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IMMOBILISATION OF ARSENIC, COPPER, MANGANESE AND LEAD IN GOLD MINE TAILINGS BY OIL PALM EMPTY FRUIT BUNCH AND RICE HUSK BIOCHARS

CLAOSTON ANAK NARDON

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By

CLAOSTON ANAK NARDON

Thesis Submitted to the School of Graduates Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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IMMOBILISATION OF ARSENIC, COPPER, MANGANESE AND LEAD IN GOLD MINE TAILINGS BY OIL PALM EMPTY FRUIT BUNCH AND RICE HUSK BIOCHARS

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Chairman: Samsuri Abd Wahid, PhD

Faculty: Agriculture

Biochar has recently received great attention due to its physico-chemical properties which affects soil fertility and contaminant immobilisation as well as serving carbon sinks and sequestration in the soil system. In this project, biochars were produced from empty fruit bunch (EFB) and rice husk (RH) by slow pyrolysis at different temperatures (350, 500 and 650 ^{o}C) and the physico-chemical properties of each biochar were analysed. The results show that the porosity (BET surface area), ash content, EC and pH value of EFB and RH biochars increased with increasing pyrolysis temperature. However the amount of biochar produced, its CEC and N, C and S content decreased with increased in temperature. The FTIR spectra were similar for RH biochars but the functional groups were more distinct in the EFB biochars spectra. There were significant reductions in functional groups as pyrolysis temperature increased, especially for the EFB biochar. However, the total acidity of the functional groups increased with pyrolysis temperature for both biochars. The first experiment that has been conducted was on adsorption studies. These studies have been done to oversee the potential of EFB and RH biochars in adsorbing As, Mn, Cu and Pb from aqueous solution of different concentrations. In this research, adsorption of As, Mn, Cu and Pb increased with increasing initial concentrations. This is due to the higher concentration gradient to overcome the mass transfer energy. The experiment also showed that adsorption of As, Mn, Cu and Pb by EFB and RH biochars fitted well to the Langmuir isotherm. The R_L values also was found between 0 and 1, and showed that the adsorption of As, Mn, Cu and Pb were a favourable process. Furthermore, to investigate the effect of biochar application in the retention of heavy metals in gold mine tailings, the tailings were incubated with different rates of RH and EFB biochars for 2, 8 and 24 weeks. The application of biochar significantly reduced the concentrations of extractable Pb, Mn and Cu in the tailings. However, the opposite was observed for

As. The addition of biochar also increased the pH of the tailings throughout the incubation periods. The EFB and RH biochars produced at 650 ^{o}C were better in reducing the extractable Cu, Pb and Mn. However, EFB650 and RH650 biochars were also the worst in reducing the extractable As in the tailings. Besides, a leaching experiment was conducted by mixing the tailings with EFB and RH biochars at different rates (0, 5, 15 and 20% (w/w)) and leached with simulated rain water (SRW) every 15 days for 2 months. The results showed that with increasing rates of both biochars, the concentrations of As, Pb, Cu and Mn in the leachates were significantly higher than the control. These experiments (adsorption, incubation and leaching studies) in aqueous solutions and tailings amended with EFB and RH biochars that were produced at 350, 500 and 650 ^{o}C showed that the capability of these biochars in reducing the available As, Cu, Mn and Pb were dependent on many aspects such as BET surface area, porosity and variety of functional groups in the biochars as well as several sorption processes, which includes adsorption to mineral (tailings) surfaces, formation of stable complexes with organic ligands, ion exchange and surface precipitation. Overall, the evidences raised by the current study proved that application of biochars as an amendment in polluted area, such as mine tailings, can adsorb or immobilized heavy metals and other pollutants, hence reducing the availability of pollutants in particular polluted area. Thus, utilization of biochar will create a cleaner environment.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

IMOBILISASI ARSENIK, KUPRUM, MANGAN DAN PLUMBUM DALAM TANAH BEKAS LOMBONG EMAS OLEH BIO-ARANG TANDAN KOSONG KELAPA SAWIT DAN SEKAM PADI

