Research Article

Photocatalytic Degradation of Organic Dyes by $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ Sensitized by H_2O_2

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$\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ was sensitized by H_2O_2 solution that significantly improved its catalytic activity under simulated natural light. Degradation of basic fuchsin was used as a probe reaction to explore the influencing factors on the photodegradation reaction. The results showed that the optimal conditions were as follows: initial concentration of basic fuchsin 8 mg/L, pH 2.5, catalyst dosage 4 g/L, and light irradiation time 4 h. Under these conditions, the degradation rate of basic fuchsin is 98%. The reaction of photocatalysis for basic fuchsin can be expressed as the first-order kinetic model. After being used continuously for four times, the catalyst kept the inherent photocatalytic activity for degradation of dyes. The photodegradation of malachite green, methyl orange, methylene blue, and rhodamine B were also tested, and the degradation rate of dyes can reach 90%–98%.

1. Introduction

In the past few years, a great deal of attention has been paid to water-treatment technology [1]. A lot of water treatment techniques including condensation, ultrafiltration, membrane separation, and adsorption have been adopted to remove persistent organic compounds and microorganisms in water [2, 3]. Especially, advanced oxidation processes (AOPs), which have the potential to completely mineralize organic compounds to CO_2 and H_2O , have shown a great potential as a low-cost and high efficiency water treatment technology [4]. Semiconductor photocatalytic process have played an important role in many advanced oxidation processes. Semiconductor materials including Ag_2O [5], Ag-loaded Bi_2WO_6 [6], TiO_2 [7, 8], bismuth tungstate [9], ZnO [10], and TiO_2 -rGO [11] have been found to exhibit high photocatalytic activity. Although TiO_2 has been investigated widely in photocatalytic degradation of organic chemicals in water under ultraviolet (UV) light, constituting only 4% of the solar light, it cannot be effectively activated under solar light irradiation due to its wide intrinsic band gap. Because the light wavelength of light sources is one of the few parameters that affects the overall photocatalytic rate, it is essential to

use solar light efficiently to achieve a high photocatalytic reaction rate. Visible-light responsive photocatalysts have been investigated quite intensively in recent years, including modified TiO_2 [12–15].

Heteropoly acid (HPA) has been extensively studied as acid or oxidation catalyst for a wide range of reactions [16, 17]. In recent years, HPA has also attracted much attention as photocatalysts owing to its photophysics and photochemical properties, analogous to these of semiconductors [18, 19]. Upon absorbing UV-near visible light irradiation, HPA will be excited to generate electron-hole pairs. The electron and hole will initiate reductive and oxidative reactions to decomposition of organic pollutants. However, several reports related to the photocatalysis of HPAs are concentrated on UV irradiation. In order to overcome their disadvantages, such as low surface area ($1\text{--}10\text{ m}^2/\text{g}$), highly soluble in polar media, and difficulty in separation, HPAs should be immobilized on a support like montmorillonite clay [20], MCM-41 [21], and TiO_2 [22] to obtain insoluble catalysts. Moreover, some support materials seem to improve the catalytic performance of the combined catalysts because of a synergistic catalytic effect [23].

In this paper, it was attempted to improve photocatalytic activity of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ according to sensitization by H_2O_2 solution. The photocatalytic degradation of some dyes having different chemical structures with the catalyst under simulated natural light irradiation was investigated.

2. Experimental

2.1. Preparation of Samples. $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ was synthesized according to reference [24, 25] by a sol-gel technique. An amount of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ was dissolved in 26 mL of H_2O , and a stoichiometric amount of TEOS was mixed with 1-BuOH. The latter was added dropwise to the aqueous solution. The resultant was allowed to be 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 vacuum and then at 90°C for 3.5 h. Thus, the silica network was fastened, and the removal of the $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ molecules from it was avoided. The particulate gel was washed with hot water for several times until the filtrate was neutral, and then the products were calcined for the required duration.

$\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ was treated by H_2O_2 as follows [26]: 1 g $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ was added into 15 mL 30% H_2O_2 solution and sonicated the mixture for 20 min. The slurry mixture was filtrated and dried at room temperature. This catalyst is denoted by $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x)$.

2.2. Characterization. The FT-IR spectra of the samples in KBr matrix were recorded on a Nicolet 5700 FT-IR spectrometer in the range $400\sim 4000\text{ cm}^{-1}$. The X-ray powder diffraction pattern of the samples was measured by a Bruker AXS D8-Advanced diffractometer (Bruker, Germany) employing $\text{Cu K}\alpha$ radiation. Scanning electron micrographs (SEM) were obtained on a Hitachi S-3400N scanning electron microscope.

