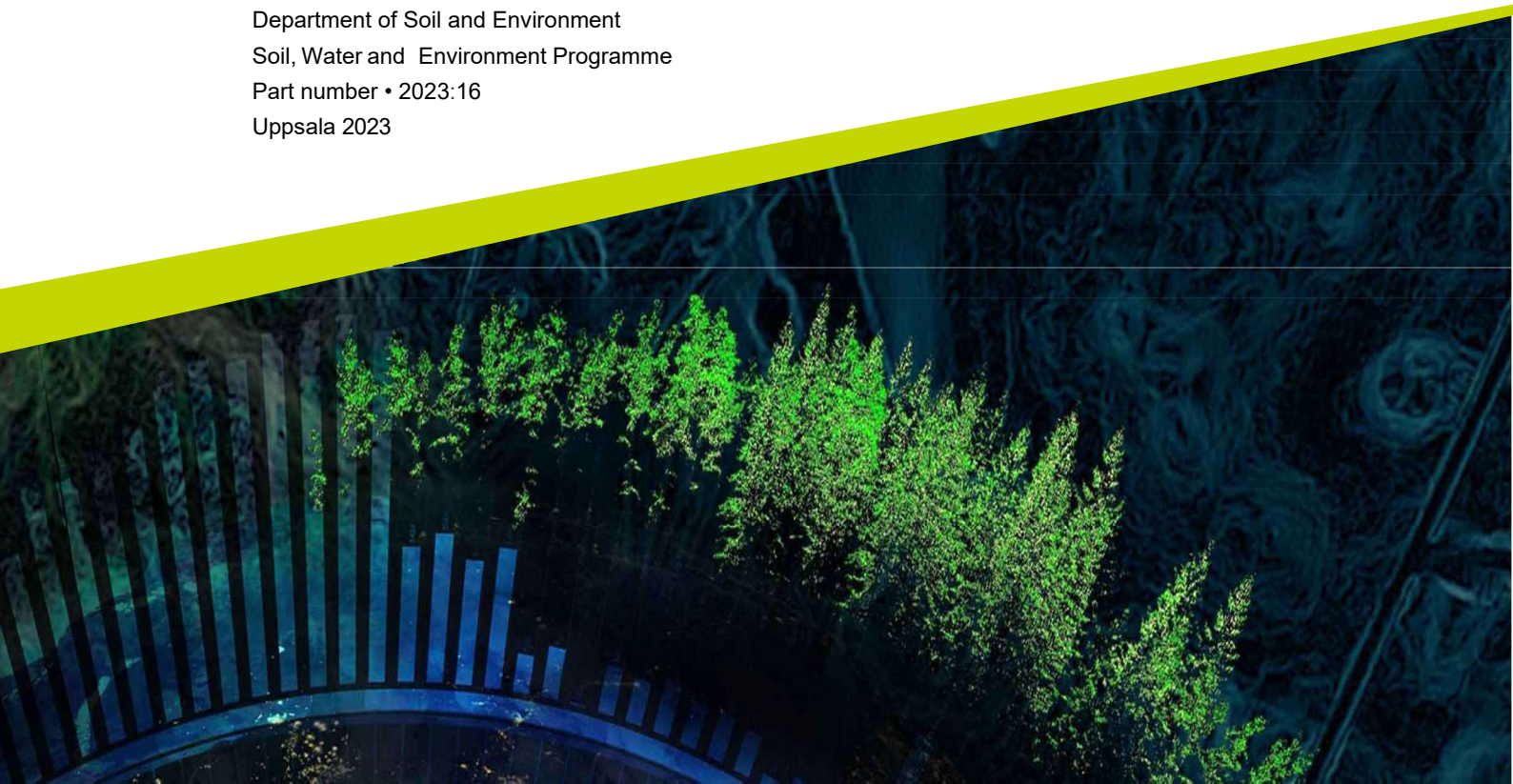




Ammonium and nitrate sorption by biochar

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Abstract

Biochar has recently drawn attention due to its ability to increase soil fertility, sequester carbon and its expected effect on reducing the leaching of elements from the soil, especially nitrogen.

The possibility of using biochar as a soil amendment to reduce the amount of nitrogen leaching, and then reducing the quantities of nitrogen fertilizers used in agriculture to avoid the bad environmental effects has become a matter of great interest.

In this study, the possibility of using biochar to reduce nitrogen leaching from soil was investigated by studying the adsorption capacity and subsequent release of ammonium (NH_4^+) and nitrate (NO_3^-) from three different biochars, vermiculite, perlite and two synthetic ion exchange resins (cation and anion exchangers). The release of NH_4^+ and NO_3^- over time from biochars and other materials were studied with a dialysis bag method.

Through the comparison of desorption between the materials with known charge and porosity properties the potential sorption mechanisms by biochar is discussed. All three kinds of biochar had negligible capacity to retain NO_3^- . The biochar behaved similarly to the cation exchange resin. This suggests that the capacity to retain NO_3^- is more dependent on the porosity of the material rather than its charge properties.

Biochar had an ability to sorb and subsequently release a significant amount of NH_4^+ over the experimental period. The results indicated that adsorption through ion exchange plays the major role in this process. There were only small differences in sorption behavior between the three kinds of biochar from different feedstock materials.

Sammanfattning

Intresset för biokol har ökat på senare tid på grund av biokolets positiva effekter på markbördighet, kolinbindning och dess potentiella bidrag till att minska utlakning av framförallt kväve. Detta ses som en möjlighet till att öka effektiviteten i kväveutnyttjandet och på så sätt minska gödslingsbehovet. I den här studien undersöktes sorptionskapaciteten och den efterföljande desorptionen av ammonium (NH_4^+) och nitrat (NO_3^-) från tre olika biokol, vermikulit, perlit och två syntetiska jonbytarmaterial (en katjon- och en anjonbytare). De tre biokolen hade framställts genom pyrolys av majshalm, kaffeskal och kokosnötskal i ett tidigare projekt.

