Effects of Environmental Conditions on Rice-straw Biochar Adsorption of Nitrate

Haitao Zhao, Tianpeng Li, Xu Yao, Zong Yu, Shengyang Zheng and Peijuan Wang

ABSTRACT

The overall aim of this study was to determine adsorption characteristics of nitrate on biochars in different environmental conditions. Biochars were produced from rice straws at 400°C, 600°C and 800°C, respectively. They were then divided into two particle sizes (1.91mm and 0.38mm). Laboratory batch sorption experiments were conducted to access the overall aqueous nitrate sorption ability of the biochars in different environmental conditions. Results showed that biochar produced at 400°C had the largest adsorption capacity for NO₃⁻-N, its removal rate of nitrate could be up to 88%. Particle size showed no significant effect on NO₃⁻-N adsorption. Biochars showed large variances on adsorption characteristics in different environmental conditions, such as contact time, initial NO₃⁻-N concentration and adsorbent dose. We concluded that 400°C rice-straw biochar can be used for NO₃⁻-N adsorption and recommended the contact time, initial NO₃⁻-N concentration, initial pH value and adsorbent dose for 12 h, 15 mg L⁻¹, 7 and 3g per 50ml, respectively.

INTRODUCTION

China is an agricultural country which is abundant in straw resource. As the most important crop in China, rice planting produces a large amount of straw every year [1]. Improper disposal of straw has caused serious air pollution and has a negative impact on the sustainable development of agriculture.

In recent years, researchers have recognized that the conversion into biochar is an effective solution to the straw resource for pyrolysis technology [2,3]. Biochar is a carbonaceous substance produced by pyrolysis of biomass under oxygen-limited conditions and at a relatively low temperature. It has a porous surface structure, high aromaticity, abundant negative surface charges and surface functional groups [4]. Due to its special structures and characteristics, biochar was reported to represent a good foreground in adsorption of heavy metal and organic contaminants [5, 6, 7].
Nitrogen (N) is an essential nutrient for plants and applying nitrate fertilizer could significantly promote root development. However, excessive application of N fertilizers has posed a serious threat to the environment. Leaching of nitrate from agricultural fields to aquatic systems may promote eutrophication in surface and groundwater [8]. Some studies showed that the amendment of biochar of soil could significantly reduce nitrate leaching [9]. Despite this, information is very limited to effects of preparation conditions and environmental conditions on rice-straw-biochar adsorption of nitrate.

The overall aim of this study was to determine adsorption characteristics of nitrate on biochars in different environmental conditions (including different durations, pH, nitrate concentrations and adsorbent dose). Biochars were produced from rice straws at 400°C, 600°C and 800°C, respectively. They were then divided into two particle sizes (1.91mm and 0.38mm). Laboratory batch sorption experiments were conducted to access the overall aqueous nitrate sorption ability of the biochars. These may help to achieve insights in utilization of biochar to adsorb nitrate and improve agricultural environment.

MATERIALS AND METHODS

Materials

Biochar samples were produced from rice straws collected from Yangzhou, China. Raw materials were cut into small pieces (30 cm) and oven-dried (105°C) for 8 hours. The straws were then converted into biochar through slow pyrolysis in an atmosphere furnace. To minimize oxygen content in reaction, a constant current of N₂ was passed through at the speed of 0.2L/min during heating stage. The pyrolysis temperature was raised to the aimed points of 400°C, 600°C and 800°C and held constant for 1 hour. After the cooling stage for 12 hours, biochar samples were then crushed into particle sizes of 10 and 40 meshes (1.91mm and 0.38mm, respectively). The resulting biochar samples were then referred to SN4-1 (400°C, 10meshes), SN4-4(400°C, 40meshes), SN6-1(600°C, 10meshes), SN6-4(600°C, 40meshes), SN8-1(800°C, 10meshes), and SN8-4(800°C, 40meshes).

Determination of Physical and Chemical Properties of the Biochars

Properties of biochar samples referred to nitrate adsorption were determined, including the BET surface area, BJH pore volume (ASAP2020 HD88, USA) and elemental C, H, N, S and O abundances (Vario EL cube, Germany). Surface functional groups of biochar samples were also analyzed by a micro infrared spectrometer (Varian Cary 610/670, USA).

The production rate was calculated as follow:

Production rate (%) = \( \frac{M_{\text{biochar}}}{M_{\text{biomass}}} \times 100 \)

Where, \( M_{\text{biochar}} \) is the mass of biochar and \( M_{\text{biomass}} \) is the mass of biomass used in pyrolysis.

