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Combined Use of Charcoal, Sago Bark Ash, and Urea Mitigate Soil Acidity and Aluminium Toxicity

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Abstract: Highly weathered tropical acidic soils are characterized by low pH, low organic matter, and aluminium and iron toxicity. These factors pose a challenge to achieving sustainable agriculture. The continued increase in the human population with the accompanied increasing food demand have negatively impacted the global N cycle partly because of excessive use N fertilizers particularly urea which is commonly used in agriculture. Ammonia volatilization from urea as an example, negatives the environmental quality. This study focuses on soil-N availability, pH, exchangeable acidity, Al^{3+}, and H^+ of a highly weathered acid soils (Bekenu series) through the combined use of charcoal, sago bark ash, and urea. To this end, an incubation study was conducted for 90 days through the combined use of charcoal, sago bark ash, and urea to determine if this approach could improve soil N availability and pH at the same time reducing exchangeable acidity, and Al^{3+}, and H^+ toxicity. The amount of urea used was fixed at 100% as the recommended rate. Charcoal and sago bark ash were varied by 25%, 50%, 75%, and 100%, respectively of the recommended rate. Selected soil physico-chemical properties were determined using standard procedures. This study revealed that combined use of charcoal, sago bark ash, and urea increased soil pH and base cations simultaneously the approach also reduced exchangeable acidity, exchangeable Al^{3+}, and exchangeable H^+. There were no significant differences in soil total N, exchangeable NH_4^+, and available NO_3^- for the combined use of charcoal, sago bark ash, and urea and urea alone because of the acid neutralizing effect of the amendments. Apart from the sago bark ash's liming effect, the high affinity of the functional groups of the charcoal for Al^{3+} might have impeded Al^{3+} from undergoing hydrolysis to produce more H^+ because a complete one mole of Al^{3+} hydrolysis produces three moles of H^+. Thus, the combined use of charcoal and sago bark ash can mitigate soil acidity and aluminium toxicity, although this approach has minimal effect on-N.

Keywords: waste management; liming agent; inorganic nitrogen; pyrolysis; functional groups

1. Introduction

Nitrogen is an essential and key nutrient in the enhancement of crop yield. Thus, to boost crop yield, modern agriculture relies on the use of inorganic fertilizers particularly synthetic fertilizers such as urea, ammonium sulphate, ammonium nitrate, anhydrous ammonia, among others [1]. Excessive use of nitrogenous fertilizers results in low nitrogen use efficiency (NUE), high surface and groundwater pollution, soil acidification, soil degradation, and decrease in soil microbial biomass [2,3].

Approximately 90% of the N fertilizer in the world is in the inorganic form called ammonium (NH_4^+). Ammonium is the predominant source of N which is commonly available for plant nutrition although the average of NH_4^+ concentration of soils is often

lower than nitrate (NO_3^-) [4]. Ammonium ions are transformed into highly mobile nitrate (NO_3^-) and nitrite (NO_2^-) by nitrifying bacteria under aerobic conditions in soils [5]. In the developing countries, urea is a popular N-based fertilizer because of its high N content (46%), easy transportation, and safety. However, urea hydrolysis increases soil pH and surface soil NH_4^+ to a level that causes NH_3 gaseous emission. Approximately, 50% of the N-based fertilizer applied is used for plant uptake. The remaining is prone to losses through surface runoff and leaching [6]. Nitrogen fertilizers are highly mobile in soils and because of this, they should be carefully used in agriculture to avoid losses through volatilization, denitrification, and leaching in particular [7]. Additionally, temperature and high rainfall contribute to the problem of N fertilizers use efficiency and this is more serious in highly weathered acid soils (for example, Ultisols and Oxisols) to cause low nutrient availability and rapid mineralization of soil organic matter [8]. Soil acidification poses a major challenge to agricultural sustainability [9]. This problem is particularly serious in highly weathered soils (Ultisols and Oxisols) whose supply of most plant nutrients with the exception of Fe, Al, and manganese (Mn) decrease with decreasing pH. For example, as base cations such as K, Ca, Mg, and Na get leached from highly weathered soils, these nutrients including ammonium and nitrate ions are replaced by Fe, Al, and Mn. In addition to the loss of organic matter, and Fe and Al hydrolysis which lead to further soil acidification, the fertility of highly weathered soils are compromised or decline with time.

Attempts have been made to reduce N losses via ammonia volatilization, leaching, immobilization, and nitrification. A technology that increases N efficacy such as an addition of organic and inorganic chemical compounds in urea as a urease inhibitor has been developed. However, this technology increases production cost by 30% [10]. Apart from urease inhibitors, biological approaches for N fixation are well established [11]. Although biological N fixation in the tropics in particular is economically and environmentally beneficial, the narrow relationships among microbial processes, micronutrients, and metabolic routes still need clarification [12]. As a result, efforts had been made to assess the feasibility and efficacy of organic residues, not only to improve soil productivity but to also enhance inorganic the efficiency od fertilizer use [13]. Therefore, it is essential to control N losses to enhance N retention using inexpensive, reliable, and environmentally friendly approaches such as adopting a combined use of sago bark ash, charcoal, and urea.

The forestry and agricultural sectors play important role in socio-economic development, particularly in developing countries. As a result, the quantity of wood wastes has increased exponentially. In the tropical areas of Southeast Asia, Sago (*Metroxylon sagu*) is one of the main starch crops grown for the starch industry [14]. Currently, Sarawak, Malaysia is one of the world's largest exporters of sago products. Approximately 43 thousand tonnes of sago starch are exported from Sarawak, Malaysia [15]. Commonly, sago bark waste is incinerated for power generation or left for natural degradation [15]. Approximately, 85% of the sago bark waste are unutilized in the sago processing mills, and this provides the opportunity for this unwanted waste to be utilized as for example, soil conditioners or amendments to improve soil N availability and pH at the same time reducing soil exchangeable acidity, Al^{3+}, and H^+ in highly weathered acid soils such as Ultisols and Oxisols. Utilizing sago bark ash as soil amendment does not only reduce this unwanted agricultural waste but it also improves soil and crop productivity. Sago bark ash or wood ash is produced through combustion and it is not only high in soluble macronutrients such as Ca, K, P, and Mg but it also has pH neutralizing effect because of its alkaline property [16]. In addition, base saturation and microbial activity can be increased following the use of sago bark ash [17]. Kilpimaa et al. [18] reported that the specific surface area, particle size distribution, pore size, and pore volume are important physical properties that influence the potential use and quality of C residues or ashes as adsorbents. Furthermore, ash hydrophilic property enables it to retain water [19] thus, increasing soil water holding capacity, moisture content, and nutrient availability.