Sorption och desorptionen av NH_4^+ och NO_3^- från biokolet och de andra materialen studerades med en dialysbaserad metod.

Den potentiella sorptionskapaciteten för de olika biokolen diskuteras genom jämförelse med hur material med känd laddning och porositet uppträder under liknande förhållanden. Alla tre biokolen hade en försumbar kapacitet att adsorbera NO_3^- . Biokolens sorptions- och desorptionsegenskaper liknade katjonbytarens. Detta indikerar att eventuell sorptionskapacitet för NO_3^- kommer att vara mer beroende på materialets porositet (vattenhållande förmåga) än på dess laddningsegenskaper.

Samtliga biokol uppvisade en liknande kapacitet för sorption av NH_4^+ under experimentet. Detta trots varierande kemiska egenskaper. Resultaten indikerar att sorption genom jonbyte är den kvantitativt mest betydelsefulla bindningsformen för NH_4^+ .

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Abbreviations

$(\text{CH}_3)_2\text{CO}$	acetone
$(\text{HO})_2\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2$	chromotropic acid
$(\text{NH}_4)_2\text{SO}_4$	ammonium sulphate
$\text{C}_6\text{H}_3\text{N}_2\text{O}_6\text{P}$	nitroaniline phosphate
CEC	cation exchange capacity
$\text{CH}_2(\text{COOH})$	malonic acid
HCl	hydrochloric acid
KBr	potassium bromide
KCl	potassium chloride
KNO_3	potassium nitrate
MWCO	molecular weight cut-off
Na_2EDTA	ethylenediaminetetraacetic acid disodium salt
$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$	sodium nitroprusside
Na_2HPO_4	sodium monohydrogen phosphate
NaCl	sodium chloride
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NH_4^+	ammonium
NH_4NO_3	ammonium nitrate
NO_3^-	nitrate
RC	regenerated cellulose
Zn	zinc
N_2O	nitrous oxide

1 Introduction and aims

N use by the microbial community and plants in the soil is a key process of the N cycle in terrestrial ecosystems. N can be applied to the soil in both organic and inorganic forms and through biochemical processes both forms can be converted to each other. Mineralization is the process in which the organic N is converted to inorganic. This process leads to NH_4^+ being released so it is called ammonification in some references (Wall, 2013). Through immobilization the organic can be converted to inorganic form by microbial activities. The C/N ratio in organic matter is the main factor which controls these processes. Low C/N ratio will lead to mineralization and high ratio will lead to immobilization (Ouyang and Norton, 2020). As it has been observed that organic nitrogen greatly increases the biodiversity of the microbial community, while the inorganic form did not affect this diversity (Ouyang and Norton, 2020). Ecosystem processes such as photosynthesis can increase when N supply increases. For example, N supply increased the photosynthetic apparatus along the sugarcane leaf by increasing chlorophyll content, the amount and activity of carboxylation enzymes, total protein, sugar content (Bassi et al., 2018).

Globally, nearly 90 % of the N fertilizer is NH_4^+ . It can be transformed to highly mobile NO_2^- and NO_3^- under aerobic conditions by nitrifying bacteria (e.g., *Nitrosospira* and *Nitrosomonas*) in agricultural soils (Li et al., 2018).

The runoff and leaching of N in the forms NH_4^+ , NO_2^- , and NO_3^- will not only affect the nutrient use efficiency of N fertilizers but will also cause environmental problems like eutrophication and poisoning of water biota (Li et al., 2018).

Soil microorganisms are responsible for N transformations through two basic processes: denitrification and nitrification.

In the first process, NH_4^+ is oxidized to NO_2^- and then to NO_3^- by different microorganisms in several steps, the most important one is the one carried out by nitrifying bacteria. An

alternative pathway for this conversion is carried out by another group of bacteria (anaerobic ammonium oxidizers) under anaerobic conditions (Sabba et al., 2010).

In the second process (denitrification), microorganisms reduce NO_3^- to N_2O and subsequently to N_2 , and it occurs under anaerobic conditions (Rysgaard et al., 1995).

Soil amendments can be used to improve the physical and chemical properties of the soil, like the porosity and water holding capacity, CEC, and soil conductivity, so it becomes a suitable medium for plant growth. Soil amendments can also positively affect biogeochemical processes in the soil, such as reducing emissions of N_2O and CH_4 , and reduce leaching of sulfates and nitrates into water sources.

Regarding N, we could potentially use suitable soil amendments with special physical and chemical properties that could sorb and continuously supply N in appropriate form to plants. At the same time, they can reduce the availability of N for microorganisms to carry out the previously mentioned processes. This will lead to reduced emissions of N_2O and reduced the amount of N leached from the soil in the form of NO_3^- and NH_4^+ .

Biochar, a carbon rich, and stable material derived from pyrolysis of biomass, has attracted attention because of its potential to enhance N retention in the soil (Li et al., 2018).

