Adsorption characteristics of ammonium onto biochar from an aqueous solution

Shamim A. Begum, A. H. M. Golam Hyder, Qwanikwia Hicklen, Taylor Crocker and Ben Oni

ABSTRACT

Ammonium contamination in water is a major concern worldwide. This study focuses on the removal of ammonium from aqueous solution by batch adsorption experiments using biochar derived from a combination of various wood chips (spruce, pine, and fir). Adsorption characteristics of ammonium onto biochar were evaluated as a function of biochar dosages, initial concentrations of ammonium, contact time and pH. Results demonstrated that ammonium removal increased with the increase of biochar dosage. The percentage of ammonium removal reached a value of 80% at a biochar dosage of 100 g/L. Ammonium removal decreased by 15% with the increase of initial ammonium concentration by 50 mg/L. The optimum pH for ammonium removal was considered in the range from 6 to 8. Ammonium removal reached its stable value within 3 days. The maximum adsorption capacity of ammonium was 0.96 mg/g for 80 mg/L of initial ammonium concentration. The adsorption isotherm followed both the Langmuir and Freundich models for ammonium adsorption onto biochar. Fourier Transform Infrared (FTIR) spectroscopy results indicated the presence of amine, amide and nitrile functional groups on the surface of biochar which could contribute to the adsorption of ammonium onto biochar. Thus, biochar derived from various wood chips showed the potential to remove ammonium from aqueous solution.

Key words | adsorption, ammonium, biochar, equilibrium concentration, isotherms, reaction kinetics

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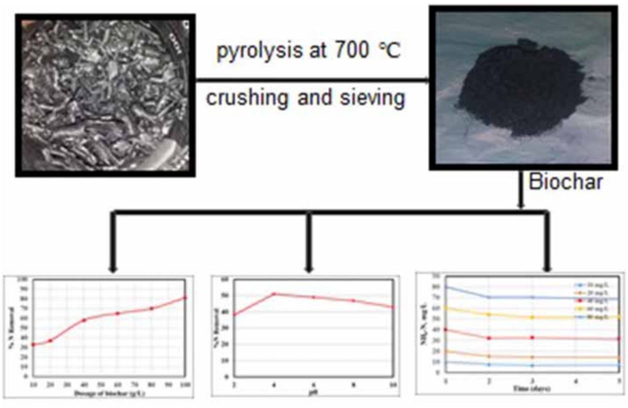
HIGHLIGHTS

- Ammonium adsorption was investigated using the biochars derived from a combination of various wood chips pyrolyzed at 700 °C.
- Ammonium adsorption onto biochars enhanced with an increase of the biochar dosage.
- Optimum pH for ammonium removal varied between 6 and 8.
- Both Langmuir and Freundlich models fitted the ammonium adsorption well.
- Surface functional groups of biochars could contribute to the ammonium adsorption onto biochars.

doi: 10.2166/aqua.2020.062

GRAPHICAL ABSTRACT



INTRODUCTION

Presence of excessive ammonium could adversely affect the natural ecosystems (Tang *et al.* 2019). Ammonium is released into the environment from municipal and industrial sources (Glavan & Pintar 2010). Ammonium contaminated water is detrimental to the health of infants, leading to serious illness and sometimes death; symptoms include shortness of breath and 'blue-baby syndrome' (EPA 2016). One major effect that excess ammonium has on the environment is eutrophication. Eutrophication causes excessive algal growth, known as algal bloom, which has various detrimental effects, such as increase of water treatment cost, decrease of oxygen content and recreational use of water (Dodds *et al.* 2009). Due to the adverse effects of ammonium on human life and environment, legislation on the standards of wastewater discharge has been strengthened in many countries (Wang *et al.* 2009). As a result, effective processes for removing ammonium from wastewater are important.

