

Determining the characteristics and potential of plant-based biochars to reduce copper uptake in maize

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ABSTRACT: Metal contamination problems have become common everywhere with several known cases of metal toxicity in the agriculture sector. Metals including copper (Cu) are important to plant metabolism in trace amounts; however, excessive amounts can cause toxicity to the plants. The biochars have potential to absorb these trace elements in soil. A study was conducted to determine the characteristics and potential of different plant-based biochars to control Cu uptake and influence on the growth of maize (*Zea mays* L.). Five biochars from different agricultural waste materials, such as rice husk (RH1 and RH2), empty fruit bunches (EFB1 and EFB2) and oil palm kernel (OPK), were selected in the study. Each biochar was applied at 20 t·ha⁻¹ on Cu contaminated soil, and maize was grown for 56 days in pots with 10 kg of acidic soil. The rice husk biochar (RH1) with a substantial number of heterogenic functional groups (alcohols and phenols, carboxylic acids and derivatives, amines, saline, alkynes) on its surface and more porous structure was able to retain more nutrients. It also give the best results in terms of reducing the Cu concentrations (1.61 mg·kg⁻¹) in plants and plant uptake (10.15 µg·pot⁻¹). Other than that, the highest plant growth parameters were also perceived in rice husk biochar applications. Hence, RH1 biochar had the most promising results in terms of controlling the plants Cu uptake and improved maize plant growth.

Key words: agricultural waste, adsorption, bioaccumulation, biochar, concentration, metal toxicity.

INTRODUCTION

Zea mays, more commonly referred to as maize, is a member of the grass family Poaceae, or true grasses. Maize is thought to have been originated 55–70 million years ago in what is now Central or South America and has since diversified into nearly 10 000 nondomestic relatives. It has the greatest global production of any crop species, around 800 million tons was produced worldwide in 2013, accounting for 32% of the total cereal production (Scott and Emery 2016). *Zea mays* ssp. are one of the world's most important crop plants, as boosting a multibillion-dollars annual revenue. In addition to its agronomic importance, maize has been a keystone model organism for basic research for nearly a century. Within the cereals, which include other plant model species such as rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), wheat (*Triticum* spp.) and barley (*Hordeum vulgare*), maize is the most thoroughly researched genetic system. Several attributes of the maize plant, including a vast collection of mutant stocks, large heterochromatic chromosomes, extensive nucleotide diversity and genic collinearity within related grasses, have positioned this species as a centerpiece for genetic, cytogenetic and genomic research (Strable and Scanlon 2009).

Globally, 14 billion metric tons of biomass are generated every year from the agricultural sector and most of them are either discarded or burnt (UNEP 2009; Asim et al. 2015). These biomass wastes include corn stalks, rice husks, straw, coconut shells, bagasse, nutshells and livestock manure. Even forestry residues, such as wood chips, bark, sawdust, timber slash



and mill scrap, can be considered as biomass waste. Instead of burning these wastes, which causes widespread ecological problems including greenhouse gasses, it is vital to find a sustainable method to manage them. In Malaysia, the bulk of agriculture biomass waste comes from the cultivation of tropical fruits, palm oil and paddy (Ghani et al. 2010). For oil palm production, 1 ton of oil palm fruit bunch process produces 0.07 ton of kernel shell, 0.146 ton of fiber and 0.2 ton of empty fruit bunch (EFB), whereas the cultivation of rice produces two types of residues: rice husk and rice straw. The husk accounts for 22% of paddy weight; however, the rice accounts for 78% (Umamaheswaran and Batra 2008).

Biomass waste generated from oil palm and rice cultivation can be used for biomass-based power generation. Alternatively, the recycling of these wastes into biochars is another way to manage them. Biochar is produced by the thermal decomposition of biomass under oxygen-limited conditions (pyrolysis), and it has been utilized in soil remediation over the recent years. It is a renewable, microporous and carbon (C) rich product that also contains nitrogen (N), hydrogen (H), oxygen (O) and ash (Lehmann et al. 2003).

The most important aspect of biochar is that it acts as a soil amendment and it increases the soil physicochemical properties. The characteristics of biochars depend on the original waste product and the condition of pyrolysis (Novak et al. 2009 b). Depending on these factors, it can have different surface areas, pore sizes, distribution of pores, pH, carbon structures, nutrient content and functional groups (Lehmann et al. 2003). Besides large amounts of biomass waste being produced in the agricultural sector, another major issue that befalls this sector is heavy metal contaminated soils. Although some heavy metals, such as copper (Cu) and zinc (Zn), are required by plants, they can become toxic in higher concentrations. Whereas heavy metals, such as arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg), can be toxic even in minimum concentrations. These heavy metals increase over time in agriculture soils due to continuous applications of fertilizers and pesticides (Neilson and Rajakaruna 2015). This is because some fertilizers are derived from waste materials that contain heavy metals, such as sewage sludge, fly ash and biosolids (Mench et al. 2010). Whereas, pesticides and herbicides contain heavy metals, like As, to kill off pests and weeds, and these heavy metals accumulate in the soil over time (Neilson and Rajakaruna 2015).

As mentioned previously, Cu is a micronutrient that is required by plants. It supports in seed production, disease resistance and regulation of water uptake. Despite being essential, it remains a highly reactive, major toxic metal (Sharma et al. 2007). High doses of Cu can cause a gradual accumulation of Cu in the soil and thereby increase Cu toxicity towards crops. This has become a prevalent issue in some plantations (Neilson and Rajakaruna 2015; Sharma et al. 2007). Recently, high concentrations of heavy metal in soils or groundwater have been reported in some countries, again proving it as a global issue (Sharma et al. 2007). Biochar may be a solution for the problem. It provides a sustainable approach to manage agriculture biomass waste, while having the potential to remediate contaminated soils (Paz-Ferreiro et al. 2014). Besides, it can also reduce dependency on inorganic fertilizers, while providing a cheap, organic soil amendment.

