

Preparation of TiO₂/C/Fe₃O₄ Magnetic Composite Catalyst and Research of its Photocatalytic Performance

Yi Yan JIANG, Ran ZHENG, Zhi Jie SHEN, Yi Ping ZHANG*

School of Science and Technology, Zhejiang International Studies University,
Hangzhou, Zhengjiang 310023, China

Email: yipingzhang@zisu.edu.cn

Abstract: TiO₂/C/Fe₃O₄ magnetic composite catalyst was prepared by using glucose as carbon source to attach an intermediate isolation layer and then wrapping TiO₂ directly on Fe₃O₄ magnetic support. The catalytic performance of the catalyst was studied by photodegrading RhB simulated wastewater under the changed external conditions such as light resource, temperature, pH and ion intensity of the solution. It was found that the photocatalytic performance under uv light was better than that of the catalyst under the visible light. The photocatalytic performance increased with the increase of temperature and acidity of the wastewater, and the decrease of the ion intensity of the wastewater. The optimum photocatalytic reaction condition was under uv light, the temperature was 75°C, pH was 1 and ion intensity was 1mmol/L. The magnetic effect was applied to the reutilization of the catalyst, and the fourth recycled catalyst still had catalytic activity, but with the increase of reusing time, the photocatalytic performance of the catalyst decreased gradually. The photodegradation rate of the recycled catalyst 90 min later was reduced from 76.20% to 57.08%, 41.80%, 28.44%, respectively, while 4 times of repeated use under uv light, 25°C, pH 1, and ion intensity 1 mmol/L.

1. Introduction

In recent years, the water pollution of organic compounds is becoming more and more serious, among which dye pollution occupies most of the water pollution of organic substances. Once a large amount of water is polluted, the dye can absorb the sunlight and reduce the transparency of the water, and then affect the growth of aquatic life in water and weaken the self-purification ability of water. In one test, most of the organic pollutants discharged from the dye industry have biological toxicity or lethality, and a considerable portion of azo, triarylmethane and anthraquinone dyes are more carcinogenic.

In the field of photocatalysis, when Fujishima et al [1] used titanium dioxide as photocatalyst to decompose water to produce hydrogen since 1972, people began to focus on TiO₂, a semiconductor material. A lot of research by scholars in related fields proved that nanoscale TiO₂ had excellent performance in photocatalytic sterilization, ultraviolet absorption, decomposition of organic matter and other application fields. Therefore, people began to apply TiO₂ to water treatment, antiseptic and deodorization, and TiO₂ was used more and more widely. However, because the average particle size of TiO₂ is about 21 nm, when it is used alone, the particles are too small to recycle.

In order to solve the problem of the above recovery difficulties involved, the concept of magnetic photocatalyst with separation function was proposed. The first magnetic photocatalyst was prepared through the deposition of titanium dioxide onto a magnetite core in 1994 by Hiroshi F et al [2]. Liu S Q [3] reviewed the photocatalytic principle, structure and application of the magnetic semiconductor



catalysts in his article. Based on the purpose of environmental protection and sewage treatment, this paper aims at magnetic TiO₂ photodegradation of organic dyes. We consulted the references of Chang S W et al [4] for the research of Ag/TiO₂/Fe₃O₄ composite catalyst on 4-chlorophenol degradation under ultraviolet light and Xiang Y et al [5] for the research of Fe₃O₄/Chitosan/TiO₂ composite catalyst on the degradation of methylene blue. With Fe₃O₄ as magnetic support, TiO₂/C/Fe₃O₄ magnetic composite catalyst was prepared and used for photocatalytic degradation of dye wastewater, the recycle and reuse can be realized because of the magnetic effect and the large particles of the catalyst.

As to achieve the best catalytic performance of the catalyst, the influence of external factors, such as the type of irradiation light source, temperature, pH and the ion intensity of the dye solution on the photocatalytic activity of magnetic photocatalyst was also studied.

