

Photodegradation of Dye Pollutants Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ Treated with H_2O_2 under Simulated Solar Light Irradiation

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Abstract. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ was prepared by a sol-gel method, and sensitized by H_2O_2 solution. Their photocatalytic effects on degradation of organic dyes were investigated under simulated natural light irradiation. Degradation of methyl orange was used as a probe reaction to explore the influencing factors of the photodegradation reaction. After used continuously for five times, the catalytic activity of the photocatalyst is not any lower. The photodegradation of methyl orange, methyl red, methyl violet, rhodamine B, malachite green and methylene blue were also tested, and the degradation rate of dyes can reach 84.6 %~98.3 %. It was found that the photodegradation reaction belongs to the first-order kinetic reaction.

Keywords: Polyoxometalate, SiO_2 , photocatalytic degradation, dye pollutant

1 Introduction

With industrialization and population growth, the problem of environmental pollution caused by organic dyes has become a worldwide problem. Those dyes are often used in textiles, papers, gasoline, additives and cosmetics [1, 2]. Conventional treatment methods, including membrane separation, ultrafiltration, condensation, adsorption, electrolytic, are not enough to degrade completely nontoxic substances [3, 4]. So, the development of high efficiency water treatment technologies to treat the wastewater is desirable. Advanced oxidation processes (AOPs) in organic pollutants degradation have attracted much attention due to their efficient decomposition ability for organic pollutants [5, 6]. Among these AOPs, photocatalytic degradation using semiconductor as catalysts, which has the potential to completely oxidize organic compounds to CO_2 , H_2O and other inorganic substances, has been investigated widely during the past decade [7-9]. Photocatalytic degradation of organic pollutants by TiO_2 has been studied for decades due to high activity, low cost, chemical stability and non-toxicity of TiO_2 [10, 11]. Because of its band gap of 3.2 eV, TiO_2 is activated only by ultraviolet (UV) light (wavelength < 387 nm). Pure TiO_2 can't be effectively activated under solar light irradiation, which limits its practical application, because UV light just accounts for less than 5 % of the solar energy that reaches the surface of the earth [12-14]. In recent years, visible light responsive photocatalysts have been extensively studied. TiO_2 modified systems have been prepared to obtain visible-light reactivity in recent years [15-18]. Polyoxometalates (POMs) have also been recently studied as efficient photocatalysts for the degradation of organic dyes and it indicates that the photocatalytic activity of POMs is comparable to that of the semiconductor TiO_2 [19-21]. When irradiated with light exceeding the HOMO-LUMO energy gap, these compounds generate the electrons and holes. Reactive oxygen species such as OH and O_2^- radicals resulting from the subsequent reaction between holes and OH- groups can effectively degrade organic pollutants [22, 23]. As a representative polyoxometalate, phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) has the highest stability and is considered as an efficient photocatalyst to degradation of textile dyes [10, 22]. Owing to low thermal stability, highly soluble in polar media, the relatively low surface area ($1\text{-}10\text{ m}_2 \cdot \text{g}^{-1}$), and the difficult separation of the product from the resulting mixture, POMs should be loaded on a carrier to improve catalytic efficiency [24-26]. SiO_2 was an ideal carrier because it exhibits higher surface area, chemical inertness, controlled porosity and well disperses POMs while

retaining the structure [27]. POMs/SiO₂ has been prepared by means of a sol-gel technique and used in some organic reactions [27]. Unfortunately, these solids present absorption bands in the region of near-UV light [28]. The use of H₂O₂ as an oxidant is much more desirable from economic and environmental points of view. However, the photodegradation rate of organic dyes in the presence of only H₂O₂ is very low [29, 30]. When added in solution H₂O₂, POMs can be partly converted into peroxides and/or superoxides. These complexes have demonstrated high activity and/or selectivity for the oxidation of organic substrates [31-33].

In this paper, to improve photocatalytic activity, H₃PW₁₂O₄₀/SiO₂ was prepared by a sol-gel technique, and sensitized by H₂O₂ solution. The photocatalytic degradation of organic dyes with the catalyst under simulated natural light irradiation was investigated.

