

ORIGINAL RESEARCH ARTICLE

Synthesis of ZnO nanometer powders doped with Ce⁴⁺ ions and the photocatalytic degradation of dying wastewater

Guishan Gu, Yuanyuan Zhang, Chi Huang, Li Sun, Xueying Wang*

School of Chemistry and Material Engineering, Changshu Institute of Technology, Changshu 215500, China. E-mail: wxy62@cslg.edu.cn

Abstract

Ce⁴⁺-doped nanometer ZnO powder was synthesized by sol-gel method. The microstructures and properties of the samples were characterized through XRD, UV-Vis and FTIR. The results indicated that the Ce⁴⁺ was successfully incorporated into ZnO, and the diameter of the nanometer was about 10.7 nm. It induced the redshifting in the UV-Vis spectra. The photocatalytic activity of the samples was investigated using methylene blue (MB) as the model reaction under irradiation with ultraviolet light. The results showed that the doping of Ce⁴⁺ could increase the photocatalytic activities of ZnO nanopowders and that the best molar ratio of Ce⁴⁺ was $n(\text{Ce})/n(\text{Zn}) = 0.05$, that the surfactant was sodium dodecyl sulfate, and that the nanometer ZnO was calcinated at 550 °C for 3 hours. Meanwhile, it inspected the effect of photocatalytic efficiency through the pH of MB, the amount of catalyst, and illumination time. The experimental results revealed that the initial mass concentration of MB was 10 mg/L, that the pH value was 7–8, that the dosage of Ce⁴⁺/ZnO photo-catalyst was 5 g/L, that the UV-irradiation time was 2 h, and that the removal rate of MB reached above 85%. Under the optimized conditions, the degradation rate of real dye wastewater was up to 87.67% and the removal efficiency of COD was 63.5%.

Keywords: Ce⁴⁺-doped Nanometer ZnO Powder; Photocatalytic Degradation; Methylene Blue

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1. Introduction

In recent years, with the increasing abundance of textile products, the substances that are difficult to biodegrade in printing and dyeing wastewater are increasing, resulting in the poor treatment effect of the simple biochemical process on printing and dyeing wastewater, which has become one of the important factors threatening the safety of water environment in China. Azo compounds and organic compounds in printing and dyeing wastewater, the discharge of phenols and amines in wastewater seriously pollute the water environment and endanger human health^[1-4]. At present, the treatment methods of dyeing wastewater mainly include adsorption, coagulation, oxidation, reduction, electrolysis, biodegradation, etc.^[5] However, above methods have the disadvantages of secondary pollution and high cost. Photocatalytic oxidation of organic pollutants is a new technology developed in recent years. Nano ZnO has become the most active research direction for the elimination and degradation of organic contaminants due to many outstanding characters, such as high catalytic activity, complete degradation, carried out at room temperature and pressure, wide application range, and other advantages^[6,7]. Nano ZnO is one of the highly active photocatalysts with great application prospects because of its high effi-

ciency and non-toxic characteristics. In recent years, its preparation and performance studies have become a hot topic in the field of catalysis research^[8-10]. It can be of extensive application.

In this paper, Zinc acetate is the raw material, ammonium ceric nitrate is dopant. Then, hydrolytic and condensation reaction in organic medium so that the solution is soldered and gelatinized, and the gel is dried and burned into powder. The samples were characterized through X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), and FT-IR (IR). The decolorization and degradation of MB were for the model reaction. It investigated the effects of cerium doping amount, calcination temperature, and calcination time on catalytic performance. At the same time, it also studied the influence of the initial pH value of the solution, reaction time, and catalyst addition on the catalytic effect. The results show that the synthesized cerium doped nano Zinc oxide powder could effectively under UV light. This experiment has the advantages of low raw material cost, easy synthesis of catalytic materials, simple operation, low requirements for equipment, and environmental protection.

