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Adsorption Process of Ammonia Nitrogen in Solution by the Modified Biochar from Corn Straw

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ABSTRACT

The biochar was prepared by pyrolyzing corn straw at 773 K temperature under an oxygen-limited condition. Then, the gained biochar samples were further modified with $MgCl_2$ solution through mixing method for 3 h at the speed of 120 rpm. The physicochemical properties of the modified biochar from corn straw were investigated by surface area analysis, elemental analysis, scanning electron microscope, X-ray diffraction and Fourier transform infrared spectroscopy spectra. The adsorption experiments of ammonia nitrogen in aqueous solution by modified biochar were carried out. The results showed that the modified biochar contains high surface area, rough surface and a lot of oxygen-containing functional groups. The adsorption process fits well with the pseudo-second-order kinetics equation and Langmuir isotherm equation. The adsorption mechanism of modified biochar to NH_4^+ ion in aqueous solution includes ion exchange and physical adsorption. The ion exchange is primary in the process of adsorption.

INTRODUCTION

With the rapid development of industry and agriculture, the emission of eutrophic substances, such as nitrogen element and phosphorus element, has also increased in China (Liu et al. 2010). The eutrophication of water bodies is harmful to environment. Therefore, research on an efficient method to treatment the eutrophication of water bodies has become a hot studying area for many scholars (Duan et al. 2012, Haseena et al. 2016).

For a long time, in order to control the eutrophication of water bodies, many scholars have begun to study on the removal methods of nitrogen and phosphorus in water bodies, such as adsorption, chemical oxygen, ions exchange and so on (Christoph & Thomas 2009, García-Martínez et al. 2018). Among these methods, the adsorption method is widely applied because of its simple operation process, high efficiency and nontoxic by-products (Qiu et al. 2018, Seabra et al. 2019). The development and utilization of adsorbents is an important research content of the adsorption method (Tokay et al. 2010). Biochar is a rich carbon solid prepared by pyrolyzing biomass under anoxic or anaerobic and low temperature conditions. It is an excellent adsorption material with well-developed pore structure, large specific surface area, rich oxygen-containing functional groups and excellent adsorption properties (Rahmati & Modarress 2009, Paz-Ferreiro et al. 2018). Therefore, in order to obtain biochar with superior adsorption performance, many scholars began to explore the effects of biochar raw materials, pyrolysis temperature and modification conditions on the physical and chemical properties of biochar (Herrera et al. 2008, Hu et al. 2017). Raw materials for the production of biochar include agricultural and forestry waste, such as straw, weeds, wood chips, manure and so on. Among them, the agricultural straw waste is the main biochar raw material. It consists mainly of cellulose, hemicellulose and lignin (Ryu et al. 2000, Moghaddam et al. 2010, Vinitnantharat et al. 2010, Siswoyo et al. 2014). In China, every year, a large amount of agricultural straw is produced, but the utilization rate of agricultural straw is very low. The new method of seeking the resource utilization of agricultural straw has been concerned by many researchers (Sprynskyy et al. 2005, Gendel & Lahav 2013).

In this paper, the biochar was prepared by pyrolyzing corn straw under an oxygen-limited condition. Then, the biochar samples were modified with $MgCl_2$ solution. The adsorption experiments of ammonia nitrogen in solution were carried out. The main object of this study is, (1) the characteristic of the modified biochar from corn straw. The obtained modified biochar from corn straw was determined by surface area analysis, elemental analysis, scanning electron microscope, X-ray diffraction and Fourier transform infrared spectroscopy spectra respectively. (2) The adsorption kinetic and adsorption isotherm of ammonia nitrogen in solution by the modified biochar were studied. (3) The adsorption mechanism of ammonia nitrogen in solution by the modified biochar is discussed in details.

MATERIALS AND METHODS

The Preparation of The Modified Biochar

The corn straws are collected from farmland in the suburbs of Dongyang City, Zhejiang Province. They were washed several times with water, and dried to a constant weight at 378 K, pulverized and passed through a 40 meshes sieve. 20 g of sample was pyrolyzed for 3 h under a nitrogen atmosphere at a temperature of 773 K. After cooling to room temperature, it was pulverized to 80 meshes. Then, the biochar from corn straw was obtained.

