

Photocatalytic Degradation of Methyl Orange by Chitosan Modified TiO₂

Ping Lu, Yuan Jing, Qiuyun Zhang, Hongkun Ying, Laisheng LI *

School of Chemistry & Environment, South China Normal University, Guangzhou, 510006, China

Email: llsh@scnu.edu.cn

Abstract: A chitosan modified TiO₂ (CTS/TiO₂) photocatalyst was prepared by a sol-gel method and used for degrading methyl orange. The photocatalyst was characterized by XRD, BET and TEM techniques. The characterization results show that the addition of chitosan can decrease agglomeration in crystallization. CTS/TiO₂ shows higher photocatalytic activity than pure TiO₂ in degrading methyl orange. During degradation of methyl orange (pH = 6.0) with the presence of CTS/TiO₂ (1.0 g/L) and UV (light intensity = 6 mW/cm²), its removal rate reaches 48 % at 60 min oxidation time, only 32 % using pure TiO₂ as photocatalyst. In addition, the degradation efficiency of methyl orange was significantly affected by oxygen flow rate, catalyst dosage and light intensity.

Keywords: chitosan modified TiO₂; photocatalysis; methyl orange

1 Introduction

The azo dyes, widely used in the process of dyeing textile, paper, leather, ceramic, cosmetics, ink, and food processing, were found to have great hazards to human health and environment due to the fact that 15 % of the dyes produced are lost during production and application [1]. The treatments of these pollutants involve chemical, physical, and biological methods [2-5], in which advanced oxidation processes (AOPs) such as sonolysis, radiolysis, and photocatalysis have emerged as useful methods for mineralizing organic compounds in aqueous media [6-8]. Photocatalytic processes have been receiving much attention, particularly for their complete destruction or mineralization of the toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents in both water and gas phases [9-12]. Among the photocatalysts applied, nanosized TiO₂ has been proved to be an excellent catalyst in the photocatalytic degradation of organic pollutants, because it is an effective, photostable, reusable, inexpensive, non-toxic and easily available catalyst [13]. Among various techniques available for the fabrication of TiO₂ nanoparticles, the sol-gel technique has been widely employed due to its low cost equipment required and highly pure products produced. However, the crystallization of titanate often takes place at high temperatures (400-600 °C), and is accompanied with high shrinkage or collapse of the mesostructure and is eventually followed by the increase in nanoparticle size and the decrease in specific surface area [14]. To aim for TiO₂ with high dispersed and unagglomerated quality, chitosan is added in TiO₂ sol before calcining, chitosan was chosen as the poly-

meric matrix because of its good forming properties, chemical resistance as well as reactive amino and hydroxyl groups, which facilitate the preferential sorption and diffusion of water molecules [15]. Methyl orange (MO) was chosen for a representation of azo dyes, photoactivity of CTS/TiO₂ was evaluated by the degradation of methyl orange.

2 Experimental

2.1 Preparation of CTS/TiO₂ catalyst

TiO₂ catalyst using tetrabutyl titanate as a titanium precursor was prepared by the sol-gel method at room temperature. 70 ml absolute alcohol, 10 ml tetrabutyl titanate and 3 ml diethanolamine were mixed as a solution at room temperature. Then it was added 4 ml deionized water drop-wise under vigorous stirring. After that, 45 ml glacial acetic acid with the dissolved CTS was added into TiO₂ sol. The mixed solution was aged for 24 h till the formation of xerogel, then ground into powder. The powder was calcined at 500 °C for 2 h, the CTS/TiO₂ was obtained.

2.2 Catalyst characterization

The crystalline phase of samples was determined using an X-ray diffractometer (Y-2000, China) employing Cu K α radiation. The surface morphology of the samples was visualized using transmission electron microscope micrographs (MODEL H-300, JAPAN). The textural properties such as specific surface area, pore volume, pore size were determined by nitrogen adsorption and desorption. Nitrogen adsorption and desorption isotherms were recorded on gas adsorption system (Micromeritics, ASAP 2020, USA).

资助信息：国家自然科学基金 (No. 20977036)

2.3 Photocatalytic experiments

A 1 L glass tubular photoreactor (h = 500 mm, ϕ_{in} = 60 mm) was employed for the photocatalytic oxidation experiments. A coaxial UV source (a 15W UV lamp with a characteristic wavelength of 254 nm) surrounded by quartz thimble (30 mm diameter). Pure oxygen was continuously bubbled into the 10 mg/L MO solution through a porous glass frit and flowed upward in the annular section between the UV lamp and the inner surface of reactor. Samples were taken at regular intervals to a UV-2800H UV-Vis spectrophotometer at λ = 470 nm to test the concentrations of MO.

