

## Changes in Potassium Sorption and pH Buffering Capacity of Tropical Acid Soils Following Application of Charcoal and Sago Bark Ash

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

<sup>1</sup>Department of Crop Science, Faculty of Agricultural Science and Forestry, Universiti Putra Malaysia, Bintulu Sarawak Campus, Bintulu 97008, Malaysia

<sup>2</sup>Faculty of Agriculture, Universiti Islam Sultan Sharif Ali, Kampus Sinaut, KM 33 Jalan Tutong Kampung Sinaut, Tutong TB1741, Brunei

<sup>3</sup>Faculty of Agro-Based Industry, Campus Jeli, Universiti Malaysia Kelantan, Jeli 17600, Malaysia

<sup>1,4</sup>Institut Ekosains Borneo (IEB), Faculty of Agriculture and Forestry Sciences, Universiti Putra Malaysia, Bintulu Sarawak Campus, Bintulu 97008, Malaysia

<sup>5</sup>Graduate School of Management Post Graduate Centre, Management and Science University, University Drive, Off Persiaran Olahraga, Section 13, Shah Alam 40100, Selangor, Malaysia

\* Correspondence: [ahmed.haruna@unissa.edu.bn](mailto:ahmed.haruna@unissa.edu.bn)

### ABSTRACT

Ultisols and Oxisols are the two dominant soils in the tropics. These soils are mostly infertile and have low cation exchange capacity because of their low pH (4 to 5). They are composed of kaolinite and sesquioxides which are prone to potassium (K) leaching. To make these soils arable, liming and fertilization are required. Nevertheless, this conventional practice alone does not mitigate K availability in such soils because of their low pH buffering capacity and low K adsorption capacity. The alkalinity of sago (*Metroxylon sagu*) bark ash and charcoal and the deprotonation of charcoal's functional groups by the carbonates and oxides of sago bark ash have potential benefits. Due to these characteristics of sago bark ash and charcoal, they could be utilized to improve soil pH buffering capacity and K adsorption capacity to prevent the leaching of K and the pollution of water bodies. Moreover, the use of charcoal and sago bark ash to amend soils is a good way of utilizing agro-wastes sustainably. Thus, the objective of this study was to determine the effects of amending tropical acid soils with charcoal and sago bark on K sorption and pH buffering capacity. The treatments evaluated were: (i) 300 g soil only, (ii) 250 g charcoal only, (iii) 250 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. Langmuir bonding energy constant ( $K_L$ ), Maximum K buffering capacity (MBC), and maximum adsorption capacity ( $q_{max}$ ) of the soil with charcoal and sago bark ash were higher than that of soil alone. However, desorption of K was not significantly affected after application of the amendments. On the other hand, the combined use of charcoal and sago bark ash improved the soil's pH buffering capacity in comparison to the untreated soil because of the inherently high CEC and alkalinity of these amendments. Therefore, this intervention could contribute to improving K fertilizer use and prevent environmental pollution and economical loss to farmers.

**Key words:** Langmuir isotherm, biochar, cation exchange capacity, soil acidity, leaching

### INTRODUCTION

Potassium in soils exist in four distinctive forms namely water-soluble potassium (K), exchangeable K, non-exchangeable K, and mineral K (Sparks 2000; Jaiswal *et al.* 2016). The kinetic and equilibrium reactions between these four forms of K in soils can determine the fate of K fertilizers applied. The K can either be lost through leaching, taken up by plants or remain in soil as reserve K. Water-soluble K is the most readily available form of K for plant uptake. Nevertheless, water-soluble K is mobile and due to the high annual rainfall in the humid tropics

most of this form of K is leached out of the soil profile, thus causing K deficiency. Hence, it is essential for the applied K to be adsorbed by the soil minerals and organic matter through electrostatic attraction, covalent bonding, or isomorphous replacement when it is not taken up by plants. However, Ultisols and Oxisols are composed of kaolinite clay minerals which have minute amounts of nutrient holding sites because the charges are only on the edges of the crystalline structure (Palanivel 2016). In addition, kaolinite minerals are stacked together by hydrogen bonding, and this prevents water and nutrients from entering between the layers of these minerals (Miranda-Trevino and Coles 2003). Hence, the low negative charge density of kaolinite results in poor K adsorption capacity.

The adsorption capacity of soils is an important property which determines the extent of leaching and redistribution of anions and cations (Wann and Uehara 1978). To temporarily hold nutrients before being taken up by plants, the high CEC of soil amendments can be exploited (Latifah *et al.*, 2017). For example, surface oxidation of aromatic rings of charcoal results in carboxylation which generates large numbers of negatively charged sites (Qiu *et al.*, 2008). This could increase the adsorption capacity of soils, enabling K to bind onto the negatively charged sites of soils. Nevertheless, to ensure timely release of the exchangeable K, soil acidification needs to be suppressed. Currently, soil acidification is accelerating because of anthropogenic activities. Soil acidification causes aluminium (Al) and iron (Fe) toxicity to plants and deficiency of nutrients such as potassium (K), phosphorus (P), calcium (Ca), and magnesium (Mg). Accumulation of Al and Fe ions in low pH soils causes the leaching of base cations in soils. In contrast, Al and Fe competition at soil exchange sites can be diminished for nutrients such as K to become more reactive in higher pH (Gazey 2018). In this situation, K could constantly move from soil solution to adsorbents or vice versa, depending on the requirements of plants. For this to occur, the pH buffering capacity of the soils must be high.

Soil pH buffering capacity is the ability of a soil to resist change in pH and increase proportionally with soil CEC and organic matter content (Moody and Aitken 1997). The application of soil amendments has been shown to increase the buffering capacity of acid soils (Shi *et al.* 2017; Xu *et al.* 2012; Perumal *et al.* 2021). Several minerals in soils enable buffering against changes in pH. For example, Ca, Mg, and K oxides, together with carbonates enhance buffer pH changes during soil acidification. Buffering capacity is important because it enables soil pH stabilization. Changes in pH can affect plants in different ways, especially by limiting the fraction of nutrients in soils that are available to plants but enhance the uptake of undesirable minerals such as Al. A high pH buffering capacity influences soil acidification and eventually increases nutrient availability in soils especially K, which is compromised at low soil pH.