2 Experimental

Synthesis of the catalysts. H₃PW₁₂O₄₀/SiO₂ was synthesized according to reference [28, 34] by a sol-gel method. An amount of H₃PW₁₂O₄₀ was dissolved in 26 ml of H₂O, and 6.3 ml of TEOS was dissolved in 25 ml 1-BuOH. The latter was added dropwise to the aqueous solution. The resultant was stirred at room temperature for 1 h, at 45 °C for 1 h, and then at 80 °C until a uniform gel was formed. The hydrogel obtained was dehydrated slowly at 45 °C for 16 h in a vacuum, and then at 90 °C for 3.5 h. The particulate gel was washed with hot water for several times until the filtrate was neutral, and then the products were calcined before being used. The acetalization of cyclohexanone with 1, 2-propanediol was used as a model reaction to optimize the preparation conditions of catalyst, and the optimum conditions are: the loading of H₃PW₁₂O₄₀ is 30 wt %; calcination temperature is 200 °C and calcination time is 4 h.

H₃PW₁₂O₄₀/SiO₂ was treated by H₂O₂ as follows [35]: 1 g H₃PW₁₂O₄₀/SiO₂ was added into 15 mL 30 % H₂O₂ solution and sonicated for 20 min. The product obtained was filtrated and dried at room temperature. This catalyst is denoted as H₃PW₁₂O₄₀/SiO₂(x).

Characterization. The FT-IR spectra of the samples in KBr matrix was recorded on a Nicolet 5700 FT-IR spectrometer in the range 400~4000 cm⁻¹. The X-ray powder diffraction patterns of the samples were measured by a Bruker AXS D8-Advanced diffractometer (Bruker, Germany) employing Cu K_α radiation. The UV-vis diffuse reflectance spectra (UV-vis/DRS) were recorded on a spectrophotometer equipped with an integrating sphere (Shmadzu UV-2550); BaSO₄ was used as a reference sample.

Photodegradation Procedure. The photo reactor was designed with an internal light source surrounded by a quartz jacket. The system was cooled by circulating water and maintained at room temperature. Simulated sunlight irradiation was provided by a 500 W xenon lamp (Nanjing Xujiang Electromechanical Factory), and the intensity of the lamp was 1200 μmol · m⁻² · s⁻¹. In a typical experiment, the catalyst was suspended in an aqueous solution of dye (150 mL) in a Pyrex reactor. Solution pH was adjusted with dilute aqueous HCl and NaOH solutions. Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of organic dyes on the catalyst surface. At given time intervals, about 3 ml suspension was continually taken from the photoreactor for subsequent MO concentration analysis after centrifuging. Decreases of the MO concentrations were monitored via an UV-visible spectrometer (Hitachi U-3010).

3 Results and Discussion

3.1 Catalyst Characterisation

The FT-IR spectra of H₃PW₁₂O₄₀, H₃PW₁₂O₄₀/SiO₂ and H₃PW₁₂O₄₀/SiO₂(x) are shown in Fig.1 (i). From the Fig.1 (i), the Keggin structure of pure H₃PW₁₂O₄₀ gives peaks at 1080, 985, 890 and 794 cm⁻¹. In addition, the band at 1662 cm⁻¹ is the bending mode of the water. When H₃PW₁₂O₄₀ is supported on SiO₂, these bands have changed. The bands at 1080 cm⁻¹ and 890 cm⁻¹ are overlapped by the characteristic band of SiO₂, while these bands at 985 and 794 cm⁻¹ shift to 950 and 803 cm⁻¹, respectively. The spectra of H₃PW₁₂O₄₀/SiO₂(x) are similar to that of H₃PW₁₂O₄₀/SiO₂. It can be concluded that the primary Keggin structure of H₃PW₁₂O₄₀ remains intact after being introduced into the SiO₂.

