https://doi.org/10.17221/276/2020-PSE

Adsorption and leaching characteristics of ammonium and nitrate from paddy soil as affected by biochar amendment

*Rujie Lv, Yong Wang, Xiuxia Yang, Yangping Wen, Xueming Tan, Yongjun Zeng, Qingyin Shang**

Ministry of Education and Jiangxi Key Laboratory of Crop Physiology, Ecology and Genetic Breeding, Jiangxi Agricultural University, Nanchang, P.R. China

**Corresponding author: qyshang@jxau.edu.cn*

Citation: Lv R.J., Wang Y., Yang X.X., Wen Y.P., Tan X.M., Zeng Y.J., Shang Q.Y. (2021): Adsorption and leaching characteristics of ammonium and nitrate from paddy soil as affected by biochar amendment. Plant Soil Environ., 67: 8–17.

Abstract: Biochar plays a key role in nitrogen cycling, potentially affecting nitrogen adsorption and leaching when applied to soils. The laboratory experiments were conducted to investigate the adsorption characteristics of rice straw biochar (RSBC) to ammonium (NH_4^+) and nitrate (NO_3^-) and the influence of RSBC on leaching characteristics of NH_4^+ and NO_3^- at different soil depths using multi-layered soil columns. The results showed that the adsorption characteristics were significantly fitted with Freundlich and Langmuir adsorption isothermal curve models. The Freundlich isotherm model indicated that RSBC has relatively higher adsorption capacity and adsorption intensity to NH_4^+ than NO_3^-. Moreover, the Langmuir isotherm model showed that the maximum adsorption capacity of RSBC to NH_4^+ and NO_3^- were 31.25 and 10.00 mg/g, respectively. The leaching experiments showed that the contents of NH_4^+ in the leachates from the soil columns showed significant differences at different depths depending on the application amount of RSBC. Compared with CK (0% RSBC amendment), the overall cumulative losses of NH_4^+ *via* leaching were decreased by 23.3, 35.1 and 13.7% after adding 2, 4 and 6% RSBC, respectively. Correspondingly, the contents of residual soil NH_4^+ in the soil column were increased significantly with the RSBC amendment at different depths. However, the losses of NO_3^- *via* leaching from the soil columns could not be retarded obviously by RSBC. Therefore, the application of an appropriate biochar rate is beneficial to retard the losses of soil NH_4^+ from paddy soil.

Keywords: N form; N leaching loss; inorganic fertiliser; nutrient; pollution; flooded condition

Nitrogen (N) is the basis of rice biomass accumulation, which plays an important role in yield formation (Huang et al. 2018, Wang et al. 2019). The world increasingly depends on inorganic fertiliser to meet the needs of a growing population for food production (Lal 2004, Bouwman et al. 2013). However, excessive N fertiliser and improper application methods not only increase input costs but also result in low N-use efficiency, high fertiliser losses through nitrate leaching and surface runoff (Hu et al. 2018), leading to a seriously polluted environment (Sun et al. 2019). Therefore, it is urgent to find an effective way to reduce nitrogen loss.

Biochar was considered as a potentially applicable material to mitigate nitrogen leaching (Gai et al. 2014). Biochar is the product of thermal degradation of organic materials in the absence of air (pyrolysis) (Lehmann et al. 2011). Biochar not only has a highly porous structure (Lin et al. 2012), but also a high specific surface area and a number of polar or nonpolar substances, which has a strong affinity to inorganic ions such as heavy metal ions, phosphate, and nitrate (Kammann et al. 2015, Schmidt et al. 2015). Many studies showed that biochar had the potential to absorb nutrients. The nitrate (NO_3^-) adsorption capacity of bamboo biochar at 900 °C was

---

Supported by the National Natural Science Foundation of China, Grant No. 31960626; by the National Natural Science Foundation of China, Grant No. 31601833, and by the National Key Research and Development Project, Project No. 2017YFD0301605.

about 1.2 mg/g (Mizuta et al. 2004). Yao et al. (2012) indicated that biochar effectively absorbed ammonium (NH_4^+) and NO_3^- by 3.7% and 15.7%. But some studies oppositely shown that biochar had limited or no adsorption capacity for NO_3^- (Hollister et al. 2013). The mechanisms attributed to adsorption of NH_4^+ onto biochar surface include: NH_4^+ reacting with acidic functional groups to form amides and amines (Spokas et al. 2011); attracting to negatively charged surfaces (Zheng et al. 2013); binding to cationic species sites on the surface of biochars (Hale et al. 2013); and π-π electron donor-acceptor interactions (Zhu and Pignatello 2015). Ding et al. (2010) indicated that the application of biochar reduced overall cumulative losses of NH_4^+ *via* leaching by 15.2% at 20 cm depth. Among the columns applied with manure, the 20 g/kg biochar treatments reduced total N by 11% (Laird et al. 2010). However, the adsorption of soil nitrogen was not permanent. Zhang et al. (2015) demonstrated that the desorption of NH_4^+ in biochar was greater than activated biochar, which ranged from 18% to 31%. The desorption of NO_3^- in activated biochar treatment at 4–5 mg/L was higher than that at 0–4 mg/L. In addition, Ding et al. (2016) proposed that biochar had great potential as a slow-release fertiliser.

In rice production, excessive use of nitrogen fertiliser causes a large amount of nitrogen leaching, leading to environmental pollution. At the same time, the burning of rice straw seriously pollutes the environment. Adding rice straw biochar (RSBC) to the soil is expected to be a method to reduce nitrogen fertiliser pollution and straw pollution. However, the effect of adding RSBC on the adsorption and leaching of NH_4^+ or NO_3^- in paddy soil was rarely studied. Therefore, the laboratory experiments were conducted to investigate the adsorption capacity and the leaching characteristics of NH_4^+ and NO_3^- at different soil depths as affected by RSBC using multi-layered soil columns. The results of this study will provide a new theoretical basis for RSBC to reduce nitrogen fertiliser leaching, improve nitrogen fertiliser utilisation efficiency and mitigate nitrogen fertiliser pollution.

