



# Article Charcoal and Sago Bark Ash Regulates Ammonium Adsorption and Desorption in an Acid Soil

Nur Hidayah Hamidi <sup>1</sup>, Osumanu Haruna Ahmed <sup>2,\*</sup>, Latifah Omar <sup>1,3</sup>, Huck Ywih Ch'ng <sup>4</sup>, Prisca Divra Johan <sup>1</sup>, Puvan Paramisparam <sup>1</sup>, Adiza Alhassan Musah <sup>5,6</sup> and Mohamadu Boyie Jalloh <sup>7,\*</sup>

- <sup>1</sup> Department of Crop Science, Faculty of Agricultural Science and Forestry, Bintulu Campus, Universiti Putra Malaysia, Bintulu 97008, Sarawak, Malaysia
- <sup>2</sup> Faculty of Agriculture, Universiti Islam Sultan Sharif Ali, Km 33 Jln Tutong Kampong Sinaut, Tutong TB1741, Brunei
- <sup>3</sup> Institut Ekosains Borneo (IEB), Sarawak Campus, Universiti Putra Malaysia, Bintulu 97008, Sarawak, Malaysia
- <sup>4</sup> Faculty of Agro-Based Industry, Jeli Campus, Universiti Malaysia Kelantan, Jeli 17600, Kelantan, Malaysia
- <sup>5</sup> Department of Business Management and Law, Faculty of Business Management and Professional Studies, Management and Science University, University Drive, Off Persiaran Olahraga Section 13, Shah Alam 40100, Selangor, Malaysia
- <sup>6</sup> Graduate School of Management Post Graduate Centre, Management and Science University, University Drive, Off Persiaran Olahraga Section 13, Shah Alam 40100, Selangor, Malaysia
- <sup>7</sup> Crop Production Programme, Faculty of Sustainable Agriculture, Universiti Malaysia Sabah, Sandakan Branch, Locked Bag No. 3, Sandakan 90509, Sabah, Malaysia
- \* Correspondence: ahmed.haruna@unissa.edu.bn (O.H.A.); mbjalloh@ums.edu.my (M.B.J.)

Abstract: Excessive N fertilizer use in agriculture results in the release of inorganic N contaminants into surface and groundwater bodies, and other negative environmental effects. The combined application of N fertilizers with charcoal and sago bark ash could help reduce these negative impacts. The objective of this sorption study was to examine the effects of the co-application of charcoal and sago bark ash with ammonium chloride in regulating the adsorption and release of NH4<sup>+</sup> in an acid soil. This soil used in the laboratory study was Bekenu series (Typic Paleudults). The treatments evaluated were: (i) 300 g soil only, (ii) 300 g charcoal only, (iii) 300 g sago bark ash only, (iv) 300 g soil + 15.42 g charcoal, (v) 300 g soil + 7.71 g sago bark ash, and (vi) 300 g soil + 15.42 g charcoal + 7.71 g sago bark ash. Regardless of the concentration of the isonormal solution, sago bark ash (T3) showed the highest  $NH_4^+$  adsorption at equilibrium (Q<sub>e</sub>) and NH<sub>4</sub><sup>+</sup> desorbed (Q<sub>de</sub>). The results for T3 for Q<sub>e</sub> and Q<sub>de</sub> were 3.88 mg L<sup>-1</sup> and  $3.80 \text{ mg g}^{-1}$ , respectively, for the 400 mg N L<sup>-1</sup> isonormal solution followed by T2 with values of 3.46 mg $L^{-1}$  and 3.30 mg g<sup>-1</sup>, respectively. For treatments T2 and T3 that resulted in higher  $Q_e$  and  $Q_{de}$  for NH<sub>4</sub><sup>+</sup>, soil was not included. However, in practical terms, any of the treatments T4, T5 and T6 that included mixing the amendments with soil are better since the results of these treatments were not significantly different in terms of  $Q_e$  and  $Q_{de}$  for  $NH_4^+$ . This is despite the fact that T4, T5 and T6 resulted in lower  $Q_e$ and  $Q_{de}$  for NH<sub>4</sub><sup>+</sup> compared to T2 and T3. The results also showed a positive linear relationship between  $NH_4^+$  adsorption and the addition of N. This indicates that  $NH_4^+$  can be retained temporarily by the amendments. The insignificant  $R^2$  (ranging from 0.10 to 0.38) of the Langmuir regression equations suggest that the NH<sub>4</sub><sup>+</sup> adsorption data did not fit the Langmuir isotherms well. Future studies could explore fitting the  $NH_4^+$  sorption data into other sorption models. The higher adsorption of  $NH_4^+$  by the treatment with charcoal is related to its high number of adsorption sites or negative charges of these materials. Incorporating charcoal and sago bark ash as soil amendments in agriculture has the potential to reduce the usage of chemical fertilizers. The reliance on commercial lime could also be reduced due to the alkaline characteristics of these materials. Therefore, the co-application of charcoal and sago bark ash could contribute to improve the utilization of N fertilizer by effectively controlling  $NH_4^+$  availability for timely crop use, reducing losses, and preventing soil and water pollution.

