Properties of Biochars Prepared from Local Biomass in the Mekong Delta, Vietnam

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Wood- (bamboo and melaleuca) and herbaceous-based (rice husk and water hyacinth) biochars, produced from local biomass by slow pyrolysis at 500 °C, 700 °C, and 900 °C, were examined for their physical and chemical properties. The wood-based biomass produced biochars with lower ash contents (<14 wt.%$_{db}$ ash) and higher fixed carbon contents ($>$ 54 wt.%$_{db}$), greater higher heating value (>23 MJ/kg), higher degree of aromaticity (with O/C, H/C, and volatile matter/fixed carbon ratios were less than 0.08, 0.51, and 0.61, respectively), and smaller amount of salt nutrients (<76 g/kg$_{db}$) compared with those of the herbaceous-based biochars. Their unique properties have generated more interest in using them as a solid fuel, for carbon sequestration, and for soil amendment. The rice husk biochars contained more than 300 g/kg$_{db}$ silica, which is potential for silicophilic plants. The water hyacinth biochars with the greatest volatile matter/fixed carbon (ranging from 0.72 to 2.35), and highest O/C ratios (0.11 to 0.18), indicating the lowest aromaticity among studied biochars and thus maybe least suitability for carbon sequestration. They also possessed a highest soluble salts content (>240 g/kg$_{db}$), highest electrical conductivity (>6489 μS/cm), and greatest liming potential (>6.56 %$CaCO_3$–eq), which may not be suitable for salt-sensitive plants or low-buffer capacity soils.

Keywords: Biochar; Physicochemical properties; Bamboo; Melaleuca; Rice husk; Water hyacinth

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INTRODUCTION

The reuse of wood and herbaceous residues for biochar production has received much attention in recent years. Biochar is a porous carbonaceous and fine-grained solid that is produced through the direct thermal decomposition of biomass in the absence of oxygen, which is a process known as pyrolysis. Agricultural and forest biomasses are often used as typical feedstocks for making biochar by pyrolysis. Because of its porous structure, biochar has received attention for multipurpose soil amendment, pollutant remediation, and carbon sequestration. In fact, biochar improves the soil properties by increasing soil moisture-holding ability, increasing cation exchange capacity, increasing organic carbon pool, while reducing nutrient leaching ability or neutralizing soil acidity (Glaser *et al.* 2002; Atkinson *et al.* 2010). Biochar also removes pollutants, *i.e.*, heavy metals, dyes, pesticides or organic wastes from aqueous solution (Uchimiya *et al.* 2011; Inyang *et al.* 2014; Mayakaduwa *et al.* 2016). On the other hand, biochar can be considered for sequestrating atmospheric carbon dioxide concentration. During the pyrolysis process, volatiles and water in biomass are driven off and the carbon atoms are rearranged into a stable form of carbon structures, which results in resistance against microbial degradation (Spokas *et al.* 2009).

The types of feedstock used and pyrolysis temperature are the two important factors that affect the physical and chemical properties of biochar that is produced. For example, biochar produced at temperatures higher than 400 °C showed higher pH values, ash contents, and specific surface areas (Gaskin *et al.* 2008; Jindo *et al.* 2014), with higher adsorption properties (Yang *et al.* 2015) than biochars produced at lower temperatures. They also possess higher proportions of carbon and stable aromatic structures (Zimmerman 2010; Guo and Chen 2014), which would result in their long-term carbon sequestration with chemical and biological stability (Spokas *et al.* 2009). As to feedstock types, wood-based biochars possessed higher carbon contents and better adsorption characteristics compared with herbaceous-based biochars (Jindo *et al.* 2014).

As a country with an agricultural tradition and nearly 40% of its territory covered by forests, Vietnam has great potential to act as a source for biomass resources (approximately 118 million ton/year) in the form of herbaceous and wood residues (Embassy of Denmark in Vietnam 2015). As of 2015, approximately 11.1 million ha of natural forest area are remaining, of which melaleuca (*Melaleuca cajuputi*) occupies 176 thousand ha (FAO 2016). It is estimated that nearly 5 million tons of wood residues are produced annually from natural forests (NL Agency 2012). The estimated residues from planted forests is much higher because of a higher annual yield. Bamboo (*Bambusa vulgaris*), which is a typical species planted in Vietnam forests, occupies more than 1.2 million ha of plantations in Southern and Northern Vietnam, and produces approximately 7 million ton of residue per year with an average annual yield of up to 13 tons/ha (NL Agency 2012). Only a small amount of these forest residues have been used for heating or cooking, and most of them are left in the forest because of logistical difficulties and low demand. In Vietnam, the southern Mekong Delta region is the highest productive agricultural sector, and accounts for approximately 50% of the total agricultural waste for the country (Vietnam 2015). Rice husks (*Oryza sativa* L.) are one of the most abundant agricultural residues in the Mekong Delta, with more than 4 million tons produced annually. However, most of it is openly burned or directly dumped into rivers or canals. Poor agricultural practices, high application rates of nitrogen and phosphorus fertilizers, and high rainfall have led to the proliferation of water hyacinth (*Eichhornia crassipes*), which poses a threat to aquatic ecosystems and human activities. The improper management of waste biomass practices in Vietnam may also contribute to environmental pollution. Therefore, producing biochar from these biomass wastes can reduce the negative effects on the environment.

When biochar is used for specific soil problems or to address specific environmental concerns, it is important to determine the optimum feedstock choice and pyrolysis protocol prior to producing the biochar (Jindo *et al.* 2014). Additionally, to optimise biochar for specific utilizations, its properties must be carefully studied and understood (Lopez-Capel *et al.* 2016). Therefore, this paper analysed some essential physico-chemical properties of wood- and herbaceous-based biochars produced at three different pyrolysis temperatures of 500 °C, 700 °C, and 900 °C. All of the biochar samples underwent the following analyses: pH, electrical conductivity (EC), liming equivalence, proximate and ultimate analyses, higher heating value (HHV), cation exchange capacity (CEC), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX). In particular, the pH and liming equivalence can predict the ability of biochars to increase the soil pH (Singh *et al.* 2017). The EC is a measurement of the amount of soluble salts in biochar solutions, which is based on the principle that biochar solutions with a higher concentration of salts have a greater ability to conduct an electrical current (Singh *et al.* 2017). The EC of a biochar is important because high rates of biochar application may adversely affect salt-sensitive plants (Joseph *et al.* 2009). The CEC can be used to evaluate the biochar ability to sorb cations in soil or water (Timmons *et al.* 2017).