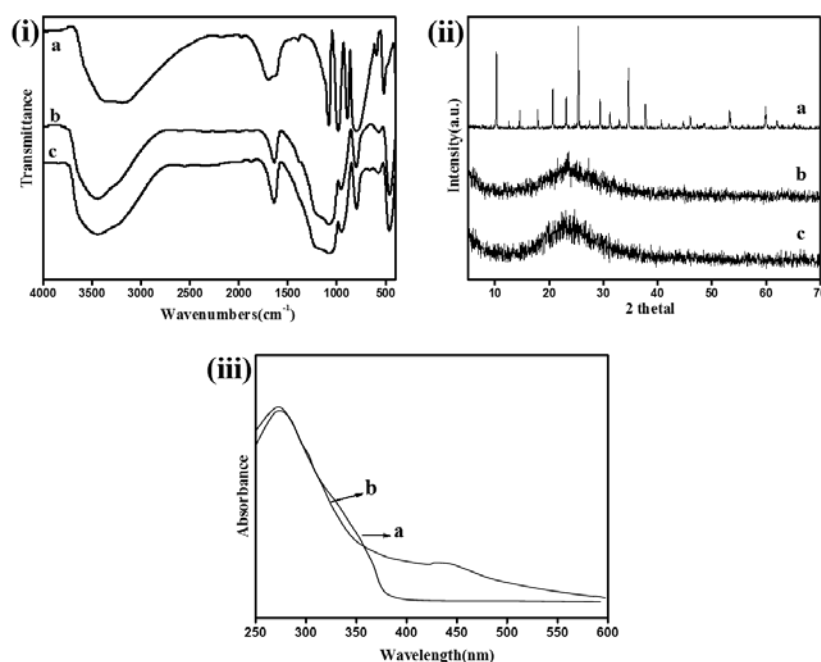


Figure 1. (i) FT-IR spectra and (ii) XRD patterns of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (a), $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (b) and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$ (c). (iii) UV-vis /DRS of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (a) and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$ (b).

POMs could be supported as molecules or aggregates on the supports. Fig.1 (ii) shows the X-ray diffraction patterns (XRD) of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (a), $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (b) and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$ (c). For $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the characteristic diffraction peaks of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with Keggin structure have peaks at $8^\circ\sim 10^\circ$, $17^\circ\sim 20^\circ$, $26^\circ\sim 30^\circ$ and $33^\circ\sim 35^\circ$. For $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$, only a broad band centered at $2\theta=24^\circ$ that can be assigned to the diffraction peaks of amorphous silica is observed, and the other signals of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ are disappeared. So it is reasonable to consider that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is amorphous and highly dispersed on the surface of silica support without any aggregation. A similar phenomenon has been reported in the literature [27, 36].

The diffusing reflectance UV-Vis spectra (UV-DRS) of the catalysts are directly related to their photochemical behavior. The UV-DRS of the samples were characterized, and the results are shown in Fig.1 (iii). It can be seen clearly the characteristic absorption peaks at 260 nm which was attributed to O-W charge transfer of the Keggin unit at W-O-W bond in the Fig.1 (iii). The characteristics of them are similar to pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$. This can be assigned to the Keggin geometry of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. It is worthy to note that an absorption tail extending from the UV to the visible region in the UV-DRS of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$. Therefore, it is concluded that the sensitizing effect has influence on the photocatalytic activity of catalyst.

3.2 Photocatalytic Activity

In order to study the effect of H_2O_2 treatment on the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$, comparison of photocatalytic activity of catalysts was carried out at the same conditions, and the results are shown in Fig. 2 (a). As seen from Fig. 2 (a), after 3 h irradiation under the same conditions, in the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$, the degradation rate of MO is about 37.0 %, while with $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$ as the catalyst, the degradation rate of 96.7 % was achieved. That may be attributed to that $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ is only illuminated by ultraviolet light, which only accounts for less than 5 % of the total solar radiation. So the photocatalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$ is higher than that of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$.

