Malaysian Journal of Soil Science 2022 Vol. 26: 88-103

Impact of Biochar Treatment on Chemical Properties of a Sandy Spodosol Developed from Marine Sediments

Syuhada, A.B.[1], Shamshuddin, J.[1*], Fauziah, C.I.[1], Arifin, A.[2] and Panhwar, Q.A.[3]

[1]Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Department of Forest Production, Faculty of Forestry, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[3]Soil & Environmental Sciences Division, Nuclear Institute of Agriculture, 70060 Tando Jam, Sindh, Pakistan

[*]Corresponding author: shamshud@upm.edu.my

ABSTRACT

An experiment using leaching columns was conducted for 72 weeks to determine the impact of biochar treatment on a sandy Spodosol. Biochar treatment was found to have a positive impact on soil chemical properties. The treated topsoil had higher exchangeable K, Ca and Mg compared to the control. Due to low clay and organic matter content, much of the cations released by biochar could not be retained in that zone. This is evidenced by the increased concentration of elements in leachates collected from the leaching columns. It means that a significant portion of the nutrients, initially in insoluble form, was susceptible to leaching or podzolization. Some of the nutrients were transported downwards and subsequently retained in the spodic horizon. The biochar treatment increased soil pH, total C and the CEC of the spodic layer with the CEC increase being positively correlated with C content. Notwithstanding, the ameliorative impact of biochar treatment is at best short-term. The application of high amounts of biochar is necessary to raise soil fertility to the level suitable for crop production. Hence, it is recommended that biochar be applied in combination with some NPK fertilizers to sustain crop growth/production in the long term.

Key words: Biochar, leaching column experiment, marine sediments, podsolization, Spodosol

INTRODUCTION

Spodosols, developed from marine sediments of Holocene age, are widespread in the coastal plains of Peninsular Malaysia (Roslan *et al.* 2010). The most important soil attribute for their low fertility is the sandy texture of such soils (have >95% sand). This pedological feature significantly affects the physico-chemical properties of the Spodosols. It can be assumed that such soils have a high proportion of drainage pores, leading to a high leaching rate. Water and dissolved substances in the soils are rapidly transported downwards and subsequently accumulate in the Spodic layer or just disappear into the groundwater.

The soils cannot sustain crop production due to their low inherent nutrient availability. It is made worse by the lack of organic matter in the topsoil that results in a low cation exchange capacity; hence, its water retention is insufficient for crop growth. Consequently, only a small area of Spodosols in the coastal plains is utilized for the production of crops (Roslan *et al.*

2011). Nevertheless Syuhada *et al.* (2016) showed that the low fertility Spodosol can, to a certain extent, be ameliorated for corn cultivation using biochar made from oil palm empty fruit bunches (EFB).

The abundant occurrence of sandy Spodosols in the coastal regions of Peninsular Malaysia raises concern among the agronomists working to formulate sustainable management practices to restore or improve their fertility. It is believed that EFB-biochar application can somewhat increase fertility of these soils. Under a high temperature environment coupled with high rainfall, the ameliorative impact is at best short-term. This is because organic matter exposed to the tropical environment is easily decomposed with the nutrients released being rapidly leached out of the soils.

Several agronomists have found biochar to provide a more enduring improvement to soil fertility (Manickam *et al.* 2015). Application of biochar is one of the ways to minimize leaching risk of nutrients as biochar is found to have a significant impact on soil quality via increases in surface area, porosity, cation exchange capacity, soil pH and water retention (Abel *et al.* 2013; Kameyama *et al.* 2012; Major *et al.* 2009). The above-mentioned effects of biochar application help curtail leaching loss of mobile nutrients, enhance microbial activities (Lehmann *et al.* 2011) and increase nutrient availability for crop uptake (Major *et al.* 2010). Thus, adding biochar into the sandy Spodosol under investigation is a feasible option to improve fertility and sustain crop growth/production.

Soil columns studies are often used to evaluate the impact of biochar application on soil chemical properties and leaching losses of nutrients (Laird *et al.* 2010; Novak *et al.* 2009). This research was conducted on loamy or clayey soils, using various types of biochar produced from different feedstock. No similar study has yet been conducted on sandy Spodosols of the humid tropics. It is plausible that some C from biochar applied into the top soil of a sandy Spodosol can be sequestrated in the spodic horizon of Spodosols under a tropical environment. Hence, the current study addressed the chemical changes that take place in a sandy Spodosol found in Peninsular Malaysia as affected by application of EFB-biochar and the ameliorative impact of applying the biochar on the infertile Spodosol.

MATERIALS AND METHODS

Soil and Biochar Used in the Study

The soil for the experiment was taken from Forest Research Institute of Malaysia (FRIM) Experimental Station in Setiu, Terengganu, Malaysia. The area is located approximately at latitude 5.54° N and longitude 102.87° E. The experimental site was planted with a forest species (*Shoreapalem banica)*. The soil had a spodic horizon below 100 cm depth, fitting well into the definition of Spodosol (Soil Survey Staff 2014). Identified as Jambu Series, the soil is taxonomically classified as sandy, siliceous, isohyperthermic family of Typic Haplorthods. According to (Roslan *et al.* 2010), quartz is the dominant mineral not only in the sand, but also in the silt and/or clay fraction of the soil. Soil samples used for the current experiment were taken from the topsoil, eluvial and spodic horizon (the dark colored bottom of the soil profile shown in *Figure 1*). They were air-dried under glasshouse conditions at Universiti Putra

Malaysia (Serdang, Malaysia), sieved (<2 mm) and kept for the leaching column experiment. The chemical characteristics of the soil are shown in Table 1.

Biochar was obtained from a local producer in Malaysia, with feedstock from oil palm empty fruit bunches (EFB). The biochar was prepared via slow pyrolysis using medium thermal process (300-350° C). With a pH of 9.73, the biochar contained 18.3 % ash, 53.3% C, 11 g kg^{-1} N, 69 g kg^{-1} K, 6.3 g kg^{-1}Ca and 5.3 g kg^{-1} Mg. The particle size of the biochar was 2 to 5 mm; but was ground to pass through 2-mm sieve and thoroughly mixed with the soil for the experiment to ensure homogeneity. A large portion of the biochar used in this study was from the < 1 mm size fraction.