A proximate analysis is a broad analysis that determines the moisture, volatile matter, fixed carbon, and ash contents. This is the most fundamental of all of the biochar analyses and is of great importance to determine the practical uses of the biochar. The moisture content consists of water physically adsorbed onto the surface and in the pores of the biochar, while the volatile matter content includes gases (H_2, CO, CO_2, CH_4, *etc.*), hydrocarbons, oxygen-containing organic compounds, some inorganic compounds, organic acids, and chemically bound water (Schernikau 2015). The biochar ash content is the inorganic residue remaining in the biochar after combustion. An ultimate analysis is the determination of the elemental composition in the biochars, *i.e.*, carbon, hydrogen, nitrogen, and oxygen. Carbon, hydrogen, and oxygen are directly used to predict the carbon sequestration ability of biochars through the H/C and O/C ratios (Lorenz and Lal 2018). They are also the main elements that contribute to the HHV of a biochar, which is an important parameter that determines if a biochar is a possible fuel candidate (Sheng and Azevedo 2005). The HHV measures the energy available in a unit mass of a biochar sample. The FTIR spectra helps to identify functional groups present on the surface of the biochar. Scanning electron microscopy is used to study the surface morphology of biochars, while EDX characterizes the elemental composition. The aim of this study was to test four hypotheses: (1) biochars derived from local biomass have fertilization potential; (2) biochars derived from bamboo and melaleuca charred at high temperature have potential for increasing C sequestered in soils or potential for producing various energy forms; (3) The rice husk biochars are a source of bioavailable silicon for silicophilic plants; and (4) The water hyacinth biochars are not suitable for salt-sensitive plants or saline soils.

In general, the objective of this paper was to explore the possibilities of utilizing locally available biomass for producing biochars.

EXPERIMENTAL

Materials

Four raw materials were used to produce biochar in this study, including bamboo (*B. vulgaris*), melaleuca (*M. cajuputi*), water hyacinth (*Eichornia crassipes*), and rice husk (*O. sativa* L., OM5451 variety). They were all collected from the Mekong Delta region of Vietnam, which is the most productive agricultural area in the country. They were selected and studied in this research because of their abundance and availability in the Vietnamese Mekong Delta region. The collected raw biomass was initially dried overnight in an oven at 105 °C. The dried raw materials were then cut into 1-mm pieces and formed into cylindrical granules for biochar production. A furnace (model VMF 165, Yamada Denki, Adachi, Tokyo, Japan) was used for pyrolysis of these granules. After the biomass granules were loaded into the centre of the furnace with a crucible, nitrogen gas was pumped into the furnace at a flowrate of 3 L/min for 30 min to remove the air from inside of the furnace. After that, the furnace temperature was increased from room temperature to 500 °C, 700

°C, and 900 °C at a heating rate of 10 °C/min. The temperature was held at the desired temperature for 2 h, and then it was allowed to cool down to room temperature. The solid biochar was collected, ground into a homogeneous powder, and put in small glass containers, which were stored at relative humidity of less than 25 % in a desiccator auto dry (SD-3 unit 1-5489-11, AS ONE Ltd., Osaka, Japan) without further treatment until they were analysed.

Methods

Physical, chemical, and energetic properties of the biochars

The biochar pH and EC were measured in a solution with a 1:100 biochar to deionized water ratio after 2 h of shaking on a shaker (Bioshaker BR-23FH, Taitec Co., Saitama, Japan) at 100 rpm and 25 °C. After this, the pH and EC were measured using a pH meter (MP220, Mettler Toledo, Taitō City, Japan) and EC meter (Laqua Twin, Horiba, Kyoto, Japan), respectively. The liming equivalence was analysed according to the procedures suggested by Singh *et al.* (2017), in which a 0.5-g air-dried biochar sample was treated with 10 mL of 1 M HCl and the mixture was allowed to sit overnight after 2 h of shaking. The excess acid was back-titrated with a standardised solution of 0.5 M NaOH until a pH of 7 was reached. The result was reported as the equivalent proportion of the liming effect of pure $CaCO_3$ (%$CaCO_3$–eq).

The moisture, volatile matter, and ash contents were determined with an electric furnace (MMF-2, AS ONE Ltd., Osaka, Japan), using a slightly modified ASTM D1762-84 (2013) method. Briefly, the moisture content was analysed by heating the biochar at 105 °C for 2 h, the volatile matter content was determined in an inert atmosphere at 900 °C ± 20 °C for 7 min, and the ash content was determined in an air atmosphere at 800 °C for 6 h. Fixed carbon is the carbon found in the biochar, which is left after volatiles in the biochar are driven off. This differs from the ultimate carbon content of the biochar because some carbon is lost in hydrocarbons with the volatiles. The fixed carbon content was calculated as follows:

$$\textit{Fixed carbon}\ (\%) = 100\% - (\textit{moisture}\ (\%) + \textit{ash}\ (\%) + \textit{volatile matter}\ (\%)) \qquad (1)$$

In other words, fixed carbon is not pure carbon but simply dry mass that is not volatile matter nor ash, which is dominated by fused aromatic carbon structure and potentially contained only a very small a part of mobile organic portion.

To determine the elemental composition, the biochar was initially ground to obtain a homogenous fine powder and dried overnight at 105 °C prior to analysis. Its carbon, hydrogen, and nitrogen contents were then analysed using a CHNS-O Analyzer Perkin-Elmer 2400 Series II instrument (Perkin-Elmer, Waltham, USA). The oxygen content was calculated with the following equation:

$$O\ (\%) = 100\% - (C\ (\%) + H\ (\%) + N\ (\%) + \textit{ash}\ (\%) + \textit{moisture}\ (\%)) \qquad (2)$$

The percentages of the C, H, N, and O elements were then used to calculate the atomic H/C, O/C, and C/N ratios of each biochar. The formula for calculating HHV with more than 90% predictions in the range of ±5% error, is based on the contents of main organic elements (in wt.%) C, H, and O (Sheng and Azevedo 2005):

$$HHV\ (\mathrm{MJ/kg}) = -1.3675 + 0.3137C + 0.7009H + 0.0318O \qquad (3)$$

For the CEC determination, a modification of the Gillman (1979) method was used. Biochar was washed in a 0.1-M $BaCl_2$ solution three times to exchange the exchangeable cations with Ba^{2+}. Then, a standard 0.02-M $MgSO_4$ solution was added to replace the Ba^{2+} and precipitation of $BaSO_4$ occurred. The CEC was calculated from the difference between the original Mg content and the Mg remaining in the standard solution.

The available nutrient contents in the biochars were analysed by EDX, using a JSM-7500F instrument (JEOL, Tokyo, Japan). At least five measurements per micrograph were performed and the average values were reported.

The FTIR measurements of the biochar were performed with a USA Thermo Nicolet Nexus 670 FTIR Spectrometer (GMI, Ramsey, USA). The KBr powder was used as a background. Approximately 1 mg of dried sample was mixed gently with 100 mg of KBr powder, and then pressed to form pellets. The FTIR spectra were obtained at a 4-cm^{-1} resolution in the region of 400 cm^{-1} to 4000 cm^{-1} with a total of 64 scans. A background FTIR spectrum of the air was collected before obtaining the FTIR spectra of the samples.

