Original research article

Durian and Mangosteen Shell-Derived Biochar Amendment on the Removal of Zinc, Lead and Cadmium

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Received 27 October 2016; Received in revised form 7 December 2016
Accepted 19 December 2016; Available online 24 March 2017

ABSTRACT

Metal contaminated soils are a major problem in Thailand. Plants that grow in this area will adsorb metal and broad impact across the food chain. Some types of biochar can immobilize metals and reduce the impact of such. This research was limited to study cadmium, zinc and lead adsorption. Durian and mangosteen shell were selected to produce biochar due to their high carbon content. The shells were firstly passed through the pyrolysis process. The chemical characterization of these biochars was then determined. The chemical characteristics of both materials were similar. Both were basic materials with pH around 10. They were high in percentage of C and TOC. Total Cd, Pb and Zn in both biochars were below the maximum allowed threshold according to biochar toxicity standard recommended by International Biochar Initiative. The buffering capability and acid neutralization capability were examined by adding acid and basic solution until the pH reached 2-12. The buffering capability of these two biochars was rather high. The values of acid neutralization capability (ANC) of biochar produced from durian and mangosteen shell were 1,464.80 meg/kg and 1,328.98 meq/kg, respectively. The study included an adsorption isotherm. Freundlich isotherm was a suitable isotherm to explain the adsorption of all three metals by biochar from durian shell, whereas Langmuir isotherm is better to explain the adsorption of metals by biochar from mangosteen shell. The adsorption capacity of both biochars was not much different.

Keywords: Biochar; Amendment; Cadmium; Lead; Zinc

Introduction

The current expansion of the economy, technology, industry and agriculture in Thailand results in increasing the discharge of metals into the soil. The soil is not suitable for growing crops. Heavy metal is chemically stable and is not degraded by natural processes. Plants grown in contaminated soil adsorb and transmit heavy metals into the food chain. The receptors suffer due to their health problem. There was a case of zinc-contamination in Paddy soil at Chulabhorn District, Nakhon Si Thammarat. This case resulted from the use of chemical fertilizers and herbicides, causing a buildup of zinc in soil to a level of 91.20 mg/kg [1]. This buildup affected farmer and rice consumers' health. According to the Toxnet database of the U.S. National Library of Medicine, the oral LD_{50}

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for zinc is close to 3 g/kg body weight [2]. Zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. The high level of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Thailand has zinc and lead mining industries. The metal spread onto the soil due to mining activity is not only zinc and lead but also cadmium. In Thailand, there was a case of rice contaminated with cadmium in Mae Tao river basins, Tak province. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage [3]. Lead is a cumulative toxicant that affects multiple body systems and is particularly harmful to young children. At high levels of exposure, lead attacks the brain and central nervous system to cause coma, convulsions and even death [3]. Soil pollution caused by the contamination of heavy metals can be treated in several ways. Soil remediation can be mainly classified into 3 systems which are physical, biological and chemical remediation. Soil replacement [4] and thermal desorption [5] are physical remediation. Plants [6] [7], animals [8] and microorganisms [9] have been studied to determine their uptake to remove heavy metals from soil. Remediation using living organisms is biological remediation. For chemical remediation, various researchers study on washing contaminated soil with inorganic eluent [10], complexing agent [11], surfactant [12], etc. Another method of chemical remediation is adding binding agents into the contaminated soil to change the water soluble form of heavy metal into insoluble form thus decreasing the migration of heavy metals to environmental media. The binding agent can be inorganic or organic material. Examples of inorganic material are apatite, slovakite [13], diatomite [14], sepiolite [15], bentonite [16] and polygorskite [17]. Many organic materials are studied such as sewage sludge [18], green waste compost [19], poultry manure [20], rice straw [21] and biochar [22]. Although biochar is a green environmental sorbent and has recently been applied to adsorb various metals in soil, not all types of biochar can be used. Some types of biochar can increase the mobility of heavy metals. Cadmium and zinc were immobilized but copper and arsenic were mobilized when using hardwood-derived biochar [23]. The mobility of copper and antimony increased by adding chicken manure-derived biochar and broiler litter-derived biochar, respectively [24] [25].

