst. Based on the above results, we can come to a conclusion that the ammonium nitrate plays an important role, like a photocatalyst, in the process of photocatalytic decolorization of dyes.

### 3.8. The change of UV–vis spectra

UV–vis absorption spectroscopy measurements were carried out using a Hitachi UV-365 spectrophotometer. The analysis range was from 200 to 900 nm. The amount of ammonium nitrate was 2.0 g/L. The initial concentrations of MO and MB were 10.6 and 2.6 mg/L, respectively. The changes in the absorption spectra of MO and MB solution during the photocatalytic process are shown in Figs. 10 and 11, respectively.

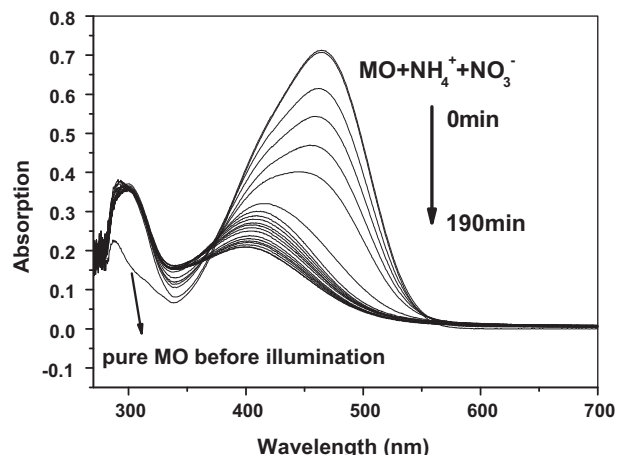


Fig. 10. Changes in the UV–vis absorption spectra of MO.

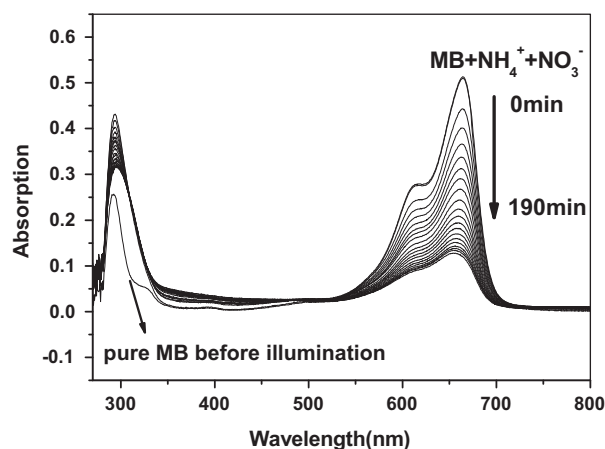

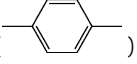
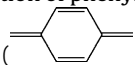


Fig. 11. Changes in the UV-vis absorption spectra of MB.

Fig. 10 shows that the spectrum of MO in the visible-light region exhibits a main band with a maximum at 464 nm before illumination. The decreased intensity of the maximum absorption peak of MO indicates a rapid degradation of the dye, and it means that the nitrogen–nitrogen double bond ( $-N=N-$ ) of the dye is broken up. From Fig. 10, it also can be seen that the location of the maximum absorption peak of MO is blue-shifted continuously during the illumination process, and it blue-shifts to 400 nm when the reaction solution is exposed to UV light for 190 min. It is because that the chromophore ( $-N=N-$ ) responsible for the characteristic color of MO is broken up and results in the decreased conjugated number of molecule, as shown in Eq. (9). Similarly, Fig. 11 shows absorption spectral changes of MB. The decreased intensity of the

maximum absorption peak is due to the photocatalytic decolorization of MB. This decrease is also believed to have much to do with the chromophore () that is responsible for the characteristic color of the dyes. It is clear that when the illumination time increases from 0 to 190 min, the location of the maximum absorption peak of MB is blue-shifted slightly from 664 nm to 655 nm, which is due to the formation of phenyl () transformed from the quinone group () of MB, and results in the decrease of conjugate number.

