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Effect of Solution pH on the Kinetic Adsorption of Tetracycline by La-modified Magnetic Bagasse Biochar

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ABSTRACT

Lanthanum-modified Fe_3O_4 nano-particles were innovatively immobilized on the bagasse biochar to prepare La-modified magnetic biochar, which demonstrated an especially high adsorption capability for the removal of tetracycline. The magnetic adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and zeta potential analysis. Through the FTIR analysis, it could be observed that La/Fe_3O_4 particles were successfully immobilized on the surface of the bagasse biochar. Zeta potential analysis showed that biochar surface became more negatively charged. Near neutral pH was more favourable for the removal of tetracycline. Elovich and pseudo-second-order kinetic models were better to fit the experimental data, indicating a chemisorption occurred in the adsorption process.

INTRODUCTION

The advent of antibiotics, especially the discovery of penicillin, has greatly helped people and animals in diseases. However, the large-scale use of antibiotics also brings a series of environmental problems because most of the antibiotics are poorly absorbed or metabolized completely (Martine 2009, Sarmah et al. 2006). The residual of antibiotics has been detected in water and soil, particularly in underground water, surface water and even in drinking water (Cetecioglu et al. 2013, Wu et al. 2013). Tetracycline ($C_{22}H_{24}N_2O_8$), as one of the broad spectrum antibiotic, is the second most widely used chemical (Mathers et al. 2011). The TC fractions lead to the increase of resistance bacterial strains and antibiotic-resistant genes, which ultimately threaten the health of human beings and the environment (Yang et al. 2017). Thus, the removal of tetracycline from aqueous solution has attracted great attention.

The industrial practices have proved the deficiency of conventional water and wastewater treatment technologies. Adsorption is considered as a promising technology for the efficient removal of tetracycline because of its high efficiency, low energy consumption and environment-friendliness. Active carbon (Choi et al. 2008), chitosan (Caroni et al. 2009), aluminium oxide and graphene oxide (Gao et al. 2012) demonstrated a high adsorption capability toward tetracycline. It is still difficult to solve the problems for adsorbent application such as adsorbent recovery and lack of cost-effective adsorbent.

Biochar and related adsorbents have been extensively studied in recent years as they are low-cost adsorbents (Ahmad et al. 2014). Biochar is mainly obtained via simple pyrolysis of biomass such as rice stalk, wheat straw and corn stalk. Meanwhile, scientists have applied the magnetic materials for the removal of arsenic, chromium, phosphorus and copper from water (Noor et al. 2017), in which the magnetic materials were easily recovered for reuse. Accordingly, it is suggested to prepare magnetic biochar for adsorption application. Additionally, our previous study proved that a very limited amount of La was capable of enhancing the adsorption of tetracycline using a La-modified diatomite (Li et al. 2015). As such, in this research, La-modified magnetic bagasse biochar was synthesized and intentionally used for adsorption removal of tetracycline. Adsorption kinetics under different pH conditions was emphatically explored and discussed.

MATERIALS AND METHODS

Chemicals: Tetracycline (TC) was purchased from Hefei Biological Science and Technology Co., Ltd. (Anhui Province, China) and used without further purification. The reagents in the analytical grade were dissolved in deionized (DI) water to prepare the solutions.

Adsorbent preparation: Sugarcane bagasse was collected from Guangxi Province, China. Detailed procedures for the preparation of sugarcane bagasse biochar can be referred to our previous study (Li et al. 2016). As the lanthanum modified magnetic particles are prepared by a chemical co-precipitation method (Li et al. 2009, Mi et al. 2017), bagasse biochar was introduced into the precursor solution. Other procedures are the same those of preparation of the lanthanum modified magnetic particles. Finally, the prepared lanthanum modified magnetic bagasse biochar was dried at 80°C for 24 h after magnetically separating and stored in a desiccator. In the following tests, the prepared magnetic sorbent is denoted as La-modified magnetic biochar.

