Oxidation of Methyl Orange Solution with Potassium Peroxydisulfate

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ABSTRACT: *Oxidation of Methyl Orange (MO) solution in potassium peroxydisulfate (KPS) homogeneous reaction system without UV irradiation was investigated. The result shows that decolorization of MO increases as the dosage of* $K_2S_2O_8$ *increases. The kinetic results demonstrate that the decolorization reaction is a pseudo first-order reaction when the concentration of MO is below 10 mg/L and Langmuir–Hinshewood kinetic model (L-H) can well described it, the value of Ea is 19.5 kJ/mol. The decolorization efficiency is low when the pH value is low (≤2). Result of CODCr shows MO can be effectively mineralized with KPS direct oxidation. The knowledge on the kinetics of the system and influence of some parameters on the system possesses both practical and theoretical values.*

KEY WORDS: *Potassium peroxydisulfate, Oxidation decolorization, Methyl orange; Kinetics, Wastewater.*

INTRODUCTION

Dyes are widely used in many industries. Some dyes are non-biodegradable, so it is difficult to remove them from the water environment. Studies have proven that most of them are toxic [1, 2]. Moreover, these dyes can not be effectively treated by the conventional wastewater treatment method in nowadays [3, 4]. Therefore, it is imperative to control the employment of these dyes and treat the effluents before being released into the aquatic environment [5].

Peroxydisulfate ($S_2O_8^{2-}$ ion) is a strong oxidant (E° =2.05V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator [6]. It has also been reported potassium peroxydisulfate (KPS) is effective for degrading organics in hazardous wastewaters in acidic or basic media through Direct Chemical Oxidation (DCO) [6]. Therefore, the potential use of peroxydisulfate at ambient temperature is of interest, but more study will be needed to better understand this process.

In this paper, study on direct oxidation of Methyl Orange (MO) with KPS was investigated. Kinetic study on oxidation of MO with KPS was investigated and the initial reaction rate and its relating factors were emphasized. Efforts were paid to draw conclusions on the apparent kinetic model, effects of initial concentration, pH and amount of oxidant.

EXPERIMENTAL SECTION

Materials and instruments

KPS was of chemical pure and MO was of analytical grade, were purchased from Cheng du Ke Long Chemical Reagents Factory and used as received. Other reagents

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were of analytical grade and were obtained from Cheng du Ke Long Chemical Reagents Factory and used as received. Deionized water was used throughout the experiments.

A closed Beaker with 100 mL volume (φ=5.4cm) was used as the reactor. A TU-1901 UV/Vis spectrophotometer was used in the experiments.

Procedures

A 100 mL MO solution containing KPS was introduced into the reactor each time in the dark room. Then the mixture was stirred continuously to keep it uniform. Samples were withdrawn at specific time intervals. Changes in the concentration of MO were measured by the spectrophotometer using Lambert-Beer law. The decolorization reaction was carried out at 300 K. To investigate the effect of pH on the decolorization efficiency, the pH value was adjusted with $HClO_4$ (0.1 mol/L) and sodium hydroxide (0.1 mol/L) solution. Before the measurement of COD_{Cr}, the reaction solution was boiled for 30 seconds to remove KPS.

In this paper, the decolorization efficiency was calculated by $(C_0-C)/C_0$, where C is the concentration of the MO after oxidation, C_0 is the initial concentration of MO before the oxidation.

RESULTS AND DISCUSSION

Direct oxidation of MO with KPS

The color of MO solution (10 mg/L) turns from orange to red immediately after KPS was added to MO solution, which indicates that MO has been oxidized. The spectra of MO demonstrates that the structure of MO has been changed and the maximum peak shifts from 460 nm to 475 nm after KPS was added to MO solution, which demonstrates that change of MO in the presence of KPS is Direct Chemical Oxidation (DCO) of the substrate by peroxydisulfate ions.

Effect of amount of the oxidant

The effect of amount of oxidant on the decolorization is shown in Fig. 1. The result indicates that the decolorization of MO increases as the dosage of the oxidant increases, when the dosage of catalyst is 400 mg in the reaction system, the decolorization of MO is up to 44%. In order to investigate the kinetics for various low concentrations, the dosage of the catalyst in our case is 50 mg.