Sorption Experiments

To investigate the ability of biochars to adsorb NO₃⁻-N, adsorption experiments were conducted by adding biochar samples to KNO₃ solution.
(1) Kinetics Study on NO₃⁻-N adsorption by biochars
   2g biochar was added to 50ml KNO₃ solution with concentration of 15mg NO₃⁻-N per liter. The mixture was then shaken in a thermostatic shaker at 25°C and 200 rpm for 1h, 3h, 6h, 12h and 24h, respectively, to achieve equilibrium. The supernatant was filtered and analyzed for concentrations of NO₃⁻-N by using UV spectrophotometer. The results of the determination were fitted by the pseudo first-order and pseudo second-order kinetic models.

(2) Effect of pH on biochar adsorption of nitrate
   2g biochar was added to 50ml KNO₃ solution with concentration of 15mg NO₃⁻-N per liter and then adjust the pH value to 3, 5, 7, 9 and 11, respectively. The mixture was then shaken in a thermostatic shaker at 25°C and 200 rpm for 12h to achieve equilibrium. The supernatant was filtered and analyzed for concentrations of NO₃⁻-N by using UV spectrophotometer.

(3) Effect of nitrate concentration on biochar adsorption of nitrate
   2g biochar was added to 50ml KNO₃ solution with concentration of 0mg, 5mg, 10mg, 15mg, 20mg and 25mg NO₃⁻-N per liter, respectively, and then adjust the pH value to 7. The mixture was then shaken in a thermostatic shaker at 25°C and 200 rpm for 12h to achieve equilibrium. The supernatant was filtered and analyzed for concentrations of NO₃⁻-N by using UV spectrophotometer.

(4) Effect of adsorbent dose on biochar adsorption of nitrate
   1g, 1.5g, 2g, 2.5g, 3g and 3.5g biochar were added to 50ml KNO₃ solution with concentration of 15mg NO₃⁻-N per liter, respectively, and then adjust the pH value to 7. The mixture was then shaken in a thermostatic shaker at 25°C and 200 rpm for 12h to achieve equilibrium. The supernatant was filtered and analyzed for concentrations of NO₃⁻-N by using UV spectrophotometer.

Calculation of Adsorption Capacity

The adsorption capacity was calculated as follow [10]:

\[ Q = \frac{(C_0 - C_e) \times V}{M} \]  

Where, Q is the amount of NO₃⁻-N adsorbed by a unit mass of biochar (mg/g) at equilibrium; C₀ and Cₑ are the NO₃⁻-N concentration in the initial and equilibrium solution (mg/L), respectively; V is the volume of the aqueous solution (L) and M is the mass of biochar (g).

Statistical Analyses

The results were expressed as means. Figures were plotted with the Origin 8.0 software. Statistical analysis was performed using SPSS 18.0. Significant differences were tested using Duncan’s multiple range test (P=0.05). Any differences between the mean values of P<0.05 were considered statistically significant.
RESULTS AND DISCUSSION

Biochar Properties

The properties and elemental composition of biochars are listed in Table 1. The biochar production rate decreased from 33.85% to 24.67% with the rise of temperature because of the greater loss of volatile constituents at the higher pyrolysis temperature [11]. As a result of the loss, positive correlation between BET surface area and pyrolysis temperature was discovered in the study, consistent with previous research [12, 13, 14]. The analysis of element revealed that carbon and oxygen were the dominate elements in biochars, 46.9%-53.3% and 12.9%-21.0%, respectively. As pyrolysis temperature increased from 400 °C to 800 °C, the content of carbon rose at first and then declined and the content of oxygen showed an opposite trend. The biochars in the study contained relatively small amount of sulfur and nitrogen.

The FT-IR spectrum indicated rice-straw biochar to be functional-group-rich as showed in Fig.1. The FT-IR spectrum of biochar at different pyrolytic temperatures showed significant differences between their characteristic peaks at different wave numbers, which is consistent with the study of Chen et al [15]. Band intensities at 3426 cm\(^{-1}\) represented –OH, whose absorption peaks decreased dramatically when the temperature rose and almost diminished at 800 °C. Similar findings were reported in previous studies [16]. The peak amplitude of Aromatic C=C and C=O at 1608 cm\(^{-1}\) rose at first and then declined, a similar trend appeared at 863 cm\(^{-1}\) in fingerprint spectrum, which reflected the change of Aromatic C-H. The absorption peaks around 1088 cm\(^{-1}\) characterize the C-O-C in biochars, which decreased significantly with rising temperature and the peak disappeared at 600 °C and 800°C. In general, the high temperature made more loss of aliphatic alkyl and hydroxyl, leading aromatic component of biochars to increase. However, aromatic substances began to decrease as the temperature kept rising and almost diminished at 800°C. These changes were also reflected in the ratio of elemental C and O (Tab.1).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Temp. (°C)</th>
<th>Production rate (%)</th>
<th>BET surface area (m(^2)·g(^{-1}))</th>
<th>Pore volume (ml·g(^{-1}))</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>400</td>
<td>33.85</td>
<td>1.02</td>
<td>0.0126</td>
<td>C: 46.90, H: 2.78, N: 0.61, S: 0.57, O: 20.96</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>27.69</td>
<td>2.57</td>
<td>0.0262</td>
<td>C: 53.28, H: 1.79, N: 0.49, S: 0.41, O: 12.87</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>24.67</td>
<td>3.07</td>
<td>0.2151</td>
<td>C: 48.130, H: 1.605, N: 0.355, S: 0.438, O: 16.486</td>
</tr>
</tbody>
</table>
Effect of Preparation Conditions on Biochar Adsorption of Nitrate