Biochar has unique physical and chemical characteristics, which may differ due to the feedstock material and the pyrolysis process parameters like the temperature and the speed of pyrolysis (Bruun et al., 2012). The specific surface area is an important characteristic of biochar, which mainly depends on the feedstock material (Chen et al., 2011). Different feedstock materials lead to different types of biochar with different surface areas. This indicates different thermal degradation and content of lignin and cellulose (El-Gamal et al., 2017). The formation process can affect the specific surface area. The surface area of the biochar increases with increasing pyrolysis temperature, since the pore-blocking substances are driven off or are thermally cracked, increasing the externally accessible surface area (Rafiq et al., 2016). Higher pyrolysis temperature causes the release of volatile matter and creates more pores (Shaaban et al., 2014). Biochar is formed through biomass pyrolysis, which is a process of dehydroxylation/ dehydrogenation and aromatization, and different functional surface groups (e.g., carbonyl, carboxyl, hydroxyl, and phenolic hydroxyl) are formed on the biochar surface (Li et al., 2013). These functional groups are important for inorganic N sorption since the ion exchange occurs between $\text{NH}_4^+/\text{NO}_3^-$ and these groups (Liu et al., 2010). Removal efficiencies of NH_4^+ and NO_3^- are positively correlated with the amount of acidic and basic functional groups, respectively (Wang et al., 2015). Acidic functional groups of biochar (e.g., hydroxyl, phenol, and carboxyl groups) are negatively charged because of the ionization of hydrogen in the solution. Positively charged NH_4^+ are electrostatically attracted to the negative's sites and exchange with H^+ . Therefore, the high content of acidic functional groups is an important factor for NH_4^+ adsorption by biochar. Basic N containing functional groups of biochar (e.g., amides, aromatic amines, and pyridinic groups) are positively charged and hydroxide ions exist simultaneously to neutralize the solution. Therefore, negatively charged NO_3^- are electrostatically attracted and anion exchange will occur between NO_3^- and OH^- (Shen et al., 2013). Biochar formation temperature (biomass pyrolysis temperature) can affect the type and amount of functional groups as well as the capacity of biochar for ion exchange (Shen et al., 2013). An increase in pyrolysis temperature will decrease the quantities of the acidic functional groups (Shen et al., 2013). It was noticed that the carboxyl groups decreased by half in corn and oak biochar when the pyrolysis temperature increases from 300 to 600 °C, and the cation exchange capability of biochar decreased accordingly (Nguyen and Lehmann. 2009). The total charge of biochar's surface is negative but positively charged sites could be found (Yin et al., 2017). Acidic functional groups can be removed, and basic groups can be created on the surface of biochar by biochar modification, and this will increase the capacity of biochar to adsorb NO_3^- (Iida et al., 2013). Biochar contains an ash fraction, which gives it an alkaline reaction, so it has a liming effect on soils. This is important in tropical areas, where the soil have a low pH (Jeffery et al., 2017). Ash, which consists mainly of metal oxides and hydroxides, can affect nutrient retention. For example, the surface of MgO becomes positively charged at a pH less than 12, and this will increase the amount of absorbed negatively charged elements such as NO_3^- (Yin et al., 2017).

The pH of the soil solution affects the adsorption of the elements, as the positive charge of the surface of biochar increases with the decrease of soil solution pH between 3 to 7 (Yin et al., 2017). Nitrate is hardly adsorbed under basic conditions because the hydroxide ions compete with the nitrate ions for the adsorption on the carbon surface (Iida et al., 2013).

Adsorption of N by biochar prepared from different feedstocks and under different formation conditions were reported (Yin et al., 2017). However, studies provide conflicting results. e.g., a considerable reduction in NH_4^+ and NO_3^- leaching was reported by the biochar made from Brazilian pepperwood and peanut hull at 600 °C (Yin et al., 2017).

Other studies mentioned that biochar has limited or no ability to adsorb NO_3^- and sometimes it can release it into environment (Gai et al., 2014).

These contradictory results can be explained by the physiochemical properties of biochar such as porosity, surface area, chemical composition, and molecular structure. The negatively charged surface, the functional groups, and a high surface area of biochar improve the water retention and increase the nutrient holding capacity of soils (Aghoghovwia et al., 2017). Therefore, conducting a more detailed study on the role of these properties for retention of N is important.

The objective of this study was to study the adsorption capacity and the subsequent desorption of NH_4^+ and NO_3^- on three different biochar and compare the results to other soil amendments and ion exchange resins.

2 Materials and methods

In this study, the ability to sorb NH_4^+ and NO_3^- by biochar, vermiculite, perlite and two ion exchange resins were compared.

2.1 Preparing samples

Biochar from three different types of feedstock; coconut shell, maize stover and coffee husk were used in the study. The biochar was analysed with respect to pH, lime value and plant- available nutrients. The plant available nutrients were determined using the Mehlich III (Mehlich, 1984) extraction with subsequent analysis by ICP-OES (Table 1). The total elemental composition of the biochar (Table 2) was analysed by the ALS Laboratory in Luleå. The biochar was fused together with LiBO_2 at 1000°C and the material was thereafter dissolved in dilute nitric acid. The extracts were thereafter analysed on ICP-OES and ICP-MS depending on element.

Table 1: Mehlich III extractable nutrients, lime value and pH for the three kinds of biochar used in this study.

	pH	Lime value	Ca	Mg	K	Na	P	Mn	B	Cu	Fe	S	Zn
----- mg/L -----													
Coconut shell	6.3	0.8	222	37.5	1150	129	39.4	8.4	0.0	0.5	64.6	48.0	2.6
Coffee husk	9.0	6.3	2664	661	16959	306	241	77.8	9.6	4.0	234	243	9.7
Maize stover	7.6	2.5	835	834	10996	662	465	80.7	0.4	0.5	128	95.0	27.4

Table 2: Total oxides content in the three kinds of biochar.

	TS	Ash	Sum oxides	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	TiO ₂
----- % -----													
Coconut shell	94.2	2.8	2.7	1.67	0.20	0.15	0.21	0.28	0.04	0.01	0.08	0.03	0.03
Coffee husk	90.5	27.4	25.6	8.14	7.43	1.58	2.96	3.92	0.45	0.07	0.23	0.45	0.42
Maize stover	94.4	10.5	10.5	5.22	0.83	0.54	0.74	1.99	0.43	0.04	0.32	0.32	0.05

To remove the ash fraction of biochar, a deionized biochar-water suspension (100 g biochar/L) was titrated down to pH 5.5 with 0.1 M HCl using an automatic titrator (Radiometer ABU901). After the titration, the suspension was allowed to stand for 24 hours. The process was repeated until the pH remained in the 5.5-6.0 interval after standing. The biochar suspension was concentrated using a 50 µm stainless steel sieve. The moisture content of the suspension was determined by drying a subsample at 105°C for 24 hours. Calculations were made to determine the amount of wet biochar to be used to obtain 2 grams of dry biochar in each treatment.