2. Experimental section

2.1 Main reagents and instruments

Main instrument: TU-1901 dual-beam UV-visible spectrophotometer (Beijing General Instrument Co., Ltd.); X-ray powder diffractor (D/max-2200/PC, Rigaku Corporation, Japan); UV-Visible spectrophotometer (Shimin Manufacturing Institute); the Fourier Infrared Spectral Analyzer (NICO-LET380, Shimjin Manufacturing Institute); Nano Ce/ZnO GGZ-125 UV HP mercury lamp (200–670 nm, 125 W, Shanghai Yaming Co., Ltd.); LG10-2.4 A high-speed centrifuge (Beijing Leibel Centrifuge Co., Ltd.).

The reagents used were analyzed pure, cerium ammonium nitrate, Zinc acetate, triethanolamine, sodium dodecyl phenyl sulfonate (SDS), polyethylene glycol-400, sodium dodecyl sulfate (SDBS), sodium stearate, oxalic acid (AR, Jiangsu Strong Chemical Co., Ltd.); methylene blue (AR, Shanghai Maikun

Chemical Co., Ltd.).

2.2 Preparation of nano Ce/ZnO

Dissolve 11.34 g of oxalic acid into 100 ml of absolute ethanol, then it obtains solution A. Dissolve 7.859 g of Zinc acetate ($\text{Zn}(\text{AC})_2 \cdot 2\text{H}_2\text{O}$) into 50 ml of distilled water, then add an appropriate amount of surfactant and ceric ammonium nitrate solution to obtain solution B. Then, slowly drop solution B into an under vigorous stirring, react for about 1.5 h, and keep it in a constant temperature (80 °C) water bath for 0.5 h. It obtains the sol. The sol was washed twice with distilled water and ethanol, dried in an 80 °C drying oven for 2 h, calcined in a muffle furnace for a certain time, cooled and ground, and finally prepared the sample. Except that ceric ammonium nitrate solution should not be added, the nano ZnO was prepared according to the above steps.

2.3 Characterization of nano Ce/ZnO

The crystal phase of the product was analyzed by XRD and Scherrer formula [$D(\text{hkl}) = K\lambda/\beta\cos\theta$]. The average grain size of the sample was calculated, the UV absorption spectrum of nanomaterials was measured by UV-Vis spectrophotometer, and the infrared spectrum of Ce/ZnO crystal was measured by Fourier infrared spectrum analysis.

2.4 Determination of the photocatalytic degradation efficiency of 1.4 nano Ce/ZnO

Weigh some amount of photocatalyst, add it to MB solution of 20 mL 10 mg/L, stir and degrade it for some time under UV irradiation, take a certain volume of solution and centrifuge it in a centrifuge tube at high speed for 5 min, take the supernatant, analyze and measure it with UV-1901 UV-V is spectrophotometer. During measurement, take distilled water as blank and measure the absorbance at 665 nm, that is, the absorbance of the liquid sample A at this time. Set the absorbance of MB solution without catalyst at 665 nm as A_0 , and calculate the degradation rate according to the following formula.

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

3. Experimental results and discussion

3.1 Characterization of nano Ce/ZnO

3.1.1 XRD analyses

Figure 1 shows the XRD spectra of pure nanoscale ZnO prepared with doped cerium nanosize ZnO(n(Ce): n(Zn) = 0.05 under optimal conditions. As shown from Figure 1, all diffraction peaks are sharp, indicating that the well crystalline generated under this condition^[11]. Compared to the standard map, it should be hexagonal, and the peaks became slightly wider after doping, but no cerium oxide peak was observed, indicating the incorporation of Ce into ZnO. The particle size of Ce/ZnO was approximately 10.7 nm, while undoped nano ZnO was about 17 nm.

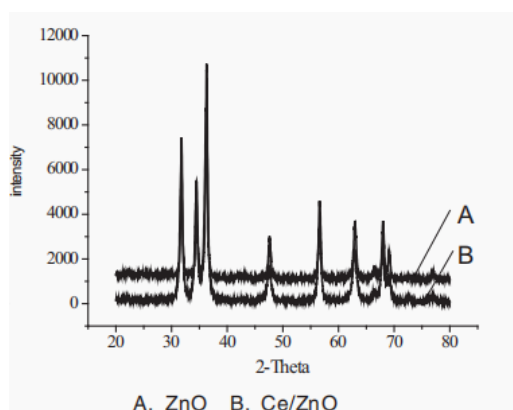


Figure 1. XRD patterns of nano ZnO and CE/ZnO.

