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Highly-Efficient Adsorptive Removal of Tetracycline Using Magnetic Sugarcane Bagasse Biochar Modified by Lanthanum

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ABSTRACT

As one of the agricultural wastes, sugarcane bagasse was easily pyrolyzed under low temperature to obtain bagasse biochar. Lanthanum-modified Fe_3O_4 particles were immobilized on the bagasse biochar to prepare La-modified magnetic biochar. The magnetic biochar was characterized by scanning electron microscope and X-ray photoelectron spectroscopy. It was found that the sizes of these biochar flakes were predominantly within 50 µm. At the same time, La species and magnetic particles are well combined with the biochar substrate. The magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 demonstrated a higher adsorption capability, which was enhanced by 69.8% compared to the raw bagasse biochar. The experimental points were quite close to curves simulated by both Langmuir and Freundlich isotherm models. From Langmuir model, the R^2 values were 0.984, 0.980 and 0.983 at 288, 298 and 308 K, respectively. The maximum adsorption capacity (q_{max}) for tetracycline reached 122.5 mg/g at 298 K and q_{max} increased with a rise in the reaction temperature, indicating the adsorption process was endothermic.

INTRODUCTION

Water resources have suffered from all kinds of pollution along with the onset of rapid industrialization in China. Various water treatment technologies were applied to solve this problem. Adsorption method has displayed promising and reliable capability for practical water and wastewater treatment on the basis of its ease of operation, universal nature and high efficiency (Qu 2008). Various adsorbents have been reported to remove the contaminants from water including clay (Cherian et al. 2018), activated carbons (Rakic et al. 2015) and biochar (Moreira et al. 2017). As a kind of environment-friendly and inexpensive material, biochar has attracted extensive interest. The resources for preparing biochar are very extensive including agricultural wastes such as corn stalk, ricestraw, wheat straw, as well as industrial wastes like sludge from water treatment plant. Sugarcane bagasse is the byproduct of sugarcane processing, which is an excellent raw material for synthesizing biochar because of its properties of abundance, economy and environment.

Recently, composite adsorbents have been hotspot owing to their better performance by combining the advantages of each composite (Qu 2008). Meanwhile, in order to recover adsorbents for repeated use, a number of studies focused on the use of magnetism for water purification and magnetic separators for separating magnetic particles rapidly (Mehta et al. 2015, Fu et al. 2018). Noor and co-workers investigated the efficient adsorption of heavy metal on magnetic biochar (Noor et al. 2017). Thus, magnetic adsorbents can well solve the problems of separation and recovery of adsorbents. Therefore, the design of low-cost and highly efficient adsorbents will be of great significance from a practical point of view.

Tetracycline is one of the antibiotics, which is the second most widely used medicine around the word (Mathers et al. 2011). The deficiency of antibiotics such as being poorly metabolized and absorbed after intake has caused environmental pollution, though they have made a big contribution to human therapy and the farming industry (Yesilova et al. 2018). Some antibiotics have been detected in municipal wastewaters, agricultural wastewater and even drinking water (Wang et al. 2016), which can induce the increase of the drug resistance of germ and ultimately threat human health and ecosystems (Yu et al. 2017). Thus, elimination of tetracycline from wastewater is extremely urgent. Recently, scientists have developed many biochars for the adsorptive removal of such antibiotics from wastewater

(Peiris et al. 2017, Moreira et al. 2017), in which these low-cost biochars demonstrated especially high adsorption capability for antibiotics removal.

Additionally, lanthanum (La), a rare earth element, exhibited excellent adsorption capacity particularly toward phosphate and fluoride in water and wastewater (Vences-Alvarez et al. 2015, Fu et al. 2018). 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. 2018). In this research, an agricultural waste sugarcane bagasse was utilized to prepare bagasse biochar, on which La-modified magnetic particles (Fe_3O_4) were immobilized. The La-modified magnetic bagasse biochar was intentionally used for adsorption removal of tetracycline. The La-modified magnetic bagasse biochar was characterized by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Batch adsorption study was carried out to explore the adsorption isotherm and adsorption performance.

