Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes

Mohammad I. Al-Wabel*, Abdulrasoul Al-Omran, Ahmed H. El-Naggar, Mahmoud Nadeem, Adel R.A. Usman*

Soil Sciences Department, College of Food & Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

HIGHLIGHTS

▶ Conocarpus wastes were pyrolyzed at different temperatures of 200, 400, 600 and 800 °C.
▶ Biochar produced at high pyrolysis temperature enjoys higher carbon stability compared to that obtained at low temperature.
▶ Biochar produced at high pyrolysis temperature may possess a higher carbon sequestration potential when applied to the soil.

ARTICLE INFO

ABSTRACT

Conocarpus wastes were pyrolyzed at different temperatures (200–800 °C) to investigate their impact on characteristics and chemical composition of biochars. As pyrolysis temperature increased, ash content, pH, electrical conductivity, basic functional groups, carbon stability, and total content of C, N, P, K, Ca, and Mg increased while biochar yield, total content of O, H and S, unstable form of organic C and acidic functional groups decreased. The ratios of O/C, H/C, (O + N)/C, and (O + N + S)/C tended to decrease with temperature. The data of Fourier transformation infrared indicate an increase in aromaticity and a decrease in polarity of biochar produced at a high temperature. With pyrolysis temperature, cellulose loss and crystalline mineral components increased, as indicated by X-ray diffraction analysis and scanning electron microscope images. Results suggest that biochar pyrolyzed at high temperature may possess a higher carbon sequestration potential when applied to the soil compared to that obtained at low temperature.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The major negative effect of burning agricultural wastes is the release of carbon dioxide gas (CO_2), which is the most important greenhouse gas produced by human activities. Carbonization of woody wastes to produce biochar, charcoal like product, has been suggested to avoid negative impacts of direct burning. As the biochar is resistant to biological decay, it is preserved in the terrestrial systems for much longer time than for example plant residues or compost therefore; the beneficial effects are extended (Lehmann, 2007; Lehmann et al., 2011). Therefore, carbonization through pyrolysis to produce biochar is a successful mean to avoid the negative impacts on human health and environment. Biochar is the black solid containing recalcitrant organic carbon (OC), which helps in global warming mitigation (Lehmann et al., 2011). In the

meantime, incorporation of biochar into soil can be used as a soil conditioner to enhance soil fertility, mainly due to its high sorptive capacity for water and nutrients (Chan et al., 2007, 2008). Recent studies showed that, in addition to reducing emission of CO_2, applying biochar to the soils increased their pH, CEC, level of a highly stable OC and nutrient content (Novak et al., 2009; Hossain et al., 2010; Major et al., 2010). Additionally, biochar application in environmental remediation as an effective adsorbent is also reported (Cao and Harris, 2010; Yao et al., 2011). Several studies demonstrated that the quality and chemical composition of biochar depend on feedstock and production conditions (Demirbas, 2004; Gaskin et al., 2008; Hossain et al., 2011; Song and Guo, 2012; Bruun et al., 2012). Therefore, it is possible to produce different types of biochars by altering feedstocks and pyrolysis conditions and selection of biochar type, in terms of its favorable contributions to soil, is mainly dependent upon both biochar and soil properties. For example, the biochars characteristics combined with their amelioration effects on soil pH were studied by Yuan et al. (2011), who reported that biochars produced from crop

* Corresponding authors. Tel.: +966 504415145; fax: +966 14678440.
E-mail addresses: malwabel@ksu.edu.sa (M.I. Al-Wabel), adelusman71@yahoo.com (A.R.A. Usman).

straws at 500 °C have greater amelioration effects on soil acidity compared with the biochars produced at 300 °C. Novak et al. (2009) investigated the influence of biochars (produced from peanut hulls, pecan shells, poultry litter and switchgrass at different temperature) on a loamy sand and found that biochars produced from different feedstocks and under different pyrolysis temperatures influenced physical and chemical properties in different ways. It might be expected that the main problematic with applying biochar to arid soils having alkaline reaction may be due to its high pH and salinity as a result of pyrolysis process. Therefore, selection of appropriate raw materials and optimization of pyrolysis technology and settings to produce suitable biochar product should be taken into our consideration.