Charcoal is another potential wood-derived product that can be used as soil conditioner or amendment. Gul and Whalen [20] defined charcoal as a carbonaceous solid

residue produced through slow and rapid pyrolysis, gasification, and hydrothermal carbonization under oxygen-deficient conditions. Charcoal as soil amendment does not only influence the nature of the sorption mechanism but it also enhances the sorption of organic pollutants [21,22]. In addition, it is highly resistant to decomposition [23]. Patel [22] reported that in carbonaceous materials, adsorption is regulated by the physical and chemical structure. Typically, charcoal is made up of C, H, N, S, ash, and oxygen [24]. Charcoal structure, composition, and characteristics such as particle size distribution, moisture content, density, ash content, and pH depend on the form, nature and origin of raw material, apart from the state of the thermal conversion cycle [25]. Additionally, Kookana et al. [26] and Jindo et al. [27] reported that charcoal is made up of inorganic and organic N and P such as amide groups, ortho-P, NH_4^+, and NO_3^-.

The high specific surface area and internal porous structure of charcoal could enhance sorption of NH_4^+ ions and retention of NO_3^- ions in soil water solution through entrapping these ions inside the pores of charcoal to improve N availability for plant uptake. Although adsorption of NH_4^+ ions on bark ash exhibits intermediate adsorption capacity compared with charcoal, it has the potential to reduce nutrient loss in addition to being ideal for highly weathered acidic soil because of its acid neutralizing properties. This present study attempts to answer the question of whether amending urea with charcoal and sago bark ash could significantly improve soil pH and N availability in addition to reducing exchangeable acidity, Al^{3+}, and H^+ of highly weathered acid soils. Therefore, this study focuses on soil urea-N availability, pH, exchangeable acidity, Al^{3+}, and H^+ of a highly weathered acid soil (Bekenu series) through the combined use of charcoal, sago bark ash, and urea. It was hypothesized that the combined use of sago bark ash, charcoal, and urea could improve soil pH and urea-N availability through reduction exchangeable acidity, Al^{3+}, and H^+.

2. Materials and Methods

2.1. Soil Sampling, Preparation, and Characterization

The soil (Bekenu series, *Typic Paleudults*) used in this present study was taken from an uncultivated secondary forest at Universiti Putra Malaysia Bintulu Sarawak Campus (Figure 1). The soil was sampled at a depth of 0–20 cm after which it was air-dried, crushed, and sieved to pass a 2 mm sieve. The soil bulk density was determined using core ring method [28]. Soil texture was determined using the hydrometer method [29]. The soil pH in water and KCl were determined using a digital pH meter at a ratio of 1:2.5 (sample: water/KCl) [30]. Soil total titratable acidity, exchangeable hydrogen, and exchangeable aluminium were determined using the titration method [31]. Soil total C was determined using loss on ignition [32] and calculated as 58% of the organic matter. Soil cation exchange capacity was determined using the leaching method [33]. Total N was determined using the Kjeldahl method [34]. Available N was determined using Keeney and Nelson [35]. Exchangeable cations (K, Ca, Mg, Na, Mn, and Fe) were extracted using the double acid method [36] after which they were determined using Atomic Absorption Spectrometry (AAnalyst 800, PerkinElmer, Norwalk, CT, USA). Except for soil texture, the selected physicochemical properties of the soil (Table 1) were within the range reported by Paramananthan [37].

Figure 1. Aerial view of location where the soil sampled in Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia.

Table 1. Selected physicochemical properties of the soil used in the incubation study.

Property	Current Study	Range *
pH (H_2O)	4.61	4.6–4.9
pH (KCl)	3.95	3.8–4.0
EC ($\mu S\ cm^{-1}$)	35.10	NA
Bulk density ($Mg\ m^{-3}$)	1.25	NA
Total Organic C (%)	2.16	0.57–2.51
Total N (%)	0.08	0.04–0.17
Exchangeable NH_4^+ (%)	0.00049	NA
Available NO_3^- (%)	0.00049	NA
CEC ($cmol\ kg^{-1}$)	4.67	3.86–8.46
Exchangeable K^+ ($cmol\ kg^{-1}$)	0.06	0.05–0.19
Exchangeable Ca^{2+} ($cmol\ kg^{-1}$)	0.02	0.01
Exchangeable Mg^{2+} ($cmol\ kg^{-1}$)	0.22	0.07-0.21
Exchangeable Na^+ ($cmol\ kg^{-1}$)	0.03	0.01
Exchangeable Fe^{2+} ($cmol\ kg^{-1}$)	1.09	NA
Exchangeable Mn^{2+} ($cmol\ kg^{-1}$)	0.01	NA
Total titratable acidity ($cmol\ kg^{-1}$)	1.15	NA
Exchangeable H^+ ($cmol\ kg^{-1}$)	0.13	NA
Exchangeable Al^{3+} ($cmol\ kg^{-1}$)	1.02	NA
Soil texture	Sand (%): 71.9 Silt (%): 13.5 Clay (%): 14.6 Sandy loam	Sand (%): 72–76 Silt (%): 8–9 Clay (%): 16–19 Sandy clay loam

Note: the values given are on dry-weight basis; NA: not available; * subjected to the soil development, range as found in Paramananthan [37].

2.2. Characterization of Charcoal and Sago Bark Ash

The charcoal used in this study was obtained from Pertama Ferroalloys Sdn Bhd, Bintulu, Sarawak, Malaysia, whereas the sago bark ash was from Song Ngeng Sago Industries, Dalat, Sarawak, Malaysia. Afterwards, the amendments were analyzed for pH in water and KCl, EC, total N, available N, and exchangeable cations (K, Ca, Mg, Na, and Fe). The results from these chemical analyses suggest that the pH of the charcoal and sago bark ash were high because of the significant amounts of the base cations in these materials (Table 2).

Table 2. Initial characterization for selected chemical properties of charcoal and sago bark ash used in the incubation study.