TABLE 1
The chemical properties of Jambu Series

Soil horizon	pH (water)	Total C	Total N	CEC	Exchangeable cation K	Exchangeable cation Ca	Exchangeable cation Mg
		---------------- % ----------------			------- (cmol$_c$ kg^{-1}) ------		
Topsoil (0 - 20 cm)	4.71	0.56	0.02	1.05	0.04	0.40	0.01
Eluvial horizon (20 - 87 cm)	4.13	0.03	0.00	0.22	0.02	0.08	0.01
Spodic horizon (>100 cm)	3.67	0.71	0.01	3.32	0.02	0.35	0.02

Soil Column Setup

Soil columns were prepared using PVC pipes of 15 cm inner diameter and 100 cm length. They were fitted with perforated PVC end-cap at the bottom to allow for the outflow of leachate to ensure the soil remained free-draining (*Figure 1*). The last 2 cm of each column was filled with a small amount of glass wool, overlain by a layer of coarse sand to minimize soil loss during leaching events. Air-dried surface soil (0-20 cm) from the eluvial (E) horizon (20-87 cm) and spodic horizon (>100 cm depth) were packed into the columns to simulate the 0-90 cm of the Spodosol profile occurring in the field (*Figure 1*). The top 0-10 cm (topsoil) and 10-40 cm of the soil profile in the columns were packed with soil from surface and E horizon, respectively.

A thin spodic layer was created at 40-45 cm depth (hereby referred to as spodic layer) with soil taken from the spodic horizon, underlain by soil from the E horizon at 45-90 cm depth. Note that the subsoil at 45-90 cm of the created soil profile was supposed to be packed with the soil taken from below the spodic horizon in the field; however, we were unable to collect it because the spodic layer was too deep below the surface (> below100 cm depth). Therefore, the soil packed below the spodic horizon of the created profile was re-constructed using soil material from the E horizon.

Each soil layer was packed in the column at an initial bulk density of 1.41, 1.69 and 1.43 g cm^{-3}(three levels of bulk density) and four depth levels at 0-10, 10-40, 40-45 and 45-90 cm depths, respectively. When all layers of the soil were packed/stabilized, there was 8 cm head space above the soil columns. The soil in the 0-10 cm depth of the leaching column (hereby called topsoil) was subjected to one of the following treatments: (1) 0 g kg^{-1}; (2) 5 g kg^{-1}; (3) 10 g kg^{-1}); and (4) 15 g kg^{-1} of biochar, designated as B0 (control), B5, B10 and B15, respectively. These rates corresponded to 0, 10, 20 and 30 t ha^{-1} with each treatment being replicated three times. A total of nine replicates for each treatment were set up so as to allow for destructive soil sampling at weeks 24, 48 and 72 consecutively.

Figure 1 shows the diagrammatic illustration of the experimental setup. The soil columns were placed upright in a glasshouse where they received water once a week over a study duration of 72 weeks, at an amount equivalent to the mean annual rainfall in Terengganu from year 2000 to 2009 of 3340 mm. The water was gently poured onto the top of each column manually. Filter paper was placed on the soil surface to help dissipate the water drops as they impacted on the upper surface of the column.

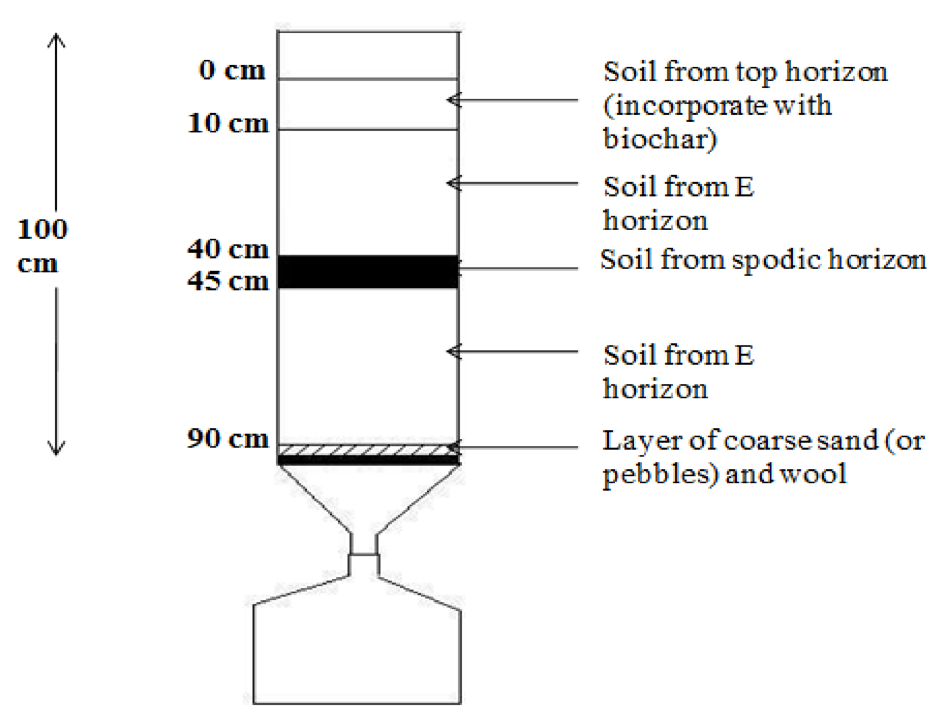


Figure 1. Diagrammatic illustration of the created Spodosol profile in a soil column

Sample Collections and Chemical Analyses

The columns were freely drained during the duration of the experiment and leachates were collected 48 hours after each leaching event. The leachates were analyzed once every 4 weeks. The concentrations of K, Ca and Mg in the leachates were determined using Optima 8300 ICP-OES spectrometer (PerkinElmer, Massachusetts, USA). Columns (n= 3) from each treatment were destructively sampled at time increments of 24, 48 and 72 weeks. The soil columns were sectioned vertically and analyzed at seven depth intervals of 0-10, 10-25, 25-40, 40-45, 45-67.5, and 67.5-90 cm below the soil surface.

The soil from the various depths was air-dried and passed through a 2-mm sieve. Soil pH was taken using a ratio of 1:2.5 soil to water; exchangeable Al was extracted with 1 M KCl at 1:10 ratio by shaking for 30 min; total C and total N were determined using TruSpec CHNanalyser (Leco, Michigan, USA); and CEC and exchangeable cations (Ca, Mg and K) were determined using ammonium acetate buffered at pH 7 (Schollenberger and Simon, 1945). The NH_4^+ ions for determination of CEC was determined by an Auto-analyser (Quik Chem 8000 Series FIA+ System, Lachat Instruments, Loveland, USA), while exchangeable cations were measured using Optima 8300 ICP-OES spectrometer (PerkinElmer, Massachusetts, USA).

