Photocatalytic Decolorization of Methyl Orange Solution with Phosphotungstic Acid

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ABSTRACT: *Photocatalytic decolorization of Methyl Orange (MO) solution has been studied using phosphotungstic acid (HPA) as photocatalyst. The decolorization reaction of MO solution is photocatalysis. The paper reveals that the optimal loading of photocatalyst for decolorization of MO solution (10 mg/L) is 0.6 g/L. The results show that the photocatalytic decolorization reaction of MO with HPA in a homogenous solution can be described by Langmuir-Hinshelwood equation; the results manifest that the reaction is first order with lower concentration, the limiting rate constant and the adsorption constant in this case are 0.3378 mg/(Lmin) and 0.5988 L/mg, respectively. The effect of pH value on the decolorization efficiency was also demonstrated, where special attention was paid on the nature of photocatalyst itself. Several observations indicate that only hydroxyl radicals participate the photocatalytic decolorization of MO with HPA under UV irradiation.*

KEY WORDS: *Phosphotungstic acid, Photocatalytic decolorization, Methyl orange; Kinetics, Wastewater treatment.*

INTRODUCTION

Organic dyes used in textile and food industries are important sources of the environmental contaminations due to their non-biodegradability and high toxicity to aquatic creatures and carcinogenic effects on humans [1, 2]. Hence, it is crucial to remove these dyes from colored effluents [3].

Conventional chemical and physical discoloration processes can not be utilized to treat effectively all these dyes [4-6]. Therefore, the interest in developing processes which can destroy these dyes effectively has been a hotspot recently. Photocatalysis by solid transition-metal oxygen anion clusters (PolyOxoMetalate (POM) is a new branch in photocatalytic chemistry, and some exciting research progresses have been achieved in recent years. In fact, many of POMs share same photochemical characteristics as the semiconduct photocatalysts, and POMs represent the analogues of semiconductor metal oxides [7-9]. The photocatalytic performance of POMs has been investigted extensively in homogeneous systems [8-17]. However, knowledge on kinetics and photocatalytic mechanism of POMs have been seldom concerned compared with semiconductor photocatalysts.

Methyl Orange (MO) is a water-soluble azo dye and widely used in many industries [18]. Methyl orange can enter the body through ingestion and metabolize into aromatic amines, which can lead to intestinal cancer [19].

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Thus, the safe removal of MO is the prime aim of our present research. In the present paper, MO was chosen as the model azo dye.

In this paper, photocatalytic decolorization of MO with phosphotungstic acid ($H_3PW_{12}O_{40}$: HPA) was investigated. The aim of this study is to study the apparent kinetic model and photocatalytic mechanism of HPA as well as the effects of different experimental parameters on the photocatalytic decolorization reaction. It was noted here that besides the understanding of the role of photocatalyst, considerations must be paid on the nature of the photocatalyst.

EXPERIMENTAL SECTION

Materials and instruments

All reagents were supplied from Cheng du Ke Long Chemical Reagent Factory and used as received. The concentration of H_2O_2 was 30 wt%. The studies were done using double distilled water and reagents of A.R grade. Water used in the experiments was fully aerated by oxygen (DO is 8.6 mg/L).

A TU-1901 UV/Vis spectrophotometer, a quartz beaker (inner diameter=5.4 cm) and a 30W medical ultraviolet lamp (Philips, with maximum emission at 254 nm) were used in the experiments.

Photochemical procedures

A quartz beaker was used as the reactor, and placed in a thermostated water bath. A 100 mL MO solution containing HPA or H_2O_2 was introduced into the reactor each time in the dark room. Then the mixture was put under the UV illumination, the distance from the lamp to the solution was 7 cm, the intensity of UV- irradiation was 950 μw/cm^2. The reaction solution was magnetic stirred continuously to keep it uniform (see Fig. 1). At regular intervals, samples were withdrawn for analysis. The concentration of MO was measured through the spectrophotometer at 510 nm (pH<3.4) or 460 nm (pH>3.4) using Lambert-Beer law. To investigate the influence of pH value on the decolorization efficiency, the pH value was adjusted with $HClO_4$ (0.1 mol/L) and sodium hydroxide (0.1 mol/L) solution.

