Cent. Eur. J. Chem. • 6(2) • 2008 • 245–252
DOI: 10.2478/s11532-008-0016-5

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Central European Journal of **Chemistry**

Photocatalytic decolorization of methyl orange solution with potassium peroxydisulfate

Research Article

Zhong Junbo[1*], Ma Di[1], Zhao Hong[2], Lian An[1], Li Min Jiao[1], Huang Shengtian[1], Li Jianzhang[1]

[1] *Departmemt of Chemistry, Sichuan University of Science and Engineering,*
Zigong, 643000, PR China

[2] *College of Environmental & Chemical Engineering,*
Dalian Jiaotong University,
Dalian,116026, PR China

Received 30 November 2007; Accepted 22 January 2008

Abstract: Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern. It has been generally agreed that methyl orange (MO) can be effectively degraded in aerated $K_2S_2O_8$ homogeneous reaction system using near-UV irradiation. In this paper photocatalytic degradation of MO solutions with $K_2S_2O_8$ was investigated, with particular attention on the possible underlying mechanisms. This report has shown decolorization efficiency of MO increases with the increasing of the dosage of the catalyst. There is no optimal amount of catalyst in our case, where special attention was paid on the nature of the photocatalyst itself. The current research revealed that the decolorization reaction is a pseudo first-order reaction when the concentration of MO is below 20 mg L^{-1} and the decolorization reaction is zero-order reaction when the concentration of MO is above 100 mg L^{-1}, but the Langmuir–Hinshewood kinetic model does not describe this. The influence of IO_4^-, BrO_3^- and H_2O_2 were investigated in detailed. Several observations indicate that the mechanism is not involved in hydroxyl radical attacks in MO degradation with $K_2S_2O_8$ by UV irradiation. The possible underlying mechanisms are direct oxidation of the MO by $S_2O_8^{2-}$ and hydrogen attraction by $SO_4^{\bullet-}$.

Keywords: *Potassium peroxydisulfate • Photocatalytic decolorization • Methyl orange • Inorganic additive • Wastewater treatment*

1. Introduction

Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern [1]. Azo dyes are characterized by the presence of one or more azo bonds (-N=N-) in association with one or more aromatic systems, which may also carry sulfonic acid groups. Many studies indicate that these dyes are toxic or carcinogenic. An additional difficulty is that, when present, these dyes are not normally removed by conventional wastewater treatment systems [2,3]. Therefore, the employment of these dyes must be controlled and the effluents must be treated before being released into the aquatic and terrestrial environment [4].

There are several methods used to decolorize the textile wastewater, but they cannot be effectively applied for all dyes [5]. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high. Ozone and hypochlorite oxidations are effective decolorization methods, but they are not desirable because of the high cost of the equipments, operating costs and the secondary pollution arising from the residual chlorine [6].

Therefore, the interest in developing processes which can destroy these dyes effectively has been a hot issue recently. Among the processes developed for the treatment of dyes, the photocatalytic oxidation process is considered to be a promising technology. Peroxydisulfate ($S_2O_8^{2-}$ ion) is a strong oxidant ($E°$ =2.05 V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator [7]. It has also been reported that potassium peroxydisulfate (KPS) can be effective for

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* *E-mail: junbozhong@sohu.com*

degrading organics in hazardous wastewaters in acidic or basic media through direct chemical oxidation (DCO) [7]. However, since the reactions of peroxydisulfate are generally slow at normal temperature, the thermal or photochemical activated decomposition of $S_2O_8^{2-}$ ion to $SO_4^{\bullet-}$ radical has been proposed as a method of accelerating the process [8,9], as summarized in the following reactions (equations 1-5):

$$S_2O_8^{2-} + \text{photons or heat} \rightarrow 2\,SO_4^{\bullet-} \quad (1)$$

$$SO_4^{\bullet-} + RH_2 \rightarrow SO_4^{2-} + H+ + RH^{\bullet} \quad (2)$$

$$RH^{\bullet} + S_2O_8^{2-} \rightarrow R + SO_4^{2-} + H^{+} + SO_4^{\bullet-} \quad (3)$$

$$SO_4^{\bullet-} + RH \rightarrow R^{\bullet} + SO_4^{2-} + H^{+} \quad (4)$$

$$2\,R^{\bullet} \rightarrow RR\ (\text{dimer}) \quad (5)$$

Therefore, the potential use of photoactivated peroxydisulfate at ambient temperature is of interest, but more study will be needed to better understand the kinetic model, effects of some inorganic additives on the decolorization and the underlying mechanisms.