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CLAOSTON ANAK NARDON

Ogos 2015

Pengerusi: Samsuri Abd Wahid, PhD

Fakulti: Pertanian

Kini bio-arang telah menerima perhatian yang meluas disebabkan oleh ciri-ciri fisiko-kimia yang mempengaruhi kesuburan tanah dan pengerakan pencemar di samping menyediakan simpanan dan pemencilan karbon di dalam sistem tanah. Dalam projek ini, bio-arang telah dihasilkan daripada tandan kosong kelapa sawit (EFB) dan sekam padi (RH) melalui pirolisis perlahan pada suhu yang berbeza (350, 500 dan 650 ^{o}C) dan ciri-ciri fisiko-kimia setiap bio-arang dianalisis. Keputusan menunjukkan nilai keronggaan (luas permukaan BET), kandungan abu, EC dan pH bio-arang EFB dan RH meningkat dengan peningkatan suhu pirolisis. Namun yang demikian, kandungan CEC, N, C dan S menurun dengan peningkatan suhu pirolisis. Spektrum FTIR pada semua bio-arang RH mempunyai bentuk yang hampir serupa tetapi spektrum biochar EFB adalah sebaliknya. Terdapat pengurangan yang signifikan kepada kumpulan fungsian pada bio-arang EFB apabila suhu pirolisis ditingkatkan. Walau bagaimanapun, jumlah keasidan pada kumpulan fungsian untuk kesemua bio-arang meningkat dengan peningkatan suhu pirolisis. Eksperimen pertama yang telah dijalankan ialah kajian penjerapan. Kajian ini telah dijalankan untuk mengetahui potensi bio-arang EFB dan RH dalam menjerap As, Mn, Cu dan Pb daripada larutan yang mengandungi kepekatan yang berbeza. Dalam penyelidikan ini, penjerapan As, Mn, Cu dan Pb meningkat dengan peningkatan kepekatan awal. Hal ini adalah disebabkan oleh daya kecerunan kepekatan yang tinggi untuk mengatasi daya pemindahan jisim. Eksperimen ini juga menunjukkan penjerapan As, Mn, Cu dan Pb oleh bio-arang EFB dan RH adalah mengikut isoterma Langmuir. Nilai R_L juga berada pada julat antara 0 dan 1, menunjukkan penjerapan As, Mn, Cu dan Pb merupakan proses yang bersesuaian. Di samping itu, untuk menyelidik kesan penggunaan bio-arang dalam pengekalan logam berat dalam tanah bekas lombong emas, tanah bekas lombong telah diinkubasi dengan kadar bio-arang RH and EFB yang berbeza selama 2, 8 dan 24

minggu. Penggunaan bio-arang mengurangkan jumlah pengekstrakan Pb, Mn dan Cu dalam tanah bekas lombong kecuali As. Penambahan bio-arang turut meningkatkan pH pada tanah bekas lombong dalam jangkamasa inkubasi. Bio-arang EFB dan RH yang dihasilkan pada suhu 650 ^{o}C merupakan bio-arang yang terbaik untuk mengurangkan pengesktrakan Cu, Pb dan Mn. Akan tetapi, bio-arang EFB650 dan RH650 merupakan bio-arang yang paling teruk dalam mengurangkan As yang boleh diekstrak dalam tanah bekas lombong. Selain itu, eksperimen larutlesap telah dijalankan dengan mencampurkan tanah bekas lombong dengan bio-arang EFB dan RH pada kadar yang berbeza (0, 5, 15 dan 20% (w/w)) dan dilarutlesapkan dengan air hujan buatan (SRW) pada setiap 15 hari selama 2 bulan. Hasil dari eksperimen mendapati peningkatan kadar bio-arang boleh meningkatkan kepekatan larutlesap As, Pb, Cu dan Mn lebih tinggi daripada rawatan kawalan. Eskperimen yang dijalankan (kajian penjerapan, inkubasi dan larutlesap) pada larutan akueus dan tanah bekas lombong yang dipinda dengan bio-arang EFB dan RH yang dihasilkan pada 350, 500 and 650 ^{o}C menunjukkan kebolehan bio-arang ini dalam mengurangkan As, Cu, Mn dan Pb bergantung pada beberapa aspek: luas permukaan BET, keronggaan dan kepelbagaian kumpulan fungsian dalam bio-arang, di samping beberapa proses serapan seperti penjerapan kepada permukaan mineral (tanah bekas lombong), pembentukan kompleks stabil dengan ligan organik, penukaran ion dan mendakan permukaan. Secara keseluruhannya, kajian yang dijalankan membuktikan penggunaan bio-arang sebagai peminda tanah dalam kawasan tercemar, seperti pada tanah bekas lombong, boleh digunakan untuk menjerap logam berat dan pencemar yang lain, lantas mengurangkan pengerakan pencemar pada sesuatu kawasan. Oleh itu, penggunaan bio-arang dapat menghasilkan persekitaran yang bersih.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Samsuri Abd Wahid, PhD
Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Ahmad Husni Mohd Hanif, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Mohd Amran Mohd Salleh, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

____
BUJANG KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Name of Member of Supervisory Committee: ______________________________