MATERIALS AND METHODS

Chemicals: All chemicals were of analytical grade and used without further purification. Tetracycline (TC) was purchased from Hefei Biological Science and Technology Co., Ltd. (Anhui Province, China). The solutions were prepared by dissolving a certain amount of reagents with deionized (DI) water.

Adsorbent preparation: Sugarcane bagasse was collected from Guangxi Province, China. Biochar derived from sugarcane bagasse was prepared according to the procedures described in our previous study (Li et al. 2016). Briefly, the pretreated raw bagasse was pyrolyzed under oxygen-limited conditions at 600°C for 2 h. Then the HCl solution (4 mol/L) was used for demineralization and finally washed it with DI water to neutral solution pH. To prepare the lanthanum modified magnetic biochar, chemical co-precipitation is one of the effective methods. In a typical procedure, desired amount of $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$ with a molar ratio of 2:1 and $La(NO_3)_3{\cdot}6H_2O$ were added into a 400 mL DI water heated up to 70°C under vigorous stirring. A desired amount of bagasse biochar was added into the mixture. Then, 2 mol/L NaOH solution was added dropwise into the above mixture until the pH reached approximately 11. Afterwards, another 1 h stirring was continued at 70°C to ensure complete growth of the particle crystals. After cooling naturally to room temperature, the precipitate was separated in a permanent magnet and washed with DI water to neutral pH. Finally, the prepared lanthanum modified magnetic biochar was repeatedly rinsed using absolute ethanol. Subsequently, the prepared sorbent was magnetically separated and dried at 80°C for 24 h and stored in a desiccator before use. The prepared sorbent is denoted as La-modified magnetic bagasse biochar.

Batch adsorption studies: A stock TC solution (500 mg/L) was diluted to get desired concentration with DI water. It was stored in a refrigerator at 277 K and used up within three days. The TC adsorption experiments were performed in a series of 100 mL conical flasks. The La-modified magnetic biochar (20 mg) was added into 50 mL TC solution. These flasks were sealed and shaken at 120 rpm for 24 h to achieve equilibrium at 288, 298 and 308 K, respectively. All the samples were collected and filtered by microporous membranes (0.45 μm) before analysis.

Characterization: The prepared La-modified magnetic bagasse biochar was characterized with a Philips Quanta-2000 scanning electron microscope. The La-modified magnetic biochar was also measured using an X-ray photoelectron spectroscopy (PHI 1600 ESCA, Perkin-Elmer Co., USA).

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

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

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

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 bagasse biochar.

RESULTS AND DISCUSSION

Optimization of the La-modified bagasse biochar: As the Fe_3O_4 modified bagasse biochar with a presumed mass ratio of Fe_3O_4 and biochar at 1:10 outperformed other Fe_3O_4 modified bagasse biochar, the magnetic biochar with a mass ratio of 1:10 for Fe_3O_4 and bagasse biochar was selected as a substrate for the corresponding lanthanum modification. Accordingly, the molar ratio of La/Fe_3O_4 is of great importance for the uptake of TC. The adsorption behaviour of TC on the magnetic composite was investigated at varying La/Fe_3O_4 ratios (1:10, 1:50, and 1:100) and the results are presented in Fig. 1. The uptake of TC by the raw bagasse biochar was only 17.8 mg/g. The TC uptake by the adsorbents with molar ratios of La/Fe_3O_4 at 1:10, 1:50 and 1:100 reached 29.7, 29.9 and 30.3 mg/g, respectively. Compared to the raw bagasse biochar, the adsorption capacity of the magnetic biochar with a presumed molar ratio of