Batch adsorption studies: The adsorption kinetics was investigated by batch experiments. A stock TC solution (500 mg/L) was diluted to get the desired concentration with DI water. The La-modified magnetic biochar (20 mg) was added into 50 mL of TC solution with a concentration of 20 mg/L. The mixtures were shaken at 120 rpm for 24 h and the temperature was controlled at 298 K. The adsorption kinetics were performed on 1000 mL solution with an initial TC concentration of 20 mg/L, in which 400 mg of the La-modified magnetic biochar was added. The mixture was magnetically stirred at a constant rate. The solution pH adjustment was conducted by adding diluted HNO_3 or NaOH solution. All the samples were collected at desired time intervals and filtered through a 0.45 μm pore-size membrane before analysis.

Characterization: The prepared La-modified magnetic biochar was characterized with Fourier transform infrared spectroscopy (FTIR) spectra (KBr pellets), which were recorded on a Nicolet NEXUS 470 FTIR spectrophotometer from 400 to 4000 cm^{-1}. A zeta potential analyser (Zetasizer 2000, Malvern Co., UK) was used to analyse the zeta potential of the raw Fe_3O_4 and the La-modified magnetic biochar with a presumed La/Fe_3O_4 molar ratio at 1:100.

Analysis of TC: The concentration of TC was measured by an UVmini-1240 spectrophotometer (Shimadzu, Japan) to monitor emissions at the wavelength of maximum adsorption (360 nm) (Figueroa et al. 2004). The adsorption capacity was calculated using the following equations:

$$q_e=(C_0-C_e)V/W \quad ...(1)$$

$$q_t=(C_0-C_t)V/W \quad ...(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min); C_0 is the initial TC concentration, while C_e and C_t (mg/L) are the concentrations of TC at equilibrium and t (min), respectively; V (L) is the volume of solution, and W (g) is the mass of La-modified magnetic biochar.

RESULTS AND DISCUSSION

Characterization of the magnetic adsorbent: It was proved that the La-modified magnetic bagasse biochar with a presumed La/Fe_3O_4 molar ratio at 1:100 had a higher adsorption capability. FTIR spectra of the raw bagasse biochar and the magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 were recorded, as illustrated in Fig. 1. After immobilization of La/Fe_3O_4, the typical FTIR absorption bands of bagasse biochar at 1620 cm^{-1} (aromatic C=C and C=O), 1376 cm^{-1} (CH_2) and 1242 cm^{-1} (C-O in the acetyl group) almost disappeared. This indicates that the biochar surface has been covered by La/Fe_3O_4 to a large extent. The weak absorption peak at 567 cm^{-1} is ascribed to the vibrations of Fe^{2+}-O^{2-}, which is consistent with the reported spectra of spinel Fe_3O_4 (Meng et al. 2005, Liese 1967). Two typical bands recorded at 884 cm^{-1} and 797 cm^{-1} can be assigned to the bending vibrations of FeOOH of α-FeOOH. This demonstrates that the bagasse biochar is well combined with the La/Fe_3O_4 particles immobilized on the surface of the biochar.

As a comparison, zeta potentials of the Fe_3O_4 substrate and the magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 were examined, as presented in Fig. 2. For both, Fe_3O_4 and the magnetic biochar, their zeta potentials declined with increasing solution pH, as a result of the

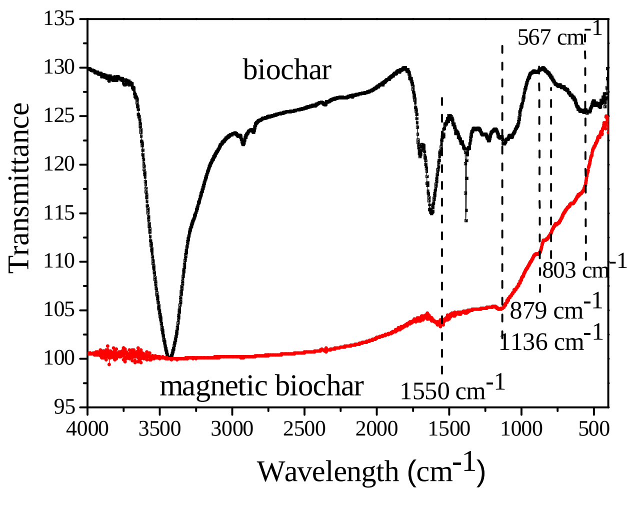

Fig.1: FTIR spectra of the raw bagasse biochar and the La-modified magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100.