3 Result and discussion

3.1 Characterization of CTS/TiO₂ catalyst

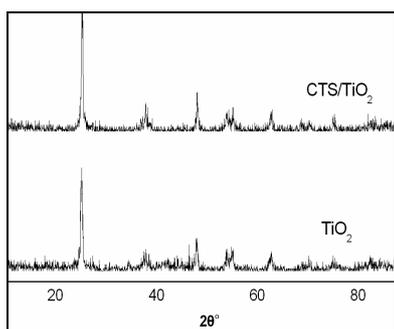


Figure 1. The XRD spectra of TiO₂ and CS/TiO₂

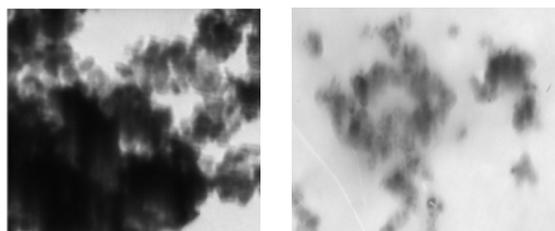


Figure 2. TEM images of TiO₂ (a) and CTS/TiO₂ (b)

Figure 1 showed XRD patterns of CTS/TiO₂ and pure TiO₂ calcined at 500 °C. All samples consist of anatase and rutile phases and no other phases can be found after calcining, which demonstrates that the addition of chitosan has no obvious influence on TiO₂ crystallizing process. Besides that, chitosan played a promote role in the process of crystallization which can be seen from appearance that anatase phase characteristic diffraction peaks became sharp and the diffraction peak intensity increased. The average crystallite sizes of TiO₂ were calculated by Scherrer's equation using the full width at half maximum of the X-ray diffraction peaks at θ = 25.3° corresponding to the most intense anatase peak. The

crystallite size of CTS/TiO₂ was 14.2 nm which was smaller than 18.5 nm of pure TiO₂. TEM photographs of CTS/TiO₂ and TiO₂ powders were displayed in Figure 2. It can be observed that the CTS/TiO₂ primary particles were relative uniform and the sizes of the primary particles which were in agreement with the value determined by XRD analysis. While the TiO₂ powders without chitosan showed a very serious agglomeration after drying and calcining in crystallizing process. The surface area and average pore size of TiO₂ and CTS/TiO₂ was showed in Table1, the surface area of CTS/TiO₂ had a slight increasing compared with pure TiO₂, the bigger average pore size was caused by CTS eliminating in calcination process.

Table1 Surface area and average pore size of TiO₂ and CTS/TiO₂

samples	Surface area (m ² /g)	Average pore size (nm)
TiO ₂	24.2	88.1
CTS/TiO ₂	28.4	105.4

3.2 Influence factors of MO degradation in photocatalytic process

3.2.1 Influence of chitosan content on TiO₂ catalyst

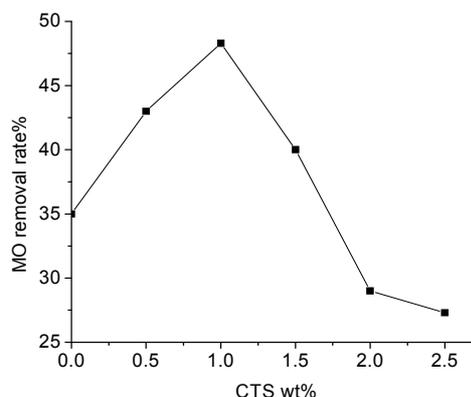


Figure 3. MO removal varies with the content of CTS added TiO₂ at 60min oxidation time

Figure 3 presented the photocatalytic activity of CTS/TiO₂ for degrading MO when the amount of chitosan increases from 0 wt% to 2.5 wt% (gas flow rate = 0.4 L/min; catalyst dosage = 1.0 g/L; light intensity = 6 mW/cm²). The effectiveness of the catalyst was strongly dependent on the adding of chitosan. Low content of CTS adding can increase the TiO₂ photocatalytic activity. First, the MO removal efficiency at 60 min oxidation time increased with chitosan content, when the content of

CTS increases to 1.0 % (w/w), its removal ratio reaches optimum (48.2 %), only 32 % using pure TiO₂ as photocatalyst. Then its photocatalytic efficiency decreased with chitosan content increase. For higher chitosan contents, it couldn't make a value of dispersant for the TiO₂ sol for condensation reaction occurred immediately.