3.1.2 Ultraviolet analysis

Figure 2 shows the UV absorption spectra of pure ZnO and cerium-doped zinc oxide prepared under optimal conditions. As shown from Figure 2, the absorption intensity of the nano zinc oxide doped UV region is much higher than the undoped nano zinc oxide with a small redshift in the UV peak, indicating successful incorporation of rare earth Ce ions into the ZnO lattice and a better crystal mass^[12,13].

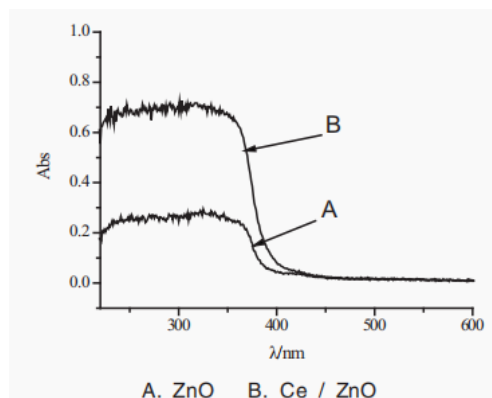


Figure 2. UV spectra of Ce⁴⁺/ZnO and ZnO.

3.1.3 Infrared spectrum analysis

It can be seen from the infrared spectrum of Figure 3 that there is a strong absorption peak around 430 cm⁻¹, which is the skeleton peak of ZnO, indicating that it got ZnO after calcination^[14]. There is a wide absorption peak at 3380–3600 cm⁻¹, and it is caused by the stretching vibration of -OH group that forms intermolecular hydrogen bond, indicating that there is strong adsorbed water on the surface of small-size Ce/ZnO nanoparticles. The adsorption activity is high, which is conducive to improving the photocatalytic properties of Ce/ZnO.

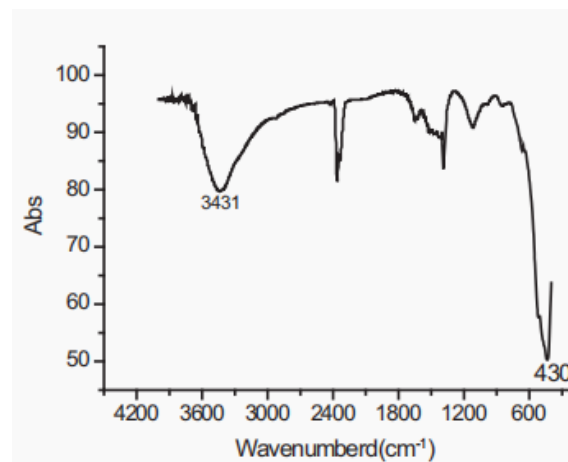


Figure 3. Infrared Spectro Spectra (FT-IR) plots of nano zinc oxide doped with cerium.

3.2 Optimization of the preparation conditions for the nanoscale Ce/ZnO

3.2.1 Effect of the different doping ratios on the photocatalytic properties

Weigh 0.1000 g of ZnO (n(Ce):n(Zn) = 0, 0.01,

0.05, 0.10, 0.20) respectively, use sodium dodecyl sulfonate as surfactant, add the catalyst with calcination temperature of 550 °C and calcination time of 3 h to 20 ml of 10 mg/L MB solution, and irradiate it under UV lamp for 2 h. Then centrifuge the reaction solution at high speed and take the supernatant. The absorption spectrum and absorbance were measured with an ultraviolet spectrometer. The absorbance at 665 nm was measured with distilled water as blank. The experimental results are shown in **Figure 4**.

