

Study on Characteristics of Ammonium Nitrogen Adsorption by Biochar Prepared in Different Temperature

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Abstract. A model was prepared for the preparation of biochar from the biomass of mushroom residue at different carbonization temperature (350 °C, 450 °C and 550 °C) for adsorption characteristics of ammonium nitrogen in water through different ammonium nitrogen concentration, reaction time, pH and temperature. The investigation result showed that the adsorptive amount of these three biochar substances increased quickly with the initial concentration (0-2 h) and the adsorption equilibrium was reached after 4 hours. The adsorptive amount of these three biochars increased with the rise of pH from 5 to 9. Different temperature preparation of biochar on ammonium nitrogen adsorption increases with the rise of temperature. Different temperature preparation of biochar on ammonium nitrogen adsorption amount is in the order of 550 °C biochar > 450 °C biochar > 350 °C biochar.

Introduction

Biochar is produced by pyrolysis under hypoxia and relatively low temperature (<700 °C) from biomass such as wood, crop waste, plant tissue and animal manure and is a source of agricultural waste utilization^[1-3]. Common biochars include straw charcoal, charcoal, bamboo charcoal, peanut shell charcoal, rice husk charcoal and so on^[4-5]. These are composed of mainly aromatic hydrocarbon and elemental carbon or graphite structure of carbon composition, containing more than 60% of the carbon, H, O, N, S and a small amount of trace elements^[6]. The biochar is a kind of porous structure material has a large specific surface area for adsorption^[7]. The present study is generally accepted that biochar is super absorbent of hydrophobic organic pollutants. Biochar can strongly adsorb phenol, polycyclic aromatic hydrocarbons, organic dyes, herbicides, pesticides, and other organic pollutants, and can significantly reduce the mobility of organic pollutants and biological effectiveness of certain heavy metals^[8-11]. Also biochar have ability of adsorption of Hg²⁺, As³⁺, Pb²⁺, Cd²⁺ and has good effect in passivation of heavy metals in the soil^[12-14].

Although biochar has good effect in the removal of heavy metals and organic pollutants, but the study of biochar on the ammonium nitrogen adsorption characteristics is little reported^[15]. Thus preparation of biochar for the utilization of agricultural wastes and waste water treatment, research on the adsorption of ammonium nitrogen in water under the influence of different factors such as ammonium nitrogen concentration, reaction time, pH value and temperature, provide theoretical reference and technical support.

Material and Methods

Experimental Material

Biochar preparation^[16]: Clean mushroom residue was air-dried(80°C), crushed and sieved(0.83mm) before their use. The material was put into 30ml ceramic crucible, when full-up, compacted and covered, after which, heated at 350 °C,450 °C and 550 °C for 4 hours in a muffle, then allowed to cool to room temperature naturally, remove standby.

Table.1 Physical and chemical properties of mushroom residue biochar.

Material	C (%)	N (%)	Specific area (m ² /g)	pH
350 °C biochar	58.31	1.11	6.43	7.35
450 °C biochar	64.38	1.08	8.93	7.96
550 °C biochar	70.05	1.27	12.02	8.22

Determine the content of element C,N by Vario EL III elementary analyzer(Elementar Co. German);Determine the specific area by specific surface area instrument SA3100,(Beckman Co. USA);Determine the pH by precise pH meter PHS-3C,(Shanghai precision scientific instrument co., LTD).

Experiment Instruments

Electronic analytical balance (ALC-210.4, Sartorius, German),Miniature plant mill(FZ102,Tianjin Tester instrument Co.,LTD),Thermostatic blast drying oven(101-2AS, Beijing Yongguangming medical instrument plant),Precision acidity meter(PHS-3C,Shanghai precision scientific instrument co.,LTD),Water-bathing constant temperature vibrator(SHZ-A, Shanghai Yuejin Medical Machinery),Specific surface area instrument(SA3100, Beckman Co. USA),Elementary analyzer(Vario EL III , Elementar Co. German),Ultraviolet Spectrophotometer(UV-2802, Shanghai Unico Instrument Co., LTD),Milipore(MILLI-Q, MILLIPORE Co., USA).

Experimental Methods

Adsorption Isotherm

0.500g biochar was weighted into centrifuge tubes (50ml) mixed with 15ml NH₄Cl solution containing diverse concentrations (10, 20, 30, 40, 50, 60mg/L). Repeat 3 times. The samples were shaken for 4 hours at a constant temperature of 25°C and centrifuged at 4000r/min for 10min, after which, a determined concentration of ammonium nitrogen by Nessler's reagent colorimetric method in supernatant was added through 0.45µm Millipore filter . According to the concentration difference of adsorption, to calculate sorbent of ammonium nitrogen, the equation as follow^[17]:

$$q = (C_0 - C_e) V / M.$$

q: adsorption of ammonium nitrogen by biochar per unit mass(mg/kg),C₀: ammonium nitrogen initial concentration (mg/L),C_e: ammonium nitrogen equilibrium concentration (mg/L) ,V: bulk(mL),M: weight of biochar(g).