To our knowledge, there is no research to date on the production and characterization of biochar produced from conocarpus wastes via pyrolysis in literature. Therefore, in this study, conocarpus residues were selected as biomass source for producing biochar. *Conocarpus erectus* L. (Button mangrove) is an evergreen tree planted in Saudi Arabia around parking lots and along streets. Its wood is hard and durable and it has high calorific value as fuel but it is most widely used for high-grade charcoal (Morton, 1981). According to the Municipal Council of the city of Riyadh, management and recycling of *Conocarpus erectus* is problematic due to its huge aboveground biomass, and widespread. Therefore, converting of conocarpus wastes into biochar may be considered as a tool for waste disposal and recycling option.

The aim of this work is to investigate the effect of pyrolysis temperature on characteristics and chemical composition of the produced biochar from conocarpus wastes to evaluate its suitability for carbon sequestration and agricultural use.

2. Methods

2.1. Production of conocarpus wastes

Conocarpus wastes were collected, dried and then chopped to small pieces. After that, pyrolysis of conocarpus wastes was performed using a closed system, which was synthesized from stainless steel and has a height of 22 cm and diameter of 7 cm. The pyrolysis process was conducted for 4 h to produce conocarpus biochars at different temperatures of 200, 400, 600 and 800 °C under oxygen-limited conditions. Char yield was calculated and the biochar samples were ground for further analysis.

2.2. Characterization of conocarpus biochar

Ash content of biochars samples were determined by dry combustion at 760 °C for 6 h (Novak et al., 2009). The ash content was determined according the following equation:

$$Ash\,content\,(\%) = (weight\,of\,ash/dry\,weight\,of\,biochar) \times 100$$

For total content of elements in biochar samples, total biochar C, H, N and S were measured by CHNS analyser. The percentage of oxygen content was estimated by difference as follows: O (%) = 100 − (C + H + N + ash) (Calvelo Pereira et al., 2011). Different atomic ratios (O/C, H/C, O + N/C, and O + N + S/C) were also calculated in this study. In addition, biochar samples were analyzed for elemental content of P, Ca, Mg, K by dry ashing at 760 °C for 6 h. The ash was dissolved in a hydrochloric acid and then analyzed. The total content of K were determined by using flame photometer. The total content of Ca and Mg was determined by titration using EDTA. Moreover, the total content of P was measured by using spectrophotometer (Sparks, 1996).

Biochar pH and electrical conductivity (EC) were measured with a glass electrode using a biochar-to-water ratio of 1:10. Biochar pH was also measured in a suspension of biochar-to-KCl ratio of 1:10. The ΔpH values were estimated by difference as follows: ΔpH = pH (biochar to KCl ratio of 1:10) − pH (biochar to water ratio of 1:10).

The titration curves exhibited the response of the biochar samples to the changes in the pH value following acid addition were determined (Kun-yu et al., 2008). The quantity of acidic and basic functional groups was measured by the Boehm method (Boehm, 1994).

2.3. Labile C and stable C in biochar

Two labile fractions of organic carbon were determined including: dissolved organic C and unstable organic C of biochar samples. Dissolved organic C (DOC) was measured in an aqueous extract (1:10). The unstable organic C was measured with potassium dichromate method as described in Song and Guo (2012). The overall stable form of carbon was calculated by the difference between the total content of carbon and unstable form of organic carbon in biochar.

2.4. Profiling of biochar structure

The thermogravimetric (TG) analyses of the biochars samples were employed to determine changes in weight of biochar in relation to temperature. Scanning electron microscope (SEM) (FEI, Inspect S50) imaging analyses of bio-char samples were conducted to identify the changes in the surfaces and structure of biochar. The Fourier transformation infrared analysis of bio-chars samples were achieved using FTIR (Nicolet 6700 FTIR) in the range of 500–4000 cm^{-1} wavenumbers to characterize the surface organic functional groups for biochar samples. X-ray diffraction analysis (XRD-7000 Shimadzu) was also carried out to identify any crystallographic structure in the produced biochars.