As can be seen from **Figure 4**, when $n(\text{Ce}):n(\text{Zn}) = 0.05$, the effect of nano Zinc oxide on MB reached the maximum degradation, and the degradation rate of MB was about 26.27%, higher than that of pure zinc oxide. The possible reason is that some Ce^{4+} ions enter the ZnO lattice during heat treatment, which result in local lattice defects and charges imbalance. To achieve charge balance, some OH^- will be adsorbed on the surface of the catalyst, which can combine with holes generated under UV irradiation to form $\bullet\text{OH}$, which can react with the adsorbed substances on the surface. In addition, some Ce^{4+} ions cover the surface of ZnO grains in the form of small clusters of CeO_2 , while Ce^{4+} ions can generate electron-hole pairs under UV excitation, which may play the synergism with the generation of electron-hole pairs by photocatalysts^[16]. The doped photocatalyst also has a strong adsorption capacity for photons, promotes the migration of photons to the catalyst surface, prevents the simple recombination of electron-hole pairs, and improves photocatalytic efficiency. However, when the content of Ce^{4+} further increases, CeO_2 covers part of the surface of zinc oxide nanoparticles, affecting the light absorption of zinc oxide^[17]. Therefore, the optimal doping degree of cerium is $n(\text{Ce}):n(\text{Zn}) = 0.05$.

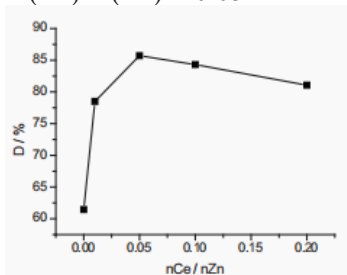


Figure 4. Effect of cerium doping on the catalytic properties of zinc oxide nanomaterials.

3.2.2 Effect of different calcination temperatures on the photocatalytic degradation effects

Figure 5 shows the photocatalytic activity of cerium doped zinc oxide nanoparticles obtained at different calcination temperatures (450–650 °C) under ultraviolet light. It can be seen from the figure that the catalytic activity of cerium doped zinc oxide nanoparticles obtained at 550 °C under ultraviolet light is the highest, and the degradation rate of MB is the highest at 2 h. The calcination temperature affects the photocatalytic performance of nano zinc oxide. In the temperature range of 500–600 °C, the catalyst has a good degradation effect on MB, but 550 °C is the highest, and the degradation rate decreases rapidly when it exceeds 600 °C. It may be that the nano zinc oxide crystal obtained at 550 °C develops best, and with the further increase of temperature, the growth rate of the ZnO crystal nucleus is accelerated, resulting in the bigger particle size and agglomeration in some parts^[15]. The particle increases while the specific surface area decreases, resulting in the decline of photocatalytic performance. Therefore, the calcination temperature is 550 °C.

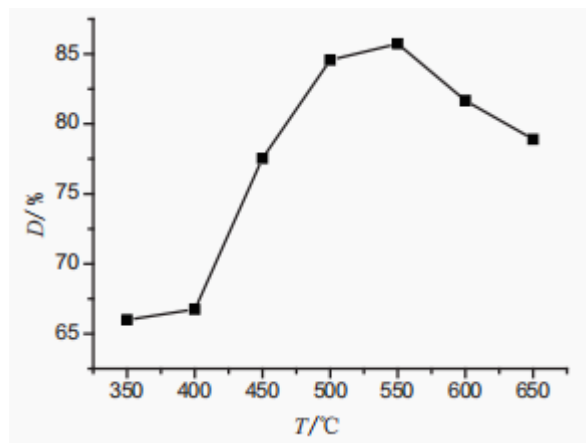


Figure 5. Effect of the calcination temperature on the photocatalytic activity of the cerium-doped nanoscale ZnO.

3.2.3 Effect of different calcination times on the photocatalytic properties

Figure 6 shows the photocatalytic activity of cerium doped zinc oxide nanoparticles under ultraviolet light when $n(\text{Ce}):n(\text{Zn}) = 0.05$, the surfactant is SDS, the calcination temperature is 550 °C, and

calcination time is different. It shows from the figure that the calcination time is in the range of 3–3.5 h, and the degradation rate of MB reaches about 85%. Because the longer the calcination time, the more small grains will be formed by the precursor. If burning time is too short, the precursor can not sufficiently decompose. Thus, the particle size of the product is coarse. Therefore, when the time is 3.0 h, the precursor can sufficiently decompose, and there are not too large grains, so the photocatalytic degradation efficiency is the highest.