The spectra of MO and MB in the UV region exhibit absorption peaks at 288 nm and 292 nm, respectively. The absorption intensity of pure MO before illumination is much lower than that of MO solution after adding  $NH_4^+$  and  $NO_3^-$ , and as well for MB. The reason is that  $NO_3^-$  in the system exhibits a strong and broad absorption peak at 298 nm, which is very close to 288 nm and 292 nm. Besides this, from Fig. 10 it also shows that, the intensity of absorption peak below 300 nm of the MO solution system hardly has change after adding  $NH_4^+$  and  $NO_3^-$ . However, from Fig. 11, it is clear that the intensity of absorption peak below 300 nm decreases with the increase in the illumination time for MB. The reason is being investigated.

### 3.9. Reaction mechanisms

From the above results, it can be implied that  $NH_4^+$  and  $NO_3^-$  take part in the reaction system synchronously. Dyes can not be

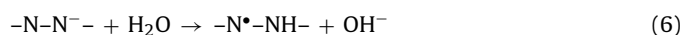
decolorized only in the presence of either  $NH_4^+$  or  $NO_3^-$ , which indicates that both  $NH_4^+$  and  $NO_3^-$  are reactants.

The specific process of photocatalytic decolorization of dyes is still unavailable in the literature. Based on the above results, a rough model was presumed to elucidate the reaction mechanism.

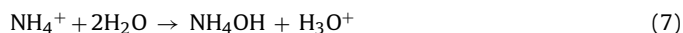
Under UV illumination, hydrated electrons are produced. The possible processes are as follows:



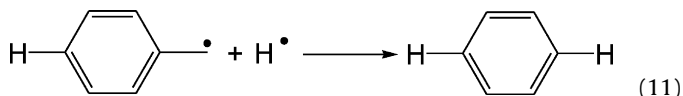
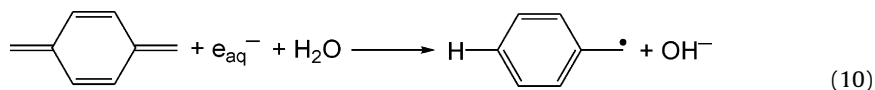
The decolorization efficiency was much higher and close to unity for  $e_{aq}^-$ . The reaction of  $e_{aq}^-$  with MO or MB led to an immediate destruction of the color. The reaction of hydrated electron with the azo group is fast and the radical anion quickly protonates forming a hydrazyl radical [13,25]:



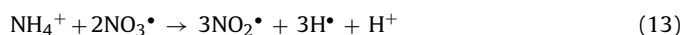
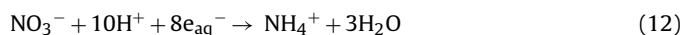
Synchronously, the solution of ammonium nitrate takes on acidity because of the hydrolyzation of  $NH_4^+$ . In acidic solution, the solvated electron reacts with proton donor, such as  $H_3O^+$ , very rapidly to produce H radical [13,26], which reacts with the hydrazyl radical in succession.



Similar processes for the photocatalytic decolorization reaction of MB are shown below in Eqs. (10) and (11), as those for the photocatalytic decolorization reaction of MO in Eqs. (5), (6) and (9).



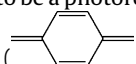
Since the amount of  $NO_3^-$  and  $NH_4^+$  is constant, there is a great possibility that  $NO_3^-$  and  $NH_4^+$  transform themselves into each other. Some reactions in aqueous solutions are probably as follows:



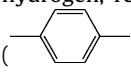
Further studies on the specific mechanisms are in progress.

## 4. Conclusions

Soluble acid dyes and basic dyes are easily photocatalytically decolorized by the bis-ions coexistence system of  $NH_4^+$  and  $NO_3^-$  in aqueous solution under UV light irradiation. The optimum concentration of ammonium nitrate is 8.0 g/L for the decolorization of both MO and MB. The photocatalytic decolorization efficiency of dyes increases as a function of the illumination time, and the reaction process follows the first order rate kinetics. The location of the absorption peak in the visible-light region is blue-shifted with the increasing in the illumination time. It is proposed that the ammonium nitrate acts as photocatalyst. The photocatalytic decolorization of dyes is also proposed to be a photoreduction reaction.

The chromophore ( $-N=N-$ ) and () reacts with



hydrogen, resulting in the formation of (–NH–NH–) and phenyl (  ), respectively. Further investigation is required to clarify the specific mechanisms of the decolorization of dyes.

### Acknowledgements

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