Statistical analysis

The significance of the differences between the biochars based on the pyrolysis temperature and biomass type was determined by the One-way ANOVA. Post hoc comparison of means was performed using Tukey-HSD procedure for the differences between the pyrolysis temperature of the same biochar. Statistical analysis was performed by using StatGraphics Centurion XV software (StatPoint, Warrenton, VA, USA). The statistical significance was set at a p-value of less than 0.05.

RESULTS AND DISCUSSION

Physical Characteristics

Biochar yields

The biochar yields are given in Table 1. The pyrolyzing temperature and feedstock type were critical factors for controlling the biochar yield. The yield fell gradually when the pyrolysis temperature was increased from 500 °C to 900 °C, similar to other studies of biochars (Rehrah *et al.* 2014; Wei *et al.* 2017). These declines are mainly due to the release of moisture and volatiles; meanwhile, hemicellulose, cellulose and lignin that are present in the biomass decompose, as the pyrolyzing temperature increases (Keiluweit *et al.* 2010). The herbaceous biomasses (rice husk and water hyacinth) showed higher biochar yields compared with the wood biomasses (bamboo and melaleuca) with biochar yields of more than 35% and less than 30%, respectively. The biochar yields of different feedstocks in this study were consistent with data from Jindo *et al.* (2014). Differences in the mineral, moisture, and ash contents in the feedstocks may have affected the amount of biochar produced (Amonette and Joseph 2009). Feedstocks with higher mineral and ash contents and a lower moisture content (such as rice husk and water hyacinth) tend to produce more biochar (Tables 1 and 2 and Fig. 2).

Cation exchange capacity

The CEC values of the biochars (Table 1) varied depending on the biomass feedstock and pyrolysis conditions. Compared with the other biochars, the rice husk-derived biochars possessed the highest CEC values and ranged from 16.14 $cmol_c/kg$ to 23.98 $cmol_c/kg$, which indicated a higher amount of exchangeable base cations in these biochars. The melaleuca and water hyacinth biochars had statistically similar CEC values, at approximately 14 $cmol_c/kg$ ($p < 0.05$). The CEC values were lower in the bamboo biochars and ranged from 11.82 $cmol_c/kg$ to 13.99 $cmol_c/kg$. Based on the pyrolysis temperature, higher CEC values were associated with an increasing pyrolysis temperature from 500 °C to 700 °C for the same feedstocks, which was followed by a decrease in the CEC at 900 °C. The mechanisms for the two contradicting trends is not fully understood. However, the increasing trend was probably caused by the presence of a higher level of oxygen surface functional groups (such as carboxyl, hydroxyl, phenolic, and carbonyl groups) formed during the oxygenation of the biochar surfaces. These oxidized functional groups may have increased the abundance of negative charges, which were likely responsible for the high CEC values in the biochar (Gomez-Eyles *et al.* 2013; Mukome and Parikh 2015). In contrast, the decreasing trend of the CEC may have been because of a loss of oxygenated (acid) functional groups, which occurred at the highest pyrolysis temperature of 900 °C (Mukome and Parikh 2015).

Proximate analysis

It was observed that higher temperatures resulted in biochars with a higher ash content and lower volatile matter and moisture contents. The moisture contents are given in Table 1, whereas the ash and volatile matter contents are presented in Fig. 1. The moisture present in each biochar decreased gradually as the pyrolysis temperature increased from 500 °C to 900 °C. The differences in the moisture contents between the biochars were small, as they fluctuated from 4 $wt.\%_{db}$ (oven-dried basis) to 5 $wt.\%_{db}$ and were statistically insignificant. Showing a similar decreasing trend, the volatile matter fraction of the biochars decreased consistently with higher pyrolysis temperatures. This was in agreement with Sadaka *et al.* (2016), who reported that volatile matter decreases with increasing pyrolysis temperature for corn stover (*Zea mays* L.). The volatile matter released from the biomass differed with the temperature, which could have been a result of the decomposition degrees of the cellulose, hemicellulose, and lignin (Demirbas and Arin 2002). The pyrolysis of the melaleuca and rice husk feedstocks generated biochars with volatile matter contents that ranged between 17 $wt.\%_{db}$ to 27 $wt.\%_{db}$ and 12 $wt.\%_{db}$ to 22 $wt.\%_{db}$, respectively; this was statistically smaller than those in the bamboo and water hyacinth biochars ($p < 0.05$). Variation in volatile matter content is likely attributable to thermal stability variances between the three main components of biomass (hemicellulose, cellulose, and lignin), and their relative abundance in each biomass (Yang *et al.* 2017). In the three components, hemicellulose produces the highest volatiles, followed by cellulose component, while lignin produced the least quantities of volatiles (Yang *et al.* 2006).

In contrast, the biochar ash content showed a gradual increase with an increasing pyrolysis temperature (Wei *et al.* 2017). Ash content is the remaining solid after all of the organic elements – Carbon (C), hydrogen (H) and nitrogen (N) – have been oxidized (Joseph *et al.* 2009). At the same pyrolysis temperature, the ash content was significantly different among the biochars. The ash content in the biochars produced from the wood biomasses (bamboo and melaleuca) was smaller ($p < 0.05$) than those produced from the herbaceous biomasses. These results were consistent with Sun *et al.* (2017), who found that wood generally had lower ash content than agricultural biomasses. In particular, there was only approximately 3 $wt.\%_{db}$ ash in the melaleuca biochars and less than 13 $wt.\%_{db}$ ash in the bamboo biochars, which was lower compared with the greater than 34 $wt.\%_{db}$ and 44 $wt.\%_{db}$ ash contents in the rice husk and water hyacinth biochars, respectively. These differences may be due to the differences in the concentrations of ash-forming elements, such as calcium carbonate, potassium silicates, iron, and other metals (Lewandowski and Kicherer 1997).

Table 1. Physical Characteristics of the Biochars Derived from the Pyrolyzed Bamboo, Melaleuca, Rice Husk, and Water Hyacinth

Feedstock	Bamboo			Melaleuca			Rice Husk			Water Hyacinth		
Pyrolysis Temperature (°C)	500	700	900	500	700	900	500	700	900	500	700	900
Yield (%)	29.8	28.4	26.6	27.6	25.1	23.7	38.3	35.9	35.3	43	39.5	35.9
CEC[a] (cmolc/kg)	13.97	13.99	11.82	14.63	15.12	14.34	16.14	23.98	19.67	14.62	14.63	14.15
Moisture[a] ($\text{wt.}\%_{db}$)	5.89	5.51	5.19	5.4	4.98	4.68	4.91	3.6	3.16	6.51	4.49	3.72
Fixed Carbon[a] ($\text{wt.}\%_{db}$)	51.56	55.06	58.88	64.18	72.88	74.82	38.66	43.1	44.67	14.66	18.95	26.14
VM/FC[b]	0.61	0.47	0.38	0.43	0.26	0.23	0.57	0.35	0.29	2.35	1.35	0.72
C/N	101.09	136.36	106.31	269.55	312.79	201.65	85.64	106.89	96.92	24.51	29.85	45.84
HHV (MJ/kg)	23.57	23.33	23.89	26.34	26.98	27.05	16.53	16.55	16.4	11.33	10.44	10.92
Liming Equivalence[a] (% $CaCO_3$-eq)	2.74	2.83	3.17	2.1	2.26	2.5	1.84	2.09	2.09	6.56	7.79	8.36