3.2.4 The effect of different surfactants

Taking $n(\text{Ce}) : n(\text{Zn}) = 0.05$, calcination temperature $550\text{ }^\circ\text{C}$, calcination time 3.0 h, adding a small amount of different surfactants, the prepared catalyst is 0.1 g, and adding 20 ml 10 mg/L MB for catalytic degradation for 2 h. The experimental results show that the catalyst prepared by adding a small amount of triethanolamine and sodium dodecyl sulfonate has a good effect on the degradation of MB. It can effectively reduce the agglomeration of nano zinc oxide, but considering the impact on the environment, the selected surfactant is sodium dodecyl sulfonate^[18].

In summary, the doping degree of CE is $n(\text{Ce}) : n(\text{Zn}) = 0.05$, the burning temperature is $550\text{ }^\circ\text{C}$, the burning time is 3.0 h, and the surfactant is sodium dodecyl sulfonate, is the optimum conditions for the synthesis of the photocatalyst.

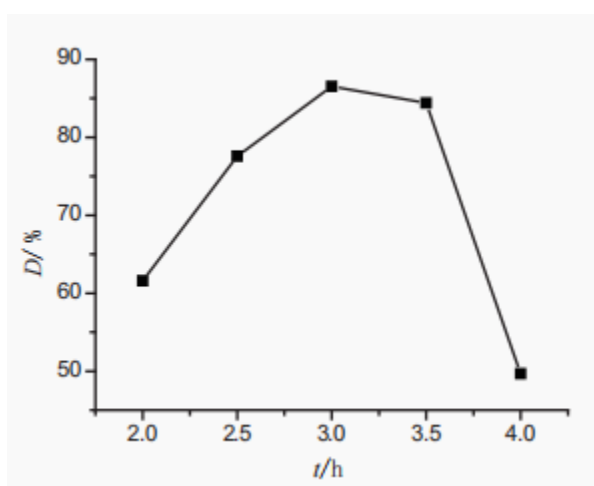


Figure 6. Effect of burning time on the photocatalytic properties of nano Ce/ZnO.

3.3 Optimization of MB degradation conditions

3.3.1 Effect of the initial pH values of the dye solution on the catalytic degradation

Take 8 parts of 20 ml and 10 mg/L MB solution, adjust the pH values of the solution to 3, 4, 5, 6, 7, 8, 9 and 10 with 1 mol/L HCl and NaOH individually, add 0.1000 g catalyst, and carry out photocatalytic degradation for 2 h. The experimental results are as in **Figure 7**. It shows from **Figure 7** that cerium doped ZnO has a high degradation rate of MB under neutral and alkaline conditions, but a low degradation rate under acidic conditions. However, when $\text{pH} = 4$, the degradation rate suddenly increases and then decreases. It may be due to that the change of catalyst surface charge caused by the change of pH value and affecting the adsorption behavior on the catalyst surface^[19,20]. MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+$) is a cationic dye. Under acidic conditions, MB molecules cannot be effectively adsorbed on the catalyst surface, resulting in low photocatalytic capacity. Under alkaline conditions, OH^- can trap holes, and the generated $\bullet\text{OH}$ harms photocatalytic degradation. Solution plays a vital role. With the increase of pH value, the OH^- content in the solution increases, and the adsorption ability of MB enhances. The combined action of the two makes MB have a high photocatalytic degradation rate under alkaline conditions^[21]. Excessive acidity and alkalinity may cause changes in the structure of nano ZnO, which is not conducive to photocatalytic degradation. Therefore, the pH value of photocatalytic degradation of MB is 7.

