

## **POTASSIUM AND NITRATE RETENTION IN THREE DIFFERENT SOIL AMENDED WITH OIL PALM EMPTY FRUIT BUNCH BIOCHAR**

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### **ABSTRACT**

The application of biochar produced from oil palm empty fruit bunch (EFB) as soil amendment to retain soil nutrients has the potential to improve agriculture production in tropical regions. A laboratory leaching study was conducted to determine the effects of different rates (0 t/ha, 10 t/ha, 20 t/ha, and 30 t/ha) of EFB biochar on potassium and nitrate retention in three different type of soil texture: clay, sandy clay loam, and sand. The sorption study showed that EFB biochar was able to sorp both potassium and nitrate ( $Q_{max}$  0.53 mg g<sup>-1</sup> and 0.23 mg g<sup>-1</sup>, respectively). However, the leaching study indicated that soil texture played a larger role in potassium and nitrate retention than biochar in condition with high soil water potential. The application of EFB biochar did not significantly affect the retention of potassium and nitrate for all three types of soil texture. The order of retention for potassium was sandy clay loam > sand > clay and clay > sandy clay loam ≥ sand for nitrate. The results suggested that high soil water potential condition, interpores between soil-biochar particles played a larger role (and therefore nutrient retention) than biochar intrapores in water retention.

**Keywords:** Biochar, soil amendment, oil palm empty fruit bunch, nutrient retention

### **INTRODUCTION**

Biochar (biological charcoal) is a carbon rich solid product, produced from the thermochemical conversion of biomass in oxygen-limited environment. Although the application of biochar alone does not provide sufficient nutrient for crop production, it work indirectly by improving soil properties [1, 2], nutrient availability [3], fertilizer use efficiency [4, 5], and reducing soil toxicity [6, 7]. The ability of biochar to retain nutrient is vital, especially for agriculture

production in tropical regions [8]. Tropical soils are highly weathered soils with poor nutrient retention capability. Nutrient loss not only reduces the efficiency of fertilizer application and affect crop production but also poses problems to the environment. This is further aggravated by mismanagement which often leads to rapid soil degradation and environmental pollution due to excessive fertilizer [9] and pesticide [10] application. Recent researches showed biochar have the capability to retain soil nutrients with varying results [11, 12, 13, 14, 15].

In Malaysia, oil palm empty fruit bunch is a potential feedstock for biochar production due to its tremendous volume and continuous availability in Malaysia. Conventionally, it is recycled as fibre fuel for energy generation in the oil extraction mills or returned to the field as mulch or compost [16, 17, 18, 19]. The conversion of EFB into biochar presents a viable option for sustainable agriculture waste management and carbon credit in the oil palm industry. EFB biochar have been produced on a pilot scale in 2009 with the development of a pilot carbonator (Universiti Putra Malaysia - Nasmeh Technologies Sdn. Bhd.). Since then, EFB biochar have been produced and studied in smaller laboratory scale with different methods and procedures [20, 21, 22]. Several glasshouse and field studies have been carried out with, focusing on different aspects such as liming potential [23], soil hydraulic conductivity [24], carbon mineralization [25], and soil amendment in SRI rice cultivation [26].

As biochar gain acceptance as a soil amendment, there has been concern raised about the testing and labelling of biochar products. Biochar may exhibit variations in characteristics when applied to the soil, depending on the feedstock used and production procedure [27, 28]. Therefore, each biochar produced need to be tested before it can be commercially available for application. To date, there are no studies that look into the nutrient retention properties of EFB biochar, especially for plant essential nutrients. Therefore, this study was carried out with the following objectives to (i) analyse selected physical and chemical properties of EFB biochar and (ii) assess the ability of EFB biochar to retain nutrient in the form of a cation ( $K^+$ ) and an anion ( $NO_3^-$ ).