[a] Values are the average of triplicates
[b] Volatile matter/fixed carbon ratio

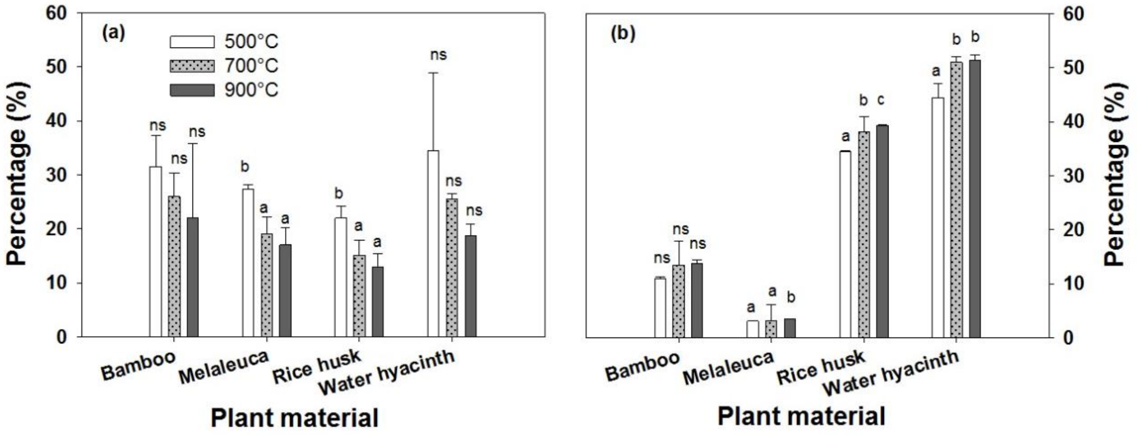

Fig. 1. (a) Volatile matter and (b) Ash contents of the biochars derived from bamboo, melaleuca, rice husk, and water hyacinth pyrolyzed at 500 °C, 700 °C, and 900 °C. Data are presented as mean ± std. Different letters in the same material indicate significantly differences between the pyrolysis temperature (p<0.05); ns: non-significant.

It was apparent from Table 1 that the fixed carbon content increased gradually in response to the pyrolysis temperature due to the increased loss of volatile matter, which was consistent with previous studies (Crombie *et al.* 2013; Sun *et al.* 2017). This increasing trend of fixed carbon may indicate that the aromaticity correlated with the pyrolysis severity (Crombie *et al.* 2013). There was also a significant difference ($p < 0.05$) between the wood- and herbaceous-based biochars, where the bamboo and melaleuca biochars had higher fixed carbon contents by more than 25% compared with the rice husk and water hyacinth biochars. The fixed carbon content showed a strong negative linear relationship with the ash content ($R^2 = 0.86$, $p < 0.05$); therefore, the fixed carbon was higher in the low ash biochars and lower in the high ash biochars. Similar findings were reported by Sun *et al.* (2017), who found the well negative correlation between fixed carbon and ash content of 60 types of biomass waste.

The volatile matter/fixed carbon (VM/FC) ratio may be used as an indicator for biochar stability in soils, where a biochar with a VM/FC ratio of 0.5 to 1.0 can be stable in soils (Novak and Busscher 2013). The gradual decrease of the VM/FC ratio in the biochars produced at higher pyrolysis temperatures may have indicated increased stability of the biochars. Except for the water hyacinth biochars produced at 500 °C and 700 °C, which had VM/FC ratios higher than 1.3, all of the biochars could have long residence times and be used for carbon sequestration.

Higher heating value

The HHV refers to the maximum amount of energy that is available from burning biochar. Table 1 shows that the HHV of the wood-based biochars were significantly higher than those of the herbaceous-based biochars (as much as 2.5-fold higher, $p < 0.05$). Anderson *et al.* (2013) also reported that biochars derived from wood biomass had higher HHV, which might have been because of the higher carbon and hydrogen contents in the wood biomass (Fig. 3). A strong negative and statistically significant correlation ($R^2 = 0.98$, $p < 0.05$) between the HHV and ash content was found, which indicated that the higher ash contents in the rice husk and water hyacinth biochars decreased their energy values. Yang *et al.* (2017) also found strong negative correlation between HHV and ash content. However, the pyrolysis temperature was not found to significantly alter the HHV of the biochars.

pH and Electrical Conductivity (EC)

Figure 2 presents the dependency of the biochar pH and EC on the feedstock and pyrolysis temperature. While the pH of the wood-based biochars generally increased as the temperature increased from 500 °C to 900 °C (*i.e.*, increased from a pH of 7 to 8 to a pH of 9 to 10), the trend was not observed in the herbaceous-based biochars produced at 900 °C (Fig. 2a). The pH values of the wood-based biochars followed the trend found in literature and increased with higher pyrolysis temperature (Conz *et al.* 2017; Sun *et al.* 2017). The trend of pH values in the herbaceous-based biochars were found similar to the results of Zheng *et al.* (2015). Theoretically, an increase in the pyrolysis temperature can abolish acidic functional groups (*e.g.*, quinone, chromene, and diketone groups); hence, the biochars tended to be more alkaline (Mukherjee *et al.* 2011; Tsai 2017). A correlation analysis was conducted on the relationship between the concentration of Na^+, Mg^+, K^+, and Ca and the biochar pH, where the sum of Na, Mg, K, and Ca was calculated using the results given in Table 2. The results showed a moderately positive relationship ($R^2 = 0.63$, $p < 0.05$), which further confirmed the dependency of the biochar pH on the soluble salts concentration. Lopez-Capel *et al*. (2016). Tsai (2017) also stated that the biochar pH is dependent on mineral salt forms with oxide, carbonate, hydroxide, and chloride (such as KOH, NaOH, $CaCO_3$, and $MgCO_3$) that can be partially dissolved in water.

In Fig. 2b, EC results varied with greater influence of the type of feedstocks rather than the pyrolysis temperature, which was in agreement with the previous results (Conz *et al.* 2017; Hossain *et al.* 2011). The highest EC values were found in the water hyacinth biochars and ranged from 6489 μS/cm to 7456 μS/cm, while the rest of the biochars showed significantly lower values. Correlation analyses were conducted to evaluate the relationship between (a) the EC and ash content and (b) the EC and soluble salts concentration (K^+, Ca^{2+}, Mg^{2+}, and Na^+). The biochar EC had been shown to be reasonably correlated with the ash content ($R^2 = 0.53$, $p < 0.05$); however, it showed a strong linear and statistically significant correlation with the soluble salts concentration ($R^2 = 0.95$, $p < 0.05$). Therefore, differences in the EC of the biochars produced using different feedstocks might have been because of differences in the ash contents and soluble salts concentrations (primarily K^+, Ca^{2+}, Mg^{2+}, and Na^+) in the biochars (Rehrah *et al.* 2014). The water hyacinth biochars produced a high ash content (more than 44 wt.%$_{db}$), and the inorganic composition was dominated by K, Ca, Mg, and Na salts (as high as 360 g/kg$_{db}$); thus, its EC values were higher. The EC values of the bamboo biochars were more than double those of the melaleuca biochars, which was also related to the higher ash and soluble salts contents. The high ash content in the rice husk biochars was attributed mainly to the presence of silica (> 300 g/kg$_{db}$) and they contained a small amount of soluble salts (< 15 g/kg$_{db}$). Their EC values were therefore the lowest, at only 65 µS/cm to 92 µS/cm.