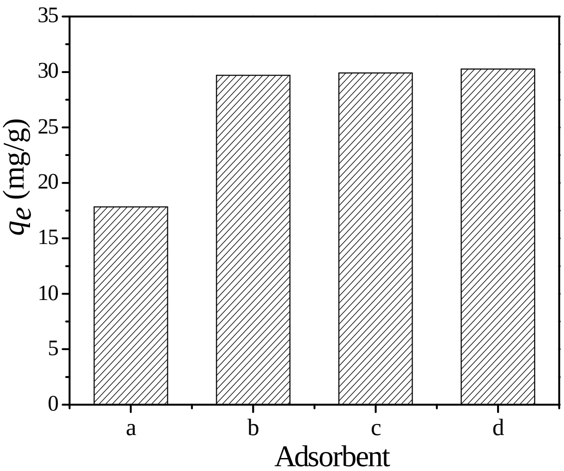

Fig. 1: Effect of the presumed molar ratio of La/Fe_3O_4 on the uptake of tetracycline. Adsorbent a is the raw bagasse biochar. Adsorbent b, c and d are those magnetic biochars with molar ratios of La/Fe_3O_4 at 1:10, 1:50 and 1:100, respectively.

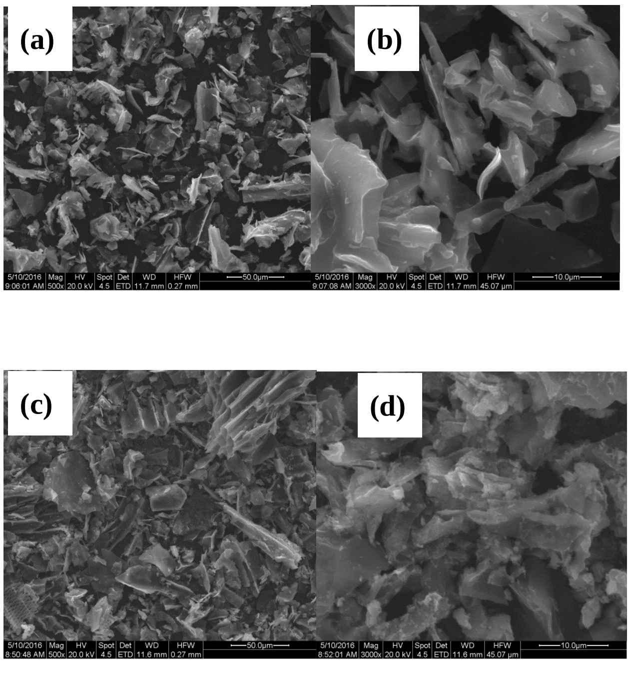

Fig. 2: Scanning electron microscopy images of the raw bagasse biochar (a, b) and the La-modified magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 (c,d).

La/Fe3O4 at 1:100 was enhanced by 69.8%. Apparently, the adsorption capability of the bagasse biochar was significantly improved because of introduction of magnetic La/Fe_3O_4, while these modified magnetic biochars with different molar ratio of La/Fe_3O_4 have a close adsorption capability. In the following tests, the La-modified magnetic bagasse biochar with the molar ratio of La/Fe_3O_4 at 1:100 was used for TC adsorption.

Characterization of the magnetic adsorbent: The scanning electron microscopy images (SEM) of the raw bagasse biochar and the magnetic biochar with a molar ratio of La/Fe_3O_4 at 1:100 are shown in Fig. 2. The raw bagasse biochar mainly consists of thin amorphous carbon flakes. The sizes of these biochar flakes are predominantly within 50 µm. After concurrent La and Fe_3O_4 immobilization, from Fig. 2, it is clearly observed that Fe_3O_4 particles are well combined with the biochar substrate. As indicated by our previous study, the Fe_3O_4 particles prepared in the same procedure are in nano-scale and they easily aggregate on the biochar surface (Li et al. 2009).

By EDX analysis, the atomic ratio of La and Fe are 0.08% and 5.36%, respectively. This equals to the molar ratio 1/22.3 between La and Fe_3O_4, which is much different from the controlled value of 1/100 in the preparation procedure. This might be attributed to the different aggregation property of La oxides and hyrdoxides. Totally, La species are scattered evenly enough within the bulk Fe_3O_4 substrate to ensure a reliable and stable adsorption capability.

