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Research Article

Removal of Organic Dyes by Nanostructure ZnO-Bamboo Charcoal Composites with Photocatalysis Function

Xinliang Yu,[1] Aimiao Qin,[1] Lei Liao,[2] Rui Du,[1] Ning Tian,[1] Song Huang,[1] and Chun Wei[1]

[1]*Key Lab New Processing Technology for Nonferrous Metals & Materials, Ministry of Education, College of Materials Science & Engineering, Guilin University of Technology, No. 12 Jiangan Road, Guilin 541004, China*
[2]*College of Environmental Science & Engineering, Guilin University of Technology, No. 12 Jiangan Road, Guilin 541004, China*

Correspondence should be addressed to Aimiao Qin; 592491245@qq.com

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Composites of nanostructure zinc oxide (nano-ZnO) and bamboo charcoal (BC) were successfully prepared via impregnation-precipitation method. The products were characterized by XRD, SEM, and EDS. Rhodamine B (RhB) and acid fuchsin (AF) were selected as the organic dyes of photocatalysis degradation under the irradiation of ultraviolet light (UV). The influence of particle size of BC, irradiation time, pH value of the solution, and additive amount of H_2O_2 on removal of the dyes has been studied. The results show that smaller particle size of BC in the composites has a better removal effect. The composites possess the highest removal capacity for RhB and AF under the conditions of pH = 2 and pH = 5.4, respectively. The optimum additive amount of H_2O_2 for 5 mL RhB and AF was 0.050 mL and 0.1 mL, with a removal rate of 93% and 99%, respectively.

1. Introduction

Nano-ZnO is considered to be one of the most promising highly active photochemical catalysts for its advantages such as high efficiency, energy saving, cleaning, nontoxicity, and no secondary pollution [1]. In the past few years, the study on its preparation method and catalytic performance has been one of the hot areas of research activities [2–4]. The photocatalysis mechanism is that, under irradiation of light, ZnO is emitted to produce a large number of electron-hole pairs in which the electrons have strong reducibility and the holes have strong oxidizability. Due to the oxidation of OH- and H_2O molecules by the holes, highly active hydroxyl free radicals ($^{\bullet}OH$) with strong oxidizability generate. Subsequently, organics are oxidized by $^{\bullet}OH$ and ultimately degraded into CO_2, H_2O, and other nontoxic inorganic small molecules [5]. At present, photocatalysis applications of ZnO concentrated on the sewage treatment and removal of interior organic contaminants [6, 7]. Most of the organics in the water can be oxidized and removed, including chloroform, carbon tetrachloride, and trichloroethylene, which are difficult to eliminate through traditional water treatment methods. In addition, heavy metal ions in the water can also be reduced by the electrons in the conduction band without affecting the beneficial mineral elements for human beings [8–10]. However, actual applications of powdery nanometer oxide photocatalysts are limited due to some disadvantages such as low light utility efficiency, difficulties in separation, and recovery [11]. Further researches will focus on development of novel nano-ZnO material which is easier to commercially produce accompanied with lower energy consumption and higher photocatalytic activity.

Bamboo charcoal (BC) prepared from pyrolysis of bamboo presents a porous structure with a surface area of 360 m^2/g and even 1000 m^2/g if further treated, which is 2–5 times higher than that of the ordinary carbon [12]. Owing to the specific structure characteristics, BC exhibits strong adsorption performance to many kinds of contamination in air and water, and thus it can be applied in air purification, sewage filtering, and food preservation as a new functional material [13–15]. However, BC is unsuitable to be used alone as an adsorbent because of the secondary pollution caused by the incomplete removal of pollutants. Besides, its adsorption performance will decrease gradually as time goes on.