Biochar sorption of NH₄⁺ and NO₃⁻ was compared with four materials. A cation-exchanger resin saturated with sodium and anion exchanger resin saturated with chloride were used as a pure cation exchanger and anion exchanger respectively. Biochar sorption was also compared with sorption on two common inorganic soil amendments, perlite, and vermiculite. Perlite has a high water holding capacity with a low surface charge since the CEC of perlite is 2.5 to 5.0 cmolc kg⁻¹ (Do and Mehmet, 2004). Perlite holds water in three ways: in between individual grains, in channels leading to the cores of the grains and on the highly irregular surfaces of each particle (Do and Mehmet, 2004). Vermiculite has a high negative surface charge since the CEC is 100 to 150 cmolc kg⁻¹ with a high porosity (Volkov and Simha, 2012). Vermiculite is an important clay mineral in soils, and it is classified as an expandable clay mineral. It is a 2:1 clay, meaning it has two Si tetrahedral sheets for every Al octahedral sheet. The surface charge of vermiculite is created through isomorphous substitution when Si⁴⁺ is replaced by Al³⁺ in the tetrahedral layer. When expanding because of heat or moisture the space between layers increases and allows the cations to go inside and occupy the

negatively charged sites (Volkov and Simha, 2012).

Three replicates were prepared for each substance. A water suspension containing 2 g of dry matter for each material was added into a 10 cm dialysis bag (Ghasemian and Rahimpour, 2022). The dialysis bags are made of a standard regenerated cellulose membrane with a molecular weight cut-off (MWCO) of 6-8 kilodalton (kD). With this membrane, the biochar particles will remain inside the tube while the NH_4^+ and NO_3^- may pass freely between the inner and outer solution. The diameter of the tube was 20.4 mm with a volume of 3.3 ml cm^{-1} . To clean the exchange sites and saturate them with Na^+ and Cl^- the dialysis bags were immersed into 800 mL of 0.1 M NaCl solution in a 1 L beaker for 24 hours and this was repeated twice. The dialysis bags were then transferred to 800 mL beakers containing 5 mM NaCl solution for 24 hours and this was repeated twice to remove excess NaCl.

The dialysis tubes were thereafter immersed in a NH_4NO_3 solution containing 1g N L^{-1} , i.e. 500 mg L^{-1} N from NH_4^+ and 500 mg N from NO_3^- for 24 hours. The process was repeated twice and after that, the dialysis tubes were transferred to a 5mM NaCl solution. At this point the sampling of the experiment starts (day zero).

2.1 Sampling

A 10 ml sample of the outer solution from all treatments were sampled on day 1, 3, 6, 13, 20, 27, 33, 40, 47, 52 and 82. A each sampling 10 mL of 5 mM NaCl solution were added to keep the volume of the dialysis system constant. Samples were kept in the fridge until analysis.

2.2 Analyzing nitrate

The method for NO_3^- analysis used is described by Nesterenko et al., (2016). It is based on the reduction of NO_3^- to NO_2^- by a reducing catalyst, zinc, and on the sub-sequent reaction of nitrite with an aromatic amine (p-nitroaniline) in acidic medium to form a diazonium salt coupled with an aromatic amine. The reaction produces a highly colored azo-dye compound. The solid-phase reagent for NO_2^- determination contained p-nitroaniline (2 mass%), chromotropic acid (2 mass%), KCl (4 mass%), KBr (12 mass%), Na_2EDTA (0.4 mass%) for masking metal cations that might be present in analyzed samples and 79.6 mass% of solid acidifier (malonic acid), zinc dust (5–10 μm) for nitrate reduction (1% relative to the amount of solid base reagent). A 0.1 mg of the mixed solid-phase reagent was weighed into a sample tube, 5 mL of standard or sample was added, and the mixture swirled for 15 s and allowed to stand for 10 minutes in room temperature for color development before measurement. The absorption of the complex was measured colorimetrically with a spectrophotometer (Genesys 20) at a wavelength of 515 nm. The concentration of NO_3^- was determined using a calibration curve made with a standard series with 0, 2, 4, 6, 8 and 10 mg L^{-1} $\text{NO}_3\text{-N}$ in the same matrix solution, 5mM NaCl, as the samples. Samples with a concentration of $\text{NO}_3\text{-N}$ outside the calibration range were diluted and re-measured.

2.3 Analyzing ammonium

Ammonium was determined using the indophenol blue method (Page et al., 1982). Alkaline phenol and hypochlorite react with ammonium to form the indophenol blue complex that is proportional to the ammonium concentration. The blue color is intensified with sodium nitroprusside. The presence of divalent cations such as Ca^{+2} and Mg^{+2} in the extraction solution may affect the success of this method for measuring ammonium, so EDTA was added as a chelating agent to remove the disturbance.

Three reagents were prepared, an EDTA reagent, a phenol-nitroprusside reagent, and a hypochlorite reagent. The EDTA reagent was prepared by adding 3 g of Na_2EDTA in 40 mL of deionized water, adjusting the pH to 7 with NaOH and the dilute to a final volume of 50 mL. The phenol-nitroprusside reagent was prepared by dissolving 3.5 g of phenol and 17 mg of sodium nitroprusside in 40 mL of NH_4^+ -free water and dilute to a final volume of 50 mL. This reagent was stored in a dark colored bottle in a refrigerator. The hypochlorite reagent was prepared by dissolving 0.74 g of NaOH in 35 mL of NH_4^+ - free water, adding 2.49 g of Na_2HPO_4 and 10 ml of the NaOCl solution (5 to 5.25% NaOCl) and finally diluted to a final volume of 50 mL. The pH was checked to ensure a value between 11.4 and 12.2. The hypochlorite reagent was prepared immediately before use to obtain optimum results, because the NaOCl concentration in this reagent decreases on standing (Carter and Gregorich 2007).