Effects of time on ammonium nitrogen adsorption by biochar

Add 0.500g biochar and 15ml NH₄Cl solution (initial ammonium nitrogen concentration is 30mg/L) into the centrifuge tubes(50mL). Whilst being shaken at a constant temperature of 25°C take one tube every 2 hours, centrifuged at 4000r/min for 10min, then determine the concentration of ammonium nitrogen by Nessler's reagent colorimetric method in supernatant through 0.45µm Millipore filter. According to the concentration difference of adsorption, calculate the sorbent of ammonium nitrogen.

Effects of pH on ammonium nitrogen adsorption by biochar

Add 0.500g biochar and 15ml NH₄Cl solution (initial ammonium nitrogen concentration is 30mg/L) into centrifuge tubes(50mL), alter the pH respectively, and shake the samples at pH: 5, 6, 7, 8 and 9 for 4 hours(constant temperature 25°C), after which, centrifuge at 4000r/min for 10min, determine the concentration of ammonium nitrogen by the Nessler's reagent colorimetric method in supernatant through a 0.45µm Millipore filter. Calculate sorbent of ammonium nitrogen accordance with concentration difference of adsorption.

Effects of temperature on ammonia nitrogen adsorption by biochar

Mix 0.500g biochar and 15ml NH_4Cl solution (initial ammonium nitrogen concentration is 30mg/L) into centrifuge tubes(50mL), shake them for 4 hours at 35, 45 and 55°C, centrifuge at 4000 r/min for 10min, determine the concentration of ammonium nitrogen by the Nessler's reagent colorimetric method in supernatant through a 0.45 μm Millipore filter. Calculate sorbent of ammonium nitrogen accordance with concentration difference of adsorption.

Results and discussion

Biochar adsorption of ammonium nitrogen adsorption isotherm

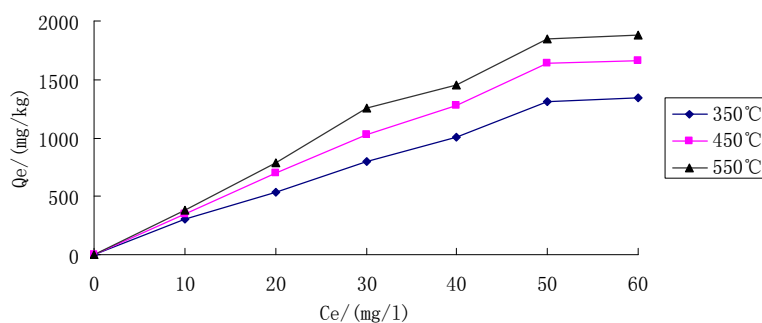


Fig.1 Effect of initial concentrations on biochar adsorption to ammonium nitrogen

Figure 1 shows the biochar prepared at different temperatures ammonium nitrogen adsorption isotherms. The figure shows that biochar is closely related to the mass concentration of the ammonium adsorption capacity and its equilibrium liquid at different temperatures prepared biochar performance of ammonium adsorption capacity increases with the increase in the concentration of equilibrium solution quality. Balance fluid mass concentration is lower, biochar adsorption quantity increases with mass concentration quickly, but when the balance of fluid mass concentration increased to a certain value, the adsorption quantity of the final balance slower with the increase of mass concentration. Among them, 550°C biochar adsorption of ammonium nitrogen adsorption capacity and adsorption rate is highest, may be related to its bigger than surface area.

Effect of time on biochar adsorption to ammonium nitrogen

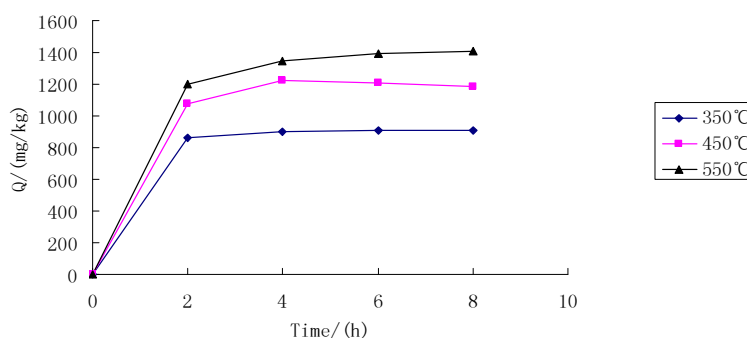


Fig.2 Effect of time on biochar adsorption to ammonium nitrogen

Determination of the reaction equilibrium, time is very important for the conduct of the adsorption kinetics and adsorption isotherms. The different oscillation time impact on biochar adsorption to ammonium are shown in Figure 2. In the initial stage (0-2h) the adsorption amount is rising rapidly. Biochar adsorption rate of ammonium slows down with the ongoing adsorption reaction. There are small changes in the amounts of adsorption after 864.91mg/kg, 1079.32mg/kg, 1201.35mg/kg and biochar ammonium adsorption after 4h is stable, basically reached a balance.

