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Agronomic benefits of durian shell biochar

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Abstract

This study investigated the chemical properties of durian shell biochar which is used as a soil amendment. It can act as a carbon sink and as a means to improve crop yield. Plant nutrient elements in this biochar are in crystalline minerals located within the complex pore structure therefore biochar production from wastes could be a very good way to reduce demand for fertilizers. XRD and SEM-EDS results demonstrate that the numerous minerals in biochar are highly soluble, such as archerite (KH_2PO_4), chlorocalcite ($KCaCl_3$), kalicinite ($KHCO_3$), and sylvite (KCl) with small amounts of poorly soluble minerals (calcite $CaCO_3$ and struvite $KMgPO_4.6H_2O$). When biochar is applied to soils at the recommended rates of tons per hectare, it will be a significant source of potassium, phosphorus and other nutrient elements. The availability of nutrients to plants will depend on properties of the biochar and the adjacent soil.

Keywords : Biochar, Durian shell, Minerals, Chemical composition
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Introduction

Durian (Durio zibethinus) called the "king of fruits" is a members of the family Bombacaceae and genus Durio (Brown, 1997). It is the most popular seasonal fruit in South East Asian countries. In 2007, Thailand produced 686,478 tonnes of durian consequently volumes of durian shell residue in excess of 48,800 tonne per year are produced (Sangkaeo, 2011). Durian shell is difficult to dispose of and it causes environmental issues including respiratory diseases, pungent smell and water contamination. However, this residue can be processed into the valuable products biochar and bio-oil by pyrolysis/carbonization.

Biochar is a black solid carbon residue formed by pyrolysis of biomass (Sukiran, et al., 2011). It is produced by heating biomass in a closed container under a limited supply of oxygen (O_2) and at moderate temperatures (<700°C) (Lehmann and Joseph, 2009). Low temperature biochar is considered to have better reactivity and greater benefits for soil fertility than high temperature biochar (>550°C) because low temperature pyrolysis (<550°C) produces biochar which has a less condensed C structure.

Most nutrient elements present in organic materials persist in biochar albeit in different compounds (Keiluweit et al., 2010) and these nutrients may be available to plants. Biochar has high alkalinity, high water retention capacity and high porosity which may be beneficial to soils and enhance plant growth. The properties of biochar are highly variable reflecting the biomass source and pyrolysis conditions consequently each feedstock for biochar production needs thorough evaluation (Singh et al., 2010).

It is now well accepted that biochar production provides the potential to better manage agricultural wastes, simultaneously improving soil fertility and enabling carbon sequestration in soil (Roberts et al., 2010). The formation of inorganic compounds (minerals) in biochar is important in determining plant nutrient availability however this process and the nature of the minerals are poorly understood.

This study aimed to determine the physical, chemical and mineralogical properties of durian shell biochar in relation to the speciation and availability of plant nutrients.

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Materials and Experimantal Procedures

Manufacture of biochars

Biochar was produced in a traditional kiln (Figure 1b) used by Thai farmers. Fuel is burnt in an outer metal cylinder to heat biomass in the inner cylinder from which air is excluded. Temperature is approximately 350°C.

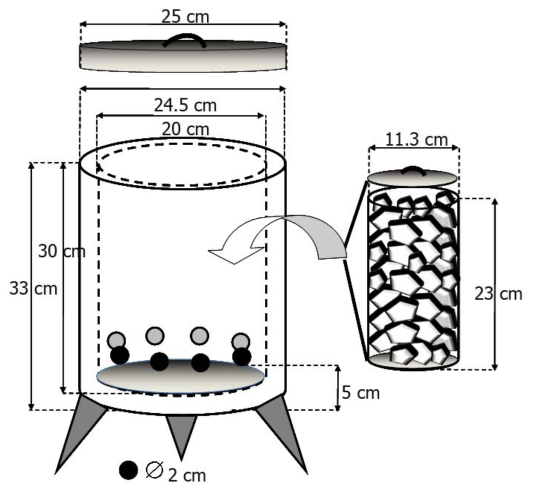

Figure 1. Traditional kiln used to manufacture biochar (uncontrolled temperatures ~350°C with limited oxygen).

Chemical analysis

The biochar was homogenised and ground for chemical analysis (size <0.3 mm). Biochar pH and electrical conductivity (EC) were measured using a 1: 5 solid: MilliQ (MQ) water (by volume) extraction. The total water soluble elements in biochar were determined by extracting the biochar with MQ water (0.3 g biochar per 10 mL MQ water) and shaking end-over-end for 12 hours. The extracted solutions were analysed by ICP-OES. The ash content of biochar was determined by dry combustion in a ventilated muffle furnace at 600°C overnight. Total carbon and nitrogen concentrations in biochar were determined using a Vario Macro elemental analyzer. Total element concentrations in biochar were determined by digesting biochar ash in 10% HCl and analysis of the solutions was by ICP-OES (Perkin-Elmer).