10 g biochar was added to the 1000 mL beaker containing 500 mL 0.01 mol/L $MgCl_2$. Then the mixture was stirred for 3 h at the speed of 120 rpm. The sample is filtered, washed with distilled water and dried to constant weight at 378 K. Then, the modified biochar by $MgCl_2$ solution was obtained.

Adsorption Experiments

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing modified biochar and 100 mL of NH_4^+ with initial concentrations in aqueous solution. The flasks were placed in a shaker at a constant temperature of 298 K and 120 rpm. The samples were then filtered and the residual concentration of NH_4^+ was analysed using Nessler reagent spectrophotometry.

Analytical Method

The concentration of NH_4^+ ion in solution was measured with a UV-1600 spectrophotometer. The adsorption capacity of NH_4^+ was calculated as following:

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

Where, C_0 and C_e (mg/L) are the initial and equilibrium concentrations of NH_4^+ in solution respectively. q_e (mg/g) is adsorption amount per unit mass of the modified biochar at adsorption equilibrium. V (mL) is volume of solution, m (g) is the mass of the modified biochar.

The physicochemical properties of the modified biochar from corn straw were investigated by surface area analysis (ASAP 2460), elemental analysis (EURO EA 3000), scanning electron microscope (Ultra 55), X-ray diffraction (Ulitma IV) and Fourier transform infrared spectroscopy spectra (Nicolet 5700).

RESULTS AND DISCUSSION

The Structural Characteristics and Properties of the Modified Biochar

The elements of C, H, O and N of the modified biochar are determined. They are 69.24%, 3.64%, 15.21% and 0.51% respectively. BET specific surface area of the modified biochar is 98.86 m^2/g, and the total of pore volume is 0.1236 cm^3/g.

The scanning electron micrograph of the modified biochar is shown in Fig. 1. From Fig.1, it can be shown that the microporous edge on the surface of the modified biochar is ablated by high temperature, and the distribution of the pores becomes disordered. It increases the surface roughness of the modified biochar, and it will benefit to improve the adsorption capacity.

The XRD spectrum is shown in Fig. 2. From Fig. 2, it can be thought that it is assigned to be broad and diffuse peak when 2θ is ranged from 15° to 22°. It is assigned to be quartz diffraction peak at 26.5°. It is assigned to be three potassium salt diffraction peaks at 28.5°, 40.6° and 50.5°. It

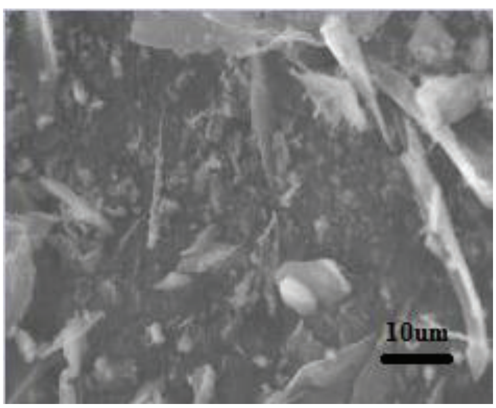

Fig. 1: SEM image of the modified biochar.

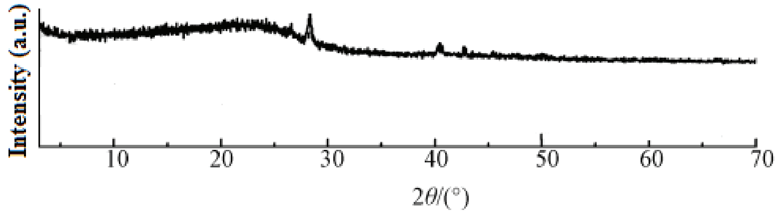

Fig. 2: X-ray diffraction spectrum of the modified biochar from corn straw.

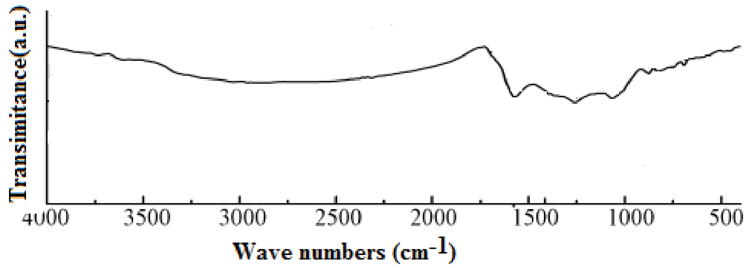

Fig. 3: Infrared spectrum of the modified biochar from corn straw.

is assigned to be diffraction peaks at 42.7°. This peak should be the characteristic peak of MgO. It indicates that Mg^{2+} ions have been loaded on the biochar.