The direct or indirect effects of charcoal and sago bark ash on K sorption and soil pH buffering capacity has been rarely reported. Therefore, understanding the ability of these amendments to resist acidification and cause changes to K sorption in soils is key in ameliorating acid soils. Towards this end, it was hypothesized that amending acid soils with charcoal and sago bark ash will improve K availability by retarding soil acidification. This will also enable timely retention and release of K into soil solution. The research questions that this study addressed were as follows: (i) will the use of charcoal and sago bark ash significantly improve pH buffering capacity of acid soils? and (ii) how much of K could be adsorbed and desorbed by charcoal and sago bark ash in response to soil solution equilibrium? This study was hence conducted to determine the effects of amending tropical acid soil with charcoal and sago bark on K sorption and pH buffering capacity.

## MATERIALS AND METHODS

### Soil Sampling, Preparation, and Selected Physico-Chemical Analyses

The soil used in this study was sampled from an uncultivated secondary forest at Universiti Putra Malaysia, Bintulu Sarawak Campus (latitude 3°12'11"N and longitude 113°04'25"E), which is a typical representative of Bekenu Series, *Typic Paleudults*. Despite the high content of Al and Fe and abundance of kaolinite clay minerals, it is a commonly cultivated soil in Sarawak, Malaysia. The area is located at 27.3 m above sea level, and experiences an annual rainfall of 2993 mm, a mean temperature of 27°C, and relative humidity of approximately 80%. The soil samples were collected at a depth of 0–20 cm using a shovel. Then, the soil samples were air dried, ground, and sieved to pass a 2-mm sieve, before they were bulked. Prior to the determination of K sorption and pH buffering capacity, 300 g of soil (Bekenu Series, *Typic Paleudults*) was mixed thoroughly with charcoal and sago bark ash in a container based on the treatments evaluated in this study. The amounts of the charcoal and sago bark ash used were derived from the respective literature [charcoal (Free *et al.* 2010; Ndor *et al.* 2015) and sago bark ash (Mandre *et al.* 2006; Ozolincius *et al.* 2007; Perucci *et al.* 2008)]. The 100% recommended rate of charcoal was 10 t ha<sup>-1</sup>, whereas that of sago bark ash was 5 t ha<sup>-1</sup>. These recommendations were scaled down to the equivalent proportions per 300 g soil. The treatments tested were as follows:

- T1: 300 g of soil only
- T2: 300 g of charcoal only
- T3: 300 g of sago bark ash only
- T4: 300 g soil + 15.42 g charcoal
- T5: 300 g soil + 7.71 g sago bark ash
- T6: 300 g soil + 15.42 g charcoal + 7.71 g sago bark ash

### Initial Characterization of Soil, Charcoal, and Sago Bark Ash

Apart from soil texture, the selected physical and chemical properties of the soil (Bekenu Series, *Typic Paleudults*) used in this study were within the range reported by Paramanathan (2000). However, the soil texture obtained was comparable to that reported in the Soil Survey Staff (2014). The sago bark ash used in this study was obtained from Song Ngeng Sago Industries, Dalat, Sarawak, Malaysia whereas the charcoal was obtained from Pertama Ferroalloys Sdn Bhd, Bintulu, Sarawak, Malaysia. The selected physico-chemical properties of the soil, charcoal, and sago bark ash are summarized in Table 1. The soil pH in water and potassium chloride (KCl) and electrical conductivity (EC) were measured in a 1:2.5 (soil: distilled water/KCl) using a digital pH meter and an EC meter, respectively (Peech 1965). Soil texture was determined using the hydrometer method (Bouyoucos 1962). Soil total carbon (TC) was calculated as 58% of the organic matter that was determined using loss of weight on ignition method (Cheftez *et al.* 1996). The soil samples were analyzed for soil bulk density using the coring method (Dixon and Wisniewski 1995). The soil CEC was determined using the leaching method (Cottenie 1980) followed by steam distillation (Bremner 1965). Exchangeable cations [K, Ca, Mg, Sodium (Na), and Fe] were extracted with 1 M ammonium acetate (NH<sub>4</sub>OAc), pH 7 using the leaching method (Cottenie 1980). Subsequently the cations were quantified using Atomic Absorption Spectrophotometry (AAAnalyst 800, Perkin Elmer Instruments, Norwalk, CT, USA). Total K was extracted using Aqua Regia method (Bernas 1968). The determination of K content in the extracts was conducted using Atomic Absorption Spectrophotometry (AAAnalyst 800, PerkinElmer, Norwalk, CT, USA). The soil-exchangeable acidity, H<sup>+</sup>, and Al<sup>3+</sup> were determined using acid-base titration method (Rowell 1994).

**TABLE 1**

Selected physical and chemical properties of Bekenu Series (*Typic Paleudults*), charcoal, and sago bark ash used in the incubation study

Property	Soil	Charcoal	Sago bark ash
pH (water)	3.95	7.74	9.99
pH (KCl)	4.61	7.31	9.66
EC ( $\mu\text{S cm}^{-1}$ )	35.10	269.33	5753.00
Bulk density ( $\text{g m}^{-3}$ )	1.25	nd	nd
------(%)-----			
Total carbon	2.16	nd	nd
Total N	0.08	nd	nd
------( $\text{mg kg}^{-1}$ )-----			
Total P	22.25	nd	nd
Total K	101.27	nd	nd
------( $\text{cmol kg}^{-1}$ )-----			
Cation exchange capacity	4.67	nd	13.13
Exchangeable acidity	1.15	0.10	nd
Exchangeable $\text{Al}^{3+}$	0.13	0.047	nd
Exchangeable $\text{H}^+$	1.02	0.05	nd
Exchangeable $\text{K}^+$	0.06	1435.20	9120.00
Exchangeable $\text{Ca}^{2+}$	0.02	2346.67	3361.20
Exchangeable $\text{Mg}^{2+}$	0.22	409.07	433.73
Exchangeable $\text{Na}^+$	0.03	99.38	348.00
Exchangeable $\text{Fe}^{2+}$	1.09	41.90	8.43
-----			
Sand (%)	71.9	nd	nd
Silt (%)	13.5	nd	nd
Clay (%)	14.6	nd	nd
Texture (USDA)	Sandy loam	nd	nd

Note: Values are on dry-weight basis; values obtained: mean  $\pm$  standard error; nd: not determined

