Adsorption and Photo-catalytic Properties of Congo Red by Cobalt Doped Porous ZnO Prepared Through Hydrothermal Method

Wenya Bao^{1,*}, Xiaofen Fu¹, Kaiqi Hu¹, and Yecong Zhao¹

¹ School of Chemical and Biological Engineering, Qilu Institute of Technology, Jinan, Shandong, 250200, China

Abstract. ZnO and cobalt doped ZnO were prepared by hydrothermal method with zinc acetate dihydrate, cobalt acetate tetrahydrate and urea as raw materials and sodium citrate as surface modifier. Congo red (CR) was used as the pollutant model for adsorption and photo-catalytic experiments. Under the same conditions, the adsorption effect of cobalt doped ZnO with different urea content on CR was investigated, and the optimum urea content was determined. Under the same conditions, the adsorption and photocatalytic properties of cobalt doped ZnO prepared with the best urea content at different annealing temperatures were studied. According to the analysis of experimental data, the adsorption effect of Co doped ZnO with urea content of 8mmol and annealing temperature of 300°C is the best, and the photocatalytic effect is also the best under the same conditions.

1 Introduction

The shortage of fresh water resources is a common global problem. China uses the most water, the utilization rate of fresh water resources is low, and the distribution of water resources in the central and western regions is not balanced. With the gradual improvement of human living standards and the development of industry, untreated industrial wastewater, printing and dyeing industry discharge sewage also increase[1]. This wastewater contains a large number of harmful substances, which are difficult to degrade and toxic. Wastewater with much organics, high chromaticity and alkalinity, once into the water, will not only change the overall quality of water, the light into the water can also be blocked. It will eventually affect the water COD and BOD, and thus affecting the survival of animals, plants and microorganisms living in the water system. This will have a great impact on the development of human society and physical health.

CR is an important industrial dye and can be used for biological dyeing, adsorption indication and acid-base indication [2]. The dye has good thermal and chemical stability and is difficult to degrade under normal conditions. And it has a carcinogenic risk to human body, so industrial wastewater containing CR needs to be treated before discharged [3].

The wastewater treatment generally includes chemical oxidation [4, 5], biodegradation [6], membrane technology [7], adsorption [8] and photo-catalysis [9]. The adsorption and photo-catalytic method has attracted much attention due to its simple operation, low cost and wide application range. Therefore, it is an urgent problem to find adsorbents with low price, large

adsorption capacity and good selectivity for wastewater treatment technology. Many nanomaterials have good adsorption and photo-catalytic properties for organic dyes. Metal oxide nanomaterials possess high stability and simple preparation and will be potential photocatalyst. Porous ZnO can be used as adsorbent due to its controllable morphology, small size and large specific surface area[10].

ZnO is a semiconductor material with a large energy gap (3.4eV) and excellent optical properties. Under ultraviolet light, valence band electrons can transition to conduction band, and it has good photocatalytic performance [11]. Porous ZnO has many active sites, multiple pores, large specific surface area and other advantages, which are the key factors to be applied in wastewater treatment [12]. Therefore, it is of great significance to explore the interrelation between adsorption and photocatalytic performance of porous ZnO.

The synthesis method of porous ZnO has been gradually mature after years of development. There are many preparation methods of porous ZnO, such as solid phase, gas phase and liquid phase, among which liquid phase is the most commonly used synthesis method. Liquid phase method generally includes sol-gel method [13], direct precipitation method [14], microemulsion method [15] and hydrothermal synthesis method [16]. Compared with other preparation methods, the hydrothermal synthesis method is simple and the prepared ZnO has the good crystallinity, easy grain dispersion, small particle size and uniform distribution.

In this paper, we use hydrothermal synthesis method to prepare ZnO and cobalt doped ZnO materials to study the adsorption performance and photocatalytic

* Corresponding author: sdbaowenya@163.com

performance of CR. The optimal urea content was determined by studying the influence of ZnO with different urea content on the adsorption performance of CR. Based on this, the influence of cobalt doped ZnO on the adsorption and photocatalytic performance of CR under different annealing temperature was discussed.

2 Experimental section

2.1 Chemicals for synthesis

Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], urea [$\text{CO}(\text{NH}_2)_2$] and Trisodium citrate [$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$] were purchased from Tianjin Damao Chemical Reagent Factory. Cobalt acetate tetrahydrate [$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] and CR was purchased from Tianjin Kemio Chemical Reagent co., LTD and Shanghai Chemical Industrial Company respectively. All chemicals used were analytical grade and without further purifying.