From Fig. 3, there is a C = O absorption peak at 1702 cm^{-1}. They were assigned to be acyclic ring C = C stretching vibration peak, C = O stretching vibration peak and phenolic hydroxyl stretching vibration peak respectively, at 1609 cm^{-1}, 1442 cm^{-1} and 1259 cm^{-1}. It was assigned to be C – O stretching vibration peak at 1068 cm^{-1}. They were assigned to be C - H stretching vibration peak between 649 cm^{-1} and 878 cm^{-1}. The modified biochar contains an increased number of oxygen-containing functional groups and an increased polarity.

Adsorption Kinetic

In order to investigate the adsorption kinetics, the adsorption test was carried out. Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.05 g modified biochar and 50 mL 25 mg/L of NH_4Cl in aqueous solution. The flasks were placed in a shaker at a constant temperature of 298 K and 120 rpm. The reaction time is 5, 10, 15, 20, 30, 40, 60, 80, 120, 180, 240, 360 and 420 min respectively. The samples were then filtered and the residual concentration of NH_4^+ was analysed using Nessler reagent spectrophotometry.

The experimental results were shown in Fig. 4. In the initial stage, the adsorption amount of NH_4^+ ion by the modified biochar increases rapidly. Then, it tends to balance slowly.

In order to describe the adsorption kinetic of NH_4^+ ion by the modified biochar, pseudo-first-order kinetic equation and pseudo-second-order kinetic equation were adopted in this study. Their equations are as follows (Eugene 2016):

$$q_t = q_e\left(1 - e^{-K_1 t}\right) \qquad \ldots(2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(3)$$

Where q_t (mg/g) and q_e (mg/g) are adsorption capacity of NH_4^+ ion solution by modified biochar at adsorption time t and adsorption equilibrium respectively. K_1 (min^{-1}) and K_2 (min^{-1}) are the adsorption rate constant.

According to Eq. (2) and Eq. (3), the results are shown in Table 1.

From Table 1, it can be shown that the adsorption process fits well with the pseudo-second-order kinetics equation according to the value of R^2 (0.9984). It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

Adsorption Isotherm

In order to investigate the adsorption isotherm, the adsorption test was carried out. Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.05 g modified biochar and 50 mL of NH_4^+ ion with initial concentrations (5, 10, 25, 40, 50 mg/L) in aqueous solution. The flasks were placed in a shaker at a constant

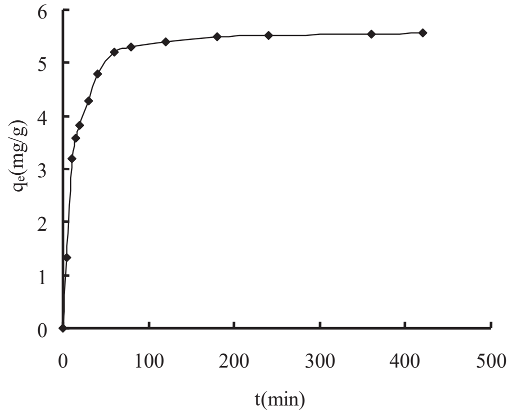

Fig. 4: The effect of reaction time on the adsorption capacity of NH_4^+ ion by the modified biochar.

Table 1: Parameters of the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation for the description of NH_4^+ ion adsorption onto modified biochar.

Pseudo-first-order kinetic equation			Pseudo-second-order kinetic equation		
K_1(min^{-1})	q_e (mg/g)	R^2	K_2 (min^{-1})	q_e (mg/g)	R^2
0.21	4.81	0.8258	0.0086	5.54	0.9984

temperature of 298 K and 120 rpm. The reaction time is 360 min. The samples were then filtered and the residual concentration of NH_4^+ was analysed using Nessler reagent spectrophotometry.

The experimental results are shown in Fig. 5. The sorption of NH_4^+ ion in aqueous solution by modified biochar increased with the initial concentration of NH_4^+ ions in aqueous solution increased.