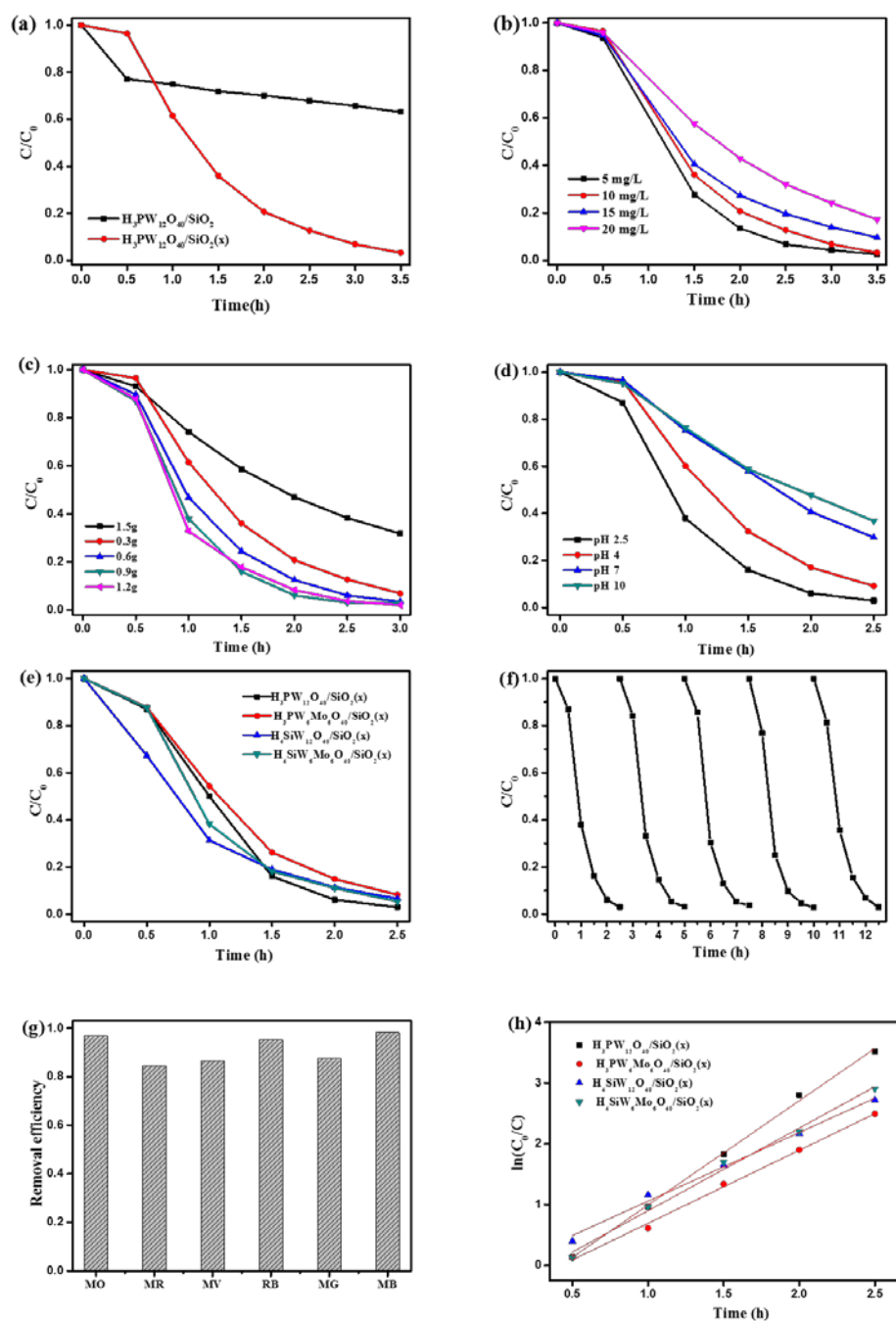


Figure 2. (a) Comparison of photocatalytic activity of catalysts; catalyst, 0.3 g; MO, 10 mg/L; pH 2.5. (b) Effect of initial dye concentration on photocatalytic activity of catalyst; catalyst, 0.3 g; pH 2.5. (c) Effect of catalyst dosage on photocatalytic activity of catalyst; MO, 10 mg/L; pH, 2.5. (d) Effect of the solution pH on photocatalytic activity of catalyst; MO, 10 mg/L; catalyst, 0.9 g. (e) Effect of polyoxometalates on photocatalytic activity of catalyst; MO, 10 mg/L; catalyst, 0.9 g; pH 2.5. (f) Recycling of the catalyst; MO, 10 mg/L; catalyst, 0.9 g; pH 2.5. (g) Photocatalytic degradation of various dyes by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(x)$; MO, 10 mg/L; catalyst, 0.9 g; pH 2.5. (h) Relation curve of $\ln(C_0/C_t)$ and time(t); MO, 10 mg/L; catalyst, 0.9 g; pH 2.5.