To prepare samples for measurement 0.5 mL from each sample was taken and 0.4 mL of EDTA reagent added. After 2 minutes 0.8 mL of the phenol-nitroprusside reagent was added. Then 1.6 mL of the hypochlorite agent was added, and the sample tube swirled. The tubes were thereafter immersed in 40 Co water bath for 30 minutes to accelerate the color formation. The absorbance at wavelength 636 nm was measured colorimetrically with a spectrophotometer. The concentration of NH_4^+ was determined using a calibration curve made with a standard series with 0, 2, 4, 6, 8 and 10 mg L⁻¹ $\text{NH}_4\text{-N}$ in the same matrix solution, 5mM NaCl, as the samples. Samples with a concentration of $\text{NH}_4\text{-N}$ outside the calibration range were diluted and re-measured.

The average accumulated amount of NO_3^- and NH_4^+ released from the dialysis tubes into the outer solution in the three replicates of each substance were calculated. At the end of the experiment, all the remaining NH_4^+ and NO_3^- in the materials were extracted with a 2 M potassium chloride (KCl) solution. The concentration of NH_4^+ and NO_3^- was measured the same way as before, but with a 2 M KCl matrix.

The extracted quantities and the total amounts of NH_4^+ and NO_3^- retained by the substances were calculated and compared. The results were presented as mg of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ per 2 g of the substance.

The standard deviation was calculated and standard deviation error bars were added to all datapoints for both nitrate and ammonium.

3 Results

3.1 Biochar pH adjustment

The pH adjustment to 5.5 of the biochars made of coffee husks, maize stover and coconut shells consumed 165, 63 and 5 ml of 0.1 M HCl respectively. The titration was repeated 6 times for the pH to become stable. The amount of acid consumed was proportional to and well correlated ($r=1.00$) with the ash amount given in Table 2.

3.2 Nitrate

The amounts of $\text{NO}_3\text{-N}$ released from the different materials are shown in Fig 1. All systems ceased releasing NO_3^- around day 40. The anion exchange resin released more than double the amount of $\text{NO}_3\text{-N}$ per g of absorbent as compared to the other materials that released very similar amounts ranging between 14.42 $\text{mg NO}_3\text{-N}$ per 2 g for vermiculite to

14.64 $\text{mg NO}_3\text{-N}$ per 2 g for maize stover biochar (Table 3).

The total amounts released by the end of the experiment (day 82) increased somewhat for all materials. (Appendix 2).

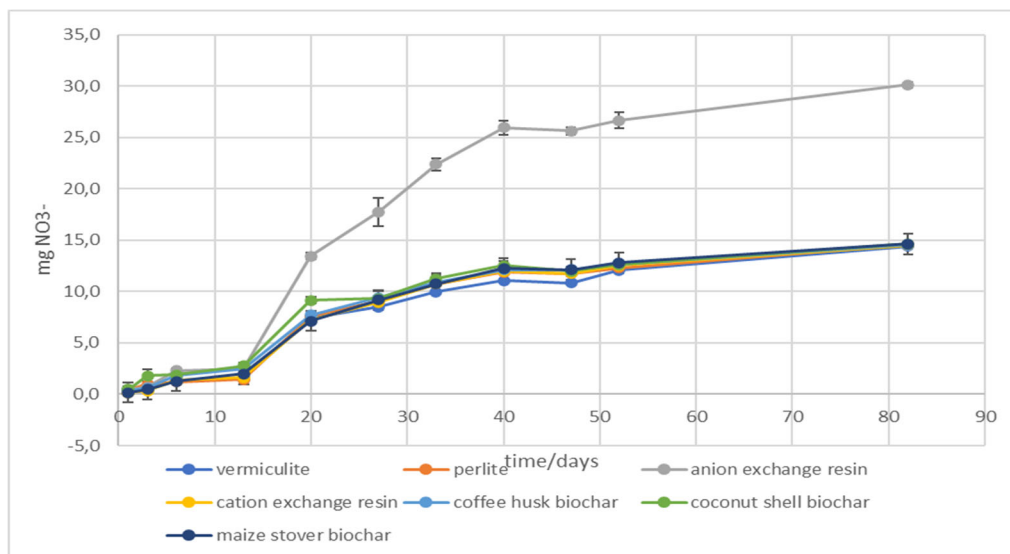


Figure 1: Released amount of NO_3^- ($\text{mg NO}_3\text{-N}/2\text{g}$) over time with standard deviation error bars.

The largest amounts were released between day 13 and 20 for all materials and all materials follow the same pattern and released NO_3^- in a similar way. There were no significant differences between the different materials except for the anion exchange material (Appendix 3 and 4).

The extraction of the remaining NO_3^- from all materials by the end of experiment shows there were almost no NO_3^- remaining, Table 3.

Table 3: Total NO₃-N released from all dialysis tubes and extracted from all substances/ mg.

	Vermiculite	Perlite	Anion exchanger resin	Cation exchanger resin	Coffee husk biochar	Coconut shell biochar	Maize stover biochar
Nitrate released from dialyses tubes	14.42	14.56	31.4	14.5	14.52	14.62	14.62
Extracted nitrate from substances	0.02	0.02	0.3	0.0	0.01	0.01	0.01
Nitrate in dialyses tubes at day 0	16.5	16.5	16.5	16.5	16.5	16.5	16.5
Nitrate released from all substances	-2.06	-1.74	14.8	-2	-1.97	-1.87	-1.87

3.3 Ammonium

Considerable amounts of NH₄⁺ were released from all materials. The cation exchanger released the highest amount followed by maize. Coffee and coconut biochar and perlite released similar amounts while vermiculite released less. Most NH₄⁺ were released between day 0 and 6 except for the anion exchanger and the different biochars follow the same pattern as the cation exchanger, Figure 4, and Appendix 5.