In order to describe the adsorption isotherm of NH_4^+ ion by the modified biochar, Langmuir isotherm equation and Freundlich isotherm equation were applied in this study. Their equations are follows (Tu et al. 2019):

$$\frac{c_e}{q_e} = \frac{c_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad \ldots(4)$$

$$\lg q_e = \lg K_F + \frac{1}{n}\lg c_e \quad \ldots(5)$$

Where q_e (mg/g) are adsorption capacity of NH_4^+ ion solution by modified biochar at adsorption equilibrium. $q_{\max}$ (mg/g) is the maximum adsorption capacity of the adsorbent under specific adsorption conditions. K_L (L/mg) and K_F (L/mg) are the adsorption rate constant. c_e (mg/L) is equilibrium concentrations of NH_4^+ ion in solution.

According to Eq. (4) and Eq. (5), the results are shown in Table 2. As shown from Table 2, the value of is 0.9326 according to the Langmuir isotherm equation. The value of R^2 is 0.8943 according to the Freundlich isotherm model. Therefore, the adsorption process of NH_4^+ ion in aqueous solution by the modified biochar fitted well with the Langmuir isotherm equation. This indicated that the surface of the adsorbent is a uniform surface. The adsorption process is a monolayer adsorption process.

Adsorption Mechanism

The adsorption mechanism of biochar on NH_4^+ ion in solution has been discussed by many researchers (Huo et al. 2012). At present, it is generally thought that the adsorption mechanism of biochar on NH_4^+ ion includes ion exchange, physical adsorption and electrostatic adsorption. In this study, biochar was modified by $MgCl_2$ solution. The surface of biochar contains a large number of functional groups, and they have a certain adsorption effect on NH_4^+ ion in aqueous solution. The reaction of biochar to NH_4^+ ion in aqueous solution is as follows:

$$\begin{aligned} &Biochar - Mg^{2+} + 2NH_4^+ + 6H_2O \rightarrow \\ &Biochar - Mg\left(NH_4^+\right)_2 \cdot 6H_2O \end{aligned} \quad \ldots(6)$$

$$\begin{aligned} &Biochar - Mg^{2+} + 2NH_4^+ \rightarrow \\ &Biochar - \left(NH_4^+\right)_2 + Mg^{2+} \end{aligned} \quad \ldots(7)$$

In a word, the adsorption mechanism of modified biochar to NH_4^+ ion in aqueous solution includes ion exchange and physical adsorption. The ion exchange is primary in the process of adsorption.

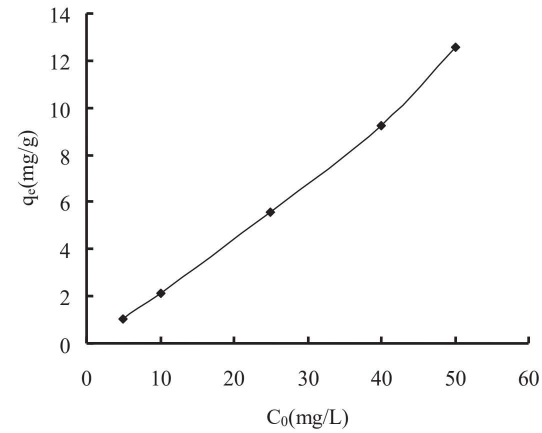

Fig. 5: The effect of initial concentration of NH_4^+ ion on the adsorption capacity of NH_4^+ ion by the modified biochar.

Table 2: Parameters of Langmuir isotherm equation and Freundlich isotherm equation for the description of NH_4^+ ion adsorption onto the modified biochar.

Langmuir			Freundlich		
q_{max} (mg/g)	K_L	R^2	K_F	n	R^2
5.12	0.26	0.9326	1.74	4.09	0.8943

CONCLUSIONS

Through the above experiments and discussions, the following results can be obtained.

1. The elements of C, H, O and N of the modified biochar were determined. They are 69.24%, 3.64%, 15.21% and 0.51% respectively. BET specific surface area of the modified biochar is 98.86 m^2/g, and the total of pore volume is 0.1236 cm^3/g. The distribution of the pores on the surface of modified biochar becomes disordered. The modified biochar contains a lot of oxygen-containing functional groups.
2. The adsorption process fits well with the pseudo-second-order kinetics equation. The predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. The adsorption process of NH_4^+ ion in aqueous solution by the modified biochar fitted well with the Langmuir isotherm equation. The adsorption process is a monolayer adsorption process.
3. The adsorption mechanism of modified biochar to NH_4^+ ion in aqueous solution includes ion exchange and physical adsorption. The ion exchange is primary in the process of adsorption.

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