Wide scan XPS spectra of the magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 were analysed to determine the existence and chemical state of the elements, as illustrated in Fig. 3. It revealed that there is a presence of C, O, Fe and La, although the content of La is very limited. This is consistent with the EDX results mentioned above. Concurrently, the complex pattern and significant broadness of O1s in Fig. 3c implies the considerable amount of impurities including iron oxide and oxyhydroxide on the magnetic biochar. As such, the above demonstrate a complex but reasonable composition of the prepared magnetic bagasse biochar.

Adsorption isotherm: Adsorption isotherm study of TC on the magnetic biochar was conducted at 288, 298 and 308 K. Typical Langmuir and Freundlich models were selected to fit the experimental data.

Langmuir isotherm model is appropriate to describe the monolayer adsorption between the adsorbate and the surface of adsorbent. The non-linear form of Langmuir adsorption isotherm is represented as (Langmuir 1916):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad ...(3)$$

Where, q_e (mg/g) is the amount of TC adsorbed onto the La-modified magnetic biochar at equilibrium, q_m (mg/g) is the maximum adsorption capacity of the adsorbent. C_e is

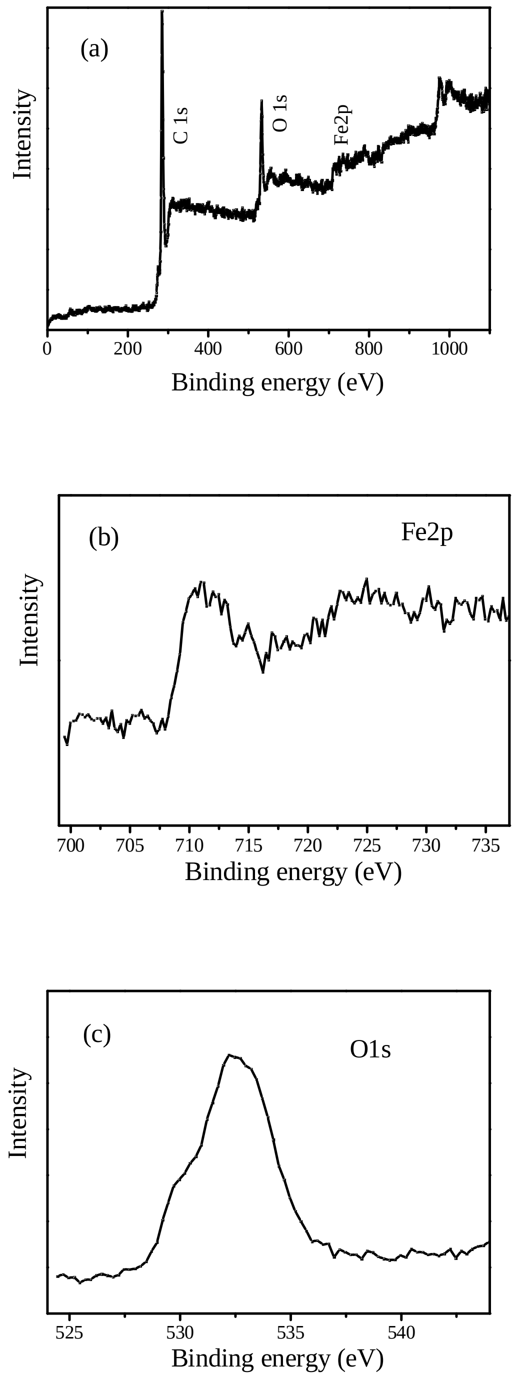

Fig. 3: Wide scan XPS spectra of the La-modified magnetic biochar with a presumed molar ratio of La/Fe_3O_4 at 1:100 (a) and the spectra of Fe2p (b) and O1s.

the equilibrium concentration of TC (mg/L), k_L (L mg^{-1}) is a constant related to the affinity of the binding sites and energy of adsorption.