The contrast experiments were carried out in two conditions: one with HPA but no illumination(I), the other with illumination 1h but no catalyst(II).

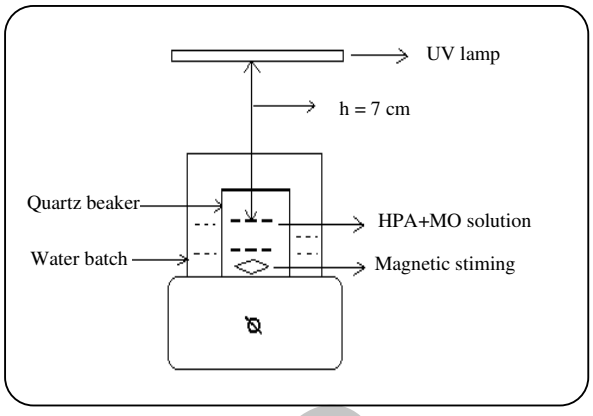

Fig.1: Schematic diagram of the batch photocatalytic reactor.

Hydroxyl radical scavenger (methanol: 4% by volume, ethanol: 3% by volume, t-BuOH: 1% by volume, NaBr:1 g/L) was added into the reaction solution separately, then the mixture was irradiated as the procedure mentioned above.

The decolorization reaction was carried out at 298K.

In this paper, the decolorization efficiency was calculated by $(C_0\text{-}C)/C_0$, where C is the concentration of the MO after irradiation, C_0 the initial concentration of MO before the irradiation in the presence of HPA.

RESULTS AND DISCUSSION

Blank experiments

The results show that the concentration of MO solution (10 mg/L) keeps the same under condition I during 20 days time period, indicating that HPA can not decolorize MO directly without UV irradiation. The concentration change of MO is 2.0% (the rate constant of photolysis is 0.0004 min^{-1}) under condition II, but compared with the declorization efficiency (79.0%) by photocatalysis with 0.6 g/L HPA, the change of concentration due to photolysis is so small that could be ignored. The results of blank tests indicate that decolorization of MO with HPA is mainly photocatalysis.

Effect of the amount of the photocatalyst

The effect of amount of HPA on decolorization efficiency is shown in Fig. 2. The result indicates that the optimal loading of HPA is around 0.6 g/L. Since more HPA leads to more reactive species, the photocatalytic decolorization efficiency increases as the dosage of HPA increases at first; then the curve drops at 0.7 g/L.

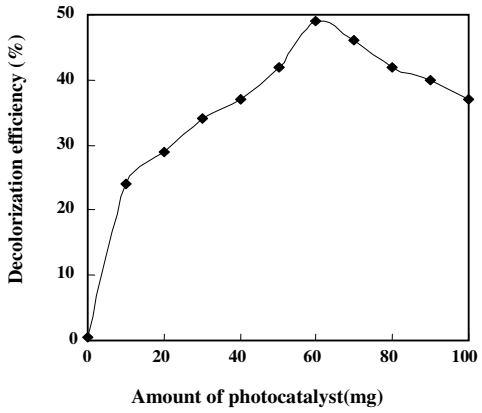

Fig. 2: Effect of photocatalyst amount on decolorization efficiency; the initial concentration of the MO solution was 10 mg/L; the reaction time was 30 mins; the volume of solution was 100 mL; pH was adjusted at 2.0 with $HClO_4$ and NaOH.

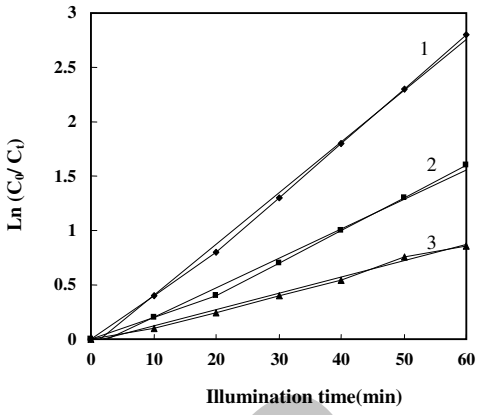

Fig. 3: $Ln(C_0/C_t)$ vs. illumination time. Initial concentration of MO (1) 5 mg/L; (2) 10 mg/L; (3) 20 mg/L; the concentration of HPA was 0.6 g/L; the volume of solution was 100 mL; pH was adjusted at 2.0 with $HClO_4$ and NaOH.

