Scientific Research

Photodegradation of Toxic Organic Pollutants by Immobilized MnPcS-TiO_2

Shulian Wang, Yan Gu, Anping Deng, Xiaorong Zhao, Yingping Huang*

Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, China Three Gorges University, Yichang Hubei, China

Email: chem_ctgu@126.com

Abstract: Immobilized MnPcS-TiO_2 was synthesized using the mesoporous TiO_2 prepared as support and N, N-dimethylformamide (DMF) as solvent to load manganese phthalocyanine tetrasulfonic acid (MnPcS). The degradation of organic dye rhodamine B (RhB) and colorless small molecule salicylic acid (SA) was used to evaluate the effect of physical and chemical factors on the catalytic activity. The results indicated that MnPcS-TiO_2 with loading amount 10μmol/g had good photocatalytic properties under visible light with 100% decolorization of RhB after 360min and 87.05% degradation of SA after 24h illumination. The photocatalytic degradation of organics by immobilized MnPcS-TiO_2 was a deep mineralization process predominating mainly by the hydroxyl radical (•OH) generated in the system.

Keywords: MnPcS-TiO_2; photocatalysis; degradation; mineralization

1 Introdution

Metal phthalocyanine compounds can extend the photocatalytic applications at neutral pH conditions and under visible light irradiation[1]. Immobilization of them on a support can enhance their photocatalytic activity and the selective usage of H_2O_2[2]. In recent years, metal phthalocyanine compounds used as light acceptor to sensitize semiconductor material TiO_2 have attracted wide attention. TiO_2 sensitized by metal phthalocyanine can increase the photoelectric conversion quantum efficiency[3] and have become a promising catalyst material for environmental remediation[4]. Metal phthalocyanine loaded on TiO_2 can enhance the stability and dispersity, so that it was a single state to improve the activity. Excited metal phthalocyanine inject the electron to the conduction band of TiO_2, which separate the photo generated charge effectively and improve the photocatalytic efficiency[5]. In this paper, immobilized photocatalyst MnPcS-TiO_2 was synthesized and the effect of physical and chemical factors on the photocatalytic activity was investigated using the degradation of RhB and SA. The results indicated that the immobilized MnPcS-TiO_2 had good photocatalytic performance which could degrade toxic organics.

2 Experimental

2.1 Preparation of mesoporous TiO_2 and MnPcS

In a typical synthesis of mesoporous TiO_2, 4.32g of $Ti(SO_4)_2$ was added to a solution of a certain amount of OP in 30mL of water with intense stirring. The mixed solution was put into the autoclave to react at 120℃ for 24h. Once the reaction finished, precipitation in the bottom of the autoclave was washed with water and ethanol several times, dried at 80℃ and calcined at 500℃ for 2h.

A round-bottom flask (50mL) with 50mg of PcS dissolved in 30mL of distilled water and 20mg of $MnSO_4 \cdot H_2O$ was heated at 100℃ with continuing stirring. Quantitative reaction solution was extracted at different intervals and measured the absorbance values at 200 – 900 nm. The changes of absorbance values and appearance of new absorption peaks were obseaved. When the changes of Q-band and B-band of PcS didn't occur any longer, the reaction should be stopped. The excess Mn^{2+} was removed using cation exchange resin (IRA200). MnPcS prepared was 2.00×10^{-3}mol/L of aqueous solution.

2.2 Preparation of MnPcS-TiO_2 complex

MnPcS-TiO_2 complex catalysts with different loading amounts (0, 5, 10, 15μmol/g) were prepared through adding a certain amount of TiO_2 into DMF which was used as load solvent with a certain volume of MnPcS and

---

Supported by the National Natural Science Foundation of China (No. 20877048), Innovation group project of Hubei Province Natural Science Foundation (No. 2009CDA020) and Innovation team plans to outstanding young of universities in Hubei Province（No: T200703）

stirring for 24h at ambient condition.