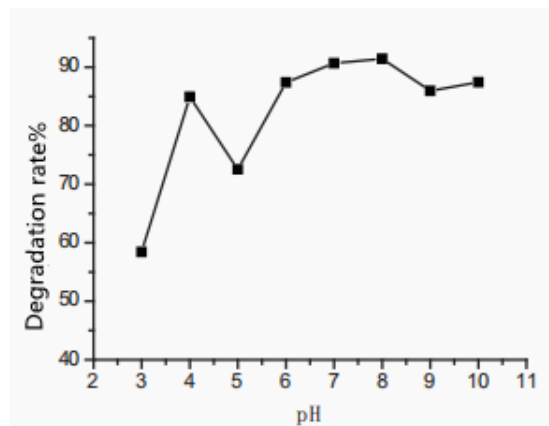


Figure 7. Effect of initial pH on MB degradation rate.

3.3.2 Effect of the catalyst dosage on the photocatalytic degradation of MB

Under the conditions of MB solution concentration of 10 mg/L, pH = 7 and photocatalyst dosage of 1 g/L, 2 g/L, 3 g/L, 5 g/L, 7 g/L and 10 g/L individually, it studied the effect of catalyst dosage on the degradation rate of MB solution. It shows from Figure 8 that the photocatalytic degradation efficiency of MB increased rapidly with the increase of catalyst dosage in the range of 1–5 g/L. When the dosage exceeds 5 g/L, the increase decreases. If the dosage of nanocatalyst continues to increase, the photocatalytic degradation efficiency of MB decreases. The reason is that when the dose of catalyst is small, it cannot utilize the light energy adequately, and the carrier produces less. With the increase of the dose of catalyst, it means more electron-hole pairs form, which accelerates the photocatalytic reaction when the amount of catalyst reaches. At 7 g/L, the degradation rate reaches the maximum. However, when the number of catalyzers increases to a certain extent, the excessive catalyzers will cause light scattering, coupled with the shielding effect between catalyst particles, so that photons cannot be used effectively, resulting in the decline of photocatalytic degradation rate^[22]. Considering the cost and environmental effects, the amount of catalyst is 5 g/L.

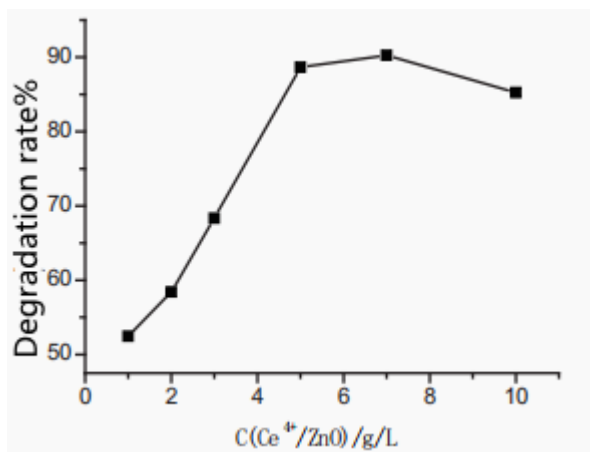


Figure 8. Effect of the catalyst dosage on the photocatalytic degradation of methylene blue.

3.3.3 Effect of light time on the photocatalytic degradation of MB

Weigh 6 parts of 0.1000 g catalyst, add 20 ml of

10 mg/L MB solution with a pH value of 7 respectively, and stir with the magnetic force for 20 min, 40 min, 60 min, 90 min, 120 min, and 150 min under the irradiation of UV light to investigate the influence of illumination time on the catalytic effect. The results show in Figure 9. It shows that in the initial stage of photocatalysis, the catalyst degradation rate of MB increases rapidly. When the photocatalytic time exceeds 60 min, the increased degradation rate slows down. It is mainly due to the strong adsorption capacity of nano materials for MB in the initial stage and more active sites on the catalyst surface, so the photocatalytic efficiency increases rapidly. With the extension of photocatalytic time, the oxygen molecules in water constantly capture electrons, and the final generation with the amount of highly active superoxide anion (O^{2-}) and hydroxyl radical (OH) also increased. Therefore, the degradation rate increased with the extension of illumination time, but the adsorption of nanomaterials gradually became saturated during the reaction. Some intermediates accumulated in nanomaterials and occupied some active sites, resulting in the reduction of photocatalytic efficiency of photocatalysts. Therefore, the increase of degradation rate slows down, that is the cause the degradation time is 2 h.

