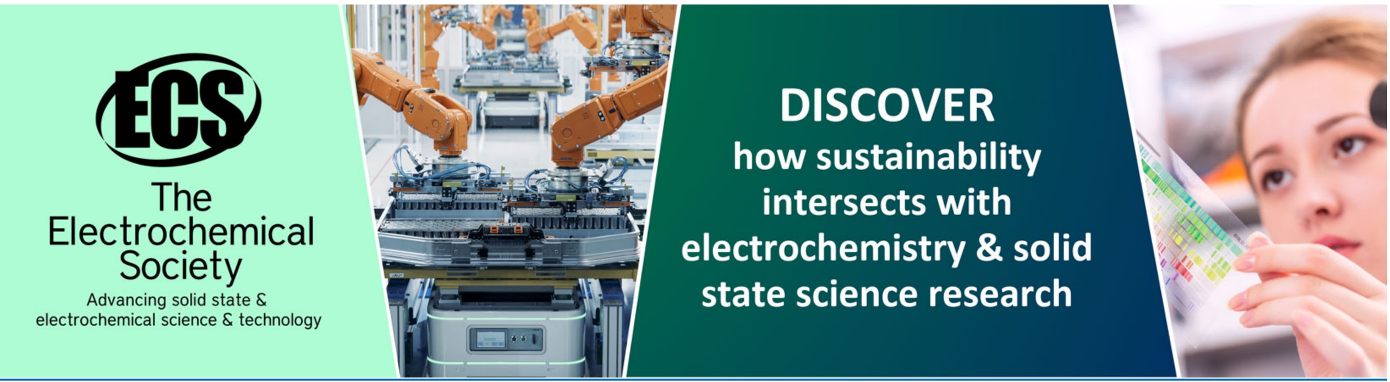
ZIF-8/ZIF-67 derived carbon for efficient removal of antibiotics in aqueous solution



ZIF-8/ZIF-67 derived carbon for efficient removal of antibiotics in aqueous solution

Hongmei Tang, Wenyao Li*, Wenjing Sun, Zhe Wang, Qiwen Hu

School of Material Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

*Corresponding author e-mail: *liwenyao314@gmail.com*

Abstract. In this paper, ZIF-8/ZIF-67 derived carbon (ZDC) was synthesized by surface modification technology and calculation process subsequently. In order to evaluate the feasibility of ZDC for antibiotic removal, the adsorption experiments were carried out by three typical antibiotics: tetracycline (TC), norfloxacin (NFO) and ofloxacin (OFO). The results showed that the maximum adsorption capacities of TC, NFO and OFO based on ZDC were 543.48, 239.8 and 340 mg/g, respectively. The adsorption capacity of ZDC was better than that of many other similar adsorbents, which is a potential adsorbent for antibiotic removal in the contaminated water.

1. Introduction

In recent years, antibiotics are widely used to treat for microbial infections, and they have become an important part for curing human diseases. According to statistics, about 10,000 tons of antibiotics are used in animal, human health, aquaculture and agricultural activities every year, so they are continuously released into the environment. [1] Because of the high-value consumption of antibiotics for various applications, and the ineffective treatment of these contaminant, thus resulted its nearly ubiquitous in the contaminated water. It is reported that about 30-90% of antibiotics have high stability and are not easy to degrade, so they can exist stably in the environment for ages. [2] Antibiotics have been shown to be toxic to aquatic organisms such as water fleas and fish, and to cause serious pollution of drinking water, thus threatening human health. [3] Therefore, it is very urgent to remove antibiotics in the contaminated water.

There are many methods to remove antibiotics in aqueous solution, during virous technologies, adsorption is recognized as the simplest and economical way, and is also one of the most effective ways to remove antibiotics. Now adsorption technology has been successfully applied to remove other different types of contaminants. In recent years, metal-organic frameworks (MOFs) have been considered as potential materials because of their high specific surface area and adjustable structure. The pore size of MOFs includes micropore, mesopore and macropore, which can be occupied by salts or other adsorbate. [4] In additional, carbon material is the most commonly used sorbent, therefore, MOFs derived carbon that keep the advantages of MOF structure could be an efficient adsorbent for removing the antibiotics in the contaminated water.

