Adsorption of Ciprofloxacin and Tetracycline by Organically Modified Magnetic Bentonite

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Abstract. In order to endow magnetic bentonite (MB) with better magnetic separation and magnetic stability, obtain stronger adsorption of antibiotics, carboxymethylcellulose-chitosan/magnetic bentonite composite (MB/CC) was prepared by modifying previously fabricated MB with carboxymethylcellulose (CMC) and chitosan (CS). The characterization of MB/CC and the adsorption properties towards ciprofloxacin (CIP) and tetracycline (TC) was investigated. The characterization results revealed that CC improves the Fe_3O_4 stability and removal capability of CIP and TC for the final product. Adsorption results indicated that MB/CC exhibited superior adsorption performance for CIP (182 $mg \cdot g^{-1}$) and TC (189 $mg \cdot g^{-1}$). Adsorptive removal of CIP and TC by MB/CC was more than 90% even after 5 cycles of adsorption-desorption process. The adsorption process fitted well with the Langmuir model and the pseudo-second order kinetic model. The main steps during the successful adsorption process of MB/CC for CIP and TC includes pore diffusion, ion exchange and electrostatic interaction. MB/CC has advantages of simplified synthesis, convenient operation and high-efficiency, which could be deemed as a promising alternative adsorbent for antibiotics removal from wastewater.

1 Introduction

Ciprofloxacin (CIP) belongs to fluoroquinolone antibiotics, and tetracyclines (TC) belongs to tetracycline antibiotics. CIP and TC are two kinds of antibiotics produced and used in large quantities in China, which are widely used in clinical medical treatment and livestock aquaculture [1-2]. CIP and TC after use are discharged into the environment in different ways and exist in various forms. Because they have certain biological toxicity, they cause great harm to the environment and hinder the healthy development of human body.

Magnetic bentonite (MB) is a kind of adsorption material developed by our research group in the early stage. It is found that MB has a certain adsorption effect on antibiotics, dyes and heavy metal ions [3]. However, the properties of Fe_3O_4 are not stable, it is easy to oxidize and agglomerate contacting with air. Moreover, some absorption points of bentonite will be occupied after Fe_3O_4 added to bentonite, thus, the adsorption capacity of MB would be reduced, and also affect the solid-liquid separation ability of MB.

Chitosan (CS) is a kind of environmental friendly material, which has remarkable adsorption capacity for organic pollutants, antibiotics and metal ions. The structure contains a large number of amino and hydroxyl groups[4]. CMC is cheap, well soluble and biodegradable polyanionic cellulose[5]. Owing to the electrostatic interaction between CS and CMC, a non-toxic, high adsorption capacity and economical CC was prepared.

2 Experimental

2.1 Materials

Bentonite (RB) was obtained from Tianjin Guangfu Fine Chemical Research Institute, chemical purity. Chitosan $(C_6H_{11}NO_4)_n$ (deacetylation degree is more than 95%, viscosity is 100-200 MPa·s), Sodium carboxymethylcellulose, $[C_6H_7O_2(OH)_2CH_2COONa]_n$ (viscosity 800-1200 MPa·s) were purchased from Aladdin reagent (Shanghai) Co., Ltd., chemical purity. $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $NH_3 \cdot H_2O$, C_2H_5OH, HNO_3, CIP ($C_{17}H_{18}FN_3O_3$) and TC ($C_{22}H_{24}N_2O_8$) were purchased from Guangdong Guanghua Chemical Reagent Co., Ltd., analytical purity.

2.2 Adsorption studies

0.2 g MB and MB/CC were added into CIP and TC solution (200 ml, 10 $mg \cdot L^{-1}$) respectively. Under the rotating speed of 150 $r \cdot min^{-1}$, the CIP and TC supernatants were adsorbed in a constant temperature water bath oscillator for 2 h, and then removed from the oscillator according to the time within 0 ~ 120 min. The absorbance values of CIP and TC supernatants were measured by ultraviolet spectrophotometer at 270 nm and

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360 nm, respectively, and the kinetic process was analyzed. A series of CIP and TC solutions with different concentration gradients ranging from 10 to 80 $mg \cdot L^{-1}$ were prepared, and 1.0 $g \cdot L^{-1}$ MB and MB/CC were added respectively. The adsorption was oscillated for 2 h at the rotating speed of 150 $r \cdot min^{-1}$. And the effect of initial concentration of solution was explored.