Processes for ammonium removal include adsorption (Saleh *et al.* 2012; Gai *et al.* 2014; Wang *et al.* 2015), ion-exchange (Leakovic *et al.* 2000), oxidation (Isaka *et al.* 2007), chemical precipitation (Zhang *et al.* 2009), and microwave radiation (Lin *et al.* 2009). Among these, adsorption is considered an effective, inexpensive, low sludge production, and simple technique for removing ammonium from water. Activated carbon is one of the most prevalent adsorbents used in adsorption process for water and wastewater treatment, but it is not the most cost efficient (Worch 2012). Therefore, various low-cost biosorbents have been used for the treatment (Hyder *et al.* 2015; Begum *et al.* 2016; Ahsan *et al.* 2018; Islam *et al.* 2019). Biochar is a low-cost, easily available and efficient carbonaceous biosorbent, which can be derived from waste materials including woody debris, corn stalks, cottonseed hulls (Uchimiya *et al.* 2011), rice husks (Zhang *et al.* 2015), sewage biosolids (Knowles *et al.* 2011), and animal manure (Song & Guo 2012). Biochar has been used extensively for the removal of heavy metals and organic contaminants from water (Hyder *et al.* 2014; Inyang & Dickenson 2015). Recent studies have also shown the potential to remove ammonium (NH_4^+-N) using biochars (Gao *et al.* 2015; Kizito *et al.* 2015; Wang *et al.* 2015; Zhang & Wang 2016; Li *et al.* 2018). Adsorption capacities of biochars depend on its physical and chemical properties on the basis of type and pyrolysis temperature of feedstock materials (Mukome *et al.* 2013; Li *et al.* 2018). Therefore, the overarching objective of this study was to evaluate the effectiveness of a commercial biochar (a bi-product from a power plant) obtained by pyrolysis of various wood chips (spruce, pine, and fir) together at 700 °C to remove ammonium from aqueous solution. The specific objectives of this study were as follows: (1) evaluate the effects of adsorbent dose, initial ammonium concentration, contact time and pH on the adsorption process;

(2) determine the adsorption isotherm; and (3) investigate the surface functional groups, which can contribute to the removal of ammonium.

MATERIALS AND METHODS

Preparation and characterization of adsorbent

The biochar used in this study was purchased from Phoenix Energy, California, USA. It is a carbonaceous granular material prepared by pyrolysis of wood chips at 700 °C. The analytical specifications of the biochar were provided by the company. The carbon content, ash, bulk density, total surface area and particle size range were 90.8%, 3.9%, 0.11 g/cm^3, 186 m^2/g and 19–150 mm, respectively. The biochar was crushed and sieved to obtain the particle with a size range 53–250 μm. The surface area and pore volume of the reduced sized biochar were determined using a NOVA 1200 surface area analyzer (Quantachrome Instruments, Boynton Beach, FL) with the Bruanuer–Emmett–Teller nitrogen adsorption method at 77 °K.

Effects of various parameters on ammonium adsorption

Adsorbent dosage

In preparation of ammonium solution, 1,000 mg/L ammonium-nitrogen (NH_4^+-N) stock solution was prepared by dissolving approximately 381.9 mg of ammonium chloride (NH_4Cl) salt in deionized water. The NH_4^+-N stock solution was diluted to working concentration of 10 mg/L for batch tests. The effect of biochar dosage on ammonium adsorption was studied in batch test using 0.10 L solution with varying biochar dosages ranging from 10 to 100 g/L. The pH of the mixture was not adjusted during batch tests. The mixture was shaken at a speed of 150 rpm using a platform shaker (New Brunswick Scientific, model: innova 2300) at room temperature for 5 days. Samples were collected at the end of test and filtered through 0.45 μm syringe filter (Sterlitech, WA, USA). Residual NH_4^+-N concentration of the filtered solution was determined using a spectrophotometer (HACH DR2800).