In Thailand there are various types of agricultural waste that have not yet been used to improve the soil capability to immobilize metals. Mangosteen and durian fruit are easy to find in Thailand. There are high amounts of carbon in both types of fruit shell, which features one of the many things that are indicative to adsorb metals. No research has been found using such fruit shells for soil remediation. This research aims to study on pyrolysis of durian and mangosteen shell. The biochars were used to adsorb Zn, Cd and Pb. The buffering capability and ANC value of the biochars were observed. The studies were also on Langmuir and Freundlish adsorption isotherm.

Materials and Methods

Biochar synthesis and characterization

Durian and mangosteen shells were collected from a nearby market during summer period. They were washed with water and left to dry under sunlight. Dried materials were then passed through the process of pyrolysis for over 10 hours. Samples of biochar were crushed and sieved through a 50 mesh size sieve before being characterized. The pH was measured in water using a pH meter (Consort, C860) at a sample water ratio of 1:100 w/v. Samples were analyzed for moisture content by drying in an oven at 110 ºC and calculating the mass loss. (ASTM 2216), organic matter by Walkley–Black titrations [26], cation exchange capacity (CEC) by the ammonium acetate method (method 9080), loss of ignition (LOI) by burning at 550 ºC and calculating the mass loss, total organic carbon (TOC) and total carbon by TOC analyser (Shimadzu, TOC-V CPH), electrical conductivity (EC) by conductivity meter, total nitrogen by Kjeldahl method, nitrate by brucine method, chloride by argentometric method, phosphate by molybdovanadophosphate method, sulfate by turbidimetric method, aluminium by colorimetric method, major and trace elements by atomic absorption spectrometry (AAS) (Perkin Elmer, AAnalyst 200) [27].

pH titration test

The pH titration test was performed to determine the buffering capacity. (CEN/TS, 2006) [28] One gram of powdered biochar was put into 100 ml distilled water. The suspension was shaken at 120 rpm/min for a period of 20 minutes. The initial pH was measured. One molar of sodium hydroxide or nitric acid at the amount of 200 microlitre was added. The pH of suspension was measured after 20 minutes shaking time. The additions were continued until reaching pH 2-12. The results from the test were used to calculate the acid neutralisation capacity (ANC) of the biochar, which is defined as the quantity of acid or base (meq/kg) required to shift the initial pH of the biochar to a pH of 4. For materials with an initial pH higher than 4, the ANC allows prediction of buffering capacity with respect to external acidic stresses.

Sorption isotherms [29]

Batch sorption tests were performed. Two grams of biochar were put into a 250 mL Erlenmeyer flask containing 0.01 M 50 mL calcium chloride. The suspension was shaken at 120 rpm for 16 hours. After a pre-equilibration time, ten different concentrations of each metal ranging from 0.1 – 10 meq/L were added. The suspensions were further shaken for 24 hours and then filtered through Whatman no. 42 filter paper under vacuum. Trace elements were determined in the solutions using atomic absorption spectrometry (AAS) (Perkin Elmer, AAnalyst 200)
The data was fitted into Langmuir and Freundlich Isotherms.

The sorbed metal concentrations were calculated using equation (1)

$$q_e = \frac{(C_0 - C_e)\,V}{m} \qquad (1)$$

Where:
q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)
C_0 = the initial concentration of adsorbate (mg/L)
C_e = the equilibrium concentration of adsorbate (mg/L)
V = the volume of contact solution (L)
m = mass of the adsorbent (g)

Langmuir adsorption isotherm:
Langmuir represented the following equation:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \qquad (2)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (2) into linear form.

$$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \frac{1}{q_m} \qquad (3)$$

Where:
C_e = the equilibrium concentration of adsorbate (mg/L)
q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).
q_m = maximum monolayer coverage capacity (mg/g)
K_L = Langmuir isotherm constant (L/mg).

$$R_L = \frac{1}{1 + (1 + K_L C_0)} \qquad (4)$$

where:

R_L = the equilibrium parameter

Freundlich adsorption isotherm:

Freundlich represented the following equation:

$$q_e = k_F C_e^{1/n} \quad (5)$$

Freundlich adsorption parameters were determined by transforming the Freundlich equation (5) into linear form.

$$\text{Log } q_e = \log k_f + 1/n \log C_e \quad (6)$$

Where:

K_F = Freundlich isotherm constant (mg/g)

n = adsorption intensity;

C_e = the equilibrium concentration of adsorbate (mg/L)

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Statistical analysis

All experiments were conducted with three replicates. Variability in the data was expressed as the standard deviation. The analyses were carried out at the $p < 0.05$ level using t tests.

Results and Discussion

Chemical characterisation

Durian and mangosteen shells became biochar after passing through the pyrolysis process. In this research, BC, DBC and MBC were used to refer to biochar, durian shell-derived biochar and mangosteen shell-derived biochar in short, respectively. The DBC and MBC were characterized and the results are shown in Table 3.1

Table 3.1 Chemical characteristics of biochars.

Parameter	Durian shell-derived biochar (DBC)	Mangosteen shell-derived biochar (MBC)
Moisture content (%)	6.13 ± 0.08	5.43 ± 0.31
pH	10.48 ± 0.10	9.85 ± 0.10
EC (mS/cm)	3.45 ± 0.06	3.69 ± 0.22
CEC (cmol/kg)	15.96 ± 0.50	29.05 ± 0.75
LOI (%)	70.08 ± 5.37	74.01 ± 2.39
TOC (%)	67.50 ± 1.50	65.57 ± 0.15
C (%)	68.31 ± 1.51	67.50 ± 0.17
DOC (%)	0.06 ± 0.01	0.05 ± 0.01
N (%)	0.31 ± 0.03	0.19 ± 0.02
NO_3^- (mg/L)	0.35 ± 0.10	0.32 ± 0.05
Cl^- (mg/L)	n.d.	n.d.
T-PO_4^{3-} (mg/kg)	1.00 ± 80.75	2.44 ± 30.78
SO_4^{2-} (mg/L)	36.35 ± 9.06	19.29 ± 6.39
Major elements		
Ca^{2+} (mg/kg)	27,523 ± 3.84	17,107 ± 9.99
Mg^{2+} (mg/kg)	1,031 ± 11.58	8,792 ± 1.21
K^+ (mg/kg)	15,846 ± 54.83	13,900 ± 33.41
Al^{3+} (mg/kg)	142 ± 0.04	241 ± 0.68
Trace elements		
Zn^{2+} (mg/kg)	57.72 ± 0.20	46.46 ± 0.61
Pb^{2+} (mg/kg)	1.82 ± 31.49	0.25 ± 7.72
Cd^{2+} (mg/kg)	0.61 ± 0.03	2.53 ± 0.77