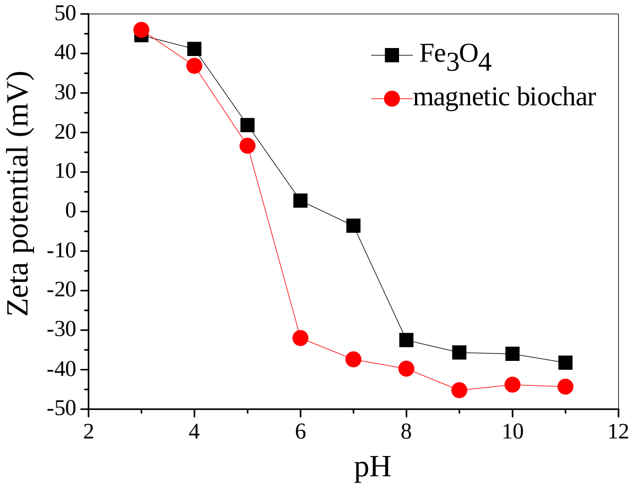

Fig. 2: Zeta potentials of the Fe_3O_4 substrate and the magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100. Adsorbent dose = 200 mg/L, ionic strength 0.01M $NaNO_3$, and equilibrium time 48 h.

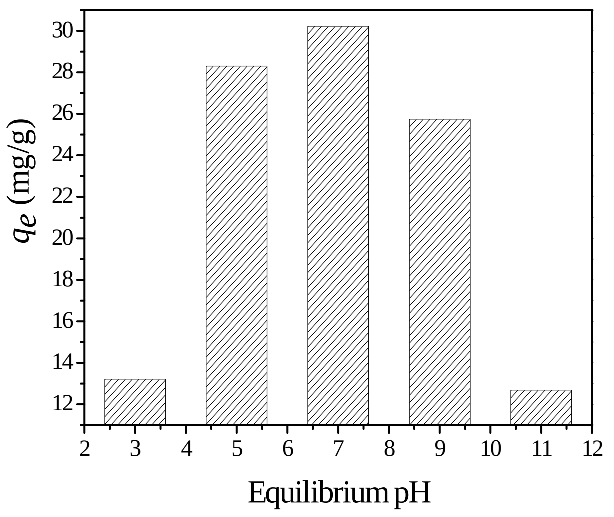

Fig. 3: Effect of solution pH on the adsorption of TC onto the La-modified magnetic biochar.

change of their surface functional groups. The zeta potentials of the magnetic biochar at different pH conditions are obviously lower than those of the Fe_3O_4 substrate particularly at pH > 5. This might be attributed to the unique property of the bagasse biochar. Actually, biochar surfaces are normally negatively charged (Ahmad et al. 2014). Considering the mass ratio of 1:10 for magnetic particles and bagasse biochar in the magnetic biochar, the properties of the bagasse biochar determine the properties of the magnetic biochar predominantly. Similarly, our previous study has demonstrated that the zeta potentials of the bagasse biochar are especially lower than those of Fe_3O_4 (Li et al. 2016). For example, at pH 7.0, the zeta potentials of Fe_3O_4, the bagasse biochar and the magnetic biochar are -3.61, -32.73 and -37.4 mV, respectively. As such, the surface properties of the magnetic biochar were typically altered by combining both bagasse biochar and La/Fe_3O_4.