Methyl Orange is a water-soluble azo dye, which is widely used in the textile, printing, paper manufacturing, pharmaceutical, food industries, and also in research laboratories. Like many other dyes of its class Methyl Orange on inadvertently entering the body through ingestion, metabolizes into aromatic amines by intestinal microorganisms. Reductive enzymes in the liver can also catalyze the reductive cleavage of the azo linkage to produce aromatic amines and can even lead to intestinal cancer [10,11]. The toxic nature of the dye is still not quantified much but its high content in living systems can prove to be harmful. Thus, the safe removal of such a dye is the primary aim of our present research. In the present paper, MO was chosen as the model azo dye.

In this paper, study on photocatalytic decolorization of MO with KPS was investigated. It was noted here that besides the understanding of the role of photocatalyst, considerations must be paid on the nature of the photocatalyst.

2. Experimental Procedures

2.1. Materials and instruments

KPS was of chemical grade and MO was of analytical grade, both were purchased from Chendu Kelong Chemical Reagents Factory and used as received.

A GBC UV/Vis 916 spectrophotometer, beaker with 100 mL volume and a 30 W medical violet lamp (Philips, with maximum emission at 254 nm) were used in the experiments. Water used in the experiments was deionized.

2.2. Procedures

Beaker with 100 mL volume (φ=5.4 cm) was used as the reactor. A 100 mL MO solution containing 50 mg KPS was introduced into the reactor each time in the dark room. Then the mixture was put under the UV illumination at a distance of 15 cm while being stirred continuously to keep it uniform. Samples were withdrawn at specific time intervals. Changes in the concentration of MO were measured by the spectrophotometer.The decolorization reaction was carried out at room temperature.

3. Results and Discussion

3.1. Blank experiments

The contrast experiments were carried out in two conditions: one with KPS but no illumination, the other with illumination but no catalyst. The results under former condition showed that the color of MO solution (6 mg L^{-1}) turned from orange to red immediately after KPS was added to MO solution, which shows that MO has been oxidized, the spectrums of MO are shown in Fig. 1. It is clear that the structure of MO has been changed and the maximum peak shifts from 460 nm to 480 nm after KPS was added to MO solution, while the absorbance at 460 nm and 480 nm are the same, which indicates that degradation of MO in the presence of KPS without illumination is direct chemical oxidation (DCO) of the substrate by peroxydisulfate ions. The result further shows that MO (6 mg L^{-1}) can be totally decolorized after 10h in the presence of KPS without illumination. While under the latter condition, the concentration of MO solutions (6 mg L^{-1}) changed so little that it could be ignored (during 10 h period), proving the stability of MO.

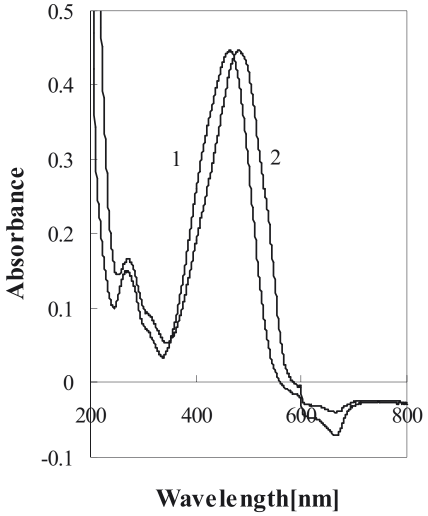

Figure 1. UV-vis spectrum of MO (1) initial MO (2)MO+$K_2S_2O_8$.