Table 1: Kinetic parameter for different initial concentration

C_0 (mgL^{-1})	K(min^{-1})	$t_{1/2}$(min)	R^2
2	0.0119	58.2477	0.9958
4	0.0107	64.7801	0.9993
6	0.0104	66.6488	0.9970
8	0.0099	70.0149	0.9978
10	0.0096	72.2028	0.9975

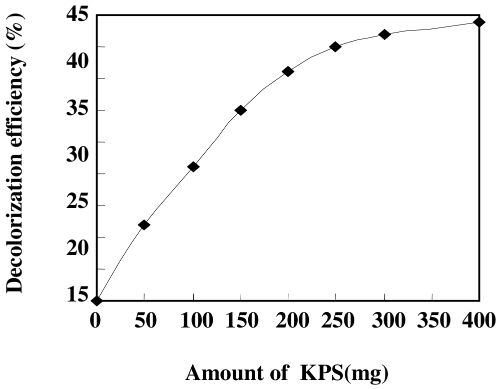

Fig. 1: Effect of amount of KPS on decolorization efficiency. the initial concentration of MO solution was 10 mgL^{-1} ; the reaction was 20 mins; the volume of the solution was 100 mL; pH of the solution was 7.0.

Kinetics on the decolorization of MO

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, K_{obs} is the observed pseudo first-order rate constant and t is the reaction time. To make the further mathematic inferences clear, all the relating kinetic parameters for MO at five low initial concentrations (≤10 mg/L) are presented in Table 1. It is clear that the rate constant is inversely proportional to the initial concentration of MO to the limit of 10 mg/L. The decrease of k_{obs} as increasing the initial MO concentration indicates that there is a competition between the instantaneous intermediates and MO for $S_2O_8^{2-}$ ion.

In order to find the effect of initial concentration on the decolorization, more detailed analysis was fulfilled based on the kinetics of decolorization. Fig. 2 shows plot of the reciprocal of the initial rate r_0^{-1} versus the reciprocal of the initial concentration C_0^{-1} for decolorization of MO.

The kinetic parameters k and K were obtained using linear least squares analysis. The value of k and K are 0.3450 mg/L min and 0.03678 L/mg, respectively. It is clear that a good fitting of the model to the experimental data may be observed thus confirming the L-H nature of the decolorization reaction mechanism.

A linear plot of lnK vs T^{-1} is often obtained, and that gives Ea of the MO in the decolorization reaction with KPS. Fig. 3 shows plot of the reciprocal of lnK versus the reciprocal of the reaction temperature. Ea was obtained using linear least squares analysis. The value of Ea is 19.5 kJ/mol.

Effect of pH on the reaction rate constant of MO

pH value is the most important parameters for the oxidation process and so it has long been of a focus to study its influence on decolorization efficiency. When the concentration of MO solution (10 mg/L) and other optimum conditions were fixed, the pH value of the mixed solution was adjusted by $HClO_4$ (0.1 mol/L) and sodium hydroxide (0.1 mo/L) solution. The effect of pH value on decolorization efficiency is shown in Fig. 4. As shown in Fig.4, the decolorization efficiency increases with the pH value at first; then the curve shows a plateau.

The structre and the concentration of oxidant all play an important role in oxidation reaction, as a whole the decolorization efficiency increases with the pH value at first; then the curve shows a plateau.

Removal of COD

When the concentration of MO solution (10 mg/L) and other conditions were fixed, the effect of reaction time on the decolorization efficiency (DC) and removal of chemical oxygen demand ($DCOD_{Cr}$) was shown in Table 2.

As shown in Table 2, it is presumed that the aromatic ring in MO molecular has been destructed in some degree, so a portion of MO has been mineralized. At the same time, the speed of removal of chemical oxygen demand is slower than that of decolorization efficiency. It is reasonable to explain this result. In MO molecular, the azo bonds (-N =N-) is the chromophore, once the azo bonds is destructed, then MO has been decolorizated, which mean the speed of removal of chemical oxygen demand is so slower than that of decolorization efficiency. This result further indicates that MO can be totally mineralized along with the reaction time.