2.3. Photocatalytic Activity Measurement. The photocatalytic activities of the samples were determined by measuring the degradation of dyes in an aqueous solution under simulated sunlight irradiation. Simulated sunlight irradiation was provided by a 500 W xenon lamp (Nanjing Xujiang Electromechanical Factory), and the intensity of the lamp was $1200\text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. Solution pH was adjusted with dilute aqueous HCl and NaOH solutions. The system was cooled by circulating water and maintained at room temperature. Before irradiation, the suspension was vigorously stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of dyes on the catalyst surface. At given time intervals, about 3 mL suspension was continually taken out from the photoreactor and centrifuged. The change of the basic fuchsin concentrations was analyzed by the UV-vis spectrophotometer (Hitachi U-3010).

3. Results and Discussion

3.1. Characterization of the $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ Catalyst. The IR spectra of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$

FIGURE 1: FT-IR spectra of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ (a) and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ (b).

FIGURE 2: The XRD patterns of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ (a) and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ (b).

are shown in Figure 1. As shown in Figure 1, the characteristic bands of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ Keggin anion at 972.9, 918.2, 774.6, and 538.6 cm^{-1} are observed for pure $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$. In addition, the band at 1618.3 cm^{-1} , which is the bending mode of the water, indicates the presence of the water. When $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ is bonded to the Si-OH group of SiO_2 , these bands have changed. However, the characteristic bands for the Keggin anion could be observed for $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$. The shifts indicate that a strong chemical interaction, not simple physical adsorption, exists between the $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ and the support.

Figure 2 shows the XRD patterns of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$. The characteristic diffraction peaks of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ that were explored at 8.0, 10.4, 20.7, 25.5, 29.2, 34.5, and 37.8° can be assigned to the diffraction characteristic peaks of crystalline $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ Keggin structure. For $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$, only a broad band at $2\theta = 22.4^\circ$ that can be assigned to the diffraction peaks of

FIGURE 3: SEM images of SiO_2 particles at different multiples.

amorphous silica appears, but no signals of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ are displayed. Thus, it can be proposed that $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ is well dispersed on the surface of silica support.

Figure 3 shows the SEM images of SiO_2 particles at different multiples. As can be seen from the figure, surface morphology of SiO_2 is spherical and massive. Silicon sphere is dispersed evenly in the whole system, and its diameter is about $4.5 \mu\text{m}$.

Figure 4 shows the SEM patterns of SiO_2 , $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$, and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ at 5000 times. Surface morphology of SiO_2 is massive, dispersed evenly in the whole system. Surface morphology of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ is net-like, and its specific surface area is relatively small. The results show that the catalyst not only uniformly dispersed in the system, but also the specific surface area is bigger than before.

3.2. Investigation of Photocatalytic Activity of Catalysts

3.2.1. Comparison of Photocatalytic Activity of Catalysts. In order to detect the catalytic activity of catalysts, the degradation of model basic fuchsin aqueous over the samples was carried out at the basic fuchsin concentration of 16 mg/L, pH 2.5 and 4 g/L of catalyst, and the results are shown in Figure 5.

As shown in Figure 5, direct photolysis of an aqueous basic fuchsin under simulated natural light irradiation for 3.5 h did not cause any changes of its concentration. In addition, the degradation rate of basic fuchsin over

$\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ is only 31.0%, while the degradation rate over $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x)$ is as high as 98%. The photocatalytic performance of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x)$ is much higher than that of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$. So, the peroxo complexes formed from the decomposition of $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ in hydrogen peroxide have played an important role in the photodegradation of dyes. Therefore, it is concluded that the sensitizing effect has a remarkable influence on the photocatalytic activity of catalyst.

3.2.2. Effect of the Initial Concentration of Dye. To investigate the effects of initial concentration on the photocatalytic degradation of basic fuchsin, this was varied from 8 mg/L to 40 mg/L, and the results are presented in Figure 6.

From Figure 6, it can be seen that the photocatalytic degradation rate of basic fuchsin decreases with an increase in the initial concentration of basic fuchsin. This phenomenon could be attributed to the excessive absorption of the basic fuchsin molecules on the surface of catalyst and a diminishing of light penetration through the solution at high initial concentration of basic fuchsin, which inhibits the process of activated catalyst. Then, the optimum of the initial concentration is 8 mg/L.

3.2.3. Effect of Catalyst Dosage. We have also investigated the effects of catalyst dosage on the degradation rate of basic fuchsin, and the results were shown in Figure 7.