## **MATERIALS AND METHODS**

### *Collection and Characterization of EFB Biochar*

The biochar used in this study was produced from oil palm empty fruit bunch through slow pyrolysis (300 – 350°C) with a rotary drum system carbonator, set up in Seri Ulu Langat Oil Palm Mill in Dengkil, Selangor. The biochar was collected, sieved with 2 mm laboratory sieve, and oven-dried before chemical analysis was carried out. The chemical characteristics of EFB biochar measured were pH ( $H_2O$  1:10 w/v), total carbon content (Model: LECO-CR-412 Carbon Analyzer), total N [29], total elemental content extracted using dry ashing method [30], and cation exchange capacity (CEC) (ammonium acetate, pH 7 method). The concentration of N, P

and CEC were determined with an auto analyser (Model: LACHAT Instrument, QuikChem FIA+ 8000 series) while the exchangeable K, Ca, and Mg content were determined using the atomic absorption spectrophotometer (Model: Perkin Elmer MDL5100). The EFB biochar surface morphology was determined using a scanning electron microscopy attached with energy dispersive X-ray spectroscopy (SEM-EDX) (Model: JSM-6400) at the Microscopy Unit, Institute of Bioscience, Universiti Putra Malaysia. The BET surface area analysis was determined on the basis of nitrogen gas sorption of carbon black (ASTM-D6556-10) using a surface area analyser (Model: BELSorp 763 Mini II) at the Institute of Advance Technology (ITMA), Universiti Putra Malaysia.

#### *Potassium ( $K^+$ ) and Nitrate ( $NO_3^-$ ) Sorption by EFB Biochar*

The sorption properties of EFB biochar of  $K^+$  and  $NO_3^-$  were determined through the batch equilibrium method. Biochar samples was pre-washed using 0.5 M hydrochloric acid and subsequently with distilled water until the solution extract showed electrical conductivity reading of below  $30 \mu S cm^{-1}$ . The washed biochar was then filtered, oven-dried, and stored in air-tight vials. An amount of 0.2 g of EFB biochar was added into centrifuge tubes and equilibrated with a series of  $K^+$  solution (KCl) containing 0, 5,10,15, 20, 25 mg/L  $K^+$  concentration. A similar set of study was carried out for  $NO_3^-$ , using  $NO_3^-$  solutions ( $KNO_3$ ) with 0, 4, 8, 12, 16, and 20 mg/L  $NO_3^-$  concentration. The mixture was equilibrated overnight at room temperature with rotary shaker at 60 rpm. After taken out from the rotary shaker, it is left to settle for 30 minutes before the solution was filtered with a syringe filter. The concentration of  $K^+$  and  $NO_3^-$  in the solution was determined using an auto-analyser (Model: LACHAT Instrument, QuikChem FIA+ 8000 series). The biochar nutrient sorption was calculated based on the difference between the initial and final concentration in the equilibrium solution. The data was then fitted into Langmuir and Freundlich adsorption isotherm equation to find the model that best fit both nutrients.

#### *Potassium and Nitrate Retention in Three Different Types of Soil Texture Amended with EFB Biochar*

A laboratory leaching study was set up to investigate the effects of EFB biochar on nutrient retention  $K^+$  and  $NO_3^-$  in three soils of different texture. The treatments are the combination of four EFB biochar application rates (0 t/ha, 10 t/ha, 20 t/ha, and 30 t/ha EFB biochar) and three different type of soil texture (clay, sandy clay loam, and sand). The study was carried out separately for both  $K^+$  and  $NO_3^-$  retention, with potassium chloride (KCl) and ammonium nitrate ( $NH_4NO_3$ ) used as  $K^+$  and  $NO_3^-$  ions source, respectively.

The soil mixture was prepared using one kilogram of each soil, thoroughly mixed with the corresponding biochar application rate (w/w). Triplicates of 100 g mixed soils for each treatment

were packed into leaching tube and flushed with distilled water several times to remove available nutrients from the soil mixture. After flushing, 100 mL of 1000 ppm concentration nutrient solution was added and left overnight to equilibrate. The leachate was collected, measured, and analysed as amount leached after nutrient solution addition (assigned as Event 1). The leaching tubes were subsequently flushed again with 100 mL distilled water for 3 subsequent events and the leachates were collected and analysed (Event 2, 3, and 4). The concentration of  $K^+$  and  $NO_3^-$  was analysed with an auto analyser (Model: LACHAT Instrument, QuikChem FIA+ 8000 series).