Property	Charcoal	Sago Bark Ash
pH (H_2O)	7.74	9.99
pH (KCl)	7.31	9.66
EC (dS m^{-1})	0.27	5.75
Total N (%)	1.54	1.37
Exchangeable NH_4^+ (%)	0.00023	0.00026
Available NO_3^- (%)	0.00023	0.00026
Exchangeable K^+ (cmol kg^{-1})	3.67	23.33
Exchangeable Ca^{2+} (cmol kg^{-1})	11.71	16.77
Exchangeable Mg^{2+} (cmol kg^{-1})	3.37	3.57
Exchangeable Na^+ (cmol kg^{-1})	0.43	1.51
Exchangeable Fe^{2+} (cmol kg^{-1})	0.15	0.03

2.3. Incubation Study Set Up

A soil incubation study was carried out for 90 days in the Soil Science Laboratory at Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia. Each treatment had three replicates. In total, 1 kg of soil was weighed using a digital balance into a polypropylene container. Only urea with different rates of charcoal and sago bark ash were used in this laboratory incubation study without applying P and K fertilizers to determine the effects of the two amendments on N availability in the soil. The recommended rate of the urea used is 60 kg N ha^{-1} (130 kg ha^{-1} urea) [38]. The amount of charcoal used was based on 10 t ha^{-1} which is equivalent to 51.4 g per 1 kg soil for this incubation study [39,40]. Additionally, the sago bark ash used was based on 5 t ha^{-1} which is equivalent to 25.7 g per 1 kg soil for this incubation study [41–43]. These amounts were scaled down from the standard fertilizer recommendation for maize (Test crop) cultivation per plant basis (based on planting density of 27,777 plants ha^{-1}). The amount of urea was fixed at 100% of the recommended rate because exceeding this rate is not economically rewarding. The charcoal and sago bark ash rates were varied by 25%, 50%, 75%, and 100%. The soil, urea, charcoal, and sago bark ash used in this incubation study were manually mixed thoroughly. Thereafter, the mixture inside polypropylene was moistened to 60% field capacity. The lids of the polypropylene were perforated for aeration. When necessary, the soil moisture content was maintained using distilled water. The samples were incubated at room temperature (26 °C) for 90 days. The treatments were assessed for 30, 60, and 90 days using factorial in a completely randomized design. The treatments evaluated are listed in Table 3.

Table 3. Treatments evaluated in incubation study.

Treatment	Soil (kg)	Urea (g)	Charcoal (g)	Sago Bark Ash (g)	Charcoal: Ash Ratio
S0	1	-	-	-	Soil only
U1	1	4.7	-	-	Urea only
C1	1	4.7	51.4	-	Charcoal only
A1	1	4.7	-	25.7	Ash only
C1A1	1	4.7	51.4	25.7	100:100
C2A2	1	4.7	38.6	19.3	75:75
C3A2	1	4.7	25.7	19.3	50:75
C4A2	1	4.7	12.9	19.3	25:75
C2A3	1	4.7	38.6	12.9	75:50
C3A3	1	4.7	25.7	12.9	50:50
C4A3	1	4.7	12.9	12.9	25: 50
C2A4	1	4.7	38.6	6.4	75: 25
C3A4	1	4.7	25.7	6.4	50: 25
C4A4	1	4.7	12.9	6.4	25:25

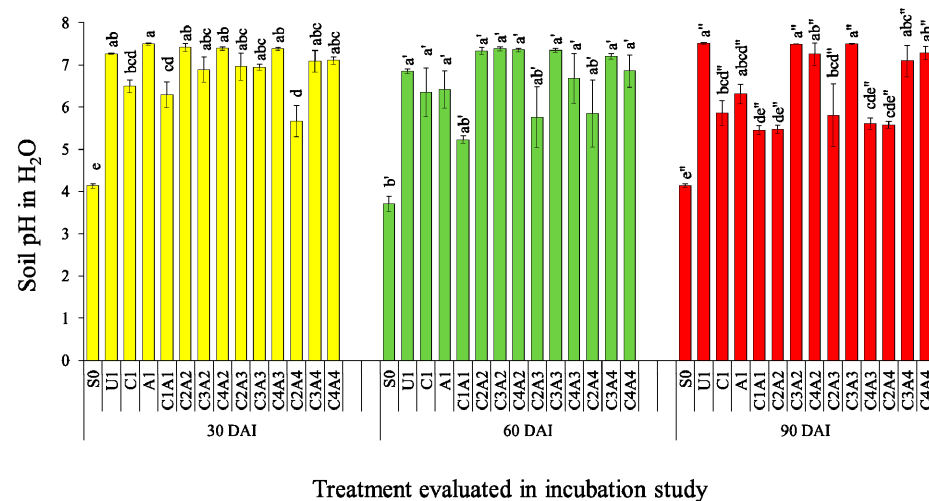*2.4. Experimental Design and Statistical Analysis*

The experimental design used in this incubation study was Completely Randomized Design (CRD) in triplicates. Analysis of Variance (ANOVA) was used to test treatment

effects whereas means of treatments were compared using Tukey's Studentized Range (HSD) test at $p \leq 0.05$. The Statistical Analysis System (SAS) version 9.4 was used for the statistical tests.

3. Results

3.1. Amending Urea with Charcoal and Sago Bark Ash on Selected Soil Chemical Properties

Throughout the incubation study, S0 had the lowest soil pH for both water and KCl, respectively (Figures 2 and 3). At 30 DAI, the soil pH in water for C2A4 was significantly different from the rest of the treatments. At 90 DAI, the soil pH in water for the treatment with urea only (U1) demonstrated no significant difference compared to A1, C3A2, C4A2, C3A3, C3A4, and C4A4. For the soil pH in KCl, at 30 DAI, 100% ash (A1) demonstrated significant difference compared with soil only (S0), 100% charcoal (C1), combination of 100% charcoal and 100% ash (C1A1), and 75% charcoal with 25% ash (C2A4). At 60 DAI, the soil pH in KCl for S0, C2A3, and C2A4 were significantly different from U1, C1, A1, C2A2, C3A2, C4A2, C3A3, C4A3, C3A4, and C4A4. At 90 DAI, the pH in water of C1, C2A2, C2A4 were significantly different from the rest of the treatments.

