Zeolitic Imidazolate Framework-67 Functionalized Chitosan Aerogel for Efficient Removal of Dye

Xiang Li[1,2], Hong Shao[3*], Qianli Ma[3], Wensheng Yu[3] and Xiangting Dong[1,3*]
[1]School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, China
[2]School of Petrochemical Technology, Jilin Institute of Chemical Technology, Jilin, China
[3]School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, China

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Abstract: As an efficient adsorbent, metal-organic framework (MOF) has been used in dye wastewater treatment. However, the morphology of MOF powder has some disadvantages, such as poor recoverability and complex operation process. The zeolitic imidazolate framework-67@chitosan aerogel (ZIF-67@CSA) was prepared by alkali freezing-thawing method, freeze drying and in situ growth method to remove dye congo red. The load mass ratio of ZIF-67on CSA is as high as 41.2 wt% ZIF-67@CSA was used to adsorb dye congo red, and the removal rate is more than 89.3%. This strategy provides an effective and universal way to prepare high loaded MOF natural polysaccharide aerogel, thus expanding its application in the field of pollutant treatment.

1 INTRODUCTION

Industries such as textiles, leather and paper produce a large amount of dye wastewater serious impact on the natural environment.

However, in order to prevent water pollution and protect human health and safety, it is necessary to properly treat dye wastewater before discharge (Yang, Han, Li, Zhu, Shi, Tang, Wang, Yue, Li, 2019, Shao, Yin, Li, Ma, Yu, Dong, 2021).

Metal-organic frameworks are regular crystalline structures supported by metal nodes and organic ligands. It has excellent properties such as large specific surface area, low density, good biocompatibility, chemical modifiability, and topological diversity (Liu, Yu, Zeng, Li, Sun, Hu, Su, 2020). Due to its exists in powder form, it cannot be used directly in practical application, resulting in different operations, resource waste and secondary pollution (Ma, Lou, Chen, Shi, Xu, 2019). In order to solve these problems, some researchers often combine polymer materials with MOF crystal.

Chitosan is one of the common natural polymer materials, which has good biocompatibility, renewability, biodegradability and economy (Wang, Zheng, Luo, Liu, Zhang, Li, Sun, Shen, Han, Wang, 2018). Chitosan aerogels have large specific surface area, high porosity, and macroporous 3D network structure, and they have excellent adsorption properties for printing and dyeing wastewater treatment (Zhao, Ma, Zhao, Rong, Tian, Zhu, 2020). However, the affinity of chitosan based adsorbent is insufficient, which limits its practical application (Qiu, He, 2019), therefore, functional modification of chitosan aerogel is needed to improve its adsorption properties.

Herein, we reported a ZIF-67@CSA material is prepared by alkali lyophilization, freeze drying and in situ growth method to remove dye congo red. In addition, ZIF-67@CSA was characterized by X-ray diffractometry. The adsorption properties and selectivity of aerogels were investigated with dye Congo red as the model.

2 EXPERIMENTAL

2.1 Materials and Characterization

Chitosan (CS), Epichlorohydrin (ECH, 99.5%), Congo red (CR), 2-methylimidazole (2-MI, 98%), cobalt nitrate ($Co(NO_3)_2.6H_2O$, 99%) were acquired

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from Aladdin. X-ray diffraction (XRD) spectra of samples were obtained on an X-ray diffractometer (D/Max 2500, Rigaku, Japan). The CR concentrations were measured at 497 nm by using an ultraviolet-visible spectrophotometer (UV-vis, UV-2501, Shimadzu, Japan).

2.2 Preparation of the ZIF-67@CSA

2.2.1 Preparation of the CSA

Chitosan aerogel (CSA) was fabricated according to the following procedure (Song, Zhu, Zhu, Zhao, Yang, Miao, Ren, Ma, Qian, 2020). A 3 wt% chitosan solution was prepared in a pre-cooled LiOH/KOH/urea (4.5 wt %/7 wt %/8 wt%) solution. Then, 5 wt% ECH was added to the CS solution and stirred at sub-zero to obtain a pre-crosslinked solution. The pre-crosslinked solution was poured into the mold and left to stand overnight at low temperature. Finally, CSA was obtained by repeated washing with deionized water and vacuum freeze-drying.

2.2.2 Preparation of ZIF-67@CSA

ZIF-67@CSA was fabricated according to the following procedure.

The CSA was immersed in 40 mL methanol containing 1.098g $Co(NO_3)_2 \cdot 6H_2O$. Then, 0.656 g of 2-methylimidazole in 40 mL of methanol was added to the above solution, ZIF-67 was grown in situ on CSA at room temperature and left to stand overnight.

and the in-situ growth of ZIF-67 on CSA was performed at room temperature for 24h. The ZIF-67@CSA was washed with methanol, deionized water and vacuum freeze-dried. ZIF-67@CSA was obtained after repeated alternate washing with methanol and deionized water, and vacuum freeze-dried.

2.3 Batch Adsorption Experiments

The adsorption experiments were conducted as follows: For all the experiments, the reacting admixtures were mechanically stirred at 150 rpm.

10 mg adsorbent was added into 20 mL CR solutions (50 mg·L^{-1}, pH=7.0).

The removal rate (%) onto the adsorbent was listed as the following (Eq. (1)):

$$\text{Removal rate} = \frac{A_0 - A_1}{A_0} * 100\% \qquad (1)$$

Where A_0 is the absorbance of initial solution; A_1 is the absorbance of residual liquid.

