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Biochar Amendment for the Immobilization of Manganese and Cadmium in the Soils of Abandoned Coal Mining in Jambi, Indonesia

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Abstract

High heavy metal contents in soil of abandoned coal mining pose a risk to the environment. Acidic conditions impose a potential mobilization and availability of toxic heavy metals to water body. The objective of this study was to reduce mobilization of manganese and cadmium in the soil by amending lignite base biochar. The immobilization was investigated in a fixed bed column experiment in which concentrations of the metals in aliquot after the column were compared. Demineralized water adjusted to pH 4.7 to mimic environmental condition was pumped up through the column and the aliquots were collected at empty head space at liquid to solid (L/S) ratios of 1, 2, 5, 8 and 10. The results show that biochar amendment improves fraction of Mn and Cd immobilization in the soil and reduces mobility and availability of the metals. Amendment of 10% biochar could immobilize Mn (30%)and Cd (1%), respectively.

1. Introduction

Approximately 400,000 ha land of total 1 million ha in Jambi Province, Indonesiahas been converted to coal mining areas with minorremediation efforts. Widespreadopen mining activitiesin the lowland areas oxidized the pyritic minerals and created acidicenvironmental conditions. Solubility and mobility of heavy metals under acidic conditions increase [1] butaffinity to associate with the soil particles decreases and weakly associated metals could actually be released to water body through cation exchange. Under this acidic condition it therefore imposes a potential threat to the environments and human health [2]. However, metals that are strongly bound to soil crystal lattice remain stable and have less threat to environments [3]. Therefore, the magnitude of risk and impact of heavy metal pollution cannot be evaluated through the total concentrations. But their level of toxicity, availability and mobility contribute to the imposed risk [4]. Other factors such as soil composition, clay and organic matter contentsalso play significant roles in regulating mobility of heavy metals in the environments [5].

High concentrations and mobilization of toxic soil heavy metals in the mining impacted areas require necessary remediation strategy to reduce the impacted in environments. Some strategies might be appliedsuch as phytoremediation [5], damping/excavation [6] and in situ metal immobilization [2,7]. In phytoremediation soil heavy metals are translocated to plant biomassthrough complex formation between plant biomass and heavy metals. However, complex formation is considered as a slow process and lowsoil fertility found in the abandoned coal mine Jambi Province [8] may hinder the absorbing plant growth. In addition, plants absorbing heavy metals may release metals back to the environment due to plant biomass destruction. Damping/excavation seems not an effective strategy for a wide-spreadabandoned coal mine land as found in Jambi Province as heavy equipment relocation to the impacted sites is not practical and economical [6].

In situ immobilization of metals usingsoil amending biochar is being considered as an effective and low cost soil remediation alternative and offers some advantages. In this case, metals are not removed from the sites but stabilized in situ,simple pyrolysistechnology is available for biochar production and thus it could be used at farmer level in the fields. This is therefore considered as a suitable strategy formetals immobilization in a wide-spread abandoned coal mine area found in Jambi [8]. In addition, abundances of low rank coal lignite found in the abandoned coal mining area are potential to be used as precursor for biochar production. A study has shown that lignite-based biochar has a high ability in immobilization of soil heavy metals due tobiochar inherent factors such as large surface areas, active functional groups as cation exchange sides and high ash contents [2]. These factors play an important role in absorbing, stabilizing and immobilizing metals. Some studies have successfully immobilized heavy metals such as Cd with biochar from straw [10] and two different soil characteristics [11], Zn, Pb, Cd and Cu metals using biochar from bamboo [12] and Zn using biochar from waste agriculture [7]. Long lasting of biochar in the environment also contributes to the mitigation of greenhouse gas emissions [9].The above mentioned examples indicatethat biochar hasa great potential to be used in environmental remediation. The objective of this study was to utilize lignite based biochar to immobilize soil manganese and cadmiumusing up-flow column bed experiment.

2. Material and Methods

2.1. Soil and lignite materials

Soils and low rank coal lignite used in this study were collected in March 2018 in area "an abandoned coal mine" located in Sungai Buluh Village, Batanghari, Jambi Province, Sumatra. The materials were transported to the lab at the Universitas Jambi approximately 30 km to the south of the sampling site.

2.2. Biochar and soil preparation

Biochar was prepared by pyrolysis of lignite (250 g) in a reactor under limited oxygen. After four hours for cooling, the recovered biochar (152 g) was grained to pass 2 mm sieve and stored in sealed plastic bags.