With synergistic reaction of absorption of BC and catalytic degradation of nanophotocatalysts, study of nanomodified BC is believed to make good sense [16]. Chuang et al. [17], Zhou et al. [18], and Zhang et al. [19] have reported that nano-TiO_2 modified BC has a good photocatalysis performance to lots of organic pollutants. However, as one of the most common semiconductor photocatalysts as TiO_2, researches on nano-ZnO modified BC are very few. In fact, ZnO has a better photocatalysis performance than TiO_2 under specific conditions [20–22]. As an efficient photocatalyst, ZnO would likely replace TiO_2 in the future owing to the same band-gap energy, similar photocatalytic mechanism, and lower cost [23]. Our previous research showed that ZnO/BC composites prepared via impregnation-precipitation method have a good removal rate of methylene blue by more than 95% [24]. Rhodamine-B (RhB) and acid fuchsin (AF) are commonly used organic dyes in industry of spin printing and dyeing and biomedicine study. Due to the high concentration in the effluents and the higher stability of these modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete removal and degradation, which are harmful to the environment and hazardous to human health. Therefore, the further study on the removal of another two basic organic dyes, RhB and AF, was carried out.

2. Materials and Experiments

2.1. Reagents and Materials. In this paper, the following chemicals were used: zinc oxide (ZnO, AR, ShanTou West Long Chemical Co., Ltd.); polyethylene glycol-6000 (PEG-6000, CP, Shantou West Long Chemical Co., Ltd.); sodium hydroxide (NaOH, AR, Guangdong Guanghua Chemical Factory Co., Ltd.); absolute ethyl alcohol (C_2H_5OH, AR, Tianjin Damao Chemical Reagent Factory); bamboo charcoal (BC, Jiangmen Jinrong Household Products Co., Ltd.); rhodamine B (RhB, AR, Tianjin Institute of Chemical Reagents); acid fuchsin (AR, Shanghai SSS Reagent Co., Ltd.); hydrochloric acid (HCl, 36–38%, AR, ShanTou West Long Chemical Co., Ltd.); and hydrogen peroxide (H_2O_2, 30%, AR, ShanTou West Long Chemical Co., Ltd.). Distilled water was used throughout the experiments.

2.2. Modification of BC by ZnO Nanoparticles. BC is modified by nano-ZnO via impregnation-precipitation method [25]. That is, BC as a carrier is soaked in soluble zinc salt solution for a period of time so that Zn^{2+} can be absorbed on the surface of BC adequately. Then NaOH as the precipitation agent is added into the solution to form precipitation with the absorbed Zn^{2+}. Under the heating conditions, nano-ZnO generated and loaded on surface of BC.

In a typical experiment, BC was ground into powder and sieved to various particle sizes: 250–550 μm, 120–250 μm, 75–120 μm, and less than 75 μm. 0.5 g as-prepared BC powder was dispersed in 30 mL mixed solution containing 0.2 g PEG-6000 and 0.086 g $ZnSO_4{\cdot}7H_2O$ with distilled water as a solvent and stirred for 4 h. Then 20 mL NaOH (0.03 mol/L) was added dropwise into above mixture and kept on stirring for 8 h. Next, the mixture was kept at 80°C for 50 min. After cooling, the products were filtered and washed repeatedly with distilled water until pH = 7. The final composites were obtained by drying at 80°C for 12 h.

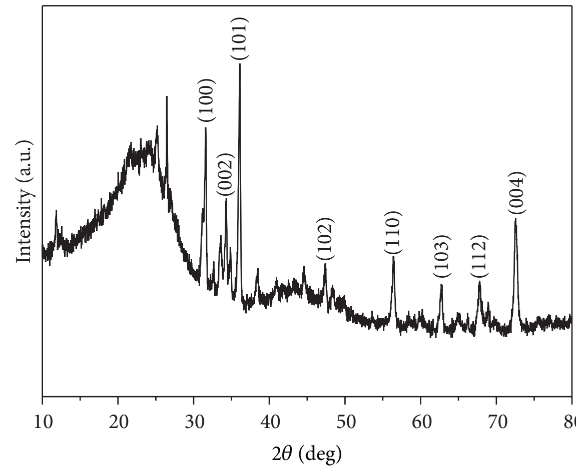


Figure 1: XRD pattern of the nano-ZnO/BC composites.

