Studies on the Synthesis and Photocatalytic Properties of Zinc Ferrite Materials

Xinxin Wang¹,a and Nan Wang²,b

¹School of Chemistry and Bioengineering, Qilu Institute of Technology, Jinan, Shandong, 250200, China
²School of Chemistry and Bioengineering, Qilu Institute of Technology, Jinan, Shandong, 250200, China

aeyah15@citicpe.net.cn, bemail: wang63ma@163.com, bemail: 1164066488@qq.com

Abstract. Zinc ferrite precursors are prepared by coprecipitation method using zinc nitrate and ferric nitrate as reactants, monohydrate ammonia and citric acid as precipitants and dispersants respectively. And zinc ferrite precursors are calcined at high temperature to obtain zinc ferrite photocatalysts at different temperatures(350℃, 450℃, 550℃). Methylene blue is used as substrates. The quality of the catalyst, the type of catalyst and the temperature of calcining are measured to study the photocatalytic performance. The results show that the preparation of zinc ferrite under 450℃ has an optimal effect on the degradation of methylene blue dye. Compared with iron oxide and zinc oxide, the photocatalytic properties of zinc ferrite are superior to that of single oxide.

1. Introduction

With the development of industry, water resources are severely polluted. Among them, most of the organic dyes in wastewater can cause distortion in animals, genetic mutations and carcinogenicity, which seriously endanger the health of the public and cause various degrees of harm to human systems [1]. The headache has always been a problem that scientists want to overcome. The general methods are difficult to meet the emission requirements, such as precipitation [2-5], membrane filtration methods [6, 7], as well as more environmentally friendly biodegradation methods. Here, photocatalytic degradation has unique advantages [8-11]. Many dyes are photosensitizers, which can accelerate the photocatalytic oxidation reaction. So the photocatalytic degradation method is of great help to the treatment of dye wastewater. In the photoreaction process, the reaction speed is accelerated due to the participation of the catalyst, and the appropriate catalyst can be used well for the degradation of pollutants. There are many types of photocatalyst materials. Common catalysts are zinc, tin, titanium, zirconium oxide, and zinc ferrite [12-14]. In particular, zinc ferrite is widely used as the photocatalyst in the fields of solar energy conversion and photocatalysis.

When zinc ferrite is used as a photocatalyst, it shows high utilization of visible light. Zinc ferrite is prepared by a combination of the solvothermal method and co-precipitation method. The photocatalytic degradation effect is measured with methylene blue solution as the catalytic target [15]. The result shows that zinc ferrite had a good catalytic effect under certain conditions. After irradiation with methyl orange, the decolorization efficiency of zinc ferrite can be as high as 95%. It can be seen that zinc ferrite has a relatively high light utilization rate and good stability, which has a good prospect
in the field of photocatalytic applications. Shen et al. also have studied the photodegradation of Congo red in dye wastewater. The catalyst used is zinc ferrite [16]. The results show that Congo red can be quickly decolorized by zinc ferrite under light irradiation and the removal rate can reach 92%. Even being used repeatedly, the degradation rate is still as high as 88%. These experimental results further show that the photocatalytic activity and stability of zinc ferrite catalysts are relatively high. The use of zinc ferrite as the photocatalyst in the photocatalytic treatment of water pollution is a relatively new approach, which can solve the problems of high energy consumption in the process, demanding experimental requirements, complicated operations, and secondary pollution [1, 4]. It plays an extremely important role in protecting the ecological environment and treating various kinds of sewage.

2. Experimental

Synthesis of Zinc Ferrite. A certain proportion of zinc nitrate powder and iron nitrate powder are dissolved in the beaker. Then, dilute ammonia is slowly added while stirring. At the same time, citric acid is added to prevent agglomeration [15], and the brown-red precipitate is formed in the beaker. Simultaneously the pH of the solution is adjusted by the pH meter. After stirring for 30 minutes, the beaker is boiled for 2 h. the obtained precipitation is vacuum filtrated, and then washed by distill water and ethanol until the filtration was colorless. After drying at 120°C overnight, zinc ferrite precursors are obtained. The precursors were respectively calcined at 350°C, 450°C, and 550°C for 2 h to obtain zinc ferrite powder.