Figure 2. Treatments on soil pH in water after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.
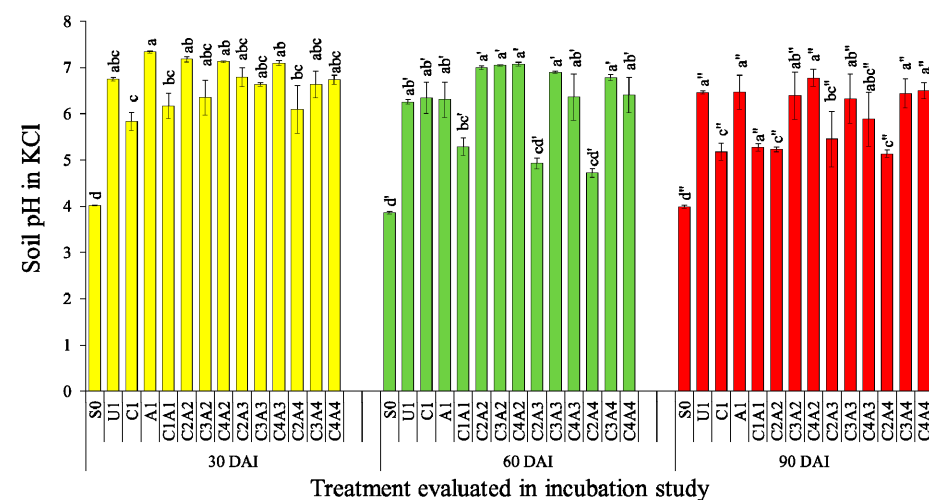
Figure 3. Treatments on soil pH in potassium chloride after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.

The interaction between time of incubation and treatment significantly affected soil exchangeable acidity (Figure 4), especially at 90 DAI. At 90 DAI, the exchangeable acidity of the soil only (S0) was significantly higher (Figure 4). Although the interaction between treatment and incubation time did not significantly affect soil exchangeable Al^{3+} (Figure 5), soil only (S0) exchangeable Al^{3+} was higher. Soil exchangeable H^+ demonstrated a decreasing pattern for 30, 60, and 90 DAI (Figure 6). At 30 DAI, the exchangeable H^+ for urea only (U1) was significantly higher. At 60 DAI, soil only (S0) had the lowest soil exchangeable H^+. However, at 90 DAI, the soil exchangeable H^+ of urea only (U1) was higher than the combined use of 75% charcoal with 75% sago bark ash (C2A2) and combined use of 50% charcoal with 75% sago bark ash (C3A2).
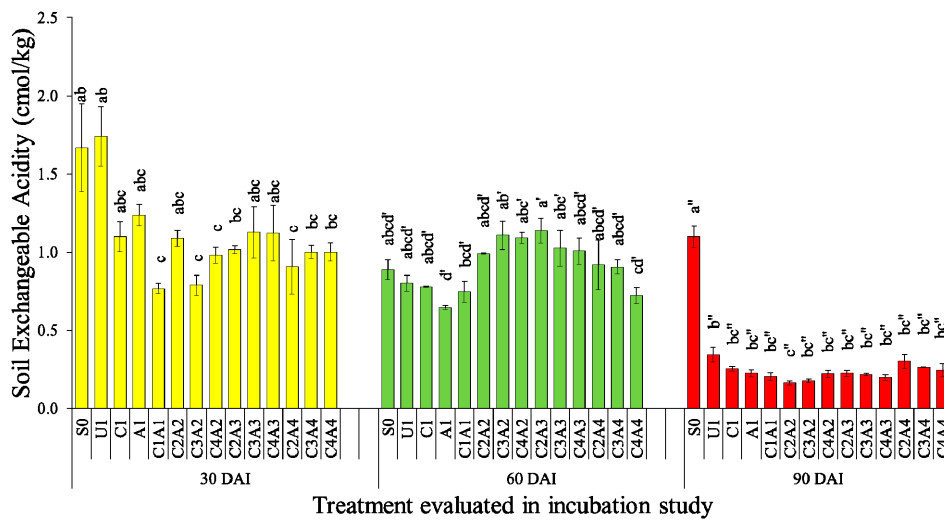

Figure 4. Treatments on soil exchangeable acidity after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \le 0.05$. Bars represent the mean values $\pm$ SE.
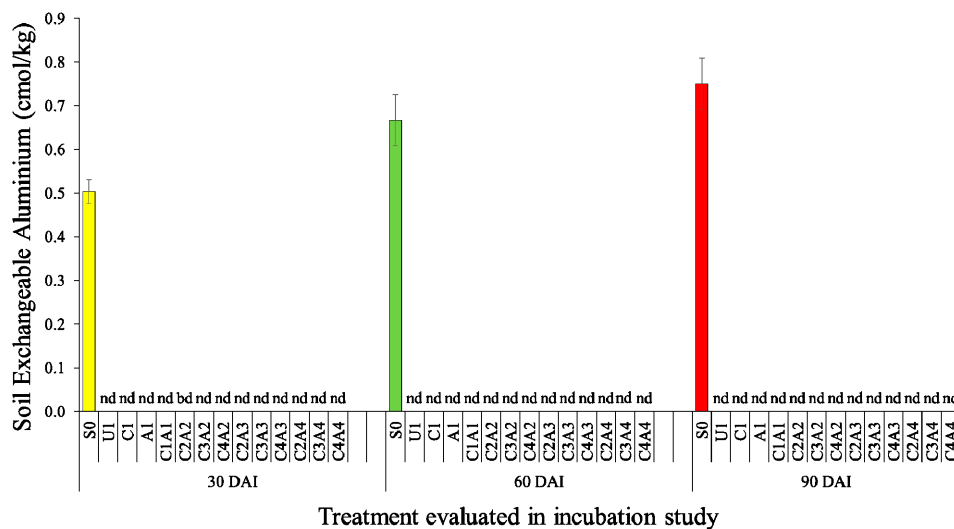