Effect of pH on biochar adsorption to ammonium nitrogen

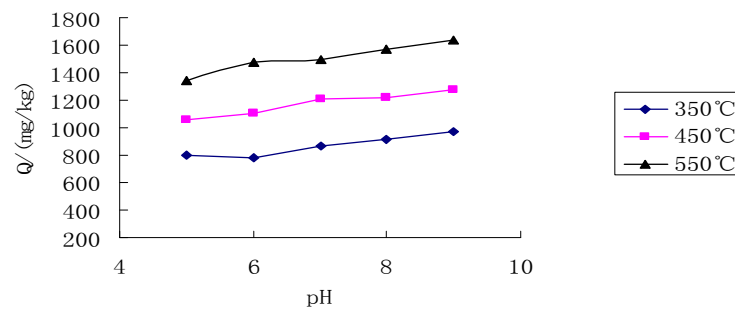


Fig.3 Effect of pH on biochar adsorption to ammonium nitrogen

Different temperature preparation of biochars on the adsorption of ammonium nitrogen under different initial pH changes as shown in figure 3. In the figure we can see that within the scope of the pH 5-9, biochar for solution of ammonium nitrogen adsorption quantity increases with initial solution pH and there was a trend toward increased slowly, but the amplitude is smaller. Initial solution pH had a greater influence on the adsorption of ammonium nitrogen. 550 °C biochar of ammonium nitrogen adsorption increased with the initial pH, adsorption capacity increased by 22% when pH 5 to pH 9. At low pH value, the concentration of H^+ is higher, NH_4^+ in biochar exchange positions form a competition relationship with H^+ , so the biochar for NH_4^+ adsorption rate is low. When pH values continue to rise, the amount of OH^- in water increased, NH_4^+ react with OH^- to form NH_3 . After the pH value reaching alkaline range, NH_4^+ and OH^- combine to form ammonium, concentration of NH_4^+ in the solution decreases gradually, leads to further reducing the concentration of NH_4^+ in water.

Effect of temperature on biochar adsorption to ammonia nitrogen

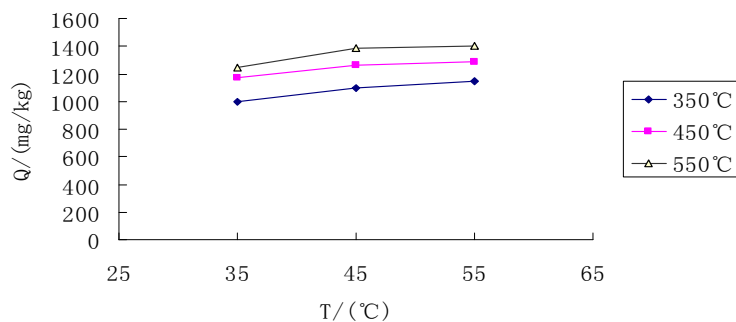


Fig.4 Effect of temperature on biochar adsorption to ammonium nitrogen

The influence of different temperature on biochar ammonium nitrogen adsorption is shown in figure 4. When the temperature rise from 35 °C to 55 °C, biochar adsorption quantity increases in the initial concentration of the solution and the reason is the higher the adsorption temperature, the greater the kinetic energy of NH_4^+ ion activity easier it into the holes in the surface of biochar increasing its adsorption quantity. Biochar adsorption quantity increases with the rising of temperature, 550 °C biochar > 450 °C biochar > 350 °C biochar indicate that different temperatures preparation of biochar type specific surface area, the higher the temperature, the greater the specific surface area and the stronger adsorption ability to ammonium nitrogen.

Conclusions

The adsorption rate of ammonium nitrogen of charcoal prepared at different temperature in the initial stage (0-2 h) is larger, the adsorption amount increased rapidly reached equilibrium after 4h. In the range of pH 5-9, the amount of biochar prepared at different temperature on ammonium nitrogen adsorption increases with the rise of pH. Different temperature preparation of biochar on ammonium nitrogen adsorption increases with the rise of temperature. Different temperature preparation of biochar on ammonium nitrogen adsorption amount is in the order 550 °C > 450 °C > 350 °C.

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