Statistical Analysis

The experimental layout for every sampling time (week 24, week 48 and week 72) was a factorial combination of four (4) different rates (0, 5, 10 and 15 g kg^{-1}) of biochar and 7 sampling depths with three replications. A completely randomized design (CRD) was used for all statistical analyses. At every sampling time, a two-way analysis of variance (ANOVA) was carried out for each variable measured with biochar rate, sampling depth and their interactions as fixed effects. Tukey's Studentized Range test was used to calculate the differences among treatment means. The functional relationship (trend comparison) between response of variables and biochar rate for variables with significant biochar rate and/or biochar rate x sampling depth interaction was performed by polynomial contrast and regression analysis.

In all cases (except for soil pH), significant regression were only detected for soil sampled in the topsoil (0-10 cm depth) and spodic layer (40-45 cm depth); thus, only regression equations for both sampling depths are reported in this paper. Thereafter, the relationship between variables for every sampling time was determined by correlation and regression analysis. Statistical analysis was performed using SAS, software version 9.1 with differences, unless otherwise stated, significant at $p \leq 0.05$.

RESULTS AND DISCUSSION

Impact of EFB-Biochar Treatment on Soil Acidity

In comparing biochar rates and soil depths, our study results detected a significant difference at every sampling time ; however, this was not the case for their interaction (Table 2). At week 24, biochar addition increased soil pH, but at week 48, only treatment B15 had a higher pH than that of the control treatment. At week 72, there was no further increase in soil pH at any rate of biochar treatment (*Figure 2a*). Linear polynomial contrast for the responses of soil pH to biochar rate was significant for soil sampled at weeks 24 and 48, while quadratic and cubic polynomial contrast was only significant for soil sampled at week 72 (Table 2). The linear regression equation so obtained demonstrated that soil pH increased by 0.06 and 0.04 unit per g kg^{-1} of biochar applied for weeks 24 and 48, respectively (*Figure 2a*). According to Joseph *et al.* (2010), the observed increase in soil pH was likely due to the dissolution of alkaline carbonates or oxides/hydroxides present in the ash fraction of the biochar. On the other hand, Ca originating from the EFB-biochar may have displaced some Al on the exchange sites which could result in a slightly lower soil pH (Egiarte *et al.* 2006).

At week 24, the topsoil had the highest soil pH (Fi*gure 2b*). However, at week 48, the pH of the topsoil showed a decreasing trend with values lower than that of the subsoil (below 40 cm depth). This was probably because of the oxidation of non-aromatic C fractions to form acidic carboxyl groups resulting from biochar addition (Cheng *et al.* 2006; Nguyen *et al.* 2010), leading to the subsequent decline in soil pH (Joseph *et al.* 2010). At week 72, the pH of the soil at every depth had decreased but with the topsoil still having the highest value.

The results seemed to indicate that the biochar-treated Spodosol became acidic again towards the end of week 72, suggesting that the ameliorative impact of EFB-biochar treatment was only short-term. The efficacy of the biochar as a soil ameliorant decreased when it had undergone ageing due to loss of K, Mg and Ca via leaching that partly contributed to the slight increase in soil acidity. Thus, EFB-biochar can only be an effective ‘liming agent’ for sandy Spodosol provided that high amounts are applied on the soil (Rabileh *et al.* 2015).

TABLE 2
Probability (p) values derived from ANOVA for chemical properties of soil

(a) Week 24

Source	pH	TC	CEC	K	Ca	Mg
Depth	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Rate	<0.0001	<0.0001	0.04	0.0002	0.18	<0.0001
Depth*rate	0.38	<0.0001	0.02	<0.0001	<0.0001	<0.0001
Rate linear	<0.0001	<0.0001	0.01	<0.0001	0.09	<0.0001
Rate Quadratic	0.001	0.72	0.29	0.35	0.20	0.07
Rate cubic	0.51	0.37	0.84	0.87	0.58	0.01

(b) Week 48

Source	pH	TC	CEC	K	Ca	Mg
Depth	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Rate	<0.0001	0.003	0.09	<0.0001	0.12	<0.0001
Depth*rate	0.32	<0.0001	0.54	<0.0001	0.01	<0.0001
Rate linear	<0.001	0.0002	0.02	<0.0001	0.02	<0.0001
Rate Quadratic	0.19	0.51	0.71	0.15	0.65	0.08
Rate cubic	0.17	0.97	0.45	0.36	0.92	0.42

(c) Week 72

Source	pH	TC	CEC	K	Ca	Mg
Depth	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Rate	0.010	0.02	<0.0001	0.01	0.08	<0.0001
Depth*rate	0.80	0.0001	0.0001	0.001	0.14	<0.0001
Rate linear	0.26	0.003	<0.0001	0.01	0.02	<0.0001
Rate Quadratic	0.02	0.37	0.12	0.17	0.27	0.57
Rate cubic	0.010	0.63	0.99	0.03	0.93	0.60