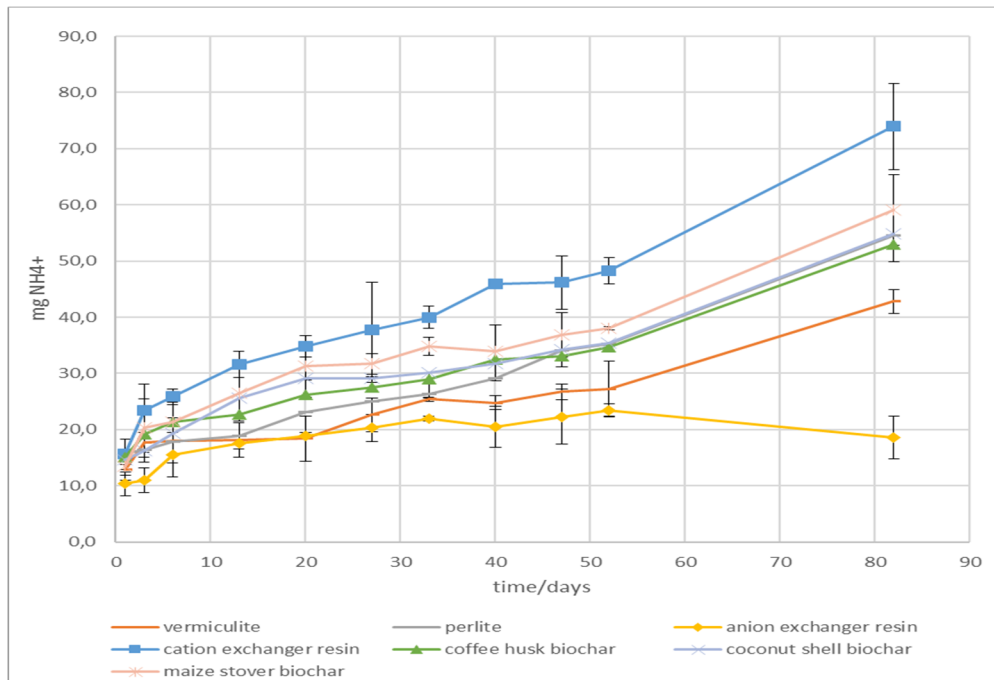


Figure 4: Released amount of NH₄⁺ (mg NH₄⁺-N/2g) over time with standard deviation error bars.

The amount of NH₄⁺ released in between sampling times were calculated. The numbers shows that vermiculite, maize stover biochar and coffee husk biochar released the highest amounts between days 1 and 3. Coconut shell biochar released the highest amount between days 6 and 13. While perlite released the highest amount later between days 40 and 47.

After extraction the remaining amount of NH_4^+ and NO_3^- three types of biochar still have the highest amount of NH_4^+ , perlite still have a considerable amount, but vermiculite and the anion exchanger have released most of the amount they retained. Total amount of NH_4^+ released from the dialysis tubes by all materials are shown in Table 4.

Table 4: Total NH_4 -N released from the dialysis tubes and extracted from all substances and the calculated amount released from all substances / mg

	Vermiculite	Perlite	Anion exchanger resin	Cation exchanger resin	Coffee husk biochar	Coconut shell biochar	Maize stover biochar
Released NH_4 -N from dialyses tubes	42.8	54.6	23.2	74.0	53.0	54.8	59.0
Extracted NH_4 -N from substances	0.2	0.8	0.2	2.6	1.6	1.0	2.6
Ammonium in dialysis tube at day 0	16.5	16.5	16.5	16.5	16.5	16.5	16.5
NH_4 -N released from substances	26.5	38.9	6.9	60.1	38.3	39.3	45.1

3.4 Ammonium vs nitrate

It is clear that there is a significant difference in the amount of NH_4^+ retained by all materials compared to the amounts of NO_3^- . Perlite retained more NH_4^+ than vermiculite. The anion exchanger resin has retained a small amount of NH_4^+ which is not expected but a higher amount of NO_3^- as expected. For the three types of biochar, maize stover biochar has retained the highest amount of NH_4^+ while coffee husk biochar retained the less.

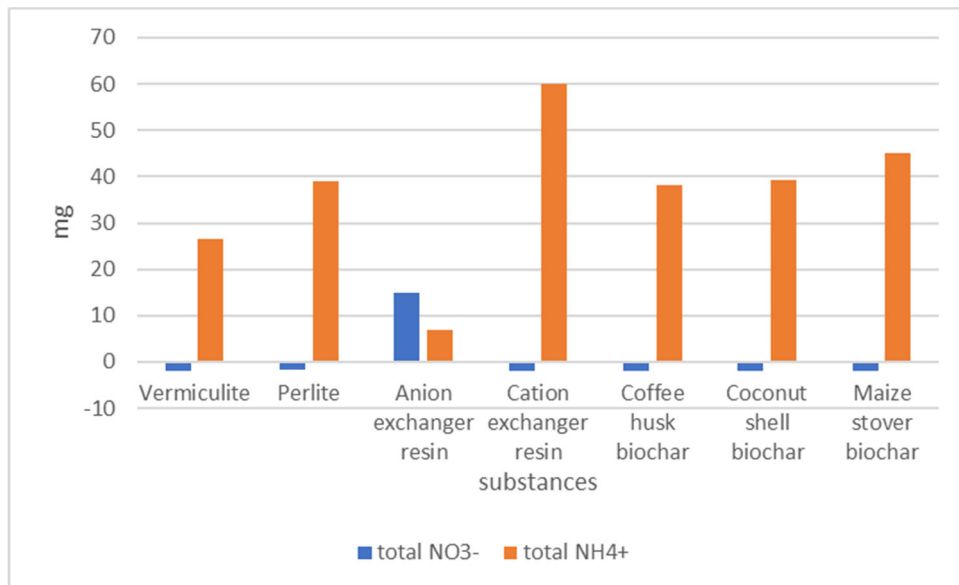


Figure 3: Total amount of NH_4 -N and NO_3 -N sorbed by all substances.

