Photodegradation of Toxic Organic Pollutants by Immobilized MnPcS-TiO₂

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Abstract: Immobilized MnPcS-TiO₂ was synthesized using the mesoporous TiO₂ 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-TiO₂ 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-TiO₂ was a deep mineralization process predominating mainly by the hydroxyl radical (•OH) generated in the system.

Keywords: MnPcS-TiO₂; photocatalysis; degradation; mineralization

1 Introduction

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 H₂O₂[2]. In recent years, metal phthalocyanine compounds used as light acceptor to sensitize semiconductor material TiO₂ have attracted wide attention. TiO₂ 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 TiO₂ 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 TiO₂, which separate the photo generated charge effectively and improve the photocatalytic efficiency[5]. In this paper, immobilized photocatalyst MnPcS-TiO₂ 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-TiO₂ had good photocatalytic performance which could degrade toxic organics.

2 Experimental

2.1 Preparation of mesoporous TiO₂ and MnPcS

In a typical synthesis of mesoporous TiO₂, 4.32g of Ti(SO₄)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°C for 24h. Once the reaction finished, precipitation in the bottom of the autoclave was washed with water and ethanol several times, dried at 80°C and calcined at 500°C for 2h.

A round-bottom flask (50mL) with 50mg of PcS dissolved in 30mL of distilled water and 20mg of MnSO₄•H₂O was heated at 100°C 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 obsereved. When the changes of Q-band and B-band of PcS didn’t occur any longer, the reaction should be stopped. The excess Mn²⁺ was removed using cation exchange resin (IRA200). Mn-PcS prepared was 2.00×10⁻³ mol/L of aqueous solution.

2.2 Preparation of MnPcS-TiO₂ complex

MnPcS-TiO₂ complex catalysts with different loading amounts (0, 5, 10, 15μmol/g) were prepared through adding a certain amount of TiO₂ into DMF which was used as load solvent with a certain volume of MnPcS and
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 BaSO4 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-TiO2. 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-TiO2. 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 (KH2PO4, pH 3.5), stationary phase C18 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 4\(^{th}\) and 10\(^{th}\) 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](image)

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 TiO2. Furthermore, the absorbance above 400nm showed a significant increase for MnPcS-TiO2 (curve a), compared with the UV-vis DRS of TiO2 (curve b). Immobilized MnPcS-TiO2 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-TiO2(10μmol/g) (curve a) and TiO2 (curve b)](image)
3.3 Determination of optimal loading amount

Figure 3 represented the degradation of RhB by MnPcS-TiO₂ with different loading amounts. The catalytic activity of MnPcS-TiO₂ 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, 15 μmol/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 TiO₂ 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 TiO₂ to prevent the absorption of light, resulting in light quantum yield lowering which worked against the catalytic activity of MnPcS-TiO₂. Therefore, the catalyst with 10μmol of MnPcS per gram of TiO₂ whose activity was slightly better than the others was the optimal loading amount under the experimental conditions.

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-TiO₂ or TiO₂ 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 TiO₂ (curve c in Figure 4 A) (k = 0.0051min⁻¹) were not as high as in the presence of MnPcS-TiO₂ (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-TiO₂), 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.
3.5 The catalyst reuse

The reuse of MnPcS-TiO₂ 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 ($k = 0.0054, 0.0046, 0.0055\text{min}^{-1}$), which indicated the combination of TiO₂ and MnPcS was extremely close without dissolution. While in the subsequent two consecutive cycles, the photocatalytic activity slightly reduced ($k = 0.0029, 0.0020\text{min}^{-1}$) 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 immobilized MnPcS-TiO₂ 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-TiO₂ was close without the phenomenon of loss and dissolution. Therefore, MnPcS-TiO₂ was relatively stable under visible light and could be reused.

3.6 The degradation of SA by the catalyst

SA without absorption under visible light ($\lambda \geq 420\text{nm}$) 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-TiO₂ could not degrade SA (curve b). Furthermore, under visible light illumination, the degradation rate of SA by TiO₂ was almost zero (curve a). While under the same condition, MnPcS-TiO₂ as photocatalyst could effectively degrade SA with 87.05% degradation rate after 24h (curve c).

3.7 The generation of radical

The concentration of H₂O₂ (Figure 7A) and •OH (Figure 7B) in the system of MnPcS-TiO₂/RhB/vis was determined. The results showed that both the relative concentration of H₂O₂ and •OH increased as the illumination time and began to decrease once reaching a level. Therefore, catalyst MnPcS-TiO₂ activated water molecules and dissolved oxygen in water to produce H₂O₂ and •OH and then degraded RhB. Figure 8 illustrated the possible mechanism of the photocatalytic degradation of RhB by MnPcS-TiO₂. The oxidation reduction potential of the singlet state 1 ($S_1$) of MnPcS ($E_{S1} = -0.63\text{eV}$ versus NHE) was higher than the oxidation reduction potential of the conduction band of TiO₂ ($E_{CB} = -0.5\text{eV}$).
versus NHE)\(^7\). While the oxidation reduction potential of triple state \((T_1)\) of MnPcS \((E_{T1} = -0.02\text{eV versus NHE})\) was lower than the oxidation reduction potential of conduction band of TiO\(_2\). MnPcS in the ground state \((S_0)\) \((E_{S0} = 1.18\text{eV versus NHE})\) 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\(_2\)O\(_2\) and •OH to achieve visible photocatalytic degradation of toxic organic pollutants. The reaction separated light-induced charge effectively and improve the photocatalytic efficiency greatly.

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\text{MnPcS}(S_0) + \text{hv} \rightarrow \text{MnPcS}^*(S_1) \quad (1)
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\[
\text{MnPcS}^*(S_1) + \text{TiO}_2(\text{CB}) \rightarrow \text{MnPcS}(S_0) + e^-(\text{TiO}_2/\text{CB}) \quad (2)
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References