2.3. Characterizations. The XRD patterns were recorded via X-ray diffractometer (Netherlands PANalytical Company). The SEM images were acquired on JSM-6380LV scanning electron microscope (NEC Electronics Corporation). Elemental analysis was taken by an OIMS energy dispersive X-ray spectroscopy and UV-VIS was tested on UV-3600 ultraviolet-visible spectrophotometer (Shimadzu Corporation) at a range of 200 nm to 800 nm.

2.4. Removal of the Organic Dyes by Nano-ZnO/BC Composites. 2 mg/L RhB and 20 mg/L AF solution were prepared firstly. Then 0.1 g nano-ZnO/BC composites were added into 5 mL as-prepared organic dyes and the formed suspension system was irradiated by UV (λ = 254 nm). After specific time, the liquid phase was separated by centrifuging (10000 r/min) and the absorbance was detected by UV-VIS.

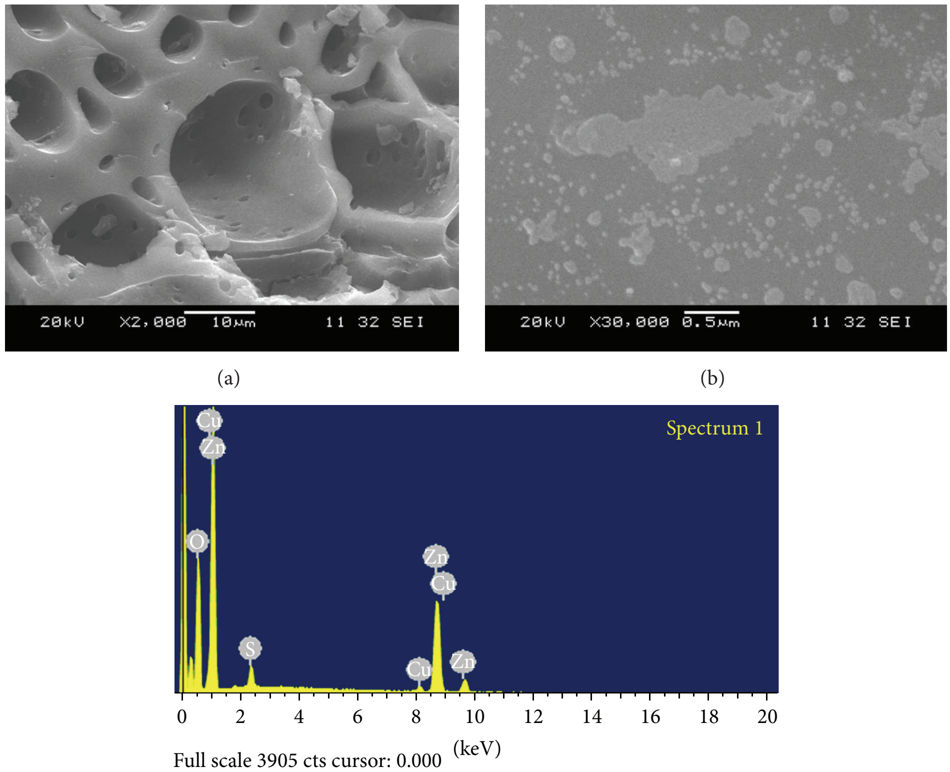
According to Lambert-Beer's law [26], the removal rate of the dyes is calculated by the following formula:

$$\text{Removal rate}\ (\%) = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\%. \tag{1}$$

In this formula, C_0 and C are defined as the initial concentration of the dyes and the concentration after photocatalysis reaction. A_0 and A are defined as the initial absorbance and the absorbance after photocatalysis reaction.

3. Results and Discussions

3.1. Structure Analysis. Figure 1 shows the XRD patterns of the ZnO/BC composites. Two broad peaks appearing around 24° and 43° indicate the typical peaks of amorphous carbon with noncrystalline structures. Typical characteristic peaks of ZnO can be observed on the diffraction patterns, which correspond to the (100), (002), (101), (102), (110), (103), (112),



(a) (b) (c)

Figure 2: SEM images (a), (b) and EDS spectrum (c) of the nano-ZnO/BC composites.

and (004) planes in the reference PDF card (JCPDS 89-0511). The XRD result suggests that BC is a typical amorphous carbon and ZnO is assigned to hexagonal zincite structure.