3.2.2 Influence of gas flow rate

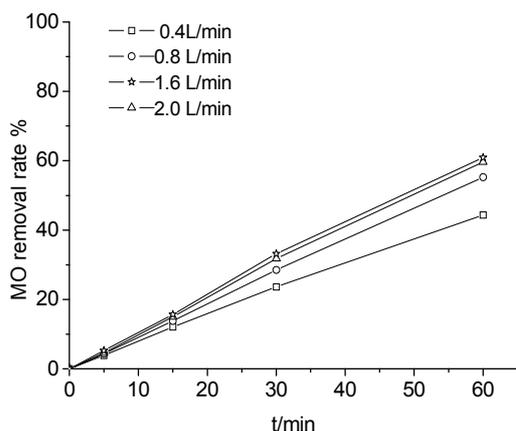


Figure 4. Effect of gas flow rate on MO removal efficiency

Gas flow rate was usually the first variables studied in a heterogeneous gas-liquid-solid reaction. Some experiments were carried out at different gas flow rate (between 0.4 L/min and 2 L/min). The effect of gas flow rate on the MO removal against time can be observed in Figure.4 (catalyst dosage = 1.0 g/L; light intensity = 0.6 mW/cm²), the MO removal first increased with the gas flow rates and the remaining dimensionless concentration profile of MO with time does not vary when it is higher than 0.8 L/min. In the heterogeneous system, the rate determining step is the gas-phase mass transfer, or surface reaction, or both of them [16]. In the region of lower gas flow rate (0.4-1.6 L/min), the apparent MO removal rate was dependant upon the gas-phase transfer rate which increased with the gas flow rate, when the gas flow was higher than 1.6 g/L, the reaction rate determining step became the surface reaction.

3.2.3 Influence of catalyst dosage

The influence of catalyst dosage on the degradation of MO in photocatalytic process can be observed in Figure.5 (gas flow rate = 0.8 L/min; light intensity = 0.6 mW/cm²). It could be seen that the degradation rate appeared to increase rapidly with catalyst concentration from 0.5 to 1.5 g/L, probably due to the increase of active sites with the suspension of catalyst loading. There was a leap increasing effect of catalyst dosage (from 0.5-1.5 g/L) on the removal rate of MO, it can reached

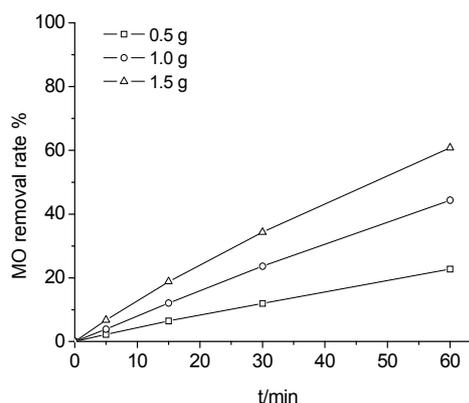


Figure 5. Effect of catalyst dosage on MO removal efficiency

60.8 % in 60min with 1.5 g/L catalyst dosage which was 16.4 %, 38.1 % higher then that with 1.0 g/L, 0.5 g/L catalyst dosage respectively.

3.2.4 Influence of light intensity

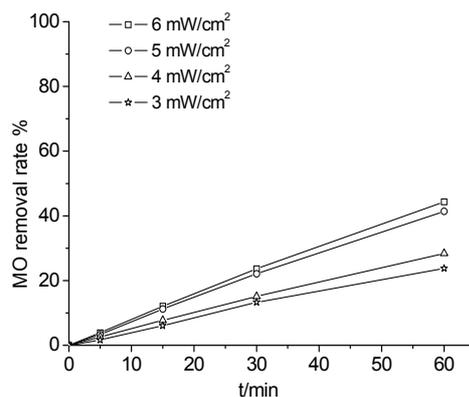


Figure 6. Effect of light intensity on MO removal efficiency

The effect of light intensity on the MO degradation was shown in Figure 6 (gas flow rate = 0.8 g/L; catalyst dosage = 1.5 g/L). The 15 w 254 nm UV lamps were used to be the light source. Light intensity played an important role in photocatalytic process. Photocatalyst can absorb more photons in higher light intensity radiated by light source. The result from Figure.6 showed that the MO removal was gradually increasing with higher light intensity. The MO removal can reach 45 % at 60 min when CTS/TiO₂ radiated in 6 mW/cm², it is 2.5 times than that radiated by UV lamp of 3 mW/cm² light intensity. And there was an obvious increasing when the light intensity enhances from 4 mW/cm² to 5 mW/cm².

4 Conclusions

CTS/TiO₂ prepared by sol-gel method characterized by

XRD, TEM and BET, CTS/TiO₂ particles generated were at the nanosized level, relative uniform and dispersed homogeneously. Chitosan adding played a promote role in the process of crystallization, ameliorate the agglomeration in calcining process of classic sol-gel method.

Compared with a series of degradation of MO with the amount of chitosan adding in TiO₂ from 0 wt% to 2.5 wt%, in a low concentration range, CTS/TiO₂ show better photocatalytic activity than pure TiO₂ and the optimum chitosan adding concentration is 1.0 %(w/w).