However, the efficiency and characteristics of biochar and its effects on plant growth performance and soil chemical properties remain a subject that requires further research. Based on previous study, biochar had the strongest sorbent compared with other organic materials, largely due to its characteristics of having high affinity and capacity for absorbing organic compounds (Yang and Sheng 2003). Another positive trait of biochar is that its absorption is comparatively less flexible than other organic materials (Sander and Pignatello 2007). Thus, some heavy metal mobility and bioavailability may be controlled by the presence of biochar (Namgay et al. 2010). Hence, this study was conducted to determine various characteristics and effectiveness of different biochars to control Cu uptake and influence on the growth of maize (*Zea mays* L.).

MATERIAL AND METHODS

Location and experimental details

The efficacy of different biochars was determined by growing maize crop on acidic soils, a common prevalence in Malaysia. The experiment was led at a glasshouse located in Rimba Ilmu, University of Malaya. The pH of experimental

soil was 5.65, total N 0.06%, available P 92.28 mg·kg⁻¹, organic C 0.51%, exchangeable K, Ca and Mg of 0.21, 0.85 and 0.18 cmolc·kg⁻¹, respectively. The soil texture was sandy loam. Five various types of biochars, including rice husk (RH1 and RH2), empty fruit bunches (EFB1 and EFB2) and oil palm kernel (OPK), were used at a rate of 20 t·ha⁻¹ with four replicates. Each treatment was planted on its own individual pot, containing 10 kg of soil. Prior to the biochar mixing, the treatment was contaminated with 60 ppm of Cu, using 5% copper sulphate (CuSO₄·5H₂O) of 60 mg·L⁻¹ Cu, and NPK fertilizer mixed in all the relevant treatments at the recommended rates. After contaminating the treatments with Cu for two weeks, biochars were mixed into the soil for two weeks before sowing the maize (three seeds·pot⁻¹). The water was given as required and treatments were harvested after 55 days. The plant height, number of leaves, plant uptake of Cu, and soil pH, cation exchange capacity (CEC), electrical conductivity (EC) and organic carbon (OC) were determined. The experiment was conducted in a complete randomized design (CRD).

Physical analysis

The surface structure of biochar was determined using the field emission scanning electron microscopy (FESEM) Hitachi-SU8220 model, Japan. Four samples of each type of biochar were magnified at different magnifications to obtain clear and detailed results. The Brunauer–Emmett and Teller (BET) surface area of biochar were calculated by measuring N₂ gas adsorption at –196 °C using a Micrometrics ASAP 2020, TRISTAR II 3020 Kr, USA, according to the single point method. Samples were degassed at 100 °C under continuous N₂ flow for 24 h prior to analysis.

Chemical analysis

The biochar pH was measured using a CRISON micro pH 2001 pH meter, while the EC was measured using a conductivity meter. Total organic C and total N were determined by the Kjeldahl digestion method (Bremner and Mulvaney 1982) and available phosphorus (P) was determined using the method of Bray No. 2 (Bray and Kurtz 1945). Dry ash and digestion with nitric acid were the combination methods used to determine the total concentration of P, K, Ca, Mg, Cu and Zn. Available Cu in soil was extracted using 0.1 M-HCl (Baker and Michael 1982). The concentrations of these elements were determined using inductively coupled plasma spectrophotometer (ICP-OES, Varian 725-ES, USA).

The functional mineral groups contained in biochar were identified by PerkinElmer Fourier-transform infrared spectroscopy (FTIR) spectrum 400, USA. One gram of each biochar sample was pressed into a thin film form and analyzed at different wavelengths. For the presence of minerals and elements, the X-ray diffraction (XRD) analysis was performed using PANalytical EMPYREAN, USA. Meanwhile, the X-ray fluorescence (XRF) spectroscopy was performed using Shimadzu Fluorescence Spectrophotometer μ-EDX 1400, Japan.

Adsorption study

The absorption of Cu on biochar was measured using the batch method. Two grams of each sample were placed in centrifuge tubes (falcon tube). The samples were then added with 0.01 mol L⁻¹·CaCl₂ solution containing various Cu concentrations (0, 20, 40, 60, 80, 100, 150 and 200 mg·L⁻¹) with three replications. The biochar mixture was stirred overnight (16 h) at room temperature (25 °C) on a rotary shaker (Lab Line Orbital Shaker, USA) at 30 revolutions per minutes (rpm). The suspension was centrifuged (Sorvall ST 16 Centrifuge Series, USA) at 3000 rpm for 15 min, followed by filtration through Whatman No. 1 filter. The concentration of Cu in the clear extract solution was determined using the inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 725-ES, USA). The Cu adsorbed by the biochar was then fixed into the Freundlich and Langmuir isotherm and calculated as follows:

$$C_e/q = 1/kq_{\max} + C_e/q_{\max} \quad (1)$$

where, C_e = concentration of Cu in equilibrium solution ($\text{mg}\cdot\text{L}^{-1}$), q = amount of Cu sorbed by the biochars ($\text{mg}\cdot\text{kg}^{-1}$), q_{max} = maximum adsorption ($\text{mg}\cdot\text{kg}^{-1}$) and k = ion bonding energy ($\text{m}^3\cdot\text{kg}^{-1}$).

Value of q was measured by the following equation:

$$q = (C_0 - C_e) V/W \quad (2)$$

where, C_0 = initial equilibrium of Cu concentration in the solution ($\text{mg}\cdot\text{L}^{-1}$), C_e = equilibrium concentration of Cu soil solution ($\text{mg}\cdot\text{L}^{-1}$), V = volume of biochar solution (cm^3) and W = weight of biochar sample (g).