**Keywords:** nutrient release and retention; sorption; soil nitrogen; fertilizer use; carbonaceous materials; soil amendments



Citation: Hamidi, N.H.; Ahmed, O.H.; Omar, L.; Ch'ng, H.Y.; Johan, P.D.; Paramisparam, P.; Musah, A.A.; Jalloh, M.B. Charcoal and Sago Bark Ash Regulates Ammonium Adsorption and Desorption in an Acid Soil. *Sustainability* **2023**, *15*, 1368. https://doi.org/10.3390/su15021368

Academic Editor: Georgios Koubouris

Received: 2 October 2022 Revised: 17 November 2022 Accepted: 22 November 2022 Published: 11 January 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

## 1. Introduction

Fertilizer use in agriculture is important for plant growth and yield. However, excessive fertilizer use on agricultural soils leads to inorganic N pollutants being released into surface and groundwater bodies [1,2]. Kumar and Padhye [3] reported that high amounts of NH<sub>4</sub><sup>+</sup> concentration causes eutrophication. Nutrients applied to soils can be retained through sorption (Adsorption and absorption). The nutrients that are adsorbed are essential fractions due to their availability for uptake by plants. Soil pH, pH buffering capacity, temperature, redox potential, and floods have significant effects on nutrient adsorption [4]. Although the average  $NH_4^+$  concentration of soils is often lower than  $NO_3^-$ ,  $NH_4^+$  is the predominant source of N that is available for plant nutrition [5]. Furthermore, because of its positive charge,  $NH_4^+$  is attracted to negatively charged soil particles, and therefore it is retained as an exchangeable cation in soils and is not easily leached, making it readily available for plant uptake. This is possible through temporary  $NH_4^+$  retention on the exchange sites of the amendments. The sorption of NH<sub>4</sub><sup>+</sup> to black carbon, particularly activated C, has been studied [6]. Pliassas et al. [7] reported that adsorption of  $NH_4^+$  onto activated C has attracted scholarly attention and is regarded as one of the most effective and well-established methods. However, activated C is expensive and it cannot be renewed or reactivated after usage. Therefore, alternative low-cost, environmentally friendly, and effective adsorbents are required and need to be researched.

Recently, the use of natural adsorbents such as agricultural waste as alternative adsorbent materials has gained popularity [8]. Charcoal and sago bark ash are produced from agricultural wastes under anaerobic combustion. These materials contain cellulose, oxides, hydroxides, carboxyl, and phenolic compounds. Charcoal has a unique pore structure and high capacity for sorption because of its high carboxylic acid content and also its resistance to biodegradation. When amendments such as charcoal or biochar are applied to soils, their interaction with soils is governed by many factors including the properties of the amendments, the soils' properties, and the nutrient retention and leaching characteristics of the mixture [9]. Therefore, this study attempted to find out whether using a combination of charcoal and sago bark ash improves  $NH_4^+$  sorption and how much  $NH_4^+$  can be adsorbed and desorbed to reduce  $NH_4^+$  leaching from soils. It was hypothesised that the combination of charcoal and sago bark ash could retain and release  $NH_4^+$ . Thus, sorption studies were carried out to examine the ability of charcoal and sago bark ash to regulate soil N availability through adsorption and release of  $NH_4^+$ .

#### 2. Materials and Methods

#### 2.1. Description of the Soil Studied, Its Collection and Analysis

The soil (Bekenu series, *Typic Paleudults*) used in this study was sampled at Universiti Putra Malaysia Bintulu Sarawak Campus ( $3^{\circ}12'20.0''$  N,  $113^{\circ}04'20.0''$  E) at 0-20 cm from an uncultivated secondary forest. Afterwards, the soil was air-dried, crushed, and sieved to pass through a 2 mm sieve for characterisation for the sorption study. The sorption study was carried out in the Soil Science Laboratory of Universiti Putra Malaysia Bintulu Sarawak Campus. Before commencing the sorption study, soil samples were analysed for their bulk density [10], texture [11], pH and electrical conductivity [12], total C [13], total N [14], exchangeable NH<sub>4</sub><sup>+</sup> and available NO<sub>3</sub><sup>-</sup> [15], exchangeable acidity, exchangeable Al, exchangeable H<sup>+</sup> [16], and soil exchangeable cations [17] using standard procedures.

#### 2.2. Initial Characterisation of Soil, Sago Bark Ash, and Charcoal

Table 1 summarizes the selected physical and chemical properties of the soil, charcoal, and sago bark ash. The selected soil properties of the examined soil (Bekenu series, *Typic Paleudults*), except for soil texture, were similar to the results of Paramananthan [18]. The soil texture obtained is comparable to that reported by the Soil Survey Staff [10]. The charcoal was obtained from Pertama Ferroalloys Sdn Bhd, Bintulu, Sarawak, Malaysia. The sago bark ash used in this study was obtained from Song Ngeng Sago Industries, Dalat, Sarawak, Malaysia.

Properties	Soil	Sago Bark Ash	Charcoal
pH (H <sub>2</sub> O)	4.61	9.99	7.74
pH (KCl)	3.95	9.66	7.31
$\overline{EC}$ (µS cm <sup>-1</sup> )	35.10	5.75	0.27
Bulk density (g m <sup>-3</sup> )	1.25	nd	nd
Total C (%)	2.16	nd	nd
Total N (%)	0.08	1.37	1.54
Exchangeable $NH_4^+$ (%)	0.00049	0.00026	0.00023
Available $NO_3^-$ (%)	0.00049	0.00026	0.00023
CEC (cmol kg $^{-1}$ )	4.67	13.13	nd
Exchangeable $K^+$ (cmol kg $^{-1}$ )	0.06	9120.00	1435.20
Exchangeable $Ca^{2+}$ (cmol kg <sup>-1</sup> )	0.02	3361.20	2346.67
Exchangeable $Mg^{2+}$ (cmol kg <sup>-1</sup> )	0.22	433.73	409.07
Exchangeable $Na^+$ (cmol kg <sup>-1</sup> )	0.03	348.00	99.38
Exchangeable $Fe^{2+}$ (cmol kg <sup>-1</sup> )	1.09	8.43	41.90
Exchangeable $Mn^{2+}$ (cmol kg <sup>-1</sup> )	0.01	nd	nd
Total titratable acidity (cmol kg $^{-1}$ )	1.15	nd	0.10
Exchangeable $H^+$ (cmol kg <sup>-1</sup> )	0.13	nd	0.05
Exchangeable $Al^{3+}$ (cmol kg <sup>-1</sup> )	1.02	nd	0.047
Sand (%)	71.90	nd	nd
Silt (%)	13.50	nd	nd
Clay (%)	14.60	nd	nd
Texture (%)	Sandy loam	nd	nd