3 RESULTS AND DISCUSSION

3.1 Design of ZIF-67@CSA

From Fig. 1, the synthetic process of ZIF-67@CSA was prepared by freeze-thaw method and in-situ growth. Firstly, chitosan was dissolved under the alkaline condition, and chitosan was dissolved by freeze thaw method. Chitosan hydrogel was prepared with ECH as crosslinking agent, and then freeze-dried into CSA, ECH and chitosan molecules are crosslinked in three different ways, as shown in Fig. 1. Then, CSA were immersed in the solution containing metal ions Co^{2+} and 2-methylimidazole in sequence, and ZIF-67 rhombic dodecahedrons was generated in situ on the surface of CSA. This is because the vacant orbitals of polyamino functional groups on CSA can form coordination bonds with Co^{2+}, and then a large number of metal active sites are generated on CSA. Further, dense layer ZIF-67 were generated in CSA. Therefore, the ZIF-67@CSA has a strong affinity for CR molecules and obtains excellent adsorption performance.

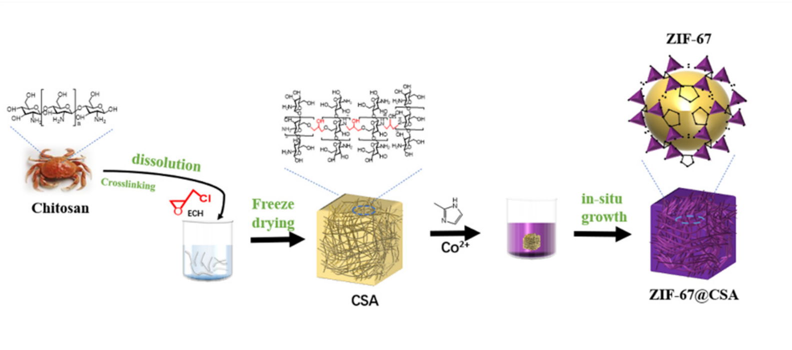

Figure 1: Schematic fabrication process of ZIF-67@CSA.

3.2 Characterization

The structures of CSA, ZIF-67 and ZIF-67@CSA were confirmed by XRD in Fig. 2. CSA have no obvious diffraction, meaning that CSA are amorphous peaks. The ZIF-67@CSA has the same peaks as the synthesized ZIF-67, which indicates that ZIF-67 are successfully grown on the surface of CSA.

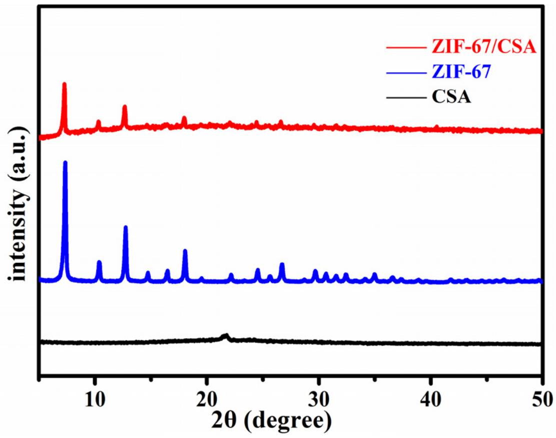

Figure 2: The XRD of CSA, ZIF-67 and ZIF-67@CSA.

3.3 Adsorption Efficiency

As shown in Fig. 3, the adsorption capacity of ZIF-67@CSA to CR is higher than that of CSA. This is because ZIF-67 has a larger load on chitosan aerogel. But the adsorption capacity of ZIF-67@CSA is lower than that adsorption capacity of ZIF-67 to CR. This is because the adsorption capacity of CSA is much lower than that of ZIF-67. The adsorption capacity of the composite aerogel in unit mass is lower than that of ZIF-67. However, the preparation of ZIF-67@CSA by powdered ZIF-67 can make the adsorbent have good recyclable properties, simple operation process and prevent secondary pollution.

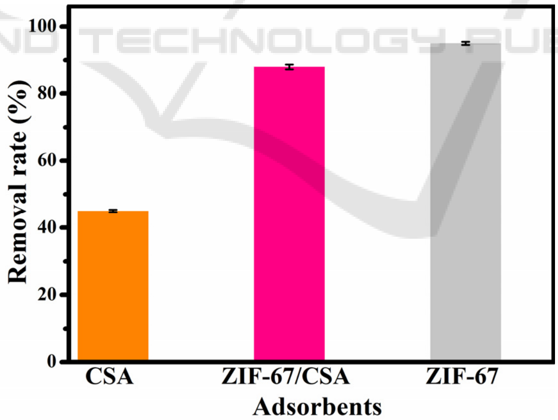

Figure 3: Removal rate of CR by CSA, ZIF-67 and ZIF-67@CSA.

4 CONCLUSIONS

In conclusion, ZIF-67@CSA was obtained by a green process of alkali dissolution, in situ growth and freeze-vacuum drying. The structure of ZIF-67@CSA was characterized by XRD. The results showed that ZIF-67 was successfully grown on CSA. The adsorption capacity of ZIF-67@CSA in CR was much higher than that of CSA. The preparation of aerogel from powdery ZIF-67 can make the adsorbent have good recyclable properties, simple operation process, and prevent Secondary pollution.

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