A plot of C_e/q versus C_e yielded a straight line with a slope of $1/q_{\text{max}}$ and intercept of $1/kq_{\text{max}}$. The slope and intercept were used to measure q_{max} and k , as well as to test changes between biochars series and Cu. The Freundlich equation is shown below:

$$\log q = \log K_f + 1/n \log C_e \quad (3)$$

where, C_e = concentration of Cu in equilibrium solution ($\text{mg}\cdot\text{L}^{-1}$), q = amount Cu sorbed by the biochars ($\text{mg}\cdot\text{kg}^{-1}$), K_f = equilibrium coefficient ($\text{m}^3\cdot\text{kg}^{-1}$) and $1/n$ = constant.

Soil analysis

The pH, EC, OC and available P of the soil were determined using the same methods for the biochar analysis. The CEC was calculated using the leaching method (Kitsopoulos 1999).

Cu concentration in plant

The dry ashing process was used to determine the total concentration of copper in plants. The P, K, Ca and Mg were extracted from the plant and then determined using the inductively coupled plasma spectrophotometer (ICP). The Cu uptake in plants was calculated using the following formula:

$$\text{Cu uptake in plants} = (\text{Plant biomass} \times \text{Cu concentration in plant}) \quad (4)$$

Statistical analysis

Analysis of variance (ANOVA), along with Tukey's test, was performed for growth parameters, soil properties and Cu uptake in plants. It was used to analyze the difference and relationship among the treatments. All statistical analyses were performed using SAS version 9.3. The experimental data was fitted to the Freundlich and Langmuir equation to determine the intensity and the capacity of the biochar to adsorb Cu. The suitability of these isotherm models for the adsorption study was measured by determining their correlation coefficient (r^2 values).

RESULTS AND DISCUSSION

Physical characterization of various biochars

The five different types of biochar from three types of agricultural wastes were used in this study. All biochar samples exhibited differing physicochemical properties and the formation of pores and surface areas were dependent on the temperature. During pyrolysis at lower temperatures no physiological changes occurred. Based on the scanning

electron microscopy, it can be observed that the biochars had different physical characteristics (Fig. 1). The EFB1 biochar possessed medium, uniformed pore sizes, with a maximum of 50 μm in diameter at 700 \times magnification. Small particle of ashes could also be perceived on the surface of the EFB1 biochar (Fig. 1b). In comparison, EFB2 biochar (Fig. 1b) had smooth, larger, well-shaped and more uniformed pore sizes, under 50 μm in diameter at 900 \times magnification. Rice husk 1 biochar showed a different pore pattern from both empty fruit branches biochars, whereby the pore shape was round and the size was different to the adjacent pores, which were not uniformly distributed with 50 μm in diameter at 700 \times magnification (Fig. 1c). Diminished and not well shaped pores were observed for RH2 biochar with 50 μm in diameter at 1000 \times magnification (Fig. 1d). Figure 1e shows that the OPK biochar had small, clumped and not uniformly distributed pores with 50 μm in diameter under 900 \times magnification. Small particles of ash were also spotted on the surface of the OPK biochar.