In conclusion, the optimum conditions for photocatalytic degradation are as follows: pH is neutral or weakly alkaline, catalyst mass is 5 g/L, and illumination time is about 2 h.

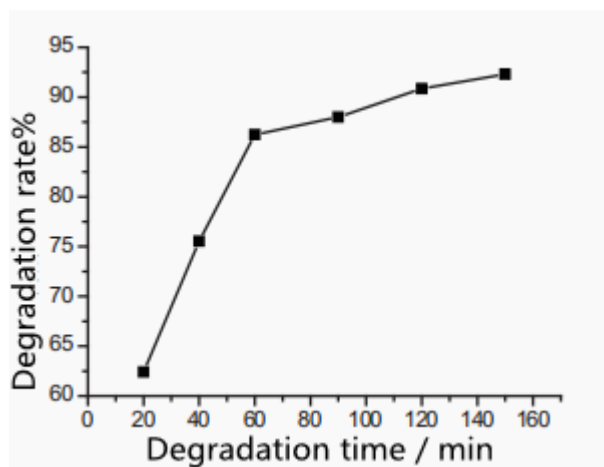


Figure 9. Effect of light time on Ce/ZnO photocatalytic methylene blue.

3.4 Practical application of the photocatalyst

It measured the actual dye wastewater in the experiment. The dye wastewater from a printing and dyeing enterprise was taken, and the decolorization rate and COD_{cr} removal rate were measured by photocatalytic degradation method and national standard method separately. Put 100 ml of the diluted wastewater into a beaker, add 0.5000 g of self-made Ce/ZnO catalyst, adjust the pH value to 7, and stir the reaction under UV light for 2 hours. Measure the decolorization rate and COD_{cr} removal rate separately. The decolorization rate was 87.67%, the COD_{cr} removal rate was 63.5%.

After 2 hours of light degradation, the dye wastewater is almost colorless, but the COD value is still high. It speculates that the organic dye molecules may not completely convert into small molecule inorganic substances in the process of light degradation. How to improve the removal efficiency of COD by photocatalyst needs further research.

4. Conclusion

a. Characterized by XRD, UV-vis and FTIR, the particle size of Ce/ZnO nanopowder prepared in this experiment is smaller than that of pure nano ZnO. The absorption ability in the UV-vis region is stronger and moves to the visible region. The broad absorption peak at 3380–3600 cm⁻¹ shows that there is strong adsorbed water on the surface of Ce/ZnO nanoparticles and high adsorption activity. These properties will help to improve the photocatalytic ability of Ce doped nano ZnO.

b. Taking MB as the photocatalytic model, the effects of cerium doping, calcination temperature and calcination time on photocatalytic performance were studied. The results showed that the degradation of MB by nano ZnO reached the maximum when n(Ce): n(Zn) = 0.05, calcination temperature 550 °C, calcination time 3.0 h and surfactant SDS.

c. It studied the effects of pH value, photocatalyst dosage, and photocatalytic time on the photocatalytic degradation of MB by Ce/ZnO nanoparticles. The results showed that the initial pH value of MB had more influence on the degradation rate, and the

degradation efficiency was higher under neutral and weak alkaline conditions. However, the hydrolysis rate is lower in strong acids. The dosage of catalyst also affects the degradation. When the dosage of catalyzers reaches 5 g/L, the catalytic efficiency is higher. The light application time also has an impact on the degradation. The changing trend shows more growth rate in the initial stage, and the increase slows down after 1 h of reaction. The longer the time is, the higher the degradation rate is. In view of the cost, the time should be 2 h after the reaction starts.

d. The composition of the actual dye wastewater is complex. The decolorization rate is 87.67% and the COD_{cr} removal rate is 63.5% when it is catalyzed by Ce/ZnO nano photocatalyst under ultraviolet light for 2 h.

Conflict of interest

The authors declare that they have no conflict of interest.

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