In this study, ZIF-8/ZIF-67 composite material was synthesised by CTAB assisted at room temperature firstly, and the ZIF-8/ZIF-67 derived carbon (ZDC) was obtained by calculation subsequently in nitrogen atmosphere. The adsorption properties of the ZDC is investigated by removing broad-spectrum antibiotics TC, NFO and OFO widely existed in water. The maximum adsorption capacity of ZDC was calculated to 543.48, 239.8 and 340 mg/g, respectively, which is a very promising antibiotic adsorbent.

IOP Conf. Series: Materials Science and Engineering **490** (2019) 022064 doi:10.1088/1757-899X/490/2/022064

2. Experiment

2.1. Experimental reagents

Reagents such as $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, HCl, anhydrous methanol, 2-methylimidazole and cetyltrimethyl ammonium bromide (CTAB) were purchased from the National Pharmaceutical Reagent Company.

2.2. Preparation method

The preparation process of ZIF-8/ZIF-67: 1.092 g $Co(NO_3)_2{\cdot}6H_2O$ is uniformly dispersed in 15 mL anhydrous methanol to form solution A; 1.232 g 2-methylimidazole is also dispersed in 30 mL anhydrous methanol to form solution B; 1.116g $Zn(NO_3)_2{\cdot}6H_2O$ is dissolved in 30 mL anhydrous methanol to obtain uniform solution C. The above solutions were all treated by ultrasonic oscillation. Slowly pour solution B into solution A to obtain a light purple suspension. Then, solution C was injected into the mixture, and 0.667 g CTAB was added slowly. Finally, the mixture was sealed and stationary at room temperature for 48 hours. At last, the product was washed and centrifuged with anhydrous methanol (centrifugal rate 10 000 rpm) for several times, and then dried in vacuum at 80 ℃ to obtain white powder products.

The preparation process of ZDC: the white powder product was put into the quartz boat and carbonized at 800 ^{o}C for 2 h (heating rate 2 ^{o}C/min) in nitrogen atmosphere to obtain the final black material. Finally, the black powder was washed with 1 M HCl aqueous solution. Then, the carbon product was rinsed several times with distilled water and dried at 60 ^{o}C overnight in vacuum oven.

2.3. Adsorption experiment

The adsorption process of three typical antibiotics is as follows: in the determination of antibiotic adsorption, 5 mg adsorbents were added to the solution of initial concentration TC, OFO, NFO (40 mg/L) and PH=7, respectively. Ultraviolet-visible spectrophotometry (G9s, Shanghai Runqee Co. Ltd.) was used to determine the absorbance of the three antibiotics at their characteristic wavelengths. On the standard adsorption curve, the concentration was calculated by measuring the absorbance of the three antibiotics before and after adsorption. The adsorption properties of ZDC is calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Among them, q_e (mg/g) is the amount of antibiotics adsorbed by each gram of ZDC under equilibrium state; C_0 is the original concentration of antibiotics (mg/L); C_e is the residual concentration of antibiotics (mg/L); V and m represent the volume of the solution (mL) and the quality of the adsorbent (g), respectively. In the whole experiment, the adsorption conditions: 5 mg adsorbent dosage, 50 mL solution volume, PH=7, room temperature.

The adsorption experiments of ZDC for three different concentrations of antibiotics are depicted in Fig. 3. The experimental data are fitted based on two adsorption models：Langmuir and Freundlich. The equation of adsorption models are expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right)\ln C_e \quad (3)$$

where q_m (mg/g) represents maximum adsorption capacity and K_L (L/mg) represents the adsorption constant. K_f ((mg/g)(L/mg)$^{1/n}$) and n represent parameters related to temperature and system.

2.4. Characterization

The morphology and structure of the adsorbent were characterized by scanning electron microscopy (SEM) (S-4800). The elemental composition of ZIF-8/ZIF-67 was characterized by X ray diffractometer (XRD, Rigaku, Cu-K_α radiation).

3. Result discussion

Figure 1 depicts the XRD pattern of the ZIF-8/ZIF-67 derived carbon (ZDC) sample. Interestingly, the ZDC sample have a sharp diffraction peak at 2θ located at 44°, 55° and 75°, which could be attributed to the graphitized of obtained carbon, corresponds to the standard card 01-075-0409. In addition, a broad diffraction peak at 25° correspond to the characteristic peaks of amorphous carbon. [5] In XRD spectra, there are no other impurity peaks such as Zn, ZnO detected. The results show that the ZDC materials can be successfully derived by simply carbonizing ZIF-8/ZIF-67 composites at high temperature.