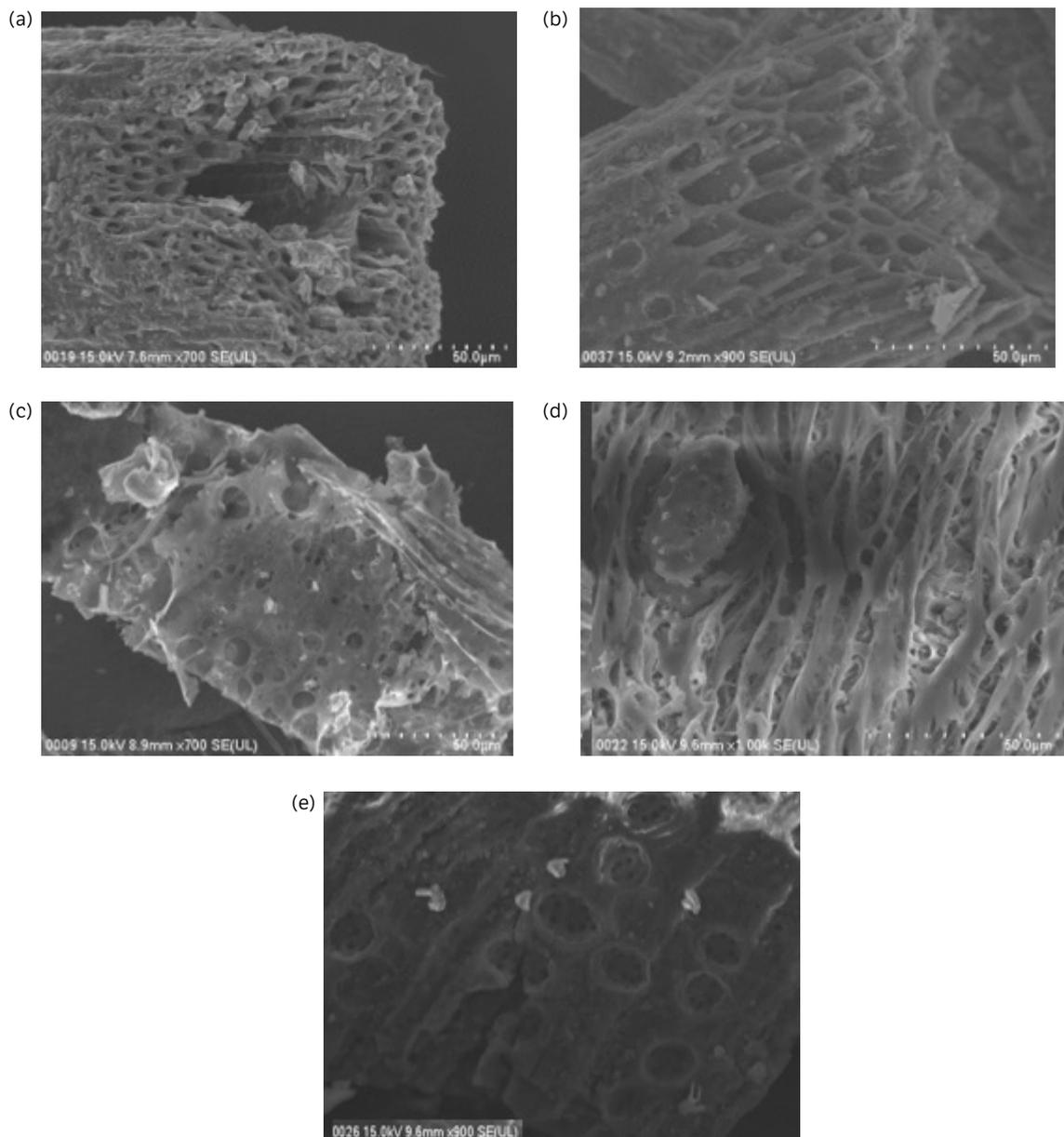


Figure 1. Field emission scanning electron microscopy imaging of biochars at different magnification. (a) biochar EFB1, (b) biochar EFB2, (c) biochar RH1, (d) biochar RH2 and (e) biochar OPK.

The formation and nature of the pores in biochars were dependent on the waste source and the biochar production method, namely the pyrolysis temperature. The surface area of biochar increased with increasing temperature, at which deformation occurred (Zarcinas et al. 2004; Lehmann and Joseph 2009). The pyrolytic temperature of a biomass affected the uptake rate of a compound by biochar as the temperature affected the degree of carbonization of a biochar. However, organic matter is completely carbonized at higher temperatures (Chen et al. 2012). At the same time, surface area was significantly increased and maximum nanopores developed, resulting in sharply enhanced adsorption rate (Zhou et al. 2010). This explained the high surface area of RH1, RH2 and OPK biochars, compared to the EFB1 and EFB2 biochars, which were produced at lower temperatures. Furthermore, the surface area of biochar was influenced by micropore volume, feedstock and production temperatures (Boateng 2007). In addition, the biochar production method, especially the temperature, has a great influence on the biochar C content. Based on the biochars used in this study, OPK biochars were found to be rich in C due to its high pyrolysis temperature. High pyrolysis temperatures produce high fractions of stable C and total C due to an increased release of volatiles (Crombie et al. 2013).

Chemical characterization of various biochars

The pH values of biochar samples varied from one another; however, all were alkaline. The highest pH was for RH2 (9.66), closely followed by EFB2 (9.46). The lowest pH was observed in RH1, with a reading of 7.87. Biochars from the pyrolysis processes were usually alkaline in nature with $\text{pH} > 7.00$ (Bagreev et al. 2001; Sari et al. 2014). Adding biochar into deionized water increases the solution pH and biochar produced at higher temperatures exhibit a higher pH. The increase of pH is likely resulted from the release of alkali salts from the feedstock during the pyrolysis process (Ahmad et al. 2012). Furthermore, because of higher temperature while producing biochar, higher amounts of ash were produced and resulted in higher pH (e.g., RH1). The highest EC ($9.37 \text{ dS}\cdot\text{m}^{-1}$) was found in EFB1 and the lowest was in RH2 ($1.33 \text{ dS}\cdot\text{m}^{-1}$). The total OC percentage varied among the different biochars. The highest OC (43.41%) and Ca (2.27%) contents were found in OPK, while the highest percentages of N (1.29%), K (5.36%), Mg (0.44%) and Cu (29.23%) were observed in EFB1 samples. For available P, the highest reading (0.21%) was obtained from RH2 (Table 1). The EC measured the soluble salts and it could be utilized as an indicator of total soluble mineral and inorganic salts content in biochar (Ding et al. 2010). Empty fruit bunches 1 has the highest amount of total soluble minerals. Biochar also influences the chemical properties of the soil, such as changing pH, EC, CEC and nutrient levels (Gundale and DeLuca 2007).

Table 1. Chemical properties of various biochars.

Biochar	pH	EC	Total OC	N	P	K	Ca	Mg	Cu
		($\text{dS}\cdot\text{m}^{-1}$)	(%)						
EFB1	8.22	9.37	42.50	1.29	0.19	5.36	0.47	0.44	29.23
EFB2	9.46	6.19	38.34	0.19	0.17	3.52	0.64	0.33	30.89
RH1	7.87	6.48	29.47	0.54	0.1	0.55	0.12	0.08	1.25
RH2	9.66	1.33	10.17	0.09	0.21	0.93	0.14	0.08	1.58
OPK	8.61	3.67	43.41	0.50	0.15	0.74	2.27	0.25	17.85

EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

Among the different biochars, EFB biochars contained higher amounts of nutrients (N, K and Mg), except for P and Ca. The depleted amount of nutrients in other biochars might be because of volatilization of few nutrients when heated at high temperature during the production procedure. The content of N in biochars was quite low, due to the high sensitivity of the nutrient in high temperatures, in comparison to the other macronutrients (Gundale and DeLuca 2006). Even at low temperatures, N can simply become free, as it is linked with several number of organic molecules (Schnitzer et al. 2007).

Brunauer–Emmett and Teller analysis

The surface area of biochar was measured using BET analysis. Table 2 shows that RH1 had the highest surface area (277.18 m²·g⁻¹), followed by OPK (141.46 m²·g⁻¹) and RH2 (85.823 m²·g⁻¹). Empty fruit bunches 1 possessed the lowest surface area among the biochars. The empty fruit branches biochar had the largest diameters of pores. Empty fruit bunches 2 had the largest diameter of mesopores at 10.843 nm width, followed by EFB1, with a diameter of 9.244 nm. The narrowest was observed in OPK, with a diameter of 1.676 nm, which can be considered as micropores. It can be proven by the FESEM imaging that EFB2 had wider pores compared to EFB1, which had the same structure but with narrower pores. Oil palm kernel had a small, narrow and bundled pore structure (Fig. 1).

