Study on Degradation Conditions of Methylene Blue by La-TiO_2/Hβ

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Abstract. The composite photocatalyst La-TiO_2/Hβ was prepared by coprecipitation method, the methylene blue (MB) was used as the target pollutant and the influence factors of degradating MB by La-TiO_2/Hβ were discussed. The results showed that the optimum conditions were that the initial mass concentration of MB was 20mg/L, the illumination time was 30 min, the dosage of oxidant H_2O_2 was 2.0mL, the catalyst dosage was 2.4g/L. Under these conditions, the degradation rate of MB by La-TiO_2/Hβ was up to 98.2%, the catalytic activity of the catalyst was unchanged after using three times.

1 Introduction

With the rapid development of the textile dye industry and dye varieties, dyeing wastewater has become an important source of waste water. Common dye wastewater treatment method has biochemical method, coagulation method, adsorption method, these methods show poor mineralization ability of dye pollutants and cause secondary pollution easily. But Semiconductor photocatalytic oxidation method is high efficiency and energy saving environmental protection technology[1]. The strong oxidizing free radicals producted by photocatalyst under the conditions of light, can degrade almost all of the organic matter thoroughly, and eventually generate H_2O, CO_2 and other small inorganic molecules, so this method shows attractive application prospect in the dye wastewater treatment.

TiO_2 is a kind of high performance semiconductor photocatalytic materials, with stable chemical properties, high catalytic efficiency, high oxidation performance, non-toxic and harmless, no secondary pollution[2], therefore TiO_2 has wide application in environment water treatment. But there are still many defects, mainly for its wide band gap width, which is mainly a response to UV light, electrons and holes easy to compound, low catalytic efficiency, nanometer TiO_2 are recycled more difficultly. For this reason, people have adopted ion doping, noble metal deposition, semiconductor compound, solid immobilized to modified TiO_2[3]. Single modification technology to improve the photocatalytic activity of TiO_2 is limited. So in this article La-TiO_2/Hβ composite photocatalyst was prepared by Lanthanum doping and solid immobilized method, MB was used as the simulated dye wastewater, the factors that influnce the effect of MB on the degradation were analyzed, and the process conditions of MB were optimized.

2 Experments

2.1 Reagent and Instrument

Hβ molecular sieve, Catalyst factory of Nankai university; Titanium sulfate (mass fraction of 15 ~ 20%); Lanthanum nitrate;Ammonia (mass fraction 15-20%); methylene blue, hydrogen peroxide (mass fraction 30%); All reagents are analytically pure, Tianjin guangfu institute of fine chemicals.

Digital display temperature control electric mixer, JJ-3, Ronghua Instrument Manufacturing Co.LTD. Jintan city, Jiangsu Province; Visible spectrophotometer, T6 xinrui, Beijing Persee General Instrument Co.LTD; Centrifugal sedimentation machine, 80-2 type, Zhongda Instrument factory Jintan city, Jiangsu Province; Thermostatic drum wind drying oven, DHG-9123 A, Shanghai Yiheng Technology Co. LTD. Box type resistance furnace SX2-4-10, electric furnace Co. LTD, Tianjin central experiment.

2.2 Preparation of La-TiO2/Hβ Composite Photocatalyst

(1) A certain concentration of sulfuric acid was added to three titanium flask, while stirring, La $(NO_3)_3 \cdot 6H_2O$ and Hβ zeolite mixed;

(2) Thermostats 30 ℃ stirring, to the above solution was slowly added dropwise a solution of aqueous ammonia, metal ions generated gradually mixed hydroxide precipitate when pH＞10 , the dropwise addition of ammonia;

(3) Continue stirring for 60 min, the precipitated product at room temperature for aging

(4) The precipitate was washed with distilled water, until no test with $BaCl_2$ solution until a white precipitate formed

(5) The precipitate was dried, ground, fired, 100-mesh standard sieved, to obtain La-TiO_2/Hβ.

2.3 Degradation of MB by La-TiO2/Hβ composite photocatalyst

A certain amount of La-TiO_2/Hβ 25mL sample into a certain concentration of MB solution, placed in a certain time 20W UV light illumination, centrifuged and the supernatant was measured using a spectrophotometer absorbance at the maximum absorption wavelength of 664nm， the degradation rate is calculated by methylene blue solution *D*.

$$D = [(A_0 - A)/A_0] \times 100\%$$

In the type, A_0 stands for methylene blue light absorbance of the sample blank; *A* stands for Light joined La-TiO_2/Hβ after MB solution absorbance.

3 Results and discussion

3.1 Effect of MB initial concentration on degradation rate

The initial concentration of MB solution had some influence on its light transmittance, so experiment at irradiation time 20min, the amount of catalyst 2.0g/L, H_2O_2 oxidant amount 1.0mL,under conditions of 10mg/L, 15mg/L, 20mg/L, 25 mg/L and 30mg/L, the degradation rate of MB was investigated, the results were showed in Figure 1.