2.2 Synthesis of samples

Porous cobalt doped ZnO samples were synthesized using a simple hydrothermal synthesis method as previously described. Typically, 2mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.028mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 6mmol $\text{CO}(\text{NH}_2)_2$ and 1mmol $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$ were dissolved and stirred in 60mL deionized water. After continuous magnetic stirring for 30min, the liquid above was transferred into Teflon reactor. Then put the Teflon reactor into the 120 °C oven for 12h. After natural cooling, the precursor was collected through washing with deionized water for three times, dried at 80 °C for 6h and annealed at different temperature (200 °C, 300 °C, 400 °C and 500 °C) for 2h in air. A black-green product (cobalt doped ZnO) was obtained, and the pure ZnO was prepared under similar reaction conditions except for the addition of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

2.3 Evaluation of adsorption performance

To investigate the effect of cobalt doped ZnO on adsorption performance, cobalt doped ZnO and pure ZnO samples were mixed with CR aqueous solution respectively in beakers under stirring in the dark. To study adsorption kinetic, 25mg of the ZnO and the cobalt doped ZnO samples are mixed with 30mL CR solution (300mg/L) respectively at different times. After centrifugation, the concentrations after adsorption of CR solutions were measured on UV-1750 ultraviolet-visible spectrometer (Shimadzu). The removal percentage (η) of as-prepared samples is calculated by Eq. (1).

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

In the above formula, A_0 and A_t are the absorbance of CR solution initially and at time t .

2.4 Evaluation of photo-catalytic performance

The CR solution with a concentration of 300mg/L was measured in 30mL in 50mL beakers, and 25mg of cobalt doped ZnO at different annealing temperatures was added. After stirring for 60min away from light for adsorption saturation, then put the suspension liquid under 200W Xenon lamp for 60min under stirring. Then centrifuge for 15 min at the speed of 10000 r/min, the concentrations of CR solutions were measured on ultraviolet-visible spectrometer. The photocatalytic degradation rate was calculated by Eq. (1).

3 Results and discussion

3.1 Effect of urea content on adsorption performance

Fig. 1. Spectrogram of absorption of CR by cobalt doped ZnO with different urea content.

As can be seen from Figure 1, when the urea content is 8mmol, the absorbance of the prepared cobalt doped ZnO to CR is the lowest at 497nm, which is 0.4353, indicating that the adsorption performance of CR is the best when the urea content is 8mmol. In addition, cobalt doped ZnO has a better adsorption effect on CR than pure ZnO. It may be that Co^{2+} occupies the position of Zn^{2+} in the ZnO lattice, resulting in a decrease in the pore diameter of ZnO, and increasing the specific surface area, thus improving the adsorption effect. The adsorption rates of each group are calculated by Formula (1), and the removal percentages are shown in Table 1.

Table 1. Removal percentage of cobalt doped ZnO with different urea content.

Urea content/mmol	Removal percentage/%
6	81.93
8	84.63
9	62.05

3.2 Effect of annealing temperature on adsorption performance

Fig. 2. Spectrogram of absorption of CR by cobalt doped ZnO with different annealing temperature.

As Figure 2 shows, when the annealing temperature is at 300°C, the absorbance of CR solution by cobalt doped ZnO is the lowest, indicating that the sample has the best adsorption ability to CR solution under this condition. When the annealing temperature is higher than 300°C, the absorbance increases gradually and the removal percentage decreases with the increase of annealing temperature. It may be because when the annealing temperature increases, the particle size and pore size of ZnO generally increase. While the specific surface area and pore volume decrease, and the pore structure begins to collapse, resulting in the decrease of surface active sites, thus affecting the adsorption effect of CR. When the annealing temperature is at 200°C, the absorbance of CR solution by cobalt doped ZnO is the highest, second only to the original solution (300mg/L). This indicates that cobalt doped ZnO has the worst adsorption ability on CR solution under this condition, which may be due to the low annealing temperature and poor crystallinity, and the precursor does not form ZnO. The removal percentage of each group are respectively calculated by Formula (1). See Table 2 for each removal percentage.

Table 2. Removal percentage of cobalt doped ZnO with different annealing temperature.

Annealing temperature /°C	Removal percentage/%
200	7.28
300	72.97
400	58.97
500	34.03

3.3 Effect of annealing temperature on photocatalytic performance

Fig. 3. Spectrogram of photocatalytic performance of CR by cobalt doped ZnO with different annealing temperature.

From Figure 3, we can see that cobalt doped ZnO has little catalytic degradation effect on CR solution at the annealing temperature of 200°C. When the annealing temperature is at 300°C, the adsorption of CR solution by cobalt doped ZnO is the lowest, indicating that the photo-catalytic degradation effect is the best. The photo-catalytic percentages of each group are calculated by Formula (1), and shown in Table 3. While the annealing temperature is higher than 300°C, the photo-catalytic degradation rate decreases with the increasing of annealing temperature. The same as the adsorption effect, the photo-catalytic ability is still the best when the annealing temperature is 300°C, indicating that the photo-catalytic effect is directly related to the adsorption effect. This may be because when the annealing temperature is 300°C, there are more active sites formed on the surface of cobalt doped ZnO, which can make good use of light source for photo-generating electrons to further improve the photo-catalytic degradation rate. When the temperature is lower than 300°C, the poor photo-catalytic degradation effect may be caused by the low temperature of the precursor annealing, resulting in poor crystallinity, structural instability, less photo-generated electrons, and slow electron transfer, etc. When the temperature is higher than 300°C, the crystal sintering may cause uneven crystal lattice and affect the photo-generated electrons of the sample, thus affecting the degradation effect of CR.