Initial ammonium concentration and contact time

In order to evaluate the effect of initial ammonium concentration and contact time, batch adsorption experiments were conducted separately with varying NH_4^+-N concentrations from 10 to 80 mg/L at 10 g/L of biochar dosage. The pH of the mixture was not adjusted during the batch test and pH value was recorded at 5. The mixture was then stirred at 150 rpm at room temperature for 5 days. Residual NH_4^+-N concentration was determined similarly as described in the previous section.

Solution pH

The pH of the solution is an important factor for the adsorption because pH affects the surface charge of adsorbent, chemical species and also the degree of ionization of surface functional groups of adsorbent during reaction (Li *et al.* 2012). Therefore, the effect of pH on the ammonium adsorption onto biochar was investigated by varying initial pH values from 2 to 10 using initial NH_4^+-N concentration of 10 mg/L. The pH values of the solution were adjusted by using 0.1 M HCl and 0.1 M NaOH. Then, 40 g/L of biochar was added to the solution. Batch tests and analysis of residual NH_4^+-N concentration were conducted according to the similar procedure described in the above section. At the end of tests using pH 4, 6 and 8, biochars were collected and air-dried overnight to analyze surface functional groups using FTIR spectroscopy at a wavenumber varying from 500 to 4,000 cm^{-1}.

Batch tests were performed in duplicate, and average values were used to represent the results. All working solutions were prepared freshly prior to batch tests. The glasswares were presoaked in 5% HNO_3 solution overnight, and then washed with tap water, rinsed three times with deionized water and dried in air before use.

Determination of adsorption isotherms (Langmuir and Freundlich)

The detail procedure to determine the adsorption isotherms is presented in Hyder *et al.* (2015). In short, Langmuir and Freundlich models are expressed linearly in Equations (1) and (2), respectively to evaluate the adsorption isotherms of ammonium onto biochar (Freundlich 1906; Langmuir 1916).

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (1)$$

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \quad (2)$$

where C_e denotes the equilibrium NH_4^+-N concentration in mg/L, q_e represents the equilibrium adsorption capacity of biochar in mg/g, q_m is the maximum adsorbed amount of NH_4^+-N per mass of biochar in mg/g, K_L is the Langmuir equilibrium adsorption constant (L/mg) related to the free energy of adsorption, K_F is the Freundlich constant $[(mg/g)(L/mg)^{1/n}]$ related to the strength of the adsorptive bond (Gupta *et al.* 1998), and $1/n$ is the adsorption intensity factor or surface heterogeneity (unit less).

For Langmuir sorption, R_L, a dimensionless separation factor was used to describe the type of isotherm and was expressed in Equation (3) (Arulkumar *et al.* 2012).

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (3)$$

where C_0 (mg/L) and K_L (L/mg) are initial NH_4^+-N concentration and Langmuir constant, respectively. Thus, the value of R_L identifies whether the adsorption process is favourable or unfavourable. The process is irreversible for $R_L = 0$, favorable for $0 < R_L < 1$, linear for $R_L = 1$ and unfavourable for $R_L > 1$ (Hameed *et al.* 2009).

The Langmuir isotherm indicates that the free energy of adsorption is independent on the surface coverage of adsorption sites, and the surface saturation of the adsorbent occurs by a monolayer coverage of adsorbate at high C_e values and a linear relationship at low C_e values (Khezami & Capart 2005).

Statistical analysis

Independent two-sample t-test was performed between the replicate values, which were obtained during the batch tests at a 95% confidence interval to determine whether the replicate values were significantly different. To verify the optimum pH value for maximum percentage of ammonium removal, a one-way ANOVA test was conducted at a 95% confidence interval. A Tukey Honestly Significant Difference (HSD) test was performed for multiple comparisons when the ANOVA test showed significant differences (p value < 0.05).