MATERIAL AND METHODS

Characterisation of soil and RSBC. The experimental soil was sampled from 0–20 cm plow layers of paddy field in Jiangxi Agricultural University (28°55'N, 115°94'E), Nanchang city, Jiangxi province, China. The soil was air-dried, passed through a 2 mm sieve, and mixed to get a homogeneous sample used in the column experiments. The RSBC used in this study were purchased from Sanli New Energy Company, Henan, China. Rice straw was collected by a cutting tractor, then shipped to and air-dried in the production plant. Pyrolysis of rice straw was performed in a vertical kiln at 550 °C, converting 35% of the biomass to biochar. The RSBC passed through a 1 mm sieve. The characteristics of the experimental soil and the RSBC are shown in Table 1.

Adsorption experiments. In order to investigate the ability of RSBC to adsorb NH_4^+ and NO_3^-, ammonium chloride (NH_4Cl) and potassium nitrate (KNO_3) were selected to obtain the adsorption isotherm in a closed system. The adsorption experiments were carried out in a series of 200 mL conical flasks containing 50 mL of NH_4^+ (or NO_3^-) solutions and 0.2 g RSBC. Specifically, 50 mL of NH_4^+ (or NO_3^-) solutions with different concentrations (10, 30, 50, 70, 100, 150, 300 and 500 mg/L) were selected and their actually initial concentration (C_0) determined by continuous flow analyser (San^{++}, Skalar, Delft, the Netherlands)

Table 1. Characteristics of the tested soil and rice straw biochar

Soil		Rice straw biochar			
Density (g/cm^3)	1.2	density (g/cm^3)	0.80	surface area (m^2/g)	120.0
pH_{H_2O}	5.2	pyrolysis temperature (°C)	550	pH_{H_2O}	10.3
Organic C (g/kg)	23.4	pore size (nm)	3.5	CEC (cmol$_+$/kg)	4.5
Total N (g/kg)	2.37	C (%)	50.5	EC (mS/cm)	110.5
NH_4^+-N (mg N/kg)	0.27	N (%)	0.86	ash content (%)	26.6
NO_3^--N (mg N/kg)	9.8	P (%)	0.24	Ca (%)	6.8
Available P (mg/kg)	24.4	K (%)	2.0	Mg (%)	0.38
Available K (mg/kg)	179.0				

CEC – cation exchange capacity; EC – electrical conductivity after completely shaken in a thermostatic shaker at 25 °C and 200 rpm for 24 h. After that, 0.2 g RSBC was added to the NH_4^+ (or NO_3^-) solutions, and the mixture was shaken in the thermostatic shaker at 25 °C and 200 rpm for 24 h to achieve adsorption equilibrium. Then, the mixtures were placed into a centrifuge with a speed of 3 000 rpm for 10 min to separate the solid from the solution. The NH_4^+ (or NO_3^-) concentration of the solution sample taken from the flasks was determined by a continuous flow analyser after filtered through a 0.45-μm membrane. For statistical analysis, including the assessment of experimental errors, all experiments were performed in triplicate. The amount of NH_4^+ (or NO_3^-) adsorbed on the RSBC was calculated as the difference between the original NH_4^+ (or NO_3^-) concentration and the remaining aqueous concentration at equilibrium. The amount of NH_4^+ (or NO_3^-) adsorbed per unit mass of RSBC was calculated as Eq. (1) (Ok et al. 2007):

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

where: Q_e (mg/g) – amount of NH_4^+ (or NO_3^-) adsorbed by RSBC at equilibrium; C_0 and C_e (mg/L) – initial and equilibrium concentration of NH_4^+ (or NO_3^-), respectively; V (L) – volume of the aqueous solution; M (g) – mass of RSBC.

The NH_4^+ (or NO_3^-) sorption data were fitted to linear Freundlich and Langmuir models, which are the most frequently used models to describe adsorption isotherms. The Freundlich adsorption model is as Eq. (2) (Gai et al. 2014):

$$\ln Q_e = 1/n \ln C_e + \ln K_F \quad (2)$$

where: K_F (mmol/g) and n – experimentally derived constants; K_F – adsorption capacity of the adsorbent; n – degree of favourable of the adsorption process (Araújo et al. 2018). 1/n ranges between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity. A lower 1/n value indicates a greater degree of heterogeneity on the biochar surface.

The Langmuir isotherm model assumes homogeneous monolayer surface sorption, which can be written as Eq. (3) (Ding et al. 2010):

$$C_e/Q_e = C_e/Q_m + 1/(Q_m K_L) \quad (3)$$

where: Q_m (mg/g) – maximum adsorption capacity of RSBC; K_L (L/mg) – Langmuir constants related to the adsorption capacity and adsorption rate. When C_e/Q_e is plotted against C_e, a straight line with a slope of $1/Q_m$ and an intercept of $1/(Q_m K_L)$ is obtained.

Leaching experiments. Figure 1 is the schematic diagram of the multi-layer soil column device improved by referring to the previous research methods (Ding et al. 2010, Gai et al. 2014). Each column had an inner diameter of 10 cm, a height of 52 cm, and four sampling ports (including three tube sections and one tap) at different heights from the top, experimentally representing four soil depths in a profile of 10, 20, 30, and 40 cm (Figure 1). The three separated sections could be well joined and sealed during an experiment. Each section had a small hole drilled in the middle on the tube sidewall for extraction of soil leachate at different layers in the profile. A simple water container was used for supplying distilled water to the column to simulate leaching.

The soil column was filled with 6 cm of quartz sand, 40 cm of soil subsamples and 6 cm of water from the bottom to top. A 6-cm thick, acid-washed quartz sand layer was placed at the bottom of each column for filtration of soil leachate. The middle section of the column (0–40 cm soil profile was marked separately on the right side of the soil column) was filled with the < 2 mm air-dried and mixed soil subsamples according to the soil bulk density in the paddy field. However, the soil placed on the top 0–10 cm of the soil profile was subjected to one of the following treatments: (1) ammonium chloride and potassium nitrate application with 0% RSBC (*w*/*w*, designated as CK); (2) ammonium chloride and potassium nitrate application with 2% RSBC (*w*/*w*, adding 17.6 g biochar); (3) ammonium chloride and potassium nitrate application with 4% RSBC (*w*/*w*, adding 35.2 g biochar); (4) ammonium chloride and