2.3 Catalyst characterization

UV-visible diffuse reflectance spectra (UV-vis DRS) of the catalyst was recorded on a U-3010 UV-vis spectrophotometer (Japan, Hitachi) using spectral grade $BaSO_4$ as the reference material.

2.4 Photocatalytic procedures and analyses

All the degradation experiments were carried out in a pyrex vessel (70mL) with 1.1mL of RhB (5.00×10^{-4}mol/L) or 1mL of SA (5.00×10^{-3}mol/L) and a certain amount of MnPcS-TiO_2. The pH of solution was adjusted to a certain value and the constant volume was 50mL. Prior to irradiation, the suspension were stirred in the dark for 30min to ensure the establishment of an adsorption/desorption equilibrium of the dye on the surface of MnPcS-TiO_2. At given irradiation time intervals, 3mL of samples were removed, centrifuged, and then filtered through a millipore filter (0.45um). The filtrates were analyzed using UV-vis spectroscopy (USA, Perkin Elmer) to examine the decomposition of RhB (λ=554nm). The content of SA was measured by high performance liquid chromatography (HPLC) (USA, Waters). The chromatographic conditions were mobile phase 45% methanol, 55% phosphate (KH_2PO_4, pH 3.5), stationary phase C_{18} column, column temperature 30℃, flow 0.70mL/min. The detection wavelength was 278nm.

3 Results and Discussion

3.1 Analysis of MnPcS absorption spectra

MnPcS was synthesized using the method of “center direct coordination”[6]. The changes of absorption spectra was measured every 2h on starting heating and reflux and the result was shown in Figure 1. The “neat” PcS showed an UV-vis spectrum with a Q-band at 624nm and a B-band at 349nm. Adding Mn^{2+} to the aqueous solution caused slight change of Q-band. As the heating going, the Q-band was observed at 719nm and B-band at 349nm and 510nm. Both the Q-band and B-band had undergone a red shift due to the coordination of manganese which brough the increase of conjugation. Similar observations were found by Liang Qiang[6] et al. However, between the 4th and 10th h, the absorbance values were almost constant, which demonstrated that MnPcS complex was prepared completely.

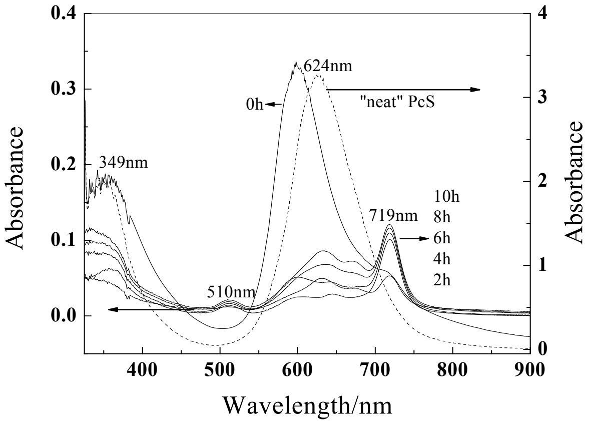

Figure 1. The change of absorption spectra for the synthesization of MnPcS in aqueous solution

3.2 UV-vis DRS of catalyst

The UV-vis DRS of catalyst was shown in Figure 2, which indicated that the UV-vis adsorption band wavelength shifted to the visible range when MnPcS was loaded on TiO_2. Furthermore, the absorbance above 400nm showed a significant increase for MnPcS-TiO_2 (curve a), compared with the UV-vis DRS of TiO_2 (curve b). Immobilized MnPcS-TiO_2 was conducive to the absorption of visible light and increased the response to the visible light range. It made photocatalytic reaction in the visible light possible. The higher absorbance at 600-800nm might be the absorbance of MnPcS.