#### Potassium Adsorption and Desorption Determination

A 2 g sample of soil was weighed into a 250 mL centrifuge bottle. This process was repeated five times per experimental unit. Isonormal K solutions of 0, 100, 200, 300, and 400 mg K L<sup>-1</sup> were prepared by dissolving potassium chloride (KCl) in 0.01 M CaCl<sub>2</sub> solution in distilled water. A 20 mL of the isonormal K solution was added to the centrifuge bottles to give 0.0, 2.0, 4.0, 6.0, and 8.0 mg of added K sample<sup>-1</sup>. The addition of isonormal solution in this adsorption study was to sustain a constant ionic strength in the mixtures (adsorbent and solution) in addition to providing competing ions for exchange sites (Kithome *et al.* 1998). The samples were shaken over night at 180 rpm using an orbital shaker. Thereafter, they were centrifuged for 15 min at 10,000 rpm. The supernatants (equilibrium solution) were collected after the centrifugation followed by analysis for K using atomic absorption spectrophotometry (AAAnalyst 800, Perkin Elmer Instruments, Norwalk, CT). The K adsorption at equilibrium ( $q_e$ ) was calculated using the formula below described by Peng *et al.* (2021)

$$q_e = \frac{(C_o - C_e) \times V}{m}$$

where

- $q_e$  = K adsorption at equilibrium ( $\text{mg g}^{-1}$ )
- $C_o$  = initial concentration of K ( $\text{mg L}^{-1}$ )
- $C_e$  = K concentration at adsorption equilibrium ( $\text{mg L}^{-1}$ )
- $V$  = volume of K solution used (L)
- $m$  = mass of sample (g)

Potassium desorption was done using the sediments of the same samples by washing the sediments with ethanol using centrifugation at 10,000 rpm for 10 min. Therefrom, the ethanol was discarded. A 20 mL of 0.01 M  $\text{CaCl}_2$  was added to the samples and shaken overnight at 180 rpm using an orbital shaker after which they were centrifuged at 10,000 rpm for 15 min. Therefrom, the supernatants were collected, and K content was determined using atomic absorption spectrophotometry (AAAnalyst 800, Perkin Elmer Instruments, Norwalk, CT). The desorbed K at equilibrium ( $q_{de}$ ) was calculated using the formula below described by Peng *et al.* (2021)

$$q_{de} = \frac{(C_{do} - C_{de}) \times V}{m}$$

where

- $q_{de}$  = K desorption at equilibrium ( $\text{mg g}^{-1}$ )
- $C_{do}$  = K concentration on sample ( $\text{mg L}^{-1}$ );  $C_{do} = C_o - C_e$
- $C_{de}$  = K concentration at desorption equilibrium ( $\text{mg L}^{-1}$ )
- $V$  = volume of 0.01 M  $\text{CaCl}_2$  solution used (L)
- $m$  = mass of sample (g)

### Potassium Adsorption Isotherm

Potassium adsorption data for the samples tested in this study were fitted to the Langmuir adsorption isotherm (Table 2). This equation was used because it enables the estimation of maximum K sorption ( $q_{max}$ ) and a constant related to K binding strength ( $K_L$ ) (Gregory *et al.* 2005). The maximum K buffering capacity (MBC) of the sample was calculated from the product of  $K_L$  and  $q_m$  (Wang and Liang 2014).

**TABLE 2**

Langmuir adsorption isotherm model used in this study and its nonlinear and linear forms

Isotherm	Nonlinear form	Linear form	Plot	Variables
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	$\frac{C_e}{q_e}$ vs $C_e$	$K_L = \frac{\text{slope}}{\text{intercept}}$ $q_m = \text{slope}^{-1}$

### pH Buffering Capacity Determination

The pH buffering capacity was determined using the titration method (Costello and Sullivan 2014). A 5 g sample of each treatment was weighed into 100 mL plastic vials. Afterwards, 0.25 M  $\text{H}_2\text{SO}_4$  was added to the samples at amounts of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 mL (1 mL = 0.1 mol  $\text{H}^+$   $\text{kg}^{-1}$  sample). Each amount of acid (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 mL) was added into a different plastic vial, after which a sufficient amount of distilled water was added to bring the total liquid addition to 50 mL (1:10 sample:distilled water). (For example, for 2 mL of 0.25 M  $\text{H}_2\text{SO}_4$ , 48 mL of distilled water was added). The suspension was stirred thoroughly for 10 sec after adding acid and equilibrated for 72 h at room temperature (26 °C). Before measuring pH at 72 h, the suspension was stirred for another 10 sec. The pH measurement was done using

a digital pH meter (SevenEasy pH, Mettler-Toledo GmbH, Greifensee, Switzerland). The pH buffering capacity of the sample or the quantity of acidity (H<sup>+</sup>) needed to reduce pH by one unit was calculated as the negative reciprocal of the slope of the linear regression, sample pH (Y-axis) versus the amount of acid added (X-axis):

$$\text{pH buffering capacity (mol H}^+ \text{ kg}^{-1} \text{ sample)} = -(1/\text{slope})$$

where slope is the fitted slope of linear regression line for each sample.

**Statistical Analysis**

Analysis of variance (ANOVA) was used to determine treatment effects, whereas the treatments means were compared using Tukey’s Studentized Range (HSD) Test at  $p \leq 0.05$ . Linear regression analysis was done to obtain the coefficient of determination (R<sup>2</sup>) for each linear regression equation. The statistical software used was Statistical Analysis System (SAS) version 9.4.

**RESULTS AND DISCUSSION**

**Potassium Concentration at Adsorption Equilibrium**

Potassium concentrations in the equilibrium solution increased with increasing amounts of K added, regardless of treatment (Table 3). This observation corroborates the findings of Choudhury and Khanif (2003), who also reported a linear increase in equilibrium solution K concentration with increasing addition of K. Regardless of the amount of K added, the soil with charcoal and sago bark ash (T6) resulted in significantly lower K in the equilibrium solution compared with the soil alone (T1). The low concentration of K remaining in the equilibrium solution of T6 suggests that the addition of the charcoal and sago bark ash increased the adsorption of K. On the other hand, charcoal alone (T2) and the soil with charcoal (T4) resulted in lower K concentration at adsorption equilibrium compared with T1 at 200 mg K L<sup>-1</sup> and higher. This indicates that charcoal facilitates K adsorption, thus reducing the concentration of K in the equilibrium solution. The high concentration of K left in the equilibrium solution for T1 is related to the abundance of kaolinite clay minerals. Melo *et al.* (2001) indicated in their findings that K sorption sites of kaolinite is limited to its external layers, and they are unable to fix K to the crystalline units.

**TABLE 3**

Treatments effects on potassium concentration at adsorption equilibrium at different isonormal potassium solutions.