Figure 5. Treatments on soil exchangeable aluminium after thirty, sixty, and ninety days of incubation. Bars represent the mean values $\pm$SE (Note: nd = not determine).
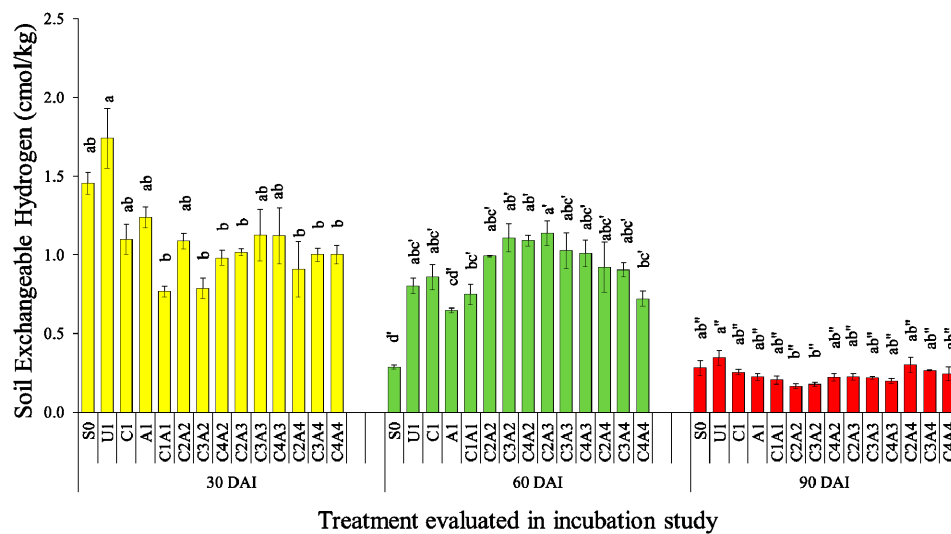
Figure 6. Treatments on soil exchangeable hydrogen ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.

Figure 7 demonstrates that the effects of the interaction between incubation period and treatment on soil CEC. Although the combination of 100% charcoal and 100% sago bark ash (C1A1) had the highest soil CEC at 30 DAI, the effect was not significantly different compared to U1, A1, C2A2, and C2A3. Soil only (S0) had the lowest soil CEC at 60 DAI but the effect was similar to U1, C3A3, C2A4, and C4A4. At 90 DAI, the soil CEC of C1, C3A3, and C2A4 were similar but significantly lower compared with C1A1.
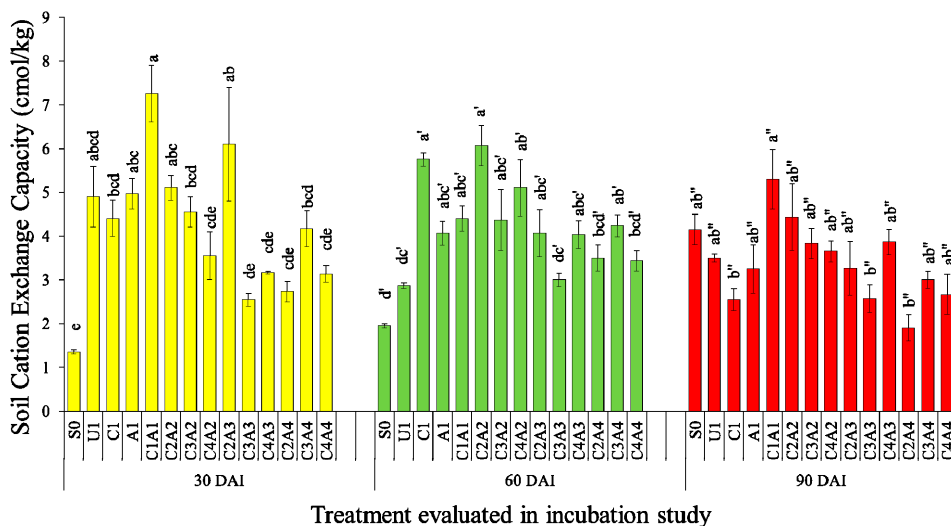

Figure 7. Treatments on soil cation exchange capacity after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.

Effects of the treatments soil total C at 30, 60, and 90 DAI are presented in Figure 8. There were no significant differences in the total C for S0, U1, and A1 regardless of the incubation period. At 30 DAI, the effects of C1 and C1A1 on soil total C were similar but significantly higher than those of S0, U1, A1, C3A2, C3A3, C4A3, C3A4, and C4A4. Although at 60 DAI, C1A1 had higher soil total C, the effect was not significantly different from those of C1, C2A2, and C3A3. At 90 DAI, the effects of C1A1 was significantly higher.
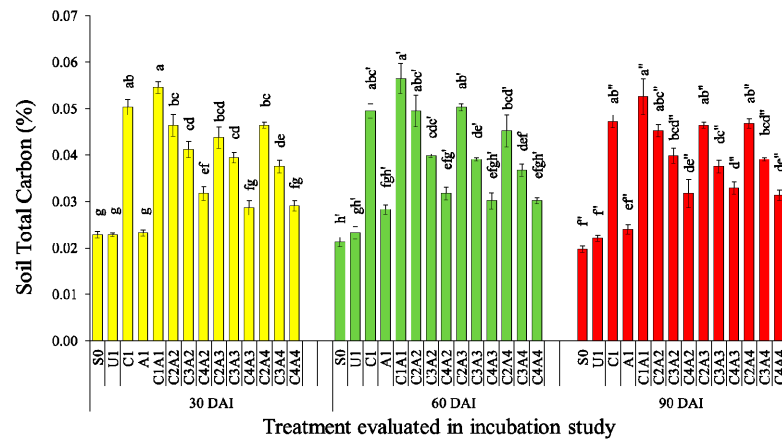
Figure 8. Treatments on soil total carbon after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.