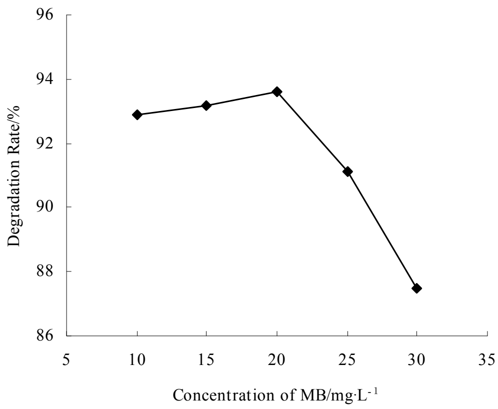

Fig.1. Influence of MB initial mass concentration on degradation rate

The results showed that with the increase of initial concentration of MB, the degradation rate of MB was first increased and then decreased. When the concentration of MB solution was 20mg/L, the degradation rate of MB was higher, up to 93.6%. The reason may be that when the concentration of MB solution was lower, in a certain light time, photocatalyst surface can accept more effective photon light, and then generate more electron hole, the parts of a hole because of strong oxidizing themselves and adsorbed on the catalyst surface reaction of MB molecules, the other parts would be electronic together diffusion migration onto the surface of the catalyst, and was captured by OH-, H_2O and O_2, generating a strong oxidation ability OH free radical, thus could fully limited degradation of MB molecules; But when the initial concentration of MB is high, transparent solution color deepening would reduce the solution rate, causing the photon number absorbed light catalyst reduction, and the surface of the catalyst would cover more the solute particle, resulting active sites reduced, thereby impeding the photocatalytic reaction. Therefore, the suitable initial concentration of methylene blue solution was 20mg/L.

3.2 Effect of illumination time on degradation rate of MB

The number of illumination time and light intensity would affect the light catalyst to produce the hole electron, so the experiment in the MB concentration of 20mg/L, dosage of catalyst 2.0g/L, oxidant amount of H_2O_2 1.0mL, under the conditions of illumination time 10min, 20min, 30min, 40min, 50min, 60min, the degradation rate of MB was investigated, the results were showed in Figure 2.

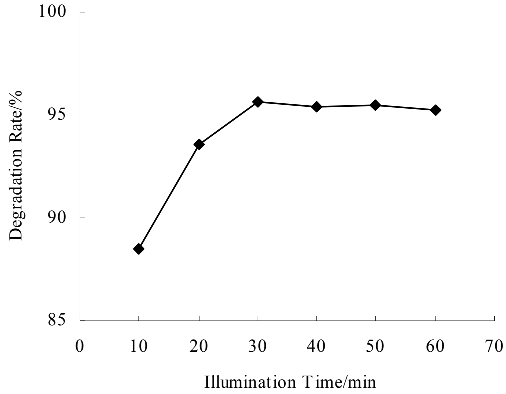

Fig.2. Influence of the illumination time on the degradation rate of MB

The results showed that with the illumination time prolonged, the degradation of MB increased firstly and then tended to be stable. The reason may be that when the illumination time was short, effective number of photons was less, the photocatalytic reaction was not sufficient, the degradation rate was low. When the illumination time was long enough, the amount of photon generation was increased, photocatalyst hole electron gradually was saturated, the photocatalytic reaction gradually tended to equilibrium, the degradation rate of changed gently. So appropriate illumination time was 30min.

3.3 Effect of Oxidant H2O2 Amount on degradation rate of MB

The oxidizing agent was introduced into the photocatalytic reaction system, would affect the number of ·OH, so the experiment in MB concentration 20mg/L, illumination time 30min, catalyst dosage 2.0g/L, under conditions of H_2O_2 0.5mL, 1.0mL, 1.5mL, 2.0mL, 2.5mL, the degradation rate of MB was investigated, the results were showed in Figure 3.

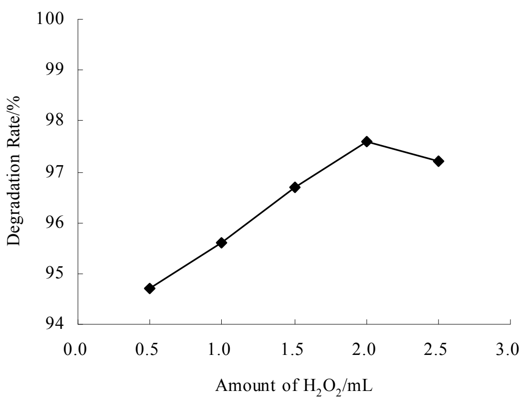

Fig.3. Influence of the dosage of H_2O_2 on the degradation rate of MB

The results showed that with the amount of plus oxidant H_2O_2 increasing, the degradation of MB solution rate showed a trend of decrease after the first increase. When H_2O_2 addition amount was 2.0 mL, the degradation of MB rate was higher, at 97.6%. This may be because of H_2O_2 was a kind of better than oxygen electron acceptor, could inhibit the light composite of electrons and holes, the ·OH radical concentration was increased effectively, the speed and efficiency of the photocatalytic reaction was improved; In addition, as a kind of efficient oxidant H_2O_2, under the action of electron and hole, could produce ·OH radical and HO_2· free radicals, these free radicals with photocatalyst oxidative MB molecules in solution, the degradation rate was increased significantly. But when a glut of H_2O_2, instead, it would become a free radical scavenger, consuming of ·OH free radicals [4], the degradation rate was declined. Therefore, the suitable amount of oxidant H_2O_2 was 2.0 mL.