2. Experimental

2.1 Preparation of TiO₂/C/Fe₃O₄ Composite Catalyst

If TiO₂ is attached directly to the magnetic support, the magnetic support will be induced photodissolution under light irradiation, which leads to the reduction of photocatalytic activity [6]. If an inert isolation layer is loaded on the surface of magnetic support, it can overcome the shortcomings to a certain extent and prevent the photochemical corrosion of magnetic support, and thus reduce the influence on photocatalytic activity of TiO₂. The thin inorganic isolation layer, such as SiO₂, Al₂O₃ and so on [7, 8], cannot completely prevent the diffusion of magnetic support material to TiO₂, thereby reducing the photocatalytic activity of TiO₂. While the intermediate isolation layer is too thick, it will block the magnetism of the support, thus affecting the recycling and utilization, so we use organic matter as the isolation layer.

Put 2.0 g Fe₂(SO₄)₃ into 500 mL three neck flask, dissolved it with 150 mL distilled water, stirred up to 60 °C for 10 min through the N₂ protection. Then added 1.5 g FeSO₄·7H₂O, the right amount of sodium dodecyl sulfate and 1 mol/L NaOH until to pH = 11, stirred the solution at 60 °C for 1 h. Pour out the solution, then add 50 mL 1 mol/L glucose solution to the black Fe₃O₄ precipitation, stirred the solution at 60 °C for 0.5 h. Added a certain amount of TiO₂, continued to stir at 60 °C for 1 h. Cooled to room temperature, after magnetic settlement, dried the precipitation at 80 °C for 12 h, then got the TiO₂/C/Fe₃O₄ composite catalyst.

2.2 Photocatalysis Reaction of TiO₂/C/Fe₃O₄ Composite Catalyst

The photocatalytic activity was determined by using the solution of rhodamine B (RhB, organic dye) as the simulated wastewater. Measured 100 mg TiO₂/C/Fe₃O₄ magnetic support composite catalyst, ultrasonic dispersed to 100 mL 1×10⁻⁵ mol/L RhB solution. First adsorbed in the dark room 30 min for balance, then irradiated under the light source. Sampled every 15 min, the RhB concentration was measured with ultraviolet visible (UV VIS) spectrophotometer, and the absorbance was recorded. The ratio (A₀-A) /A₀ was calculated, that is, the degradation rate, where A₀ was the initial absorbance, and A was the absorbance after a certain time of photocatalysis, and the degradation rate-time curve was obtained.

2.3 Characterization of TiO₂/C/Fe₃O₄ Composite Catalyst

The morphology of the catalyst was observed by scanning electron microscope (SEM).

3. Results and discussion

3.1 Influence of Types of Light Sources on Catalytic Performance

Ultraviolet light (UV, 254 nm) and sunlight (visible light) as the light sources were used to study the photocatalytic degradation performance of TiO₂/C/Fe₃O₄ composite catalysts respectively for RhB simulated wastewater. The absorbance of RhB simulated wastewater under the degradation of different light sources at different time was recorded. The ratio of absorbance reduction after

photodegradation(A_0-A) and initial value (A_0) of RhB simulated wastewater was the index of degradation rate, and the degradation rate (%) - degradation time (t) curve was plotted. Figure 1 is a comparison of the photocatalytic degradation performance of the catalyst under different light sources.

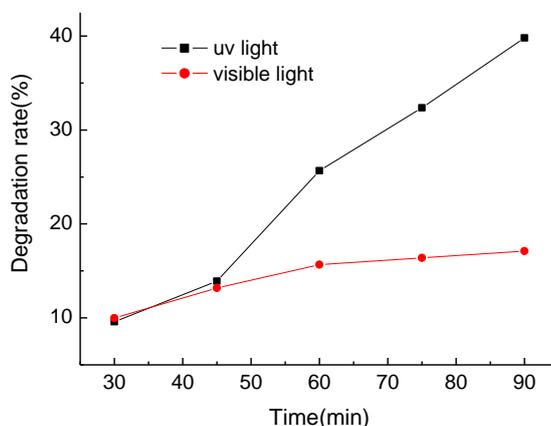


Figure 1 Comparison of the Photodegradation Performance of Composite Catalysts under Different Light Sources