2.5. Statistical analysis

The statistical analysis of the data was performed by using Statistica for Windows statistical software (StatSoft, 1995).

3. Results and discussions

3.1. Yield and ash content of conocarpus biochar

The yield and ash content of biochar produced at different pyrolysis temperatures are presented in Table 1. The results showed that the yield of conocarpus biochar was reduced by increasing pyrolysis temperature and ranged from 51.33% to 23.19%. Specifically, the yield of biochar was reduced from 51.33% at 200 °C to 31.86%, 27.22%, 23.19% at 400, 600 and 800 °C, respectively. This decline in yield content is mainly due to the destruction of some compounds such as cellulose and hemicellulose as well as combustion of organic materials with increased pyrolysis temperature (Demirbas, 2004; Cao and Harris, 2010). Muradov et al. (2012) attributed the decrease in biochar yield with temperature to increased volatilization rate of the organic compounds. Yang et al. (2004) suggested that moisture is evolved at 220 °C, hemicelluloses are decomposed at 220–315 °C, and cellulose is decomposed at 315–400 °C, whereas the decomposition of lignin occurs at 400 °C. Novak et al. (2009) explained the high recovery of biochar at the low pyrolysis temperatures by minimal condensation of aliphatic compounds, and lower losses of CH$_4$, H$_2$ and CO. In addition, they attributed the decline in biochar yield with increased temperature to dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures.

By contrast to biochar yield, the biochar ash content increased significantly with increasing pyrolysis temperature. Similarly, Ozç-

Table 1
Effect of pyrolysis temperature on yield and ash of biochar.

Parameters	Feedstock	Pyrolysis temperature (°C)			
		200	400	600	800
Yield (%)	–	51.33 ± 2.38	31.86 ± 1.19	27.22 ± 0.57	23.19 ± 0.65
Ash (%)	3.18	4.53 ± 0.07	5.27 ± 0.04	8.56 ± 0.02	8.64 ± 0.01

Table 2
Effect of pyrolysis temperature on pH, EC and ΔpH of biochar derived from conocarpus wastes.

Pyrolysis temperatures (°C)	EC (dS m^{-1})	pH (Water)	pH (KCl)	ΔpH
200	0.76 ± 0.004	7.37 ± 0.01	6.69 ± 0.01	−0.68 ± 0.02
400	1.34 ± 0.01	9.67 ± 0.01	9.51 ± 0.02	−0.16 ± 0.03
600	9.03 ± 0.04	12.21 ± 0.02	12.52 ± 0.01	0.31 ± 0.03
800	10.26 ± 0.04	12.38 ± 0.02	12.70 ± 0.01	0.32 ± 0.01

imen and Ersoy-Meriçboyu (2010) found that the ash content of feedstock was higher than that in biochar, mainly due to the mineral matter forming ash remains in biochar following carbonization. The percentage of ash content was increased from 3.18% for feedstock to 4.53%, 5.27%, 8.56 and 8.64% for biochar pyrolyzed at 200, 400, 600 and 800 °C, respectively (Table 1). In general, the low ash content could be explained by low silica content of woody feedstock. It has been reported that the ash content of biochar produced from woody materials was lower than that produced from some grasses and straws (Amonette and Joseph, 2009).

3.2. pH and EC of conocarpus biochar

The results of this study showed that the feedstock samples have an acidic pH of 5.41 (in 1:10 ratio of biochar to water). However, the produced biochars lie in the range of weakly basic to alkaline, depending on pyrolysis temperature. Among biochar samples, the lowest pH value (7.37) was recorded at lowest pyrolysis temperature (200 °C). However, this value increased sharply and reached 9.67 (at 400 °C), 12.21 (at 600 °C) and 12.38 (at 800 °C). These increases in pH values are mainly due to separating of alkali salts from organic materials by increased pyrolysis temperature (Yuan et al., 2011). As indicated by the data of ΔpH, the biochar samples at 200 and 400 °C showed net negative surface charge, whereas 600 and 800 °C biochar samples indicated a net positive surface charge.