To determine the optimum initial concentration of dye for degradation of MO, the photodegradation of MO was carried out at various initial concentration levels. As it can be seen in Fig. 2 (b), the degradation rate decreased with increasing of initial concentration of MO. This might be ascribed to the

excessive adsorption of the MO molecules on the surface of catalyst and a diminishing of light penetration through the solution, which inhibits the process of activated catalyst. It should be noted that degradation rate of MO is decreased only by 1 % under the initial concentration of dye increased from 5 mg/L to 10 mg/L. Thus, the initial concentration of the 10 mg/L is more appropriate.

The influence of catalyst dosage on the degradation of MO is depicted in Fig. 2 (c). The degradation rates were found to be strongly influenced by catalyst dosage. The results indicated that with an increase in catalyst dosage, the degradation rate increases due to an increase in active sites. After 2 h irradiation, the dye was almost completely degraded at 0.9 g of catalyst. So, 0.9 g is used as the optimum catalyst dosage.

The pH value is an important parameter in photocatalytic degradation of organic compounds because of the photocatalysis that takes place on the surface of photocatalyst. The effect of pH on the photocatalytic degradation rate of MO was investigated at different pH (pH 2.5, 4, 7, and 10). The results are shown in Fig. 2 (d). It was found that the degradation rate decreased with increasing pH of the solution, and the highest degradation rate was achieved at pH = 2.5.

The effect of the kind of POM on photocatalytic degradation of organic compounds was investigated, keeping all the other experimental conditions constant, and the results were shown in Fig. 2 (e). From Fig. 2 (e), we observed that they exhibited excellent catalytic activity in the degradation of organic compounds. The activity of various POM in the reaction follows the order of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x}) > \text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(\text{x}) > \text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x}) > \text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(\text{x})$.

Reusability of the catalyst was studied under the optimized conditions. After the reaction finished, the catalyst was recovered by filtering and washed with distilled water. The recovered catalyst was treated again by H_2O_2 for the next degradation run. The results are presented in Fig. 2 (f). It was observed that deactivation of the catalyst was hardly observed after five cycles, indicating the high stability of the catalyst. This result indicated that the high activity of the catalyst remains intact after photocatalysis degradation.

In order to sufficiently test the efficiency of the degradation of this catalyst for organic dye pollutants, we chose other five colorful dyes including methyl orange(MO), methyl red(MR), methyl violet(MV), rhodamine B(RB), malachite green(MG) and methylene blue(MB) as reactants. The results are shown in Fig. 2 (g). The degradation rate of organic compounds can reach 84.6 % ~ 98.3 % at the optimized conditions. Therefore, the catalysts have good prospects of application in treatment of organic pollutants.

It is well known that the photodegradation of organic dyes mainly follows the first-order kinetics, which follows Langmuir-Hinshelwood kinetics [3]. The kinetic expression can be presented as follows:

$$\ln(C_0 / C_t) = k t$$

where k is the rate constant related to the reaction properties of the solute which depends on the reaction conditions and the photocatalytic activity increases with increasing this value. C_0 is the initial concentration, and C_t is the concentration of dye at time t . The kinetics of photocatalytic degradation of MO over $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$, $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(\text{x})$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2(\text{x})$, and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(\text{x})$ were studied under optimized conditions. The results are shown in Fig. 2 (h). The results show that a plot of $\ln(C_0/C_t)$ versus "time" exhibits a nearly straight line, and the linear correlation coefficients (R) are ca. 0.998, 0.996, 0.991, and 0.991, respectively. It can be seen that the degradation reactions belong to the first-order kinetic reaction. The rate constants were calculated to be 1.7, 1.2, 1.1, and 1.4 h^{-1} .

4 Conclusion

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ was prepared by a sol-gel method, and sensitized by H_2O_2 solution that significantly improved its catalytic activity under simulated natural light irradiation. Degradation of methyl orange was used as a probe reaction to explore the influencing factors of the photodegradation reaction. The optimum condition is that initial concentration of methyl orange is 10 mg/L, the pH is 2.5, and catalyst dosage is 0.9 g, the degradation rate of methyl orange is as high as 97.0 % after 2 h under simulated natural light irradiation. The reaction of photocatalysis for methyl orange can be expressed as the first-order kinetic model. After used continuously for five times, the catalytic activity of the photocatalyst is not any lower. The photodegradation of methyl orange, methyl red, methyl violet, rhodamine B, malachite green and methylene blue were also tested, and the degradation rate of dyes can reach 84.6 %~98.3 %.

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