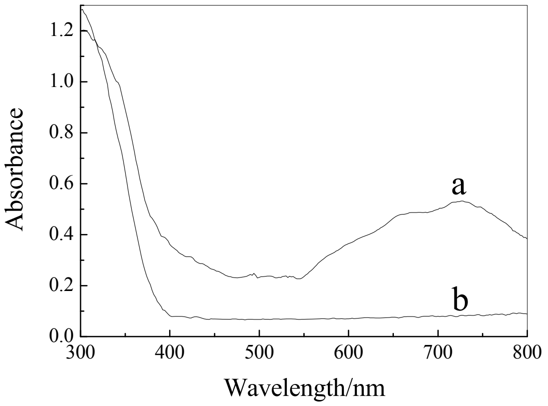

Figure 2. UV-visible diffuse reflectance spectra of MnPcS-TiO_2(10μmol/g) (curve a) and TiO_2 (curve b)

3.3 Determination of optimal loading amount

Figure 3 represented the degradation of RhB by MnPcS-TiO_2 with different loading amounts. The catalytic activity of MnPcS-TiO_2 first increased and then decreased slightly with the increasing of loading amount. The photodegradation reaction of RhB under visible light irradiation followed a first-order kinetics. When the loading amounts were 0, 5, 10, 15μmol/g, the k were 0.0105 (curve a), 0.0104 (curve b), 0.0133 (curve c) and 0.0028min^{-1} (curve d), respectively. This was because little MnPcS would not fully occupy the surface of TiO_2 while excess MnPcS led to excited state quenching and degradation effect weakening. Extra MnPcS acted as a light filter and occured reunion and held the catalytic activity of sites on the surface of TiO_2 to prevent the absorption of light, resulting in light quantum yield lowering which worked against the catalytic activity of MnPcS-TiO_2. Therefore, the catalyst with 10μmol of MnPcS per gram of TiO_2 whose activity was slightly better than the others was the optimal loading amount under the experimental conditions.

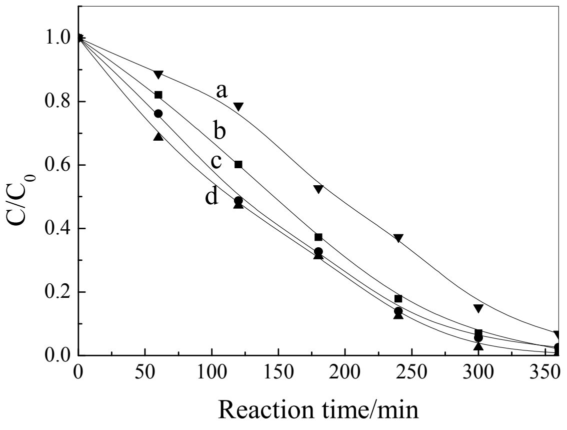

Figure 3. Degradation of RhB by MnPcS-TiO_2 with different loading amount (a: 0; b: 5μmol/g; c: 10μmol/g; d: 15μmol/g) [RhB]=1.10×10^{-5}mol/L; pH=6.88; [MnPcS-TiO_2]=0.20g/L

3.4 The photocatalytic degradation kinetics curves of RhB under optimal conditions

Figure 4 was the photocatalytic degradation kinetics of RhB under the optimal conditions. In the presence of MnPcS-TiO_2 or TiO_2 in the dark, no significant degradation was observed (curve a and b in Figure 4A). In control experiments under irradiation with visible light, the degradation rates of RhB in the heterogeneous solutions containing TiO_2 (curve c in Figure 4 A) (k = 0.0051min^{-1}) were not as high as in the presence of MnPcS-TiO_2 (curve d in Figure 4 A) (k = 0.0104min^{-1}) under otherwise identical conditions. After illumination for 360min, the maximum absorption peak of RhB disappeared completely (Figure 4 B). Besides, the photodegradation of RhB was also evident from the color change on the catalyst surface. Before irradiation, the catalyst was fresh peach red, due to the absorbed dye of RhB. The solution became colorless after exposure to visible light for 360min (curve d in Figure 4 A). Further irradiation for another 30min changed the catalyst to blue (inherent color of MnPcS-TiO_2), indicating that RhB both on the surface of support catalyst and in solution was efficiently degraded. However, in the other three cases (curves a-c in Figure 4 A), the color of catalysts in the RhB solution remained fresh peach red during the same reaction time.