The effects of preparation conditions on biochar adsorption of NO$_3^-$-N are illustrated in Fig.2, 3, 4, 5. Within all the treatments, SN4 (biochars produced at 400 °C) had a significantly greater NO$_3^-$-N sorption ability than other two samples. And the results showed a slight difference between SN6 and SN8 while SN8 had a slender lead on adsorption capacity in a given environmental condition. It is generally accepted that increase in pyrolysis temperature may improve the sorption ability of biochars to aqueous nitrate because of the higher aromaticity, weaker polarity and higher specific surface areas[17, 18, 19]. However, results in this study showed biochars made at a relatively lower temperature (400 °C) had the strongest adsorption capacity. The relatively poor thermal stability of rice straw and abundant organic groups in SN4 biochar may be the major factors. The consumption of these rich organic groups was accompanied with the increase of pyrolysis temperature (Fig.2). And a higher specific surface area may contribute to the slight difference of adsorption capacity between SN6 and SN8 biochar (Tab.1).

It can be seen in the figures that grinding process had little effect on adsorption of NO$_3^-$-N, especially for SN6 and SN8 biochars. The grinding process made a little reduction on sorption ability of SN4 biochar due mainly to the decline of adsorption sites on its surface. However, the difference was insignificant, which is consistent with the study of Xu et al [20].
Kinetics Study on NO$_3$-N Adsorption by Biochars

The Kinetic curves of NO$_3$-N on rice-straw biochars are presented in Fig.2. It is clear that SN4 and SN8 biochars had similar sorption isotherms of NO$_3$-N. During the previous 6-hour adsorption period, a high rate of adsorption was found and the adsorption capacity had achieved over 75% of adsorption equilibrium. A similar result was also reported by Öztürk et al [21], they considered that the reason for the high speed was the existence of abundant surface adsorption points in the early period. These points provided a large number of sites for NO$_3$-N adsorption on biochar. However, these points decreased gradually with the increase of time, which slowed down the rate of adsorption. It took about 12 hours to reach adsorption equilibrium for both SN4 and SN8 biochar.

In order to study the controlling mechanisms of the adsorption process, the results of the determination were fitted by the pseudo first-order and pseudo second-order kinetic models.

A simple kinetic analysis of adsorption is the pseudo-first-order differential equation [22, 23].

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

where $q_e$ and $q_t$ are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time $t$ (h), respectively, and $k_1$ (l/h) is the rate constant of first-order adsorption.

The pseudo-second-order model can be expressed in the form [22, 23]

$$\frac{t}{q_t} = \left( \frac{1}{K_2 q_e^2} \right) + \left( \frac{1}{q_e} \right) t$$

where $q_e$ and $q_t$ are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time $t$ (h), respectively, and $k_2$ is the pseudo-second-order rate constant ($g \cdot (mg^{-1} \cdot h^{-1})$).

Kinetic parameters for adsorption-rate expressions of NO$_3$-N on biochar are listed in Tab.2. Both the pseudo first-order and pseudo second-order kinetic models fitted well with NO$_3$-N adsorption on SN4 biochar and the fitting effect of pseudo second-order kinetic models was better as shown in the table, which indicates that NO$_3$-N adsorption on SN4 biochar was a complex process including physical and chemical adsorption while the chemical adsorption played a dominate role in the
whole adsorption process. The phenomenon answered the description of abundant organic groups in SN4 biochar (Fig.1). Conversely, for SN8 biochar, the adsorption of NO$_3^-$-N was mainly the physical one due to its high specific surface area (Tab.1) and the great loss of organic groups at a high temperature (Fig.1). The kinetic parameters also showed that biochars produced at 600 °C had negligible adsorption ability of nitrate nitrogen.