4 Discussion

Ash is a major content of biochar, it is formed by the degradation and mineralization of biomass materials during pyrolysis (Yu et al., 2022). The ash content in biochar differs due to the feedstock material (Jeffery et al., 2017). When the biochar with all its components is added to the soil, the ash will dissolve in a relatively short time (Ambaye et al., 2021) while the biochar proper remains with its carbon structure. To simulate the biochar function in soil without interference of the ash, the ash must be removed from the biochar.

Ash is made of oxides and hydroxides which are not stable at low pH (Jeffery et al., 2017), so to remove it we acidified the biochar suspension. Some amount of ash is trapped in the biochar pores. Waiting for a while after reaching the required value of pH during titration will allow the ash to be dissolved in the pores and the pH of the suspension will go up again. Therefore, we repeated the titration until the biochar suspension reached the required value of pH and stayed stable at that pH. The observed proportionality between the amount of acid added and the experimentally determined ash content is supporting that the ash removal procedure worked.

In the first day at the start of the experiment, large amounts of NH_4^+ was recorded. Most of this originated from the inner solution of the dialysis tubes because it contains 33 ml of NH_4NO_3 solution at the start of the experiment. Theoretically we should get a similar amount of NO_3^- . Theoretically, 16.5 mg of NH_4^+ -N and NO_3^- -N that originates from the inner solution will be released from the solution in the dialysis tubes to the matrix solution. The rest of the amounts recorded would have been initially retained by the tested adsorbents. All materials except the anion exchanger exhibited some capacity to retain NH_4^+ since we recorded 42.8 mg for vermiculite to 74 mg for the cation exchange resin.

For NO_3^- the total amount released from the tested adsorbents ranged between 14.4 mg (vermiculite) and 14.6 mg (maize biochar), while the anion exchange resin released the highest amount, 31.4 mg. The numbers for most materials are close to 16.5, which indicate that all the amount of NO_3^- released to the matrix solution came from the original concentration in the dialysis tube solution. This means that the substances did not sorb any amount of NO_3^- . The result is expected since the biochar surface is negatively charged (Gai et al., 2014). This can explain why some studies show that biochar cannot affect the NO_3^- leaching (Gai et al., 2014). When we subtract the amount that was present in the dialysis tube solution from the total amount, we find that the anion exchanger resin had absorbed about 14.8 mg of NO_3^- . No other material indicated any adsorption capacity for NO_3^- . Since all the NO_3^- measured in the system came from the solution in the dialysis tubes, including the absorbed fraction, the absorption can only play a small role in NO_3^- sorption by biochar.

Maize stover biochar has released 45.1 mg, the largest amount of NH_4^+ , then coconut shell biochar and coffee husk biochar that released 38.3 and 39.3 mg respectively.

The amounts of NH_4^+ extracted from biochar at the end of the experiment show

the ability of biochar to continue releasing NH_4^+ for a relatively long time, longer than vermiculite and perlite.

Using the water holding capacity determined during the samples preparation (Appendix 1), we can say that the determined water content is much greater than the amount theoretically retained in the pores. This indicates that the amounts of NH_4^+ held in the pores of biochar is small compared with the total amounts of NH_4^+ released from the three types of biochar.

This indicates that electrostatic sorption plays the major role in NH_4^+ sorption by biochar (Li et al., 2016).

Perlite has released more NH_4^+ than vermiculite, this was unexpected since vermiculite has a higher CEC than perlite (Do and Mehmet. 2004). Porosity properties might explain that but since we do not have a certain measurement for both of them so we cant be sure if the perlite porosity is the explanation. The results show that biochar has some potential to play a role in N retention in the form of NH_4^+ but the effect will be very limited for N in the form of NO_3^- as mentioned by Li et al. (2018).

The behavior of the biochar was more similar to the cation exchange resin than to the anion exchange resin, which is logical because the biochar has a negatively charged surface (Gai et al., 2014). Nitrogen retention by biochar is controlled by the porosity and surface charge properties (Zhang et al., 2020) but the study shows that the surface charge plays the major role for NH_4^+ . The low standard error shows that sample means are closely distributed around the population mean and that the sample is representative of the population. Two measurements for NH_4^+ at day 27 and 82 seem to be less reliable than the other measurement.

The CEC of biochar differs deeply due to the feedstock materials (Hu et al., 2022). This should lead to a considerable difference in biochar sorption of NH_4^+ between biochars. However, our study did not find such differences in NH_4^+ sorption between the biochars types we studied.

The results of this study are supported by many other studies dealing with nitrogen sorption by biochar such as Hou (2021), Li (2018) and Liao (2018) which reach the same results which indicate that biochar have no effect on nitrate sorption but has a good effect on ammonium sorption.

5 Future work

This part aims to summarize how parts of the methods and results could be improved by future research. Some suggestions for future research based on this study are that one could make more measurements to facilitate the comparison between materials such as CEC for all materials and the ash free biochar. Gathering as much information as possible related to biochar production conditions, which make the comparison with other studies results more relevant. Since the results did not differ between the feedstock materials, more focus could be directed to the pyrolysis conditions to investigate if biochar that is more efficient in retaining nitrogen can be produced.

6 Conclusions

Biochar has limited or no ability to retain NO_3^- but can retain NH_4^+ .

NH_4^+ is sub-sequently released from biochar over a relatively long period of time.

The results indicate that biochar can be used to decrease NH_4^+ leaching from the soil profile.

The three tested types of biochar had the same behavior with regard to NH_4^+ and NO_3^- sorption.

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8 Popular science summary

Nitrogen (N) is one of the major plant nutrients. Its availability in the soil in a suitable form for the plant is a decisive factor for increased production. However, excessive N fertilization may have bad consequences on the environment and climate. On one hand, N in the form of nitrous gas (N_2O) is a greenhouse gas released from the activity of denitrifying microorganisms in the soil. On the other hand, leaching N from soil in the form of nitrate (NO_3^-) to groundwater, rivers, and lakes, down to the seas and oceans, leads to eutrophication.

Therefore, finding materials that help reduce the amount of fertilizer used in agriculture by maintaining an adequate stock of N to feed the plant through the season and prevent the leaching of NO_3^- from the soil is an urgent need.