The calculation formulas of adsorption removal of CIP and TC by MB and MB/CC are shown in (1) and (2):

$$q = (C_0 - C_t)/m \quad (1)$$

$$R = (C_0 - C_t)/C_0 \times 100\% \quad (2)$$

Where C_0 is the concentration of CIP and TC before adsorption ($mg \cdot L^{-1}$). C_t is the concentration of the supernatant of CIP and TC were adsorbed at t (min) ($mg \cdot L^{-1}$). m is the dosage of MB and MB/CC ($g \cdot L^{-1}$). q is the adsorption capacity of MB and MB/CC for CIP and TC ($mg \cdot g^{-1}$). R is the adsorption efficiency (%) of adsorbates on MB and MB/CC.

3 Results and discussion

3.1 Effect of pH and initial concentration of CIP and TC

The adsorption efficiency of antibiotics on MB and MB/CC were changed significantly at pH were 2 ~ 6 and 7 ~ 10. The solution was acidic at pH 2 ~ 6, CIP and TC existed in the form of cation after hydrolysis, and reacted with $-OH$, $-NH_2$ on the surface of the MB/CC, thus the adsorption percentage of CIP and TC on MB/CC was higher. With the increase of pH, OH^- in the solution increased, CIP and TC gradually deprotonated, the combining ability with $-OH$, $-NH_2$ gradually weakened. Therefore, the removal efficiency of CIP and TC on MB and MB/CC were decreased[6].

The adsorption efficiency of CIP and TC first increased and then reached the adsorption equilibrium gradually[7]. This was due to the more adsorption sites on MB and MB/CC to be occupied at the initial concentration of CIP TC is low, thus the adsorption efficiency of CIP and TC on MB and MB/CC was faster. When the initial concentration increased, the adsorption process has been reached adsorption saturation and the adsorption sites was limited, hence, the adsorption capacity of CIP and TC on MB and MB/CC was not increased.

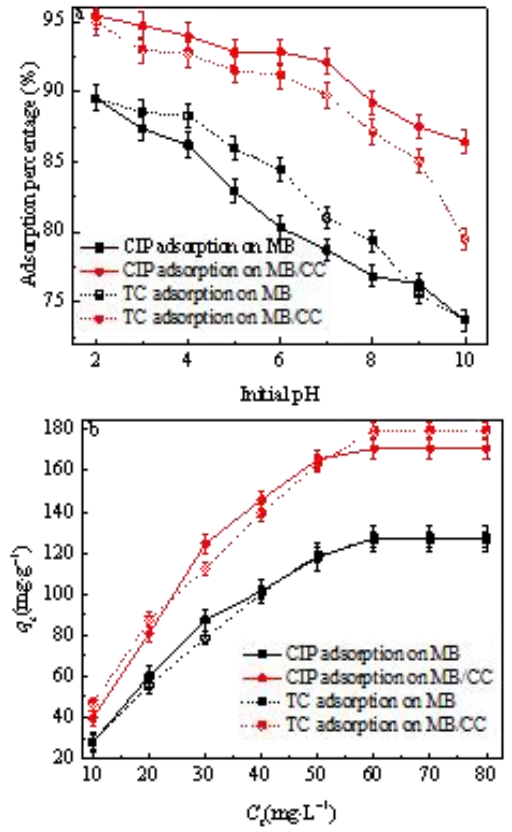
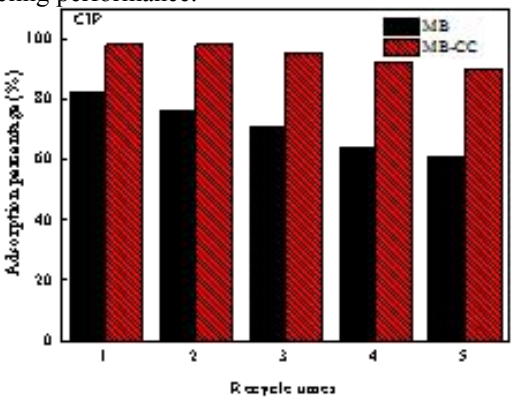


Fig. 1. Effect of (a) pH and (b) initial concentration on the adsorption of CIP and TC.