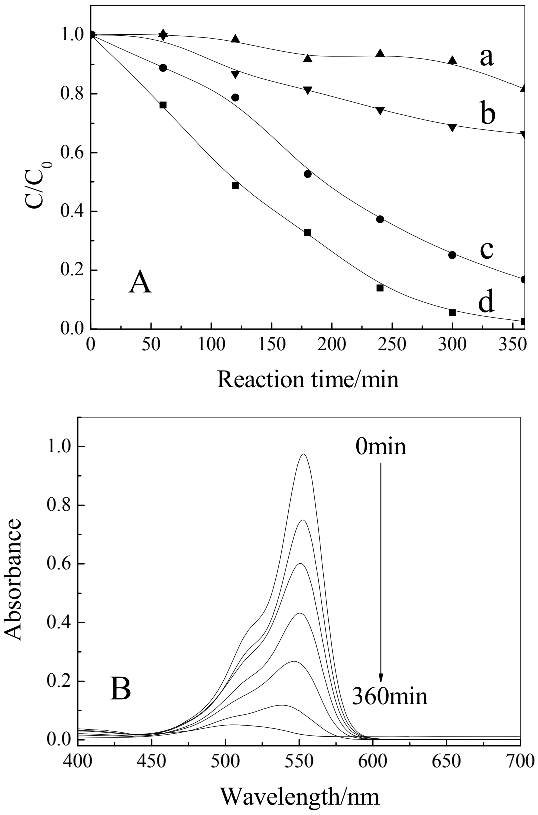

Figure 4. Degradation of RhB by MnPcS-TiO_2 [RhB]=1.10×10^{-5}mol/L; pH=6.88; MnPcS-TiO_2]=0.20g/L a: MnPcS-TiO_2/RhB/dark; b: TiO_2/RhB/dark; c: TiO_2/RhB/vis; d: MnPcS-TiO_2/RhB/vis

3.5 The catalyst reuse

The reuse of MnPcS-TiO_2 was examined for degradation of RhB during a five consecutive cycle experiment. Each experiment was carried out under identical conditions. After each experiment, the solution residue was filtered, washed and the solid was dried. The dried catalyst samples were used again for the degradation of RhB, employing similar experimental conditions. The results were showed in Figure 5, which confirmed that the photocatalytic activity maintained. In the former three consecutive cycles, the catalyst showed good stability and had no significant attenuation phenomenon (k = 0.0054, 0.0046, 0.0055min^{-1}), which indicated the combination of TiO_2 and MnPcS was extremely close without dissolution. While in the subsequent two consecutive cycles, the photocatalytic activity slightly reduced (k = 0.0029, 0.0020min^{-1}) for the possible loss of catalyst during the degradation. During the photoreaction process, no MnPcS was found in the solution, as measured by UV/vis spectroscopy. The results indicated the mmobilized MnPcS-TiO_2 was an efficient and rather stable photocatalyst for the degradation of toxic organic pollutants in water under visible light. After each cycle, the content of Mn was measured by atomic absorption spectrophotometry (USA, Varian). In the five consecutive cycles, there was no free of Mn was detected which indicated that the coordination of Mn and PcS in MnPcS-TiO_2 was close without the phenomenon of loss and dissolution. Therefore, MnPcS-TiO_2 was relatively stable under visible light and could be reused.