The electrical conductivity (EC) has been used to give an indication for the salinity. The EC values in the samples of biochar produced at 200 and 400 °C, respectively, were 0.76 and 1.34 dS m^{-1}. However, these values sharply increased with the pyrolysis temperature up to 600 and 800 °C and amounted to 9.03 and 10.26 dS m^{-1}, respectively (Table 2). These results suggest that biochar produced at high pyrolysis temperature (especially at 600 and 800 °C), when applied to the soil, may increase soil salinity and subsequently provide undesirable impacts on the plant growth. It has been reported that the negative impacts of high salinity on the plant growth could be due to the following reasons: (1) the low osmotic potential of the soil solution, resulting in water stress, (2) specific ion effects, resulting in salt stress, and (3) nutrient imbalances (Martinez-Ballesta et al., 2006).

3.3. Acid neutralizing ability and Boehm titration for conocarpus biochars

In this study, titration curves exhibit the response of the biochar samples to the changes in the pH value as acid is added (Fig. 1). The results indicated that biochar samples pyrolyzed at a high temper-

ature, especially at 800 °C, had a higher buffering capacity than those at a low temperature. This high buffering capacity can be explained by the presence of some functional groups that lead to strong buffering capacity. Our results suggest that the increased quantity of surface basic groups with temperature might be responsible for buffering the solution strongly.

In this connection, the functional groups on the surface of biochars can be selectively measured by titration according to Boehm. The amounts of the surface acidic and basic of the biochar are shown in Fig. 2. In fact, the functional groups could be considered as a property to determine the sorptive capacity of biochars for ionic solutes (Song and Guo, 2012). The results of this study showed that the total surface acidity was higher in biochars produced at the low-pyrolysing temperature than in those produced at high-temperature. The surface acidic groups in the sample of biochars produced at 200, 400, 600 and 800 °C, respectively, were 4.17, 1.46, 0.57, and 0.22 mmol/g biochar.

By contrast, the total surface basicity increased with increasing pyrolysis temperature. The surface basic groups in the sample of biochars produced at 200, 400, 600 and 800 °C, respectively, were 0.15, 2.00, 3.40 and 3.55 mmol/g biochar. Generally, the obtained data of surface acidic and basic groups are consistent with the increased pH values of conocarpus biochars when pyrolysis temperature increased.
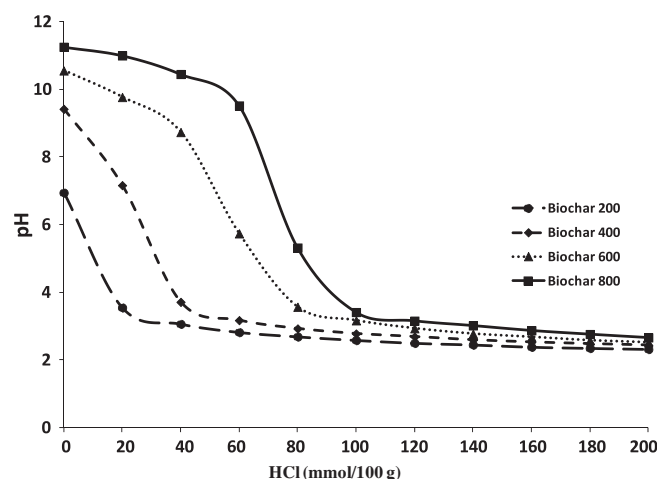
Fig. 1. Titration curves for conocarpus biochars pyrolyzed at different temperatures.
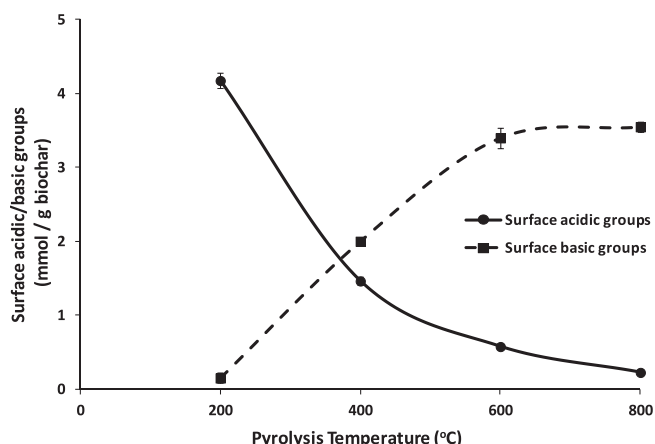
Fig. 2. Effect of pyrolysis temperature on surface functional groups of conocarpus biochar.