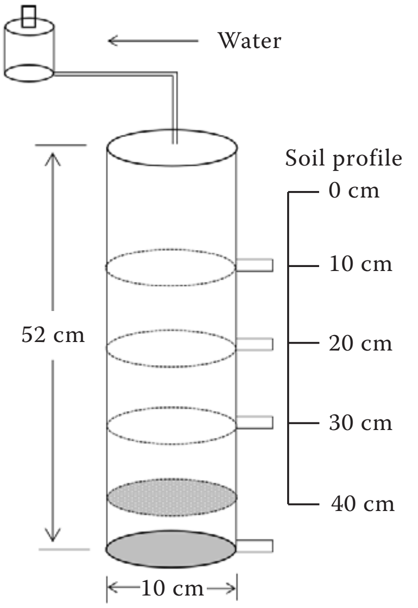

Figure 1. Schematic diagram of the multi-layer soil column device used in this study

potassium nitrate application with 6% RSBC (*w*/*w*, adding 52.9 g biochar), with four replicates for each treatment. The amount of N fertiliser used in the above treatments was the same, that was, ammonium chloride added at a rate of 0.29 mg N per g of soil and 256.4 mg N per column, and potassium nitrate added at a rate of 0.15 mg N per g of soil and 135.9 mg N per column. In addition, two layers of 2 mm nylon mesh were placed on the inner wall of each sampling ports. The leaching experiment was conducted at 25 ± 2 °C in the laboratory.

Before starting the nitrogen leaching experiment, 1 600.0 mL distilled water was added from the top over a period of 3 days in order to have a homogeneously moist soil column at field capacity. The total soil porosity and water holding capacity in the columns were about 55% and 45%. Distilled water was added and maintained a 6 cm water layer to simulate flooding status.

Sampling time and methods. Leachate samples were extracted at different depths in the soil column profile through sampling ports at 3 days in the initial stage and 7 days in the following stage. All the sampling ports were sealed when not sampled. The outlet of the upper three layers of soil was sealed when not sampled. Sealed the outlet of the upper three layers of soil when it was not sampled. Leachate samples were extracted at different depths in the soil column profile through each sampling port at 1, 7, 14, 21, 28 and 42 days. Leachates were collected about 30 mL and refrigerated at 4 °C for testing. The outlet of the upper three layers of soil was sealed when not sampled. Opened the bottom exit and received the leachates in a small-necked bottle. Recorded the extract volume on days 7, 14, 21, 28, and 42, shake evenly and remove 30 mL for analysis. At the end of the last leaching, the soil was removed from the soil column, and 50 g was taken out to be stored. All of the samples were stored in the dark at 4 °C in an icebox before analysis.

Determination of NH_4^+ and NO_3^- content. Soil NH_4^+ and NO_3^- were extracted after shaking for 60 min with 2 mol/L KCl followed by a 10-min standing and then filtered through quantitative filters. The leachates were filtered with quantitative filter paper. The NH_4^+ and NO_3^- contents of soil and leachates were determined using San^{++} Continuous flow analyser (Skalar, Delft, the Netherlands).

Statistical analysis. The results were expressed as means and standard deviations. Figures were plotted with the Origin 8.5 software (OriginLab, Northampton, USA). Statistical analysis was performed using the software of JMP, ver. 5.1 (SAS Institute, Cary, USA, 2003). Any differences between the mean values with $P < 0.05$ were considered statistically significant. Regression was used to evaluate the fitness of the prediction models to the experimental data in this study. The suitability of the model fitting was assessed using R^2 values and Akaike information criterion (AIC) values.

RESULTS

Adsorption of NH_4^+ and NO_3^- by RSBC. The equilibrium adsorption isotherms of NH_4^+ and NO_3^-, which are essential to understand the mechanism controlling the RSBC adsorption process, are presented in Figure 2. With the concentration of NH_4^+ (or NO_3^-) increasing in solution, the amount of them adsorbed by RSBC at equilibrium increased accordingly. The adsorption characteristics were significantly fitted with Freundlich and Langmuir adsorption isothermal curve models (Figures 3 and 4). NH_4^+ and NO_3^- absorption data can be introduced into the linear Freundlich and Langmuir models. The formulas of Freundlich and Langmuir models were shown below.

$$NH_4^+\text{: Freundlich } \ln Q_e = 0.300\ln C_e + 0.625;\ R^2 = 0.964 \quad (4)$$

$$\text{Langmuir } C_e/Q_e = 0.032C_e + 1.918;\ R^2 = 0.996 \quad (5)$$

$$NO_3^-\text{: Freundlich } \ln Q_e = 0.578\ln C_e + 0.186;\ R^2 = 0.910 \quad (6)$$

$$\text{Langmuir } C_e/Q_e = 0.100C_e + 2.308;\ R^2 = 0.997 \quad (7)$$

From the Freundlich model, we can see that NH_4^+ had a greater K_F value and lower 1/n value com-

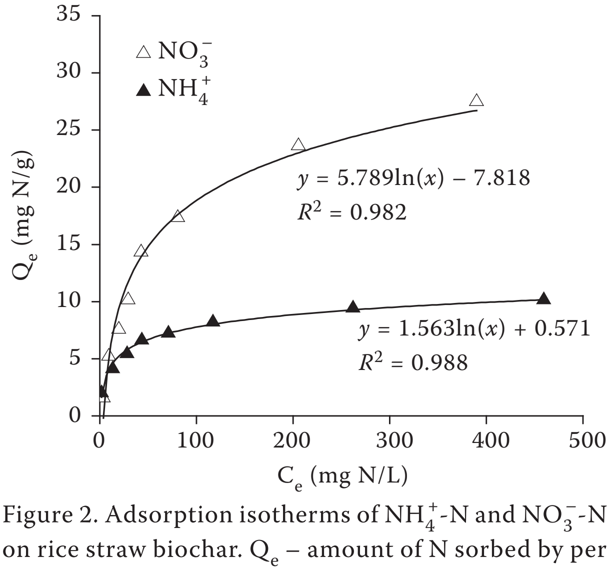

Figure 2. Adsorption isotherms of NH_4^+-N and NO_3^--N on rice straw biochar. Q_e – amount of N sorbed by per unit mass of biochar at equilibrium; C_e – concentration of N in the solution at equilibrium

