Removal of Nitrate from Water by Reed Straw Biochar with Different $FeCl_3$ Modification Method

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Abstract: Nitrate contamination became an ever-increasing serious environmental problem and some conventional methods had the higher operating costs and the lower efficiency. In order to develop low-cost technology for aqueous nitrate treatment, various agro-forest residuals have attracted a great deal of research attention to preparing biochar adsorbents for nitrate adsorption. In our study, reed straw biochar was prepared from wetland plant residuals at different pyrolysis temperatures (300ºC, 400ºC, 500ºC, 600ºC and 700ºC). Meanwhile, biochar was modified by $FeCl_3$ with different methods to optimize their adsorbent performance. The results show that the optimal preparation conditions could achieve at carbonization temperature of 600ºC for 2 h, followed by soaking in $FeCl_3$ solution for 24 hours in alkaline condition, for which the highest adsorption capacity could reach at 1.97 mg/g after modification. SEM images show that a large amount of iron oxides were loaded on the surface of biochar, as well as in the pores of biochar, promoting the removal of nitrate. This study can provide a theoretical basis for the comprehensive utilization of agro-forest waste and nitrate removal.

1 INTRODUCTION

Unreasonable discharge of industrial nitrogen-containing wastewater, random stacking of solid wastes such as domestic waste and nitrogen-containing waste residue, unreasonable use of nitrogen-containing pesticides and fertilizers will lead to a large number of NO_3-N into the water environment, resulting in NO_3-N pollution in water environment (JesúsGarcía-Fernández, 2018). Due to the limited self-purification capacity of water and the natural degradation capacity of microorganisms, NO_3-N gradually accumulates in the environment, and the concentration continues to increase (Liu 2021). Enriched NO_3-N makes the water eutrophication, a large number of algae cover the water surface so that sunlight can not be transmitted, the photosynthesis of aquatic plants is weakened, and the respiration is enhanced, resulting in the death of a large number of aquatic organisms such as fish, and the deterioration of water quality (Huang 2017). In order to reduce the damage of NO_3-N pollution to the water environment and human health, it is of great significance to seek economical and effective technology to control the concentration of NO_3-N in water.

In recent years, the use of low-cost and effective adsorbents to adsorb pollutants is the focus of scholars (Cao 2019). As a new type of environment-friendly adsorbent, biochar has strong adsorption capacity for heavy metals and organic pollutants because of its easily available raw materials and rich surface functional groups. Biochar has become one of the main ways of resource utilization of agricultural

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waste (HussainLAHORI 2017). The adsorption performance of biochar can be improved by modifying biochar (Chen 2014). Ordinary biochar has large specific surface area and high porosity. Biochar can be modified to change its surface structure (Zhu 2017), increase surface functional groups, enhance the adsorption capacity of biochar to NO_3-N and improve the removal rate of NO_3-N. Some studies have shown that iron oxides have high affinity and adsorption selectivity for oxygen-containing anions in water (Namasivayam 2005). Wheat straw biochar was prepared by Li et al and modified with $FeCl_3$. The results showed that when the mass ratio of Fe/C was 0.7, the maximum NO_3-N adsorption capacity of iron modified biochar was 2.47 mg/g fitted by Langmuir isothermal adsorption model, while that of unmodified biochar was only 0.13 mg/g (Li 2015). Dewage et al prepared Douglas fir biochar and modified it with $FeCl_3$. It was found that Fe particles in the form of α-Fe_2O_3 and Fe_3O_4 could lead to magnetization of biochar and produce a large number of adsorption sites (Dewage 2018). However, few people have studied the treatment of pollutants in water by $FeCl_3$ modified reed straw biochar.

As a kind of wetland aquatic plant, reed straw was made into biochar to explore its adsorption capacity to nitrate nitrogen in water environment. reed straw biochar was modified by $FeCl_3$ to determine the modification conditions with the best adsorption capacity. The related properties of biochar (modified biochar) were analyzed by scanning electron microscope (SEM) and X-Ray diffraction (XRD). The purpose of this study is to provide a scientific basis for the resource utilization of aquatic plants in wetlands and the pollution control of nitrate nitrogen in water.