As to the effect of the amount of HPA on photocatalytic decolorization, it is interesting that there is a maximum amount of HPA, but it is not clear to explain why the decolorization efficiency drops dramatically upon further addition of the catalyst. A similar phenomenon has also been reported and discussed by *Hu & Xu* in dealing with textile dye X3B using HPA as photocatalyst in 2004 [20]. This phenomenon was observed when we dealt with other dyes using HPA as photocatalyst. *Hu & Xu* ascribed this result to the fact that HPA has a limited solubility in water[20], but we think this explanation is not convincible. Under our experimental condition the mass range of HPA is 0∼100 mg, 100 mg HPA can be completely dissolved in 100 mL water, however decolorization efficiency by 100 mg HPA is lower than that of 60 mg HPA. Einaga and *Misono* [21] reported the photocatalytic degradation rate of 4-chlorophenol with HPA was proportional to the catalyst concentration in the optically dilute region and when the catalyst concentration higher than 0.7 mM, the rate was saturated duo to the complete light absorption by catalyst. The results provide substantial evidence that the literature data on effect of the amount of the photocatalyst is circumstantial, depending on substrate and the mode of investigation. So the underlying mechanism remains to be unraveled.

Kinetics on the decolorization of MO

In general, for TiO_2 heterogeneous reaction system, the kinetics would follow the Langmuir-Hinshelwood (L-H) model [22-25]. Some researchers reported that the kinetics also follow the L-H model for homogeneous reaction system [26, 27].

$$r=dC_t/dt=kKC_t/(1+KC_t) \quad (1)$$

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; C_t is the concentration of the MO under study; and t is the reaction time. If $KC_t<<1$, then $r\approx KkC_t$, $\ln(C_0/C_t)= Kkt= k_{obs}t$, thus the reaction is first order kinetics, where $k_{obs} =Kk$, k_{obs} is the observed pseudo first-order rate constant, C_0 and C_t is the the initial concentration of MO and the concentration at time t, respectively.

The logarithmic transforms for concentration versus irradiation time curves are shown in Fig. 3 (MO≤20 mg/L). As shown in Fig. 3, 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. The slope of a liner plot of $\ln(C_0/C_t)$ versus time gives k_{obs}. 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) of the lines in Fig. 3 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. The decrease of k_{obs} with the initial MO concentration increasing indicates that there is a competition between the instantaneous intermediates and MO for reactive species [24]. We believe that two factors

Table 1: Parameter and reaction kinetic equation for different initial concentration.

C_0 (mg/L)	reaction kinetic equation	rate constant	$t_{0.5}$(min)	R^2
5	$\ln(C_0/C_t)$=0.0471t-0.0714	0.0471min^{-1}	16.23	0.9977
10	$\ln(C_0/C_t)$=0.0271t-0.0714	0.0271 min^{-1}	28.21	0.9931
20	$\ln(C_0/C_t)$=0.0150t-0.0350	0.0150 min^{-1}	48.54	0.9931

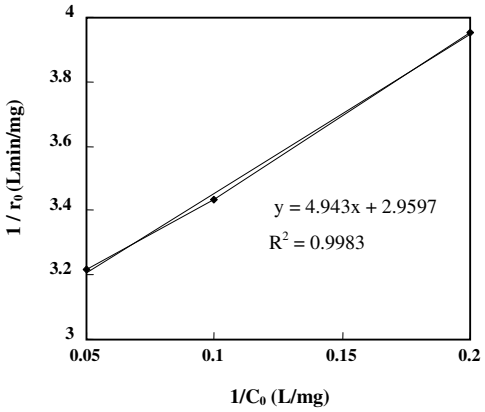

Fig. 4: The linear transformation of $1/r_0$ vs. $1/C_0$.

should be considered, one is that in the process of decolorization higher concentration of MO would produce more intermediates. Intermediates would compete with MO for reactive species. The other is that a rise in MO concentration induces an inner filter effect and hence the solution becomes more and more impermeable to UV radiation [28].