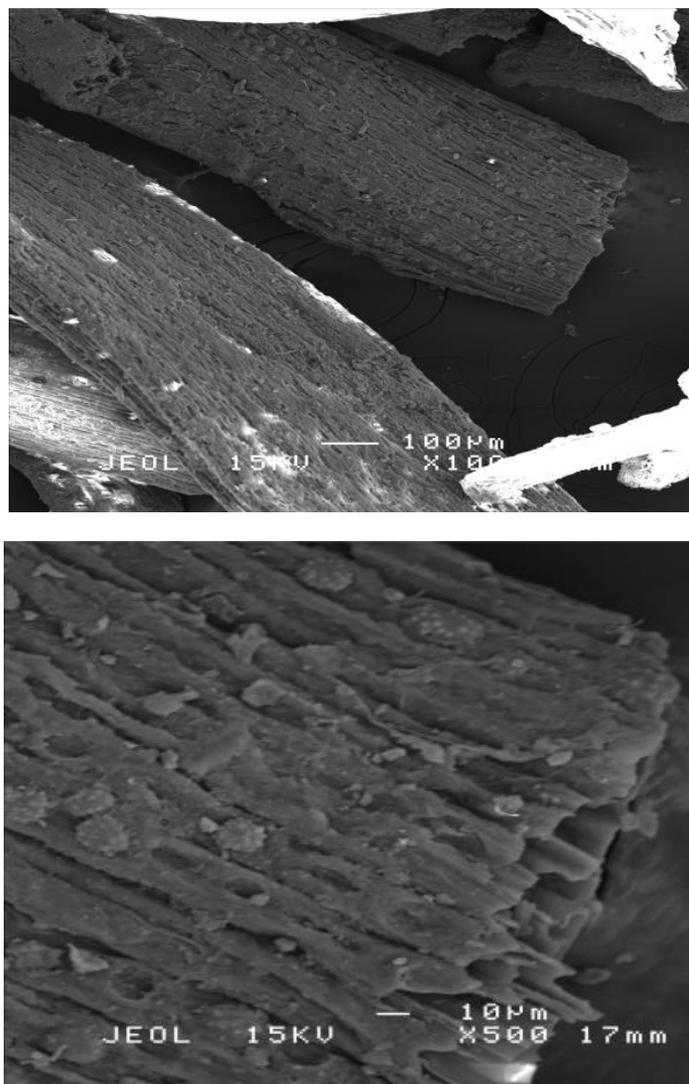
#### *Experimental design and Statistical Analysis*

The laboratory leaching study was carried out in a completely randomized design (CRD) with four different EFB biochar application rates and three different soil textures in triplicates (4 rates x 3 soils x 3 reps). The data was analysed using analysis of variance (ANOVA) and significant treatment means were separated by Duncan multiple range test (DMRT) at 95% confidence level (SAS Ver. 9.3).

## **RESULTS**

#### *Physical and Chemical Characteristics of EFB biochar*

The EFB biochar have the pH of 8.6, CEC value of 59.9  $cmol_{(+)}/kg$ , and elemental composition of 43.7% C, 1.1% N, 0.2% P, 2.5% K, 0.3% Mg, and 0.4% Cu. The SEM images of EFB biochar strand showed rough surfaces with the parallel running fibrils exposed at its end (Figure 1). The structure of the EFB fibre strand remained mostly intact. Similar findings was reported by [22] with EFB biochar produced at 350°C that was filled with under-developed pores due to the lack of tissue devolatilization which happened at higher temperature (500°C). Along the fibrils are circular craters with silica spheres attached to it. The presence of the silica bodies in oil palm EFB were also reported by [31], which suggested its formation from silica deposited through the network of siliceous pathways found within the fibrous strand matrix during growth. The BET surface area of EFB biochar was determined to be 17.07  $m^2/g$ , with pore volume of 0.18  $cm^3/g$  (less than 0.0842  $\mu m$  radius) and 0.20  $cm^3/g$  (less than 0.0914  $\mu m$  radius). The pore size was 0.0419  $\mu m$  (adsorption average pore diameter) and 0.0459  $\mu m$  (desorption average pore diameter).