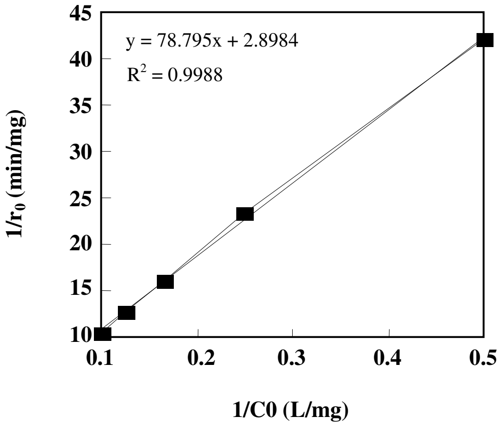

Fig. 2: The linear transformation of $1/r_0$ vs. $1/C_0$.

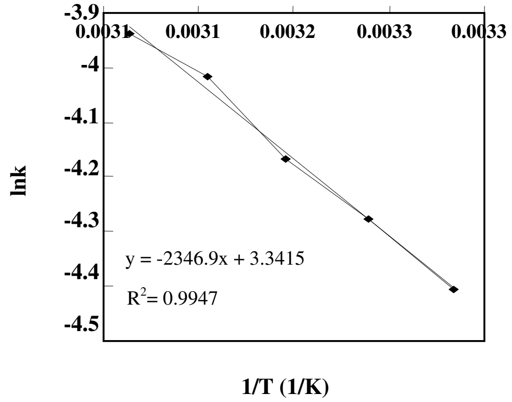

Fig. 3: The relationship between lnK and T^{-1}.

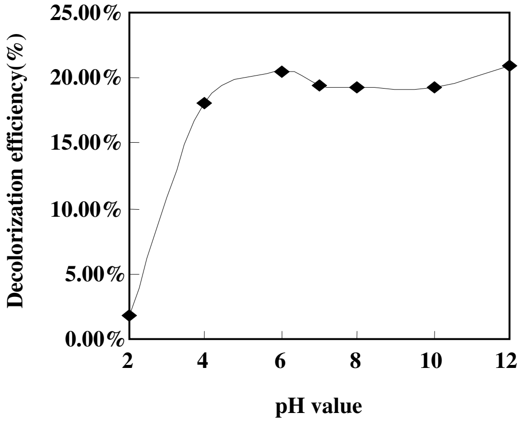

Fig. 4: Effect of pH value on decolorization efficiency; the initial concentration of MO solution was 10 mg/L; the reaction was 20 mins; the volume of the solution was 100 mL; pH was adjusted with $HClO_4$ and NaOH.

CONCLUSIONS

The paper reveals that MO can be effectively decolorized with $K_2S_2O_8$ direct oxidation. The result shows that decolorization of MO increases as the dosage of $K_2S_2O_8$ increases. The kinetic results demonstrate that the decolorization reaction is a pseudo first-order reaction when the concentration of MO is below 10 mg/L and Langmuir-Hinshewood kinetic model (L-H) can well described it, the value of Ea is 19.5 kJ/mol. The decolorization efficiency is low when the pH value is low (≤ 2), however more detailed reason needs to be further investigated in the near future. Results of COD_{Cr} shows MO can be effectively mineralized with $K_2S_2O_8$ direct oxidation

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Abbreviations

MO	Methyl orange
KPS	Potassium peroxydisulfate
L-H	Langmuir-Hinshelwood
DC	Decolorization efficiency
$DCOD_{Cr}$	Removal of chemical oxygen demand using potassium dichromate oxidation

Nomenclature

C_0	Initial concentration of MO, mg/L
C_t	Concentration of MO at moment t, mg/L
t	Reaction time, min
K_{obs}	The observed pseudo first-order rate constant, 1/min
k	L-H rate constant, mg/Lmin
K	Langmuir adsorption constant, L/mg

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