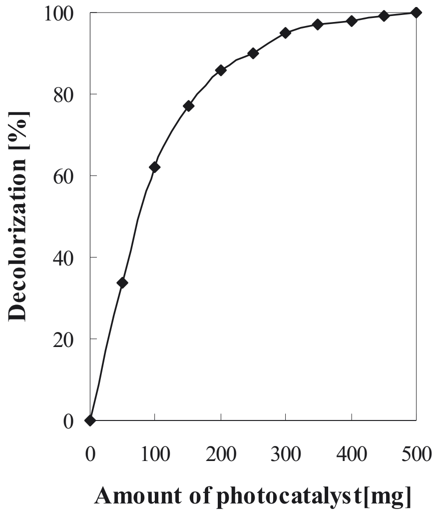

Figure 2. Effect of photocatalyst on decolorization efficiency.

3.2. Effect of amount of the photocatalyst

The initial concentration of MO solution was 10 mg L^{-1} and the reaction time was 20 min. The effect of amount of photocatalyst on the decolorization was shown in Fig. 2. The result indicates that the decolorization of MO increases with the increasing of the dosage of the catalyst. When the dosage of the catalyst is 5 g L^{-1}, the decolorization of MO is up to 100%. This result illustrates that there is no optimal amount of catalyst in our case, this result is not the same as the results reported by Zhu *et al.* [12,13] in dealing with dyes using phosphotungstic acid as photocatalysts. It is plausible that this difference is caused by the nature of the photocatalyst itself (note that phosphotungstic acid has a limited solubility in water), where special attention was paid on the nature of the photocatalyst itself.

In order to investigate the kinetics for various concentrations, the dosage of the catalyst in our case is 500 mg L^{-1}.

3.3. Kinetics on the decolorization of MO

In general, for TiO_2 heterogeneous reaction system, the kinetics would follow the Langmuir-Hinshelwood (L-H) model [14-17]. Mylonas [18] and Turchi [19] reported that the kinetics also follow the L-H model for homogeneous reaction systems whose degradation mechanisms involve hydroxyl radical attack.

$$r = -\frac{dCt}{dt} = \frac{kKCt}{1+KCt} \qquad (6)$$

Where *r* is photocatalytic degradation rate; *k* is L–H rate constant; *K* is the Langmuir adsorption constant of the MO in the photocatalytic degradation reaction; and C_t is the concentration of the MO under study.

Fig. 3 and Fig. 4 show information on the kinetics of photocatalytic decolorization for eight various concentrations under identical conditions. Fig. 3 is a plot of normalized concentrations versus irradiation time for MO at three high initial concentrations (≥100 mg L^{-1}), it is clear that C_t vs. *t* is in linear form, which shows that the decolorization rates fit a zero-order model well, that is the $C_t = C_0 - k_0 t$ describes the tendency well, where C_0 and C_t are the concentration of MO at time *0* and *t*, respectively, and k_0 is the observed zero-order rate constant. Fig. 4 is a plot of normalized concentrations versus irradiation time for MO at five low initial concentrations (≤20 mg L^{-1}). The decolorization rates fit a first-order model well, that is, the integral equation of $ln(C_0/C_t) = K_{obs}t$ describes the tendency well, where C_0 and C_t are the concentration of MO at time *0* and *t*, respectively, and K_{obs} is the observed pseudo first-order rate constant. The slope of a liner plot of $ln(C_0/C_t)$ versus *t* gives the apparent decolorization rate constant. To make the further mathematic inferences clear, all the relating kinetic parameters, such as the reaction rate constants (K_{obs}), half-life ($t_{0.5}$), and interrelated coefficients (R^2) of the lines in Fig. 3 and Fig. 4, are all presented in Table 1. It is clear that the rate constant is inversely proportional to the initial concentration of MO to the limit of 20 mg L^{-1}. The decrease of k_{obs} as increasing the initial MO concentration indicates that there is a competition between the instantaneous intermediates and MO for the oxidant.