Soil samples were cleaned from detritus such as stones, plant materials and other artefact and air dried at room temperature for 7 days.The solid was grained to pass 2 mm sieve and stored in sealed plastic bags.

2.3. Biochar and soil characterisation

The pH was measured in suspension soil:solution ratio of 1:2.5 g g^{-1}, biochar:solution ratio 1:5 gr ml^{-1}. The electrical conductivity of the biochar was determined in a filtered suspension biochar:solution ratio 1:5 ml ml^{-1} with distilled water. Soil moisture was determined by drying in an oven. Sieved sample (0.50 g) was weighed in aluminum plates of known weight, then dried in an oven at 105^{o}C to a constant weight, and then after cooling to room temperature the sample was placed in a desiccator for 15 minutes before re-weighing.

Specific surface area of the soil was determined by halo molybdenum spotting test [13]. Ten elemental heavy metals Pb, Cd, Mn, Zn, Ni, Fe, Cr, Na, Co and Ca in the soils and water collected from the mining site were determined using Inductively Plasma Optical Emission Spectroscopy (ICP-OES) Varian 715-ZEISS. Surface morphology of biochar was determined by Scanning Electron Spectroscopy (SEM) EVO MA 10. All samples were analyzed in duplicate.

2.4. Heavy metal immobilisation experiments

Biochar (0, 5, 10 and 15%) was added and mixed to the soil thoroughly. Transparent acrylic column of 4.8-cm ID and 50-cm long was set up by adding 1 cm^{-3} gravels and nylon sponge at base to facilitate liquid flow and on top to secure integrity of the soil particles. The soil of 235 gr was added into the column and pressed to ensure of 10-cm high to represent field soil density of 1.31 gr cm^{-3}. It needs to emphasize that higher soil densities up to 2.1 gr cm^{-3}were found in the fields caused liquid blocking in the column and thus could not be implemented in this experiment.

Demineralized water adjusted to pH of 4.7 to mimic the environmental condition was flowed through from column base with a peristaltic pump and aliquots were collected at empty head space at liquid to solid (L/S) ratios of 1, 2, 5, 8 and 10. The concentrations of Mn and Cd in the aliquots were analyzed with AAS.

2.5. Calculation of immobilisation efficiency of Mn and Cd

Immobilization efficiency of Mn and Cd is calculated from the different between the Mn and Cd concentrations in the aliquots after columns with and without biochar addition.

$$Immobilization\ efficiency\ (\%) = \frac{Co - C_1}{Co} \times 100\%$$

Where C_o is concentration (mg/L) of Mn or Cd in aliquots after the column without biochar addition, C_1 is the concentration (mg/L) of Mn or Cd in the aliquots after the column with biochar addition.

2.6. Determination of surface specific area

Methylene blue (MB) solution (1 g MB + 200 mL of deionized water) was prepared [13]. Soil (10 g) was mixed with deionized water (30 mL) and then MB solution was slowly added (with 0.5 mL increment). After the addition, the suspension was mixed by a magnetic stirrer (1 min), then a small drop was removed and placed onto Whatman filter paper 41. Un-adsorbed MB forms a permanent blue halo around the soil aggregate onto the filter paper, this indicates that the MB has replaced cations in the double layer and coated the entire surface. The surface area is determined from the MB amount addedtothe end point with the following equation:

$$SSA = \frac{1}{319{,}89}\ x\ \frac{1}{200}(0{,}5\ N)AvA_{MB}x\frac{1}{10}$$

where N=number of MB increments added to the soil suspension solution; Av=Avagadro's number ($6.02x10^{23}$) mole; and A_{MB}=area covered by one MB molecule (typically assumed to be 130 $Å^2$).

3. Results and discussion

3.1. Soil and water heavy metals

The soilsused in this study were collected from abandoned coal mining, Sungai Buluh, Batanghari, Jambi Province. The soils show yellowish to red color could be Ultisol soil and Podsolic soil (ultisol). Density of the soils ranged from 1.3 to 2.1 g cm^{-3} and acidity (pH) of 4.9.pH of the water collected from the site ranged from 4.7 to 5.0.Ten most abundant heavy metals in the soil and water wereanalyzed with ICP-OESas given in table 1.

Table 1. Ten elemental heavy metals in soils and waters collected from abandoned coal mining, SungaiBuluh, Batanghari, Jambi Province.