Scanning electron microscopy and EDS

Fractured biochar grains were placed on a carbon tape which adhered to an aluminium stub and were coated with carbon prior to examination using secondary and backscattered electron images and using energy dispersive X-ray spectroscopy (EDS) on a JEOL 6400 SEM operated at a 15 kV electron beam accelerating voltage. SEM images of biochar enabled recognition of plant organs that had been altered to carbon and the associated mineral grains. EDS provided quantitative analyses of micron-size volumes to determine the chemical composition of mineral grains on the surface and inside voids in biochar. Image analysis was used to measure pore size of biochar.

X-ray diffraction analysis

Minerals were determined by conventional X-ray diffraction (CXRD) analysis using a Philips PW- 3020 diffractometer with a graphite diffracted beam monochromator (CuKα, 50 kV, 20 mA). The ground biochars (size <0.05 mm) were scanned from 4 to 65° 2θ, using a step size of 0.02° 2θ and a scan speed of 0.04° 2θ sec^{-1}. Synchrotron X-ray diffraction (SXRD) was used to confirm the identity of trace mineral constituents using powder samples in glass capillaries, and patterns were analysed over an angular range of 4-60° 2Theta. The wavelength was set at ~1.0Å to provide dispersion/ resolution of reflections that was superior to CXRD.

Results and Discussion

X-ray diffraction analysis

Based on synchrotron XRD, kalicinite ($KHCO_3$) is the dominant mineral in durian biochar. Archerite (KH_2PO_4), calcite ($CaCO_3$), chlorocalcite ($KCaCl_3$), struvite ($KMgPO_4.6H_2O$) and sylvite (KCl) are minor constituents (Table 1). The solubility in water of these mineral constituents is high except for calcite ($CaCO_3$) and struvite so the availability to plants of nutrient elements in the minerals might be mostly limited by diffusion into soil of the ions in the solution retained in pores in biochar grains.

Chemical properties

Table 2 shows chemical properties, total elements and water soluble elements in durian shell biochar which is an alkaline material (pH 9.9) with high EC 4,750 µs cm^{-1}. This may provide additional value in applications to acidic soils. It has moderate ash content (14%) as has been reported in other studies (Nuithitikul, et al., 2010;

Wilaipon 2011; Daosukho, et al., 2012). The concentration of sodium in this sample is low (non detectable) and the sample contains minor As (0.16 mg kg^{-1}). Durian shell biochar has high levels of potassium, magnesium, calcium and phosphorous at 50.7, 8.1, 4.8 and 3.8 g kg^{-1} respectively, whereas silicon, aluminium, sulphur levels are quite low (1472, 82 and 869 mg kg^{-1}). The water soluble potassium content in this sample is very high (22,926 mg kg^{-1}) because of the soluble crystalline potassium minerals and this biochar can be considered to be a potassium fertiliser. Phosphorus (1,103 mg kg^{-1}), magnesium (125 mg kg^{-1}) and sulfur (193 mg kg^{-1}) are quite soluble adding to the fertilizer value of the material. The water solubility of calcium is very low (16 mg kg^{-1} Ca) as most Ca is present in calcite however calcite is likely to dissolve in acid soils. Yamamoto et al., 2006 suggested that a typical biochar application rate for acid soil in Indonesia is 15.25 t ha^{-1} (2.44 t rai^{-1}), therefore when durian shell biochar is applied at this application rate, it provides KCl at 1.48 t ha^{-1} (0.24 t rai^{-1}).

Scanning electron microscopy

The morphology of durian shell biochar is shown in Figures 2 and 3. It has a highly porous structure with numerous cellular microstructures inherited from the original plant material. The cellular microstructure of durian shell biochar contains numerous interconnecting pores that will allow access into the biochar to soil solution which will dissolve soluble minerals. According to image analysis results, this material has a wide variation of pore sizes. The average pore size in this biochar is approximately 3 µm, ranging from 0.26 to 23.7 µm, so that in soil capillary attraction of water will occur followed by diffusion of dissolved ions through water-filled pores. All minerals that had been identified using conventional and synchrotron XRD were also detected as discrete crystals or in mixtures by SEM with EDS. The chemical composition and corresponding atomic ratios of mineral grains confirm the identity of minerals as shown in the attached examples (Figure 3).