**Table 1.** Selected physical and chemical properties of soil, sago bark ash, and charcoal used in the sorption study.

Note: the values are on a dry weight basis; nd = not detected.

#### 2.3. Soil Ammonium Adsorption and Desorption

Two grams of soil were placed into a 250 mL centrifuge bottle for each treatment. There were three replicated for each treatment. A range of N solutions (0, 100, 200, 300, and 400 mg N L<sup>-1</sup>) was prepared by dissolving ammonium chloride (NH<sub>4</sub>Cl) in 0.2 M NaCl solution in distilled water. Subsequently, 20 mL of the prepared isonormal N solutions were poured into the centrifuge bottles to give 0, 1000, 2000, 3000, and 4000 µg of added N sample<sup>-1</sup>. The isonormal solutions were used in this adsorption study to provide competing ions for exchange sites, in addition to preserve a constant ionic strength in the mixtures between the adsorbent and the solution [19]. The samples were then shaken using an orbital shaker for 24 h at 180 rpm, after which the samples were centrifuged at 10,000 rpm for 15 min. The N content in each supernatant (equilibrium solution) was then determined using the steam distillation method [14]. The amount of N adsorbed per g soil was determined by subtracting the initial amount of N supplied from the amount in the equilibrium solution. The adsorbed N was calculated as µg per g soil. The amount of NH<sub>4</sub><sup>+</sup> adsorbed at equilibrium (Q<sub>e</sub>) was calculated using the following formula:

$$Q_e = ((C_o - C_e) \times V)/(M)$$

where  $C_o$  = the initial concentration of the isonormal solution (mg L<sup>-1</sup>),  $C_e$ = the equilibrium concentration of the isonormal solution (mg L<sup>-1</sup>), V = the volume of the isonormal solution (L), and M = the mass of the sample (g).

After the N adsorption part of the experiment, the same samples (sediments in centrifuge bottles) were rinsed with ethanol and centrifuged for 10 min at 10,000 rpm [19]. Thereafter, the ethanol was discarded. Then, a 20 mL of 2 M KCl was added and shaken using an orbital shaker for 24 h at 180 rpm. Thereafter, the samples were centrifuged for 15 min at 10,000 rpm. Then, the supernatants were collected, and the N contents determined as the desorbed N content using the steam distillation method [14]. The amount of  $NH_4^+$ desorbed at equilibrium  $(Q_{de})$  (mg g<sup>-1</sup>) was calculated using the following formula:

$$Q_{de} = ((C_{do} - C_{de}) \times V)/(M)$$

where  $C_{do} = NH_4^+$  concentration on the sample (mg L<sup>-1</sup>);  $C_{do} = C_o - C_e$ ,  $C_{de} = NH_4^+$ concentration at the desorption equilibrium (mg  $L^{-1}$ ), V = the volume of the isonormal solution (L), and M = the mass of the sample (g).

The amounts of the materials used were calculated based on the literature for charcoal [20,21] and sago bark ash [22–24] where 10 and 5 t ha<sup>-1</sup> are equivalent to 15.42 g and 7.71 g, respectively. The treatments evaluated in the sorption study and their initial pH are summarised in Table 2.

Code for the Treatments	Details of the Treatments	Initial pH
T1	Soil only (300 g)	5.31
Τ2	Charcoal only (300 g)	7.76
Т3	Sago bark ash only (300 g)	9.78
T4	Soil + charcoal $(300 \text{ g} + 15.42 \text{ g})$	6.51
T5	Soil + sago bark ash $(300 \text{ g} + 7.71 \text{ g})$	6.41
Τ6	Soil + charcoal + g sago bark ash (300 g +15.42 g + 7.71)	6.65

#### 2.4. Experimental Design and Statistical Analysis

Table 2. Sorption study treatments and their initial pH.

The treatments were arranged in Completely Randomized Designed (CRD) in triplicates. Analysis of Variance (ANOVA) was used to determine treatment effects whereas means of treatments were compared using Tukey's Studentized Range (HSD) test at  $p \leq 0.05$ . PROC REG was used to test linear regression analysis and to obtain coefficients of determination  $(R^2)$  for each linear regression equation. The Statistical Analysis System (SAS) version 9.4 was used for the statistical tests.