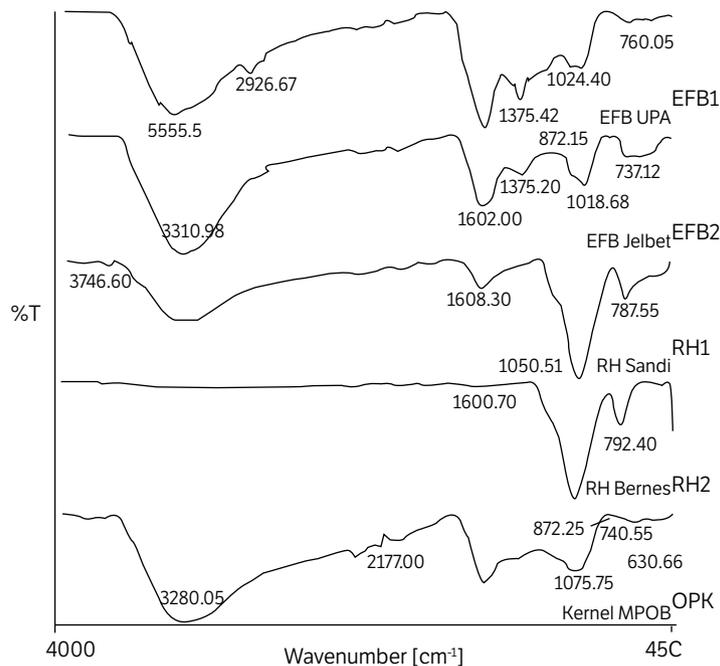
Table 2. Brunauer–Emmett and Teller surface area and porosity of biochar.

Biochar	Surface area (m ² ·g ⁻¹)	Micropore volume (cm ³ ·g ⁻¹)	Internal surface area (m ² ·g ⁻¹)	Average pore diameter (nm)
EFB1	1.54	0.0036	1.36	9.24
EFB2	1.70	0.0046	1.64	10.84
RH1	277.18	0.1411	245.09	2.03
RH2	85.82	0.0138	53.50	3.34
OPK	141.46	0.0592	121.66	1.67

EFB = empty fresh fruit bunch, RH = rice husk, OPK = oil palm kernel.

Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra of various biochars were analyzed with wavelengths ranging from 400 to 4000 cm⁻¹ (Fig. 2). The biochars had different minerals and a substantial number of functional groups, which mostly contained alcohol, phenols and carboxylic. The least number of functional groups were found in EFB1 and RH2 samples. As the pyrolytic temperature of biochar improved, the functional groups decreased due to pyrolysis (Table 3).



EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

Figure 2. Fourier infrared spectra of various biochars.

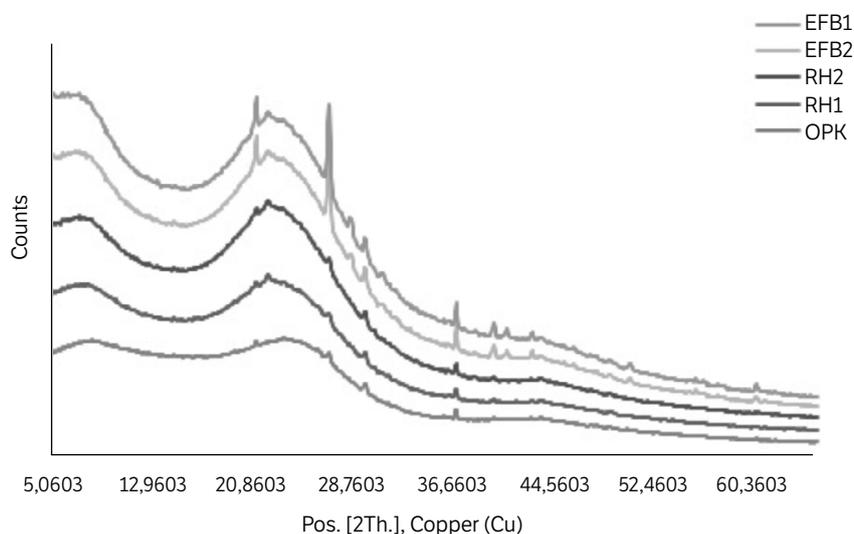
Table 3. Summary of FTIR spectra of various biochars.

Biochar	Peak (cm ⁻¹)	Assignment		Strength	Functional group
		Stretching	Bending		
EFB1	3353.05	N-H (2 amines)	-	Weak	Amines
	2926.67	O-H	-	Strong	Alcohols and phenols
	1024.4	C-N	-	Medium	Amines
	760.05	-	C-H	Strong	Arenes
EFB2	3310.98	O-H	-	Strong	Alcohols and phenols
	1602	-	N-H (1i- amide)	Medium	Carboxylic acids and derivatives
	1018.68	O-C	-	Strong	Carboxylic acids and derivatives
	872.15	-	=C-H,=CH ₂	Strong	Alkenes
RH1	3298.6	O-H	-	Strong	Alcohols and phenols
	1608.3	-	N-H (1i- amide)	Medium	Carboxylic acids and derivatives
	1050.31	C-N	-	Medium	Amines
	2323.05	Si-H	-	Strong	Saline
	787.5	-	C-H	Strong	Alkynes
RH2	1600.7	-	NH ₂ (1 amine)	Strong	Amines
	792.94	-	C-H	Strong	Alkynes
	2307.6	Si-H	-	Strong	Saline
	1048.54	Si-OR	-	Strong	Alkoxysilane
OPK	3328.05	O-H	-	Strong	Alcohols and phenols
	2177	C=C	-	Weak	Arenes
	1074.75	O-C	-	Strong	Carboxylic acids and derivatives
	872.25	NH ₂ and N-H	-	Weak	Amines
	740	-	C-H	Strong	Alkynes

EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

X-ray diffraction (XRD)

The XRD analysis confirmed the presence of various patterns (Fig. 3) and minerals in the biochar samples (Table 4). The XRD analysis of biochar indicated that EFB2 had the highest number of minerals (5): epsomite, magniotriplite, heterosite, periclase and nanosite. The other biochars, with the exception of RH1, had only one type of mineral. The low mineral content in the biochar might be influenced by the pyrolysis temperature.



EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

Figure 3. XRD pattern of various biochar.

Table 4. Summary of XRD analysis.

Biochar	Minerals	Chemical formula	Peak, d-spacing [Å]
EFB1	Moganite	SiO ₂	3.332
	Epsomite	MgSO ₄ ·7(H ₂ O)	4.212
EFB2	Magniotriplite	(Mg,Fe ²⁺ ,Mn)2(PO ₄)F	3.330
	Heterosite	Fe ³⁺ PO ₄	2.452
	Periclase	MgO	2.107
	Nasonite	Pb ₆ Ca ₄ Si ₆ O ₂₁ Cl ₂	1.810
RH1	-	-	-
RH2	Cuprite	Cu ₂ O	2.471
OPK	Anglesite	PbSO ₄	3.009

EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

X-ray fluorescence (XRF) analysis

The XRF was used for elemental analysis of the composition of the biochar samples. Empty fruit bunches 1 and EFB2 had high amounts of K, which reaffirmed the findings of the chemical analysis (Table 5). Whereas RH1 and RH2 had high amount of Si and OPK showed high amount of Fe and Ca, which also reaffirmed the chemical analysis findings. The XRF analysis also confirmed that the hard protective shells of plants contained a high silica content, which was exhibited in biochars made from these materials. Hence, biochar made from rice husk would have high silica content.

Table 5. Chemical composition of biochars.

Biochar	Compounds (%)											
	K ₂ O	Fe ₂ O ₃	Cl	NiO	I	CaO	BaO	ZnO	MnO	SiO ₂	Cr ₂ O ₃	NiO
EFB1	82.80	8.55	4.69	2.53	1.41	-	-	-	-	-	-	-
EFB2	53.91	9.63	-	-	-	27.04	4.64	1.80	1.46	-	-	1.50
RH1	3.99	0.25	-	-	-	1.81	-	-	0.21	93.46	-	0.25
RH2	4.79	0.12	-	-	-	0.91	-	-	0.09	93.90	-	0.78
OPK	16.71	34.54	-	-	-	37.17	-	-	-	-	1.18	10.45

EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

Biochar adsorption isotherm for Cu

The isotherm defines the association among the mass adsorbed substances with the sorbent when the adsorption process reaches equilibrium. In this study, the absorbed substance is Cu, whereas the sorbent is biochar. The experimental data was fitted to the Freundlich and Langmuir equation (Table 6) to determine the intensity and the capacity of biochar to adsorb Cu. The suitability of these isotherm models for the adsorption study was measured by determining their correlation coefficient (r² values). Most correlation coefficient (r²) values were > 0.9 and this meant that the data fitted well with the models. The highest adsorption value, q_{max}, (5128.21 mg·kg⁻¹) was found in the RH1 samples.

The Freundlich isotherm is created on the theory of the heterogeneous superficial energies of the sorbent. The adsorption coefficient, k_p, denotes the amount of Cu concentration adsorbed into biochar for a unit of equilibrium concentration. It processes the adsorption capacity of biochar for Cu, where the greater k_f designates the biochar preference to adsorb solute. The kf showed higher adsorption of Cu on RH2 biochar in contrast with the rest of the biochars.

Table 6. Adsorption parameters of Freundlich and Langmuir equation for Cu.

Biochar	Langmuir model			Freundlich model		
	q_{\max} ($\text{mg}\cdot\text{kg}^{-1}$)	k ($\text{m}^3\cdot\text{kg}^{-1}$)	r^2	K_f ($\text{m}^3\cdot\text{kg}^{-1}$)	n	r^2
EFB1	2000	0.063	0.9987	6.46	0.622	0.974
EFB2	909	0.239	0.9932	10.20	0.458	0.967
RH1	5128	0.065	0.991	12.74	0.864	0.972
RH2	4977	0.058	0.990	45.64	1.168	0.921
OPK	4889	0.0219	0.9707	8.64	0.463	0.948

q_{\max} : maximum adsorption, k : binding affinity, k_f : equilibrium coefficient, n : binding affinity, EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel.

The biochar samples had a number of functional groups, namely alcohol, phenols and carboxylic. All biochars had alcohols, phenols and carboxylic functional groups, except for RH2, while amines dominated all biochars except for EFB2. Both rice husk biochars had silicon functional groups, such as saline and alkoxy silane. This might be due to the rich silica content in rice husks (Uchimiya et al. 2013). The most diverse functional group was OPK, with six different functional groups. As OPK underwent the highest pyrolysis temperature, it can be determined that temperature did not decrease functional groups of biochars. Therefore, it is more likely that the source of biomass waste is the biggest contributing factor to functional groups in biochars (Khare et al. 2017; Pintor et al. 2012). The functional groups have a strong interaction with heavy metals through electrostatic attraction, ion exchange and surface complexation (Amonette and Joseph 2009). Minerals also act as additional adsorption sites, which contribute to the biochar adsorption capacity for heavy metals (Xu et al. 2013). Hence, biochar functional groups might assist in controlling Cu uptake by plants, which meant OPK had promising attributes.

In addition, the Langmuir isotherm showed that the maximum adsorption capacity of molecules on the biochar surface at the same energy (Hameed et al. 2007) and maximum adsorption value were observed in RH1. The high adsorption of RH1 was caused by its surface area ($245.09 \text{ m}^2\cdot\text{g}^{-1}$) and high number of functional groups (O-H, N-H, C-N, Si-H and C-H). High surface areas and pores enable easier accessibility to metals. Biochar has the potential to change the physical and chemical properties of soil (Glaser et al. 2002). These effects may enhance water availability to crops and even prevent soil erosion. Perhaps the most significant factor of the biochar interaction with soil is its effect on soil pH. Malaysia's soil is highly weathered, making it highly acidic. As soil acidity is a key factor that controls metal mobility in soils (Ali et al. 2013) and plants are mostly susceptible to heavy metal toxicity. The ability of biochar to increase soil pH unlike most other organic amendments (Novak et al. 2009 a) increases the sorption of these metals, thus reducing their bioavailability for plant uptake. Besides retaining heavy metals, biochar treated soils also increased their CEC (Chibuike and Obiora 2014).