Treatment	Potassium concentration at adsorption equilibrium, C <sub>e</sub> (mg L <sup>-1</sup> )				
	0	100	200	300	400
	Added K (mg K L <sup>-1</sup> )				
T1	nd	77.63 <sup>a</sup> ± 3.90	163.65 <sup>a</sup> ± 4.80	250.58 <sup>a</sup> ± 11.26	336.85 <sup>a</sup> ± 2.58
T2	nd	60.13 <sup>ab</sup> ± 4.73	137.58 <sup>bcd</sup> ± 3.95	214.58 <sup>bc</sup> ± 4.44	295.02 <sup>b</sup> ± 4.06
T3	nd	60.13 <sup>ab</sup> ± 4.73	143.63 <sup>abc</sup> ± 5.53	235.55 <sup>ab</sup> ± 7.91	325.21 <sup>a</sup> ± 5.77
T4	nd	52.18 <sup>b</sup> ± 2.87	122.00 <sup>cd</sup> ± 3.45	213.54 <sup>bc</sup> ± 6.76	264.96 <sup>c</sup> ± 5.75
T5	nd	66.54 <sup>ab</sup> ± 3.56	155.58 <sup>ab</sup> ± 5.11	238.09 <sup>ab</sup> ± 1.16	332.08 <sup>a</sup> ± 2.79
T6	nd	50.23 <sup>b</sup> ± 4.24	116.78 <sup>d</sup> ± 8.11	184.55 <sup>c</sup> ± 4.88	262.62 <sup>c</sup> ± 6.38

Note: nd: not detected; different letters within a column indicate significant difference of means ± standard error using Tukey’s test at  $p \leq 0.05$

**Potassium Adsorption**

Regardless of the concentration of the isonormal K solution used, the soil with charcoal and sago bark ash (T6) resulted in the highest K adsorption at equilibrium ( $q_e$ ) (Table 4). There were no significant differences in the amount of K adsorbed for sago bark ash alone (T3) and the soil with sago bark ash (T5) compared to the soil alone (T1) at all concentrations of the isonormal K solutions. On the other hand, the effect of the soil with charcoal alone (T4) on the amount of K adsorbed was significantly higher compared with the soil alone (T1), regardless of the concentrations of isonormal K solution used. The improvement in the adsorbed K with the inclusion of charcoal is consistent with the surface oxidation of the aromatic rings of the charcoal which creates negative-charged sites (Biedereman and Harpole 2013; Major *et al.* 2010). The low K adsorption of the sago bark ash relates to  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  of this amendment. Dissolution of these compounds releases cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Low negative charge density of acid soils and competition with divalent cations released from dissolution reactions, hinders K adsorption (Vasconcelos *et al.* 2010). Nevertheless, the co-application of charcoal and sago ash overcomes this limitation. The dissolution of  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  also releases anions to deprotonate the oxygen-containing functional groups on the charcoal, thus providing more adsorption sites for the cations including K (Shi *et al.* 2017). This explains why T6 resulted in the highest K adsorption at equilibrium in spite of the presence of the sago bark ash.

**TABLE 4**  
Treatments effects on the amounts of potassium adsorbed at equilibrium at different concentrations of added potassium.

Treatment	Potassium adsorption at equilibrium, $q_e$ (mg g <sup>-1</sup> )			
	100	200	300	400
	Added K (mg K L <sup>-1</sup> )			
T1	0.22 <sup>b</sup> ± 0.04	0.36 <sup>d</sup> ± 0.05	0.49 <sup>c</sup> ± 0.11	0.63 <sup>c</sup> ± 0.03
T2	0.40 <sup>ab</sup> ± 0.05	0.62 <sup>abc</sup> ± 0.04	0.85 <sup>ab</sup> ± 0.04	1.05 <sup>b</sup> ± 0.04
T3	0.40 <sup>ab</sup> ± 0.05	0.56 <sup>bcd</sup> ± 0.06	0.64 <sup>bc</sup> ± 0.08	0.75 <sup>c</sup> ± 0.06
T4	0.49 <sup>a</sup> ± 0.03	0.78 <sup>ab</sup> ± 0.03	0.86 <sup>ab</sup> ± 0.07	1.35 <sup>a</sup> ± 0.06
T5	0.33 <sup>ab</sup> ± 0.04	0.44 <sup>cd</sup> ± 0.05	0.62 <sup>bc</sup> ± 0.01	0.68 <sup>c</sup> ± 0.03
T6	0.50 <sup>a</sup> ± 0.04	0.82 <sup>a</sup> ± 0.08	1.15 <sup>a</sup> ± 0.05	1.37 <sup>a</sup> ± 0.06

Note: Different letters within a column indicate significant difference of means ± standard error using Tukey’s test at  $p \leq 0.05$

**Langmuir Adsorption Isotherm**

The assumptions of Langmuir adsorption model are the occurrence of monolayer adsorption and the adsorption sites on the surface have the same force on the adsorbate (Srividya and Mohanty, 2009; Abdelnaeim *et al.*, 2016). Therefore, once an adsorption site is occupied by the adsorbate, it can no longer adsorb other adsorbates. Based on the significant regression coefficient ( $R^2$ ), the effects of soil alone (T1), charcoal alone (T2), sago bark ash alone (T3), soil with sago bark ash (T5), and soil with charcoal and sago bark ash (T6) were best fitted to Langmuir adsorption model (Table 5). Apart from the soil with charcoal (T4), all the treatments resulted in strong and positive regression coefficients ( $R^2 \geq 0.90$ ). Insignificant  $R^2$  of the Langmuir regression equations for T4 implies that the K adsorption data do not fit Langmuir adsorption model and the data could be fitted to other K adsorption models such as Freundlich and Temkin (Perumal *et al.* 2021).

The Langmuir bonding energy constant ( $K_L$ ) determines the affinity of adsorbent towards the adsorbate. High values of  $K_L$  suggest strong binding of K (adsorbate) by the treatments (adsorbents). Soil alone (T1) resulted in the lowest  $K_L$  because Al and Fe ions predominate at low pH and displaces K from soil colloids (Gazey 2018). The charcoal and sago bark ash in the treatments improved the  $K_L$ . The affinity of these amendments for K was higher because of their high CEC and alkalinity (Table 1).

The maximum K buffering capacity (MBC) is the maximum amount of K (adsorbate) loadable on an adsorbent. Higher MBC enables soils to hold more K in the exchange sites, thus preventing leaching in addition to enabling future redistribution. The maximum K buffering capacity was highest in soil with charcoal and sago bark ash (T6). The deprotonation of charcoal's functional groups by the carbonates and oxides of sago bark ash creates more adsorption sites for the K, thereby increasing the MBC of T6 compared to soil alone (T1). Soil alone (T1) resulted in the lowest MBC, and this is attributable to the low K sorption capacity of 1:1 lattice structure of the kaolinite clay mineral (Schneider *et al.* 2013).