## 3. Results and Discussion

## Effects of Amendments on Ammonium Adsorption and Desorption

The amount of ammonium in the equilibrium solution increased with increasing the amount of N (Table 3). For the ammonium content in the equilibrium solution of the sago bark ash, only (T3) was the lowest (Table 3), which could be attributed to the inherent nutrients in the sago bark ash of CaCO<sub>3</sub>, CaO, and MgO. The dissolution of these compounds releases Ca<sup>2+</sup> and Mg<sup>2+</sup> cations, which results in a low negative charge density in acid soils and inhibits NH<sub>4</sub><sup>+</sup> adsorption because of the competition with the divalent cations. Moreover, there is limited N in the sago bark ash (Table 1). In addition, the lower N in the ash was because the N was lost during pyrolysis. At 100 mg N  $L^{-1}$  for the equilibrium solution, the effects of T1, T4, T5, and T6 were not significantly different but their effects were significantly higher than those of T2 and T3. A similar trend was shown by the T1, T4, T5, and T6 treatments for the 300 mg N  $L^{-1}$  NH<sub>4</sub><sup>+</sup> concentration, where T2 and T3 resulted in a significantly lower NH4<sup>+</sup> concentration at the equilibrium solution compared with T1, T4, T5, and T6. At 200 mg N  $L^{-1}$ , T3 resulted in the lowest  $NH_4^+$ concentration with the equilibrium solution. At 400 mg  $L^{-1}$ , T4 resulted in significantly higher NH<sub>4</sub><sup>+</sup> concentration than T3, but its effect was similar to T1, T5, and T6.

	Ammonium Concentration at Adsorption Equilibrium, C <sub>e</sub> (mg				
Treatments	0	100	200	300	400
Added N (mg N L <sup>-1</sup> )					
T1	nd	38.76 $^{\rm a} \pm 5.22$	$68.65\ ^{a}\pm 11.64$	100.64 $^{\mathrm{a}} \pm 13.33$	91.30 $^{\rm ab} \pm 17.2$
T2	nd	$17.51 \text{ b} \pm 1.07$	$35.96$ $^{\mathrm{ab}}\pm6.74$	$32.69 \text{ b} \pm 2.44$	$54.17  {}^{ m bc} \pm 8.57$
T3	nd	$2.80^{ ext{ b}} \pm 0.40^{ ext{ }}$	$5.37^{\text{ b}} \pm 1.17$	$5.37^{\text{ b}} \pm 1.02$	$11.68 \text{ c} \pm 3.99$
T4	nd	46.47 $^{\mathrm{a}}\pm3.67$	68.18 a $\pm$ 11	104.61 $^{\mathrm{a}}\pm9.91$	116.75 a $\pm$ 9.76
T5	nd	42.26 $^{\mathrm{a}}\pm3.53$	51.37 $^{\mathrm{a}}\pm7.28$	$88.03\ ^{\mathrm{a}}\pm7.48$	$81.49~^{ m ab}\pm 12.75$
T6	nd	38.53 $^{\mathrm{a}}\pm5.96$	53.94 $^{\mathrm{a}}\pm7.19$	77.99 a $\pm$ 6.06	92.23 $^{\rm ab} \pm 13.35$

**Table 3.** Treatments effects on ammonium concentration adsorbed at equilibrium for different concentrations of added nitrogen.

Note: nd = not detected. Means with different letter(s) indicate significant differences between treatments according to Tukey's HSD test at  $p \le 0.05$ , that is <sup>a</sup> > <sup>b</sup> > <sup>c</sup>. Mean values  $\pm$  standard error.

Generally, the amount of ammonium adsorbed increased with increasing concentration of the isonormal solution (Table 4). This result is consistent with that of Jellali et al. [25] who also reported that the increased driving forces of the  $NH_4^+$  concentration gradient and an increase in the contact probability between the  $NH_4^+$  and the adsorbent explain the higher sorption capacity observed at the initial concentrations.

**Table 4.** Treatments effects on the amount of ammonium adsorption for different initial concentrations of isonormal solution (NH<sub>4</sub>Cl-NaCl).

	Ammonium	Adsorption under E Isonormal Solut	Different Initial Conion, Q <sub>e</sub> (mg L <sup>-1</sup> )	ncentration of	
Treatments	100	200	300	400	
	Added N (mg N L <sup>-1</sup> )				
T1	$0.61 \ ^{\mathrm{b}} \pm 0.05$	$1.31~^{\rm b}\pm0.12$	$1.99 \ ^{b} \pm 0.13$	$3.09 \text{ bc} \pm 0.17$	
T2	$0.82~^{\rm a}\pm0.01$	$1.64~^{\mathrm{ab}}\pm0.07$	$2.67~^{a}\pm0.02$	$3.46~^{\rm ab}\pm0.09$	
T3	$0.97~^{\mathrm{a}}\pm0.00$	$1.95~^{\mathrm{a}}\pm0.01$	$2.95~^{\rm a}\pm0.10$	3.88 a $\pm$ 0.04	
T4	$0.54~^{ m b}\pm 0.04$	$1.32 \ ^{ m b} \pm 0.11$	$1.95 \ ^{ m b} \pm 0.10$	$2.83~^{\rm c}\pm0.10$	
T5	$0.58~^{ m b}\pm 0.04$	$1.49~^{\rm b}\pm0.07$	$2.12^{\text{ b}}\pm 0.07$	$3.19 \ ^{ m bc} \pm 0.13$	
T6	0.61 $^{\rm b} \pm 0.06$	$1.46^{\text{ b}}\pm0.07$	$2.22^{b} \pm 0.06$	$3.08 \text{ bc} \pm 0.13$	

Note: Means with different letter(s) indicate significant differences between treatments according to Tukey's HSD test at  $p \le 0.05$ , that is <sup>a</sup> > <sup>b</sup> > <sup>c</sup>. Mean values  $\pm$  standard error.