Biochar has recently drawn attention as a material that can be used as a soil amendment that can achieve the previous goals. However, there are conflicting results regarding its ability to retain N.

In this study, the ability of three kinds of biochar to retain N and subsequently release it was investigated. The sorptive properties of the biochars were compared with vermiculite and perlite, two well-known soil amendments.

The results confirm the inability of biochar to retain N in the form of NO_3^- . The study confirmed that adsorption plays a greater role in nitrate retention than desorption but that

the adsorption capacity is very small.

The study showed that biochar can retain and subsequently release a significant amount of NH_4^+ and the results indicated that adsorption plays a great role in this process. Despite different feedstock, the three kinds of biochar showed similar capacity to retain NH_4^+ .

In general, most studies focus on studying the role of biochar as a soil amendment with all its components, including ash, where the results overlap due to the ability of the oxides to form negatively or positively charged surfaces based on the pH of the soil solution.

Studying the carbon structure of biochar in isolation from the ash may provide a deeper understanding of the long-term mechanisms by which biochar can affect many soil properties, especially those closely related to the environment and climate change.

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10 Appendixes

Appendix 1

Calculation of the wet amount of biochar needed to get (2) g of dry biochar and the water hold capacity of the three kinds of biochar (wet biochar).

	empty plate g	plate wet biochar g	wet biochar g	after drying g	water content g	biochar content g	wet biochar needed to get 2 g of dry biochar	water contnt in 2 g of wet biochar ml	water needed to be added to the dialyses bag	water content wet % weight
Maize	21.7	22.7	0.9	21.9	0.8	0.167	11.7	9.7	23.3	82.9
Coconuts	16.4	17.4	1	16.8	0.55	0.74	4.3	2.3	30.6	54
Coffee	13.8	14.8	1	14.2	0.65	0.38	5.4	3.4	29.6	62.8

Appendix 2

Nitrate released during the time series/ mg.

	vermiculite	perlite	anion exchange resin	cation exchange resin	coffee husk biochar	coconut shell biochar	maize stover biochar
1	0.4	0.4	0.5	0.2	0.4	0.5	0.2
3	0.5	1.0	0.7	0.4	0.6	1.8	0.5
6	1.4	1.2	2.3	1.3	1.8	1.9	1.3
13	1.5	1.4	2.5	1.6	2.5	2.8	2.0
20	7.4	7.6	13.5	7.3	7.7	9.1	7.1
27	8.5	9.0	17.7	9.0	9.4	9.3	9.2
33	10.0	10.7	22.4	10.7	10.9	11.2	10.8
40	11.0	11.9	26.0	12.0	12.1	12.5	12.2
47	10.8	11.8	25.6	11.8	12.1	12.0	12.1
52	12.1	12.3	26.6	12.5	12.7	12.6	12.8
82	14.4	14.6	30.1	14.5	14.5	14.6	14.6

Appendix 3

Ammonium released during the time series.

	vermiculite	perlite	anion exchanger resin	cation exchanger resin	coffee husk biochar	coconut shell biochar	maize stover biochar
1	12.8	15.8	10.3	15.6	15.1	14.6	13.5
3	17.7	16.3	11.0	23.4	19.1	16.2	20.3
6	18.0	17.9	15.5	25.8	21.4	19.3	21.4
13	18.1	18.8	17.6	31.5	22.6	25.6	26.4
20	18.4	23.1	18.8	34.8	26.1	29.1	31.3
27	22.6	25.0	20.3	37.8	27.5	29.1	31.7
33	25.4	26.4	22.0	40.0	29.0	30.1	34.8
40	24.8	29.2	20.5	46.0	32.5	31.7	33.9
47	26.7	34.1	22.3	46.2	33.0	34.2	36.9
52	27.2	35.3	23.5	48.2	34.7	35.4	38.0
82	42.8	54.6	18.6	73.9	53.0	54.8	59.1

Appendix 4

Standard deviation for nitrate measurement

	vermiculite	perlite	anion exchange resin	cation exchange resin	coffee husk biochar	coconut shell biochar	maize stover biochar
1	0.177	0.153	0.284	0.119	0.155	0.141	0.343
3	0.062	0.287	0.103	0.175	0.083	0.555	0.341
6	0.308	0.167	0.250	0.072	0.412	0.216	0.280
13	0.073	0.152	0.292	0.170	0.431	0.316	0.376
20	0.073	0.152	0.292	0.170	0.431	0.316	0.376
27	0.757	1.359	1.399	1.247	0.856	0.739	1.520
33	1.276	0.516	0.603	1.201	1.174	0.310	1.347
40	1.588	0.579	0.689	1.479	1.423	0.416	1.854
47	1.666	0.559	0.352	1.527	1.121	0.456	1.738
52	1.175	0.149	0.763	1.773	0.884	0.174	0.824
82	0.066	0.076	0.267	0.105	0.023	0.055	0.054

Appendix 5

Standard deviation for ammonium measurement

	Vermiculite	Perlite	Anion Ex	Cation EX	Coffee husk biochar	Coconut shell biochar	Maize stover biochar
1	0.939	0.576	2.161	2.722	5.603	4.327	2.484
3	1.706	0.692	2.250	4.681	4.215	2.037	5.188
6	4.055	1.484	3.969	1.365	6.009	3.940	3.375
13	3.058	1.98	1.091	2.347	7.951	3.780	4.929
20	4.062	1.979	0.621	1.934	3.444	3.315	2.525
27	3.029	3.851	2.366	8.346	5.268	0.785	1.828
33	0.320	1.022	0.418	1.981	1.380	4.515	1.549
40	1.295	2.158	3.636	0.8	2.480	3.072	4.644
47	1.361	3.26	4.870	4.802	5.845	3.054	3.939
52	5.002	0.923	1.107	2.35	0.545	0.476	0.255
82	2.180	5.237	3.758	7.692	9.362	4.892	6.309

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