https://doi.org/10.17221/276/2020-PSE

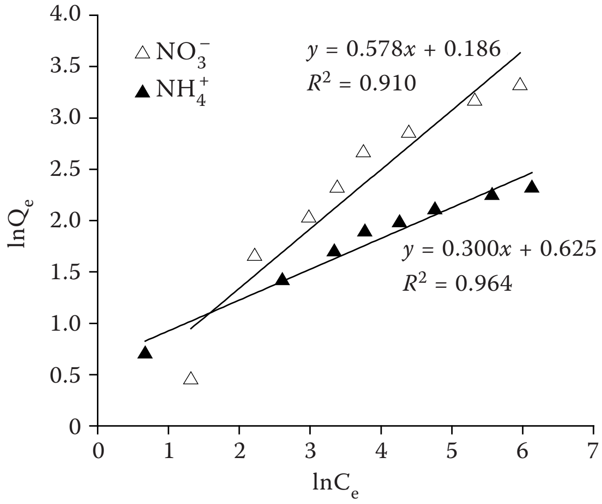

Figure 3. Linear plot of Freundlich isotherm of NH_4^+ and NO_3^- adsorption on biochar. Q_e (mg N/g) – amount of N adsorbed by rice straw biochar at equilibrium; C_e (mg N/L) – equilibrium concentration of N

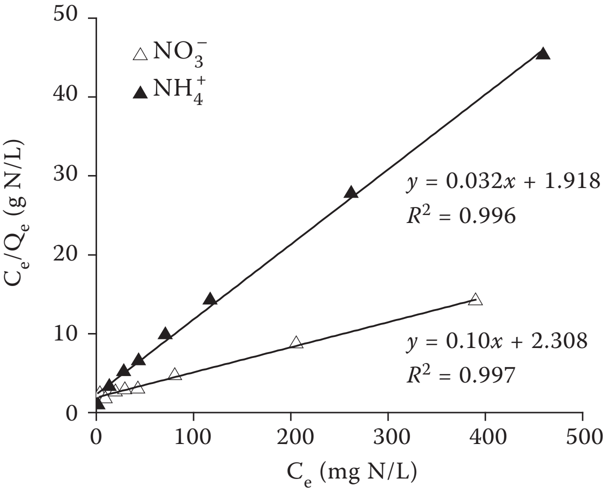

Figure 4. Linear plot of Langmuir isotherm of NH_4^+-N and NO_3^--N adsorption on biochar. Q_e (mg N/g) – amount of N adsorbed by rice straw biochar at equilibrium; C_e (mg N/L) – equilibrium concentration of N

pared with NO_3^- in the isotherm, which indicates that RSBC has relatively high adsorption capacity and intensity to NH_4^+. However, sorption of NH_4^+ and NO_3^- to RSBC was better fitted to the Langmuir isotherm model, with higher R^2 values than that of the Freundlich model. The maximum adsorption capacity of RSBC to NH_4^+ and NO_3^- were 31.25 and 10.00 mg/g, respectively.

Effect of RSBC on leaching of NH_4^+ from soil column. The maximum concentration of NH_4^+

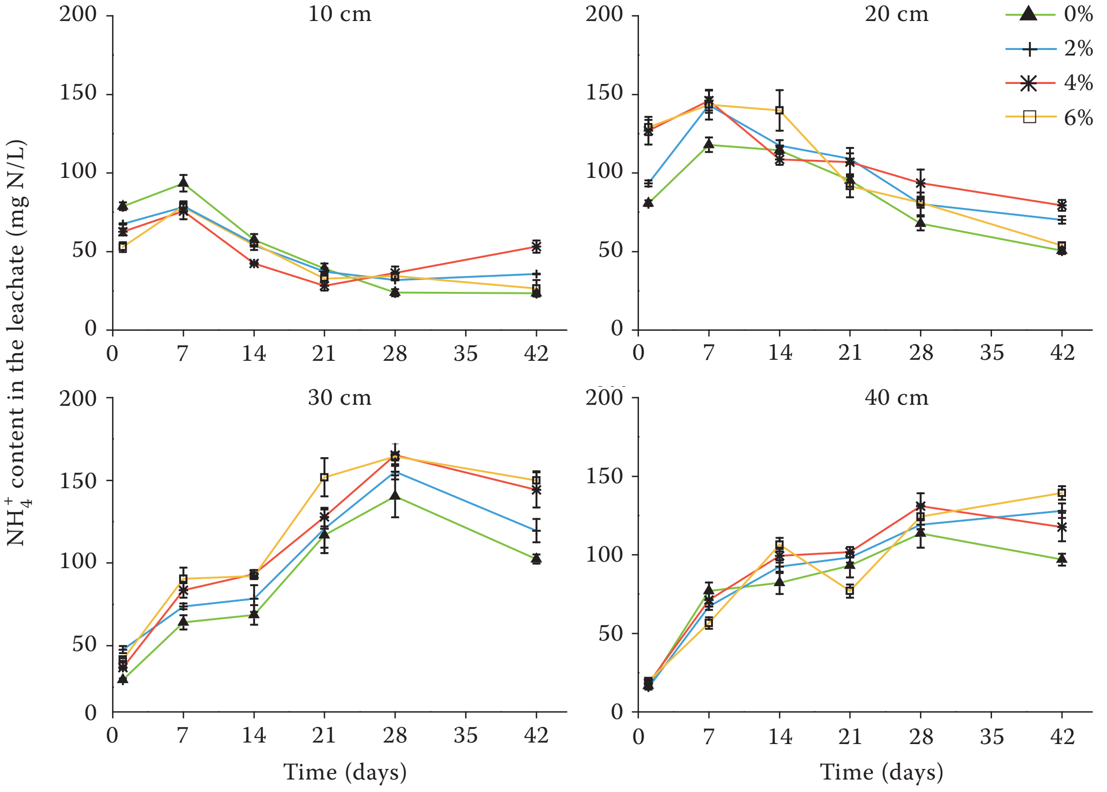

Figure 5. Temporal dynamics of NH_4^+-N content in the leachate from soil columns at 10, 20, 30 and 40 cm depths (treatment: adding 0, 2, 4 and 6% rice straw biochar, respectively)