Table 1. Mineralogical composition of biochar expressed on a semiquantitative basis (based on synchrotron XRD) and the solubility in water of these mineral constituents.

Mineral name	Chemical Formula	Semiquantitative quality	Solubility in water (mg L^{-1}) Weast (1983)
Archerite	KH_2PO_4	x	Soluble
Calcite	$CaCO_3$	x	14
Chlorocalcite	$KCaCl_3$	x	Soluble
Kalicinite	$KHCO_3$	xxx	224,000
Struvite	$KMgPO_4.6H_2O$	x	Slightly soluble
Sylvite	KCl	x	238,000

Table 2. Properties including total elemental composition* of durian shell biochar and water soluble** elements in biochar.

Ash	C	N	pH	EC	Si*	Al*	Ca*	Mg*	Na*	K*	P*	S*	Fe*	Mn*	As*
(---------%--------)				(µs cm^{-1})	(-------------------------------------total mg kg^{-1}-------------------------------)										
14	65	1.0	9.9	4750	1472	82	4820	8147	nd	50715	3803	869	55	53	0.16
					Si**	Al**	Ca**	Mg**	Na**	K**	P**	S**	Fe**	Mn**	As**
					(-----------------------------water soluble mg kg^{-1}-----------------------------)										
					nd	nd	16	125	nd	22926	1103	193	0.64	0.24	nd

* = digest of biochar ash in 10% HCl, measured by ICP-OES and converted to biochar basis, ** = 1: 5 biochar: H_2O extract measured by ICP-OES, nd = not detected.

Conclusions

Biochar was created from durian shell. XRD and chemical results were found to match particles seen in the SEM images and identified the mineral forms of plant nutrient elements in durian shell biochar. The potassium minerals sylvite (KCl), kalicinite ($KHCO_3$), archerite (KH_2PO_4), chlorocalcite ($KCaCl_3$) and struvite ($KMgPO_4.6H_2O$) are present and as these minerals are soluble in water, durian shell biochar is a potential potassium fertilizer. Calcite ($CaCO_3$) is also present in durian biochar however as this mineral has low water solubility its dissolution to release Ca will depend *inter alia* on the pH of soil solution and diffusion of reactants (hydrogen ions, Ca) through pores in biochar. Biochar is an alkaline material that can be used to neutralise acidic soil. The beneficial properties of durian shell biochar suggest that it has a high potential for agronomic use.