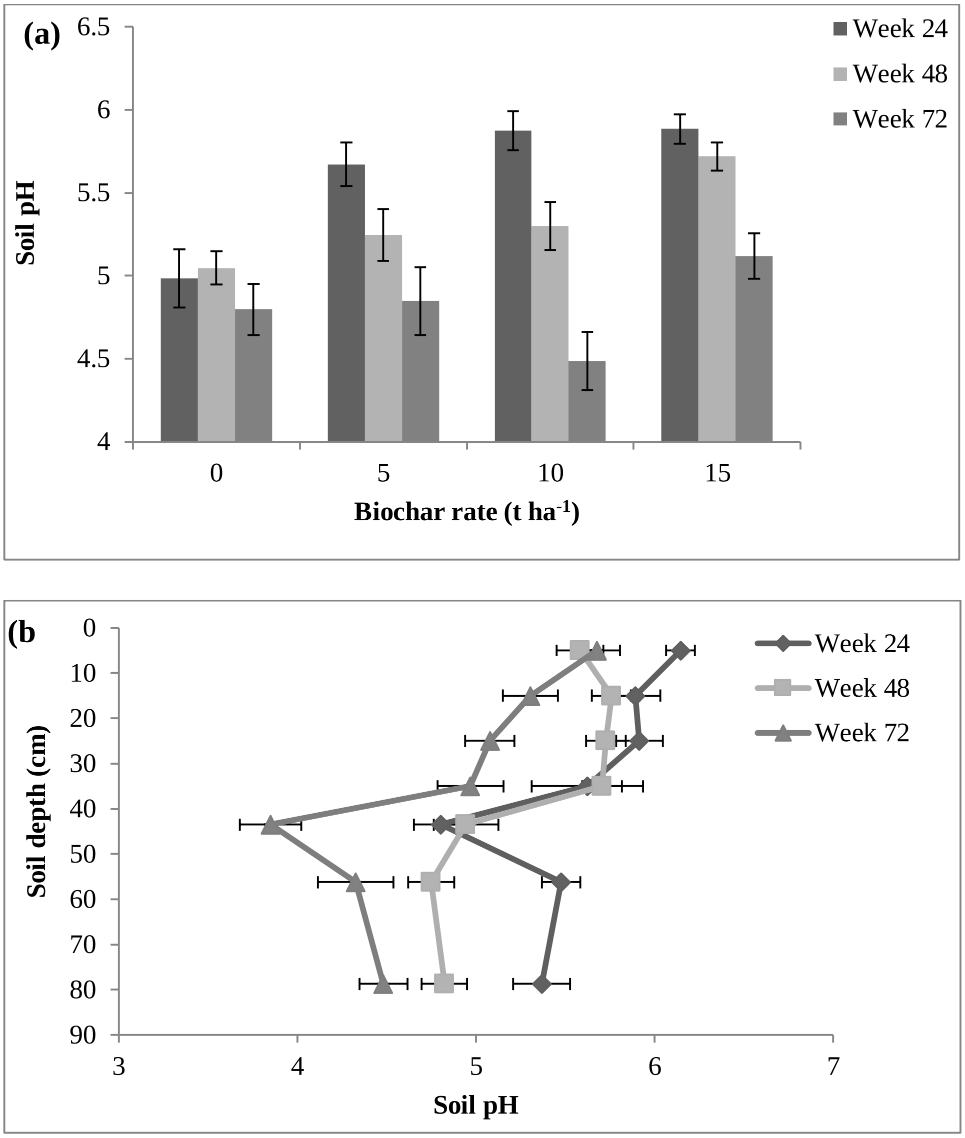


Figure 2. Interaction effects of biochar rate × sampling time (a) and depth × sampling time (b) on soil pH. Error bars represent ± standard error of the means; (a) n = 21, (b) n = 12. Points in (a) and (b) are placed at the center of the depth increment they represent. Significant at p≤ 0.05.

Impact of EFB-biochar treatment on soil C content

Figure 3 shows the impact of biochar treatment on soil C content of the treated samples. Polynomial contrast and regression analyses indicated that the response of total C in the topsoil increased linearly with every g kg^{-1} increase in EFB-biochar rate applied at 0.36, 0.50 and 0.29 % for weeks 24, 48 and 72, respectively (Table 3). Total C in the biochar treated top soil was higher than that of the control treatment for every sampling time, indicating that a large amount of the applied biochar remained in place even after being subjected to the continuous wet-dry cycles for 72 weeks. However, only soils in the columns treated with B15 were significantly higher compared to that of the control treatment (*Figure 3a*).

The biochar-treated soil in the spodic layer appears to have a significantly higher C content compared to that of the control treatment for week 24 only. This result suggests that some C from the topsoil had moved down to the subsoil via leaching or perhaps by the process of podzolization. Total C in the spodic layer increased linearly by 0.18% ($R^2=0.71$, $P<0.001$) with every g kg^{-1} of EFB-biochar added (Table 2). At every sampling time, soil without EFB-biochar treatment showed significantly higher C in the topsoil and spodic layer compared to that of the other soil depths. A similar trend was observed for the biochar-treated soils, but their total C was higher. This finding is consistent with that of Lehmann *et al.* (2007), which means that in real situations in the field, some C from EFB-biochar is transported downwards over time.

Total C of the treated soil columns in the topsoil and spodic layer showed a small decrease with time (*Figure 3b*). The recalcitrant nature of the biochar does not mean that it remains unchanged forever (Atkinson *et al.* 2010). Schmidt and Noack (2000) noted that besides having recalcitrant aromatic ring structures, biochar contains some easily degradable aliphatic and oxidized C structures. Hence, some of the unstable C in the EFB-biochar might have undergone change through oxidation and mineralization. However, this is not consistent with the finding of Laird *et al.* (2010) who reported no detectable loss of biochar C during the 72 weeks of their soil column study. The soil tested by Laird *et al.* (2010) was a Mollisol dominated by 2:1 phyllosilicates (smectite and vermiculite) with high CEC that can curtail C loss via leaching. Note that the clay fraction of the sandy Spodosol under study was dominated by kaolinite which has low CEC (Roslan *et al.* 2010).

Addition of EFB-biochar to the sandy Spodosol containing some kaolinite increased C in the topsoil, but its level decreased as the biochar aged with time. This is due to the effects of exposure to the high soil temperature and leaching environment, resulting in rapid mineralization of C in the EFB-biochar. The biochar-C could have been leached as dissolved organic materials, which was eventually transported down the soil column. It was possible that some of the dissolved C accumulated or was temporarily trapped in the spodic layer via the process of podzolization. Because of the loose soil structures in the re-packed spodic layer or possibly due to the presence of low amount of 2:1 phyllosilicates,the dissolved C could have continued to move further below the said layer.

The assumed podzolization process occurring in the soil columns during the period of the experiment could have been promoted by special microbes existing in the Spodosol, which was identified by Zainuri (1981) as fungi species. According to Lundström *et al.* (2000) and Van Schöll *et al.* (2008), fungi could play a crucial role in the podzolization of Spodosols. Hydroxyl, aliphatic and quinone are the dominant functional groups present in biochar (Liu *et al.* 2015). Accordingly, the organic C released into the soil by the decomposition of the EFB-biochar could form stable Al-Fe-complexes, which is the key mechanism of the podzolization process.

The biochar-treated soil had significantly higher C in the spodic layer compared to that of the control treatment. This means that some C in the topsoil had been transported down the soil profile via leaching and/or the process of podzolization. If the latter could be proven to occur in the studied soil, it is plausible that some C from the EFB-biochar can be sequestered in the spodic layer of sandy Spodosols in the tropics.