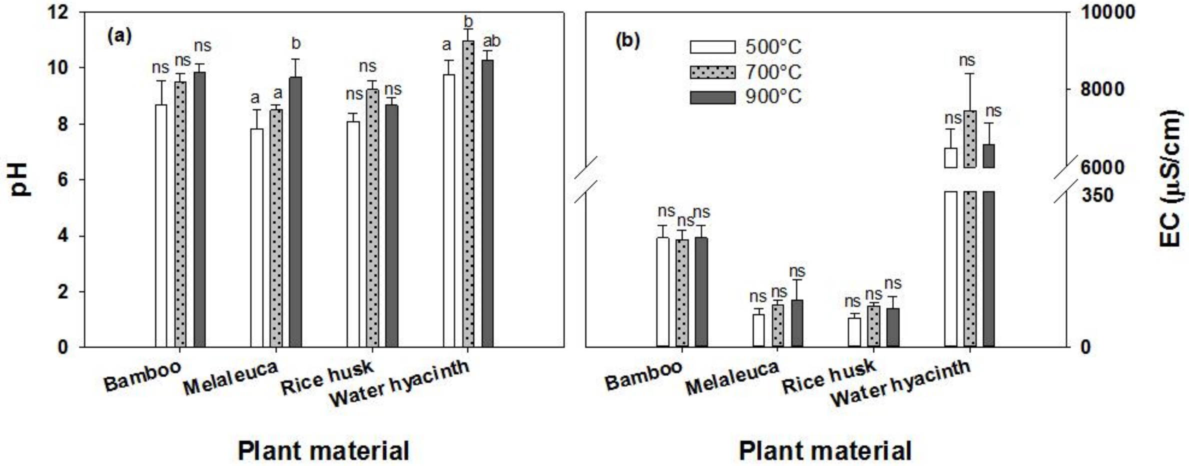

Fig. 2. (a) pH and (b) EC of the biochars derived from bamboo, melaleuca, rice husk, and water hyacinth pyrolyzed at 500 °C, 700 °C, and 900 °C. Data was presented as mean ± std. Different letters in the same material indicate significantly differences between the pyrolysis temperature ($p<0.05$); ns: non-significant.

To test the ability of the 12 biochars to increase the soil pH, the liming equivalence was determined (Table 1). The highest liming equivalence was found with the water hyacinth biochars and ranged from 6.56 %$CaCO_3$–eq to 8.36 %$CaCO_3$–eq, while the rest of the biochars had a liming equivalence of less than 3.17 %$CaCO_3$–eq. The biochars produced with the same feedstock and different pyrolysis temperatures also showed different liming equivalence values, where a greater liming equivalence was found for the biochars produced at a higher temperature, this was in agreement with other previous studies (Khanmohammadi *et al.* 2015; Singh *et al.* 2017). The liming equivalence was found to be extremely well correlated with the ash content ($R^2 = 0.99$, $p < 0.05$). However, no relationship was found in the rice husk biochars, which had the second highest ash content (34 wt.%$_{db}$ to 39 wt.%$_{db}$) and lowest liming equivalence (< 2.09 %$CaCO_3$–eq) among the studied biochars. These results were similar to the observations of Singh *et al.* (2017). The chemical composition of the ash would be a key reason for this result. For example, the greatest liming potential was found for the water hyacinth biochars, this attributed to the high amount of calcite and other carbonate minerals (such as magnesite) in their ash. In contrast, the ash in the rice husk biochars contained mainly elements of silica (> 300 g/kg$_{db}$) and a small amount of calcium and magnesium (< 5 g/kg$_{db}$ Ca and < 3 g/kg$_{db}$ Mg, Table 2), resulted in the smallest liming potential among the four studied biochars.

Elemental Characteristics

Figure 3 shows that the biochars had high C contents and low H, N, and O contents; the concentrations of these elements statistically varied. The biochars made from the wood-based materials had significantly greater C contents than those made from the herbaceous materials and were as much as 2.4-fold higher ($p < 0.05$). Ma *et al.* (2018) also found higher C content in woody compared to herbaceous biomasses. The water hyacinth biochars contained the lowest C and H contents and the highest O and N contents. With an increase in the pyrolysis temperature, the C content increased, while the H and O contents decreased. Losses in the H and O may have been because of the breaking of weaker bonds within the biochar structure, and the biochar became highly carbonaceous at a higher temperature as a result (Capareda 2013). It is well known that the proportion of aliphatic C decreases and the proportion of aromatic C increases with an increasing pyrolysis temperature. Because of the pyrolysis temperature, the aliphatic C, O, and H were removed because of losses of water, H_2, CO, and CO_2 from the biomass through heating and reorganisation of the chemical structure of the material (*i.e.*, changing from long molecular chains to a ring-like structure with six C atoms) (Schimmelpfennig and Glaser 2012).