N.d. = not detected

The moisture content of DBC and MBC were in the same range of BC from tree bark, vine shoot [30] and many other BCs reported in the literature. Dried BC can be easily eroded by wind. Biochar produced from durian shell showed a little higher pH value than BC produced from mangosteen shell. BC from difference sources would have different pH values. Another researcher reported that the pH of BC from apple tree branch, rice husk and oak tree were 10.04, 9.4 and 8.85, respectively when using 600°C pyrolysis temperature. The pH of BC also depends on the pyrolysis temperature [31]. Usually, the lower the pyrolysis final temperature, the lower is the pH in the BC structure, due to the remaining of carboxyl and hydroxyl groups on its structure. In this research, the pyrolysis temperature was higher than 500°C so the pH of BCs were quite high. This implied that there was a large number of negative ions that could combine with heavy metals in the soil. Addition of DBC and MBC can also improve the soil pH in acid soil. The response will depend on the amount of biochar added and initial soil pH as well as length of the addition. In general, BC produced below 400°C showed not only a low pH but also low electrical conductivity (EC), and small surface area. [32] The EC of DBC and MBC were not considered to be low and the value of both types of biochar were not significantly different ($p<0.05$). The EC values were close to biochar from rice bran produced above 400°C. CEC is one of many factors involved in soil fertility. Organic matter in BCs hold on to positively charged nutrients because they have negatively charged sites on their surface, and opposite charges attract. The BC or soil can then "exchange" these nutrients with plant roots. If a BC has a low cation exchange capacity, it is not able to retain such nutrients well, and the nutrients are often washed out with water. The CEC of DBC and MBC were low. If we considered only CEC value, it may not be a good material to retain nutrients. The value of LOI, TOC, C and DOC of DBC and MBC were low but close to the value from tree bark-derived biochar and vine shoot-derived biochar [30]. The value of organic carbon was related to CEC value. In fact, biochar amendments can play both roles, and cause decrease and increase of soil pH. These are related to the evolution of the organic matter added to soil and its decomposition level. Small organic molecules (right after addition to soil) are decomposed by microorganism action that produce amounts of CO_2 and organic acids which decrease soil pH. The organic molecules of DBC and MBC were low so there would not have such a problem. The percentage of nitrogen of BC was very much lower than other organic amendment materials. Nitrate, chloride, sulfate and phosphate ions contained in BC can combine with metals. DBC and MBC were low in such ions. Liming power of biochar depends basically on its ashes content, which is not really biochar but one of its fractions (mineral fraction). Ash content of biochar is very variable and depends on the feedstock. And the liming effect of the biochar ashes depends on its base content (Ca, Mg, K, Al and Na). DBC and MBC contained large amounts of major elements. The amounts of Pb, Cd and Zn were lower than the maximum allowed threshold according to the biochar toxicity standard recommended by International Biochar Initiative [33] The recommended values cannot exceed 121-300 mg/kg for Pb, 1.4-39 mg/kg for Cd, and 416-7,400 mg/kg for Zn.

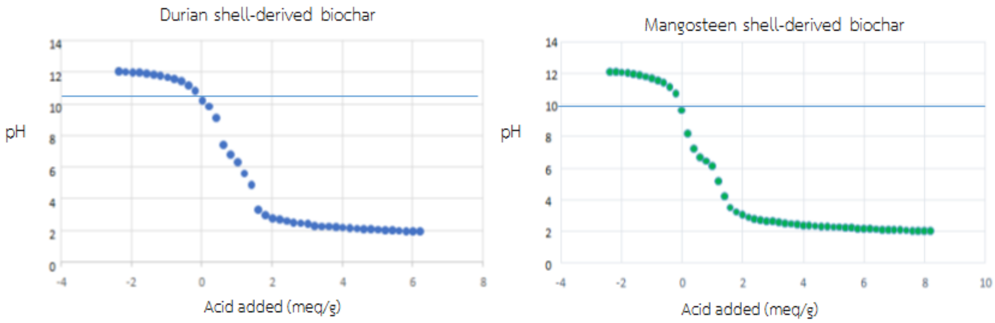

Fig. 1. pH titration curves for durian shell-derived biochar and mangosteen shell-derived biochar.

Neutralization capacity

The results from the pH titration test are shown in fig. 1. Fig. 1 is a graph showing the relationship between the volume of acid added (positive value) or base added (negative value) and the changing of pH value. The initial pHs of biochar produced from durian and mangosteen were equal to 10.48 and 9.85, respectively. In the first period of nitric acid adding, pH was decreased rapidly. After the pH reached 2, the pH value did not change much. In the first period of sodium hydroxide addition, the pH value also rose sharply until the pH value reached 1 2 and then the pH was also unchanged. The pH titration curve patterns of DBC and MBC were similar to the curves of tree bark-derived biochar and vine shoot-derived biochar reported in literature [30]. However, when adding an acid to tree bark-derived biochar and vine shoot-derived biochar, the pH dropped more quickly. It indicated that the buffering capacities of DBC and MBC were a little higher than tree bark-derived biochar and vine shoot-derived biochar. But when comparing with other organic amendment materials like compost from municipal organic waste, green waste and compost from food left over [30], DBC and MBC were not as good as those materials.