The maximum adsorption capacity ( $q_{max}$ ) determines the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface of the adsorbent. The higher  $q_m$  of the soil with charcoal and sago bark ash (T6) in comparison with soil alone (T1) suggests that the soil can hold more K on its exchange sites, thus preventing leaching. Because leaching depletes water-soluble K, it is essential to maintain the exchangeable K such that this pool is activated to replenish the K in soil solution.

**TABLE 5**  
Treatments effects on potassium sorption parameters of the isotherm described by Langmuir equation

Treatment	Estimated by Langmuir equation				
	Regression equation	R <sup>2</sup>	q <sub>max</sub> (mg g <sup>-1</sup> )	K <sub>L</sub> (L mg <sup>-1</sup> )	MBC (L mg <sup>-1</sup> )
T1	y = 0.71x + 311.80	0.93 *	1.41	2.28 × 10 <sup>-3</sup>	3.21 × 10 <sup>-3</sup>
T2	y = 0.54x + 130.69	0.95 *	1.85	4.13 × 10 <sup>-3</sup>	7.64 × 10 <sup>-3</sup>
T3	y = 1.08x + 94.29	0.98 *	0.93	1.15 × 10 <sup>-2</sup>	1.07 × 10 <sup>-2</sup>
T4	y = 0.52x + 93.13	0.69 ns	1.92	5.58 × 10 <sup>-3</sup>	1.07 × 10 <sup>-2</sup>
T5	y = 1.03x + 151.44	0.95 *	0.97	6.80 × 10 <sup>-3</sup>	6.60 × 10 <sup>-3</sup>
T6	y = 0.41x + 84.99	0.98 *	2.44	4.82 × 10 <sup>-3</sup>	1.18 × 10 <sup>-2</sup>

Note: R<sup>2</sup>: regression coefficient; q<sub>max</sub>: maximum adsorption capacity; K<sub>L</sub>: Langmuir constant related to the binding energy; MBC: maximum K buffering capacity; ns: not significant at  $p \leq 0.05$ ; Asterisk (\*): significant at  $p \leq 0.05$

### Potassium Concentration at Desorption Equilibrium

Potassium concentrations in the equilibrium solution increased with increasing amounts of K added, regardless of treatments (Table 6). Among the treatments, the soil with charcoal and sago bark ash (T6) resulted in the highest K concentration at desorption equilibrium (Cde), regardless of the concentration of isonormal K solution used. The trend of K concentration at desorption equilibrium was opposite to the trend of K concentration at adsorption equilibrium for all the treatments (Table 3). The low K concentration at desorption equilibrium of soil alone (T1) indicates that it is prone to desorption of K. In summary, a decrease in K concentration at desorption equilibrium reflects an increase in K desorption.



**TABLE 6**  
Treatments effects on potassium concentration at desorption equilibrium at different isonormal potassium solutions

Treatment	Potassium concentration at desorption equilibrium, $C_{de}$ (mg L <sup>-1</sup> )				
	0	100	200	300	400
Added K (mg K L <sup>-1</sup> )					
T1	nd	14.68 <sup>c</sup> ± 2.43	26.73 <sup>d</sup> ± 4.31	38.71 <sup>c</sup> ± 9.14	52.19 <sup>c</sup> ± 5.16
T2	nd	34.88 <sup>ab</sup> ± 4.17	57.14 <sup>bc</sup> ± 3.38	77.15 <sup>bc</sup> ± 5.36	99.03 <sup>b</sup> ± 5.45
T3	nd	34.30 <sup>ab</sup> ± 4.28	48.03 <sup>cd</sup> ± 4.39	55.28 <sup>bcd</sup> ± 3.85	65.24 <sup>c</sup> ± 6.19
T4	nd	43.01 <sup>ab</sup> ± 3.26	73.36 <sup>ab</sup> ± 3.16	79.16 <sup>b</sup> ± 3.98	128.63 <sup>a</sup> ± 5.13
T5	nd	28.53 <sup>bc</sup> ± 2.82	37.20 <sup>cd</sup> ± 3.36	51.99 <sup>cd</sup> ± 1.89	58.38 <sup>c</sup> ± 2.95
T6	nd	47.10 <sup>a</sup> ± 4.31	78.75 <sup>a</sup> ± 7.18	108.97 <sup>a</sup> ± 5.58	131.56 <sup>a</sup> ± 7.04

Note: nd: not detected; Different letters within a column indicate significant difference of means ± standard error using Tukey’s test at  $p \leq 0.05$

**Potassium Desorption**

Potassium desorption at equilibrium ( $q_{de}$ ) for the soil with charcoal and sago bark ash (T6) was significantly lower than that of soil alone (T1) when 100 mg K L<sup>-1</sup> was used as an isonormal solution. However, when the K solution concentration was increased to 200 mg K L<sup>-1</sup> and beyond, there were no significant differences in the amounts of K desorbed for all the treatments. This is because desorption of K occurs at a rate that is slower than adsorption. Hundal and Pasricha (1998) also reported that the equilibrium time for desorption was approximately three fold of the values for equilibrium time of adsorption. Such lower rates of desorption than adsorption for K have also been reported by Sparks *et al.* (1980) for *Paleudult* from the Coastal Plain of Virginia. The insignificant effect of T6 on potassium desorption at equilibrium compared to T1 can be ascribed to an absence of plants which does not elucidate the effects of plant-soil interaction response.

**TABLE 7**  
Treatments effects on the amounts of potassium desorbed at equilibrium at different concentrations of added potassium.

Treatment	Potassium desorption at equilibrium, $q_{de}$ (mg g <sup>-1</sup> )			
	100	200	300	400
Added K (mg K L <sup>-1</sup> )				
T1	0.077 <sup>a</sup> ± 0.015	0.096 <sup>a</sup> ± 0.016	0.107 <sup>a</sup> ± 0.022	0.110 <sup>a</sup> ± 0.003
T2	0.050 <sup>ab</sup> ± 0.006	0.053 <sup>a</sup> ± 0.021	0.083 <sup>a</sup> ± 0.012	0.059 <sup>a</sup> ± 0.017
T3	0.056 <sup>ab</sup> ± 0.006	0.083 <sup>a</sup> ± 0.020	0.092 <sup>a</sup> ± 0.045	0.096 <sup>a</sup> ± 0.023
T4	0.048 <sup>ab</sup> ± 0.004	0.047 <sup>a</sup> ± 0.006	0.073 <sup>a</sup> ± 0.030	0.064 <sup>a</sup> ± 0.013
T5	0.049 <sup>ab</sup> ± 0.013	0.072 <sup>a</sup> ± 0.026	0.099 <sup>a</sup> ± 0.014	0.095 <sup>a</sup> ± 0.003
T6	0.027 <sup>b</sup> ± 0.002	0.045 <sup>a</sup> ± 0.009	0.065 <sup>a</sup> ± 0.008	0.058 <sup>a</sup> ± 0.008