It was found that the degradation rate of basic fuchsin increases with an increase in the amount of catalyst from 1 g/L to 4 g/L, then decreases when the catalyst dosage is higher

FIGURE 4: SEM images of SiO_2 (a), $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ (b), and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2$ (c).

than 4 g/L. This may be attributed to the scattering effect. The high turbidity of catalyst decreased the penetration depth of solar radiation [22]. So, the optimum amount of catalyst is 4 g/L.

3.2.4. Effect of pH. The pH value is one of the most important parameters in the photodegradation of organic compounds. The effect of pH on the photodegradation rate of basic fuchsin was also investigated at different pH. The results are shown in Figure 8.

From Figure 8, it can be seen that the degradation rate increased with decreasing pH of the solution, then decreases when pH of the solution is lower than 2.5. This is mainly ascribed to the variations of surface charge properties of the photocatalyst.

3.2.5. Effect of HPA. The effect of the kind of HPA on photocatalytic degradation of organic compounds was examined, and the results were shown in Figure 9.

From Figure 9, it can be seen that the kind of HPA plays an important role in the photocatalytic reaction. After 3.5 h irradiation under simulated natural light

irradiation, the degradation rate of basic fuchsin over $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x)$, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(x)$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2(x)$, $\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x)$, and $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$ is 98%, 96%, 68%, 82%, and 68%, respectively. The activity of various HPA in the reaction follows the order $\text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x) > \text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2(x) > \text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}/\text{SiO}_2(x) > \text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2(x) > \text{H}_4\text{SiW}_6\text{Mo}_6\text{O}_{40}$.

3.3. Photocatalytic Degradation of Various Dyes. In order to determine the feasibility of the catalyst in treatment of some dyes having different chemical structures, we attempted to choose other dyes such as methyl orange, rhodamine B, malachite green, and methylene blue as reactants. The results are shown in Figure 10. The degradation rate of dyes can reach 90%~98% at the optimized conditions. Therefore, the catalysts have good prospects of application in treatment of organic pollutants.

3.4. Reuse of the Catalyst. Reusability of the catalyst was also studied under the optimized conditions. After the reaction finished, the catalyst was recovered and washed with distilled

FIGURE 5: Comparison of photocatalytic activity of catalysts.

FIGURE 7: Effect of catalyst dosage on photocatalytic activity of catalyst.

FIGURE 6: Effects of initial dye concentration on photocatalytic activity of catalyst.

FIGURE 8: Effects of the solution pH on photocatalytic activity of catalyst.

water and ethyl alcohol. The recovered catalyst was treated again by H_2O_2 for the next degradation run.

The results are shown in Figure 11. It was observed that a decrease in catalytic activity is observed with its subsequent reuse. However, the degradation rate of basic fuchsin can reach 87% in the fifth run. So, it can be concluded that the high catalytic activity is retained in a next run.

3.5. Kinetic Analysis. The kinetics of photocatalytic degradation of basic fuchsin by $H_4SiW_6Mo_6O_{40}/SiO_2(x)$, $H_3PW_{12}O_{40}/SiO_2(x)$, $H_4SiW_{12}O_{40}/SiO_2(x)$, and $H_3PW_6Mo_6O_{40}/SiO_2(x)$ was studied under optimized conditions. The results are shown in Figure 12.

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. 0.985, 0.991, 0.994, 0.986, and 0.997, respectively. It can be concluded that the photodegradation reactions follow the first-order kinetics, which follow Langmuir-Hinshelwood kinetics. The rate constants were calculated to be 0.85, 0.45, 0.29, 0.15, and $0.99\ h^{-1}$.

4. Conclusion

$H_4SiW_6Mo_6O_{40}/SiO_2$ was prepared by a sol-gel method and sensitized by H_2O_2 solution. Degradation of basic fuchsin was used as a probe reaction to explore the influencing factors

FIGURE 9: Effect of HPA on photocatalytic activity of catalyst.

FIGURE 10: Photocatalytic degradation of various dyes using $H_4SiW_6Mo_6O_{40}/SiO_2(x)$ as a catalyst.

on the photodegradation reaction. The results showed the optimal conditions were as follows: initial concentration of basic fuchsin 8 mg/L, pH 2.5, catalyst dosage 4 g/L, and light irradiation time 4 h. Under these conditions, the degradation rate of basic fuchsin is 98%. The photodegradation of other dyes such as malachite green, methyl orange, methylene blue, and rhodamine B were also tested, and the degradation rate of dyes can reach 90%–98%. The high activity and stability of the catalyst is well retained after 5 runs. The reaction of photocatalysis for basic fuchsin can be expressed as the first-order kinetic model.

FIGURE 11: Recycling of the catalyst.

FIGURE 12: Relation curve of $\ln(C_0/C)$ and time (t).

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