3.4. Elemental content of conocarpus biochars

The elemental content of biochars is presented in Table 3. The data showed that carbon content increased with temperature, but the loss of O, H and S was recorded. The increase in carbon content with temperature is due to increasing degree of carbonization. However, these decline in O and H elements may be attributed to breaking of weaker bonds in biochar structure and highly carbonaceous materials yielded with increased temperature (Imam and Capareda, 2012; Demirbas, 2004). The decrease in S with temperature could be explained by the volatilization of sulfur during pyrolysis process. Though it has been reported by many authors that pyrolysis temperature lead to reduce N content of biochars (Song and Guo, 2012), relative increases in N content were observed in samples of biochar with temperature in this study. Our results suggest that temperature could conserve N in wood chars. This can be explained by incorporation of N into complex structures that are resistant to heating and not easily voltilized (Gaskin et al., 2008). In consistent with our results, Calvelo Pereira et al. (2011) also found that N enrichment relative to the original feedstock was recorded upon charring of woody material.

The results of the present study showed that other essential nutrients (Ca, Mg, K and P) increased with pyrolysis temperature, mainly due to concentrated of these elements in biochar samples with temperature. Additionally, these elements might not be lost by volatilization (Novak et al., 2009). As compared to nutrients content in feedstock, the total content of Ca, Mg, K and P increased by 232%, 199%, 304% and 68%, respectively, when pyrolysis process conducted at a temperature of 800 °C. This increase in alkaline elements could be responsible for liming effects induced by biochar pyrolyzed at high temperatures.

Table 3
Effect of pyrolysis temperature on elemental composition of biochar.

Parameters	Units	Feedstock	Pyrolysis temperature (°C)			
			200	400	600	800
C	%	44.96	64.19	76.83	82.93	84.97
O	%	45.82	26.61	14.16	6.55	4.87
H	%	5.41	3.96	2.83	1.28	0.62
N	%	0.62	0.69	0.87	0.71	0.90
S	%	2.81	2.28	1.72	0.91	0.58
Ca	g kg^{-1}	20.3	43.4	51.8	64.7	67.5
Mg	g kg^{-1}	2.61	3.43	3.98	4.79	7.81
K	g kg^{-1}	0.29	0.38	0.54	0.90	1.15
P	g kg^{-1}	0.80	0.84	0.88	1.11	1.34

Table 4
Effect of pyrolysis temperature on the atomic ratios of biochar.

Atomic ratio	Feedstock	Pyrolysis temperature (°C)			
		200	400	600	800
O/C	1.019	0.414	0.184	0.079	0.057
H/C	0.120	0.062	0.037	0.015	0.007
(O + N)/C	1.033	0.425	0.196	0.088	0.068
(O + N + S)/C	1.095	0.461	0.218	0.099	0.075

The calculated atomic ratios of O/C, H/C, (O + N)/C, and (O + N + S)/C are presented in Table 4. The results showed that feedstock samples have highest values of these ratios, whereas these ratios tended to decrease with pyrolysis temperature. The decrease in the O/C ratios with temperature is associated with dehydration reactions and resulting in less hydrophilic biochar surface (Chun et al., 2004; Ahmad et al., 2012). In addition, the decrease in the H/C ratio is associated with degree of carbonization. The lowest H/C ratio (0.007) at 800 °C suggests that the biochar is highly carbonized, indicating higher aromaticity at 800 °C compared to other employed temperature, especially at the lowest one (200 °C). By contrast, among biochar samples, the highest H/C ratio (0.062) found at 200 °C indicates that the biochar has considerable quantities of organic materials. These results are in agreement with those obtained by Ahmad et al. (2012). The highest ratio of the (O + N)/C at 200 °C indicates that biochar samples contains polar functional groups which tended to decrease with temperature (low O + N/C), suggesting an increase in aromaticity and a decrease in polarity of biochar produced at a temperature of 800 °C (Ahmad et al., 2012).