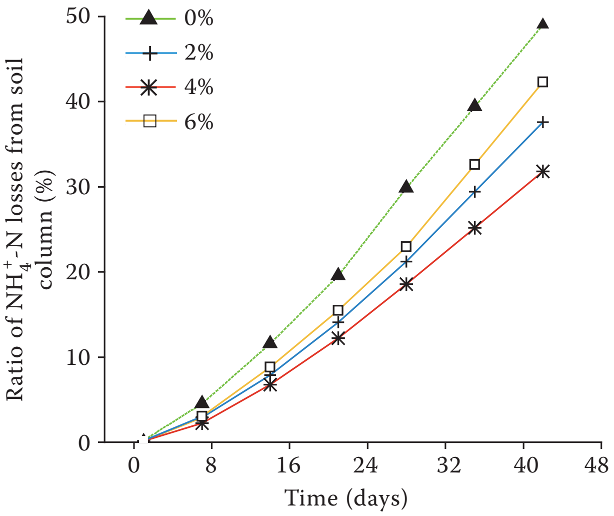

Figure 6. The ratio of cumulative losses of NH_4^+-N in the leachates from soil column with different biochar application rates (treatment: adding 0, 2, 4 and 6% rice straw biochar, respectively)

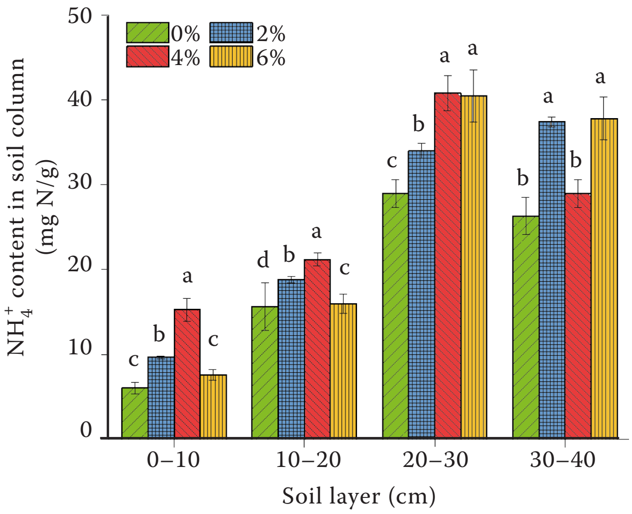

Figure 7. The content of NH_4^+-N per g of soil in soil column at different layers after the experiment (treatment: adding 0, 2, 4 and 6% rice straw biochar, respectively). Within a layer, values followed by different letters are significantly different at $P < 0.05$

leached from the soil column at 10, 20, 30, and 40 cm depths appeared on 7, 7 to 14, 28 and 28 to 42 days, respectively (Figure 5). During the first week of the experiment, compared with CK treatment (0% RSBC amendment), the NH_4^+ content leached from the soil column at 10 cm depth was decreased obviously by 14.3, 20.6 and 32.9% for the treatments with 2, 4 and 6% RSBC amendment (Figure 5). However, the NH_4^+ content in leachates from 10 cm depth declined rapidly for CK thereafter. Compared with CK, as a consequence, NH_4^+ content in the leachates from 10 cm depth increased by 52.0, 126.4, 13.0% for the treatments with 2, 4 and 6% RSBC amendment after the experiment, respectively. In terms of other soil depths, NH_4^+ content in leachates at most sampling days for the treatments with 2, 4 and 6% RSBC amendment was higher than that of CK treatment (Figure 5).

Compared with CK, the cumulative losses of NH_4^+ in the leachates from the soil column were decreased by 23.3, 35.1 and 13.7% after the experiment with 2, 4 and 6% RSBC amendment, respectively (Figure 6). Among treatments, there were significant differences in cumulative losses of NH_4^+ in the leachates during each sampling time (Table 2). These suggested that NH_4^+ leaching from soil can be significantly reduced with additional RSBC amendment.

The residual NH_4^+-N content ranged from 6.03 to 40.77 mg N/g among different treatments and layers of soil column (Figure 7). Compared with CK, the content of residual soil NH_4^+ was increased significantly for the treatment with biochar amendment in the soil column (except for 4% RSBC in 30–40 cm soil layer, and 6% RSBC in 0–10 cm and 10–20 cm soil layers). Particularly, the highest content of residual NH_4^+ in the soil column was observed in the treatment with 4% RSBC amendment (except for 30–40 cm soil layer).

Effect of RSBC on leaching of NO_3^- from soil column. The change of NO_3^--N content ranged from 1.14 to 2.94 mg N/L of the leachates at the 10, 20 and 30 cm depths. It varied from 115.97 mg N/L to

Table 2. Analyses of variance for the influence of different treatment on cumulative losses of NH_4^+-N and NO_3^--N in the leachates from soil columns

	df	Time (days)					
		1	7	14	21	28	42
NH_4^+	3	54.6**	81.3**	101.6**	136.5**	146.7**	444.6**
NO_3^-	3	1.00^{ns}	0.16^{ns}	0.15^{ns}	0.13^{ns}	0.11^{ns}	0.08^{ns}