The extrapolation of the photocatalytic degradation rate to time=0 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 degradation reaction [23, 24].

$$\frac{1}{r_0} = \frac{1}{kKc_0} + \frac{1}{k} \qquad (2)$$

In order to ascertain the effect of initial concentration on the photocatalytic decolorization, more detailed analysis was fulfilled based on the kinetics of photocatalytic decolorization. Based on the first order kinetics results: $\ln(C_0/C_t)$=kt+a, where k is kinetic constant, t is reaction time, a is a constant, then C_t= C_0exp(-kt-a), theoreticly, r_0 is equal to C_0kexp(-a). Fig. 4 shows a plot of the reciprocal of the initial rate r_0^{-1} versus the reciprocal of the initial concentration C_0^{-1} for photocatalytic decolorization of MO. The kinetic parameters k and K were obtained using linear least squares analysis. The value of k and K is 0.3378 mg/(L.min) and 0.5988 L/mg, respectively. By substituting the k and K values into Eq. (2), the analytical relationship between r_0 and C_0 is obtained. 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 photocatalytic decolorization reaction mechanism.

Langmuir-Hinshelwood model is a mechanism for surface catalysis in which the reaction occurs between species that are adsorbed on the solid surface for heterogeneous reaction system. *Turchi & Ollis* [27] reported that the reaction which occurs between two species in the fluid phase also follows L-H model, the reaction between ·OH radical and solution–phase molecule in a homogenous system can be described by L-H model, but they did not give a clear explanation on the K (Langmuir adsorption constant in the L-H model).

Some researchers reported that Langmuir-Hinshelwood model can be used to describe the kinetics in the homogenous system. *Ozer & Ferry* [29] reported that photocatalytic oxidation of chlorinated organics with polyoxometalate could be adequately modeled by the Langmuir-Hinshelwood approach, the plot of the initial rate vs the initial concentration yielded K values of 314, 264, and 132 M^{-1} for $H_4SiW_{12}O_{40}$, $HNa_2PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, respectively. However, they did not give a clear explanation on the *K. Hu et al* used L-H model to describe the $(W_7O_{24}^{6-})0$ $rate_0^{-1}$ against $(RCl)_0^{-1}$[30]. They claimed the K value reflects the tendency of precomplexation between $(W_7O_{24}^{6-})$ and organic substrates. Some researchers argued the catalytic effect of phosphotungstic acid on the decomposition of organic compounds is a precomplexation of phosphotungstic acid with organic compounds and subsequent reactions [17, 31].

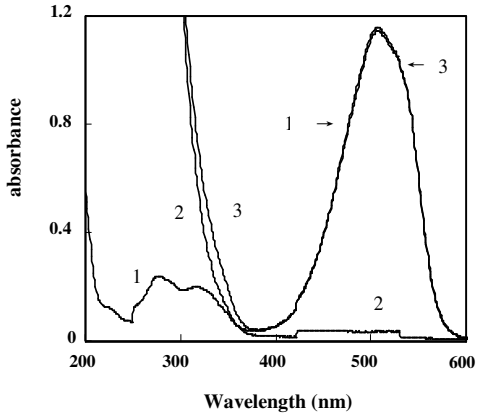

Fig. 5: Spectrum of MO and HPA; (1) MO (pH=2.0); (2) HPA (pH=2.0); (3) MO+HPA (pH=2.0); The concentration of MO was 10 mg/L; the concentration of HPA was 0.6 g/L; the volume of solution was 100 mL; pH was adjusted at 2.0 with $HClO_4$ and NaOH.

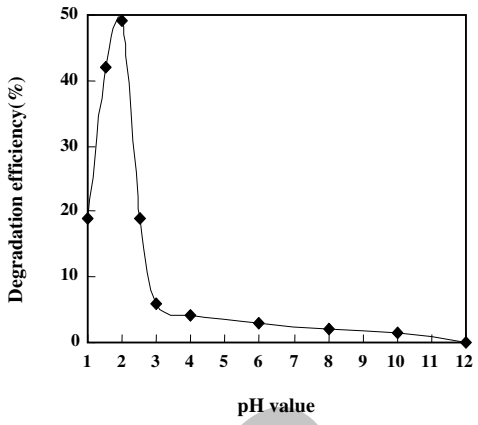

Fig. 6: Effect of pH value on the decolorization efficiency; the concentration of MO solution (10 mg/L); the concentration of HPA was 0.6 g/L; the volume of solution was 100 mL; pH was adjusted by $HClO_4$ and NaOH solution. The reaction time was 30 mins.