Note: Different letters within a column indicate significant difference of means ± standard error using Tukey’s test at  $p \leq 0.05$

### **pH Buffering Capacity of Soil, Charcoal, and Sago Bark Ash**

Table 8 shows the results of the effects of soil alone (T1), charcoal alone (T2), sago bark ash alone (T3), soil with charcoal (T4), soil with sago bark ash (T5), and soil with charcoal and sago bark ash (T6) on pH buffering capacity. These treatments resulted in negative linear relationships between their pH and the amount of acid added with all the regression coefficients ( $R^2 \geq 0.90$ ) (Figure 1). The fact that pH of the treatments decreased linearly with added mmol  $H^+$  suggests an occurrence of soil acidification. Treatment 1 resulted in the lowest pH buffering capacity compared with other treatments and this explains why T1 showed the highest decrease in pH with addition of mmol  $H^+$ . This is due to the inherent properties of Bekenu series which has low CEC, BSP, and carbon content but high Al and Fe ions (Table 1). In acid soils, pH is buffered by Al and Fe ions. The addition of  $H^+$  into soil solution causes Al and Fe hydroxides to solubilize so as to neutralize the change in pH. However, this reaction is reversible because Al and Fe ions are unstable and are adsorbed on exchange complexes *via* hydrolyzation, generating hydrogen ions as products. For each 1 mole of  $Al^{3+}$  that undergoes complete hydrolysis, three  $H^+$  are released (Goulding 2016).

Among the treatments, sago bark ash alone (T3) resulted in the highest pH buffering capacity because the ash contains substantial amounts of  $CaCO_3$ ,  $CaO$ , and  $MgO$  and they serve as pH-neutralizing compounds (Saarsalmi *et al.* 2004). Alternatively, the soil with sago bark ash (T5) showed lower buffering capacity compared with T3 because for T3, the source of acidification comes from  $H_2SO_4$  alone, whereas for T5, the soil also contributes to acidification. Nevertheless, incorporation of sago bark ash (T5) improved pH buffering capacity of the soil in comparison with T1. The dissolution of pH-neutralizing compounds in the ash releases organic anions which consume  $H^+$  added into soil solution and slows acidification.

Charcoal alone (T2) and the soil with charcoal (T4) resulted in better pH buffering capacity compared with T1, but lower than those of T3 and T5. The incorporation of charcoal adds to the CEC and organic matter content of the treatments. The surface oxidation of oxygen-containing functional groups on the charcoal creates negative-charged sites to increase CEC which could consume the added  $H^+$  and retard acidification (Yuan and Xu 2011). The lower pH buffering capacity of the charcoal in comparison with sago bark ash relates to the charcoal's resistance to decomposition (Paustian *et al.* 2016) and smaller particle size of the ash which facilitates a rapid reaction.

The co-application of charcoal and sago bark ash (T6) improved the soil pH buffering capacity compared with the soil with single amendment application (T4 and T5). This is related to the inherently high CEC and alkalinity of the amendments (Table 1). The dissolution of carbonates and oxides from the ash neutralized the active acidity in the soil in addition to dissociating  $H^+$  from the functional groups of the charcoal. This in turn enables chelation of exchangeable acidity pool in the soil by the charcoal. Subsequently, base cations such as  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  from the amendments could immobilize  $H^+$  released from the functional groups and buffer acidification. This mechanism entirely relies on pH of the soil wherein functional groups adsorb  $H^+$  with decreasing pH and dissociate them with increasing pH (Xu *et al.* 2012).

**TABLE 8**

Summary of pH buffering capacity as affected by soil alone, amendments alone, and soil with the amendments

Treatment Code	Initial pH	pH Buffering Capacity (mol H <sup>+</sup> kg <sup>-1</sup> sample)	Regression Coefficient, R <sup>2</sup>
T1	5.31 ± 0.05	0.25	0.92 *
T2	7.76 ± 0.06	0.29	0.90 *
T3	9.78 ± 0.00	0.34	0.92 *
T4	6.51 ± 0.03	0.26	0.97 *
T5	6.41 ± 0.02	0.28	0.93 *
T6	6.65 ± 0.03	0.29	0.92 *

Note: Asterisk (\*) represent significant difference at  $p \leq 0.05$ ; the values given are mean ± standard error.