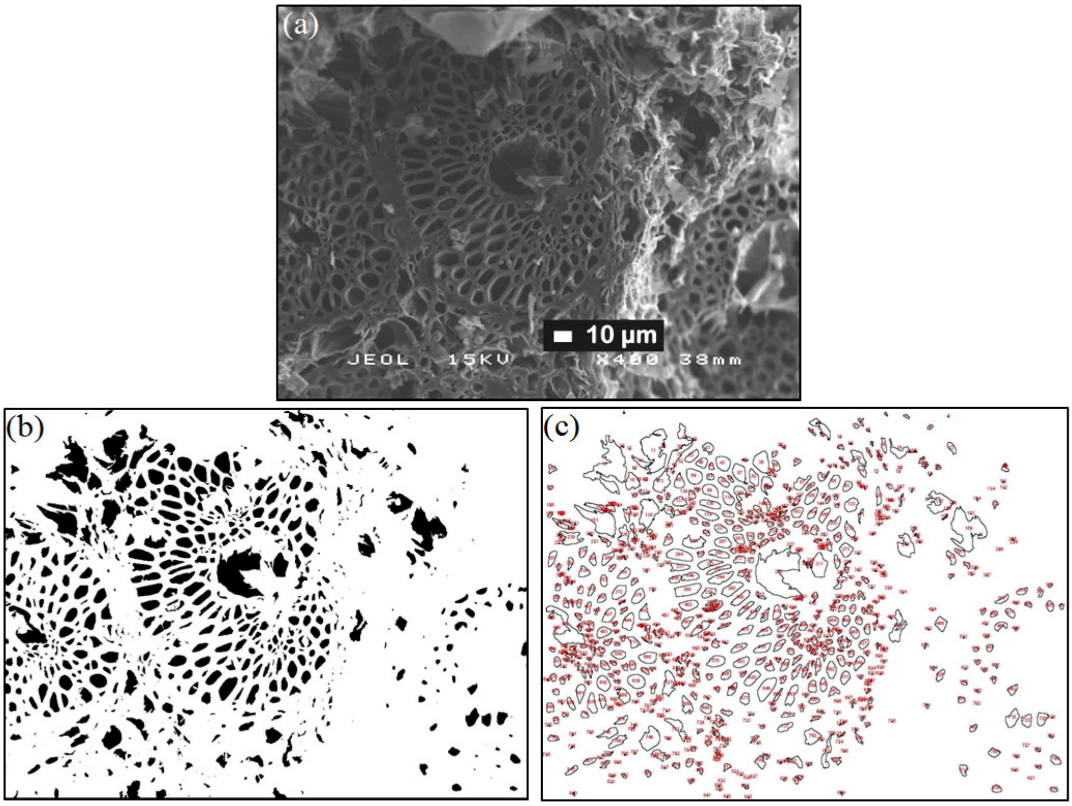

Figure 2. A SEM image of durian shell biochar at low magnification that was used for the image analysis to determine pore abundance and geometry (a) secondary scanning electron (SE) image; (b) SE image after thresholding by the ImageJ program and (c) outlines of pores for the calculation of circularity and feret dimension of pores.

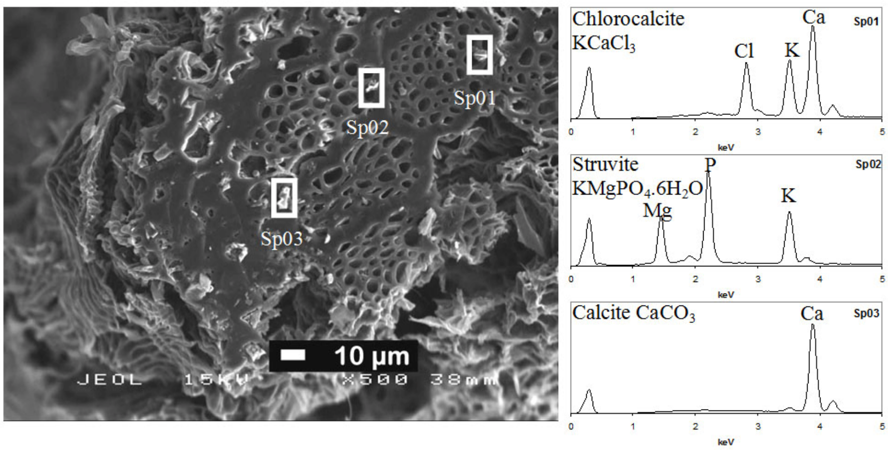

Figure 3. Secondary electron micrograph and x-ray spectra enabling the identification of minerals present in biochar.

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Reference

1. Brown, M.J. (1997). *Durio-A Bibliographic Review.* New Delhi : IPGRI Office for South Asia.

2. Daosukho, S., Kongkeaw, A. and Oengeaw, U. (2012). The development of durian shell biochar as a nutrition enrichment medium for agricultural purpose : Part 1 chemical and physical characterization. *Bull. Appl. Sci.* **1(1)** : 133-141.

3. Keiluweit, M., Nico, P.S., Johnson, M.G. and Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Tech.* **44(4)** : 1247-1253.

4. Lehmann, J. and Joseph, S. (2009). *Biochar for Environmental Management: Science and Technology*. London : Earthscan.

5. Nuithitikul, K., Srikhun, S. and Hirunpraditkoon, S. (2010). Influences of pyrolysis condition and acid treatment on properties of durian peel-based activated carbon. *Bioresour. Technol*. **101(1)** : 426-429.

6. Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R. and Lehmann, J. (2010). Life cycle assessment of biochar systems : Estimating the energetic, economic and climate change potential. *Environ. Sci. Technol.* **44** : 827-833.

7. Sangkaeo, W. (2011). The processing of durian shell as power sources: The comparison of durion shell charcoal and durian shell charcoal mixed with charcoal dust and sawdust on traits, quality, cost and opinions of consumers. *Res. Jour. Pibulsongkram Rajabhat U.* **7(13)** : 51-59.

8. Singh, B., Singh, B.P. and Cowie, A.L. (2010). Characterisation and evaluation of biochars and their application as a soil amendment. *Aust. J. Soil. Res.* **48(7)** : 516-525.

9. Sukiran, M.A., Kheang, L.S., Bakar, N.A. and May, C.Y. (2011). Production and characterization of bio-char from the pyrolysis of empty fruit bunches. *Am. J. Appl. Sci.* **8(10)** : 984-988.

10. Weast, R.C. (1983). *Handbook of Chemistry and Physics*. 64th ed. Cleveland, Ohio : CRC.

11. Wilaipon, P. (2011). Durian husk properties and its heating value equation. *Am. J. Appl. Sci.* **8(9)** : 893-896.

12. Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S. and Ogawa, M. (2006). Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil. Sci. Plant. Nutri.* **52** : 489-495.