3.5. Labile and fixed C of biochar

It is very important to evaluate the effects of production temperature on the stability of biochar C against biological decay. Therefore, fixed and labile pools via unstable (oxidizable C by acidic dichromate) and dissolved organic C were evaluated. As can be seen from the results given in Fig. 3, the fixed carbon (stable pool) increased with increasing pyrolysis. However, unstable organic carbon and dissolved organic carbon decreased with temperature. Similarly, Song and Guo (2012) found that the recalcitrant portion of biochar OC resistant to oxidation increased as the pyrolysis temperature was elevated. In this study, it was observed that the rates of increases or decreases in different pools of C were very high when temperature increased from 200 to 400 °C. However,
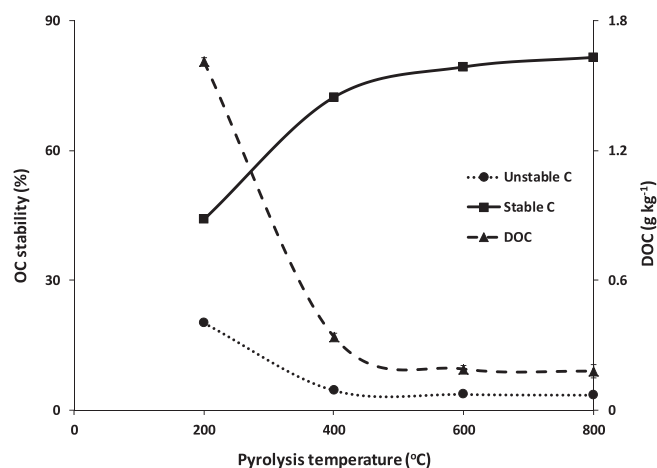

Fig. 3. Effect of pyrolysis temperature on overall C stability and dissolved organic carbon (DOC) for conocarpus biochar.

with further temperature, these rates were decreased to a small extent. Our results suggest that acidity and alkalinity of biochars are related with these different fractions of carbon as well as acidic/basic groups of biochars. It can be concluded generally that biochars produced at high temperature could be resistant to biological decay and preserved in the terrestrial systems for much longer time than for biochars produced at the lowest one, thus resulting in slowly release of CO_2 to the atmosphere. In an incubation experiment to study application effect of biochars pyrolyzed at different temperatures on CO_2-efflux, Calvelo Pereira et al. (2011) found that high temperature biochar induced a lower CO_2 efflux than low temperature biochar.

3.6. FTIR, SEM, TG and XRD analysis for conocarpus biochar

The FTIR analysis revealed that a high peak at about 3400 cm^{-1} was observed in the spectra of feedstock (data not shown), indicating the presence of O–H stretching and strong hydrogen bonding. However, the intensity of this peak decreased with increasing pyrolysis temperature, suggesting an ignition loss of OH at the increased temperature (Yuan et al., 2011) The absorption peaks at 2925, 1734, 1621 cm^{-1} were also found in the spectra of feedstock (with higher intensity) or biochars pyrolyzed at low temperature (with lower intensity) and these peaks are evidence for C–H stretching, C=O stretching of the ester bond and C=C stretching in the aromatic ring, respectively. In addition, some appeared peaks for feedstock ranged from 700 to 1600 cm^{-1} suggested the presence of cellulosic and ligneous constituents. The vibrations, which lie in the range of 1500–1640 cm^{-1}, are mainly responsible for lignin in feedstock. However, these peaks tended to be diminished at a pyrolysis temperature of 600 and 800 °C. These data in consistent with those of atomic ratios indicate that polar functional groups tended to be diminished with temperature (as indicated by lowest O + N/C ration), resulting in an increase of aromaticity and a decrease in polarity of biochar produced at a highest temperature. Novak et al. (2009) reported that pyrolysis at a temperature below 400 °C exhibits aliphatic C structures, whereas increases in pyrolysis temperature to above 400 °C represent poly-condensed aromatic C-type compounds in biochar.