**Figure 1: SEM image of EFB biochar at 100x (left) and 500x magnification (right).**

*Potassium and Nitrate Sorption Properties of EFB Biochar*

The  $K^+$  sorption data was best fitted to the Langmuir adsorption model, with the  $R^2$  of 0.97 (Table 1). The maximum adsorption capacity ( $Q_{max}$ ) of EFB biochar for  $K^+$  was  $0.53 \text{ mg g}^{-1}$  with K value of  $0.02 \text{ L mg}^{-1}$ . The  $NO_3^-$  sorption data was best fitted to the Freundlich model, with  $R^2$  value of 0.93 (Table 1). The maximum adsorption capacity of EFB biochar for  $NO_3^-$  was  $0.23 \text{ mg g}^{-1}$  with K value of  $0.34 \text{ L mg}^{-1}$ .

**Table 1: Sorption isotherm obtained by fitting the data with the Langmuir and Freundlich isotherms for EFB biochar.**

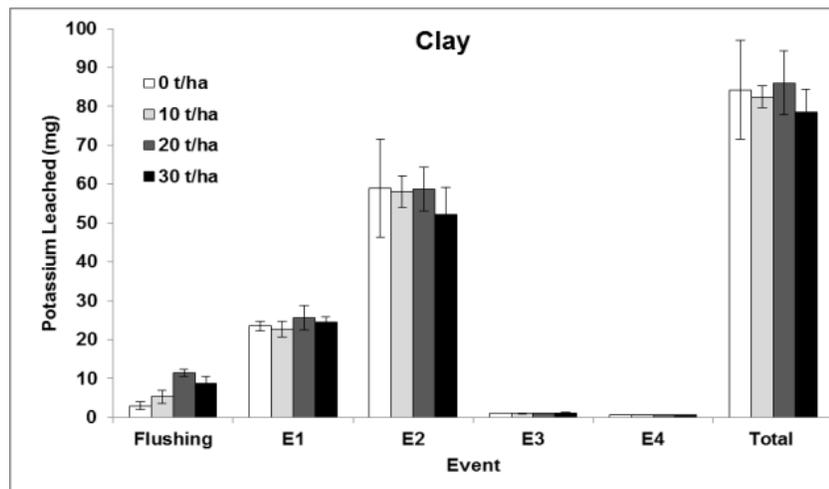
Nutrient	Langmuir model		
	$Q_{max}$ ( $mg\ g^{-1}$ )	K ( $L\ mg^{-1}$ )	$R^2$
K	0.53	0.02	0.97
$NO_3^-$	0.58	0.58	0.82
Nutrient	Freudlich model		
	n	K	$R^2$
K	1.10	0.02	0.88
$NO_3^-$	0.23	0.34	0.93

*Effects of EFB Biochar on Potassium Retention in Soils of Different Texture*

Significant amount of  $K^+$  was flushed from treatments with EFB biochar application (5.3 - 11.5 mg in clay soil, 2.9 - 3.4 mg in sandy clay loam soil, and 9.5 – 44.0 mg in sand soil when compared to the control treatment (1.3 – 3.0 mg), indicating EFB biochar itself was a source of  $K^+$  (Figure 2). Soil texture rather than the EFB biochar application rate affects the  $K^+$  retention after the nutrient solution was added (Event 1); sand showed the highest amount of  $K^+$  leached (42.2 – 43.0 mg), followed by sandy clay loam (26.2 – 28.0 mg) and clay (22.7 – 25.6 mg). Inversely, this meant that clay and sandy clay loam soils retained more  $K^+$  compared with sand. There was no significant difference between the EFB biochar treatment and the control treatment for all soil texture. In the subsequent leaching event (Event 2), clay soil showed higher amount of  $K^+$  leached compared with the other two soils. The  $K^+$  amount leached from Event 2 in clay soil more than doubled to 52.2 – 59.0 mg (113 – 155%) when compared with Event 1. In sandy clay loam treatments, the amount of  $K^+$  leached was 41 – 55% lower (11.8 -15.5 mg) compared with Event 1 while in sand treatments, the reduction was between 76 – 79% (9.0 – 10.2 mg). Traces amount of  $K^+$  was detected in the leachate in the next two subsequent events (Event 3 and ); 0.6 to 1.1 mg in clay soil, 0.2 to 0.4 mg in sandy clay loam soil, and 0.1 – 0.2 mg in sand. In total, clay soil showed the highest amount of  $K^+$  leached (78.5 – 86.1 mg), followed by sand (51.8 – 53.0 mg), and sandy clay loam (38.2 – 44.0 mg). This inversely meant that the order of  $K^+$  retention is as follow: sandy clay loam > sand > clay.