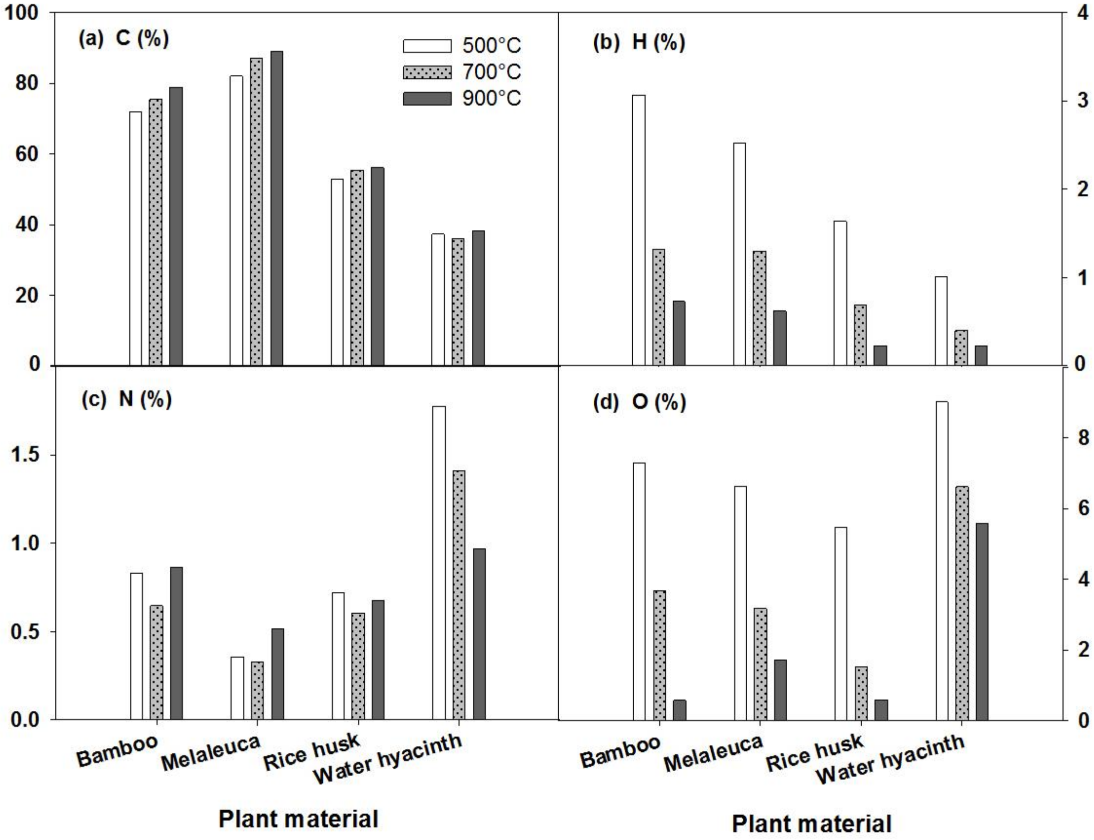

Fig. 3. (a) C, (b) H, (c) N, and (d) O contents in the biochars derived from bamboo, melaleuca, rice husk, and water hyacinth pyrolyzed at 500 °C, 700 °C, and 900 °C (values are the average of duplicate analyses on an oven-dry ash-free basis)

To compare the carbon sequestration ability of the 12 biochars, the H/C and O/C ratios were displayed in van Krevelen diagrams (Fig. 4). Although the 12 biochars had ratios that were within the recommended range ($H/C < 0.6$ and $O/C < 0.4$) suited for sequestering carbon (Schimmelpfennig and Glaser 2012), there were some differences in the H/C and O/C ratios between the different feedstocks and pyrolysis temperatures. The H/C and O/C ratios of the biochars decreased gradually with an increasing pyrolysis temperature, which might have been because of the removal of polar surface functional groups, losses of O and H, and increase of aromatic C with an increasing pyrolysis temperature (Cantrell *et al.* 2012). Therefore, biochars produced at a higher temperature would be less polar and would have a greater stability and aromaticity, which may lead to a more hydrophobic character. The diagram showed that at the same pyrolysis temperature, there was significantly higher O/C ratio in the water hyacinth biochars ($p < 0.05$), while the other biochars were closely spaced, which suggested similar behaviors. In combination with the reported higher VM/FC ratios from the proximate analysis, it was concluded that the water hyacinth biochars may be the least suited for carbon sequestration among the studied biochars.

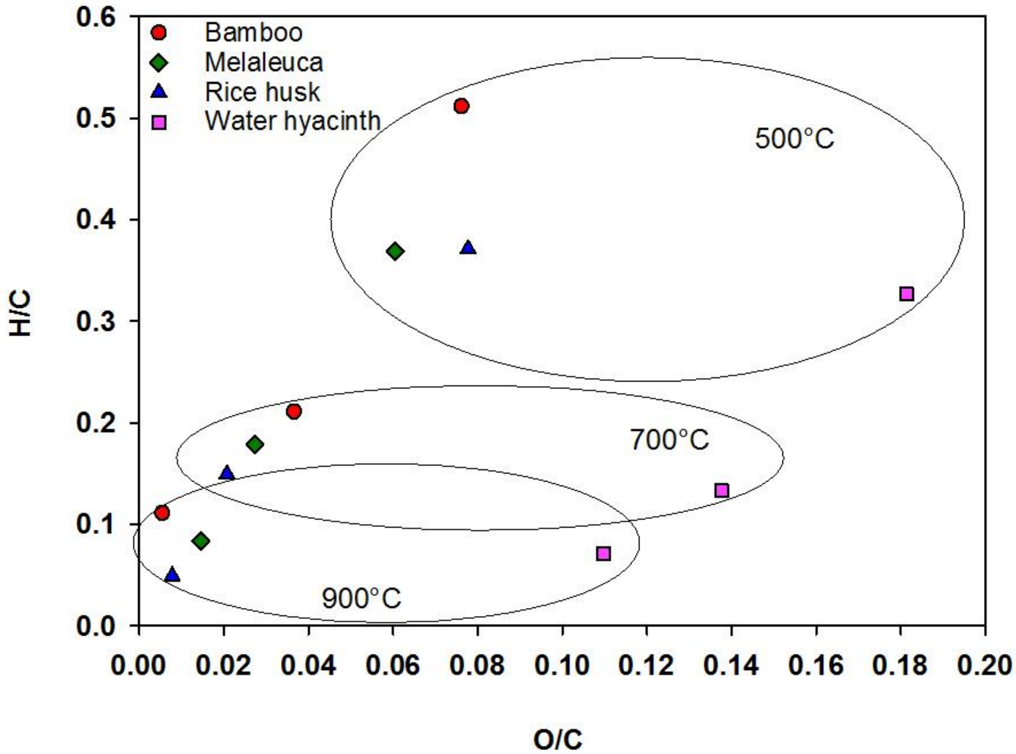

Fig. 4. van Krevelen plot (H/C *versus* O/C ratios) of the biochars derived from bamboo, melaleuca, rice husk, and water hyacinth pyrolyzed at 500 °C, 700 °C, and 900 °C

The C/N ratios in the biochars, where different feedstocks produced variable C/N ratios, are also included in Table 1. The wood-based biochars had a statistically higher C/N ratio than the biochars made from herbaceous residues ($p < 0.05$); this was consistent with data analysed by Sun *et al.* (2017). During pyrolysis, the N content either decreased or increased, and this trend was not well understood or explained. Volatilisation of gaseous NH_3 and N-containing volatile organic compounds may have led to the losses in the N content; meanwhile, recalcitrant N occurring in heterocyclic compounds may have been able to increase the N content (Kazi *et al.* 2010). An increasing trend of the C/N ratio was found when the pyrolysis temperature increased from 500 °C to 700 °C, and then suddenly decreased at 900 °C, except for the water hyacinth biochar produced at 900 °C. Most of the biochars possessed a C/N ratio greater than 30, and only the water hyacinth biochars produced at 500 °C and 700 °C had C/N ratios of less than 30. The high range of C/N ratios in the biochars indicated that they may lead to increased N immobilisation by microorganisms in soils. However, N immobilisation may not have necessarily occurred in the biochars because of the large, highly recalcitrant C fraction (Chan and Xu 2009). Most of the N in biochars is incorporated into heterocyclic C structures and thus is unavailable for use by both microbes and plants (Jeffery *et al.* 2015). The N immobilisation process is dependent upon the magnitude of the labile C fraction; however, the C content determined by the ultimate analysis consisted of both relatively stable aromatic C and relatively labile aliphatic C (Steiner *et al*. 2016). Therefore, the C and N of the labile fraction may be more useful when expressing the C/N ratio of biochars (Cross *et al.* 2016).