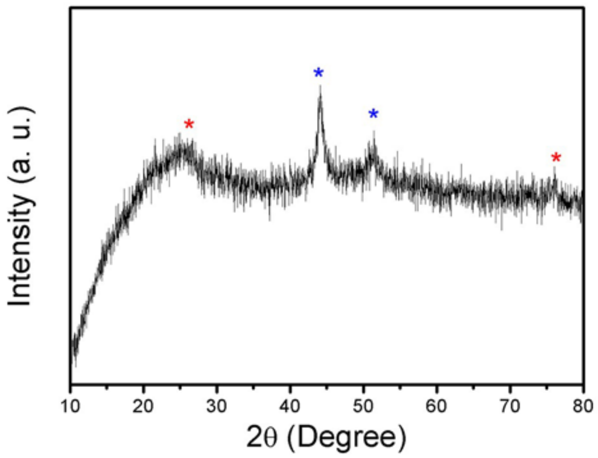


Figure 1. XRD pattern of obtained ZDC sample.

The morphology of the obtained samples was characterized by SEM. As shown in figures 2a, the ZIF-8/ZIF-67 composites show nearly homogeneous micro-particles (~1 μm). As shown in Figure 2b, the surface of ZDC were collapse and the defects of the particles calcined in nitrogen atmosphere are caused by the carbonization of organic matter during high temperature calcination.

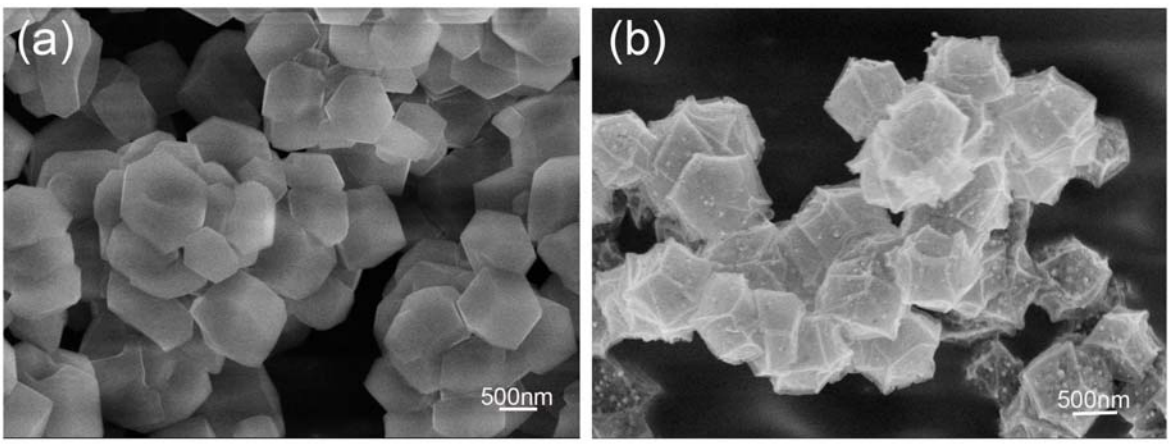


Figure 2. SEM morphology of (a) ZIF-8/ZIF-67 and (b) ZDC sample.

From Fig. 3, it is concluded that the adsorption of TC, NFO and OFO on ZDC conforms to Langmuir and Freundlich models, but considering the correlation fitting coefficient (R^2) in Table 1, Langmuir model can describe the adsorption process well. According to the fitting results of Langmuir model, the adsorption capacity of ZDC for three antibiotics is TC (543.48 mg/g), NFO (239.8 mg/g) and OFO (340 mg/g), respectively. Compared with other inorganic adsorbents in Table 2, ZDC is more effective in adsorbing three antibiotics, so it is a very potential adsorbent for antibiotic removal in the contaminated water.