RESULTS AND DISCUSSIONS

Textural properties of biochar

After reducing the particle size between 53 and 250 μm, the surface area (BET), pore volume, and average pore diameter of the biochar were found as 285 m^2/g, 0.1507 cm^3/g and 2.117 nm, respectively. The surface area of the biochar increased from a value of 186 m^2/g to 285 m^2/g due to the size reduction.

Effects of parameters on ammonium adsorption

Adsorbent dosages

The biochar dosage has a significant influence on the adsorption of ammonium. The maximum percentage of ammonium removal was 80% using 100 g/L of biochar at an initial ammonium concentration of 10 mg NH_4^+-N/L (Figure 1(a)). The percentage of ammonium removal increased with the increase of biochar dosage, which could be due to the increased number of available adsorption sites as the biochar amount increased in the solution. Other researchers also observed the increased ammonium adsorption with the increase of biochar amount up to a certain value. However, further increase of biochar dosage decreased the ammonium adsorption onto biochars (Kizito *et al.* 2015; Xue *et al.* 2019).

Effects of initial ammonium concentration

To observe the effects of initial ammonium concentration on the adsorption of ammonium onto biochar, initial NH_4^+-N concentrations were varied from 10 to 80 mg/L (Figure 1(b)). The percentage of ammonium removal decreased steadily with the increase of initial NH_4^+-N concentration. About 31% ammonium was removed with an initial NH_4^+-N