Application of charcoal and sago bark ash increased soil exchangeable K^+ (Figure 9). The treatment with 100% of sago bark ash only demonstrated the highest effect on exchangeable K^+ at 30 DAI, compared with S0, U1, C1, C1A1, C2A2, C3A2, C4A2, C2A3, C3A3, C4A3, C2A4, C3A4, and C4A4. The effects of the treatments without sago bark ash (S0, U1, and C1) on exchangeable K^+ were similar at 60 DAI but significantly lower than with sago bark ash alone (A1). At 90 DAI, the treatments with 25% of sago bark ash had similar effects on soil exchangeable K^+ compared with those without sago bark ash. Exchangeable Ca^{2+} increased with the increasing amount of charcoal and sago bark ash (Figure 10). Soil only (S0), urea only (U1), and charcoal only (C1) had significantly lower soil exchangeable Ca^{2+} at 30 DAI compared with sago bark ash only (A1). However, at 60 DAI, U1 and C1 effects on exchangeable Ca^{2+} were similar to those with sago bark ash only and the combinations of charcoal and sago bark ash (A1, C1A1, C2A2, C3A2, C4A2, C2A3, C3A3, C4A3, C2A4, C3A4, and C4A4). At 90 DAI, S0 had the lowest soil exchangeable Ca^{2+}. Although S0 had the lowest exchangeable Ca^{2+} its effect was similar to C1A1, C2A2, C4A3, and C2A4. The soil exchangeable Mg^{2+} (Figure 11) of U1 and C1 were similar at 30 DAI and 60 DAI. At 30 DAI, sago bark ash alone (A1) demonstrated the highest effect on soil exchangeable Mg^{2+}. At 60 DAI, the soil exchangeable Mg^{2+} of S0 was similar to those of C2A3 and C2A4. At 90 DAI, most of the treatments effects were similar.
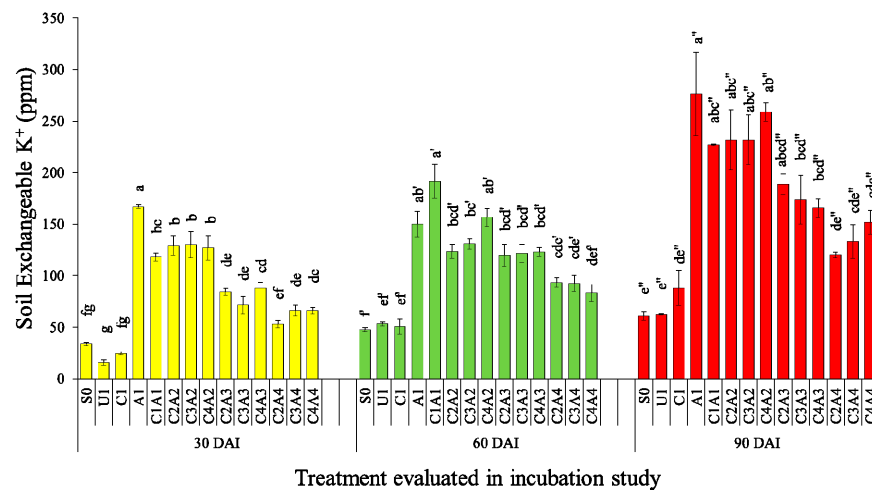

Figure 9. Treatments on soil exchangeable potassium ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.
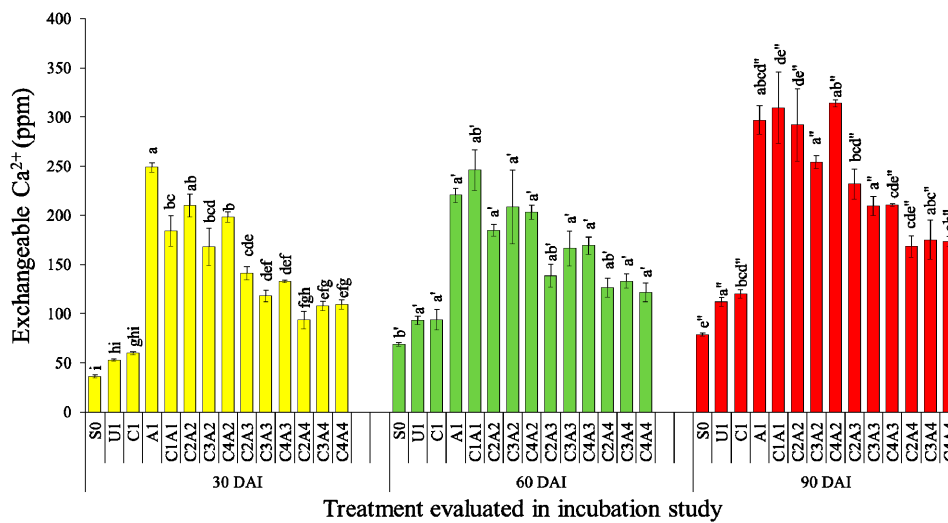
Figure 10. Treatments on soil exchangeable calcium ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \le 0.05$. Bars represent the mean values $\pm$ SE.
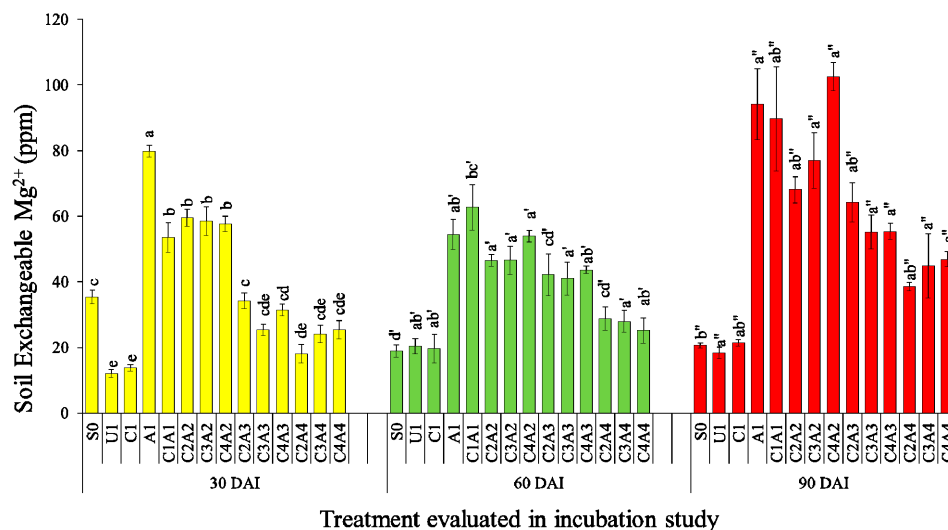

Figure 11. Treatments on soil exchangeable magnesium ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \le 0.05$. Bars represent the mean values $\pm$ SE.