3.4 Effert of dosage of catalyst on degradation rate of MB

The dosage of catalyst had an influence on the number of free radicals in the reaction system and the light transmittance of the solution, so the experiment in MB solution concentration 20 mg/L, illumination time 30 min, H_2O_2 amount 2.0 mL, under the conditions of dosage of catalyst 1.6 g/L, 2.0 g/L, 2.4 g/L, 2.8 g/L, 3.2 g/L, the degradation rate of MB was investigated, the results were showed in Figure 4.

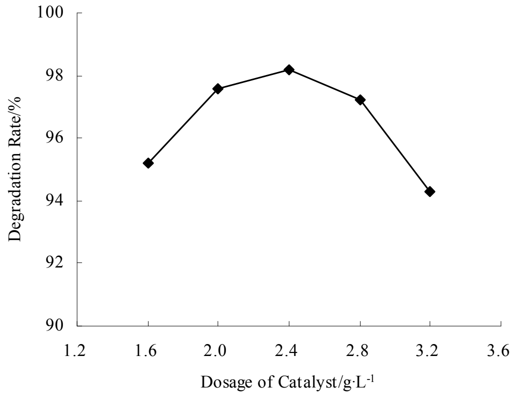

Fig.4. Influence of the dosage of catalyst on the degradation rate of MB

The results showed that with the increasing of the dosage of photocatalyst, the degradation rate of MB showed a trend of decrease after the first increase. When the catalyst was 2.4 g/L, the maximum degradation rate reached at 98.2%. This was because when the MB concentration was certain, according to the mechanism of photocatalytic reaction, increasing the dosage of catalyst, the number of electron hole generated by light excitation was increased, also resulting in the reactive group was increased, and the active site used for light catalytic degradation of unit volume of waste water increasing[5], making the photocatalytic reaction rate was increased, the degradation rate was increased follow it. And continuing to increase the dosage of catalyst, the reaction had been balanced, but too much catalyst particles had an effect of light scattering and shielding to a certain extent, solution transmittance decreased, resulting in a decline in catalyst light absorption efficiency and a low degradation rate. As a result, the suitable dosage of catalyst was 2.4 g/L.

3.5 Effect of catalyst using times on degradation rate of MB

The reusability of catalyst was related to the catalyst can be recycled, the reusability experment was that each sample was treated by the centrifugal separation, washing, drying, the catalytic activity of La-TiO_2/Hβ was investigated again. The using times of used catalysts were inspected under the conditions of MB solution 20mg/L, illumination time 30min, the amount of H_2O_2 2.0mL, the dosage of catalyst 2.4g/L, the results were showed in Figure 5.

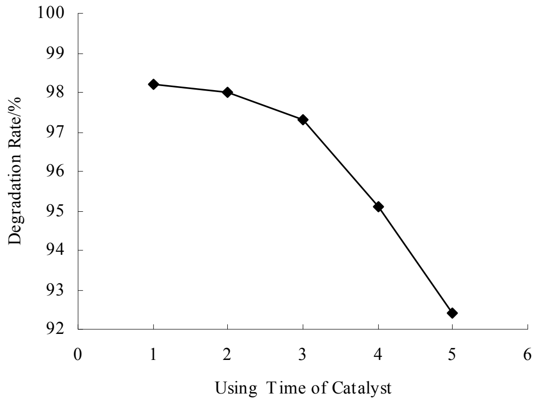

Fig.5. Influence of the using times of catalyst on the degradation rate of MB

It was seen from Figure 5 that the catalytic activity of La-TiO_2/Hβ composite photocatalyst was changed little after used three times, the activity was decreased after used the fourth and the fifth times. The reason may be that while the catalyst circulation was used three times, the surface of photocatalyst could also provide enough active sites and the active groups to degradation of MB molecules. The degradation of MB rate decreased when fourth and fifth time, may because the catalyst surface could absorb a certain amount of MB, but washing and drying treatment was difficult to remove, led to a decrease in the effective active surface of the catalyst, active site was insufficient.

4 Conclusion

The La-TiO_2/Hβ composite photocatalyst which was prepared by co-precipitation had an excellent effect on degradation of MB. The degradation conditions on the MB solution (25mL) were optimized by single factor experiments. The results showed that under the conditions of the initial MB concentration 20mg/L, illumination time 30min, amount of oxidant H_2O_2 2.0mL, the dosage of catalyst 2.4g/L, the degradation rate of MB reached 98.2%. Its activity had little change when La-TiO_2/Hβ composite photocatalyst after used three times repeatedly.

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