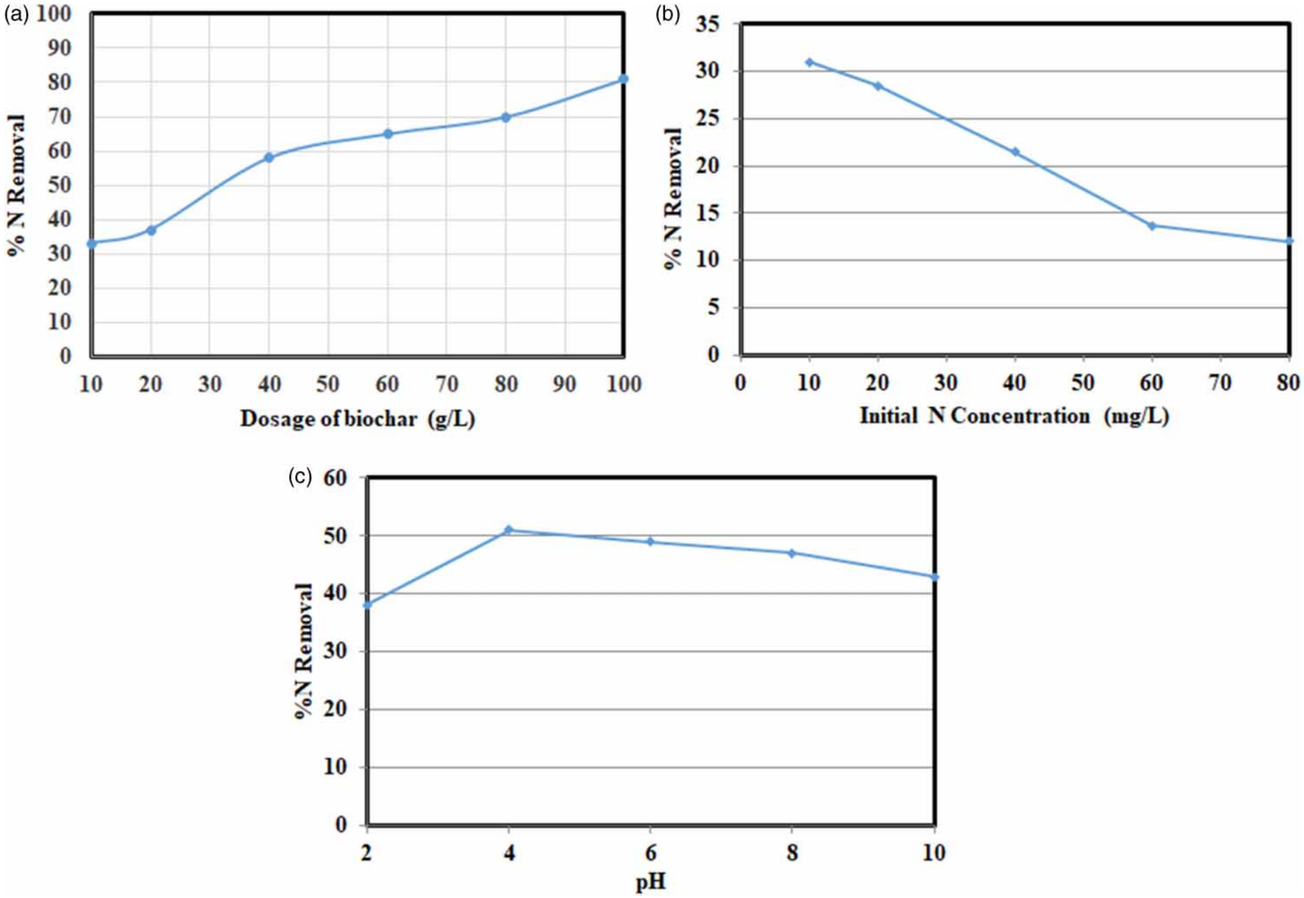


Figure 1 | Percentage of ammonium removal due to the effect of (a) biochar dosage (initial ammonium concentration = 10 mg NH_4^+-N/L; pH = 6.6), (b) initial ammonium concentration (biochar dosage = 10 g/L; pH = 5) and (c) pH of the solution (initial ammonium concentration = 10 mg NH_4^+-N/L; Biochar dosage = 40 g/L).

concentration of 10 mg/L with a biochar dosage of 10 g/L at a pH of 5. The ammonium removal was 12% at an initial NH_4^+-N concentration of 80 mg/L by keeping other parameters constant. It may be due to the presence of lower amount of ammonium ions at low initial concentration compared to the availability of excess unoccupied active sites on the biochar (Qu *et al.* 2008; Nidheesh *et al.* 2012). Thus, the percentage of ammonium removal was higher at low initial NH_4^+-N concentration. Similar results were also observed by other researchers (Vassileva *et al.* 2008; Kizito *et al.* 2015).

Effect of solution pH

To identify the effect of pH, further batch tests were conducted using biochar dosage of 40 g/L with the variation of pH from 2 to 10 at an initial NH_4^+-N concentration of 10 mg/L. The percentage of ammonium removal increased from 38% to 51% with the increase of pH value from 2 to 4 as shown in Figure 1(c) and remained stable up to pH value of 6. Subsequently, the percentage of ammonium removal decreased slowly with the increase of pH, and finally reached a value of 43% at pH 10. The less removal of ammonium at pH lower than 4 can be attributed to the high protonation of functional groups on the biochar surfaces resulting in a partial positive charge. It can compete with NH_4^+ ions in aqueous solution for adsorption onto biochar surfaces as ammonium exists mainly in the form of NH_4^+ in acidic environment (Maranon *et al.* 2006). At high pH, the decreasing trend of ammonium removal was observed which may be due to the conversion of NH_4^+ to $NH_{3(aq)}$ form. The electrostatic attraction mechanism was not effective at this pH resulting in the reduction of ammonium removal (Thurston et al. 1979; Vu et al. 2017).

The one-way ANOVA test results show that the percentage of ammonium removal was significantly different for various pH values. Therefore, Tukey HSD test was performed for multiple comparisons among pH values to identify the optimum pH value (Table 1). From Table 1, the percentage ammonium removal was not significantly different between pH values of 4 and 6, 4 and 8, and 6 and 8. Even though the percentage removal of ammonium is maximum at pH 4 (Figure 1(c)), Tukey HSD test indicates that the percentages of ammonium removal at pH 4, 6 and 8 were not significantly different. Thus, the pH value between 6 and 8 can be considered as the optimum pH as they are close to the pH value of natural waters.