The data of TG analysis indicated that weight loss of feedstock was at a temperature of about 100 °C (data not shown), mainly due to moisture volatilization of raw materials. The obtained curves showed that the weight loss began to increase sharply from 300 °C for biochars produced at 200 and 400 °C, whereas this loss was found at 400°C for biochar samples produced at 600 and 800 °C. It was generally observed that higher mass loss was recorded at lower pyrolysis temperature and this loss tended to decline with increasing biochar production temperature. As expected, the occurred weight loss followed the order feedstock > 200 °C biochar > 400 °C biochar > 600 °C biochar > 800 °C biochar. Cao and Harris (2012) suggested that mass loss between 200 and 580 °C for biochars is mainly due to combustion of organic matter remaining in the biochar samples. However, they reported that the occurred loss at higher pyrolysis temperature attributed to decomposition of calcite. Our results suggest that cellulose loss and porosity of biochar increase with increasing pyrolysis temperature, as indicated by SEM image (data not shown). SEM revealed that conocarpus biochar underwent clear structural modifications as compared with feedstock image. Moreover, the development of pores in biochar samples enhanced with increasing temperature (especially at 600 and 800 °C), which may result in significant improvement in the pore properties of biochars. Additionally, it is possible that an increase in crystalline of mineral components and formation of highly ordered aromatic structures of biochar with increasing pyrolysis temperature (Kloss et al., 2012; Kim et al., 2012).

The XRD spectra of the produced biochar samples have different peaks (data not shown), suggesting the presence of mineral crystals. It was noticed that feedstock samples have the main peaks at d = 5.80 and 3.89 Å, which indicate the presence of organic compounds and represent crystal structure of cellulose in wood (Ertas and Alma, 2010; Kim et al., 2012; Wang et al., 2009). The appeared peak at d = 5.80 in the samples of feedstock became sharp in those of 200°C biochar. In addition, biochar produced at 200°C showed new peaks appeared at 3.63 and 2.35 Å. The obtained peaks at 5.80, 3.63 and 2.35 Å indicate the presence of whewellite [Ca(C$_2$O4)·H$_2$O] in the feedstock or 200 °C biochar. However, these peaks were diminished with higher temperature (400–800 °C), indicating the decomposition of cellulose and calcium oxalate. Wang et al. (2009) also found that the peaks of cellulose in raw pine wood and its biochar produced at 300 °C vanished at 400 °C. The presence of whewellite in the feedstock and 200 °C biochar is somewhat more consistent with the results of Kloss et al. (2012), who found a calcium oxalate mineral (whewellite; main peaks at 5.97, 5.82, and 2.35) in the feedstock of poplar wood and its biochar produced at 400 °C. They also revealed that whewellite structures disappeared at 525 °C and were completely replaced by calcite. In the current study, there was similarity in the XRD patterns of biochar samples produced at 400 and 600 °C and whewellite structures were replaced by calcite (3.03 Å). In biochars produced at 600 and 800 °C, the presence of calcite is also confirmed by the other obtained peaks at d = 2.48, 2.09, 1.91 and 1.87 Å. The obtained sharp peaks (at d = 3.03) for biochar pyrolyzed at 400 and 600 °C indicate that the structure of calcite is well-crystallized. However, these peaks were diminished with biochar pyrolyzed at 800 °C, suggesting that decomposition of calcite is possible under higher pyrolysis temperature.

4. Conclusions

The results of this study indicated that biochars produced at low temperature have the lowest values of pH and EC and the highest concentrations of unstable organic carbon and dissolved organic carbon compared with those produced at high temperature. Therefore, in terms of their favorable contributions to soils having high alkalinity, high salinity and low organic matter content, biochars produced at low pyrolysis temperatures may afford preferred impacts on agricultural systems in the arid regions. Future studies should focus on the optimization of biochar application for both agronomic and environmental purposes and carbon budget for agricultural systems enriched with biochar.

Acknowledgements

References

Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.K., Yang, J.E., Ok, Y.S., 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresour. Technol. 118, 536–544.

Amonette, J.E., Joseph, S., 2009. Characteristics of biochar: Microchemical properties. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, United Kingdom, pp. 33–52.