*Temperature=25°C, pH=5, ion intensity=10 mmol/L

As can be seen from Figure 1, the photocatalytic degradation of the composite catalyst by uv light was obviously better than that of visible light. The wavelength of ultraviolet light is shorter, the energy is higher, and the reaction is more sufficient. The degradation rate of RhB simulated wastewater was only 17.11% after the visible light degradation of 90 min, it was far away from the degradation rate of 39.81% under UV light source.

3.2 Influence of Reaction Temperature on Catalytic Performance

Using ice water bath and constant temperature water bath to change the temperature of catalytic solution respectively, the photocatalytic degradation performance of $\text{TiO}_2/\text{C}/\text{Fe}_3\text{O}_4$ composite catalyst under uv light for RhB simulated wastewater was studied. The absorbance of RhB simulated wastewater under the degradation of different temperature at different time was also recorded. The comparison of the photodegradation performance of composite catalysts at different temperature was shown in Figure 2.

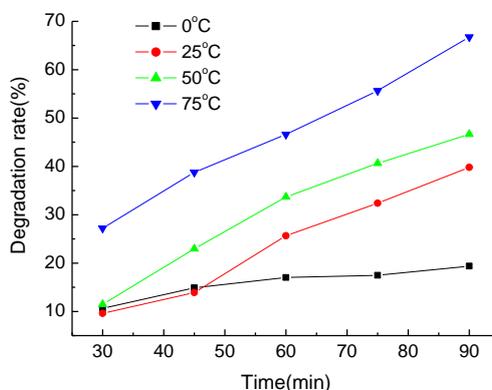


Figure 2 Comparison of the Photodegradation Performance of Composite Catalysts at Different Temperature

*uv light, pH=5, ion intensity=10 mmol/L

It can be seen from Figure 2, with the increase of temperature, the rate of degradation was also increasing, that is accord with the principle of thermal dynamics. The degradation rate of RhB simulated wastewater was obviously enhanced at 75 °C, which was up to 66.75% 90 min later.

3.3 Influence of pH on Catalytic Performance

The photocatalytic degradation performance of $\text{TiO}_2/\text{C}/\text{Fe}_3\text{O}_4$ composite catalyst used in RhB simulated wastewater was studied by changing the pH of the catalytic solution. With the absorbance data under different pH after different degradation time, we got Figure 3, comparison of the photodegradation performance of composite catalysts at different pH.

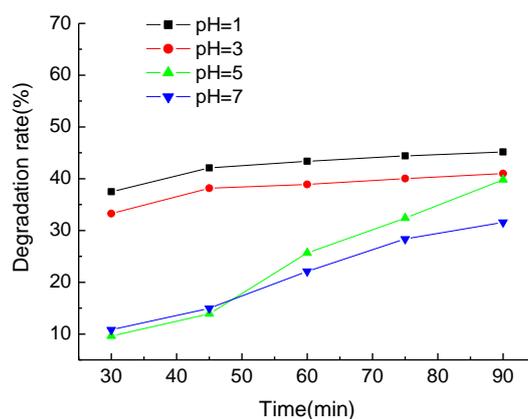


Figure 3 Comparison of the Photodegradation Performance of Composite Catalysts at Different pH
*uv light, temperature=25°C, ion intensity=10 mmol/L

From Figure 3, it can be seen that the catalytic rate increased with the increase of the acidity of the solution. This is because positive ion adhered on the surface of the catalyst, and rhodamine B molecules existed in the presence of negative ions under acid condition, there was electrostatic attraction between the two molecules, which will speed up the adsorption process and the photocatalytic reaction. The degradation rate of RhB simulated wastewater was 45.15% after 90 min when pH=1.