To further investigate the effect of the initial concentration on the reaction rate constants, suppose: $K_{obs} = aC_0^n$, where *a* is a constant and *n* is the exponent of the initial concentration. The relationship between K_{obs} and C_0 is shown in Fig. 5. The values of *a* and *n* are 0.2994 and -1.2123, respectively.

It is clear that the apparent reaction rate constant reduces along with increasing the initial concentration.

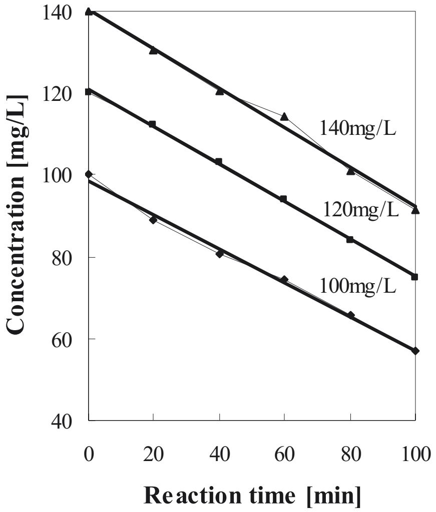

Figure 3. Plot of photocatalytic decolorization of MO vs. irradiation time.

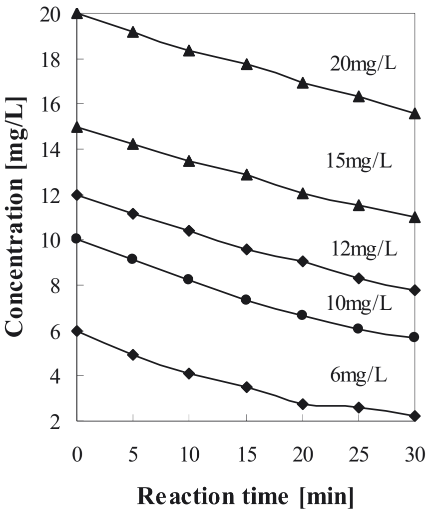

Figure 4. Plot of photocatalytic decolorization of MO vs. irradiation time.

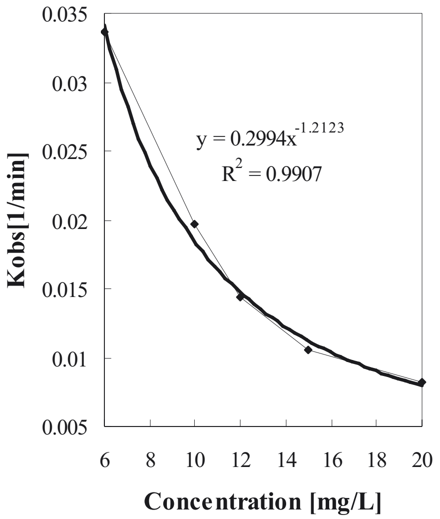

Figure 5. The relationship between K_{obs} and C_0.

Table 1. Kinetic parameter for different initial concentration.

C_0 (mg L^{-1})	rate constant	$t_{0.5}$ (min)	r_0 (mg L^{-1} min^{-1})	R^2
6	0.0336 min^{-1}	20.63	0.2016	0.9911
10	0.0197 min^{-1}	35.19	0.1970	0.9949
12	0.0144 min^{-1}	48.14	0.1728	0.9994
15	0.0105 min^{-1}	66.01	0.1575	0.9981
20	0.0082 min^{-1}	84.53	0.1640	0.9991
100	0.4149 mg L^{-1}min^{-1}	118.81	0.4149	0.9950
120	0.4543 mg L^{-1}min^{-1}	132.85	0.4543	0.9991
140	0.4818 mg L^{-1}min^{-1}	145.65	0.4818	0.9941

In the process of decolorization, the higher initial concentration is, the more intermediates appear, and the stronger negative effects on the apparent reaction rate constant. As to the negative effect of initial concentration, it can be speculated to be caused by the limited dosage of oxidants which is fixed in our case because the intermediates would compete with MO for oxidant. Considering the results above, the adsorption process can be excluded from the rate-determining step; hence the oxidation reaction is probably the rate-determining step.