3.2. Morphology and Component Analysis. The SEM images and the EDS analysis of the composites are shown in Figure 2. Figure 2(a) illustrates that BC presents a typical honeycomb structure with a large number of macropores with the diameter of 1–15 μm on the cross section. Figure 2(b) reveals that ZnO particles are mostly less than 50 nm in diameter and some are aggregated because of the high surface energy. The EDS result in Figure 2(c) shows that, besides Cu introduced by sample stage, O and Zn are mainly detected and the calculated atom ratio is close to 1 : 1. A small amount of S may derive from BC.

3.3. Photodegradation Studies of the Organic Dyes

3.3.1. Effect of Particle Size of BC. Table 1 presents the influence of particle size of BC on the removal of the organic dyes under UV for 15 min. The removal rates of RhB and AF increase by 41.49% and 25.20% when the particle size of BC decreases from 250–550 μm to ≤75 μm. The reason should be attributed to the stronger adsorption of the smaller particle with larger specific surface area. But if particle size is too small, preparation time will be longer and separation of the liquid-solid phase would be more difficult. So the particle size should be controlled to a specific region according to actual requirement.

Table 1: Influence of particle size of BC on removal of the organic dyes.

Particle size/μm	Removal rate of RhB/%	Removal rate of AF/%
250–550	43.46	61.60
120–250	54.32	73.76
75–120	55.79	81.56
≤75	84.95	86.80

3.3.2. Effect of Time. The influence of irradiation time of UV on the removal of the organic dyes is shown in Figure 3. It can be seen that the removal rate increases rapidly in the beginning and becomes stable after 60 min, which is because the concentration of the dyes falls down over time and the diffusion layer thickness surrounding the adsorbent particles decreases [27].

3.3.3. Effect of pH Value. Figure 4 shows the influence of the pH value of the solution on the removal of the organic dyes under UV for 15 min. The pH value was adjusted by HCl and NaOH. It is clear that the removal rate of two organic dyes is affected greatly by pH value. At lower pH value, the removal rate of RhB is higher than that under neutral and alkaline condition. It should be noted that when the pH value is 2.0, the removal rate reaches to 65% after only 15 min photocatalysis reaction. However, strong acid condition plays an opposite role in the removal of AF compared with RhB.