Influence factors of degradation of MO in photocatalytic process were also investigated, gas flow rate, catalyst dosage and light intensity can influence the MO removal rate in photocatalytic process, The optimization of variables in photocatalytic process concluded gas flow rate = 0.8 g/L; catalyst dosage = 1.5 g/L and light intensity = 5 Mm/cm² were obtained.

Acknowledgments

The authors are grateful for the financial support from National Natural Science Foundation of China (contract No. 20977036).

References

- [1] H. Destailats, A.J. Colussi, J.M. Joseph, M.R. Hoffmann, Synergistic Effects of Sonolysis Combined with Ozonolysis for the Oxidation of Azobenzene and Methyl Orange[J], *Journal of Physics and Chemistry A*, 2000, 104(39), P8930-8935.
- [2] V.K. Gupta, R. Jain, S. Varshney, Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents[J], *Journal of Colloid and Interface Science*, 2007, 312(2), P292-296.
- [3] J.T. Li, M. Li, J.H. Li, H.W. Sun, Drastically enhanced ultrasonic decolorization of methyl orange by adding CCl₄[J], *Ultrasonics Sonochemistry*, 2007, 14(2), P253-258.
- [4] L.M. Wang, L.H. Zhu, W. Luo, Y.H. Wu, H.Q. Tang, Decolorization of azo dye direct scarlet 4BS solution using exfoliated graphite under ultrasonic irradiation[J], *Ultrasonics Sonochemistry*, 2007, 14(2), P241-245.
- [5] X.B. Cheng, R. Jia, P.S. Li, S.Q. Tu, Q. Zhu, W.Z. Tang, X.D. Li, Purification of a new manganese peroxidase of the white-rot fungus *Schizophyllum* sp. F17, and decolorization of azo dyes by the enzyme[J], *Enzyme and Microbial Technology*, 2007, 41(3), P258-264.
- [6] I.Gültekin, N.H.Ince, Degradation of aryl-azo-naphthol dyes by ultrasound, ozone and their combination: Effect of α -substituents[J], *Ultrasonics Sonochemistry*, 2006, 13(3), P208-214.
- [7] H.J. Ma, M. Wang, R.Y. Yang, W.F. Wang, J. Zhao, Z.Q. Shen, S.Yao, Radiation degradation of Congo Red in aqueous solution[J], *Chemosphere*, 2007, 68(6), P1098-1104.
- [8] L. Wojnárovits, T. Pálfi, E. Takács, Kinetics and mechanism of azo dye destruction in advanced oxidation processes[J], *Radiation Physics and Chemistry*, 2007, 76(8-9), P1497-1501.
- [9] Laisheng Li, Wanpeng Zhu, et al., Photocatalytic ozonation of dibutyl-phthalate over TiO₂ film[J], *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, 175(2-3), P172-177.
- [10] L.C. Chen, F.R. Tsai, C.M. Huang, Photocatalytic decolorization of methyl orange in aqueous medium of TiO₂ and Ag-TiO₂ immobilized on γ -Al₂O₃[J], *Journal of Photochemistry and Photobiology A: Chemistry*, 2005, 170(1), P7-14.
- [11] Laisheng Li, Wanpeng Zhu, Pengyi Zhang, Qiuyun Zhang, Zulin Zhang, TiO₂/UV/O₃-BAC processes for removing refractory and hazardous pollutants in raw water[J], *Journal of Hazardous Materials*, 2006,128(2-3), P145-149.
- [12] Laisheng Li, Pengyi Zhang, Wanpeng, Wenya Han, Zuling Zhang, Comparison of O₃-BAC, UV/O₃-BAC and TiO₂/UV/O₃-BAC processes for removing organic pollutants in secondary effluents[J], *Journal of Photochemistry and Photobiology A: Chemistry*, 2005, 171(2), P145-151.
- [13] A. Haarstrick, O.M. Kut, E. Heinzle, TiO₂-Assisted Degradation of Environmentally Relevant Organic Compounds in Wastewater Using a Novel Fluidized Bed Photoreactor[J], *Environmental Science Technology*, 1996, 30(3), P817-824.
- [14] Qiaorong Sheng, Ye Cong, Shuai Yuan, Jinlong Zhang, Masakazu Anpo. Synthesis of bi-porous TiO₂ with crystalline framework using a double surfactant system. *Microporous and Mesoporous Materials*, 2006, 95(1-3), P220-225.
- [15] Nawawi, M., Ghazali, M., Huang, R.Y.M., Pervaporation dehydration of isopropanol with chitosan membranes[J], *Journal of Membrane Science*, 1997, 124(1-2), P53-62.
- [16] Pinyu Kuo, Grace W.M. Lee. Decomposition of gas-phase toluene by the combination of ozone and photocatalytic oxidation process (TiO₂/UV, TiO₂/UV/O₃, and UV/O₃)[J], *Applied Catalysis B: Environmental*, 2007, 75(1-2), P29-38.