Effect of solution pH on TC adsorption: Solution pH is one of the key factors influencing the uptake of TC onto the La-modified magnetic biochar. As illustrated in Fig. 3, the effect of solution pH was investigated and the highest uptake of TC was observed at pH 7.0. Electrostatic attraction/repulsion between TC and the magnetic biochar is thought to be the predominant adsorption mechanism. However, the adsorption of TC onto the magnetic biochar might be quite complicated as the magnetic biochar contains both carbonaceous component, biochar and inorganic component including oxides and oxyhydroxides of La and Fe. TC (H_2L) is an amphoteric compound with pK_a values at 3.3, 7.7 and 9.7 (Liu et al. 2012). Its predominant species are deduced to be cation (H_2L^+) at pH<3.3, zwitterions (H_2L^0) at 3.3<pH<7.7, and negatively charged anions (HL^-, L^{2-}) at pH>7.7. Meanwhile, from Fig. 3, the magnetic biochar is quite positively charged at pH<5.0 while particularly negatively charged at pH>6.0. Between pH 5.0 and pH 6.0, there is a sharp decrease from a positively charged surface to negative-charged. It can be deduced that both TC and the magnetic biochar are highly positively or negatively charged under acidic and basic conditions, respectively. This is not beneficial for the uptake of TC. Differently, at near neutral pH conditions, TC molecules are zwitterions and their negative charge density increases gradually with the increasing pH. It is speculated that the attraction force between TC and the magnetic biochar achieves the maximum at near neutral pH conditions, which is consistent with the highest uptake of TC at pH 7.0.

Adsorption kinetics: The adsorption kinetics of TC onto the magnetic biochar was investigated at solution pH 7.0, 9.0 and 11.0, respectively. Typical kinetic models, including pseudo-first-order, pseudo-second-order and Elovich models, were used to fit the experimental data. The mathematical representations of the non-linear and linear models of pseudo-first-order and pseudo-second-order kinetics are those in literature (Lagergren 1898, Ho & McKay 1999):

$$q_t = q_e(1 - e^{-k_1 t}) \quad ...(3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad ...(4)$$

$$q_t = \frac{k_2 q_e^{\,2} t}{(1 + k_2 q_e t)} \quad ...(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad ...(6)$$