Boehm, H.P., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32, 759–769.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biol. Biochem. 46, 73–79.

Calvelo Pereira, R., Kaal, J., Camps Arbestain, M., Pardo Lorenzo, R., Aitkenhead, W., Hedley, M., Macías, F., Hindmarsh, J., Maciá-Agulló, J.A., 2011. Contribution to

characterisation of biochar to estimate the labile fraction of carbon. Org. Geochem. 42, 1331–1342.

Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour. Technol. 101, 5222–5228.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2008. Using poultry litter biochar as soil amendments. Aust. J. Soil Res. 46, 437–444.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2007. Agronomic values of green waste biochar as a soil amendment. Aust. J. Soil Res. 45, 629–634.

Chun, Y., Sheng, G., Chiou, C.T., Xing, B., 2004. Compositions and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655.

Demirbas, A., 2004. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. J. Anal. Appl. Pyrolysis 72, 243–248.

Ertas, M., Alma, M.H., 2010. Pyrolysis of laurel (Laurus nobilis L.) extraction residues in a fixed-bed reactor: characterization of bio-oil and bio-char. J. Anal. Appl. Pyrolysis 88, 22–29.

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Am. Soc. Agric. Biol. Eng. 51, 2061–2069.

Hossain, M.K., Strezov, V., Chan, K.Y., Nelson, P.F., 2010. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (Lycopersicon esculentum). Chemosphere 78, 1167–1171.

Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J. Environ. Manage. 92, 223–228.

Imam, T., Capareda, S., 2012. Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures. J. Anal. Appl. Pyrolysis 93, 170–177.

Kim, K.H., Kim, J., Cho, T., Choi, J.W., 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresour. Technol. 118, 158–162.

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H., Soja, G., 2012. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. J. Environ. Qual. 41, 990–1000.

Kun-yu, Z., Hui-ping, H., Li-juan, Z., Qi-yuan, C., 2008. Surface charge properties of red mud particles generated from Chinese diaspore bauxite. Nonferrous Met. Soc. China 18, 1285–1289.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota – a review. Soil Biol. Biochem. 43, 1812–1836.

Lehmann, J., 2007. A handful of carbon. Nature 447, 143–144.

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333, 117–128.

Martinez-Ballesta, M.C., Silva, C., López-Berenguer, C., Cabañero, F.J., Carvajal, M., 2006. Plants aquaporins: new perspectives on water and nutrient uptake in saline environment. Plant Biol. 18, 535–546.

Morton, J.F., 1981. Atlas of Medicinal Plants of Middle America. Bahamas to Yucatan. C.C. Thomas, Springerfield, IL.

Muradov, N., Fidalgo, B., Gujar, A.C., Garceau, N., T-Raissi, A., 2012. Production and characterization of Lemna minor bio-char and its catalytic application for biogas reforming. Biomass Bioenergy 42, 123–131.

Novak, J.M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., Das, K.C., Ahmedna, M.A., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195–206.

Ozçimen, D., Ersoy-Meriçboyu, A., 2010. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. Renew. Energy 35, 1319–1324.

Song, W., Guo, M., 2012. Quality variations of poultry litter biochar generated at different pyrolysis temperatures. J. Anal. Appl. Pyrolysis 94, 138–145.

Sparks, D.L., 1996. Methods of Soil Analysis. Soil Society of American, Madison, WI.

StatSoft Inc., 1995. Statistica for Windows (Computer Program Manual). StatSoft Inc., Tulsa, OK.

Wang, Z., Cao, J., Wang, J., 2009. Pyrolytic characteristics of pine wood in a slowly heating and gas sweeping fixed-bed reactor. J. Anal. Appl. Pyrolysis 84, 179–184.

Yang, H.P., Yan, R., Chin, T., Liang, D.T., Chen, H.P., Zheng, C.G., 2004. Thermogravimetric analysis – Fourier transform infrared analysis of palm oil wastes pyrolysis. Energy Fuels 18, 1814–1821.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. Bioresour. Technol. 102, 6273–6278.

Yuan, J., Xu, R., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour. Technol. 102, 3488–3497.