*Effects of EFB Biochar on Nitrate Retention in Soils of Different Texture*

The amount of NO<sub>3</sub><sup>-</sup> leached during column flushing was between 0.01 to 0.02 mg in clay soil, 0.16 to 0.19 mg in sandy clay loam, and 0.00 to 0.01 in sand (Figure 3). In Event 1, the amount of NO<sub>3</sub><sup>-</sup> leached was 15.0 - 16.0 mg in clay, 18.6 – 20.3 mg in sandy clay loam and 18.3 - 18.6 mg in sand, indicating that clay soil showed higher NO<sub>3</sub><sup>-</sup> retention, followed by sand and sandy clay loam soil. In Event 2, amount of NO<sub>3</sub><sup>-</sup> leached reduced for all treatments with sand showing the highest amount of NO<sub>3</sub><sup>-</sup> leached; 0.0 - 0.1 mg in clay, 0.0 - 0.3 mg in sandy clay loam, and 2.9 - 3.6 mg in sand. The amount of NO<sub>3</sub><sup>-</sup> leached increased in Event 3 for clay and sandy clay loam (0.2 - 1.3 mg and 0.4 - 0.8 mg, respectively) but reduced for sand (to range of 2.0 mg). In the final leaching event (Event 4), sandy clay loam showed higher amount of NO<sub>3</sub><sup>-</sup> leaching (between 0.2 - 0.8 mg) while the amount for clay and sand fall below 0.1 mg. In total, the amounts of NO<sub>3</sub><sup>-</sup> leached are 16.1 – 17.1 mg in clay, 20.3 -22.0 mg in sandy clay loam and 21.9 - 22.2 mg in sand. In term of total NO<sub>3</sub><sup>-</sup> retained, the soil with highest to lowest NO<sub>3</sub><sup>-</sup> retained are in the following order: clay > sandy clay loam ≥ sand.