Owing to the complex mechanism of reactions, it is difficult to develop a model for the dependence of the photocatalytic decolorization rate on the experimental parameters for the whole treatment time. Thus, kinetic modeling of the photocatalytic process is usually restricted to the analysis of the initial rate of photocatalytic decolorization. This can be obtained from the initial slope to the curves and the initial concentration in an experiment in which the variation of the concentration is measured as a function of time. The extrapolation of the photocatalytic degradation rate to time equal to zero avoids the possible interference from by-products. The initial photocatalytic decolorization rate (r_0) is observed to be a function of the initial concentration (C_0). A linear plot of r_0^{-1} vs. C_0^{-1} is often obtained, and that gives k as the L–H rate constant and K as the Langmuir adsorption constant of the MO in the photocatalytic decolorization reaction [14,16].

$$r_0 = \frac{kKc_0}{1+Kc_0} \tag{7}$$

The equation is further expressed in a linear form:

$$\frac{1}{r_0} = \frac{1}{kKc_0} + \frac{1}{k} \tag{8}$$

In order to find the effect of initial concentration on the photocatalytic decolorization, more detailed analysis was fulfilled based on the kinetics of photocatalytic decolorization. The linear relationship between initial rate r_0^{-1} and the initial concentration C_0^{-1} for photocatalytic decolorization of MO is r_0^{-1} = -11.561C_0^{-1}+6.7332 (R^2=0.7169) using linear least squares analysis (see Fig. 6). It is clear that the experimental data do not abide by the L-H model thus confirming the photocatalytic decolorization reaction mechanism is not based on hydroxyl radical attack in one way.

3.4 Effect of H_2O_2

Adding other powerful oxidizing species to TiO_2 suspension is a routine procedure and often leads to an increase of the rate of the degradation. When initial concentration of MO is 10 mg/L, reaction time is 20 min, the effect of H_2O_2 on the photocatalytic decolorization of MO was shown in Fig. 7.

As shown in Fig. 7, the optimal amount of H_2O_2 is around 1.5 g L^{-1}. The photocatalytic decolorization efficiency increases with the dosage of H_2O_2 at first; then the curve drops sharply at 4.50 g L^{-1}. When the amount of H_2O_2 exceeds a proper value (here, 1.5 g L^{-1}),

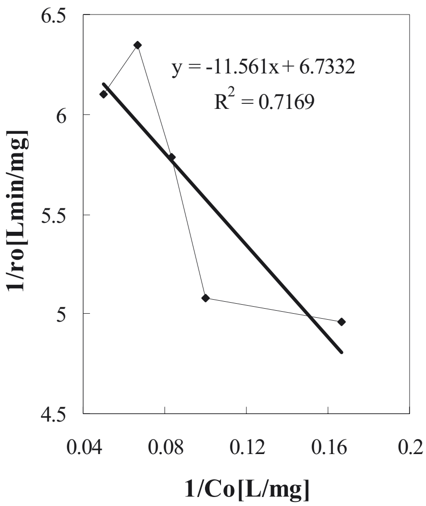

Figure 6. The linear transformation of $1/r_0$ vs. $1/C_0$.

the decolorization efficiency is reduced.

The presence of H_2O_2, on one hand, contributes to the amount of $^{\bullet}OH$ radicals [20-23]:

$$H_2O_2 + h\upsilon \xrightarrow{\lambda<380nm} 2HO^{\bullet} \quad (9)$$

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet} \quad (10)$$

$$HO_2^{\bullet} + H_2O_2 \longrightarrow H_2O + O_2 + {}^{\bullet}OH \quad (11)$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (12)$$

on the other hand it acts as a hole to recombine ·OH when concentration of H_2O_2 is too high, which are detrimental to the photocatalytic degradation[24].