Regardless of the concentration of the isonormal solution used, T3 had the highest NH4<sup>+</sup> adsorption at equilibrium (Qe). Among the treatments, T2 and T3 resulted in a significantly higher amount of NH4<sup>+</sup> adsorbed in the 100 mg L<sup>-1</sup> isonormal solution compared with T1, T4, T5, and T6. This trend was similar to that for the 300 mg  $L^{-1}$ isonormal solution. At 200 mg N  $L^{-1}$ , the combined use of charcoal and sago bark ash (T6) resulted in similar effects compared to those of T1, T2, T4, and T5. The sago bark ash only (T3) adsorbed higher  $NH_4^+$  than the soil with charcoal only (T2), but the effect of T2 was comparable to those of T1, T5, and T6. This observation is related to the initial pH of the treatments because pH is one of the important variables in the sorption process and it impacts the surface charge of the sorbent, degree of ionisation, and adsorbate speciation [26]. Treatment 2 and T3 had pH values greater than 7. When the pH was greater than 7, the sorption capacities were higher than the values at low pH, indicating that neutral or alkaline conditions are favourable for  $NH_4^+$  removal. In solution,  $NH_4^+$  is present in ionised ( $NH_4^+$ ) and the non-ionised (NH<sub>3</sub>) forms. According to Maraňón et al. [27], N exists as  $NH_4^+$  when pH is below 7. When the pH decreases, competition between  $H^+$  and the  $NH_4^+$  in the solution increases at the exchange sites of the sorbents surface. This results in low NH<sub>4</sub><sup>+</sup> sorption capacity by the adsorbents. At high pH,  $NH_4^+$  is transformed to  $NH_3$ , which could be lost through volatilization.

adsorption. The insignificant  $R^2$  (ranging from 0.10 to 0.38) of the Langmuir regression equations suggest that the NH<sub>4</sub><sup>+</sup> adsorption data did not fit the Langmuir isotherms (Table 5). This is because the Langmuir isotherm is the simplest theoretical model for a monolayer adsorption, and this model assumes that all the sorption sites have an equal adsorbate affinity [28]. This finding is consistent with that of Palanivell [4] who also reported that N adsorption, regardless of treatment (crude humic, biochar, and clinoptilolite zeolite), does not fulfil the assumptions of the Langmuir approach [29]. Therefore, it is advised to incorporate the NH<sub>4</sub><sup>+</sup> sorption data into other sorption models such as Freundlich, to have a better understanding of the relationship between equilibrium and NH<sub>4</sub><sup>+</sup> adsorption.

Table 5. Langmuir isotherms variables for ammonium adsorption for the different treatments.

Treatment	<b>Regression Equation</b>	<b>R</b> <sup>2</sup>	$q_m$ (mg g $^{-1}$ )	b (mg $g^{-1}$ )	MBC
T1	y = 0.24x + 24.62	0.18	4.16	$9.74  imes 10^{-3}$	0.04
T2	y = 0.36x + 5.72	0.38	2.78	0.063	0.18
T3	y = 0.09x + 1.48	0.30	11.11	0.061	0.68
T4	y = 0.229x + 33.57	0.12	4.37	$6.82 imes10^{-3}$	0.03
T5	y = 0.235x + 21.43	0.11	4.26	0.011	0.05
T6	y = 0.26x + 23.093	0.10	3.85	0.011	0.04

The maximum  $NH_4^+$  uptake  $(q_m)$  per unit mass of the adsorbent in the monolayer context is highest in sago bark ash only (T3). This suggest that T3 required less  $NH_4^+$  to saturate the adsorbent because of its lower adsorption sites. Kithome et al. [19] also found that the amount of  $NH_4^+$  sorption increased with increasing the pH (4 to 7). The lower maximum  $NH_4^+$  uptake  $(q_m)$  for T2 and T6 suggests that charcoal has higher adsorption sites and it requires more  $NH_4^+$  to saturate the charcoal. In terms of bonding energy constant (b), soil only demonstrated the lowest. The sago bark ash reduced the bonding of energy constant (b) because of the contribution of the acid functional groups, the carbonate dissolutions, and the CEC on the soil buffering capacity, particularly at a pH above 4.5 [30,31]. A similar finding has been reported by Luo et al. [32] who revealed that the changes in the buffering capacity are influenced by the CEC, the carbonates concentration, and the base saturation. The sago bark ash only (T3) resulted in the highest maximum buffering capacity (MBC). This is possible because of the charge characteristics of the amendments.

The treatment effects on the amount of  $NH_4^+$  desorbed at equilibrium at the different concentrations of the added N are summarised in Table 6. Among the treatments, there were no significant differences in  $NH_4^+$  desorbed for T2, T4, and T6, but the effects of these treatments were significantly higher than T3 at 100 mg N L<sup>-1</sup>. Similar results on  $NH_4^+$ desorbed were observed at 200 mg N L<sup>-1</sup>. At 300 mg N L<sup>-1</sup>, charcoal only (T2) resulted in a significantly higher desorbed  $NH_4^+$  than sago bark ash only (T3). At 400 mg N L<sup>-1</sup>, the combined use of charcoal and sago bark ash with soil (T6) resulted in a similar effect on the desorbed  $NH_4^+$  as those of soil only (T1), soil with charcoal only (T4), and soil with sago bark ash only (T5). The higher  $NH_4^+$  desorption for the treatments with charcoal (T2, T4, and T6) compared with those for soil only (T1) and sago bark ash only (T3) suggests that these treatments can release  $NH_4^+$  into the solution. The higher  $NH_4^+$  desorption of the charcoal suggests that charcoal can temporary retain  $NH_4^+$ , although the CEC of the charcoal is high.