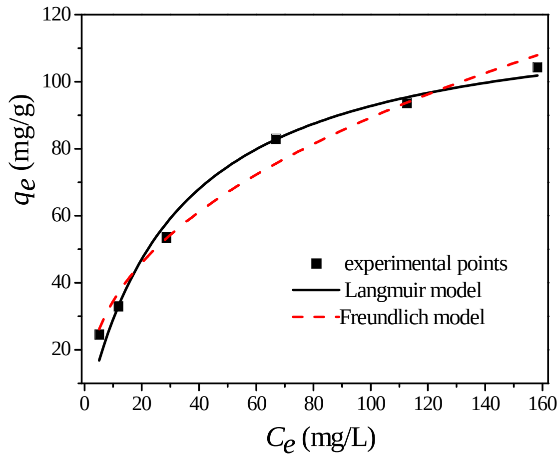

Fig. 4: Langmuir and Freundlich isotherms for TC adsorption on the La-modified magnetic biochar at 298 K.

Table 1: Simulated isotherm parameters at different temperatures for the adsorption of TC on the La-modified magnetic biochar.

	Isotherm parameters		
	288 K	298 K	308 K
Langmuir			
q_{max} (mg/g)	79.6	122.5	154.6
k_L (L/mg)	0.03	0.031	0.036
R^2	0.984	0.980	0.986
Freundlich			
k_F (mg/g)R^2	9.04	13.35	17.71
nR^2	2.51	2.42	2.43
R^2R^2	0.973	0.980	0.978

The Freundlich isotherm can be used to describe the multilayer adsorption onto a heterogeneous surface and the equation is expressed as (Freundlich 1906):

$$q_e = k_F C_e^{\frac{1}{n}} \quad ...(4)$$

Where, q_e is the amount of TC adsorbed onto the La-modified magnetic biochar (mg/g), C_e is the equilibrium concentration of TC (mg/L), q_m is the maximum adsorption capacity of the adsorbent (mg/g), n is the Freundlich linearity index, k_F is the Freundlich constants related to the adsorption capacity.

From the curves simulated in Fig. 4 and the isotherm parameters listed in Table 1, both Langmuir and Freundlich isotherm models fitted the experimental data well as the experimental points are quite close to the simulated curves. The correlation coefficients (R^2) of Langmuir and Freundlich models at three temperatures are quite close, and most of them are higher than 0.980. By Langmuir model, the calculated maximum adsorption capacities (q_{max}) at 288, 298 and

308 K were 79.6, 122.5 and 154.6 mg/g, respectively. It indicates that the adsorption capacity of TC on the magnetic biochar increases with the rising temperature. The adsorption process is deduced to be an endothermic process.

CONCLUSION

Composite adsorbent La-modified magnetic biochar was creatively prepared by immobilizing La/Fe_3O_4 particles (mainly Fe_3O_4) onto the biochar derived from sugarcane bagasse via co-precipitation method. The sizes of these biochar flakes are predominantly within 50 µm. La/Fe_3O_4 particles are scattered evenly enough within the biochar substrate to ensure a reliable adsorption performance. The La-modified magnetic bagasse biochar with the molar ratio of La/Fe_3O_4 at 1:100 performed better for TC adsorption. Both Langmuir and Freundlich isotherm models fitted the experimental data well as the experimental points are quite close to the simulated curves. By Langmuir model, the maximum adsorption capacities (q_{max}) at 298 K achieved as much as 122.5 mg/g. The uptake of tetracycline increases with a rise in the reaction temperature and the adsorption process is endothermic.

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REFERENCES

Cherian, C., Kollannur, N.J., Bandipally, S. and Arnepalli, D.N. 2018. Calcium adsorption on clays: Effects of mineralogy, pore fluid chemistry and temperature. Appl. Clay Sci., 160: 282-289.

Figueroa, R.A., Leonard, A. and MacKay, A.A. 2004. Modeling tetracycline antibiotic sorption to clays. Environ. Sci. Technol., 19: 55-64.