**TABLE 2. KINETIC PARAMETERS FOR ADSORPTION-RATE EXPRESSIONS OF NO$_3^-$-N ON RICE-STRAW-BIOCHAR.**

<table>
<thead>
<tr>
<th>biochar</th>
<th>pseudo-first order kinetic model</th>
<th>pseudo second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\ln(q_e - q_t) = \ln q_e - K_1 t$</td>
<td>$\frac{t}{q_t} = \left( \frac{1}{K_2 q_e^2} \right) + \left( \frac{1}{q_e} \right) t$</td>
</tr>
<tr>
<td>q$_e$</td>
<td>K$_1$</td>
<td>R$^2$</td>
</tr>
<tr>
<td>SN4-1</td>
<td>25.710</td>
<td>0.651</td>
</tr>
<tr>
<td>SN4-4</td>
<td>24.465</td>
<td>0.863</td>
</tr>
<tr>
<td>SN6-1</td>
<td>0.665</td>
<td>32.034</td>
</tr>
<tr>
<td>SN6-4</td>
<td>0.878</td>
<td>23.209</td>
</tr>
<tr>
<td>SN8-1</td>
<td>3.071</td>
<td>0.261</td>
</tr>
<tr>
<td>SN8-4</td>
<td>3.358</td>
<td>0.221</td>
</tr>
</tbody>
</table>

**Effect of Environmental pH on Biochar Adsorption of Nitrate**

The sorption curves of NO$_3^-$-N on rice-straw biochar at different pH values are presented in Fig.3. In general, effects of initial pH values on nitrate sorption were insignificant. However, a slight fluctuation occurred in the adsorption process as initial pH value changed, especially on SN4-1 biochar. With the rise of initial pH value, adsorption capacity increased constantly until the pH value reached 7. It is opposite to the findings of previous studies, which reported that treatment of biochars with acid tends to produce positive sites on the biochars, by protonation of surface -OH groups that would cause an increase in electrostatic adsorption of anions. Reason for the results in this study could probably be the formation of the hydrogen bond by undiscouraged carboxylic groups and alkyl carbon chains at a relatively low pH value, which strengthened its stability and led to the decline of adsorption capacity. However, corresponding mechanism was still unclear and further studies are needed. After the peak value, adsorption capacity began to decrease because the rise of negative charge density on biochar surface strengthened the electrostatic repulsion, which inhibited the adsorption of anions, for example, nitrate.
Effect of Nitrate Concentration on Biochar Adsorption of Nitrate

The sorption isotherms of NO$_3^-$-N on rice-straw biochar at different initial nitrate concentrations are presented in Fig. 4. It is clear that biochars released nitrate in deionization (DI) water (0mg NO$_3^-$-N per liter). SN4 biochar released much more NO$_3^-$-N than the other two ones for lower loss of N (Tab.1). Adsorption capacity by SN4 biochar increased dramatically and peaked at 0.227 mg g$^{-1}$ in the solution of 15mg NO$_3^-$-N per liter. There was then a slight downward trend when the concentration continued to climb, consisted with Liu’s study on Pb$^{2+}$ and Cd$^{2+}$ adsorption by biochar [24]. It suggested that SN4 biochar reached adsorption saturation at that point and desorption occurred in following process. SN8 biochar adsorption had a similar trend with a more significant desorption. It is because SN8 biochar adsorption was a physical adsorption (Tab.2) which is a reversible process [25]. Compared with SN4 and SN8 biochars, there was almost no response of SN6 biochar to concentration change as showed in the figure.
Effect of Adsorbent Dose on Adsorption of Nitrate

Effects of adsorbent dose on adsorption of NO$_3^-$-N by rice-straw biochar are presented in Fig.5 and Fig.6. As the increase of biochar application amount, a significant rise occurred in NO$_3^-$-N removal rate in a given environmental condition by SN4 biochar, from 46% to 88%. However, the adsorption capacity of NO$_3^-$-N by a unit mass of biochar decreased as showed in Fig.6. This illustrated the great regularity of SN4 biochar structure and its homogeneous distribution in adsorption[26]. There was no significant difference between NO$_3^-$-N removal rate of 3g and 3.5g biochar added as the adsorption equilibrium was achieved when adsorbent dose reached 3g.

The NO$_3^-$-N removal rate by SN6 biochar increased slightly and its adsorption capacity was almost unchanged, which demonstrated its weak sorption ability of NO$_3^-$-N. There was no significant difference between treatments using SN8 biochar. It was probably because the Van der Waals force became so weak that the adsorption cannot continue in a relatively low concentration of NO$_3^-$-N solution in spite of the increase of biochar application amount. Further studies are needed in this regard to fully understand the exact mechanisms.
CONCLUSION

Pyrolysis temperature had a great effect on the biochar chemical and physical characteristics, which further influenced NO$_3^-$-N adsorption ability of the biochars. Biochar produced at 400°C had the largest adsorption capacity for NO$_3^-$-N. Particle size showed no significant effect on NO$_3^-$-N adsorption. Biochars showed large variances on adsorption characteristics in different environmental conditions.

Therefore, we concluded that 400°C rice-straw biochar can be used for NO$_3^-$-N adsorption. According to this study, we recommended the contact time, initial NO$_3^-$-N concentration, initial pH value and adsorbent dose for 12 h, 15 mg L$^{-1}$, 7 and 3g per 50ml, respectively.

REFERENCES