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Preparation of Perovskite Oxide $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ and Photocatalytic Degradation of Dye Wastewater

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ABSTRACT

Perovskite oxide $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ was prepared using sol-gel method, and it was used as catalyst in photocatalytic degradation of dyestuff wastewater. Using acid magenta as degradation material, the influence factors on the photocatalysis activity were investigated, such as the pH value, the dyestuff concentration, the quantity of the catalyst, the quantity of the additional oxidant (H_2O_2) and so on. The results indicate that the degradation rate of the dyestuff may get to 96% when the doped ratio of Co is $x=0.4$, the quantity of catalyst is 0.2g/L, the concentration of acid fuchsine was 10 mg/L, and the pH value of dyestuff solution is 7. H_2O_2 can improve the photocatalytic degradation rate.

1. Introduction

Organic dyestuff wastewater is one of the most common organic pollutants in production. If it is not treated before discharge, it will cause environmental pollution, which directly or indirectly affects human health. The degradation of dyestuff wastewater traditionally use the methods like adsorption, flocculation and biological oxidation, but satisfactory effect often cannot be obtained. With the progress of science and technology, some new dye wastewater treatment technologies started to show their unique effect. Among them, photocatalytic oxidation technology is one of the typical representatives. Photocatalytic degradation technology has the advantages of high efficiency, energy saving, wide range of catalysis and non-toxic. It can effectively remove various organic pollutants in water, and has a wide application prospect [1]. Photocatalytic oxidation technology requires the use of photocatalyst. There are many kinds of photocatalysts. The perovskite complex oxide is one of the materials being found have photocatalytic activity. Perovskite composite oxides often expressed as a universal formula ABO_3 . Because of its variable structure and abundant physical and chemical properties, it has an important position in the fields of functional materials, solid state physics and solid state chemistry. In the past few decades it had widespread attention [2,3]. In addition to the development and utilization of the conventional magnetics and electrical properties of perovskite compounds, some photocatalytic properties of them are also being developed. One of the research focuses on perovskite oxide nanoparticles with lanthanum at A site because of its special structure and properties.

In this work, perovskite oxide $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ was prepared using sol-gel method, and acid fuchsine was selected as target dye to study its photocatalytic degradation property. The influences of initial dye concentration, initial pH value, the influence of H_2O_2 on the decolorization rate were studied, which can provide certain theoretical basis for practical application, and has certain practical significance.

2. Experimental

2.1 Experimental instruments and chemical reagents

Experimental instruments: UV752 UV-VIS spectrophotometer, 30 w UV lamp, 80-2 Centrifugal sedimentation machine, Magnetic stirrer, FA22048 Electronic balance, HH-2 Digital constant temperature water-bath water, Electrothermal blowing oven, RJM - 28-10 Muffle furnace.

Chemical reagents: lanthanum nitrate, cobalt nitrate, manganese nitrate, citric acid, ethylene glycol, nitric acid, hydrogen peroxide, sodium hydroxide, acid fuchsine.

2.2 Preparation of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ samples

According to the molar mass ratio of $\text{La}(\text{NO}_3)_3$ 、 $\text{Co}(\text{NO}_3)_3$ 、 $\text{Mn}(\text{NO}_3)_2$, The corresponding mass was weighed and put into four-mouth flask and diluted with a small amount of water: 40 ml 0.36 mol/L citric acid and 40 ml 1.2 mol/L ethylene glycol were measured and poured into the above solution, a moderate amount of nitric acid was added to adjust pH value at 1.5, and they were heated at 45 °C water bath for 20 min. And then the temperature of water bath was raised to 80 °C and continue heating. In the process of water bath heating, stirring is constant until the solution become yellow, forming sticky wet gel.

The wet gel was put into drying oven for several hours until the reagent flames in a divergent manner when the reagent encounters open flame. Then the reagent calcine at 700 °C for four hours and obtaining the product [4].

2.3 Photocatalytic degradation experiments

A certain amount of acid fuchsine was put into beaker, and a suitable amount of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ was added and put it on the magnetic stirrer. The UV lamp was fixed in a certain distance from the mixture of liquid surface. Then the mixture of liquid was stirred at a certain speed for a period of time. After that, the upper mixture was took and put in a centrifugal pipe to centrifugal deposit for 20 min. Then the supernatant fluid was took and determined using UV752 UV-VIS spectrophotometer to measure the absorbance ($\lambda_{\text{max}}=665\text{nm}$). According to the absorbance A of the solution before and after reaction, the degradation rate of methyl orange D % was calculated. The calculation equation is as follow:

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

where A_0 is the absorbance of the sample before irradiation, A is the absorbance of the sample after irradiation [11].

3. Results and discussion

3.1 The influence of Co doping on the photodegradation rate of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$

When the concentration of acid fuchsin is 10 mg/L, the dosage of catalyst is 0.2 g/L, and the pH value of the solution is 7, the changes of discoloration rate with X value are shown in Figure 1.

Figure 1. The influence of Co doping on decolorization rate.

As is shown in Figure 1, the photocatalysis activity of the samples with Co doping is better than that of undoped samples. The photocatalysis of the sample is better when the doping quantity is $X = 0.4$. The reasons for this result are as follows: The radius of Co^{3+} (0.061 nm) is smaller than Mn radius (0.070 nm). The blending of Co^{3+} makes the average ionic radius of ions at B site reduced. The tolerance factor increases and tolerance factor increases resulting in the decrease of the binding energy between B-O. Low binding energy on the one hand can prompt to generate oxygen vacancy on catalyst surface, and it also is advantageous to chemical adsorption, which improves the efficiency of the photocatalytic reaction. The electronegativity of Co^{3+} (1.70) is greater than Mn (1.60), so when Co replaces Mn, the forbidden band width is reduced, and the ray with long wavelength can stimulate valence band electrons to form electronic - air three holes pair and oxidation-reduction reaction, making the dye molecules more easy to degrade [5]. Therefore, the optimal X value is 0.4.