Heavy Metals	Water		Soil			
	A	B	Soil-0	Soil-12	Soil-34	Soil-56
	(mg/L)	(mg/L)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)
Ca	5,531	27,769	417,939	421,223	265,778	818,531
Na	1,948	1,304	56,150	49,119	34,006	59,566
Fe	0,393	0,421	3.03*	3.54*	4.09*	1.86*
Zn	0,188	0,468	30,895	23,644	12,701	52,279
Cr	0,059	0,137	7,101	7,391	6,062	8,112
Mn	0,049	0,055	16,677	7,524	14,042	28,734
Ni	0,013	0,083	3,792	2,434	<0,410**	10,927
Pb	<0,037**	0,304	<1,674**	<1,674**	<1,674**	<1,674**
Cd	<0,003**	<0,003**	1,969	4,153	5,047	1,762
Co	<0,003**	<0,003**	<1,140**	<1,140**	<1,140**	<1,140**

*inpercentage **belowdetectionlimit

Table 1 shows that the most dominant heavy metals found the soils are iron (Fe), calcium (Ca), sodium (Na), Zinc (Zn), Manganese (Mn), Chromium (Cr), Nickel (Ni), Cadmium (Cd), respectively. Lead (Pb) and Cobalt (Co) arebelow limit detections. In the water samples three metals (Ca, Na and Fe) are predominant while other three metals (Pb, Cd and Co) are all below the detection limit.The most abundant heavy metal in our solid sample is iron with average concentration of 3.13%. While in the water samples calcium is the most abundant element with concentration up to 27.77 mg L^{-1}.We notify that Cdis the only element with high concentrations in the soils but in the water it is below detection limit. This probably indicates that Cd is strongly associated with soil minerals of low solubility at the environmental condition. Cobalt is the only element with concentration of below limit detection in both water and soil samples.

3.2. The effect of biochar amendment on Mn immobilisation

The effects of biochar amendment on immobilization of Mn were studied using up-flow fixed bed column experiments are shown in figure 1. The concentration of Mn in the solid after deionized water pH 4.7 passed through the soil column at various L/S ratios. The soil in the column was amended with biochar (0, 5, 10 and 15%). The concentrations of Mn in the soil without biochar (0%) amendment are low compared to that of soils with 5, 10 and 15% biochar amendment. A substantial increase in Mn immobilization is observed at low L/S ratios(1 and 2)at all biocharconcentrations (5, 10 and 15%). However, no significant increase is observed at higher L/S ratios (5, 7 and 9).The addition of 5, 10 and 15% biochar to the soils immobilizes 7.13, 9.25 and 12.71% Mn, respectively at L/S of 1. At the L/S ratio of 2 the amount of Mn immobilized is about 15.81, 20.18 and 23.41%, respectively. We notify that at higher L/S ratios (5, 8 and 10) and biochar amendment (10 and 15%) there are no significant improvements in Mn immobilization. This probably indicates that labile fractions of Mn in the soil might have been mobilized during the L/S ratios of 1 and 2. Similar results have been reported in several articles [10,12] using biochar from straw [10] and soils of different characteristics [12].