Effects of biochars on soil properties

The application of biochars affected the soil pH. However, the general pH values were below 7.0 (5.26–6.0), indicating that the acidic nature of the soils persisted despite biochar applications. The highest pH (5.93) was observed in OPK biochar (Table 7). From the data obtained, the soil applied with empty fruit branches-based biochar had shown higher pH than the rice husk biochars. The application of biochar on Cu polluted soils significantly increased the mean values ($p < 0.05$) of soil organic C (OC). The highest values were observed in soils amended with EFB1 (0.88%) followed by RH2 (0.84%). The increase in OC due to the addition of biochar could be caused by the presence of high amount of organic carbon in the biochar itself (Table 1).

Among the biochar treatments, OPK had the highest increase in soil pH; however, EFB1 showed the highest OC, while EFB2 had the highest concentrations of available P. It is also significant to note that, since the characteristics of biochar vary widely depending on its method of production and the material used in its production, the effect of biochar amendments on the availability of Cu in soil differs (Ippolito et al. 2012; Yuan and Xu 2011). The availability of P in soil is also highly dependent on the range of the soil pH. The application of biochar can increase P availability in soils at the ideal pH from 6.5 to 7.0 (Ippolito et al. 2012) and it has been described that biochar can enhance the CEC in soils (Chan et al. 2007), which changes soil pH and makes available soil P for plants (Zwetsloot et al. 2016). Moreover, increase in soil pH reduces the activity of iron (Fe) and

aluminum (Al), further contributing to increase in available P. The addition of mineral P fertilizers can made P-availability in soils and similarly increase the efficiency of metal P mineral formations, which increases metal solubility in soil suspensions by inducing the formation of heavy metal P precipitation (Yuan and Xu 2011). All biochar treated soils in the study showed an increase in soil pH, organic matter and available P, when compared to the control treatment. Therefore, it can be concluded that biochar improves soil properties, while improving the soil ability to retain heavy metals, such as Cu.

Table 7. Effect of biochars on soil properties at harvest.

Treatment	pH	EC (dS·m ⁻¹)	OC (%)	CEC (cmolc·kg ⁻¹)	Av. P (mg·kg ⁻¹)
Control	5.29c ± 0.01	68.15a ± 3.22	0.53e ± 0.01	11.64a ± 0.90	105.42b ± 4.41
F	5.29c ± 0.02	71.06a ± 3.59	0.55e ± 0.01	12.30a ± 0.87	118.83ab ± 6.11
EFB1	5.75b ± 0.04	70.23a ± 2.60	0.88a ± 0.03	10.51a ± 0.66	141.63ab ± 1.22
EFB2	5.65b ± 0.01	55.56a ± 3.66	0.77bc ± 0.02	10.64a ± 0.27	151.67a ± 5.67
RH1	5.39c ± 0.03	62.18a ± 2.61	0.84ab ± 0.02	9.95a ± 1.82	147.13a ± 8.37
RH2	5.41c ± 0.03	61.72a ± 4.82	0.68cd ± 0.02	9.43a ± 0.73	148.29a ± 3.74
OPK	5.93a ± 0.04	66.93a ± 6.11	0.66d ± 0.01	11.30a ± 2.23	146.21a ± 3.79

Control = without fertilizer or biochar, F = fertilizer only, EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel. Means followed by the same letter within a column are not significantly different (Tukey's test, p > 0.05).

The influence of biochar to the CEC of Cu contaminated soils was not significantly different (p > 0.05). Theoretically, the result should have been slightly different. However, differences in the experimental design of the present study may also be a contributing factor in the patterns observed. Basically, the application of various biochars in this study did not alter the CEC of the soil (Table 7). Meanwhile, the application of various biochars had significantly increased the available P in the soil related to the control treatment; however, no significant variation was found among the applied treatments.

Copper concentration in soil and in plants

Copper is an essential micronutrient, needed by plants in low concentrations for normal and healthy plant growth. All the experimental treatments were contaminated with 60 ppm of Cu, except control. After harvesting, all the biochar amended treatments found less than 15 ppm of Cu concentration (Table 8). To maintain crop quality, the maximum permitted concentration (MPC), is 30 ppm of Cu (Kitsopoulos 1999; Zarcinas at al. 2004), which meant that all biochars studied were able to absorb and control Cu mobility in the soil. The biochar amended treatments had a significantly higher (p < 0.05) concentration value than the control treatment. The highest available Cu in soil was found in OPK (5.21 mg·kg⁻¹) and the lowest was in control (2.82 mg·kg⁻¹).

Table 8. Effect of biochar on Cu concentration in soil and plant uptake.

Treatment	Total Cu concentration in soil	Available Cu in soil	Cu concentration in plant	Cu uptake in plant
	(mg·kg ⁻¹)		(µg·pot ⁻¹)	
Control	4.84c ± 0.33	2.92c ± 0.11	0.78c ± 0.06	10.53d ± 0.54
F	5.55c ± 0.38	2.64c ± 0.07	1.19b ± 0.08	18.73c ± 1.59
EFB1	12.99ab ± 0.61	5.09b ± 0.17	1.61a ± 0.13	39.76a ± 3.31
EFB2	13.78ab ± 0.63	6.17b ± 0.34	0.94c ± 0.03	25.53bc ± 1.05
RH1	12.25b ± 0.56	5.52b ± 0.17	0.38d ± 0.04	13.14d ± 0.83
RH2	13.25abc ± 0.42	5.26b ± 0.07	0.52d ± 0.03	18.25c ± 0.96
OPK	14.23a ± 0.54	8.30a ± 0.77	1.31b ± 0.07	38.87a ± 1.473

Control = without fertilizer or biochar, F = fertilizer only, EFB = empty fresh fruit bunch, RH = rice husk, OPK = oil palm kernel. Means followed by the same letter within a column are not significantly different (Tukey's test, p > 0.05).