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (13)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (14)$$

So adding is a tricky factor in the photodegradation as discussed above. Theoretically, the optimal amount of H_2O_2 should be just the value fit for the degradation. In our case, with the help of H_2O_2 (1.5 g L^{-1}), the degradation of 10 mg L^{-1} MO is accelerated (see Fig. 8),the first-order rate constants of two processes are 0.0197 min^{-1}, 0.0295 min^{-1}, respectively. The difference is obvious, compared with the system without H_2O_2, the first-order rate constant has increased 49.75%. It is clear that the increase in decolorization rate is caused by the presence of H_2O_2. Fig. 8 also illustrates that the change of the concentration of the MO keeps following a logarithmic tendency as the irradiation time elapses. It still abides by a pseudo first-order reaction model, which further confirms that the hydrogen peroxide accelerates the reaction rate by providing a proper amount of $^{\bullet}OH$ radicals for the degradation reaction without affecting the rate-determining step; therefore it cannot alter the kinetic model of the reaction as demonstrated by the experiments.

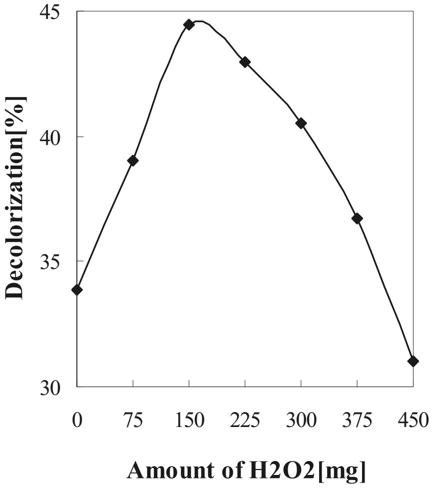

Figure 7. Effect of H_2O_2 on photocatalytic decolorization.

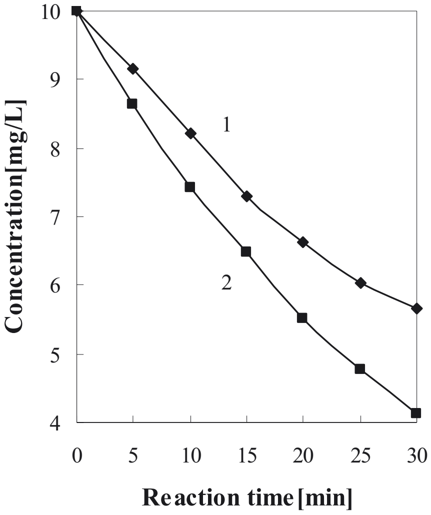

Figure 8. The promotion effect of hydrogen peroxide on the photocatalytic decolorization (1)KPS (2) KPS+H_2O_2.

3.5 Effect of IO_4^- and BrO_3^-

The inorganic oxidants such as KIO_4, $KBrO_3$, can also be used as additives to enhance the photocatalytic degradation rates of organic substrates [25]. The influence of the inorganic additives must be accurately checked before their application since they may exhibit negative effect depending on experimental parameters. The concentration of MO was 10 mg L^{-1}, when other conditions were fixed, the effect of 50 mg KIO_4 and 50 mg $KBrO_3$ on the photocatalytic decolorization was shown in Fig. 9.

As illustrated by the Fig. 9, the photocatalytic decolorization is greatly promoted, the first-order rate constants of three processes are 0.0102 min^{-1} (K_{obs1}), 0.0308 min^{-1}(K_{obs3}), 0.040 min^{-1} (K_{obs4}), and 0.0412 min^{-1}(K_{obs5}), respectively. The result indicates that KPS and IO_4^- have a synergy which leads to the promotion of decolorization rate, but the presence of