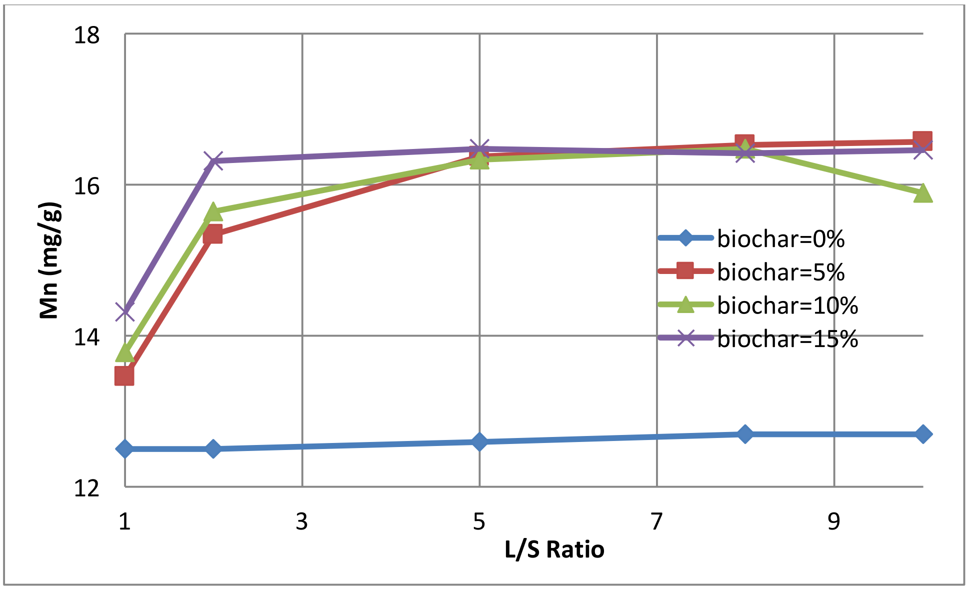

Figure 1. Effect of biochar amendment (0, 5, 10 and 15%) and liquid to solid ratios (L/S) (1, 2, 5, 8 and 10) on immobilisation of soil Mn studied using up flow bed column experiment

3.3. The effect of biochar amendment on Cd immobilisation

Similar to that of manganese, cadmium immobilization was also studied using the same experimental set up. At the L/S ratio of 1, the amount of labile Cd found in the liquid is variable, but at higher L/S ratios the amount of Cd in the liquid shows a continuous improvement as shown in Figure 2.

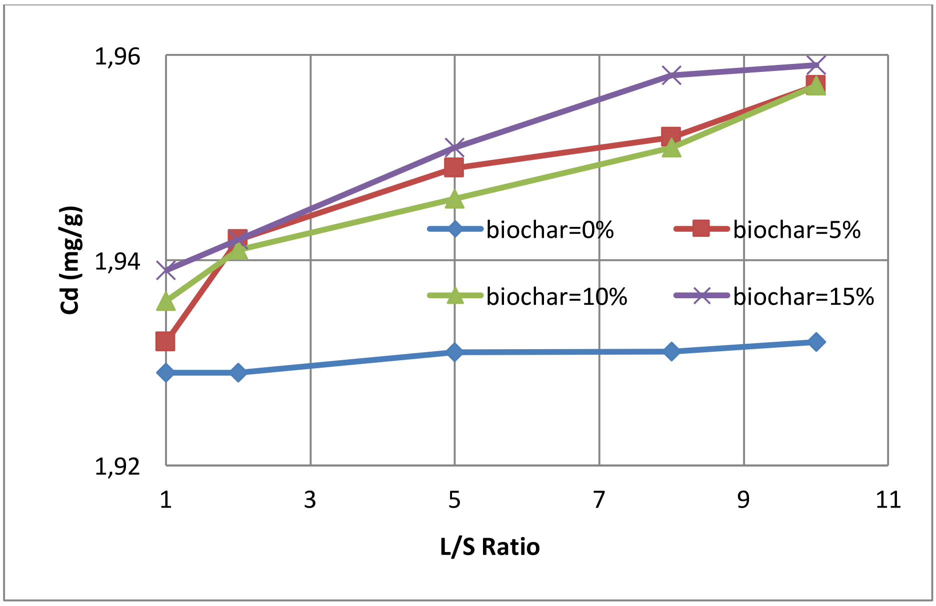

Figure 2. Effect of biochar amendment (0, 5, 10 and 15%) and liquid to solid ratios (L/S) (1, 2, 5, 8 and 10) on immobilisation of soil Cd studied using up flow bed column experiment.

This might indicate a slow mechanism process of Cd immobilization in the soils studied. This probably also explains below detection limit of Cd is found in the water samples collected in the area from where the soil samples were obtained.

It appears that Mn and Cd show different of immobilization mechanisms in the soils studied as indicated in Figures 1 and 2. Both metals might be interacting with different parts of the biochar in the soil mixture and they might also associate with different minerals of the soils.

This could probably be related to a small amount of Cd found in the soil samples so that amendment of 5% biochar is appropriate amount for biochar to immobilize weakly bound Cd to the soil particles. However, the improve in the amount of liquid passed through the solid as indicated by the increase in the L/S ratios is followed by the increase in the soil Cd immobilization. According to [14] the main mechanisms responsible for Cd^{2+} removal using biochar were cation exchange and cation-π bonding. Cadmium removal could achieve adsorption capacity of 81.10 mg Cd/g as a result of the increase of the specific surface area, number of oxygen containing functional groups and the pore size and structure of biochar.

Conclusion

Soils from abandoned coal mining of Sungai Buluh contain high concentrations of some heavy metals. Amendment of lignite-based biochar to the soils in up-flow column experiment is able to immobilize approx. 20% of Mn and Cd in the biochar amended soils. Biochar amendment could be potential strategy to mobilize Mn and Cd contamination in the soils of Sungai Buluh abandoned coal mining.

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