Nutrient Characteristics

The nutrient contents of the biochars are shown in Table 2. There was an unclear effect of the pyrolysis temperature on the nutrient availability. The data illustrated that an increasing pyrolysis temperature produced mixed results in the available nutrients in the biochars, as reported by Ippolito *et al.* (2015). While some nutrients, such as Fe and Zn, increased from 500 °C and reached their maximum values at 700 °C, other nutrient contents showed increasing and decreasing trends with an increasing pyrolysis temperature.

Table 2. Mean Mineral Analyses of the Biochars Derived from the Pyrolyzed Bamboo, Melaleuca, Rice Husk, and Water Hyacinth

Feedstock	Bamboo			Melaleuca			Rice Husk			Water Hyacinth		
Pyrolysis Temperature (°C)	500	700	900	500	700	900	500	700	900	500	700	900
Si (g/kg$_{db}$)	37.2	75.4	41.3	11.2	9.2	24.8	312.7	417.9	311.8	14	15.4	18.9
P (g/kg$_{db}$)	3.2	6.4	9.5	1.9	2.3	4.1	0.6	1.7	1.8	5.6	6	7.9
Ca (g/kg$_{db}$)	8.7	10	13.8	14.9	16.4	16.5	4.9	4.5	5.2	58.4	75.9	71.8
K (g/kg$_{db}$)	29.5	43.2	39.6	8.3	7.8	11.3	9.1	7.4	6.9	166.2	267.5	227.3
Na (g/kg$_{db}$)	1.5	2.7	1	3.3	2.9	2.6	0.3	1.8	0.6	3.2	3	5.3
Mg (g/kg$_{db}$)	9.3	20.4	14.5	5.1	4.1	4	1.3	1.0	3.2	13.1	13.1	16.4
Al (g/kg$_{db}$)	1.8	1.2	1.1	1.2	3.3	2.7	1.7	1.5	1.8	4.8	6.1	7.7
Fe (g/kg$_{db}$)	11.9	6.1	2.4	3.9	6.5	2.5	4.8	5.2	5.3	7.5	8.6	8.7
Cu (g/kg$_{db}$)	41.1	61.1	62.7	48.3	57	47.9	27.8	36.1	27.6	34.9	36.0	39.0
Zn (g/kg$_{db}$)	29.8	50	45.6	44.6	41.4	32	27.6	23.9	19.2	25.5	30.5	28.7

Significant differences in the available nutrients were observed among the four types of biochar. In comparison, the available Ca, K, and Al in the water hyacinth biochars were significantly higher than in the other biochars. The rice husk biochars contained a statistically significant amount of Si, but lower contents of the other elements (*e.g.*, P, Ca, K, Na, Mg, Cu, and Zn), consistent with data reported by Prakongkep *et al.* (2013). The bamboo biochars were generally richer in Si, K, P, Mg, and Cu than the melaleuca biochars. The variation in the nutrient concentrations in the biochars may have been because of differences in the type of soil or water, available plant nutrients, and chemicals added to manure during plant growth. For example, the growth of water hyacinth is favoured in water that is rich in nutrients, especially N, P, K, and Ca (Labrada *et al.* 1994). In contrast, rice plant species need large quantities of Si for their development. In the Mekong Delta, melaleuca mainly grows with little or no human disturbance or intervention in natural forests, which are typically low in nutrient contents compared with planted bamboo forests and agricultural soils. During growth, these plants take up nutrients from the soil or water and assimilate them into their biomass structures; therefore, they accumulate and concentrate in the corresponding biochar during pyrolysis.

FTIR Characteristics

The FTIR spectra are presented in Fig. 5. The infrared band assignments were interpreted based on the characteristic vibrations in the biochars produced from the wood and herbaceous residues (Guo and Chen 2014; Mukome *et al.* 2014; Parikh *et al.* 2014; Xiao *et al.* 2014).

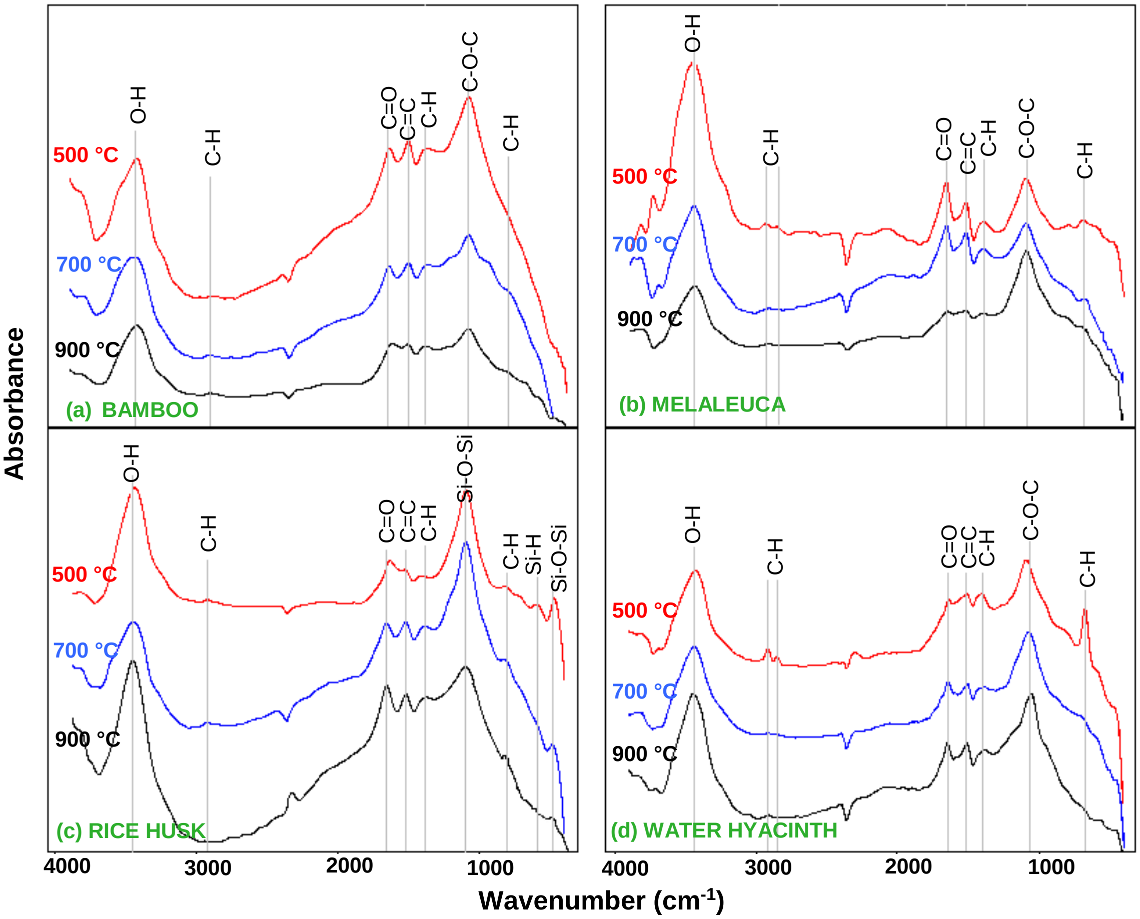

Fig. 5. FTIR spectra of the biochars derived from (a) bamboo, (b) melaleuca, (c) rice husk, and (d) water hyacinth pyrolyzed at 500 °C, 700 °C, and 900 °C