TABLE 3

Regression equation for the response of total C and CEC in the topsoil

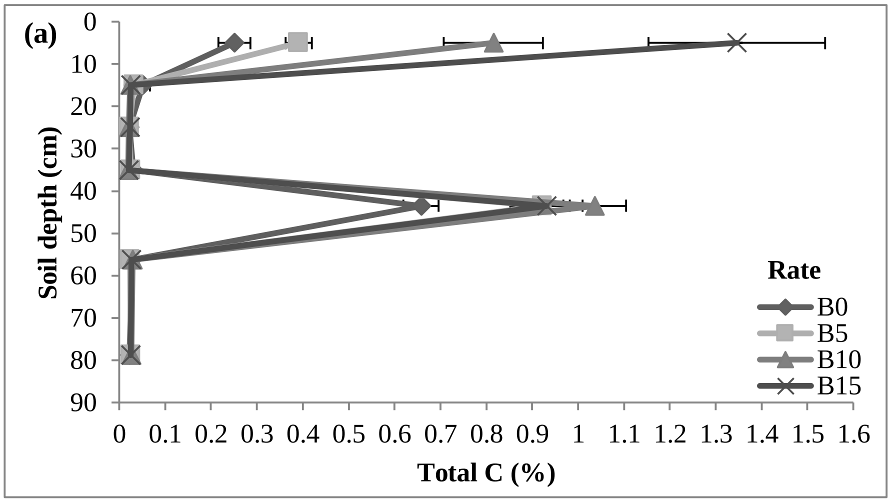
		Equation R^2	
Soil properties and depth	Week 24	Week 48	Week 72
Total C (%)			
0-10cm	$y=0.363x-0.108$ $R^2=0.81$***	$y=0.504x-0.455$ $R^2=0.59$**	$y=0.29x-0.115$ $R^2=0.61$**
40-45cm	$y=0.182x+0.557$ $R^2=0.71$***	$y=0.068x+0.632$ $R^2=0.43$*	ns[a]
CEC (cmol$_c$ g kg^{-1})			
0-10cm	$y=0.364x+0.032$ $R^2=0.65$**	nd[b]	$y= 0.473x+0.037$ $R^2=0.8$***
40-45cm	ns	nd	ns

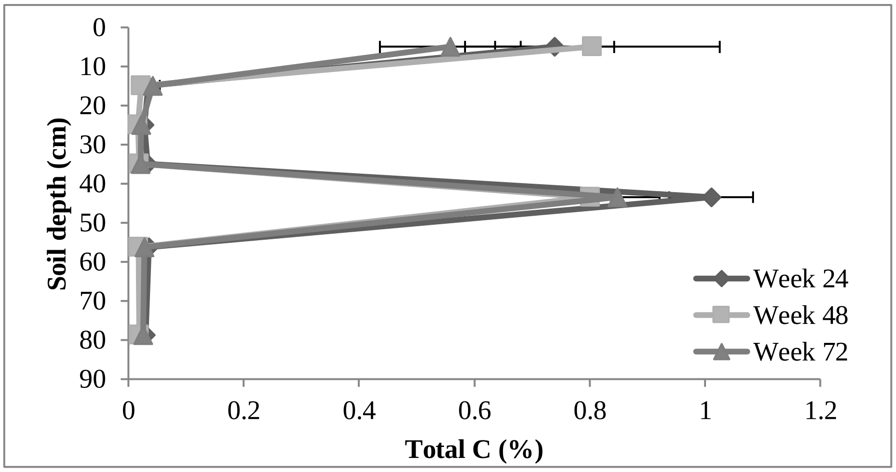
Topsoil and spodic layer to biochar rate for the soil sampled at weeks 24, 48 and 72.

[a] Not significant at $p>0.05$

[b] Not determined because there was no significant effect of biochar rate or biochar rate x depth interaction for CEC of soil sampled at week 48

* Significant at $p\leq0.05$, ** significant at $p\leq0.01$, *** significant at $p\leq0.001$





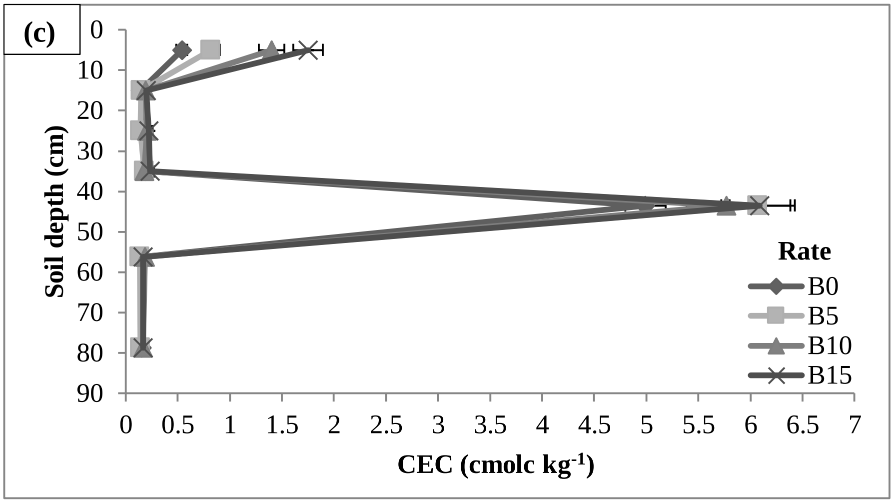


Figure 3. Interaction effect of biochar rate × depth (a), depth × sampling time (b) on soil total C %, and (c)biochar rate × depth on the CEC. Error bars represent ± standard error of the means (n = 9). Points are placed at the center of the depth increment they represent. Significant level: $p \leq 0.05$.

Impact of EFB-Biochar Treatment on Soil CEC

A significant effect of biochar rate x depth interaction on CEC of the soil was observed at weeks 24 and 72 (Table 2). At week 24, only soil treated with B15 significantly increased the topsoil CEC compared to that of the control (*Figure 3c*), while at week 72, the CEC of the soil at the same depth increased significantly in the soil treated with B10 and B15. There was a significant linear polynomial contrast for the response of CEC to the biochar treatment at weeks 24 and 72 (Table 2). Regression analysis (R^2=0.65, P<0.01; R^2=0.8, P<0.001, for weeks 24 and 72, respectively) showed that the CEC increased by 0.36 and 0.47 unit for every g biochar kg^{-1}soil applied at weeks 24 and 72 (Table 3). No significant difference was found in the spodic layer due to EFB-biochar treatment.

Soil in the spodic layer was initially quite high in CEC, with values higher than that of the other layers in the soil profile. This is expected as the spodic horizon of a Spodosol contains high amounts of organic matter. Due to EFB-biochar addition, the CEC of the soil in the spodic layer was also significantly higher than that of the control treatment. The CEC of the topsoil appears to show an increasing trend with the rate of biochar addition but not significantly different. This is consistent with the finding of other researchers who reported the ability of biochar to only slightly increase the CEC of a soil (Novak *et al.* 2009; Steiner *et al.* 2007).