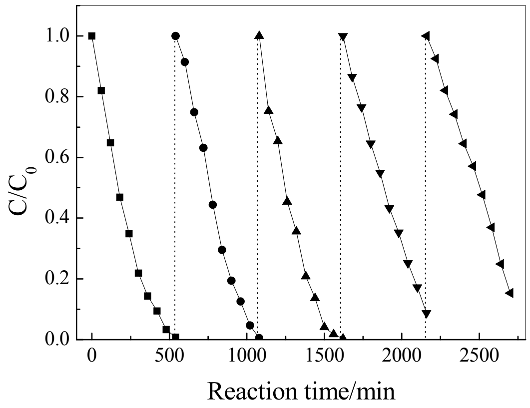

Figure 5. Reuse of catalyst in the degradation of RhB for five cycles
[RhB]=1.10×10^{-5}mol/L; pH=6.88; [MnPcS-TiO_2]=0.20g/L

3.6 The degradation of SA by the catalyst

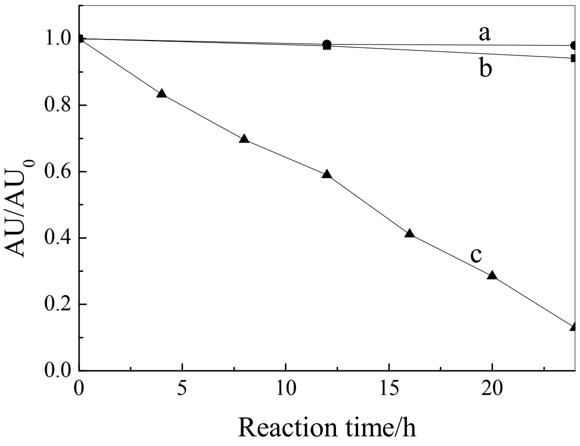

Figure 6. Photodegradation of SA by TiO_2 and MnPcS-TiO_2
a: TiO_2/SA/vis; b: MnPcS-TiO_2/SA/dark; c: MnPcS-TiO_2/SA/vis

SA without absorption under visible light (λ⩾ 420nm) was selected as a target degradation product to ensure that the degradation of organics was the excitation rather than sensitization of catalyst. The concentration of SA during the degradation process was measured using HPLC method and the results were shown in Figure 6. In the absence of visible irradiation, MnPcS-TiO_2 could not degrade SA (curve b). Furthermore, under visible light illumination, the degradation rate of SA by TiO_2 was almost zero (curve a). While under the same condition, MnPcS-TiO_2 as photocatalyst could effectively degrade SA with 87.05% degradation rate after 24h (curve c).

3.7 The generation of radical

The concentration of H_2O_2 (Figure 7A) and • OH (Figure 7B) in the system of MnPcS-TiO_2/RhB/vis was determined. The results showed that both the relative concentration of H_2O_2 and •OH increased as the illumination time and began to decrease once reaching a level. Therefore, catalyst MnPcS-TiO_2 activated water molecules and dissolved oxygen in water to produce H_2O_2 and •OH and then degraded RhB. Figure 8 illustrated the possible mechanism of the photocatalytic degradation of RhB by MnPcS-TiO_2. The oxidation reduction potential of the singlet state 1 (S_1) of MnPcS (E_{S1} = -0.63eV versus NHE) was higher than the oxidation reduction potential of the conduction band of TiO_2 (E_{CB} = -0.5eV versus NHE)[7]. While the oxidation reduction potential of triple state (T_1) of MnPcS (E_{T1} = -0.02eV versus NHE) was lower than the oxidation reduction potential of conduction band of TiO_2. MnPcS in the ground state (S_0) (E_{S0} = 1.18eV versus NHE) was easy to absorb visible light to translate from the ground state (S_0) to the S_1 state (equation (1)) which transferred the electrons directly to the conduction band of TiO_2 (equation (2)). The electrons in the conduction band of TiO_2 activated water molecules and dissolved oxygen in water to produce H_2O_2 and •OH to achieve visible photocatalytic degradation of toxic organic pollutants. The reaction separeted light-induced charge effectively and improve the photocatalytic efficiency greatly.

$$\mathrm{MnPcS}(S_0) + h\nu \rightarrow \mathrm{MnPcS}^*(S_1) \quad (1)$$

$$\mathrm{MnPcS}^*(S_1)+\mathrm{TiO_2(CB)}\rightarrow \mathrm{MnPcS}(S_0)+ e^-(\mathrm{TiO_2/CB}) \quad (2)$$