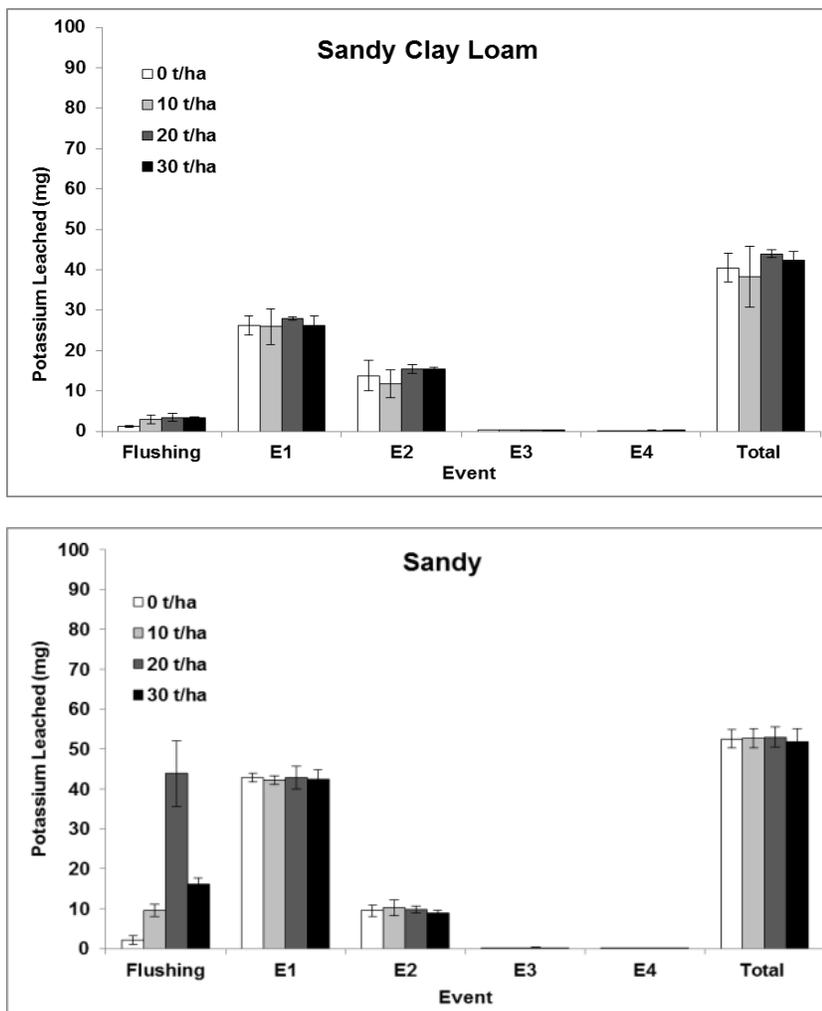
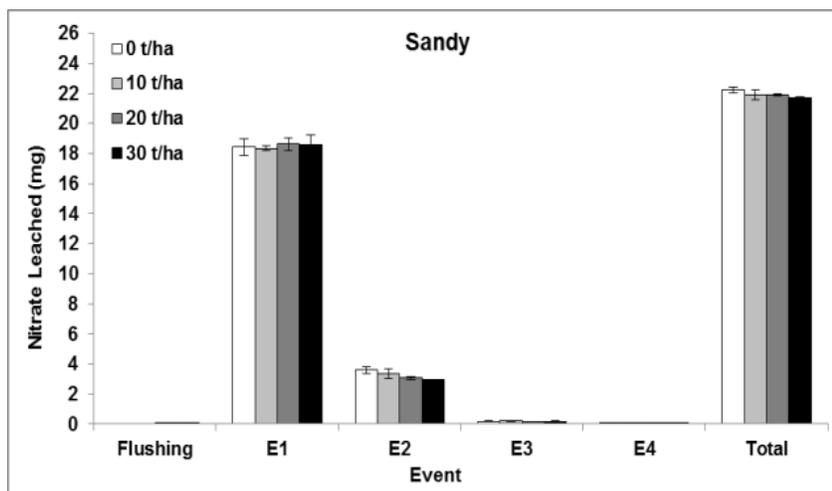
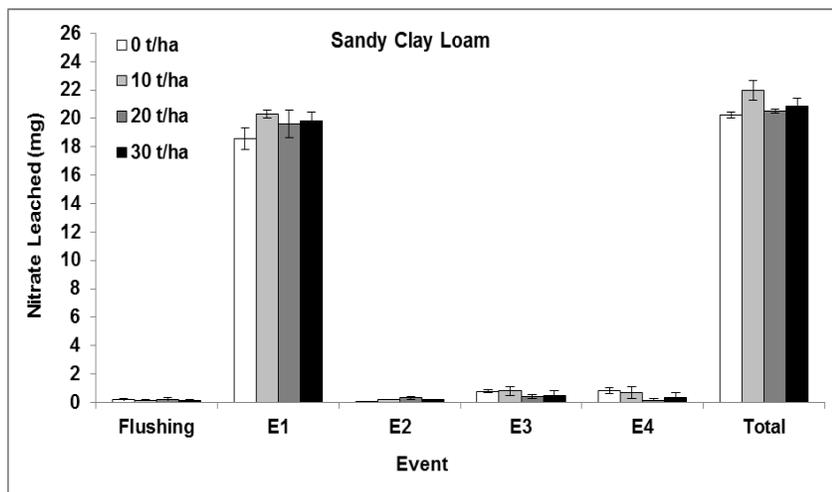
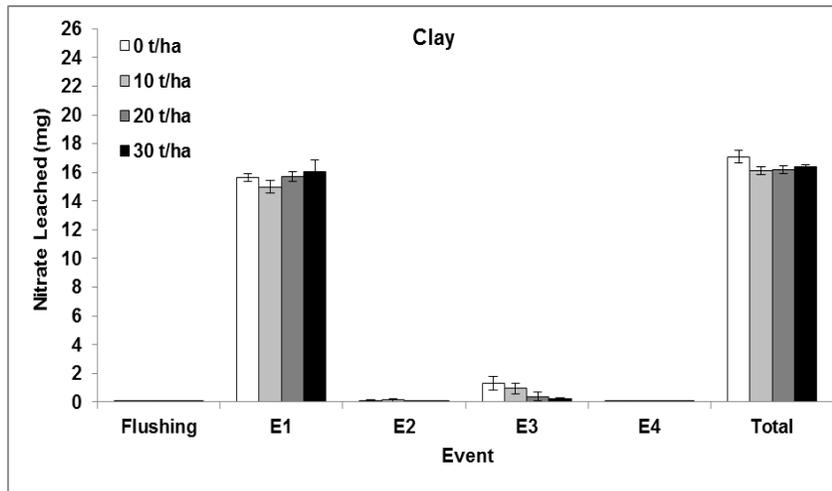