Mylonas et al. [32] also observed a precomplexation between POMs and substrate.

Ozer and Co-worker reported that 1,2-dichlorobenzene degradation over TiO_2 with O_2 or POM+O_2 systems can be modeled by the Langmuir-Hinshelwood (saturation kinetics) model [33], but they did not report the precomplexation between POMs and substrate or the value for K in POM+O_2 homogeneous reaction system.

The UV-Vis spectra of MO and HPA are shown in Fig. 5, it is clear that no new absorption appear when MO and HPA co-exist in the solution, from 360 nm~600 nm, the spectrum of MO in the mixed solution(MO and HPA) is almost the same as that of MO, but this result can not exclude exclusively any precomplexation between MO and HPA. Up to now, it is difficult for us to ascertain whether or not the precomplexation between POMs and organic substrates exist, more detailed studies are needed in the near future. If there is a precomplexation between POMs and organic substrates, we think that K also can reflect the tendency of precomplexation between HPA and MO.

Effect of the pH value on the decolorization efficiency

The pH value is one of the most important experimental parameters for the photocatalytic process and so it has long been of a focus to study its influence on decolorization efficiency. As shown in Fig. 6, the decolorization efficiency increases as the pH value increases at first; then the curve drops sharply when pH is above 2.0, while there is a maximum value at about pH =2.0. The stability of HPA in aqueous solution is strongly dependent on pH. When pH =2.5, parts of HPA would transform to $PW_{11}O_{39}^{7-}$. The photocatalytic activity decreases above pH =2.0(pH =2.0~7.0), corresponding to the change of the absorbance of the ligand to metal charge transfer band [21]. When pH is above 7.0, the following reaction would occur, which causes the low decolorization efficiency of MO.

$$H_3PW_{12}O_{40}+27NaOH \rightarrow Na_3PO_4+12Na_2WO_4+15H_2O \quad (3)$$

Photocatalytic mechanism of HPA

In order to comprehend the mechanism, the possible participation of hydroxyl radicals as the main reactive species for MO decolorization was examined (MO:10 mg/L). When hydroxyl radicals scavenger ethanol [20], methanol [34], t-BuOH (t-BuOH is an effective hydroxyl radicals scavenger [35, 36], t-BuOH reacts quickly with hydroxyl radicals with a rate constant of 6.0×10^8 $M^{-1}s^{-1}$ [35]) and sodium bromide [37] were added, the hydroxyl radicals scavengers exert great influence on the decolorization reaction, the decolorization reaction rate constant decreases greatly (k_{obs} drops from 0.0271 min^{-1} to 0.0183 min^{-1},0.01541min^{-1},0.0041 min^{-1} and 0.0004 min^{-1}, respectively) (see Fig. 7). The results obtained here

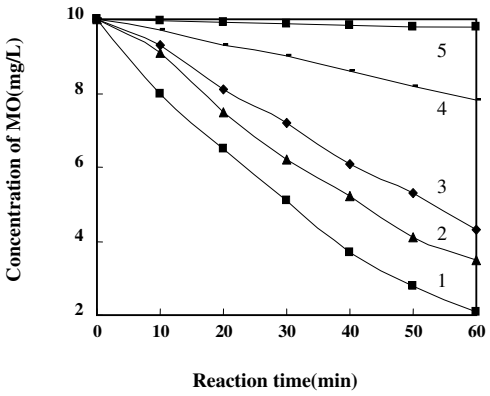

Fig. 7: Effect of ·OH scavengers on the decolorization reaction; (1) HPA; (2) HPA+ methanol (4% by volume); (3) HPA+ ethanol (3% by volume); (4) HPA + t-BuOH (1% by volume); (5) HPA +NaBr (100 mg); the concentration of MO solution (10 mg/L); the concentration of HPA was 0.6 g/L; the volume of solution was 100 mL; pH was adjusted at 2.0 by $HClO_4$ and NaOH.

