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WO_3-ZnO Supported on Molecular Sieves as Efficient Material for the Decolorization of Methylene Blue by Adsorption and Photocatalysis

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Abstract. Over the past few decades, nano-sized semiconductor powders for use as photocatalytic degradation of organic pollutants have attracted attention due to many advantages. In this research, a new composite material WO3-ZnO/molecular sieves (MS) was synthesized by precipitation method and hydrothermal method. The degradation activities of the WO3-ZnO/MS composite material were evaluated through photodegradation of methylene blue (MB). It was found that the degradation rate of MB increased with an increase in the time, and the composite material was effective for the decolorization of MB. The decolorization rate of MB increased with an increase in the material dosage. The decolorization rate of MB decreased with an increase in the initial concentration. The temperature affected the adsorption capacity of the composite material but the temperature had little effect on photodegradation. The results also indicated that MB was not easily decomposed under strong acid condition, while more easily under weakly acidic and alkaline conditions. Our results will serve as a foundation for future applications of photocatalytic degradation.

Keywords: nano-sized semiconductor powders; new composite material; composite material.

1. Introduction

Approximately 15% of the dyes produced worldwide are lost within the water during synthesis and processing [1]. In China, about 1.6 billion tons of dye-containing wastewater is produced every year. Instead of biological processes, physicochemical techniques have been considered as the decolorization of colored solutions due to the low biodegradability [2]. Over the past few decades, nano-sized semiconductor powders for use as photocatalytic degradation of organic pollutants have attracted attention due to its low energy consumption, easy operation, high degradation efficiency, and non-secondary pollution.

There are many kinds of semiconductor photocatalysts used for degrading organic pollutants, such as TiO_2, ZnO, WO_3, SnO_2, etc. ZnO is recognized as a suitable material for photocatalysis application because of its non-toxicity, high photosensitivity, less cost and protection towards the environment [3]. Nevertheless, ZnO also shows some disadvantages in the applications [4]. One way to enhance the photocatalytic efficiency by avoiding the recombination of photo generated charge carriers is combining other semiconductors with ZnO nanostructures, such as WO_3, TiO_2, Fe_2O_3 etc. Among these WO_3 is another promising photocatalyst for many optoelectronic applications [5], [6].

However, the disadvantages of easy aggregation, difficulty in separation, and difficulty in recovery of nano-powder are also increasingly apparent. Therefore, searching the appropriate catalyst carriers and developing an effective loading processes prove to be the key to the industrialization of photocatalysis. In this study, combining the excellent adsorption capacity of molecular sieves (MS) and the synergistic effect of WO_3-ZnO compound photocatalyst, WO_3-ZnO/MS composite material was prepared by precipitation method and hydrothermal method. The degradation activities of the WO_3-ZnO/MS composite material were evaluated through photodegradation of methylene blue (MB). The effects of various parameters like the amount of material, the initial concentration, the temperature and pH values were examined. Our results will serve as a foundation for future applications of photocatalytic degradation.

2. Experimental Section

Approximately 15% of the dyes produced worldwide are lost within the water during synthesis and processing [1]. In China, about 1.6 billion tons of dye-containing wastewater is produced every year. Instead of biological processes, physicochemical techniques have been considered as the decolorization of colored solutions due to the low biodegradability [2]. Over the past few decades, nano-sized semiconductor powders for use as photocatalytic degradation of organic pollutants have attracted attention due to its low energy consumption, easy operation, high degradation efficiency, and non-secondary pollution.

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2.1 Materials

All the chemicals used were of analytical grade and without any further purification. Sodium tungstate, Sodium carbonate, Zinc sulphate, Absolute ethanol were purchased from Xilong Scientific Co., Ltd. CTAB, molecular sieve, methylene blue were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled Water was used in all the experiments. 150W mercury lamp used for photosource.

2.2 Preparation of WO_3-ZnO Composites

The precursor solution of WO_3 was prepared by dissolving a small amount of CTAB into sodium tungstate solution and an excess of 1.5 molL-1 HNO_3 was gradually added to it, stirred for 2h. The precipitate was repeatedly washed with absolute ethanol and distilled water and dried at 80℃ for 2h to obtain $WO_3 \cdot H_2O$.

The precursor solution of ZnO was prepared by adding a small amount of CTAB into the zinc sulfate solution and an excess of sodium carbonate solution was gradually added to it, stirred for 2h. The precipitate was repeatedly washed with absolute ethanol and distilled water and dried at 80℃ for 2h to obtain $ZnCO_3 \cdot 2Zn\ (OH)_2 \cdot H_2O$.

The preparation of WO_3-ZnO composites were mixed the above two products with a mass ratio of 1:3, ground for 1h and then calcined in a vacuum calcining furnace at 350℃ for 2h.

2.3 Synthesis of WO_3-ZnO/MS

The molecular sieve and the WO_3-ZnO composites were mixed in a certain mass ratio, after adding some distilled water, the mixture was stirred for 1h and placed in a hydrothermal reactor at 120℃ for 8h. Then the autoclave was cooled to room temperature naturally. After being taken out and centrifuged, the precipitate was washed with absolute ethanol and placed in a vacuum calciner at 400℃ for 4h to obtain the WO_3-ZnO/MS composite material.