$^*P < 0.05$; $^{**}P < 0.01$; ^{ns}non-significant

https://doi.org/10.17221/276/2020-PSE

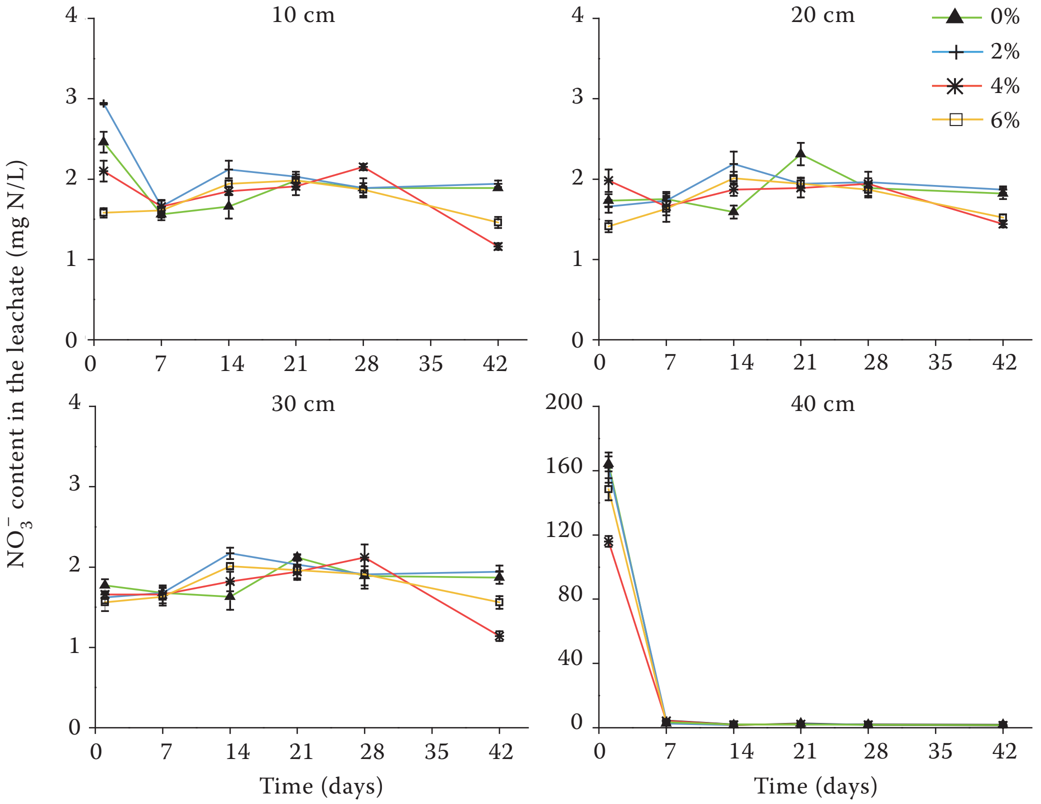

Figure 8. Temporal dynamics of NO_3^--N content in the leachate from soil column at 10, 20, 30 and 40 cm depths (treatment: adding 0, 2, 4 and 6% rice straw biochar, respectively)

164.27 mg N/L during the first week at 40 cm depth, while then gradually decreased to background levels (Figure 8). As a result, the cumulative loss of NO_3^--N from the soil column in all treatments almost all occurred in the first week (Figure 9). In addition, there were no differences in cumulative losses of NO_3^--N among treatments during each sampling time (Table 2). It suggested that the addition of RSBC had no significant effect on the NO_3^- leaching from the soil. The residual value of NO_3^- content ranged from 0.34 to 0.54 mg/g at the four soil layers. There was no difference between the 2% treatment and CK for the four soil layers, but they were obviously higher than 6% and 4% treatments (except for 6% treatment at 30–40 cm soil layer).

DISCUSSION

Adsorption characteristics of NH_4^+ and NO_3^- in solution by biochar. In most soils, NH_4^+ and NO_3^- are the predominant sources of nitrogen available for plant nutrition. Biochar was considered as a potentially applicable material to mitigate nitrogen leaching. The equilibrium adsorption isotherms of NH_4^+ (or NO_3^-), which are essential to understand the mechanism controlling the biochar adsorption process. With the concentration of NH_4^+ (or NO_3^-) increasing in solution, the amount of them adsorbed

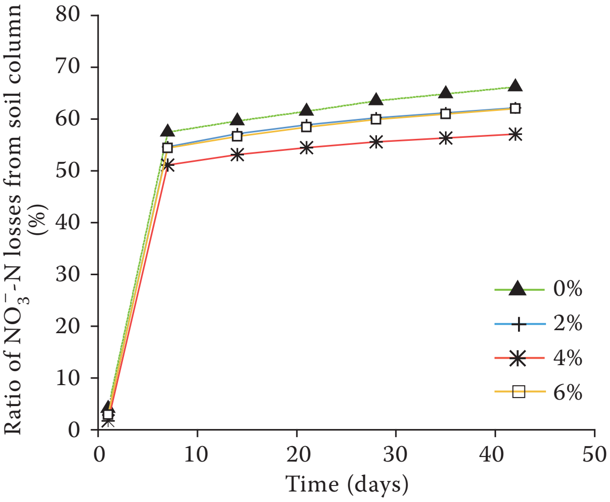

Figure 9. The ratio of cumulative losses of NO_3^--N in the leachates from soil column with different biochar application rates (treatment: adding 0, 2, 4 and 6% rice straw biochar, respectively)

by RSBC at equilibrium increased accordingly. Since plenty of pores were formed during the pyrolysis of rice straw at high temperature (Lin et al. 2012), RSBC has achieved high physical adsorption capacity, which is one of its important characteristics, with a large specific surface area (Table 1, the specific surface area of the tested RSBC reached 120 m^2/g when carbonised at 550 °C). From the Freundlich model, however, our results showed that RSBC has relatively high adsorption capacity and intensity to NH_4^+. From the Langmuir model, moreover, we can see that the maximum adsorption capacity of RSBC to NH_4^+ and NO_3^- were 31.25 and 10.00 mg/g, respectively. These may be mainly due to a large amount of negative charge in biochar, which enhances the chemical adsorption ability to retain cations (e.g., NH_4^+) and thus inhibit cation loss by leaching (Gai et al. 2014).

Leaching characteristics of NH_4^+ from paddy soil as affected by biochar amendment. Noted that the greater NH_4^+ losses occurred in the control treatment, which was mainly due to the fact that most of the leachate came from the 0–10 cm soil layer, while the rate of NH_4^+ loss at this layer was significantly higher in control than other treatments during the first two weeks (Figure 5). Nonetheless, the leaching loss of NH_4^+ from different soil layers of the control treatment was obviously lower than RSBC treatments at the end of the leaching experiment (42 days). This suggested that more NH_4^+ in the control treatment had been leached, which led to a decrease of soil NH_4^+ availability. Similarly, some studies also showed that the cumulative leaching losses of soil NH_4^+ from multi-layered soil columns were substantially reduced by biochar addition (Ding et al. 2010). The reason may lie in the porous structure of biochar that reduces the NH_4^+ transport due to the adsorption capability of biochar (Spokas et al. 2011, Kammann et al. 2015, Schmidt et al. 2015, Zhang et al. 2015). Our present adsorption experiments also suggested that RSBC has relatively high adsorption capacity and adsorption intensity to NH_4^+ in solution. Therefore, NH_4^+ could be absorbed by biochar, which led to an increase of residual NH_4^+ content in the soil column (Figure 7). Although the cumulative losses of NH_4^+ from the soil column were less for 4% RSBC treatment than 2 % RSBC treatment, the cumulative losses of NH_4^+ were higher for 6% RSBC treatment than other treatments with RSBC amendment. Excessive application of biochar would increase soil porosity but also increase the water storage capacity of the soil (Lu 2014, Nelissen et al. 2015). In this study, indeed, the soil water content is higher for the treatments with 6% RSBC amendment than the treatments with 4% RSBC amendment, thus accelerating the dissolution of NH_4^+ and flowed out with the liquid phase. Therefore, the cumulative nitrogen loss does not decrease with the increase of biochar addition from 4% RSBC to 6% RSBC.