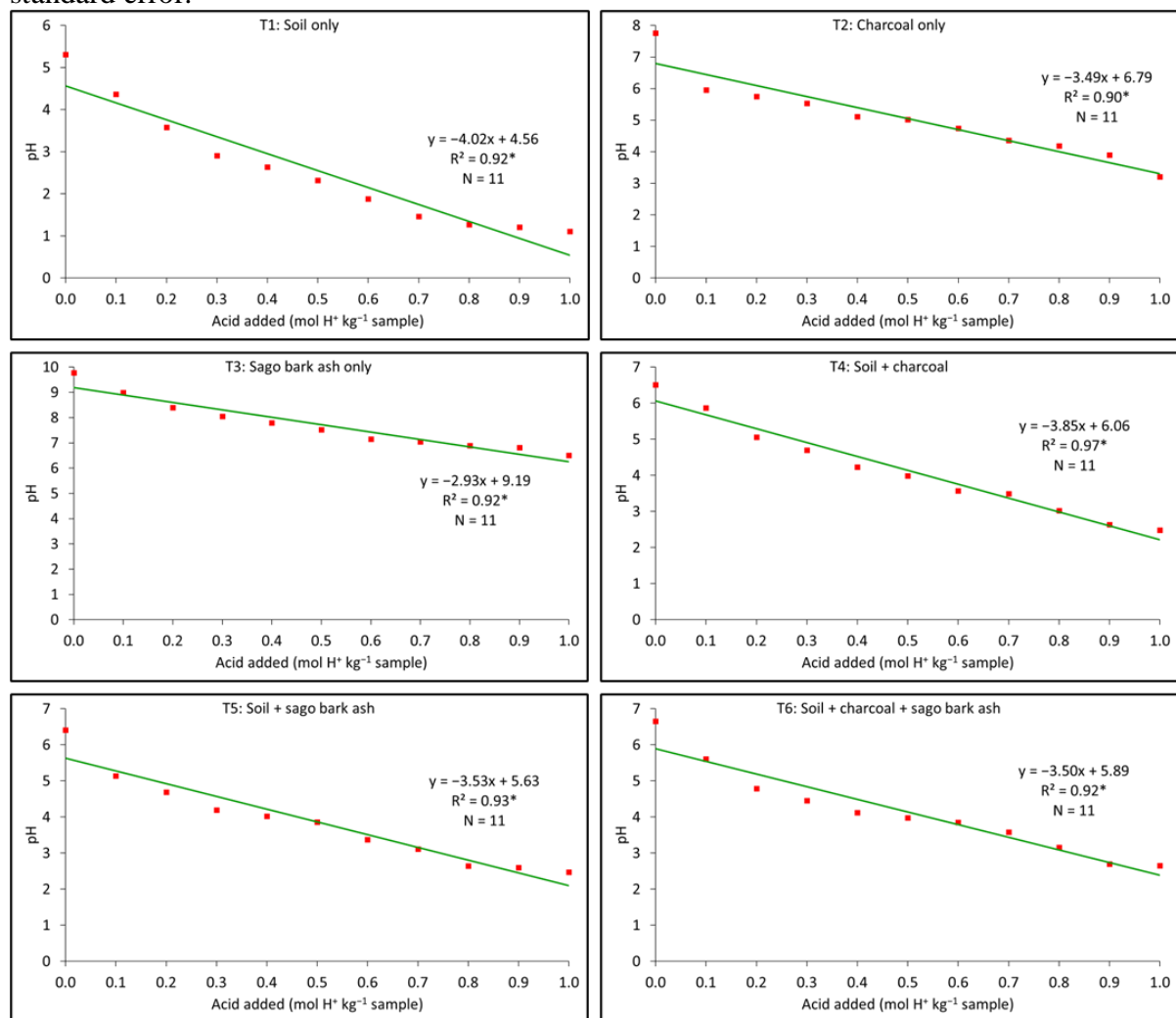


Figure 1. Linear regression between dilute sulphuric acid added (mol H<sup>+</sup> kg<sup>-1</sup> sample) and pH of suspension for the various treatments. Asterisk (\*) indicates significant difference at  $p \leq 0.05$ .

## CONCLUSION

The co-application of charcoal and sago bark ash to acid soils improves K adsorption. This happens because the deprotonation of the functional groups of charcoal, which is facilitated by the dissolution of carbonates and oxides of sago bark ash, creates more adsorption sites for the soil to hold K. This explains why Langmuir bonding energy constant ( $K_L$ ), Maximum K buffering capacity (MBC), and maximum adsorption capacity ( $q_{max}$ ) of T6 are higher than that of soil alone (T1). However, desorption of K is not significantly affected by the application of the amendments. On the other hand, co-application of charcoal and sago bark ash to acid soil improves pH buffering capacity because of the inherently high CEC and alkalinity of the amendments. Knowledge about the ability of the amendments to adsorbed K and buffer acidification is essential to provide a basis for mitigating loss of K in tropical acid soils. Nonetheless, the effect of co-applying charcoal and sago bark ash at different rates on the physicochemical properties of soils needs to be determined to avoid setbacks. Thereafter, a further study could be embarked on.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Putra Malaysia for financial assistance and providing research facilities. Our appreciation is also extended to colleagues and staff of Universiti Putra Malaysia (Malaysia), Universiti Malaysia Kelantan (Malaysia), Management & Science University (Malaysia), and Universiti Islam Sultan Sharif Ali (Brunei Darussalam) for their technical support and collaboration.

## REFERENCES

- Abdelnaeim, M.Y., I.Y. El Sherif, A.A. Attia, N.A. Fathy, M.F. El-Shahat. 2016. Impact of chemical activation on the adsorption performance of common reed towards Cu (II) and Cd (II). *International Journal of Mineral Processing* 157: 80-88.
- Bernas, B. 1968. New method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry. *Anal. Chem.* 40: 1682–1686.
- Biederman, L.A. and W.S. Harpole. 2013. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy* 5: 202–214.
- Bouyoucos, G.J. 1962. Hydrometer method improved for making particle size analyses of soils 1. *Agron. J.* 54: 464–465.
- Bremner, J.M. 1965. Total Nitrogen. In *Methods of Soil Analysis: Part 2* ed. C.A. Black, D.D. Evans, L.E. Ensminger, J.L. White, F.F. Clark and R.C. Dinauer. American Society of Agronomy: Madison, WI, USA, pp. 1149–1178.
- Chefetz, B., P.H. Hatcher, Y. Hadar and Y. Chen. 1996. Chemical and biological characterization of organic matter during composting of municipal solid waste. *J. Environ. Qual.* 25: 776–785.
- Choudhury, A.T.M A. and Y. M. Khanif. 2003. Potassium adsorption behaviour of three Malaysian rice soils. *Biological Sciences-PJSIR.* 46(2): 117-121.
- Costello, R.C. and D.M. Sullivan. 2014. Determining the pH buffering capacity of compost via titration with dilute sulfuric acid. *Waste Biomass Valorization.* 5: 505–513.
- Cottene, A. 1980. Soil testing and plant testing as a basis of fertilizer recommendation. *FAO Soils Bull.* 38: 70–73.
- Dixon, R.K. and J. Wisniewski. 1995. Global Forest systems: An uncertain response to atmospheric pollutants and global climate change? *Water Air Soil Pollut.* 85: 101–110.
- Free, H.F., C.R. McGill, J.S. Rowarth and M.J. Hedley. 2010. The effect of biochar on maize (*Zea mays*) germination. *N. Z. J. Agric. Res.* 53: 1–4.
- Gazey, C. 2018. Effects of Soil Acidity; Agriculture and Food Department of Primary Industries and Regional Development Government of Western Australia. Available online:

- <https://www.agric.wa.gov.au/soil-acidity/effects-soil-acidity?page=0%2C1> (accessed on 22 April 2021).
- Goulding, K.W.T. 2016. Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom. *Soil Use Manag.* 32: 390–399.
- Gregory, T., C.L. Karns and K.D. Shimizu. 2005. A critical examination of the use of the Freundlich isotherm in characterizing molecularly imprinted polymers (MIPS). *Anal. Chim. Acta* 528: 107–13.
- Hundal, L. S. and N.S. Pasricha. 1998. Adsorption-desorption kinetics of potassium as influenced by temperature and background anions. *Geoderma* 83(3-4): 215-225.
- Jaiswal, D.K., J.P. Verma, S. Prakash, V.S. Meena and R.S. Meena. 2016. Potassium as an important plant nutrient in sustainable agriculture: A state of the art. *Potassium Solubilizing Microorg. Sustain. Agric.* 21–29, [https://doi.org/10.1007/978-81-322-2776-2\\_2](https://doi.org/10.1007/978-81-322-2776-2_2)
- Kithome, M., J.W. Paul, L.M. Lavkulich and A.A. Bomke. 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Science Society of America Journal* 62(3): 622-629.
- Latifah, O., O.H. Ahmed and N.M.A Majid. 2017. Short term enhancement of nutrients availability in *Zea mays* L. cultivation on an acid soil using compost and clinoptilolite zeolite. *Compost Science & Utilization* 25(1): 22-35.
- Major, J., M. Rondon, D. Molina, S.J. Riha and J. Lehmann. 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil* 333: 117–128.
- Mandre, M., H. Pärn and K. Ots. 2006. Short-term effects of wood ash on the soil and the lignin concentration and growth of *Pinus sylvestris* L. *For. Ecol. Manag.* 223: 349–357.
- Melo, V. F., Singh, B., Schaefer, C. E. G. R., Novais, R. F. and Fontes, M. P. F. 2001. Chemical and mineralogical properties of kaolinite-rich Brazilian soils. *Soil Science Society of America Journal.* 65(4):.1324-1333.
- Miranda-Trevino, J.C. and C.A. Coles. 2003. Kaolinite properties, structure and influence of metal retention on pH. *Appl. Clay Sci.* 23: 133–139.
- Moody, P.W. and R.L. Aitken. 1997. Soil acidification under some tropical agricultural systems. 1. Rates of acidification and contributing factors. *Soil Research* 35(1): 163-174.
- Ndor, E., S.N. Dauda and E.D. Azagaku. 2015. Response of maize varieties (*Zea mays*) to biochar amended soil in Lafia, Nigeria. *J. Exp. Agric. Int.* 5: 525–531.
- Ozolincius, R., R. Buozyte, and K.I. Varnagiryte. 2007. Wood ash and nitrogen influence on ground vegetation cover and chemical composition. *Biomass Bioenerg.* 31: 710–716.
- Palanivell, P. 2016. Organic and Mineral Amendments on Rice (*Oryza sativa* L.) Yield and Nutrients Recovery Efficiency. Ph.D. Thesis, Universiti Putra Malaysia, Seri Kembangan, Malaysia.
- Paramanathan, S. 2000. *Soil of Malaysia: Their Characteristics and Identification*; Academy of Sciences Malaysia: Kuala Lumpur, Malaysia, Vol. 1, pp. 11–125.
- Paustian, K., J. Lehmann, J. S. Ogle, D. Reay, G.P. Robertson and P. Smith. 2016. Climate-smart soils. *Nature* 532: 49–57.
- Peech, H.M. 1965. Hydrogen-ion Activity. In *Methods of Soil Analysis Chemical and Microbiological Properties*, ed. C.A.Black, D.D. Evans, J.L. White, L.E. Ensminger and F.E Clark. American Society of Agronomy: Madison, WI, USA, pp. 914–926.
- Peng, H., A. Jiang and H. Wang. 2021. Adsorption and desorption characteristics of phosphorus on sediments in Panzhuhua Section of Jinsha River, China. In *IOP Conference Series: Earth and Environmental Science*. IOP Publishing; Bristol, United Kingdom, pp. 042059.
- Perucci, P., E. Monaci, A. Onofri, C. Vischetti and C. Casucci. 2008. Changes in physico-chemical and biochemical parameters of soil following addition of wood ash: A field experiment. *Eur. J. Agron.* 28: 155–161.
- Perumal, P., O.H. Ahmed, L. Omar and N.M. Abdul Majid. 2021. Nitrogen, phosphorus, and potassium adsorption and desorption improvement and soil buffering capacity using clinoptilolite zeolite. *Agronomy* 11(2):379-398.
- Qiu, Y., H. Cheng, C. Xu and G.D. Sheng. 2008. Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. *Water Res.* 42: 567–574.
- Rowell, D.L. 1994. *Soil Science: Methods and Application*; Longman Publishers Ltd: London, UK, 169 p.

- Saarsalmi, A., E. Mälkönen and M. Kukkola. 2004. Effect of wood ash fertilization on soil chemical properties and stand nutrient status and growth of some coniferous stands in Finland. *Scand. J. For. Res.* 19: 217–233.
- Schneider, A., R. Tesileanu, R. Charles and S. Sinaj. 2013. Kinetics of soil potassium sorption–desorption and fixation. *Commun. Soil Sci. Plant Anal.* 44: 837–849.
- Shi, R.Y., Z.N. Hong, J.Y. Li, J. Jiang, M.A.A. Baqay, R.K. Xu and W. Qian. 2017. Mechanisms for increasing the pH buffering capacity of an acidic Ultisol by crop residue-derived biochars. *Journal of Agricultural and Food Chemistry.* 65(37): 8111-8119.
- Soil Survey Staff. 2014. *Keys to Soil Taxonomy* (12th ed.). USDA-Natural Resources Conservation Service: Washington, DC, USA.
- Sparks, D.L. 2000. Bioavailability of soil potassium, D-38-D-52. In *Handbook of Soil Science*, ed. M.E. Sumner. CRC Press: Boca Raton, FL, USA.
- Sparks, D.L., L.W. Zelazny and D.C. Martens. 1980. Kinetics of potassium exchange in a Paleudult from the coastal plain of Virginia. *Soil Science Society of America Journal* 44(1):37-40.
- Srividya, K. and K. Mohanty. 2009. Biosorption of hexavalent chromium from aqueous solutions by *Catla catla* scales: equilibrium and kinetics studies. *Chemical Engineering Journal.* 155(3):666-673.
- Vasconcelos, R.F.B.D., J.R.B. Cantalice, V.S.D. Oliveira, J.D.J.D. Costa and D.M. Cavalcante. 2010. Estabilidade de agregados de um Latossolo Amarelo distrocoeso de tabuleiro costeiro sob diferentes aportes de resíduos orgânicos da cana-de-açúcar. *Revista Brasileira de Ciência do Solo.* 34:309-316.
- Wang, L. and T. Liang. 2014. Effects of exogenous rare earth elements on phosphorus adsorption and desorption in different types of soils. *Chemosphere* 103: 148–155.
- Wann, S.S and G. Uehara. 1978. Surface charge manipulation in constant surface potential soil colloids: II. Effect on solute transport. *Soil Sci. Soc. Am. J.* 42: 886–888.
- Xu, R.K., A.Z. Zhao, J.H. Yuan and J. Jiang. 2012. pH buffering capacity of acid soils from tropical and subtropical regions of China as influenced by incorporation of crop straw biochars. *Journal of Soils and Sediments* 12(4): 494-502.
- Yuan, J.H. and R.K. Xu. 2011. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic Ultisol. *Soil Use and Management.* 27(1): pp.110-115.