2 MATERIALS AND METHODS

2.1 Preparation of Biochar from Reed Straw

In this study, the reed was defoliated, washed and crushed into powder with a powder mesh of about 60-80 mesh. The reed straw powder was washed with a large amount of deionization and dried in an oven at 105°C. Under the conditions of 10°C/min heating gradient, 120 min combustion residence time and oxygen limitation, reed powder was prepared at five operating temperatures of 300ºC, 400ºC, 500ºC, 600 ºC, 700 ºC respectively, and BC300, BC400, BC500, BC600 and BC700 were obtained.

2.2 Preparation of Biochar from Different Modified Reed Straw

Different preparation methods are as follows：

(a) Reed straw was pre-modified with $FeCl_3$ solution and rotated in shaker for 24 hours, then carbonized at 600°C for 2 hours in muffle furnace under oxygen-limited condition;

(b) Reed straw was carbonized at 500°C for 1 h, soaked in $FeCl_3$ solution for 24 h, then washed with deionized water for five times (filtrate Ph was about 4.3), then dried;

(c) Reed straw was carbonized at 600°C for 2 h, soaked in $FeCl_3$ solution, adjusted to alkaline solution, soaked 24 h, washed with deionized water for five times (filtrate Ph was about 4.5);

(d) Reed straw was pre-soaked with Hcl solution for 24h, then rinsed with deionized water for five times (filtrate Ph was about 4), carbonized at 600°C in muffle furnace under oxygen limitation for 2 h, removed and soaked with $FeCl_3$ for 12 h, then dried;

(e) Reed straw was carbonized at 600°C for 2 hours, soaked in Hcl solution for 24 hours, then washed with deionized water for five times (filtrate Ph = 5.5), then dried, soaked in $FeCl_3$ solution for 12 hours, and dried.

2.3 Preparation of Nitrate Solution

Accurately weigh KNO_3 (analytical purity) 0.14436 g in the beaker, add appropriate amount of deionized water to dissolve, fix the volume to 1 L, obtain the NO_3-N reserve solution of 20 mg/L, avoid light and store at 4°C.

2.4 Experiment on Determination of Adsorption Effect of NO_3-N

Configure the KNO_3 solution of 20 mg/L, adjust the solution pH to about 7, weigh 0.2 g reed straw biochar (modified straw biochar), add it to the 50 ml capacity flask of KNO3 solution containing 20 mg/L, shake in the shaker for 24 hours, and then use 0.22 μm filter membrane to determine the concentration of NO_3-N in the supernatant. Thus, the adsorption effect of reed straw biochar (modified straw biochar) on NO_3-N after 24 h adsorption was calculated. NO_3-N was detected by CleverChem Anna automatic discontinuous chemical analyser, and the SEM characterization of reed straw biochar was measured. X-Ray powder diffraction (XRD) is used to scan the crystal structure of the material in the range of 10-60 degrees using Bruker D4 Endeavor Powder X-Ray diffractometer.

2.5 Analytical Methods

The adsorption capacity of biochar to NO_3-N is calculated by formula (1):

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

Among them, q_e (mg/g) is the equilibrium adsorption capacity; C_0 (mg/L) is the initial concentration of NO_3-N in the water sample; C_e (mg/L) is the concentration of NO_3-N in the adsorption equilibrium; M (g) is the amount of biochar added; V (L) is the volume of the water sample.

The experimental data were plotted using Excel 2016 and Origin 2018 software.

3 RESULTS AND DISCUSSION

3.1 Effect of Biochar at Different Preparation Temperatures on the Adsorption Properties of Nitrate Nitrogen

It can be seen from figure 1 that for the solution with the same NO_3-N concentration (20.381mg/L), the adsorption capacity of reed straw biochar is in the order of BC600 > BC700 > BC300 > BC500 > BC400 under the preparation conditions of 300°C, 400°C, 500°C, 600°C and 700°C. The three kinds of biochar BC300, BC400 and BC500 had negative adsorption effect on NO_3-N, while under the preparation conditions of 600°C and 700°C, the adsorption effect of reed straw biochar on NO_3-N was close to that of reed straw biochar.