Table 3. Photo-catalytic degradation rate of cobalt doped ZnO with different annealing temperature.

Annealing temperature /°C	Photo-catalytic degradation rate/%
200	8.49
300	90.12
400	68.92

500	41.46
-----	-------

4 Conclusion

In this study, ZnO and cobalt doped ZnO prepared by hydrothermal synthesis method with different urea content and annealing temperature. The results show that the adsorption and photo-catalytic performance on CR solution were the best with the urea content of 8mmol and the annealing temperature at 300°C.

Acknowledgments

The research was supported by the student innovation program of Qilu Institute Technology (DC2019072).

References

1. S. Hokkanen, A. Bhatnagar, M. Sillanpää. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity[J]. *Water research*, 2016, 91: 156-173.
2. Y. Zheng, B. Zhu, H. Chen, W. You, C. Jiang, J. Yu, Hierarchical flower-like nickel(II) oxide microspheres with high adsorption capacity of Congo red in water, *J. Colloid Interface Sci.* (2017),504, 688–696.
3. M.H. Beyki, M. Bayat, F. Shemirani. Fabrication of core-shell structured magnetic nanocellulose base polymeric ionic liquid for effective biosorption of Congo red dye[J]. *Bioresource technology*, 2016, 218: 326-334.
4. A.J. Santos, I. Sirés, A.P.M. Alves, et al. Vermiculite as heterogeneous catalyst in electrochemical Fenton-based processes: Application to the oxidation of Ponceau SS dye[J]. *Chemosphere*, 2020, 240: 124838.
5. C.W. Zhu, C.Q. Jiang, S. Chen, et al. Ultrasound enhanced electrochemical oxidation of alizarin red on boron doped diamond (BDD) anode: effect of degradation process parameter[J]. *Chemosphere*, 2018, 209: 685-695.
6. W. Sun, C. Zhang, J. Chen, et al. Accelerating biodegradation of a monoazo dye Acid Orange 7 by using its endogenous electron donors[J]. *Journal of hazardous materials*, 2017, 324: 739-743.
7. W. Chen, J. Mo, X. Du, et al. Biomimetic dynamic membrane for aquatic dye removal[J]. *Water research*, 2019, 151: 243-251.
8. H. Jin, J. Yuan, H. Hao, et al. The exploration of a new adsorbent as MnO₂ modified expanded graphite[J]. *Materials Letters*, 2013, 110.
9. Q. Li, T. Zhao, M. Li, et al. One-step construction of Pickering emulsion via commercial TiO₂ nanoparticles for photocatalytic dye degradation[J]. *Applied Catalysis B: Environmental*, 2019, 249: 1-8.
10. A. Serrà, Y. Zhang, B. Sepúlveda, et al. Highly reduced ecotoxicity of ZnO-based micro/nanostructures on aquatic biota: Influence of architecture, chemical composition, fixation, and photocatalytic efficiency[J]. *Water research*, 2020, 169: 115210.
11. J. Wang, S. Fan, Y. Xia, et al. Room-temperature gas sensors based on ZnO nanorod/Au hybrids: Visible-light-modulated dual selectivity to NO₂ and NH₃[J]. *Journal of hazardous materials*, 2020, 381: 120919.
12. X.L. Li, J. Zhang, Y.C. Jiang, et al. Highly efficient biode-colorization / degradation of congo red and alizarinyellow by chloroperoxidase from *Caldariomyces fumiga-go*: catalytic mechanism and degradation pathway[J]. *Industrial & Engineering Chemistry Research*, 2013, 52: 13572-13579.
13. P.C. Bhomick, A. Supong, M. Baruah, et al. Pine Cone biomass as an efficient precursor for the synthesis of activated bio-carbon for adsorption of anionic dye from aqueous solution: isotherm, kinetic, thermodynamic and re-generation studies[J]. *Sustainable Chemistry and Pharmacy*, 2018, 10: 41-49.
14. C. Lei, M. Pi, C. Jiang, et al. Synthesis of hierarchical porous zinc oxide (ZnO) microspheres with highly efficient adsorption of Congo red[J]. *Journal of colloid and interface science*, 2017, 490: 242-251.
15. X. Han, J. Harris, L. Šiller. Synthesis of porous zinc-based/zinc oxide composites visol-gel and ambient pressure drying routes. *Journal of Materials Science*. 2018, 018, 2138.
16. D. Pinheiro, S. Devi, A. Jose, R. Bharadwa. Effect of surface charge and other critical parameters on the adsorption of dyes on SLS coated ZnO nanoparticles and optimization using response surface methodology[J]. *Journal of Environmental Chemical Engineering*, 2020, 8(4).
17. A. Ishizumi, Y. Kanemitsu. Structural and luminescence properties of Eu-doped ZnO nanorods fabricated by a microemulsion method[J]. *Applied Physics Letters*, 2005, 86(25).
18. O. Akhavan, M. Mehrabian, K. Mirabbaszadeh, et al. Hydrothermal synthesis of ZnO nanorod arrays for photocatalytic inactivation of bacteria[J]. *Journal of Physics D: Applied Physics*, 2009, 42(22): 225305.