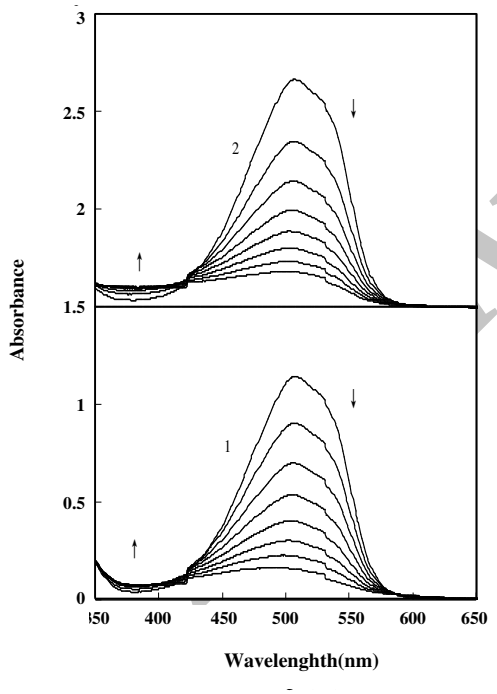

Fig.8: The spectral changes during MO photocatalytic decolorization by HPA (1) at reaction time of 0, 10, 20, 30, 40, 50, 60,70 min, respectively; H_2O_2 (2) at 0, 1.5, 3, 4.5, 6.0, 7.5, 9.0,10.5 min ; the concentration of MO was 10 mg/L; the concentration of HPA was 0.6 g/L; the volume of solution was 100 mL; pH was adjusted at 2.0 by $HClO_4$ and NaOH; the volume of H_2O_2 (30%) was 1.5 mL.

support that the hydroxyl radicals participate the decolorization of MO by HPA photocatalysis.

When sodium bromide was added in to the reaction system, the photocatalytic reaction was totally retarded, the k_{obs} is the same as the rate constant of photolysis (0.0004 min^{-1}), which indicates that the photocatalytic mechanism of MO with HPA is only the attack of hydroxyl radicals. Some researchers reported that one of the photocatalytic mechanisms of POM ($PW_{12}O_{40}^{3-}$) is the direct reaction of the excited POM with substrate [38]. In our case, the direct reaction of the excited $PW_{12}O_{40}^{3-}$ with MO can be excluded, because 100 mg sodium bromide in the phtocatalytic reaction system press the reaction besides the photolysis reaction.

Since H_2O_2 is oxidant used widely and it's oxidation mechanism is only the attack of hydroxyl radicals, H_2O_2 can produce ·OH radicals under UV irradiation [39]. So H_2O_2 was employed here as a standard for comparison the photocatalytic mechanism with HPA, if the photocatalytic mechanism of HPA only concerns hydroxyl radical attack as that of H_2O_2, the spectral changes recorded during MO photocatalytic degradation by H_2O_2 and HPA would follow the same spectral changes. The spectral changes recorded during MO photocatalytic decolorization by H_2O_2 and HPA are shown in Fig. 8.

As shown in Fig. 8, from 423 nm∼580 nm (H_2O_2 and HPA absorption at λ< 350 nm overlap with MO), spectral changes during MO photocatalytic decolorization by H_2O_2 and HPA follow the same spectral changes. No new peaks appear during the photocatalytic decolorization reaction, which indicates that the decolorization mechanism of MO with HPA is only the attack of hydroxyl radical, this result is in good consistent with the result of effect of hydroxyl radical scavengers on the decolorization reaction.

CONCLUSIONS

The paper reveals that the decolorization reaction of MO is photocatalysis and the optimal amount of HPA for decolorization of MO (10mg/L) is 0.6 g/L. The results demonstrate that the decolorization is a pseudo first-order reaction when the concentration of MO is below 20 mg/L and Langmuir–Hinshewood kinetic model describes it well. Mathematical inference shows that the limiting rate constant and the adsorption constant in this case is 0.3378 mg/(L.min) and 0.5988 L/mg, respectively.

The effect of pH value on the decolorization efficiency was also demonstrated, where special attention was paid on the nature of photocatalyst itself. Though there is lack of the direct evidence for hydroxyl radicals participation, several observations indicate that only hydroxyl radicals are involved in photocatalytic decolorization mechanism of MO with HPA under UV irradiation.

Abbreviations

MO	Methyl orange
POM	Polyoxometalate
L-H	Langmuir-Hinshelwood

Nomenclature

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

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