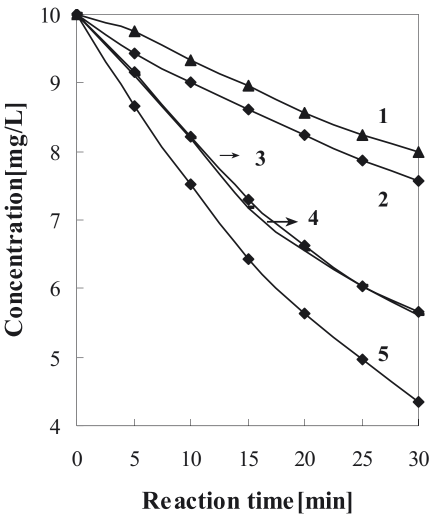

Figure 9. The promotion effect of IO_4^- and BrO_3^- on the photocatalytic decolorization; (1) BrO_3^- (2) KPS (3) IO_4^- (4) IO_4^- + KPS (5) BrO_3^- + KPS.

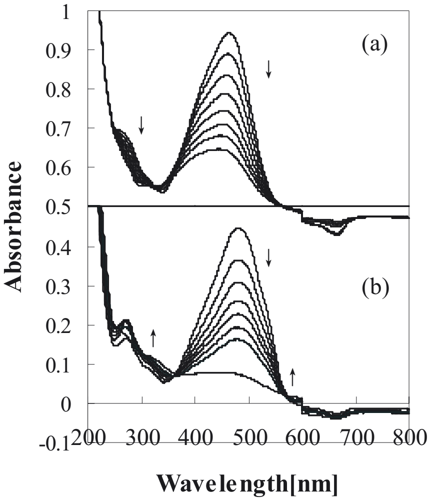

Figure 10. The spectral changes recorded during MO photodegradation by H_2O_2 (a) reaction time of 0, 10, 20, 30, 40, 50, 60, 70 min, respectively and $K_2S_2O_8$ (b) at reaction time of 0, 5, 10, 15, 20, 25, 30, 40, 50 min, respectively.

IO_4^- can not alter the kinetic model of the reaction as demonstrated by the experiments, the photocatalytic decoloration reaction is still pseudo first-order. Furthermore, $K_{obs4}<K_{obs2}+K_{obs3}$,which shows that the synergy between KPS and IO_4^- is not very strong. The result indicates that KPS and BrO_3^- have a synergy which leads to the promotion of decolorization rate, but the presence of BrO_3^- can not alter the kinetic model of the reaction as demonstrated by the experiments, the photocatalytic decoloration reaction is still pseudo first-order. Furthermore, $K_{obs5}>K_{obs1}+K_{obs2}$, which shows that the synergy between KPS and BrO_3^- is very strong. It is notable that the synergy between KPS and BrO_3^- is stronger than that of KPS and IO_4^-. It is plausible that this difference is caused by the nature of the additive itself, but the underlying reason is unclear, more attention should be focused on this question. Based on the results, the photocatalytic ability of the three oxidants used in UV system was found to be in the order of $IO_4^- > S_2O_8^{2-} > BrO_3^-$.

3.6 Comparison of $K_2S_2O_8$ with H_2O_2

Since H_2O_2 is a photocatalyst used widely, its degradation mechanism is known to only involve hydroxyl radical attack, the presence of H_2O_2 contributes to the amount of $^{\bullet}$OH radicals. So H_2O_2 was employed here as a standard for comparison in the degradation mechanism with $K_2S_2O_8$ based on the fact that the two reaction systems are homogeneous reaction systems. The amount of H_2O_2 and $K_2S_2O_8$ were 500 mg L^{-1} and pH of MO solution (6 mg L^{-1}) was 5.64. The intermediates formed from MO photodegradation appear different from that of H_2O_2 (Fig. 10a). In H_2O_2 photocatalysis (Fig. 10a), the intermediates have a broad band in the range of about 324–620 nm, while the products formed from $K_2S_2O_8$ reaction (Fig. 10b) exhibit a broader band in about 357-560 nm and the peak disappears with the irradiation time, while at the same time, the absorbance in the range of about 262–357 nm and 560-600 nm increases with the irradiation time ($K_2S_2O_8$ absorption at $\lambda<246$ nm overlaps with MO). These facts illustrate that the degradation mechanism of MO with $K_2S_2O_8$ is greatly different from that of MO with H_2O_2. This indicates that the degradation of MO with $K_2S_2O_8$ is not the attack of radical attack in one way, this result is in good agreement with the kinetics.