Figure 2 : Effect of EFB biochar on potassium retention by leaching event in three types of soil with different texture. The treatments were: 0 t/ha EFB biochar (□), 10 t/ha EFB biochar (◻), 20 t/ha EFB biochar (◼), and 30 t/ha EFB biochar (■). Vertical bar represents the standard deviation.



**Figure 3 : Effect of EFB biochar on nitrate (right) retention by leaching event in three types of soil with different texture. The treatments were: 0 t/ha EFB biochar (□), 10 t/ha EFB biochar (▤), 20 t/ha EFB biochar (▥), and 30 t/ha EFB biochar (■). Vertical bar represents the standard deviation.**

## DISCUSSION

The EFB biochar showed chemical and physical characteristics of a potential soil amendment. The alkaline pH of biochar (pH 8.6) may act as a liming agent when applied to the soil. Biochar have been reported to increase soil pH and exchangeable bases, when either applied individually or with other liming materials [32, 33]. Biochar improve soil pH through its physiochemical properties (carbonaceous components, base cations and organic anions, large surface area and enhancement of soil CEC) and the inhibition of soil nitrification [34]. The EFB biochar have a moderate carbon content of 43.7%, which is expected for biochar produced through slow pyrolysis, similar to those reported by [22]. The EFB biochar contained essential nutrients for crops (N, K, Ca, and Mg), which is likely derived from the biochar ash content. The SEM image and BET analysis showed that EFB biochar contained surface area and many pores, important site for soil processes to occur.

The results from the sorption isotherm showed that EFB biochar was able to sorp both cation  $K^+$  and anion  $NO_3^-$ , although biochar was not expected to actively retain much  $NO_3^-$  due to the negative charges on its surface. Biochar oxidation decrease anion sorption capability, reducing surface positive charge until it eventually disappeared totally [35]. The nutrients could be indirectly retained by the porous space within the fibre structure of the EFB biochar (which existence was shown in the SEM and BET analysis). There are some studies that showed biochar being able to retain  $NO_3^-$  albeit mostly through indirect methods. [36] gave several possible mechanisms on how biochar maybe able to influence soil  $NO_3^-$  retention: (i) microbial immobilization of  $NO_3^-$ , (ii) improvement in soil water retention from soil physical properties alteration (micropores and mesopores), (iii) reduction of  $NO_3^-$  to ammonium ( $NH_4^+$ ) by soil microorganisms, and (iv) direct absorbance of  $NO_3^-$  though anion exchange reaction of fresh biochar surface. [37, 38] reported organic coating of the biochar was able to capture and slow release nitrate, although the mechanism of nitrate uptake by biochar was not fully understood. The washing of biochar prior to the sorption study may have also encouraged the sorption of  $NO_3^-$ . The washing of biochar with acid and deionized water removed ash from biochar surface, creating additional sorption sites that facilitate the sorption of  $NO_3^-$  [39]. The ability of the biochar to retain nutrient make it a potential soil amendment for agriculture production to improve soil fertility and retention of applied chemical fertilizers for plant uptake.