Photocatalytic Performance Measurement. Methylene blue solution is used to simulate the dye wastewater. A series of standard methylene blue solutions are prepared. The absorbance is measured with a visible spectrophotometer. In the course of the experiment, a certain amount of the photocatalytic reaction solution is taken out every 20 minutes, and the supernatant is centrifuged. The absorbance is measured at 664 nm.

3. Results and discussion

Because the relationship between the detected absorbance and the concentration after photocatalysis is in accordance with Lambert-Beer's law, the photodegradation effect of zinc ferrite can be evaluated by calculating the photodegradation rate. The calculation formula of degradation rate (η) is as follows:

\[ \eta = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\% \]

In the formula, A0 represents the absorbance of the reference solution; At represents the absorbance of the sample at t min during photodegradation; η represents the degradation rate of the substrate solution.

Drawing of Methylene Blue Standard Curve. Methylene blue standard solutions were prepared at concentrations of 1 mg/L, 5 mg/L, 10 mg/L, 15 mg/L, and 20 mg/L, respectively. And the absorbance was measured at 664 nm. The standard curve of methylene blue is drawn, as shown in Figure 1.
As can be seen from Figure 1, the linear equation of the absorbance and concentration curve is: 
\[ A = 0.04432 + 0.1006c \]
where the linear correlation coefficient \( R^2 = 0.9896 \), and \( c \) is the concentration of the methylene blue solution.

Infrared Spectral Characterization. In the zinc ferrite molecule, each O\(_2\)- is shared by one tetrahedral cation and three octahedral cations. All vibrations of O\(_2\)- are related to both tetrahedron and octahedron. Therefore, the infrared spectrum of zinc ferrite is characterized by two strong absorption band in the range from 600 cm\(^{-1}\) to 410cm\(^{-1}\). The infrared spectrum of zinc ferrite obtained at calcination temperature of 450\(^\circ\)C is taken as an example. It can be seen that two strong absorption peaks appear in the crystal in the range of 600-410cm\(^{-1}\) from the Figure 2. It shows that the prepared crystals are zinc ferrite crystals. A weak absorption peak appears in the wavenumber range of 1200-1000cm\(^{-1}\), which is the characteristic peak of the C-C skeleton shrinking vibration.

![Figure 2. Infrared spectrum of zinc ferrite obtained at calcination temperature of 450°C](image-url)

Analysis of Calcination Temperature on Degradation Effect. Three portions of zinc ferrite catalyst with different calcination temperatures (350°C, 450°C, 550°C) are added to 200 mL 10 mg/L
methylene blue solution, respectively. And then the solutions are dispersed ultrasonically for 5 min to make the dispersion uniform. The above solutions are stirred for 30 min without light reaction to ensure the equilibrium of adsorption and desorption. Then, a purple light is used to perform the irradiation reaction for 2 h. The samples are taken out every 20 minutes. Using distilled water as a reference, the absorbance is measured at 664 nm with a visible spectrophotometer.

![Figure 3. Effect of zinc ferrite at different calcination temperatures on the degradation rate of methylene blue](image)

Different calcination temperatures are the key factors for the product which has good catalytic properties. The zinc ferrite crystals are formed at different calcination temperatures, and the efficiency of photocatalytic degradation will be different. As shown in Figure 3, the zinc ferrite has a higher activity when the calcination temperature is 450°C. The activity is relatively lower at 550°C. It shows the lowest at 350°C. This change occurs due to the agglomeration of the product during the calcination process. The degradation effect is significantly increased when the calcination temperature is increased from 350°C to 450°C, and the high-temperature agglomeration occurs at 550°C [14]. The porous structure of the zinc ferrite nanocrystals after calcinations is changed. The crystal diameter increases, and the specific surface area of the particles decreases. So the catalytic effect decreases.

Comparison of Different Catalysts on Degradation Effects. Zinc ferrite obtained at calcination temperature of 450°C, iron oxide, and zinc oxide are added to 200 mL 10 mg/L methylene blue solution, respectively. The operation method is the same as described above. Finally, samples are taken out every 20 minutes and the absorbance is measured. It can be seen from Figure 4 that the maximum degradation efficiency of zinc ferrite on methylene blue can reach 77.2%. Compared with the degradation rate of zinc oxide (65.89%) and the degradation rate of iron oxide (46.39%), zinc ferrite has a higher catalytic effect.
4. Conclusion
In this study, zinc ferrite powers are prepared by co-precipitation method and high-temperature calcination. The photocatalytic effect of zinc ferrite on organic dyes (methylene blue) are studied by changing the calcination temperature of zinc ferrite precursor and comparing different catalysts. The results show that the properties of zinc ferrite prepared by calcination at 450°C are the best and the photocatalytic performance of zinc ferrite is better than that of a single oxide.