	Ammonium Concentration at Desorption Equilibrium, $C_{de}$ (mg g <sup>-1</sup> )				
Treatments	0	100	200	300	400
Added N (mg N L <sup>-1</sup> )					
T1	nd	$6.30~^{ab}\pm0.81$	$9.57~^{\mathrm{ab}}\pm0.84$	11.91 $^{\mathrm{ab}}\pm0.4$	12.61 <sup>ab</sup> ±0.40
T2	nd	7.24 $^{\mathrm{a}}\pm0.23$	10.74 $^{\rm a}\pm1.30$	$16.81^{a} \pm 3.59$	15.88 $^{\rm a} \pm 1.63$
T3	nd	$3.04^{\text{ b}} \pm 0.23$	$4.90^{\text{ b}} \pm 0.00$	$6.77 \ ^{ m b} \pm 0.62$	$8.64 \ ^{ m b} \pm 2.69$
T4	nd	$8.41^{\rm a}\pm1.46$	10.74 $^{\mathrm{a}}\pm0.23$	14.71 $^{\mathrm{ab}}\pm2.53$	14.01 $^{\mathrm{ab}}\pm0.00$
T5	nd	$6.07~^{ m ab}\pm 0.62$	$9.57~^{\mathrm{ab}}\pm1.82$	12.14 $^{\mathrm{ab}}\pm1.68$	13.08 $^{\mathrm{ab}}\pm0.23$
T6	nd	$6.77~^a\pm0.23$	10.97 $^{\mathrm{a}}\pm0.62$	$15.18 ^{\text{ab}} \pm 1.63$	14.71 $^{\rm ab}\pm1.62$

**Table 6.** Treatments effects on the amount of ammonium desorbed at equilibrium for different concentrations of added nitrogen.

Note: nd = not detected. Means with different letter(s) indicate significant differences between treatments according to Tukey's HSD test at  $p \le 0.05$ , that is <sup>a</sup> > <sup>b</sup> > <sup>c</sup>. Mean values  $\pm$  standard error.

Table 7 summarises the effects of treatments on the amount of  $NH_4^+$  desorbed for the different concentrations of the isonormal solution ( $Q_{de}$ ). Among the treatments, charcoal only (T2) and sago bark only (T3) resulted in no significant differences for the amount of  $NH_4^+$  desorbed at the 100 mg N L<sup>-1</sup> isonormal solution, but they were significantly higher than others (T1, T4, T5, and T6). At 200 mg N L<sup>-1</sup>, with the exception of T3, the effects of the rest of the treatments on the amount of  $NH_4^+$  desorbed were similar. Sago bark ash only (T3) resulted in the highest amount of  $NH_4^+$  desorbed were similar. Sago bark ash only (T3) resulted in the highest amount of  $desorbed NH_4^+$  at 300 mg N L<sup>-1</sup> followed by charcoal only (T2). However, at 300 mg N L<sup>-1</sup>, the  $NH_4^+$  desorbed due to soil only (T1), soil with charcoal (T4), soil with sago bark ash (T5), and soil with the combined use of charcoal and sago bark ash (T6) were similar. At 400 mg N L<sup>-1</sup>, there was no significant difference between T2 and T3 for  $NH_4^+$  desorption. The insignificant findings between soil only and soil with amendments suggest that these amendments are more effective in absorbing  $NH_4^+$  than adsorbing this ion.

**Table 7.** Treatments effects on the amount of ammonium desorption for different initial concentrations of isonormal solution (NH<sub>4</sub>Cl-NaCl).

	Ammonium	Desorption under D Isonormal Soluti	Different Initial Coron, ${ m Q}_{ m de}$ (mg g $^{-1}$ )	ncentration of			
Treatments	100	200	300	400			
	Added N (mg N L <sup>-1</sup> )						
T1	$0.55^{\text{ b}} \pm 0.05$	$1.22^{\text{ b}} \pm 0.12$	$1.87~^{\rm c}\pm0.13$	$2.96 {}^{bc} \pm 0.18$			
T2	0.75 $^{\rm a}\pm 0.01$	$1.53~^{ m ab}\pm 0.06$	$2.50 \ ^{\mathrm{b}} \pm 0.02$	$3.30~^{\mathrm{ab}}\pm0.09$			
T3	0.94 $^{\mathrm{a}}\pm0.00$	1.90 $^{\rm a}\pm 0.01$	$2.88~^a\pm0.02$	3.80 $^{\rm a}\pm 0.04$			
T4	$0.45~^{ m b}\pm 0.05$	$1.21 {}^{\rm b} \pm 0.11$	$1.81~^{\rm c}\pm0.08$	$2.69\ ^{ m c}\pm 0.09$			
T5	$0.52~^{ m b}\pm 0.04$	$1.39 { m \ b} \pm 0.08$	$2.00\ ^{ m c}\pm 0.07$	$3.05 \text{ bc} \pm 0.13$			
T6	$0.55~^{\mathrm{b}}\pm0.06$	$1.35 \ ^{ m b} \pm 0.07$	$2.07~^{\rm c}\pm0.07$	$2.93 \ ^{\mathrm{bc}} \pm 0.14$			

Note: Means with different letter(s) indicate significant differences between treatments according to Tukey's HSD test at  $p \le 0.05$ , that is <sup>a</sup> > <sup>b</sup> > <sup>c</sup>. Mean values  $\pm$  standard error.