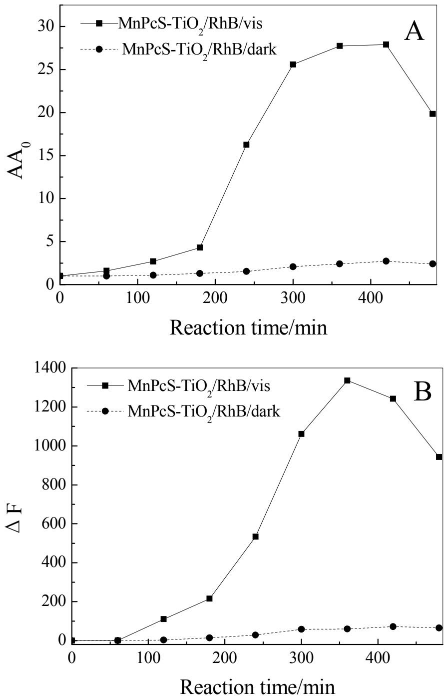

Figure 7. Measurement of H_2O_2 (A) and •OH (B)

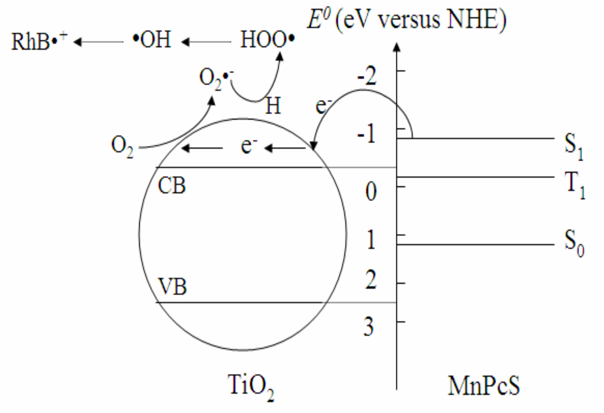

Figure 8. Possible mechanism for the degradation of RhB

References

[1] Tao X, Ma W H, Zhao J C, et al. A Novel Approach for the Oxidative Degradation of Organic Pollutants in Aqueous Solutions Mediated by Iron Tetrasulfophthalocyanine under Visible Light Radiation[J]. *Chem. Eur. J.*, 2002, 8(6), P1321-1326.

[2] Tao X, Ma W H, Zhao J C, et al. Efficient degradation of organic pollutants mediated by immobilized iron tetrasulfophthalocyanine under visible light irradiation[J]. *Chem.Commun.*, 2003, P80-81.

[3] Yuan Hui, Zhao Gaoling, Han Gaorong. Effect on photocatalysed property of TiO_2 thin film by the preparation of high-purity metal phthalocyanin[J]. *J.Funct.Mater.*, 2005, 36(4), P580-582(Ch).

[4] Sorokin A, Meunier B, Séris J L. Efficient Oxidative Dechlorination and Aromatic Ring Cleavage of Chlorinated Phenols Catalyzed by Iron Sulfophthalocyanine[J]. *Science*, 1995, 268, P1163-1166.

[5] Iliev V, Tomova D, Bilyarska L, et al. Phthalocyanine modified TiO_2 or WO_3-catalysts for photooxidation of sulfide and thiosulfate ions upon irradiation with visible light[J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2003, 159, P281–287.

[6] Liang Qiang, Han Aixia, Zhang Fushi. Synthesis and Application of Manganese (Ⅱ) Tetrasulfophthalocyanine[J]. *Chinese Journal of Applied Chemistry*, 2004, 21(12), P1290-1294(Ch).

[7] Fang Y F, Huang Y P, Liu D F, et al. Photocatalytic degradation of the dye sulforhodamine-B: A comparative study of different light sources[J]. *Journal of Environmental Sciences*, 2007, 19, P97-102.