The acid neutralization capacity (ANC) is defined as the quantity of acid or base (meq/kg) required to shifting the initial pH of the biochar to a pH of 4. The ANC value of DBC (1,464.80 meq/kg) was greater than the ANC value of MBC (1,328.98 meq/kg). The reason was partly from the higher initial pH of DBC. The major elements (Ca^{2+} and K^{+}) were also greater in DBC as described earlier. The ANC value of DBC and MBC were about two fold greater than the ANC value of tree bark-derived biochar and vine shoot-derived biochar. The ANC value of other organic amendment materials such as compost from municipal organic waste were very much higher. The low ANC for the BCs could be due to very low content of organic acids as well as low content in phenolic and carboxylic functional groups [30].

Sorption isotherm

Langmuir and Freundlish isotherms were taken into consideration in this research. The results are shown in table 2.

Table 2. Langmuir and Freundlish isotherm constants for the adsorption of Pb, Cd and Zn on MBC and DBC.

		Langmuir isotherm			Freundlish isotherm		
		q_m	K_L	R^2	K_F	1/n	R^2
Pb	MBC	16.18	0.12	0.9590	45.60	0.74	0.8395
	DBC	2.75	0.27	0.9359	42.70	0.28	0.9819
Cd	MBC	67.11	0.06	0.8095	38.21	0.15	0.7947
	DBC	4.68	0.08	0.7209	1.36	0.16	0.8379
Zn	MBC	12.48	0.07	0.9300	7.87	0.16	0.8635
	DBC	3.94	0.15	0.9791	3.48	0.81	0.9812

The Langmuir isotherm model fitted the data of Pb and Zn adsorption on MBC well with R^2 value in the range of 0.9300-0.9590, implying that chemisorption of these two metals may be on a monomolecular layer and occur on the homogeneous surfaces of MBC. The maximum adsorption capacity (q_m) of MBC on all three metals was higher than that of DBC. This may due to the higher CEC value in MBC. Moreover, the amount of major elements was lower in MBC so there were more adsorption sites left to adsorb metal. The q_m of MBC on Pb was 16.18 mg/g, close to some reported values in the literature such as hickory biochar (12.2-16.30 mg/g) [34] and oak bark biochar (13.10 mg/g) [35]. The q_m of DBC on Pb was 2.75 mg/g, close to various reported values such as pine wood bark biochar (3.00 mg/g) [35], rice husk (1.84-2.40 mg/g) and pine wood biochar (3.89-4.25 mg/g) [36]. The q_m of Zn was similar to Pb. The q_m of Cd on MBC was 67.11 mg/g, close to data of the adsorption on *Canna indical* derived biochar (63-140 mg/g) reported in the literature [36]. The R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for Pb, Zn and Cd adsorption onto MBC at all initial concentration used in this research were greater than 0 but below 1 indicating that Langmuir isotherm was favorable. The Freundlish isotherm was better to explain the adsorption of all metals on DBC. This isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. The K_f is an indicator for adsorption capacity, while 1/n is a function of the adsorption strength. The K_f of Cd adsorbed on DBC was quite low, whereas the K_f of Cd adsorbed on MBC was close to data of the adsorption on *Canna indical* derived biochar (19-52 mg/g) reported in the literature [37]. The K_f of Pb adsorbed on DBC and MBC was much lower than the K_f of Pb adsorbed on hickory biochar [34].

Conclusions

Biochar produced from durian shell and mangosteen shell were appropriate to apply to adsorb cadmium, lead and zinc in soil. DBC and MBC were also evaluated as an alternative low-cost adsorbent to soil to raise pH of acid soil. From the pH titration curve of DBC and MBC, the pH dropped quite rapidly after adding acid. The ANC value of DBC (1,464.80 meq/kg) and MBC (1,328.98 meq/kg) were not so high. From the adsorption isotherm study, the Langmuir isotherm model fitted the data of Pb, Cd and Zn adsorption on biochar from mangosteen well, whereas the Freundlish isotherm was better to explain the adsorption of the metals on biochar from durian.

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