3.4 Influence of Ion Intensity on Catalytic Performance

The ion intensity of catalytic solution was changed based on NaNO_3 as standard substance, and the photocatalytic degradation performance of $\text{TiO}_2/\text{C}/\text{Fe}_3\text{O}_4$ composite catalyst in RhB simulated wastewater was plotted in Figure 4.

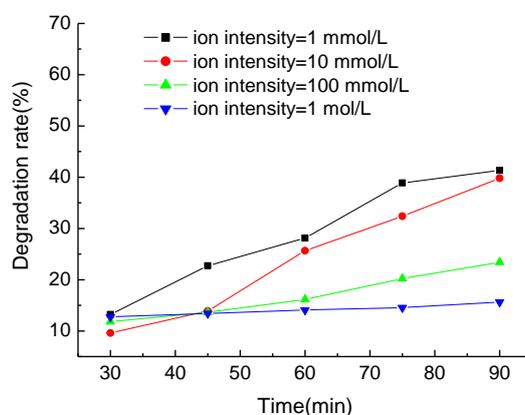


Figure 4 Comparison of the Photodegradation Performance of Composite Catalysts in Different Ion Intensity

*uv light, temperature=25°C, pH=5

Figure 4 shows that the degradation effect of the composite catalyst decreased with the increase of the solution ionic intensity, the best catalytic performance appeared as the ionic intensity was 1mmol/L, the value of degradation rate was 41.32% after 90 min. This is due to the increase of ion intensity of the solution will enhance the agglomeration of composite catalyst, which made the catalyst surface area reduce, hydroxyl radicals on the catalyst surface will also decrease, and the hydroxyl radical played an important role in the photodegradation of the catalyst, so the catalytic performance of catalyst dropped down.

3.5 Reuse of Composite Catalyst

After the recovery of the catalyst, the photocatalytic experiment was carried out again according to the above operation. Figure 5 is a comparison of the photodegradation performance of the recycled composite catalyst.

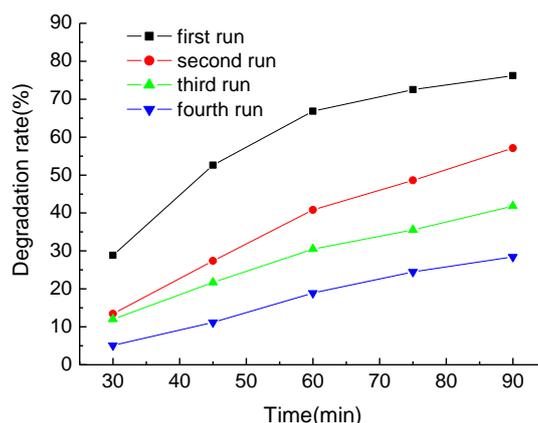


Figure 5 Comparison of Photodegradation Performance of the Recycled Catalyst

*uv light, temperature=25°C, pH=1, ion intensity=1 mmol/L

As can be seen from Figure 5, with the increase of reusing times, the photocatalytic performance of the catalyst decreased gradually. When the reaction condition was uv light, temperature=25°C, pH=1, ion intensity=1 mmol/L, the photodegradation rate of the recycled catalyst after 90 min was reduced

from 76.20% to 57.08%, 41.80%, 28.44% , respectively, while 4 times of repeated use. The most important factor was the loss of TiO₂ active components during reusing process.

3.6 SEM Characterization

Figure 6 is a diagram of the SEM of the prepared composite catalyst.