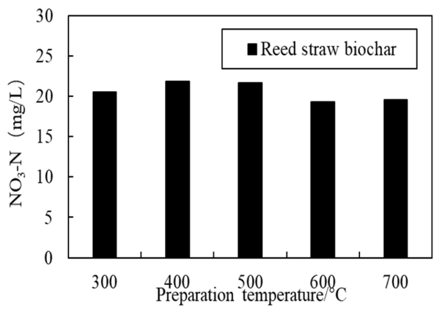

Figure 1: Adsorption effect of reed straw biochar prepared at different temperatures for NO_3-N.

As shown in figure 2, with the increase of the pyrolysis temperature of straw biochar material, the concentration of NO_3-N in the target solution decreases gradually. The higher the pyrolysis temperature, the higher the adsorption capacity of straw biochar to NO_3-N, and the adsorption capacity of BC600 and BC700 to NO_3-N is the largest compared with other biochar. This should be due to the fact that the surface of biochar prepared by high temperature pyrolysis has more pore structure than that of biochar prepared at 300°C ~ 500°C. With the increase of pyrolysis temperature, the porosity and specific surface area of biochar are increasing, and the porosity is becoming more and more perfect. In the SEM diagram of the original reed, due to the crushing of the reed straw, the surface of the reed straw is rough and the electrical conductivity is poor. In the SEM diagram of BC300, biochar is not carbonized completely and does not form complete porosity, which will lead to poor electrical conductivity of biochar. In the SEM diagram of BC400 and BC500, the porosity of biochar has been gradually formed. In the SEM diagram of BC600, the porosity of reed carbon is relatively complete, and the voids are larger, and there are many small holes in the voids, which may cause NO_3-N to adhere to the voids more easily. In the SEM diagram of BC700, the porosity of reed carbon has been completely formed, and the arrangement is relatively neat, and the inner surface of the pore is smooth.

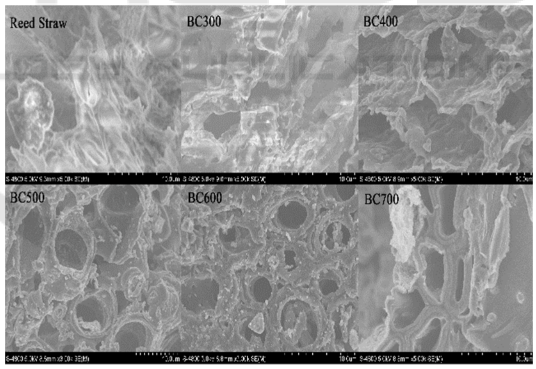

Figure 2: Micro-morphology pictures of SEM (10 μm) prepared by biochar at different temperatures.

3.2 Effect of Biochar Modified by Different Methods on Adsorption Properties of NO3-N

As shown in figure 3, the effect of (c) method is the best among the five modification methods, reaching 1.97 mg /g. In (c) method, Ph, is adjusted to $FeCl_3$ solution to make it alkaline. NaOH can interact with carbon matrix to increase the porosity and specific surface area of biochar. At the same time, it can also increase the amount of -OH, -COOH and cation exchange capacity. $FeCl_3$ is easy to form iron hydroxide under alkaline conditions. Iron hydroxide is easier to combine with the surface functional groups in biochar to form iron oxide, and it is easy to be loaded in biochar. The effect of (b) is not as good as that of (c), which may be due to the fact that the porosity is not as good as that of (c) due to the lack of carbonization time. Although the adsorption effect of (d) and (e) is not as good as that of (c), they also have better adsorption capacity, which may be due to the effect of HCI solution, because the surface elemental composition of biochar changes when soaked in acid solution: on the one hand, the C content decreases and the O content increases due to the loss of organic carbon in biochar, on the other hand, the relative content of C increases due to the decrease of ash content in biochar. In addition, the increase of oxygen-containing functional groups on the surface of biochar can also increase its O content. Therefore, acid modification can effectively increase the number and variety of oxygen-containing functional groups on the surface of biochar, and greatly increase the porosity of the materials. In (d) method and (e) method, the modification order of HCl solution is different, and the reed straw treated with HCI solution does not play a key role in carbonization. On the contrary, the carbonized reed carbon produces a large amount of CO and H_2O due to soaking in HCI solution, which makes the pore structure of biochar more developed, increases the specific surface area and reduces the crystallinity of cellulose in the process of biomass carbonization. The improvement of its pore structure leads to the increase of the porosity of biochar, which makes the oxide of Fe more easily attached to it.