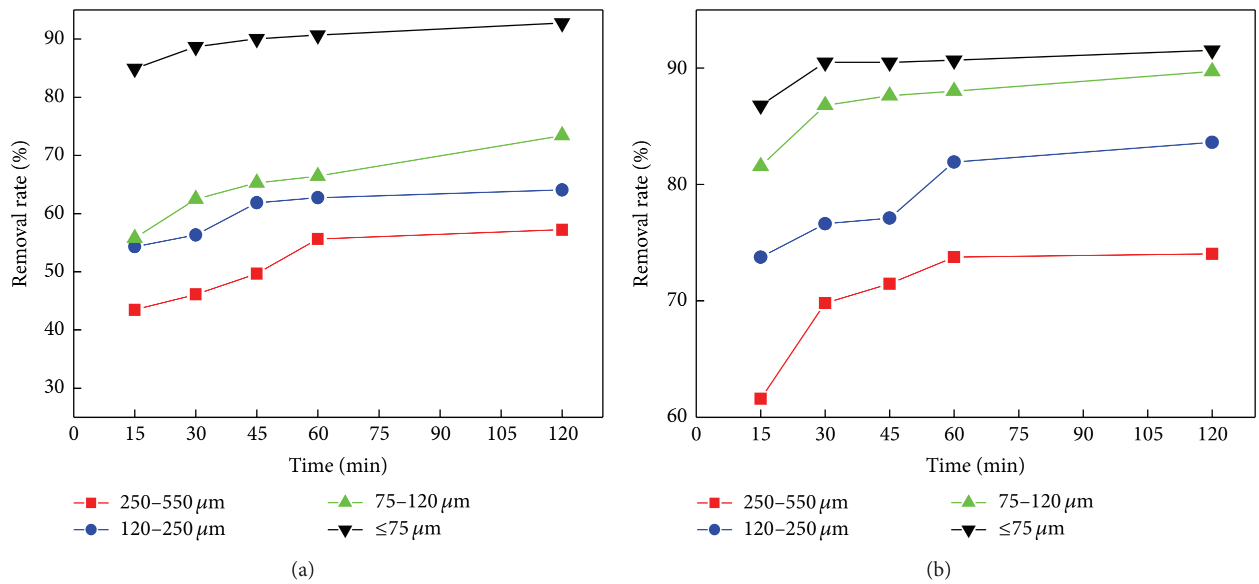


Figure 3: Influence of irradiation time of UV on the removal of the organic dyes by nano-ZnO/BC composites with different particle size of BC: (a) RhB, (b) AF.

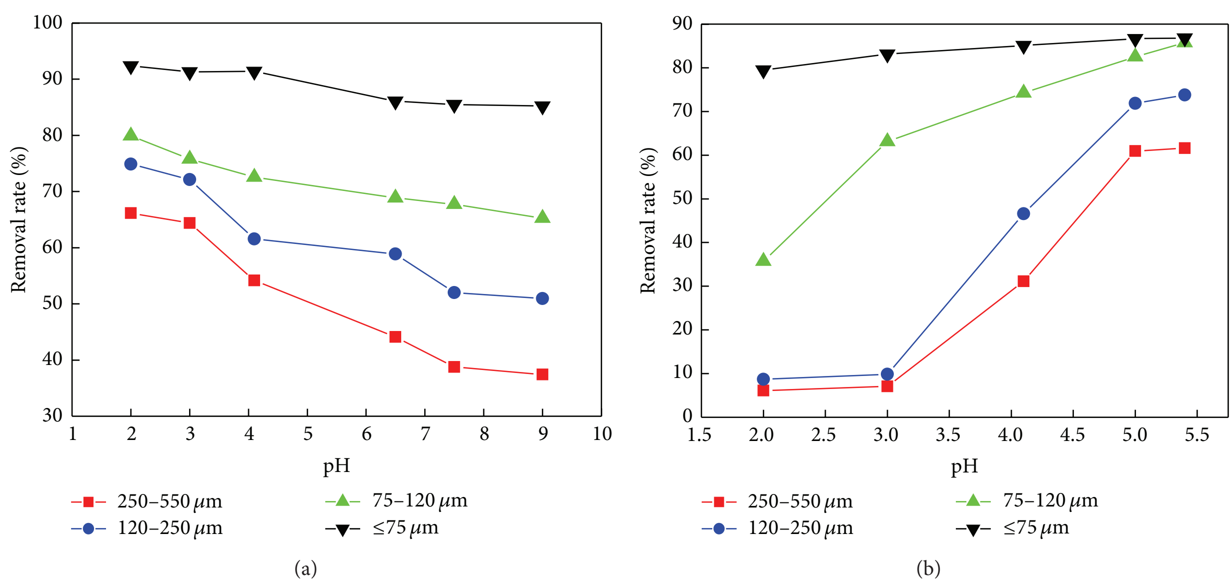


Figure 4: Influence of pH value on removal of the organic dyes by nano-ZnO/BC composites with different particle size of BC: (a) RhB, (b) AF.

The removal rate of AF improves much as the pH value increases. Therefore, pH value has different influences on removal of different organic dyes, for it affects not only the surface properties of ZnO but also the dissociation of dye molecules and the formation of hydroxyl radicals [28].