Effect of contact time

Ammonium concentration in the solution decreased with time until 3 days. Then, ammonium concentration reached a stable value for all initial ammonium concentration when contact time was further increased as shown in Figure 2. This indicates that the adsorption of ammonium onto biochar reached the point of saturation after 3 days (Vu et al. 2017). The ammonium removal rate was faster until 2 days. The slight uptake of ammonium was observed up to an equilibrium level in day 3 for all initial ammonium concentrations. The ammonium concentrations decreased to 7 mg/L, 14.5 mg/L, 32.6 mg/L, 51.8 mg/L and 70.4 mg/L for an initial concentrations of 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L respectively in 3 days. The maximum ammonium adsorption capacities were 0.3, 0.55, 0.74, 0.82, and 0.96 mg/g for initial ammonium concentrations of 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L, respectively. The ammonium adsorption capacities of various biochars are presented in Table 2.

Table 1 | Tukey HSD test for % ammonium removal at various pH values

pH Values	Mean difference in % ammonium removal	HSD Value	Comments
2 and 4	10.667	10.485	Significant difference
2 and 6	11.667	10.485	Significant difference
2 and 8	11.667	10.485	Significant difference
2 and 10	5.000	10.485	Not Significant difference
4 and 6	1.000	10.485	Not Significant difference
4 and 8	1.000	10.485	Not Significant difference
4 and 10	5.000	10.485	Not Significant difference
6 and 8	0.000	10.485	Not Significant difference
6 and 10	6.667	10.485	Not Significant difference
8 and 10	6.667	10.485	Not Significant difference

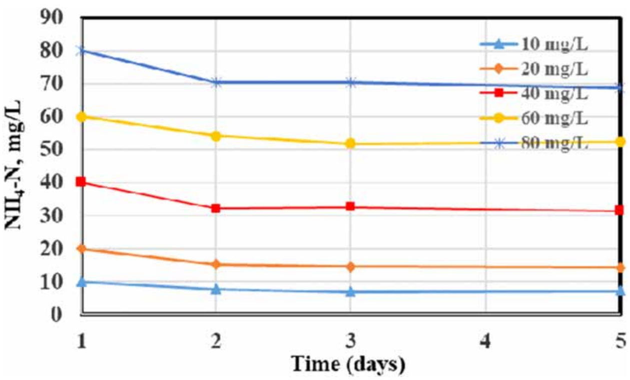


Figure 2 | Variation of ammonium concentrations with time for different initial ammonium concentrations: pH of 5, bone-char of 10 g/L.

Generally, the adsorption capacity of the adsorbent is expected to improve at a higher initial ammonium concentration due to the greater driving force from concentration gradient (Ho 2004). A higher initial concentration leads to higher collisions between the biochar and ammonium species, resulting in a driving force that is able to overcome all mass transfer resistances between the solid and aqueous phases (Anupam et al. 2011).

Evaluations of the adsorption isotherms (Langmuir and Freundlich)

Langmuir and Freundlich isotherm models were used to investigate the relationship between adsorbate in liquid and solid (Hameed et al. 2008). The adsorption isotherms of ammonium onto biochar were tested by varying initial NH_4^+-N concentrations from 10 to 80 mg/L at 10 g/L of biochar dosage with pH of 5 for 5 days. These two models are the most common isotherms used to describe solid-liquid adsorption systems, and presented in Figures 3(a) and 3(b) for ammonium removal. The isotherm coefficients for these two models are presented in Table 3 for ammonium removal. Since, the maximum adsorption capacity (q_m) obtained from the experimental result and Langmuir

Table 2 | Ammonium adsorption capacities of biochars at various operating conditions