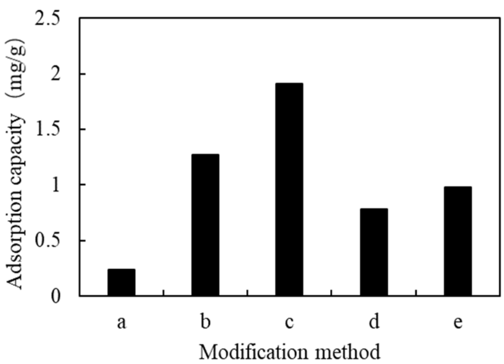

Figure 3: Adsorption effect of NO_3-N on biochar under different modified methods.

As shown in figure 4, most of the biochar has a porous structure in the (a) ~ (e) modification method. In (a) modification method, the porous structure of biochar and very few Fe oxide particles attached to the surface of biochar have large and small pore structure, which may be caused by carbonization time of only 1 h. In (c) method, the crystallization of oxides containing a large amount of iron in the pores can be observed, which may indicate that $FeCl_3$ solution modification is more successful than the previous methods. Due to the pre-treatment of reed straw by HCl immersion in (d) method, the solution is slightly acidic after washing, and the pores are destroyed and not round, which may make the adsorption effect not as good as that of (e) method. In the SEM diagram of (e) method, it is obvious that the iron oxides have been attached to the pores, which is because the carbonized pores are amplified by HCl solution.

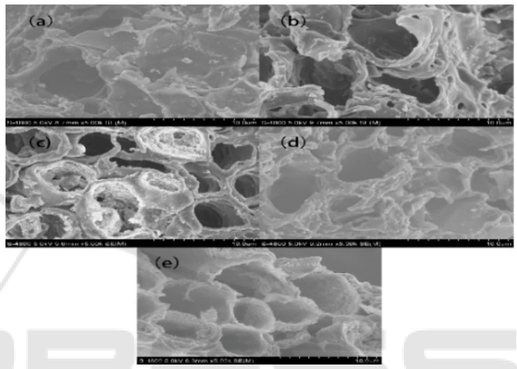

Figure 4: SEM (10 μm) micro-morphology pictures prepared by different modification methods of biochar.

Figure 5 shows the XRD pattern of biochar modified by $FeCl_3$ solution, which does not show the characteristic diffraction peak of iron, indicating that the two kinds of modified biochar are amorphous. Hu et al also reached a similar conclusion (Hu 2016). The iron-bearing particles are amorphous, which may have a good adsorption effect on NO_3-N.

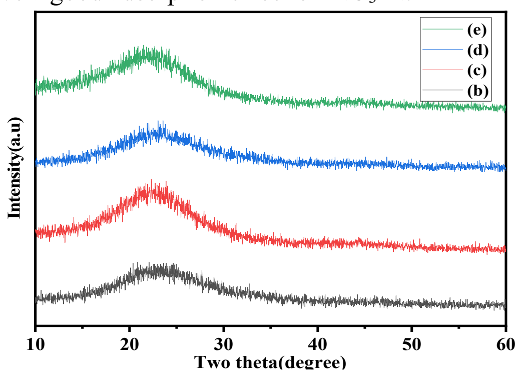

Figure 5: XRD pattern of biochar modified by $FeCl_3$ solution.

4 CONCLUSIONS

The main results are as follows:

(1) The biochar of reed straw loaded with iron oxide was prepared by the activation of $FeCl_3$, and the preparation conditions with the best adsorption capacity of NO_3-N were obtained, that is, carbonization at 600ºC for 2 h and soaking in $FeCl_3$ solution (alkaline) for 24 h. The adsorption capacity under the optimal conditions is 1.97 mg/g .

(2) The porosity of reed straw biochar prepared under the optimal preparation conditions is higher than that of biochar prepared by other methods; biochar has a porous structure and loaded with a variety of iron oxide components.

(3) Acid modification reagents can change the specific surface area and pore structure of biochar, and increase the porosity of biochar; Appropriate amount of alkali modification not only increases the specific surface area and porosity of biochar, but also increases the number of -OH and -COOH of biochar.

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