#### 4. Conclusions

This study revealed that the combined use of charcoal and sago bark ash improves  $NH_4^+$  adsorption but reduces  $NH_4^+$  desorption. This indicates that these soil amendments have a high affinity for  $NH_4^+$ , which enables temporary retention of  $NH_4^+$  by the amendments. The results for T3 for  $Q_e$  and  $Q_{de}$  were 3.88 mg L<sup>-1</sup> and 3.80 mg g<sup>-1</sup>, respectively, for the 400 mg N L<sup>-1</sup> isonormal solution followed by T2 with values of 3.46 mg L<sup>-1</sup> and 3.30 mg g<sup>-1</sup>, respectively. For treatments T2 and T3, which resulted in higher  $Q_e$  and  $Q_{de}$  for  $NH_4^+$ , soil was not included. However, in practical terms, any of the treatments T4, T5 and T6 that included mixing the amendments with soil are better since the results of these treatments were not significantly different in terms of  $Q_e$  and  $Q_{de}$  for  $NH_4^+$ . This is

despite the fact that T4, T5 and T6 resulted in lower  $Q_e$  and  $Q_{de}$  for NH<sub>4</sub><sup>+</sup> compared to T2 and T3. The results also showed a positive linear relationship between NH<sub>4</sub><sup>+</sup> adsorption and the addition of N. This indicates that NH<sub>4</sub><sup>+</sup> can be retained temporarily by the amendments. The insignificant or low R<sup>2</sup> (ranging from 0.10 to 0.38) of the Langmuir regression equations suggest that the NH<sub>4</sub><sup>+</sup> adsorption data did not fit the Langmuir isotherms well. Future studies could explore fitting the NH<sub>4</sub><sup>+</sup> sorption data into other sorption models. The negatively charged surface of the charcoal aided nutrient retention due to the high number of adsorption sites. It is envisaged that the sorption efficiency could be enhanced by changing the processing conditions such as the pyrolysis temperature during the production of these soil amendment materials. The incorporation of charcoal and sago bark ash has the potential to reduce the use of chemical fertilizers and reliance on commercial lime. Therefore, the co-application of these amendments could contribute to improving the use of N fertilizer by effectively controlling NH<sub>4</sub><sup>+</sup> availability for timely crop uptake, reduced losses, and prevention of soil and water pollution.

Author Contributions: Conceptualization, N.H.H., O.H.A., L.O., H.Y.C. and M.B.J.; methodology, N.H.H., P.D.J., P.P. and L.O.; validation, O.H.A., L.O. and H.Y.C.; formal analysis, O.H.A., and M.B.J.; investigation, N.H.H.; resources, O.H.A., L.O., H.Y.C. and N.H.H.; data curation, N.H.H., P.P. and P.D.J.; writing—original draft preparation, N.H.H.; writing—review and editing, O.H.A., M.B.J., and A.A.M.; visualization, N.H.H., P.D.J., P.P. and A.A.M.; supervision, O.H.A., L.O. and H.Y.C.; project administration, O.H.A., M.B.J. and A.A.M.; funding acquisition, O.H.A., M.B.J. and A.A.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Ministry of Higher Education, Malaysia with grant number [FRGS/1/2016/WAB01/UPM/02/2].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available within article.

Acknowledgments: The authors would like to acknowledge the Ministry of Higher Education, Malaysia for financial assistance and the collaboration with, and facilities provided by, Universiti Putra Malaysia (Malaysia), Universiti Malaysia Sabah (Malaysia), Universiti Malaysia Kelantan (Malaysia), Management and Science University (Malaysia), and Universiti Islam Sultan Sharif Ali (Brunei Darussalam).

Conflicts of Interest: The authors declare no conflict of interest.

### References

- 1. Gai, X.; Wang, H.; Liu, J.; Zhai, L.; Liu, S.; Ren, T.; Liu, H. Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. *PLoS ONE* **2014**, *9*, e113888. [CrossRef] [PubMed]
- Scott, H.L.; Ponsonby, D.; Atkinson, C.J. Biochar: An improver of nutrient and soil water availability-what is the evidence? CAB Rev. Perspect. Agric. Veter Sci. Nutr. Nat. Resour. 2014, 2014, 1–19. [CrossRef]
- 3. Kumar, R.; Padhye, L.P. Fate of environmental pollutants. Water Environ. Res. 2017, 89, 1603–1633. [CrossRef] [PubMed]
- 4. Palanivell, P. Organic and Mineral Amendments on Rice (*Oryza sativa* L.) Yield and Nutrient Recovery Efficiency. Ph.D. Thesis, Universiti Putra Malaysia, Serdang, Malaysia, 2016.
- 5. Marschner, P.; Rengel, Z. Nutrient availability in soils. In *Marschner's Mineral Nutrition of Higher Plants*; Academic Press: Cambridge, MA, USA, 2012; pp. 315–330.
- 6. Seredych, M.; Bandosz, T.J. Template-derived mesoporous carbons with highly dispersed transition metals as media for the reactive adsorption of dibenzothiophene. *Langmuir* **2007**, *23*, 6033–6041. [CrossRef]
- Pliassas, E.; Pivnenko, K.; Gidarakos, E. Adsorption of ammonium ions (NH<sub>4</sub><sup>+</sup>) onto bioadsorbent: Case of cotton waste. In Proceedings of the CRETE 2012, 3rd International Conference on Industrial and Hazardous Waste Management, Chania, Greece, 12–14 September 2012.
- 8. Khalil, A.; Sergeevich, N.; Borisova, V. Removal of ammonium from fish farms by biochar obtained from rice straw: Isotherm and kinetic studies for ammonium adsorption. *Adsorpt. Sci. Technol.* **2018**, *36*, 1294–1309. [CrossRef]
- 9. Mukherjee, A.; Zimmerman, A.R. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar-soil mixtures. *Geoderma* 2013, 193–194, 122–130. [CrossRef]