3.2. Amending Urea with Charcoal and Sago Bark Ash on Soil Total Nitrogen, Exchangeable Ammonium, and Available Nitrate

Soil total N at 30, 60, and 90 DAI are summarized in Figure 12. At 30 DAI, C2A3 increased soil total N compared with S0, A1, and C3A3. At 60 DAI, C2A4 significantly improved soil total N compared with C1A1. However, at 90 DAI, soil total N was similar regardless of treatment. At 30 DAI, there were significant differences for soil exchangeable NH_4^+ (Figure 13). At 60 DAI, S0 had the lowest soil exchangeable NH_4^+ compared with C1 and C4A2. Charcoal only (C1) demonstrated a similar effect compared to other treatments except for S0, A1, C1A1, and C3A3. Soil exchangeable NO_3^- at 30 DAI suggests that C4A2 had a similar effect as C3A3, C4A3, and C3A4 (Figure 14). However, at 60 DAI, the sago bark ash only (A1) demonstrated the highest soil NO_3^-. Treatment C3A3 had the highest soil exchangeable NO_3^- but its effect was similar to urea alone (U1) and charcoal alone (C1).
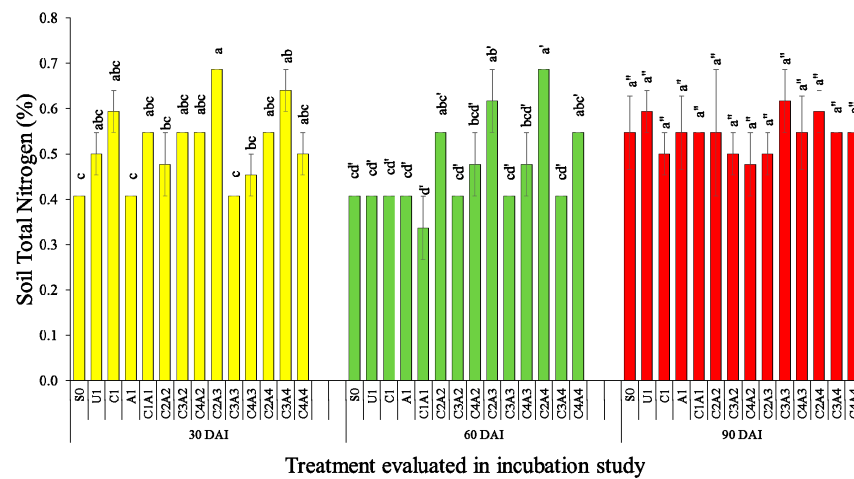
Figure 12. Treatments on soil total nitrogen after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.
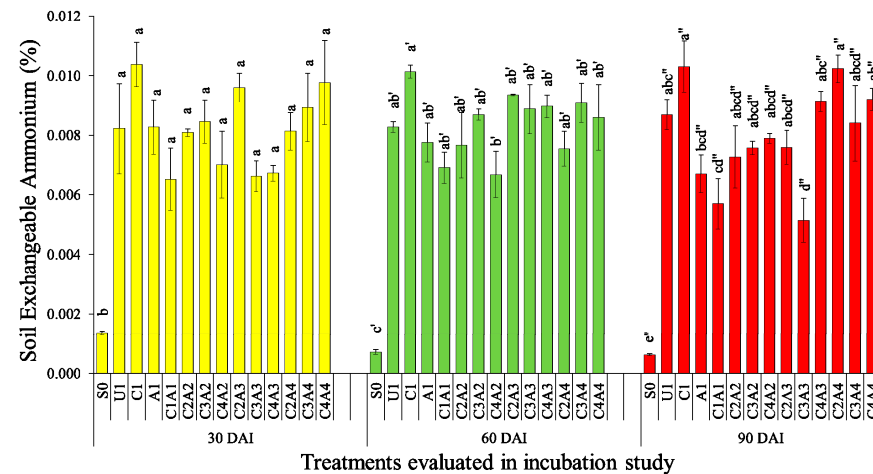

Figure 13. Treatments on soil exchangeable ammonium ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.
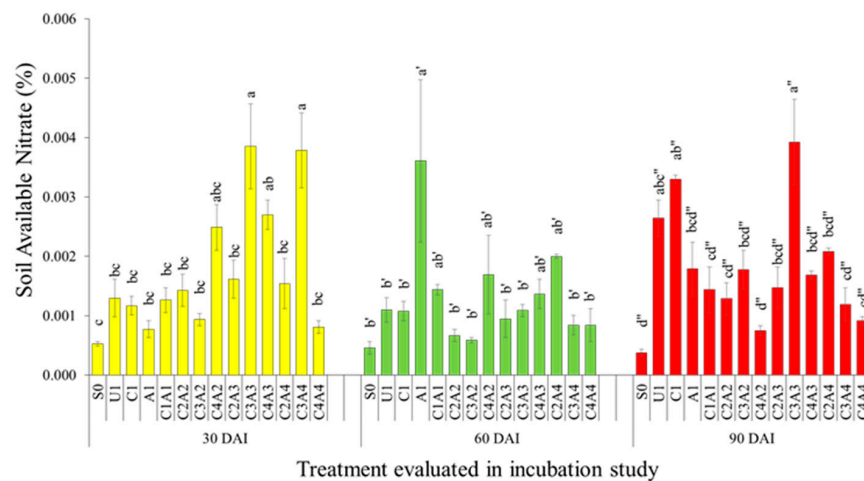

Figure 14. Treatments on soil available nitrate ions after thirty, sixty, and ninety days of incubation. Means with different letter(s) within the same incubation period indicate significant difference between treatments by Tukey's HSD test at $p \leq 0.05$. Bars represent the mean values $\pm$ SE.

4. Discussion

4.1. Effects of Treatments on Selected Soil Physicochemical Properties

Figures 2 and 3 suggest that the treatment without urea (S0) had the lowest soil pH in water and KCl because the treatments with urea underwent urea hydrolysis to produce OH^- ions [44]. This partly explains why soil pH generally increases with increasing urea hydrolysis because the OH^- ions which are produced during hydrolysis are able to neutralize H^+ ions. Moreover, the treatments with charcoal and sago bark ash increased the soil pH because of their basic cations. Furthermore, the functional groups of the charcoal and ash such as the carboxylic–COOH group contributed to the increase in soil pH because of the dissociation of OH^- ions to also neutralize H^+ ions. Additionally, the sago bark ash is not only alkaline because of its acid neutralizing property, but it is also high in soluble base macronutrients [16] and OH^- ions. This qualifies sago bark ash as a soil liming material.