IOP Conf. Series: Materials Science and Engineering **490** (2019) 022064 doi:10.1088/1757-899X/490/2/022064

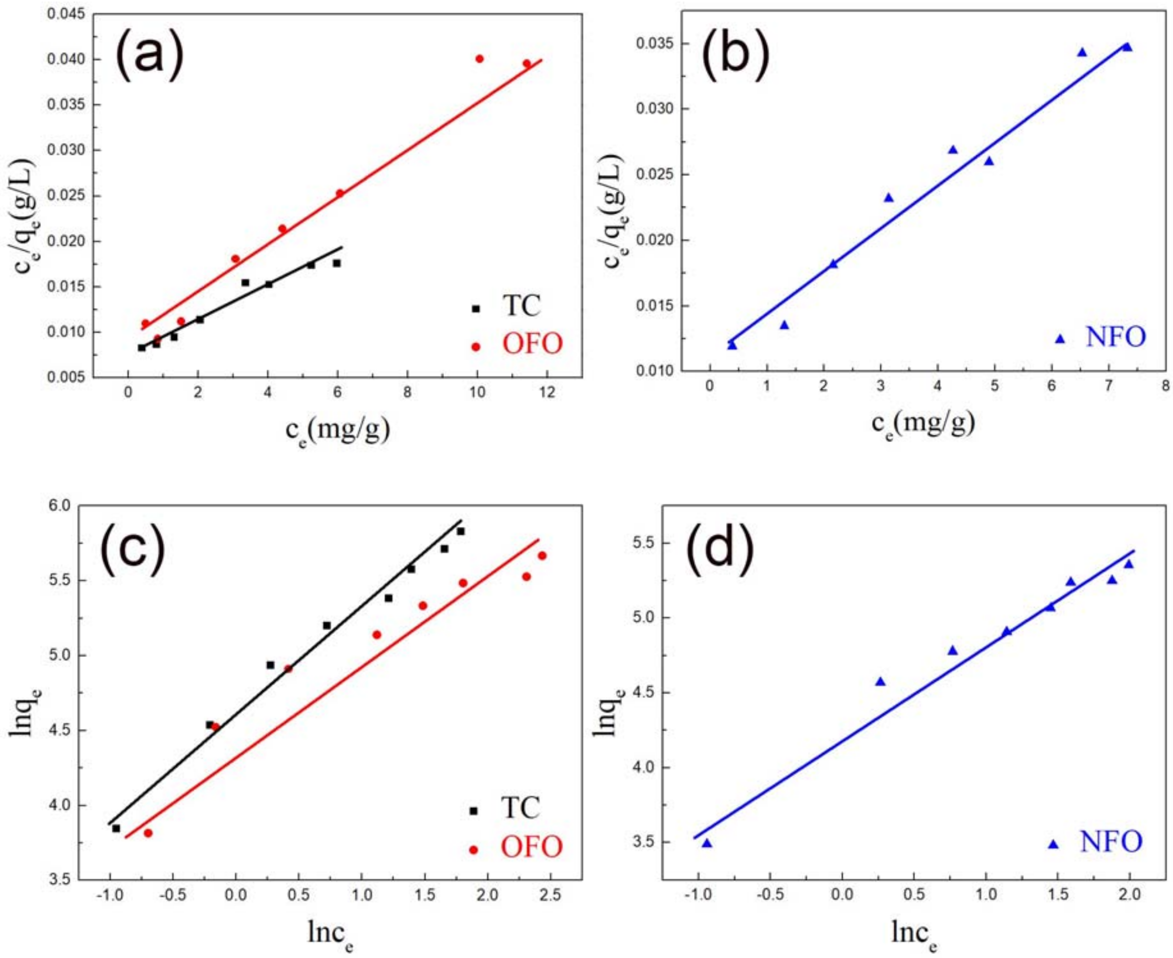


Figure 3. Isothermal adsorption curves of Langmuir (a, b) and Freundlich (c, d) of the models for ZDC towards TC, OFO and NFO.

Table 1. The model fitting data parameters of ZDC adsorption to antibiotics

	Langmuir			Freundlich		
Pollutions	K_L(L/mg)	q_m(mg/g)	R^2	k_f	n	R^2
TC	0.243	543.48	0.953	101.7	1.457	0.98
NFO	0.395	239.8	0.970	73.59	1.909	0.843
OFO	0.365	340	0.981	88.22	1.915	0.91

Table 2. Comparison of the TC, NFO and OFO adsorption ability of ZDC with other reported inorganic adsorbents.