The occurrence of the maximum NH_4^+ concentration in the leachate was delayed with the decline of soil depth. This indicated that NH_4^+ was sinking over time. At 10 cm depth, however, the NH_4^+ content in the leachates decreased with the increase of RSBC addition on 1 day. It might be attributed to the strong adsorption capacity of RSBC to NH_4^+, resulting in a decrease in the NH_4^+ content of the soil liquid phase, and finally, the NH_4^+ content in leachates decreased. The higher the amount of RSBC addition, the stronger the adsorption capacity of NH_4^+ and the lower the content of NH_4^+ in the leachates. With the continuous leaching, the content of NH_4^+ of each treatment in the leachates gradually decreased on days 21 and 28, but the sequence of values was completely reversed. It was reported the biochar had both adsorption and desorption to NH_4^+ (Zhang et al. 2015), and the desorption amount of NH_4^+ was gradually larger than that of adsorption from day 21 to 28. In this experiment, NH_4^+ had a dynamic equilibrium among solid phase, liquid phase, and biochar. There was also a dynamic equilibrium between the adsorption and desorption of NH_4^+ by RSBC. With the leaching of NH_4^+ in the liquid phase, the equilibrium content of the solid phase and the adsorption and desorption of RSBC changed. When NH_4^+ in the liquid phase reduced to a certain degree, the reverse reaction occurred between the adsorption and desorption of the RSBC, and the desorption capacity was greater than that of the adsorption. Thus, RSBC released the adsorbed NH_4^+ at the early stage, and the NH_4^+ content in the leachates increased.

The NH_4^+ content in the leachates was relatively stable for 0% RSBC from 28 days to 42 days at 10 cm soil depth but increased for 2, 4 and 6% RSBC. This may be mainly due to the fact that the desorption of NH_4^+ by RSBC was greater than the adsorption capacity. With the continuous decrease of the concentration of NH_4^+ in the soil liquid phase, as a result, a large amount of NH_4^+ adsorbed by biochar in the early stage can be released, thus increasing the NH_4^+ content in the leachates. After the experiment, the NH_4^+ content in soil column and leachate at 10 cm and 20 cm soil depths were highest for the treatments

https://doi.org/10.17221/276/2020-PSE

with 4% RSBC amendment. This means that there is an optimal amount of biochar for the adsorption capacity of soil NH_4^+. The trend of NH_4^+ content at 20 cm soil depth was different from 10 cm depth on the first day of leaching. This was probably because of the downward migration and lateral diffusion of NH_4^+ across the soil.

Compared with CK (0% RSBC amendment), the NH_4^+ content leached from the soil column at 10 cm depth was decreased greatly during the first week of the experiment, while it increased obviously after the experiment, for the treatments with 2, 4 and 6% RSBC amendment (Figure 5). In addition, NH_4^+ content in leachates from other soil depths for the biochar treatments was higher than that of CK treatment at most sampling days (Figure 5). It was likely to be related to the dual characteristics of adsorption and desorption to soil NH_4^+ by biochar (Ding et al. 2016). Compared with CK, the treatments with RSBC amendment in 0–10 cm soil layer had a strong adsorption capacity for soil NH_4^+ at the beginning of leaching, and more NH_4^+ were retained in the soil. With the decrease of NH_4^+ content in the leachate, the NH_4^+ adsorbed by biochar was gradually released into the soil liquid phase. Therefore, the NH_4^+ content in leachate for the RSBC treatments was higher than that of the CK after a while.

Combined with adsorption tests, we speculated that compared with CK, 2, 4 and 6% RSBC adsorbed NH_4^+ at the early leaching period and released the adsorbed NH_4^+ in the later stage of leaching. It was consistent with the adsorption and sustained release effects of biochar proposed by Ding et al. (2016). The addition of RSBC reduced the cumulative losses of NH_4^+ in the leachates from soil columns, which was consistent with previous research results (Sika and Hardie 2013). 4% RSBC had the best effect in this experiment. Therefore, RSBC not only reduced the leaching of NH_4^+ in soil but also had great potential as a slow-release fertiliser to achieve better management of soil nutrients for maximum bioavailability (Ding et al. 2016), which played an important role in reducing agricultural nitrogen pollution.

Leaching characteristics of NO_3^- from paddy soil as affected by biochar amendment. The NO_3^- content decreased quickly in the leachates in 40 cm depth of soil column during the initial 7 days (Figure 8), and almost all of the cumulative losses of NO_3^- in the leachates came from these days (Figure 9). This result suggested that the NO_3^- retention by paddy soil and biochar is very weak. The Freundlich model in the adsorption experiment also showed that the sorption capacity and sorption intensity of NO_3^- by biochar was lower than NH_4^+. This may be mainly because the surface of soil particles and biochar usually carried negative charges so that it can inhibit the adsorption of anions (e.g., NO_3^-). Therefore, soil NO_3^- is easily lose downwards. Indeed, the soil NO_3^- has been leached to the bottom layer before the leachate can be collected regardless of whether biochar was added or not. Therefore, the NO_3^- content of leachates at 40 cm depth was higher than other depths on the first day but decreased quickly in the leachates at this depth during the initial 7 days.