3.2 Recycling performance

After 5 adsorption-desorption cycling experiments, the adsorption efficiency of CIP and TC on MB decreased from 82% and 61% to 61% and 42% respectively, while the adsorption efficiency of CIP and TC by MB/CC decreased from 98% and 96% to 90% and 91% respectively, which indicated that MB/CC has good recycling performance.



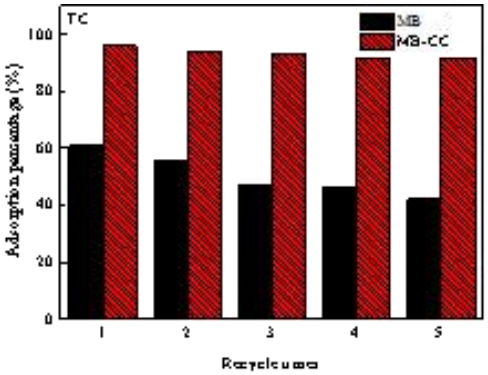


Fig. 2. Recycling performance of CIP and TC on MB and MB/CC.

3.3 Adsorption kinetics and isotherms studies

The R^2 were 0.999 (Langmuir adsorption isotherm model), the Langmuir adsorption capacities of MB and MB/CC for CIP were 147 mg·g^{-1} and 182 mg·g^{-1}, and for TC were 136 mg·g^{-1} and 189 mg·g^{-1}, respectively. The adsorption process was more consistent with Langmuir model, and belongs to monolayer adsorption [7]. The K_L values of CIP and TC adsorbed by MB/CC were much higher than those on MB, which indicated that MB/CC had stronger adsorption capacity for CIP and TC.

Table 1. Fitting parameters of CIP and TC adsorption isotherm models of MB and MB/CC.

	Langmuir model			Freundlich model			
	K_L/L·mg^{-1}	$q_{m,cal}$/mg·g^{-1}	R^2	K_f/mg·g^{-1}	1/n	R^2	$q_{m,exp}$/mg·g^{-1}
MB/CC(CIP)	1.27	182	0.999	51.3	0.41	0.939	170
MB/CC(TC)	1.31	189	0.999	68.2	0.43	0.955	179
MB(CIP)	0.28	147	0.999	36.1	0.37	0.937	127
MB(TC)	0.55	136	0.999	45.7	0.39	0.958	126

The maximum adsorption capacities ($q_{e,cal}$) of CIP and TC on MB/CC were 181 mg·g^{-1} and 191 mg·g^{-1}, and on MB were 102 mg·g^{-1} and 119 mg·g^{-1}, respectively, which are closer to the actual adsorption capacities ($q_{e,exp}$) measured by experiments. In conclusion, the adsorption process of CIP and TC on MB/CC was more consistent with the quasi second-order kinetic model, which indicated that the adsorption process was a process of fast initially, then slowed down n and finally reached equilibrium [8].