Throughout the incubation study, there was reduction in soil exchangeable acidity, Al^{3+}, and H^+. The treatment without urea (S0) had significantly higher soil exchangeable acidity than those with urea because there was no urea hydrolysis in S0. This indicates charcoal and sago bark ash can reduce soil acidity. The reduction of soil exchangeable Al^{3+} is directly related to the ability of the amendments to increase soil pH through the prevention of Al^{3+} ions from undergoing hydrolysis to produce H^+ ions. It is known that if one mole of Al^{3+} ions undergoes complete hydrolysis, three moles of H^+ ions are produced to cause soil acidity. Thus, it is reasonable to suggest that the use of the two amendments in this present study did not only increase the soil pH but they were also capable of fixing Al^{3+} [45]. Although Al^{3+} can be reduced during urea hydrolysis, sago bark ash and charcoal were also responsible in the reduction of soil acidity. This is because the functional groups of these amendments have a high affinity for Al^{3+} and Fe^{2+} to impede the hydrolysis of these acid cations.

The increase in the exchangeable base's cation such as K^+, Ca^{2+}, and Mg^{2+} in the soils with sago bark ash is related to K, Ca, and Mg contents of the sago bark ash. Decreasing soil acidity with increasing soil base saturation is partly associated with soil base cations [17]. The inconsistency in the soil CEC could be associated with the function of the charcoal as adsorbent which is relatively short although it has the potential to remain in soils for many years, as the pores become clogged [46]. The soil with charcoal demonstrated higher soil total C because of the recalcitrant C of the charcoal. Demirbas et al. [24] stated that typical charcoal is made up of C, H, N, S, ash, and oxygen. Sago bark ash does not contribute a significant amount of C because of the tendency for the combustion of sago bark to produce ash volatilizing C.

4.2. Treatments on Total Nitrogen, Exchangeable Ammonium, and Available Nitrate

At 30 and 60 DAI, the effects of the treatments soil total N were almost similar. At 90 DAI, there were no significant differences among the treatments because urea is highly soluble in water such that it hydrolyzed rapidly. The availability of soil exchangeable NH_4^+ following the application of urea was significantly different from the soil without urea (S0). Regardless of the incubation period, the treatments with 100% charcoal had the highest soil exchangeable NH_4^+ although the effect was not different from those with urea alone (U1) or with the two amendments. Although NH_4^+ ions are the predominant form of N for plant uptake, the true potential of charcoal and sago bark ash as efficient adsorbents to retain NH_4^+ in this study is not glaring because this experiment involved no planting of test crops. Charcoal and sago bark ash has a high capacity to sorb NH_4^+ ions because of their physical and chemical properties. Charcoal is an amendment with high-specific surface area and high in CEC because of its porous structure and surface electrostatic properties [47,48]. These properties enable charcoal to alter nutrient accessibility such as retention of NH_4^+ ions through nutrient soil inputs [49,50]. Amending soil with charcoal can enhance retention of NH_4^+ in soils because of its affinity for NH_4^+ sorption compared with soils. However, in acidic soils, the NH_4^+ adsorption capacity decreases because, at low pH, the competition between H^+ and NH_4^+ for the active sites of the charcoal surface increases

to cause low NH_4^+ adsorption capacity [51]. Conversely, when pH values are greater than eight, the NH_4^+ ions are transformed to NH_3 gas, causing depletion in NH_4^+ adsorption capacity. This explains why the optimum pH for NH_4^+ adsorption ranges between five and eight [52–54]. The combination of ash and charcoal as amendment increases soil pH to enhance NH_4^+ retention on the large surface area (exchange sites) of charcoal. Similar to charcoal, adsorption of NH_4^+ on the surface of the wood ash is influenced by its specific surface area and porosity. Although charcoal exhibits higher adsorption capacity, ash also has the potential as an intermediate adsorption material [55]. Gómez-Rey et al. [56] suggested that in N limited soils, co-application of ash and N fertilizers is essential to balance soil N immobilization. Increasing soil pH causes dissociation of H^+ from hydroxyl and carboxylate groups to provide negatively charged surface adsorption sites in a manner that enables NH_4^+ ions retention. This reaction causes NH_4^+ ions to remain in their available form from being leached from soils. Moreover, NH_4^+ can be trapped through a process called ammonium fixation between the layers of clay minerals that exhibit swelling and shrinking properties [57,58]. In this present study, the inconsistent results on soil exchangeable NO_3^- are because NO_3^- is highly mobile in soil water solution. Jury and Nielson [59] stated that the movement of NO_3^- is governed by mass flow and diffusion within the soil solution. Nitrates ions are repelled by negatively charged soil surfaces and because of this, they are prone to leaching if they are not utilized by microorganisms or taken up by plants. Nitrogen forms are easily transformed in soils. Commonly, soils are unable to adsorb NO_3^- because at their natural pH, anion exchange capacity is insufficient. Because NO_3^- ions are negatively charged, they are repelled by the negatively charged soil colloid. With the aid of charcoal's unique pore structure, soil water is trapped inside charcoal pores and nitrate remains in available formed until plant uptakes. Therefore, to obtain conclusive information on NO_3^- ions, a leaching study could be carried out.

5. Conclusions

This study had revealed that combined use of charcoal, sago bark ash, and urea does not only increase soil pH and base cations but the approach also reduces exchangeable acidity, exchangeable Al^{3+}, and exchangeable H^+ although this intervention has minimal effect on soil total N, exchangeable NH_4^+, and available NO_3^-. Apart from the sago bark ash's liming effect, the high affinity of the functional groups of the charcoal for aluminium ions might have impeded these acidic ions (Al^{3+}) from undergoing hydrolysis to produce more hydrogen ions because a complete one mole of aluminium ions hydrolysis produces three moles of hydrogen ions. Thus, the combined use of charcoal and sago bark ash can mitigate soil acidity and aluminium toxicity although this approach has minimal effect on urea-N. The findings of this study are being verified in our ongoing greenhouse and field experiments with sorghum as a test crop. The presence of the test crop in the greenhouse and field experiments could provide more insights on our incubation study results.

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