It is believed that the small increase in the topsoil CEC was due to the addition of C released by the EFB-biochar (Chan *et al.* 2008). This is shown by the linear relationship between CEC and C at every sampling time (R^2=0.62, P<0.001; R^2=0.41, P<0.001; R^2= 0.66; P< 0.001, at weeks 24, 48 and 72, respectively) (Figure 4). The CEC of the topsoil was respectively increased by 3.44, 2.93 and 4.1 $\text{cmol}_c\ \text{kg}^{-1}$ for every 1 % increase in C content, at weeks 24, 48 and 72. Liang *et al.* (2006) and Atkinson *et al.* (2010) explained the occurrence of a phenomenon by the oxidation of C present in the biochar that oxygenates functional groups, and producing negative charge. The CEC of fresh biochar is relatively low; however, it increases during the period of incubation in soil due to the oxidation of biochar surfaces and/or adsorption of organic acids (Cheng *et al.* 2006). This notion is supported by the findings of another study (Laird *et al.* 2010).

A slight increase in the topsoil CEC is indicative of oxidation of the easily degradable C present in the EFB-biochar. Note that soil sampled from the E horizon was not significantly affected by addition of the EFB-biochar, which was probably due to the very low clay mineral and/or C content in that zone. By and large, the CEC of the biochar-treated soil in the leaching columns except for the spodic layer remained very low (< 3 $\text{cmol}_c\ \text{kg}^{-1}$). This suggests that a large amount of EFB-biochar (at least 15 g kg^{-1}) is needed to increase the CEC of the sandy soil significantly. In spite of ameliorative impact on the soil, application of EFB-biochar at the proposed rate is considered not a feasible agronomic practice due to the high cost of producing EFB-biochar (Manickam *et al.* 2015).

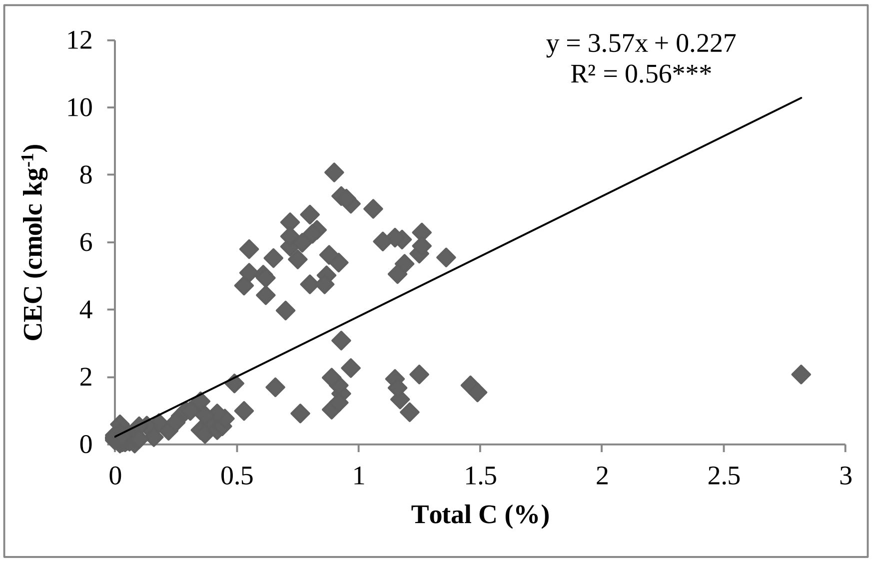


Figure 4. Impact of EFB-biochar treatment on relationship between CEC and total C in the soil

Effects of EFB-Biochar Treatment on Leachate Composition

Leachate K

Potassium concentration in the leachates increased with increasing biochar rates, but decreased with time (*Figure 5a*). This is due to the continued leaching of K from the soil, evidenced by the higher concentration of K in the leachate at the beginning of the leaching event compared that of the latter. It is known that K is not tightly bound to the biochar (Milligan *et al.* 2008); therefore, it is subjected to immediate leaching after the EFB-biochar was applied. Furthermore, leaching of K is dependent on the concentration of other cations, especially Ca. Note that Ca is the dominant cation in soil and thus it competes with K for the exchange sites. If a limited number of cation exchange sites is available, divalent cation is preferentially exchanged. This is due to the greater force of attraction to the exchange sites for a divalent ion compared to that of a monovalent ion (Hodson and Langan 1999). Therefore, K is more available for movement within the leachate as explained by Novak *et al.* (2009).

Leachate Ca

Calcium concentration initially increased with biochar rate, but it dramatically dropped up to week 12 (*Figure 5b*). This result reflects the increasing amounts of Ca added into the soil column with higher rates of biochar application and demonstrates that some of the Ca in EFB-biochar is easily soluble and partly mobile (Lehmann *et al.* 2011). At week 72, Ca concentration in the leachates of the control treatment was higher compared to that of the biochar treatments, indicative of the high retention ability of the EFB-biochar for Ca. We hypothesized that the presence of EFB-biochar in the soil would slow down the eventual loss of Ca from the soil. This hypothesis is supported by the increasing availability of Ca in the treated topsoil.

Leachate Mg

Magnesium concentration in the leachates for all treatments showed a declining trend for the first 24 weeks of the experiment (*Figure 5c*). Thereafter, Mg concentration due to B5 treatment increased to the maximal level at week 48. This can be attributed to the mobilization of the exchangeable Mg that was accumulated in the spodic layer for the first 24 weeks. During this time, Mg present in the spodic layer could have been released due to proton exchange at the exchange sites, and as leaching continued, Mg became soluble and was leached out of the soil columns. Nutrients such as Ca and Mg are below the level required for healthy plant growth (Palhares *et al.* 2000).

Contribution of EFB-biochar to soil fertility

The topsoil of the current study contained high amounts of sand; consequently, its CEC was very low. Hence, the less strongly-held K present on the exchange sites of the topsoil treated with the EFB-biochar could have been easily leached out. The translocation of K through the soil column may be also be related to the dissolved C because the EFB-biochar contained organic ligands with affinity to form soluble complexes with minerals (McBride *et al.* 1997). Thus, the formation of organo-mineral complexes by organic ligands from EFB-biochar is an important mechanism to retain some nutrients in the topsoil.

EFB-biochar applied into the topsoil could have undergone degradation and ageing with the time. It is possible that microbial breakdown is one of the degradation mechanisms. It is also possible that part of the applied EFB-biochar was degraded due to long-term exposure to high soil temperature and a strong leaching environment. Be that as it may, we believe that degradation and ageing of biochar led to greater surface oxidation, resulting in a slight CEC increase, which enhanced cation retention in soil under treatment. It appears that the availability of K, Mg and Ca in the zone of EFB-biochar application (topsoil) was still low for crop requirement (Egiarte *et al.* 2006). This means that application of EFB-biochar alone is unable to sustain crop production on the nutrient-deficient Spodosols in Malaysia or even Southeast Asia.