3.2 The influence of pH value of dye solution on $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ photodegradation rate

X is 0.4, the concentration of acid magenta is 10 mg/L, the dosage of catalyst is 0.2 g/L, and the pH value of the solution is at 2, 3, 5, 7 and 8, respectively. When $\text{pH} > 8$, the acid magenta solution will fade, so the maximum pH value is 8. The decolorization rate changes with the pH value are shown in Figure 2.

Figure 2 The influence of pH value on decolorization rate.

As is shown in Figure 2, the decolorization rate of acid fuchsin solution increases with the increase of the pH value of the solution. The degradation effect is obvious in the weak alkaline condition. This is because the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ excited electrons from the forbidden band to the conduction band, forming electrons and cavities under UV irradiation. Highly active cavities react with OH^- in the water, and oxidize it into $\cdot\text{OH}$, and then the electrons and holes react with the materials dispersed in the water respectively. In the weak

alkaline solution, the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ surface has a negative charge, which is beneficial to the migration of the cavity to the surface of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$, and reacting with electron donor to form $\cdot\text{OH}$ free radical with high oxidizability. [6]. Therefore, the photocatalytic degradation effect is better under weak alkaline conditions. Because when the pH value is 7 or 8, the decolorization rate has little difference. Considering that the discharge fluid should have no harm to the environment, so the optimal pH value is 7.

3.3 The influence of initial concentration of dye solution on $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ photodegradation rate

X is 0.4, the concentration of acid fuchsin solution is 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L respectively, and the quantity of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ is 0.2 g/L, the pH value is 7. The changes of decolorization rate with the initial concentration are as shown in Figure 3.

Figure 3. The influence of initial concentration of dye solution on decolorization rate.

It can be seen from Figure 3 that the photocatalytic degradation rate is the best when the concentration of acidic fuchsin solution is 10 mg/L. This indicates that there is a suitable concentration in photocatalytic degradation of dye wastewater. In the process of photocatalysis, photocatalyst and dye have a catalytic reaction equilibrium. The quantity of catalyst is restricted with the concentration of dye solution. For a certain concentration of dye solution, increasing the amount of catalyst means more photons will be utilized. However, over a certain amount will affect the utilization of light. In addition, when the concentration of dye waste is increased, the color of dye solution will become darker, which will affect light transmittance and thus degrade the efficiency. Therefore, the concentration of dye wastewater should be considered in degradation. The optimal initial concentration of acidic fuchsin is 10 mg/L.

3.4 The effect of catalyst dosage on photodegradation rate

X is 0.4, the dosage of the catalyst $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ is 0.1 g/L, 0.2 g/L, 0.3 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L respectively, the concentration of acid fuchsin is 10 mg/L, and pH value is 7. The decolorization rate varies with the amount of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ are as shown in Figure 4.

Figure 4 influence of the dosage of the catalyst $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ on decolorization rate.

As is shown in Figure 4, the decolorization rate of dye solution increases with the increase of the catalyst dosage, and the decolorization rate of acid fuchsin can reach above 96% when the catalyst dosage is 0.2 g/L. However, when the catalyst dosage exceeds a certain value, even if the catalyst dosage is increased, the variety of decolorization rate is not obvious. This is because at the beginning of the catalyst increase, increasing the amount of catalyst means that more effective photons are

generated, thus accelerating the rate of photocatalytic reaction. However, when the dosage of the catalyst increases to a certain extent, the amount of $\cdot\text{OH}$ free radicals produced by photocatalysis is certain. And the excessive catalyst will cause the scattering of the light, and the masking of the light can reduce the production rate of the effective photon, resulting in the decrease of the photocatalytic reaction rate. Therefore, the optimal dosage is determined at 0.2g/L for $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$.

3.5 The influence of H_2O_2 on the photodegradation rate of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$

X is 0.4, the concentration of H_2O_2 is 0.04 mol/L, the concentration of acid fuchsin is 10 mg/L, the pH value is 7, and the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ is 0.2g/L. The influence of H_2O_2 on decolorization rate is shown in Figure 5.

Figure 5. influence of H_2O_2 on decolorization rate.

As is shown in Figure 5, when the concentration of H_2O_2 is 0.04 mol/L, the photocatalytic reaction rate is accelerated, and the rate of decolorization of 90 min is 96%. This is because a certain amount of oxidant can promote the reaction. The oxidant as a good electron acceptor can capture e^- on the catalyst surface, weaken the compound process of cavitation and electronic as far as possible, to make them more effective participate target reaction. In addition, the addition of a moderate amount of oxidants can also counteract the tendency of the reaction system to be hypoxic, making the reaction faster. Therefore, H_2O_2 can increase the rate of photocatalytic degradation.

4. Conclusions

(1) Perovskite composite oxides $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ was prepared using sol-gel method. Co doping can change the ionic radius at B site, electronic structure, and electronegativity, eventually increasing the degradation rate. The photocatalysis of the sample is better when the doping quantity is $X = 0.4$.

(2) When the initial pH value is 7 and the catalyst amount is 0.2g/L, the concentration of the acid fuchsin solution is 10 mg/L, the catalytic degradation effect is the best. The degradation rate of the acid magenta solution can reach over 96%.

(3) The addition of H_2O_2 increases the degradation reaction rate of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ photocatalytic for acidic fuchsin.

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