2.4 Degradation Tests

The degradation activities of the WO_3-ZnO/MS composite material were evaluated through photodegradation of methylene blue (MB). The experiment was carried out in a self-made photoreactor of 500mL. The photoreactor was kept at 25℃ by circulating water to avoid the heating effect.

The WO_3-ZnO/MS composite material was added into the photoreactor containing 200mL MB solution. Before light illumination, the reaction system was allowed to vibrate and stir slowly under dark conditions for 40min to reach the adsorption–desorption equilibrium of MB on the composite material. Then the reaction system was exposed directly to a 150W mercury lamp. The concentrations of the solutions were monitored colorimetrically by using a UV-vis spectrophotometer (Shimadzu

UV-2450) at the wavelength of 663nm. The dye degradation rate (DR) was calculated from the equation:

$$DR(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where A0 is initial absorbance of MB and at is absorbance of MB at time t.

3. Results and Discussion

Approximately 15% of the dyes produced worldwide are lost within the water during synthesis and processing [1]. In China, about 1.6 billion tons of dye-containing wastewater is produced every year. Instead of biological processes, physicochemical techniques have been considered as the decolorization of colored solutions due to the low biodegradability [2]. Over the past few decades, nano-sized semiconductor powders for use as photocatalytic degradation of organic pollutants have attracted attention due to its low energy consumption, easy operation, high degradation efficiency, and non-secondary pollution.

There are many kinds of semiconductor photocatalysts used for degrading organic pollutants, such as TiO_2, ZnO, WO_3, SnO_2, etc. ZnO is recognized as a suitable material for photocatalysis application because of its non-toxicity, high photosensitivity, less cost and protection towards the environment [3]. Nevertheless, ZnO also shows some disadvantages in the applications [4]. One way to enhance the photocatalytic efficiency by avoiding the recombination of photo generated charge carriers is combining other semiconductors with ZnO nanostructures, such as WO_3, TiO_2, Fe_2O_3 etc. Among these WO_3 is another promising photocatalyst for many optoelectronic applications [5], [6].

3.1 Effect of Ratios of Molecular Sieves and WO_3-ZnO

The degradation rates of MB using WO_3-ZnO/MS composite material at different mass ratios were described in Fig. 1, where the initial concentration was 10 mgL-1, the amount of material was 50mg. It showed the degradation rate of MB increased with an increase in the time, and the decolorization rate reached more than 80% in 1h, indicating that the composite material was effective for the decolorization and removal of MB. The highest adsorption of MB on the composite material appeared when the mass ratio of molecular sieves and WO_3-ZnO was 1:1. The maximum degradation rate of MB on the composite material appeared when the mass ratio of molecular sieves and WO_3-ZnO was 1:3.

3.2 Effect of the Amount of Material

The effect of the amount of material on degradation of MB was presented in Fig. 2, where the initial concentration was 10mgL^{-1}, and m (MS): m (WO_3-ZnO)=1:3. It showed that the decolorization rate of MB increased with an increase in the amount of material.

3.3 Effect of the Initial Concentration

The effect of the initial concentration on degradation of MB was presented in Fig. 3, where the amount of material was 40mg, and m(MS):m(WO_3-ZnO)=1:3. It showed that the decolorization rate of MB decreased with an increase in the initial concentration. This was mainly because the light passing through the solution will decrease when the concentration is too high, which will reduce the absorption of light. On the other hand, when the adsorption of MB on the material is saturated, they have no chance in contact because of the limited active sites on the surface of the material.

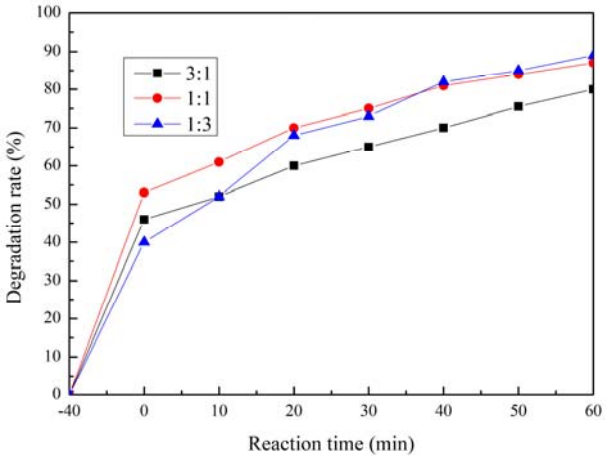

Figure 1. Degradation of MB using WO3-ZnO/MS composite material.