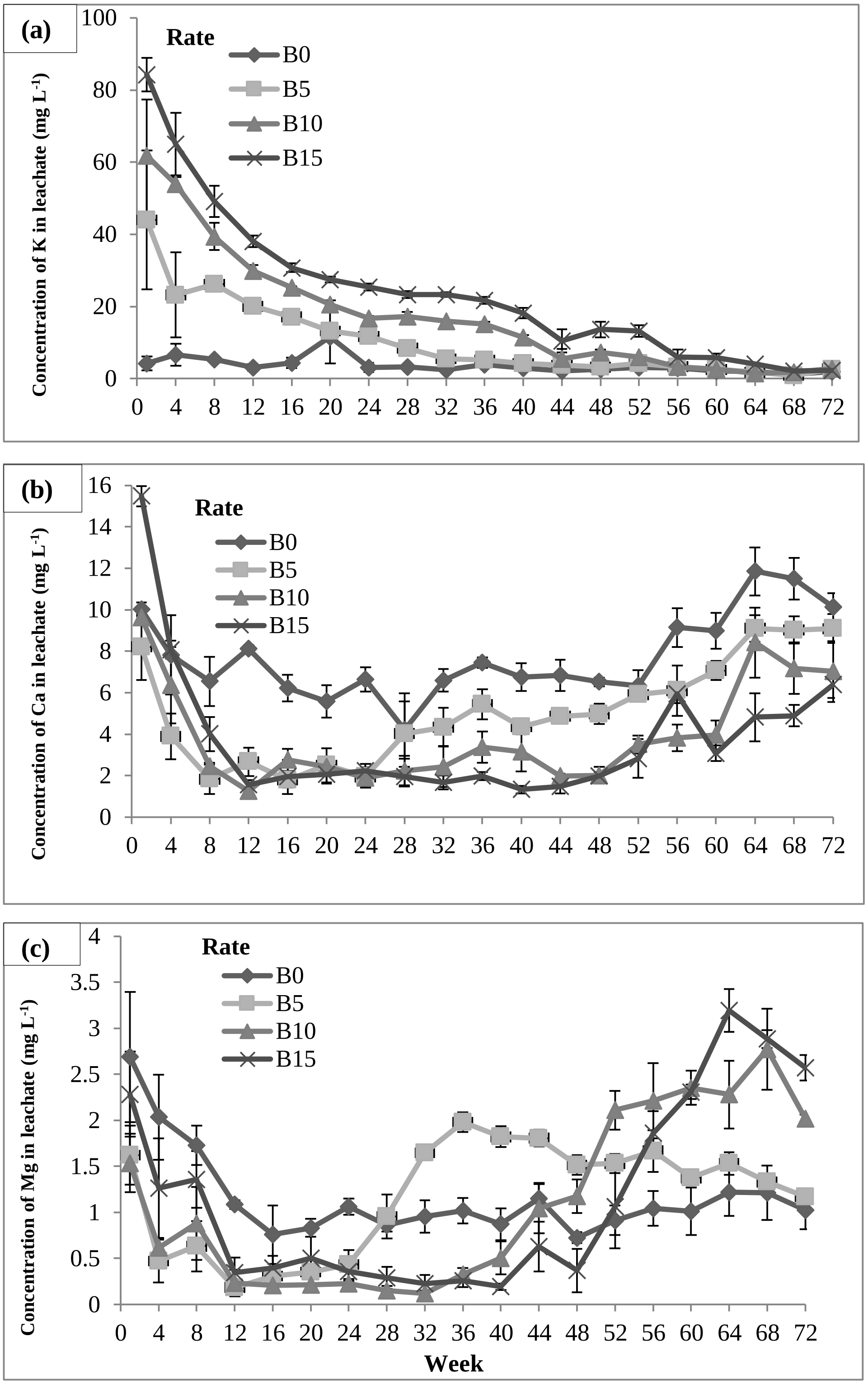


Figure 5. Effects of biochar application on the concentration of K in the leachates (a), K in the leachates (b), Ca in the leachates (c) Mg collected from soil columns during the 72 weeks of the study. The first point on the graph represents the concentration of Mg in the leachate collected at week 1 of the leaching event. Error bars represent ± standard error of the means (n = 3).

CONCLUSIONS

Treating a sandy Spodosol with EFB-biochar had a positive impact on soil chemical properties. Soils treated with the biochar had higher exchangeable K, Ca and Mg compared to those of the control treatment. The higher K, Ca and Mg concentration in the leachates collected from the biochar-treated soils compared to that of the control during the first week means that a significant portion of the nutrients initially present in the biochar was in soluble form, susceptible to leaching losses. To reduce leaching rates, the CEC of the soil needs to be significantly increased via biochar treatment. The C and CEC of the treated topsoil and those of the spodic layer were increased with treatment; the CEC was positively correlated with the soil C content. The ameliorative impact of EFB-biochar application failed to create a favorable condition for crop growth because it was only a short-term event. Application of high amounts of biochar is necessary to enhance soil fertility to sustain crop growth. At the rate applied during the experiment, the EFB-biochar was unable to provide sufficient nutrients for crop requirement to sustain it growth. Hence, its application at that rate is not a feasible agronomic practice without undergoing innovation in the method of application. Organic acids released by the EFB-biochar could have played a role in transporting the organo-metal-complexes down the soil columns via the process of podzolization. This suggests that some C present in the biochar could have been sequestered in the spodic layer of the biochar-treated Spodosol within the period of 72 weeks.

ACKNOWLEDGEMENTS

We wish to express our utmost appreciation to Universiti Putra Malaysia (UPM) for the financial and technical supports given during the conduct of the research. The study was financed by UPM under Research University Grant Scheme (RUGS), number 01-03-10-0983-RU (Vote: 91988).

REFERENCES

Abel, S., A. Peters, s. Trinks, H. Schonsky, M. Facklam and G. Wessolek. 2013. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. *Geoderma* 202: 183-191.

Atkinson, C.J., J.D. Fitzgerald and N.A. Hipps. 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil*. 337: 1-18.

Chan, K.Y., L.A. van Zwitten, I. Meszaros, A. Downie and S. Joseph. 2008. Using poultry litter biochars as soil amendments. *Aust. J. Soil Res*. 46: 437-444.

Cheng, C., J. Lehmann, J.E Thies, S.D. Burton and M.H. Engelhard. 2006. Oxidation of black carbon by biotic and abiotic processes. *Organic Geochem*. 37: 1477-1488.

Egiarte, G. M., A. Camps, E. Ruiz-Romera and M. Pinto. 2006. Study of the chemistry of an acid soil column and the corresponding leachates after addition of an anaerobic municipal sludge. *Chemosphere* 65: 2456-2467.