Table 2. Fitting parameters of CIP and TC adsorption kinetic models of MB and MB/CC.

	quasi first-order kinetic model			quasi second-order kinetic model			
	k_1×0.01/ min^{-1}	$q_{e,cal}$/ mg·g^{-1}	R^2	k_2×0.01/ g·mg^{-1}·min^{-1}	$q_{e,cal}$/ mg·g^{-1}	R^2	$q_{e,exp}$/ mg·g^{-1}
MB/CC(CIP)	0.003	92	0.466	0.36	181	0.999	170
MB/CC(TC)	0.006	103	0.588	0.41	191	0.999	179
MB(CIP)	0.002	68	0.582	0.32	102	0.999	127
MB(TC)	0.005	77	0.673	0.35	119	0.999	126

3.4 Adsorption mechanism

(1) Pore diffusion: MB/CC was equipped with abundant mesopores which can accommodate the adsorption process of CIP and TC on MB/CC.
(2) Ion exchange: CIP and TC exist in the form of cation at the solution is acidic, thus K^+, Ca^{2+}, Na^+ and Mg^{2+} in bentonite can adsorption CIP and TC through ion exchange.
(3) At acidic, CIP and TC exist in the form of cation. Hence CIP and TC combine with MB/CC (negative charge) through the electrostatic attraction.

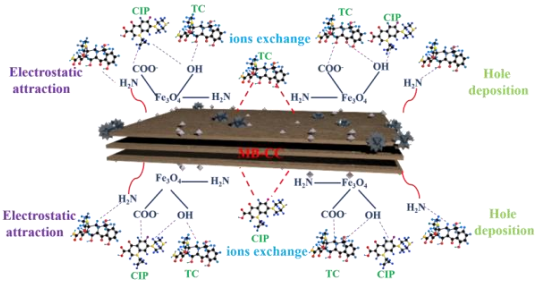


Fig. 3. Proposed mechanism for CIP and TC adsorption on MACB-CC.

4 Conclusions

CMC and CS were used as organic modifiers, and MB/CC was prepared by microwave solid-liquid phase

synthesis. The removal efficiency of CIP and TC on MB were above 80%, whileon MB/CC were above 90% at pH 2 ~ 6. The adsorption process of CIP and TC on MB/CC was more consistent with Langumir isotherm model and quasi second-order kinetic model. The adsorption process of CIP and TC on MB/CC belongs to monolayer adsorption, and the adsorption process was a process of fast initially, slowed down then and finally reached equilibrium.

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References

1. S.J. Olusegun and N.D.S. Mohallem, Comparative adsorption mechanism of doxycycline and Congo red using synthesized kaolinite supported CoFe2O4 nanoparticles. Environ. Pollut. **260**, 114019 (2020)
2. Y. Youngbeom, H.C. Yang, C. Jaewon, C. Soohoon and K.M. Sung, Multi-barrier approach for removing organic micropollutants using mobile water treatment systems. Sci. Total. Environ. **639**, 331-338 (2018)
3. C. Cazzorla, G. Bensi, G. Biasucci, V. Leuzzi, F. Manti, A. Musumeci, F. Papadia, V. Stoppioni, A. Tummolo, M. Vendemiale, G. Polo and A. Burlina, Living with phenylketonuria in adulthood: The pku attitude study. Mol. Genet. Metab. Rep. **16**, 39-45 (2018)
4. H. Wang, L. Wang and S. Ye, Construction of Bi2WO6-TiO2/strach nanocomposite films for visible-light catalytic degradation of ethylene. Food. Hydrocolloid. **39**, 75-90 (2018)
5. L. Xu, X. Xu, G. Cao, S. Liu, Z.Y. Duan, S.M. Song and M.J. Zhang, Optimization and assessment of Fe-electrocoagulation for the removal of potentially toxic metals from real smelting wastewater. J. Environ. Management. **218**, 129-138 (2018)
6. J. Zheng, D.J. Luo and Y.H. Qiao, Surface complexation modeling of U(VI) sorption on GMZ bentonite in the presence of fulvic acid. Radiochim. Acta. **105**, 33-41 (2016)
7. F.L. Fu and Q. Wang, Removal of heavy metal ions from wastewaters: a review. J. Environ. Management. **92**, 407-418 (2011)
8. D. Colangelo, F. Torchio, D.M.D. Faveri and M. Lambri, The use of chitosan as alternative to bentonite for wine fining: Effects on heat-stability, proteins, organic acids, colour, and volatile compounds in an aromatic white wine. Food. Chem. **264**, 301 (2018)