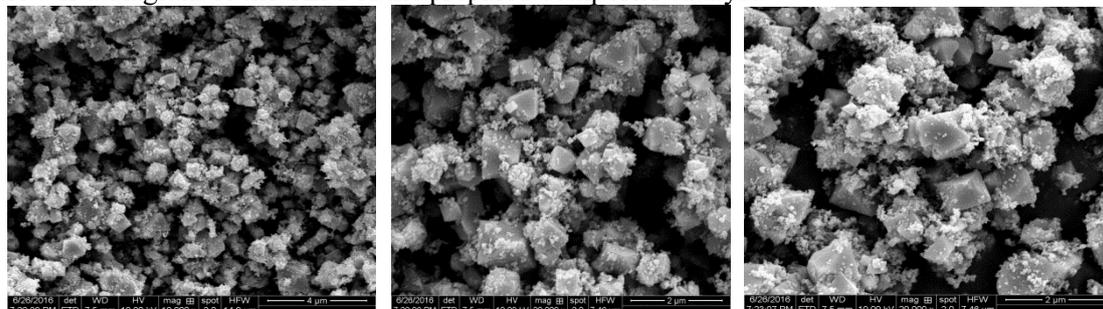


Figure 6 Diagram of SEM of TiO₂/C/Fe₃O₄ composite catalyst

It can be seen from Figure 6 that the small particles of TiO₂ are attached to the surface of crystalline granular Fe₃O₄ with different degree clusters, this proved the successful preparation of the composite catalyst.

4. Conclusion

(1) In this paper, we prepared magnetic Fe₃O₄ support using ferric sulfate and ferrous sulfate first, then covered it with glucose as an inert carbon layer, at last, coated TiO₂ directly on the surface of the support, the TiO₂/C/Fe₃O₄ composite catalyst was prepared successfully.

(2) As the prepared magnetic TiO₂/C/Fe₃O₄ composite catalyst was applied for the RhB dye wastewater, the photocatalytic performance under uv light was better than that of the catalyst under the visible light. The photocatalytic performance increased with the increase of temperature and acidity of the wastewater, and the decrease of the ion intensity of the wastewater. The optimal photodegradation condition was 75 °C, pH=1, ion intensity=1mmol/L.

(3) The recovery experiments of the magnetic TiO₂/C/Fe₃O₄ composite catalyst showed that the recovered catalyst can still photodegrade rhodamine B wastewater after four reutilizations, but the catalytic performance decreased with the reuse time of the catalyst. It is in accordance with the original design purpose of this paper, solving the recycling difficult problems caused by the too small TiO₂ particles, which can be of a certain economic value and use value after the improvement in the future.

References

- [1] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode[J]. *Nature*, 1972, 238: 37-38.
- [2] Hiroshi F, Yukiko H, Michichiro Y, Shoichi A. Magnetic photocatalyst[P]. Japanese Patent, JP6154620 (A), 1994.
- [3] Liu S Q. Magnetic semiconductor nano-photocatalysts for the degradation of organic pollutants[J]. *Environmental Chemistry Letters*, 2012, 10(3): 209-116.
- [4] Chang S W, Chung W J, Yu S H, Lee S J. Photocatalytic degradation of 4-chlorophenol using a Ag/TiO₂/Fe₃O₄ composite under UV-A irradiation[J]. *Desalination and Water Treatment*, 2015, 54(13): 3646-3653.
- [5] Xiang Y, Wang H, He Y, Song G W. Efficient degradation of methylene blue by magnetically separable Fe₃O₄/chitosan/TiO₂ nanocomposites[J]. *Desalination and Water Treatment*, 2015, 55(4): 1018-1025.
- [6] Watson S, Beydoun D, Amal R. Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO₂ crystals onto a magnetic core[J]. *Journal of Photochemistry and*

- Photobiology A: Chemistry, 2002, 148(1-3): 303-313.
- [7] Su T L, Chiou C S, Chen H W. Preparation, Photocatalytic Activity, and Recovery of Magnetic Photocatalyst for Decomposition of Benzoic Acid[J]. International Journal of Photoenergy, 2012, Article ID 909678, 8 pages.
- [8] Harraz F A, Mohamed R M, Rashad M M, Wang Y C, Sigmund W. Magnetic nanocomposite based on titania–silica/cobalt ferrite for photocatalytic degradation of methylene blue dye[J]. Ceramics International, 2014, 40(1): 375-384.