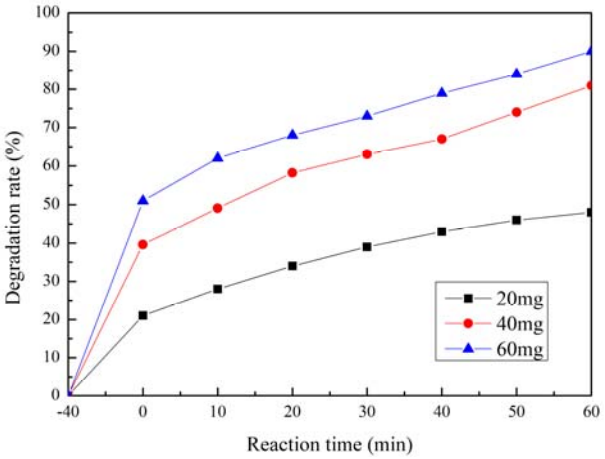

Figure 2. Effect of the amount of material on degradation of MB.

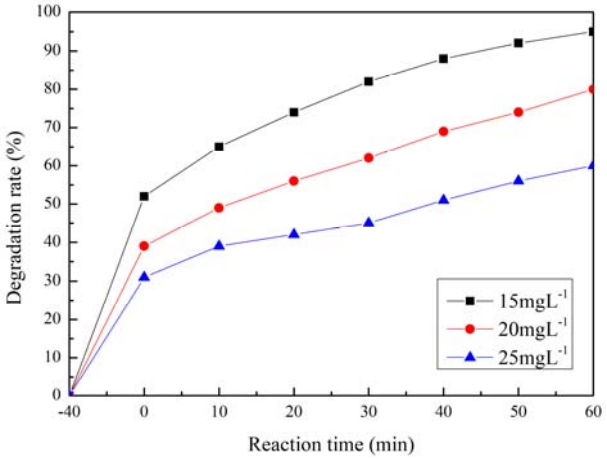

Figure 3. Effect of the initial concentration on degradation of MB.

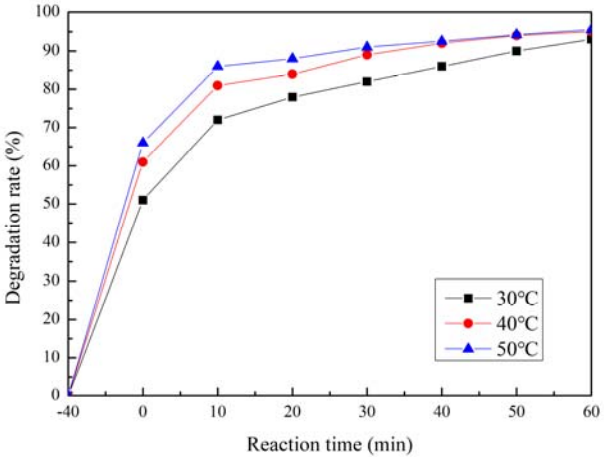

Figure 4. Effect of the temperature on degradati-on of MB.

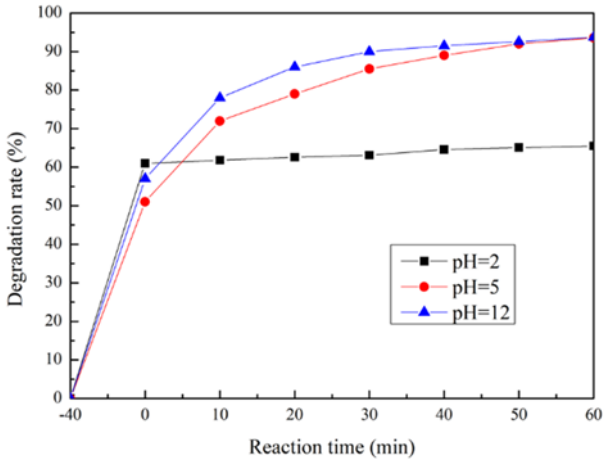

Figure 5. Effect of the pH value on degradation of MB

3.4 Effect of the Temperature

The effect of temperature on degradation of MB was presented in Fig. 4, where the initial concentration was 10mgL-1, the amount of material was 40mg, and m(MS):m(WO_3-ZnO)=1:3. It showed the temperature affected the adsorption capacity of the composite material. The degradation efficiency reached more than 92% at different temperatures, indicating that the temperature had little effect on photodegradation.

3.5 Effect of the pH Value

The effect of the pH value on degradation of MB was presented in Fig. 5, where the initial concentration was 10 mgL^{-1}, the amount of material was 40mg, and m(MS):m(WO_3-ZnO)=1:3. When the pH of the solution was 2, the adsorption rate of MB on the composite reached 60.6% (highest), and the subsequent degradation rate did not change basically. When the pH was 5 or 12, the degradation rate was significantly increased (more than 90%) in 1h after radiation. It indicated that MB was not easily decomposed under strong acid condition, while the decolorization of MB proceeded more easily under weakly acidic and alkaline conditions.

4. Conclusion

A new composite material WO_3-ZnO/MS was synthesized by precipitation method and hydrothermal method. The degradation rate of MB increased with an increase in the time, and the composite material was effective for the decolorization of MB. The decolorization rate of MB increased with an increase in the amount of material. The decolorization rate of MB decreased with an increase in the initial concentration. The temperature affected the adsorption capacity of the composite material but the temperature had little effect on photodegradation. The results also indicated that MB was not easily decomposed under strong acid condition, while more easily under weakly acidic and alkaline conditions.

Acknowledgments

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