In order to understand the mechanism, the possible involvement of hydroxyl radicals as the main reactive species for MO degradation was then examined (MO:10 mg/L). When the •OH scavenger ethanol [12] (99.9%, 1 mL) and methanol [26] (99.9%, 1 mL) were added, the reaction rate was decreased greatly(the decolorization efficiency decreased from 33.8% to 24.4%,20.1% respectively after 30 min), the primary alcohol present may consume the excited $SO_4^{\bullet-}$ by hydrogen attraction, the evidence obtained here can not support that the $^{\bullet}$OH radicals are involved in the degradation of MO by $S_2O_8^{2-}$ photocatalysis.

The increased reaction rate was observed (Fig. 11) in the presence of other •OH scavengers, sodium bromide [27], but it is not clear how to explain why the sodium bromide can promote the photocatalytic decolorization of $K_2S_2O_8$. It is plausible that the promotion of the reaction rate is associated with the photocatalytic mechanism of $K_2S_2O_8$, and a more detailed mechanism needs to be further investigated in the near future. In addition, the

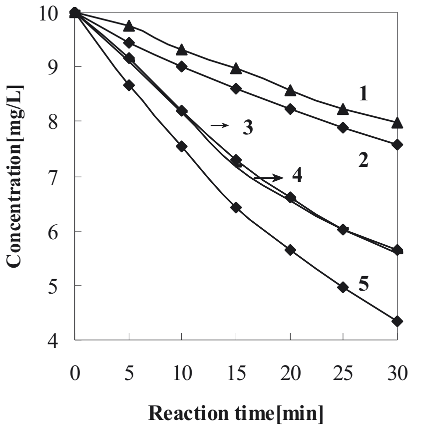

Figure 11. Photocatalytic degradation of MO by $K_2S_2O_8$ (1) $K_2S_2O_8$+methanol (1% by volume) (2) $K_2S_2O_8$+ ethanol (1% by volume) (3) $K_2S_2O_8$ (4) $K_2S_2O_8$+Na_2SO_4 (100 mg) (5) $K_2S_2O_8$+KBr (100 mg).

presence of other $^{\bullet}OH$ scavengers, sodium sulfate [28] has no influence on the decolorization reaction. The evidence obtained here supports that the $^{\bullet}OH$ radicals are not involved in the degradation of MO by $K_2S_2O_8$ photocatalysis. The result here and the result of the kinetics illustrate that the $^{\bullet}OH$ radicals are not involved in the degradation of MO by $K_2S_2O_8$ photocatalysis.

Because of some difference between H_2O_2 and $K_2S_2O_8$, based on the results and the references, it is plausible that the underlying mechanisms are direct oxidation of the MO by $S_2O_8^{2-}$ and hydrogen attraction by $SO_4^{\bullet-}$.

4. Conclusions

This report has shown that the textile dye of MO in water can be degraded by UV irradiation in the presence of $K_2S_2O_8$. For this reaction, decolorization of MO increases with the increasing of the dosage of the catalyst, there is no optimal amount of catalyst in our case. The work revealed that the decolorization reaction was a pseudo first-order reaction when the concentration of MO is below 20 mg L^{-1} and the decolorization reaction was zero-order reaction when the concentration of MO is above 100 mg L^{-1}, but Langmuir–Hinshewood kinetic model can not describe it. IO_4^-, BrO_3^- and H_2O_2 can greatly promote the photocatalytic decolorization of MO. Several observations indicate that the mechanism is not involved in hydroxyl radical attacks in MO degradation with $K_2S_2O_8$ by UV irradiation. The possible underlying mechanisms are direct oxidation of the MO by $S_2O_8^{2-}$ and hydrogen attraction by $SO_4^{\bullet-}$.

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