Freundlich, H.M.F. 1906. Uber die adsorption in lasungen. J. Phys. Chem., 57: 385-470.

Fu, H.Y., Yang, Y.X., Zhu, R.L., Liu, J., Usman, M., Chen, Q.Z. and He, H.P. 2018. Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetite. J. Colloid Interf. Sci., 530: 704-713.

Langmuir, I. 1916. Kinetic model for the sorption of dye aqueous solution by clay-wood sawdust mixture. J. Am. Chem. Soc., 38: 2221-2295.

Li, G.T., Wong, K.H., Zhang, X.W., Hu, C., Yu, Jimmy C., Chan, R.C.Y. and Wong, P.K. 2009. Degradation of Acid Orange 7 using magnetic Ag Br under visible light: The roles of oxidizing species. Chemosphere, 76:1185-1191.

Li, G.T., Zhu, W.Y., Zhu, L.F. and Chai, X.Q. 2016. Effect of pyrolytic temperature on the adsorptive removal of p-benzoquinone, tetracycline, and polyvinyl alcohol by the biochars from sugarcane bagasse. Korean J. Chem. Eng., 33(7): 2215-2221.

Li, G.T., Feng, Y.M., Zhu, W.Y. and Zhang, X.W. 2015. Enhanced adsorptive performance of tetracycline antibiotics on lanthanum modified diatomite. Korean J. Chem. Eng., 32(10): 2109-2115.

Mathers, J.J., Flick, S.C. and Cox, L.A. 2011. Longer-duration uses of tetracyclines and penicillins in U.S. food-producing animals: Indications and microbiologic effects. Environ. Int., 37: 991-1004.

Mehta, D., Mazumdar, S. and Singh, S.K. 2015. Magnetic adsorbents for the treatment of water/wastewater- A review. J. Water Process Eng., 7: 244-265.

Moreira, M.T., Noya, I. and Feijoo, G. 2017. The prospective use of biochar as adsorption matrix-A review from a lifecycle perspective. Bioresour. Technol., 246: 135-141.

Noor, N.M., Othman, R., Mubarak, N.M. and Abdullah, E.C. 2017. Agricultural biomass-derived magnetic adsorbents: Preparation and application for heavy metals removal. J. Taiwan Inst. Chem. E., 78: 168-177.

Peiris, C., Gunatilake, S.R., Mlsna, T.E., Mohan, D. and Vithanage, M. 2017. Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: A critical review. Bioresour. Technol., 246: 150-1

Qu, J.H. 2008. Research progress of novel adsorption processes in water purification. J. Environ. Sci., 20:1-13.

Rakic, V., Rac, V., Krmar, M., Otman, O. and Auroux, A. 2015 The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons. J. Hazard. Mate., 282: 141-149.

Vences-Alvarez, E., Velazquez-Jimenez, L.H., Chazaro-Ruiz, L.F., Diaz-Flores, P.E. and Rangel-Mendez, J.R. 2015. Fluoride removal in water by a hybrid adsorbent lanthanum-carbon. J. Colloid Interf. Sci., 455: 194-202.

Wang, H.X., Wang, N., Wang, B., Zhao, Q., Fang, H., Fu, C.W., Tang, C.X., Jiang, F., Zhou, Y., Chen, Y. and Jiang, Q.W. 2016. Antibiotics in drinking water in Shanghai and their contribution to antibiotic exposure of school children. Environ. Sci. Technol., 50: 2692-2699.

Yesilova, E., Osman, B., Kara, A. and Tümay Özer, E. 2018. Molecularly imprinted particle embedded composite cryogel for selective tetracycline adsorption. Sep. Purif. Technol., 200: 155-163.

Yu, B.W., Bai, Y.T., Ming, Z., Yang, H., Chen, L.Y., Hu, X.J., Feng, S.C. and Yang, S.T. 2017. Adsorption behaviors of tetracycline on magnetic graphene oxide sponge. Mater. Chem. Phys., 198: 283-290.