In the soil leaching experiment, RSBC immobilised less NO_3^- than NH_4^+ in soil, and NO_3^- was leached out at the beginning of leaching. On the one hand, it was probably due to the difference of adsorption properties for NH_4^+ and NO_3^- by RSBC from the adsorption experiment. The sorption capacity and sorption intensity of NO_3^- by biochar was weaker than that of NH_4^+. On the other hand, denitrification converts a large amount of NO_3^- into NO_2^-, NO, N_2O and N_2 resulting in low NO_3^- content in paddy soil under flooded conditions. In addition, the negative charge of biochar and soil repelled NO_3^- in soil leaching experiment. Therefore, a large amount of NH_4^+ was retained in the soil, and NO_3^- was excluded from the soil. In conclusion, the cumulative loss of NO_3^- was higher compared to NH_4^+, and the content of the leaching solution and soil of NO_3^- was lower than that of NH_4^+.

REFERENCES

Araújo C.S.T., Almeida I.L.S., Rezende H.C., Marcionilio S.M.L.O., Léon J.J.L., de Matos T.N. (2018): Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (*Solanum lycocarpum*) using Langmuir, Freundlich and Temkin isotherms. Microchemical Journal, 137: 348–354.

Bouwman L., Goldewijk K.K., Van Der Hoek K.W., Beusen A.H.W., Van Vuuren D.P., Willems J., Rufino M.C., Stehfest E. (2013): Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900–2050 period. Proceeding of the National Academy of Sciences of the United States of America, 110: 20882–20887.

Ding Y., Liu Y.G., Liu S.B., Li Z.W., Tan X., Huang X., Zeng G., Zhou L., Zheng B. (2016): Biochar to improve soil fertility. A review. Agronomy for Sustainable Development, 36: 36.

Ding Y., Liu Y.X., Wu W.X., Shi D.Z., Yang M., Zhong Z.K. (2010): Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, and Soil Pollution, 213: 47–55.

Gai X.P., Wang H.Y., Liu J., Zhai L.M., Liu S., Ren T.Z., Liu H.B. (2014): Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PloS One, 9: e113888.

Hale S.E., Alling V., Martinsen V., Mulder J., Breedveld G.D., Cornelissen G. (2013): The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere, 91: 1612–1619.

Hollister C.C., Bisogni J.J., Lehmann J. (2013): Ammonium, nitrate, and phosphate sorption to and solute leaching from biochars prepared from corn stover (L.) and oak wood (spp.). Journal of Environmental Quality, 42: 137–144.

Hu A.Y., Tang T.T., Liu Q. (2018): Nitrogen use efficiency in different rice-based rotations in southern China. Nutrient Cycling in Agroecosystems, 112: 75–86.

Huang M., Fan L., Chen J.N., Jiang L.G., Zou Y.B. (2018): Continuous applications of biochar to rice: effects on nitrogen uptake and utilization. Scientific Reports, 8: 11461.

Kammann C.I., Schmidt H.-P., Messerschmidt N., Linsel S., Steffens D., Müller C., Koyro H.-W., Conte P., Stephen J. (2015): Plant growth improvement mediated by nitrate capture in co-composted biochar. Scientific Reports, 5: 11080.

Laird D., Fleming P., Wang B.Q., Horton R., Karlen D. (2010): Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma, 158: 436–442.

Lal R. (2004): Soil carbon sequestration impacts on global climate change and food security. Science, 304: 1623–1627.

Lehmann J., Rillig M.C., Thies J., Masiello C.A., Hockaday W.C., Crowley D. (2011): Biochar effects on soil biota – a review. Soil Biology and Biochemistry, 43: 1812–1836.

Lin Y., Munroe P., Joseph S., Henderson R., Ziolkowski A. (2012): Water extractable organic carbon in untreated and chemical treated biochars. Chemosphere, 87: 151–157.

Lu S.G., Sun F.F., Zong Y.T. (2014): Effect of rice husk biochar and coal fly ash on some physical properties of expansive clayey soil (Vertisol). Catena, 114: 37–44.

Mizuta K., Matsumoto T., Hatate Y., Nishihara K., Nakanishi T. (2004): Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. Bioresource Technology, 95: 255–257.

Nelissen V., Ruysschaert G., Manka'Abusi D., D'Hose T., De Beuf K., Al-Barri B., Cornelis W., Boeckx P. (2015): Impact of a woody biochar on properties of a sandy loam soil and spring barley during a two-year field experiment. European Journal of Agronomy, 62: 65–78.

Ok Y.S., Yang J.E., Zhang Y.S., Kim S.J., Chung D.Y. (2007): Heavy metal adsorption by a formulated zeolite-Portland cement mixture. Journal of Hazardous Materials, 147: 91–96.

Schmidt H.P., Pandit B.H., Martinsen V., Cornelissen G., Conte P., Kammann C.I. (2015): Fourfold increase in pumpkin yield in response to low-dosage root zone application of urine-enhanced biochar to a fertile tropical soil. Agriculture, 5: 723–741.

Sika M.P., Hardie A.G. (2013): Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil. European Journal of Soil Science, 65: 113–119.

Spokas K.A., Novak J.M., Venterea R.T. (2011): Biochar's role as an alternative N-fertilizer: ammonia capture. Plant and Soil, 350: 35–42.

Sun X., Zhong T., Zhang L., Zhang K.S., Wu W.X. (2019): Reducing ammonia volatilization from paddy field with rice straw derived biochar. Science of the Total Environment, 660: 512–518.

Wang J., Fu P.H., Wang F., Fahad S., Mohapatra P.K., Chen Y.T., Zhang C.D., Peng S.B., Cui K.H., Nie L.X., Huang J.L. (2019): Optimizing nitrogen management to balance rice yield and environmental risk in the Yangtze River's middle reaches. Environmental Science and Pollution Research, 26: 4901–4912.

Yao Y., Gao B., Zhang M., Inyang M., Zimmerman A.R. (2012): Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere, 89: 1467–1471.

Zhang H., Voroney R.P., Price G.W. (2015): Effects of temperature and processing conditions on biochar chemical properties and their influence on soil C and N transformations. Soil Biology and Biochemistry, 83: 19–28.

Zheng H., Wang Z.Y., Deng X., Zhao J., Luo Y., Novak J., Herbert S., Xing B.S. (2013): Characteristics and nutrient values of biochars produced from giant reed at different temperatures. Bioresource Technology, 130: 463–471.

Zhu D.Q., Pignatello J.J. (2005): Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. Environmental Science and Technology, 39: 2033–2041.

Received: May 29, 2020
Accepted: December 12, 2020