The Cu concentration in the maize plants differ among the different types of biochar applied. However, all biochar treatments increased Cu uptake associated to the control treatment (Table 8). The highest Cu concentration and uptake was observed in the EFB1 treatment. Despite having the highest concentration, the Cu uptake was not in amounts that could affect the plants growth. Rice husk biochars were promising, since they had less concentration of Cu than the control treatment. This clearly indicates that rice husk biochar had the potential to control Cu uptake in plants (Ippolito et al. 2012).

Effect of various biochars on *Zea mays* L. growth

The use of biochar showed a positive effect on maize grown in Cu contaminated soils (Table 9). Among all treatments, the highest plant height (68.27 cm) was found in RH1. The highest plant biomass (34.73 g) and leaf chlorophyll contents (45.03) were observed in RH2 applications. Meanwhile, there was no significant difference in plant biomass for the other treatments.

Table 9. Effect of biochar on the plant growth performances of maize.

Treatment	Plant height (cm)	Plant biomass (g)	Leaf chlorophyll content (SPAD values)
Control	41.73b ± 2.57	17.03c ± 1.37	33.37c ± 1.14
F	44.90b ± 3.95	24.13b ± 1.17	40.03abc ± 0.27
EFB1	61.11a ± 1.97	24.70b ± 0.05	39.23abc ± 1.22
EFB2	59.67a ± 0.27	27.27b ± 1.77	36.20bc ± 2.87
RH1	68.27a ± 0.94	26.87b ± 0.89	32.60c ± 1.09
RH2	67.30a ± 2.05	34.73a ± 1.41	45.03a ± 1.34
OPK	60.43a ± 2.77	29.82ab ± 2.28	41.30ab ± 1.72

Control = without fertilizer or biochar, F = fertilizer only, EFB = empty fruit bunch, RH = rice husk, OPK = oil palm kernel. Means followed by the same letter within a column are not significantly different (Tukey's test, $p > 0.05$).

The amounts of Cu in maize are in low amounts. However, the lowest Cu uptake among all the biochar treatments was observed in RH1. This meant that RH1 had the best potential to reduce the bioavailability of Cu. Furthermore, it should also be noted that maize plants in RH1 treatment had the best growth performance in terms of height and number of leaves. All biochars studied had the potential to not only improve the growth performance of maize plants, but also to retain soil Cu, preventing it to be up taken by the plants at toxic levels (Beesley et al. 2011). However, RH1 exhibited the best results in retaining the most Cu while providing the best growth performance of the maize plants. The different processes of adsorption and desorption are the most important mechanisms that managed bioavailability of heavy metals ions in the soils. Instead, desorption mechanism in soil to the release of heavy metal ions from various processes of retention and adsorption is the main contributor to the steady state of heavy metals such as Cu, Zn and Cd in the soil (Aishah et al. 2018).

Correlations of soil properties with plant biomass and Cu uptake

Correlation analysis was carried out in order to understand the relationship between soil properties with plant biomass and Cu uptake in plants. All soil factors were analyzed, including the pH, CEC, OC and available P. A significant positive correlation was observed among the pH and Cu uptake in the maize plants (Table 10). Available P also exhibited a significant positive correlation with the plant biomass, while CEC had a significant negative correlation with the plant biomass. Phosphorus is often recommended as a row applied starter fertilizer for increasing early growth of plants. Low available phosphorus is a primary constraint to plant growth, because phosphorus is usually bound to soil ingredients that make it unavailable to plants (Yuan and Xu 2011).

Table 10. Correlation of soil properties with plant biomass and Cu uptake in plants.

Soil properties	Correlation coefficient	
	Plant biomass	Cu uptake in plants
pH	0.32750	0.74919**
EC	-0.26938	0.28339
OC	0.30638	0.15650
Available P	0.65520*	0.19857
CEC	-0.17856	0.18132

* Significant, ** significant at $p < 0.01$.

CONCLUSION

The five plant-based biochars exhibited different physicochemical properties. The RH1 biochar had the most porous in structure, having highest BET surface area, including with a substantial number of functional groups. The porous structure and heterogenic functional groups on surface area meant that it was able to retain nutrients. All biochars contained relatively low amounts of nutrient conformation, which was most likely vanished due to volatilization throughout the biochar production. The potential adsorption of biochar is influenced by pH, surface area, functional groups and organic matter contents. Combination of these characteristics created Cu adsorption potential. Regardless, all biochar amended treatments not only showed the ability to retain Cu, but also facilitated significant maize plant growth. This study was conducted to determine the characteristics and potential of different plant-based biochars to control Cu uptake and influence on the growth of Maize (*Zea mays* L.), where, among the biochars studied, RH1 showed the most promising results, as it retained the most soil Cu while providing the best growth performance of the maize plants. Thus, RH1 can be a useful soil amendment to reduce Cu bioavailability for plants.

AUTHORS' CONTRIBUTION

Conceptualization: Abdullah R.; **Methodology:** Abdullah R. and Ishak C. F.; **Investigation:** Abdullah R., Ishak C. F., Osman N., Halim N. S. A. and Panhwar Q. A.; **Writing – Original Draft:** Abdullah R. and Panhwar Q. A.; **Writing – Review and Editing:** Abdullah R., Ishak C. F., Osman N., Halim N. S. A. and Panhwar Q. A.; **Funding Acquisition:** Abdullah R., Ishak C. F. and Osman N.; **Resources:** Abdullah R., Ishak C. F. and Osman, N.; **Supervision:** Abdullah R.

DATA AVAILABILITY STATEMENT

Data will be available upon request.

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