Antibiotics	Adsorbents	q_m(mg/g)	Condition	Ref
Tetracyclie	Fe_3O_4/PAN	257.07	PH=6	[1]
	MWCNT/MIL-53(Fe)	364.37	PH=7	[6]
	Fe/Zn-biochar	102	PH=6	[7]
	ZDC	543.48	PH=7	This paper
Norfloxacin	MT-BC	25.53	PH=7	[3]
	MICs	7	PH=7	[8]
	ZDC	239.8	PH=7	This paper
Ofloxacin	M-CCNs@MIP	58.48	PH=7	[9]
	Cassava residue-derived biochar	3.00	PH=7,	[10]
	ZDC	340	PH=7	This paper

IOP Conf. Series: Materials Science and Engineering **490** (2019) 022064 doi:10.1088/1757-899X/490/2/022064

4. Conclusion

In conclusion, ZIF-8/ZIF-67 derived carbon (ZDC) material was synthesized by adding CTAB during the preparation of ZIF-8/ZIF-67 composite and carbonizing at 800 ^{o}C in nitrogen atmosphere. When it used as adsorbing material to remove residual antibiotics in the environment, the test results show that the synthesized ZDC material has a strong adsorption capacity for three typical antibiotics, i.e., TC (543.48 mg/g), NFO (239.8 mg/g) and OFO (340 mg/g), respectively. All in all, this study provides a briefness and efficient method to prepared ZDC materials for removing antibiotics from the polluted water.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (51602193, 21601122), Shanghai "Chen Guang" project (16CG63).

References

[1] Q. Liu, L. B. Zhong, Synthesis of Fe_3O_4/Polyacrylonitrile Composite Electrospun Nanofiber Mat for Effective Adsorption of Tetracycline, ACS Appl. Mater. Interfaces. 7 (2015) 14573-14583.
[2] V. Sharmaa, R. V. Kumara, K. Pakshirajanb, G. Pugazhenthia, Integrated adsorption-membrane filtration process for antibiotic removal from aqueous solution, Powder Technol. 321 (2017) 259-269.
[3] J. H. Zhang, M. Y. Lu, J. Wan, Y. H. Sun, Effects of pH, dissolved humic acid and Cu^{2+} on the adsorption of norfloxacin on montmorillonite-biochar composite derived from wheat straw, Biochem. Eng. J. 130 (2018) 104-112.
[4] D. N. R. Sousa, S. Insa, A. A. Mozeto, Equilibrium and kinetic studies of the adsorption of antibiotics from aqueous solutions onto powdered zeolites, Chemosphere. 205 (2018) 137-146.
[5] C. Young, R. R. Salunkhe, J. Tang, C. C. Hu, M. Shahabuddin, E. Yanmaz, M. S. A. Hossain, Zeolitic imidazolate framework (ZIF-8) derived nanoporous carbon: The effect of carbonization temperature on the supercapacitor performance in an aqueous electrolyte, Phys. Chem. Chem. Phys. 18 (2016) (42) 29308-29315.
[6] W. P. Xiong, G. M. Zenga, Z. H. Yanga, Adsorption of tetracycline antibiotics from aqueous solutions on nanocomposite multi-walled carbon nanotube functionalized MIL-53 (Fe) as new adsorbent, Sci. Total Environ. 627 (2018) 235-244.
[7] Y. Y. Zhoua, X. C. Liua, Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: Adsorption mechanism and modelling, Bioresour. Technol. 245 (2017) 266-273.
[8] X. H. Wua, M. J. Huanga, Recognizing removal of norfloxacin by novel magnetic molecular imprinted chitosan/c-Fe_2O_3 composites: Selective adsorption mechanisms, practical application and regeneration, Sep. Purif. Technol. 165 (2016) 92-100.
[9] Z. H. Hua, Y. F. Wang, A. M. Omera, Fabrication of ofloxacin imprinted polymer on the surface of magnetic carboxylated cellulose nanocrystals for highly selective adsorption of fluoroquinolones from water, Int. J. Biol. Macromol. 107 (2018) 453-462.
[10] P. Huanga, C. J. Ge, D. Fenga, Effects of metal ions and pH on ofloxacin sorption to cassava residue-derived biochar, Sci. Total Environ. 616-617 (2018) 1384-1391.