Hodson, M.E. and S.J. Langan. 1999, A long-term soil leaching column experiment investigating the effects of variable sulfate loads on soil solution and soil drainage chemistry. *Environ. Pollut.* 104: 11-19.

Joseph, S.D., M. Camps-Arbestain, Y. Lin, P. Munroe, C.H. Chia, J. Hook, L. Van Zwieten, S. Kimber, A. Cowie, B.P. Singh, J. Lehmann, N. Foidl, R.J. Smernik and J.E. Amonette. 2010. An investigation into the reactions of Biochar in Soil. *Aust. J. Soil Res.* 48: 501-515.

Kameyama, K., T. Miyamoto, T. Shiono and T. Shinogi. 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. *J. Environ. Qual.* 41: 1131-1137.

Laird, D.A., P. Fleming, B. Wang, R. Horton and D.L. Karlen. 2010. Biochar impact on nutrient leaching from Midwestern agricultural soil. *Geoderma* 158: 436-442.

Lehmann, J., M.C. Rilling, J. Thies, C.A, Masiello, W.C. Hockaday and D. Crowley. 2011, Biochar effects on soil biota: A review. *Soil Biol. Biochem.* 43(9): 1812-1839.

Lehmann, L. 2007. Bio-energy in the black. *Front. Ecol. Environ.* 5(7): 381-387.

Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, O.J. Skjemstad, J. Thie, F.J. Luizao, J. Peterson and E.G. Neves. 2006. Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Amer. J.* 70: 1719-1730.

Liu,P, C.J. Patacek, D.W. Blowes, W. R. Berti and R.C. Landis. 2015. Aqueous leaching of organic acids and dissolved organic carbon from various biochars at different temperatures. *J. Environ. Qual.* 44: 684-695.

Lundstrom, U.S., N. Van Breemen, D.C. Bain, P.A.W. Van Hees, R. Giesler, J.P. Gustafsson, H. Ilvesniemei, E. Karltun, P.A. Melkerud, M. Olsson, G. Riise, O. Wahlberg, A. Bergelin, K. Bishop, R. Finlay, A. GJongmas, T. Masnusson, H. Mannerkoski, A. Nordgren, L. Nyberg, M. Starr and L.Tau Strand. 2000. Advances in understanding the podzolozation process resulting from multidisciplinary study of three coniferous forest soils in the Nordic Countries. *Geoderma* 94: 335-353.

Major, J., M. Rondon, D. Molina, S.J. Riha and J. Lehmann. 2010. Maize yield and nutritioleyn during 4 years after biochar application to a Colombian Savanna Oxisol. *Plant Soil.* 333: 117-128.

Major, J., J. Lehmann, M. Rondon and C. Goodale. 2009. Fate of soil applied black carbon: Downward migration, leaching and respiration. *Glob. Change Biol.*16: 1366-137.

Manickam, T., G. Cornelissen, R.T. Bachmann, I.Z. Ibrahim, J. Mulder and S.E. Hale. 2015. Biochar application in Malaysian sandy and acid sulfate soils: Soil amelioration effects and improved crop production over two cropping seasons. *Sustainability* 7: 16756–16770.

McBride, M.B., B.K. Richards, T. Steenhuis, J.J. Russo and S. Sauve. 1997. Mobility and solubility of toxic metals and nutrients in soils fifteen years after sludge application. *Soil Sci.* 162(7): 487-500.

Milligan, E.E., A.A. Bomke and W.D. Temple. 2008. Compost layering effects on poultry litter leaching: A column study. *Compost Sci. Utilization.* 16(3): 171-182.

Nguyen, B.T., J. Lehmaan, C.W. Hockaday, S. Joseph and C.A. Masielllo. 2010. Temperature sensitivity of black carbon decomposition and oxidation. *Environ. Sci. Tech.* 44: 3324-3331.

Novak, J.M., W.J. Busscher, D.L. Laird, M. Ahmedna, D.W, Watts and M.A.S. Niandou. 2009. Impact of biochar amendment on soil fertility of a southeastern coastal plain soil. *Soil Sci.* 174: 105-112.

Palhares, M. 2000. Recommendation for fertilizer application for soils via qualitative reasoning. *J. Agric. Sys.* 67: 21-30.

Rabileh, M.A., J. Shamshuddin, Q.A. Panhwar, A.B. Rosenani and R.A. Anuar. 2015. Effects of addition of biochar and/ or dolomitic limestone application on the properties of Ultisols cropped to maize under glasshouse conditions. *Can. J. Soil Sci.* 95: 37- 47.

Roslan, I., J. Shamshuddin, C.I. Fauziah and A.R Anuar. 2011. Fertility and suitability of the Spodosols formed on sandy beach ridges interspersed with swales in the Kelantan-Terengganu Plains of Malaysia for kenaf production. *Malays. J. Soil Sci.* 15: 1-24.

Roslan, I., J. Shamshuddin, C.I. Fauziah and A.R. Anuar. 2010. Occurrence and properties of soils on sandy beach ridges in the Kelantan-Terengganu Plains, Peninsular Malaysia. *Catena* 83(1): 55-63.

Schmidt, M.W.I. and A.G. Noack. 2000. Black carbon in soils and sediments: Analysis, distribution, implications and current challenges. *Glob. Biogeochem.Cyc.*14: 777-794.

Soil Survey Staff. 2014. *Keys to Soil Taxonomy* (12th Edn). Washington DC, USA: USDA and NRCS.

Schollenberger, C.J. and R.H. Simon, 1945. Determination of exchange capacity and exchangeable bases in soil: ammonium acetate method. *Soil Sci*. 5: 13-24.

Steiner, C., W.G. Teixeira, J. Lehmann, T. Nehls, J. L.W. de Macedo, W.E.H. Blum and W. Zech. 2007. Long-term effects of manure, charcoal and mineral fertilization on crop production and fertility of a highly weathered Central Amazonian upland soil. *Plant Soil.* 291: 275-290.

Syuhada, A.B., J. Shamshuddin, C.I. Fauziah, A.B. Rosenani and A. Arifin. 2016. Biochar as a soil amendment: Impact on chemical properties and corn nutrient uptake in a Podzol. *Can. J. Soil Sci.* 96: 400-412.

Van Schöll, L., T.W. Kuyper, M.M Smits, R. Landeweert, E. Hoffland and N. van Breemen. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil* 303: 35-47.

Zainuri, M. 1981. Study of selected coastal sandy soils from Peninsular Malaysia. MSc. Thesis, Ghent University, Ghent, Belgium.