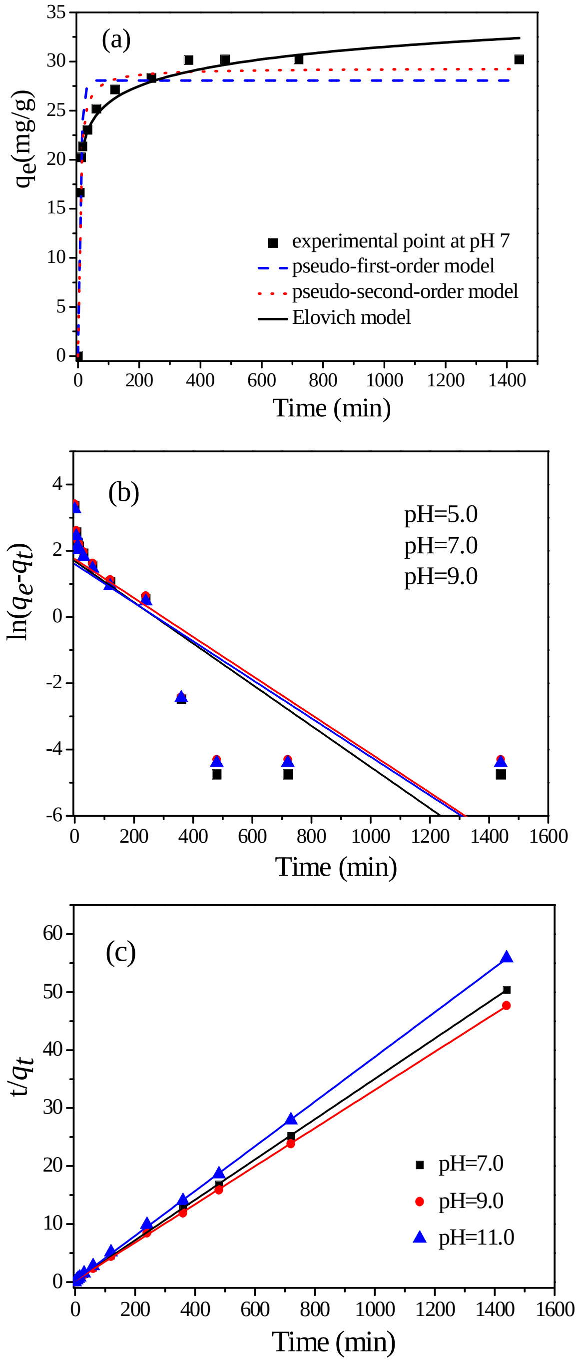

Fig. 4: Non-linear (a) and linear (b,c) adsorption kinetics for pseudo-first-order and (b) pseudo-second-order (c) simulation of TC onto the La-modified magnetic biochar.

Where, q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g/mg min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

The Elovich model, used to describe chemisorption occurring on the solid-liquid interface, can be written as (Kithome 1988):

$$q_t = k\ln(t) + \mathrm{a} \qquad ...(7)$$

Where, a (g·mg/min) and b (mg/g) are constants.

The experimental kinetic data at the three pH conditions were fitted by the three kinetic models, and the simulated curves are presented in Fig. 4. From the non-linear kinetic fitting curves presented in Fig. 4a, it is noted that the Elovich and pseudo-second-order kinetic models better described the experimental points than pseudo-first-order model under the three pH conditions. The calculated nonlinear kinetic parameters are given in Table 1. The correlation coefficients (R^2) of Elovich and pseudo-second-order models are all higher than 0.975, while those R^2 values of Elovich model are only slightly higher than those of pseudo-second-order model. In contrast, the R^2 values of pseudo-first-order model are less than 0.914. Meanwhile, by linear kinetic fitting presented in Fig. 4b and c, pseudo-second-order kinetic model described the adsorption performance particularly better than pseudo-first-order model. The calculated nonlinear kinetic parameters shown in Table 1 demonstrate that the correlation coefficients (R^2) of pseudo-second-order model are all 0.999 while those of pseudo-first-order model are all lower than 0.692. Furthermore, the calculated q_e values using linear pseudo-second-order kinetic model are much close to the experimental values as well. As such, pseudo-second-order kinetic model fitted the experimental data better. Totally, it can be inferred that chemisorption occurred between TC molecules and the La-modified magnetic biochar.

CONCLUSION

The La-modified magnetic bagasse biochar was creatively prepared via a simple co-precipitation method. The bagasse biochar is well combined with the La/Fe_3O_4 particles immobilized on the surface of the biochar by FTIR analysis. By zeta-potential analysis, biochar surface became more negatively charged after immobilization of the magnetic particles. The favorable solution pH for the uptake of tetracycline was observed at near neutral. Elovich and pseudo-second-order kinetic models fitted the experimental data better, which indicated that chemisorption occurred between TC molecules and the La-modified magnetic bagasse biochar. In short, the La-modified magnetic biochar possesses a high adsorption capacity and can be recycled by magnetic separation.

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Table 1: Non-linear kinetic parameters for the adsorption of TC onto the La-modified magnetic biochar.

Model	pH=5	pH=7	pH=9
Pseudo-first-order model			
k_1 (min^{-1})	0.128	0.129	0.129
q_e (mg/g)	26.6	28.1	24.0
R^2	0.9140.902	0.9140.901	0.913
Pseudo-second-order model			
k_2 (g/mg·min)	0.0074	0.00702	0.00827
q_e (mg/g)	27.7	29.3	25.0
R^2	0.9750.971	0.9750.967	0.975
Elovich model			
a	13.6	14.4	12.3
k	2.34	2.47	2.10
R^2	0.9850.984	0.9850.982	0.985

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