3.3.4. Effect of Additive Amount of H_2O_2. Figure 5 shows the influence of additive amount of H_2O_2 on the removal of the organic dyes under UV for 15 min. A considerable improvement of the removal rate can be observed due to an increase of $^{\bullet}OH$ in the solution after a small amount of H_2O_2 is added. For RhB, the removal rate reaches a relatively high level when the amount of H_2O_2 is 0.05 mL. However, as concentration increases continuously, the removal rate begins to decrease. The reason may be that excess H_2O_2 acts as a hole or $^{\bullet}OH$ scavenger or reacts with ZnO and forms peroxo compounds, which are detrimental to the photocatalysis action [29]. For AF, the removal rate increases significantly when the additive amount of H_2O_2 is less than 0.1 mL. It should be emphasized that when the particle size of BC is less than 75 μm, the removal rate of AF is close to 100% by the addition of only a little H_2O_2 solution. Therefore, more H_2O_2 is not necessarily better to assure a higher removal rate. To avoid waste, the optimum amount of H_2O_2 in this experiment is 0.05 mL and 0.1 mL for 5 mL RhB and 5 mL AF.

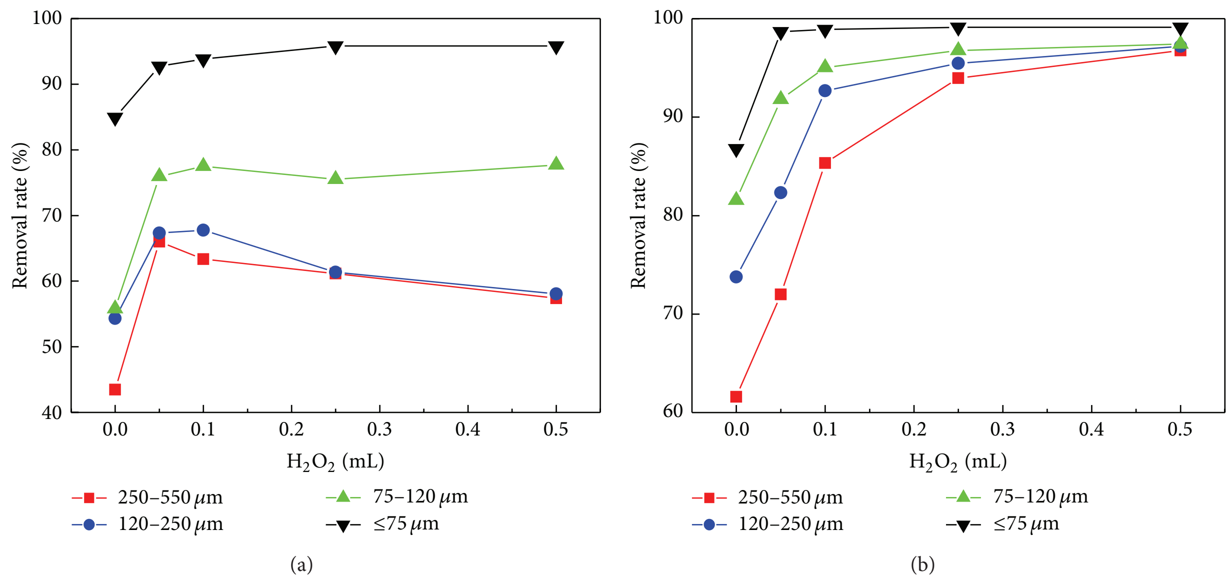


FIGURE 5: Influence of additive amount of H_2O_2 on removal of the organic dyes by nano-ZnO/BC composites with different particle size of BC: (a) RhB, (b) AF.

4. Conclusions

Nano-ZnO/BC composites were prepared via impregnation-precipitation method. The impact factors such as particle size of BC, irradiation time, pH value of solution, and additive amount of H_2O_2 on the photocatalysis properties of the composites are discussed. The results show that the as-prepared ZnO/BC composites are assigned to wurtzite of hexagonal crystal structure. Smaller particle size of BC shows better removal effect on the dyes. The removal rate of RhB is much higher under strong acid condition but it is better for removal of AF under weak acid condition. In addition, a certain amount of H_2O_2 contributes to the removal of the dyes for the enhanced oxidation of solution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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