- Soil Survey Staff. Soil Survey Field and Laboratory Methods Manual; Soil Survey Investigations Report No. 51, Version 2.0.; Burt, R., Ed.; U.S. Department of Agriculture, Natural Resources Conservation Service: Washington, DC, USA, 2014.
- 11. Bouyoucos, G.J. Hydrometer Method Improved for Making Particle Size Analyses of Soils 1. Agron. J. 1962, 54, 464–465. [CrossRef]
- Peech, M. Hydrogen-Ion Activity. In *Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties;* American Society of Agronomy: Madison, WI, USA, 1965; Volume 9, pp. 914–926.
- Chefetz, B.; Hatcher, P.G.; Hadar, Y.; Chen, Y. Chemical and Biological Characterization of Organic Matter during Composting of Municipal Solid Waste. J. Environ. Qual. 1996, 25, 776–785. [CrossRef]
- 14. Bremner, J.M. Studies on Soil Organic Matter: Part I. The Chemical Nature of Soil Organic Nitrogen. J. Agric. Sci. 1949, 39, 183–193. [CrossRef]
- 15. Keeney, D.R.; Nelson, D.W. Nitrogen—Inorganic forms. In *Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties* 9.2.2, 2nd ed.; John Wiley & Sons: Hoboken, NJ, USA, 1983; Volume 9, pp. 643–698. [CrossRef]
- 16. Rowell, D.L. Soil Science: Methods and Applications; Longman Scientific & Technical: Essex, UK, 1994.
- 17. Cottenie, A. Soil testing and plant testing as a basis of fertilizer recommendation. FAO Soils Bull. 1980, 38, 70–73.
- 18. Paramananthan, S. Soils of Malaysia: Their Characteristics and Identification; Academy of Sciences Malaysia: Kuala Lumpur, Malaysia, 2000; Volume 1.
- 19. Kithome, M.; Paul, J.W.; Lavkulich, L.M.; Bomke, A.A. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.* **1998**, *62*, 622–629. [CrossRef]
- Free, H.F.; McGill, C.R.; Rowarth, J.S.; Hedley, M.J. The effect of biochars on maize (*Zea mays*) germination. N. Z. J. Agric. Res. 2010, 53, 1–4. [CrossRef]
- 21. Ndor, E.; Dauda, S.N.; Azagaku, E.D. Response of maize varieties (*Zea mays*) to biochar amended soil in Lafia, Nigeria. *J. Exp. Agric. Int.* **2015**, *5*, 525–531. [CrossRef]
- Mandre, M.; Pärn, H.; Ots, K. Short-term effects of wood ash on the soil and the lignin concentration and growth of *Pinus sylvestris* L. For. Ecol. Manag. 2006, 223, 349–357. [CrossRef]
- Ozolincius, R.; Buozyte, R.; Varnagiryte, K.I. Wood ash and nitrogen influence on ground vegetation cover and chemical composition. *Biomass Bioenergy* 2007, 31, 710–716. [CrossRef]
- 24. Perucci, P.; Monaci, E.; Onofri, A.; Vischetti, C.; Casucci, C. Changes in physico-chemical and biochemical parameters of soil following addition of wood ash: A field experiment. *Eur. J. Agron.* **2008**, *28*, 155–161. [CrossRef]
- Jellali, S.; Wahab, M.A.; Anane, M.; Riahi, K.; Jedidi, N. Biosorption characteristics of ammonium from aqueous solutions onto *Posidonia oceanica* (L.) fibers. *Desalination* 2011, 270, 40–49. [CrossRef]
- Anirudhan, T.S.; Rijith, S.; Tharun, A.R. Adsorptive removal of thorium (IV) from aqueous solutions using poly (methacrylic acid)-grafted chitosan/bentonite composite matrix: Process design and equilibrium studies. *Colloids Surfaces A Physicochem. Eng. Asp.* 2010, 368, 13–22. [CrossRef]
- Maranon, E.; Ulmanu, M.; Fernandez, Y.; Anger, I.; Castrillón, L. Removal of ammonium from aqueous solutions with volcanic tuff. J. Hazard. Mater. 2006, 137, 1402–1409. [CrossRef]
- 28. Bulut, Y.; Aydın, H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination* **2006**, *194*, 259–267. [CrossRef]
- Oros, I.; Krstić, J.; Kovačević, I. Adsorption feasibility in the Cr (total) ions removal from waste printing developer. *Global Nest J.* 2012, 14, 18–23.
- Bloom, P.R. Soil pH and pH buffering. In *Handbook of Soil Science*; Sumner, M.E., Huang, P.M., Li, Y., Eds.; CRC Press: Boca Raton, FL, USA, 2000; pp. B333–B352.
- Nelson, P.N.; Su, N. Soil pH buffering capacity: A descriptive function and its application to some acidic tropical soils. *Soil Res.* 2010, 48, 201–207. [CrossRef]
- Luo, W.T.; Nelson, P.N.; Li, M.-H.; Cai, J.P.; Zhang, Y.Y.; Yang, S.; Wang, R.Z.; Wang, Z.W.; Wu, Y.N.; Han, X.G. Contrasting pH buffering patterns in neutral-alkaline soils along a 3600 km transect in northern China. *Biogeosciences* 2015, 12, 7047–7056. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.