Biochar	Solution pH	Pyrolysis temperature (°C)	Surface area (m^2/g)	Particle size (mm)	Adsorption capacity (mg/g)	References
Cotton stalk	10	300	–	0.9–1.2	19.2	Gao et al. (2015)
Wood	7	600	273.623	0.25–1.25	44.64	Kizito et al. (2015)
Rice husk	7	600	10.995	0.25–1.25	39.8	Kizito et al. (2015)
Switchgrass	7	800	–	<0.5	10.47	Li et al. (2018)
Water oak	7	400	–	<0.5	3.82	Li et al. (2018)
Digested sludge	6–8	450	20.86	<1	1.4	Tang et al. (2019)
Maple wood	–	500	–	0.149–0.85	<1	Wang et al. (2015)
Wood chips	5	700	285	0.053–0.250	0.96	This study

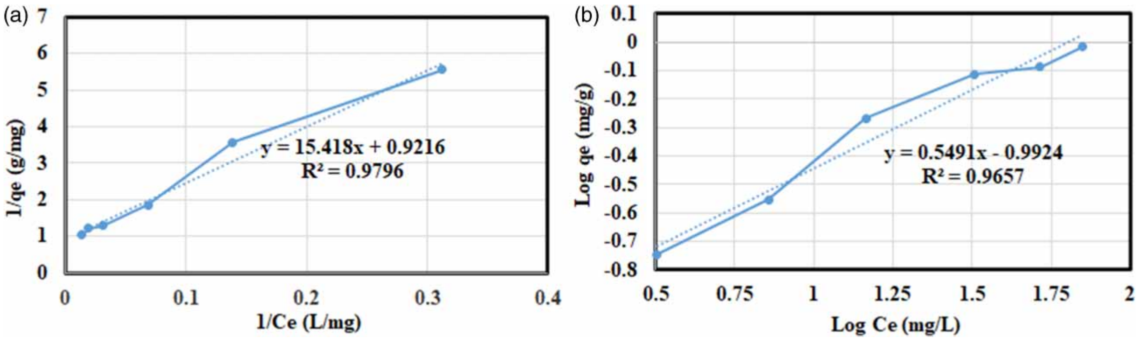


Figure 3 | Adsorption isotherm model for ammonium removal using (a) Langmuir Isotherm and (b) Frendlich Isotherm.

Table 3 | Coefficients of Langmuir and Freundlich models for ammonium removal

Langmuir model			Experimental	Deviation	Freundlich model		
R^2 –	K_L (L/mg)	q_m (mg/g)	q_m (mg/g)	q_m %	R^2 –	K_F (mg/g) $(L/mg)^{1/n}$	$1/n$ –
0.9796	0.06	1.1	0.96	13%	0.9657	0.102	0.5491

model was not similar, the deviations of q_m value obtained from the experimental result to Langmuir model were 13% for ammonium adsorption. The value of R_L, the essential characteristics of Langmuir dimensionless separation factor or equilibrium parameter, was obtained between 0 and 1 which indicates the favorable adsorption process of ammonium onto the biochar (Hameed et al. 2009).

It is clear from Figures 3(a) and 3(b) that the adsorption data of ammonium onto biochar fit the Langmuir model better with R^2 values of 0.9796 as compared to the Freundlich model R^2 values of 0.9657. The suitability of Langmuir model can be interpreted to mean that the adsorption of ammonium took place largely by chemisorption within the monolayer on the biochar. On the contrary, R^2 value from Freundlich model is higher than 0.95 which suggests some level of physical adsorption (Kizito et al. 2015). Other studies also reported that the ammonium adsorption onto biochar followed both the Langmuir and Freundlich models (Liu et al. 2010, 2013; Zhu et al. 2012; Kizito et al. 2015). The results of these studies indicate the heterogenous nature of the biochar surfaces (Kizito et al. 2015).