However, the leaching study showed that soil texture played a large role in nutrient retention when compared with biochar application, which could be attributed to the mechanism of water retention in a soil-biochar matrix. [40] posit that biochar intrapores (pores inside particles) affect water retention in low soil water potential while the biochar-soil interpore (pores between particles) dominates water retention in higher soil water potential. The leaching study was carried out in a high soil water potential condition (at 100% water holding capacity), suggesting that inter pores between soil-biochar particles played a larger role in water retention (and therefore nutrient retention) than biochar intrapores. The treatment with sand showed better  $K^+$  retention when compared to the finer clay soil due to the effect of biochar application on soil porosity. Soil with high porosity encouraged leaching through vertical movement of water that remove nutrients out of the rooting zone. Soil pores structure can affects soil water movement. Micropores ( $< 30 \mu\text{m}$ ) are able to retain water from flowing downwards while mesopores ( $30 - 80 \mu\text{m}$ ) permit water movement via soil matric potential differences from wetter to drier region. Macropores ( $> 80 \mu\text{m}$ ) allows leaching events through rapid gravitational water flow through soil. Biochar application in the larger particle sands created smaller pores where water and nutrient could be retained. The effect was reversed in finer particle clay soil as biochar application increase pore size, allowing more downward movement of water and nutrient. Biochar affects soil particle arrangement and aggregates formation, which influences soil properties such as micropore surface area, and moisture retention; with the magnitude of changes depending on the soil texture [41]. [42] reported that wood biochar was able to improve water infiltration rates better in coarse-textured soil than finer-textured soils.

The ability of biochar to retain nutrients may vary with factors such as soil type, biochar feedstock and production process, and the nutrient type. [43] and [44] showed nitrogen leaching reduction in column experiments conducted with wood char and bamboo biochar, respectively. [12] found different types of biochars (sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo) exhibit differing adsorption properties for different nutrients (nitrate, ammonium and phosphate). [45] reported biochar was irrelevant in soil-water retention in a sandy loam soil without vegetation cover; no possible reason for the findings was given. [46] reported insignificant effect of biochar (produced from herbaceous plant cuttings) application (at rates of up to 50 t/ha) on the soil water retention and hydraulic conductivity in a sand, which was attributed to the biochar's strong hydrophobic behaviour. [47] reported that pyrolysis temperature affect the nutrient status of a sewage sludge biochar, which enhanced nutrient leaching in a Typic Plinthudult soil.

## CONCLUSION

The study demonstrated that EFB biochar has suitable chemical properties (alkaline pH 8.6, 43.7% C, 59.9 cmol<sub>(+)</sub>/kg CEC), and physical properties (17.07 m<sup>2</sup>/g surface area and pore volume of 0.20 cm<sup>3</sup>/g) to be applied as a soil amendment for crop production. The EFB biochar was capable of adsorbing K<sup>+</sup> and to a certain extent sorbs NO<sub>3</sub><sup>-</sup>, likely due to sorption into the pores of the biochar structure rather than adsorption to the biochar surface itself. However, the leaching study showed that K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> were affected by the soil texture rather than biochar application rate. The retention of K<sup>+</sup> in the soil followed the order: sandy clay loam > sand > clay while NO<sub>3</sub><sup>-</sup> retention in soil followed the order: clay > sandy clay loam > sand. This study was limited to the effect of EFB biochar nutrient retention in high soil water potential; more detailed studies are needed to study the mechanism of nutrient retention by soil and biochar.

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