Acknowledgments
The authors are thankful to Research Project Foundation of Qilu Institute of Technology (No. QL19K 054) for financial support of this work.

References
[1] H.G. Kim, D.W. Hwang and J.S. Lee: An undoped, single-phase oxide photocatalyst working under visible light. J. Am. Chem. Soc. Vol. 126 (2004), p. 8912
[2] Y.S. Fu and X. Wang: Magnetically separable ZnFe2O4-graphene catalyst and its high photocatalytic performance under visible light irradiation. Ind. Eng. Res. Vol. 50 (2011), p. 7210
[3] X.V. Cao, L. Gu and X.M. Lan: Spinel ZnFe2O4 nanoplates embedded with Ag clusters: preparation, characterization, and photocatalytic application. Mater. Chem. Phys. Vol. 106 (2007), p. 175
[4] S.H. Yu, T. Fujino and M. Yoshimura: Hydrothermal synthesis of ZnFe2O4 ultrafine particles with high magnetization. Sens Actuators, B: Chemical Vol. 256 (2003), p. 420
[5] B.G. Veronica, S.P. Regino and T.F.J. Maria: Superparamagnetism and interparticle interactions in ZnFe2O4 nanocrystals. J. Mater. Chem. Vol. 22 (2012), p. 2992
[6] Y. Li, G.Z. Dai and C.J. Zhou: Formation and optical properties of ZnO:ZnFe2O4 superlattice microwires. Nano Res. Vol. 3 (2010), p. 326
[7] J.X. Qiu, C.Y. Wang and Y.M. Gu: Photocatalytic properties and optical absorption of zinc ferrite nanometer films. Mater Sci. Eng. B Vol. 112 (2004), p. 1
[8] H. Lee, J.C. Jung and H. Kim: Preparation of ZnFe2O4 catalysts by a co-precipitation method using aqueous buffer solution and their catalytic activity for oxidative dehydrogenation of n-butene to 1,3-butadiene. Catal. Lett. Vol. 122 (2008), p. 281
[9] F. Li, H.B. Wang and L. Wang: Magnetic properties of ZnFe2O4 nanoparticles produced by a low-temperature solid-state reaction method. Magn. Mat. Vol. 309 (2007), p. 295
[10] C. Nordhei, K. Mathisen and I. Bezverkhyy: Decomposition of carbon dioxide over the putative cubic spinel nanophase cobalt, nickel, and zinc ferrites. J. Phys. Chem. C. Vol. 112 (2008), p. 6531

[11] H.L. Zhu, X.Y. Gu and D.T. Zuo: Microemulsion-based synthesis of porous zinc ferrite nanorods and its application in a room-temperature ethanol sensor. Nanotechnol. Vol. 19 (2008), p. 405

[12] M. Wang, Z.H. Ai and L.Z. Zhang: Generalized Preparation of Porous Nanocrystalline ZnFe₂O₄ Superstructures from Zinc Ferrioxalate Precursor and its Superparamagnetic Property. Phys. Chem. C Vol. 112 (2008), p. 13163

[13] M. Veith, M. Haas and V. Huch: Single Source Precursor Approach for the Sol-Gel Synthesis of Nanocrystalline ZnFe₂O₄ and Zinc-Iron Oxide Composites. Chem. Mater. Vol. 17 (2005), p. 95

[14] Q. Wang and T. Feng: Study on the relationship between the preparation methods of zinc ferrite and micromorphology and sensitive properties. J. Cera. Vol. 4 (2013), p. 543

[15] F. Cao, X.Y. Li and Z.P. Qu: Synthesis of zinc ferrite nanocrystals and its catalytic decolorization performance. Enviro. Pollu. Prev. Vol. 8 (2006), p. 891

[16] D. Shen, J.H. Pan and R. Jiang: Decolorization of ZnFe₂O₄/graphene nanosheet composites for photocatalytic dye wastewater. Prin. Dy. Auxi. Vol. 2 (2015), p.29