Surface functional groups by FTIR spectroscopy

The FTIR spectra of raw biochar and biochar tested at pH 4, 6 and 8 are presented in Figure 4. It shows that the IR

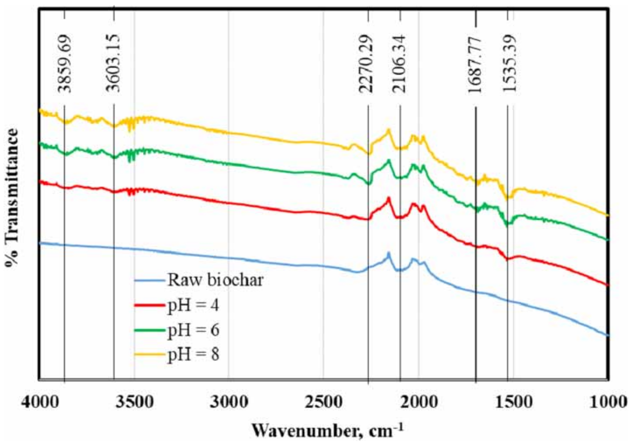


Figure 4 | FTIR spectra with the variation of pH values.

spectrum of biochar tested at pH 4, 6 and 8 changed after being used in the tests. The FTIR spectroscopy confirmed the presence of different functional groups in the raw biochar and biochar used in the batch tests at pH 4, 6 and 8 to remove ammonium from the water. The FTIR spectra of raw biochar and biochar tested at pH 4, 6 and 8 showed the C–C triple bond stretching at wavenumbers of 2,106.34 cm^{-1}. At pH 4, 6 and 8, the FTIR spectra of biochar showed almost similar pattern. The symmetric and asymmetric stretching vibrations of N–H bond were observed at 3,859.69 and 3,603.15 cm^{-1}, respectively, which might correspond to the amine and amide functional groups. The peak at 2,270.29 cm^{-1} could be due to the C–N triple bond stretching, which indicates the alkyl nitrile formation. In addition, the N–H bending vibration at 1,535.39 cm^{-1} could also be an indication of the amine and amide functional groups, and C=O stretching vibration at 1,687.77 cm^{-1} could be attributed to the amide functional group (Silverstein *et al.* 2005). Therefore, the higher ammonium removal at pHs of 4, 6 and 8 could be influenced by the formation of amine, amide and nitrile functional groups on the surface of biochar.

CONCLUSIONS

In this study, biochar derived from woodchips was used to adsorb ammonium from the aqueous solution. About 80% ammonium removal was achieved using 100 g/L of biochar at an initial NH_4^+-N concentration of 10 mg/L at pH 6.6. Ammonium removal decreased by 15% with the increase of initial ammonium concentration by 50 mg/L. Even though the highest ammonium removal was obtained at pH 4, there was not significant difference in ammonium removal at pH 4, 6 and 8. Therefore, the optimum pH value was considered between 6 and 8 for ammonium removal as it is close to the pH value of natural waters. The maximum adsorption capacity of ammonium was 0.96 mg/g for 80 mg/L of initial ammonium concentration after 3 days. Both Langmuir and Freundlich models showed a good fit for ammonium adsorption onto the biochar. The ammonium removal could occur due to the formation of amine, amide and nitrile functional groups on the biochar surface. The results obtained in this study suggest that biochar derived from the combination of various wood chips at a pyrolysis temperature of 700 °C is a promising adsorbent to remove ammonium from water and wastewater resources. Therefore, a filtration unit incorporating the biochar as an adsorbent can be operated based on the effects of operating conditions, and adsorption isotherm obtained in this study in a full-scale water and wastewater treatment plant for the removal of ammonium from the contaminated waters.

ACKNOWLEDGEMENTS

This study was made possible by the support of the United States Department of Energy – National Nuclear Security Administration (DOE-NNSA). The contents of this paper are the sole responsibility of the authors and do not reflect the views of the US Department of Energy or the United States Government.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this article.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 17 June 2020; accepted in revised form 29 October 2020. Available online 9 December 2020