Over the entire temperature range, the peak strengths of the spectra changed slightly. Increasing the pyrolysis temperature led to spectra with decreased intensities of the O-H, aliphatic C-H, and C-O-C peaks and increased intensities of the peaks representative of aromatic moieties. The O-H peaks slightly decreased in the biochars produced at 500 °C to 900 °C because of dehydration reactions. The aliphatic C-H band was almost eliminated in the higher temperature biochars, which indicated that aliphatic C-H bonds had been broken into CO_2 and H_2O. The cleavage of hemicellulose and cellulose were recognized because of the slight reduction in the peaks at approximately 1040 cm^{-1} (corresponding symmetric C-O-C ester) in the biochars.

Increasing the pyrolysis temperature resulted in increasing aromatic C groups, with minor contributions of carbonyl-C, O-alkyl-C, and alkyl-C moieties (Novak *et al.* 2009). However, it was rather difficult to observe this trend in the FTIR spectra because of unclear peaks for aromatic and other forms of recalcitrant C. The existence of the peaks at approximately 785 cm^{-1} and 1319 cm^{-1}, which corresponded with aromatic C-H groups, and the slight elimination of the peaks at approximately 2926 cm^{-1}, which corresponded to aliphatic C-H groups, may have indicated the forming of aromatic rings during pyrolysis. Also, the existence of aromatic C=C and C=O groups, which were the absorption peaks at approximately 1590 cm^{-1} and 1641 cm^{-1}, respectively, were also maintained during pyrolysis at 500 °C to 900 °C.

There was some overlap of groups that appeared in the adsorption bands in the region of 1040 cm^{-1} to 1100 cm^{-1}, which made making definitive assignments difficult. While the C-O-C symmetric stretching of pyranose rings and guaiacyl monomers of cellulose and hemicellulose were identified at approximately 1040 cm^{-1} to 1100 cm^{-1}, Si-O-Si asymmetric vibrations also appeared in this range (Lee *et al.* 2010). Similarly, it was difficult to distinguish between the bending of networked Si-O-Si symmetrical vibrations and hemicellulose aromatic C-H bonds in the adsorption band at 785 cm^{-1} to 897 cm^{-1}. Nevertheless, considering the high Si content in the rice husk biochars, as was determined by the EDX, the broad bands near 1040 cm^{-1}, 785 cm^{-1}, and 467 cm^{-1} likely resulted from Si-O-Si functional groups (*i.e.*, asymmetric, symmetric, and flexural Si-O-Si), as well as Si-H stretching vibrations recognized as the broad peak from 469 cm^{-1} to 800 cm^{-1}. In contrast, for the low Si-containing biochars, *i.e.*, bamboo, melaleuca, and water hyacinth, the C-O-C symmetric stretching bands and aromatic C-H bonds were identified by peaks centered at approximately 1040 cm^{-1} and 785 cm^{-1}, respectively. Therefore, it was concluded that the peaks were almost similar and only varied slightly in the peak strengths of the spectra between the biochars, except for that of the rice husk biochars with Si-containing groups.

CONCLUSIONS

Briefly, the melaleuca- and bamboo-derived biochars possessed less than 14 $wt.\%_{db}$ ash, less than 246 $\mu S/cm$ EC, less than 3.17 $\%CaCO_3$–eq, and less than 76 g/kg_{db} soluble salts; therefore, they can be applied to most kinds of plants and soils. The high HHV values of greater than 23 MJ/kg also suggested their potential use for producing various energy forms, such as steam, heat, and fuels (*i.e.*, biogas, syngas, bio-oils, and solid fuel). Their O/C, H/C, and VM/FC ratios were less than 0.08, 0.51, and 0.61, respectively, which may have meant that they are also suited for sequestering carbon. The rice husk biochars possessed more than 300 g/kg_{db} Si, which can be useful for silicophilic plants, such as rice.

The water hyacinth biochars possessed pH values greater than 9.8, greater than 6.56 %$CaCO_3$–eq, greater than 6489 μS/cm EC, and greater than 240 g/kg_{db} soluble salts; therefore, a high rate application of these biochars to soil can significantly increase the soil pH, EC, and soluble salts concentration for plants or soils, which may not be suitable for salt-sensitive plants or low-buffer capacity soils.

Based on the results presented and discussed above, the following conclusions were highlighted:

1. Higher pyrolysis temperatures produced biochars with higher ash contents, fixed carbon contents, pH values, EC values, liming equivalences, HHVs, and proportions of carbon; however, they had lower volatile matter and moisture contents.
2. The effect of the pyrolysis temperature on the available nutrients, C/N ratio, and CEC showed mixed trends, with an initial increase from 500 °C to 700 °C and then a subsequent decrease at 900 °C. The CEC results indicated that the biochars produced at 700 °C possessed high CEC values and may have had a greater capacity to maintain adequate quantities of essential nutrients, such as Ca^{2+}, Mg^{2+}, and K^+, in soils with a low CEC, *i.e.*, through electrostatic interactions. They also may have had a stronger adsorption capability for cationic organic compounds or metals than those produced at 500 °C and 900 °C.
3. The bamboo and melaleuca resulted in low ash biochars (14 wt.%$_{db}$ ash) with high fixed carbon contents (> 54 wt.%$_{db}$), whereas the water hyacinth and rice husk resulted in high ash biochars (> 34% ash) with low fixed carbon contents (< 45 wt.%$_{db}$).
4. It was concluded that the bamboo and melaleuca biochars may be more suitable to use as solid fuels because of their high HHVs, as soil amendment because of the relatively low amount of salt nutrients, or for carbon sequestration because of their high degree of aromaticity and stability (*i.e.*, low H/C, O/C, and VM/FC ratios).
5. The rice husk biochars contained more than 300 g/kg Si, which makes it an excellent bioavailable silicon source for silicophilic plants.
6. The water hyacinth biochars contained a high soluble salts concentrations and EC values, which likely makes them unsuitable for use in soil that already has a high level of soluble salts. Their high pH and liming equivalence values may also make them inapplicable for low-buffer capacity sandy soils.

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