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LIST OF ABBREVIATIONS

g/mol	gram per mol
mg/kg	milligram per kilogram
µg/L	microgram per litre
g/cm^3	gram per centimetre cube
^oC	degree Celcius
%	percentage
µm	micrometre
ms	millisecond
BET	Brunauer, Emmet and Teller
K_L	Langmuir constant
Q_m	Langmuir maximum adsorption capacity
K_F	Freundlich constant
1/n	affinity of sorbate to sorbent
mm	millimetre
EC	electrical conductivity
pH	concentration of hydrogen ion
CEC	cation exchange capacity
g	gram
N	normality
mL	millilitre
EFB	empty fruit bunch
RH	rice husk
M	molarity
kW	kilowatt
K	Kelvin
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
mg/g	milligram per gram
ppm	part per million
SRW	simulated rain water
wt/wt	weight over weight
m^2/g	meter square per gram
HTT	highest temperature treatment
cm^{-1}	per centimetre
dS/cm	desi Siemens per centimetre
$cmol_+/kg$	centimol charge per kilogram
meq/g	milliequivalent per gram
kg H_2SO_4/t	kilogram of sulphuric acid per tonne
mg	milligram
mg/L	milligram per litre
ICP-OES	Inductively Coupled Plasma/Optical Emission Spectrometry
cm	centimetre
mM	millimolar

CHAPTER 1

INTRODUCTION

1.1 General background

Mining industry produced large quantities of solid wastes as by-products from its operations. Specifically, mining activities will also discharge high quantities of potential toxic materials bearing volatiles and dust particles into the environment, thus creating pollution. Besides, mining areas are associated with dissolved metals from the oxidation of sulphide-bearing minerals that are exposed to weathering conditions. This will result in acidic effluents with high amount of dissolved metals such as cadmium, copper and zinc, and other metalloids such as arsenic and selenium.

Crushing, grinding and other physical and chemical processes in mining activities generate waste products known as tailings and usually the tailings are disposed off *in-situ*. Besides tailings, other solid mining wastes and other related wastes from the mining industry is summarized in Table 1. The tailings are typically in the form of particulate suspension, i.e. a fine grained sediment-water slurry and represents the most voluminous waste at the mine sites. The physical and chemical processes of breakdown the mineral in the mining require addition of chemical additives. Although most of the additives are reused and recovered in the process, some of the chemicals may remain in the tailings. However, some of the chemical additives are decomposed naturally but many of them may be bound strongly and long lasting within the tailings. Besides, the tailings contain enormous concentration of non-economic minerals such as silicates, oxides, hydroxides, carbonates and sulphides that have never been collected throughout the mineral processing. Hence, these ingredients when mixed with the tailings may result in mixture which is partly toxic and bring harm to ecosystem. Since the tailings contain both solid waste mixed with water during the mining operation, the mixtures will gradually dry after the end of the mining process, hence redox reaction would be taking place and change the stability of some elements which can be leached out into the environment. The inappropriate management of tailings resulted in the destruction of ecological landscape, decrease in biological diversity, contributing to the contamination of soil substrates, migration of heavy metals to the surrounding environment and groundwater pollution.

Heavy metals in soil are ubiquitous, rising from both anthropogenic and natural sources with trails including the rocks, parent materials, application of water as well as local and long-range atmosphere and fluvial deposition of emissions from dust and mining. Heavy metals that are related with tailings, show capability to accumulate and build-up in sediments and soils, and are not biodegradable. Under highly acidic conditions, metals including Fe, Mn, Cu, Al, Pb, Cd, Zn and As will be released from the tailings and bring toxicity to plant and animals. Furthermore, mine tailings contain sulphide minerals such as pyrite (FeS_2), arsenopyrite (FeAsS), galena (PbS), and sphalerite [(Fe, Zn)S]. As tailings exposed to the air, oxidation, precipitation, adsorption and desorption may occur, as oxidation of sulphide minerals resulting in contamination of the surrounding soil and groundwater by releasing As and heavy metals in sulphide-bearing minerals (Jang et al., 2005). Besides, As and heavy metals originated from mine tailings may cause fatal sickness in human beings through food and water due to the easiness of the metals to accumulate in the internal organ.

Table 1. Summary of mining activities and their wastes (Sutthirat, 2002)

Activities	Mining wastes
Open pit and underground mining	Waste rocks, overburden soils, mining water, atmospheric emissions
Mineral processing, coal washing, mineral fuel processing	Tailings, sludge, mill water, atmospheric emissions
Pyrometallurgy, hydrometallurgy, electrometallurgy	Slag, roasted ores, flue dusts, ashes, leached ores, process water, atmospheric emission

Various treatments have been developed and known for treatment of such polluted environment. The real challenge is to select the economical technique that has the least adverse effect on the environment. Methods for removing metals from environment mainly consist of physical, chemical and biological techniques. Example of the treatments include foam filtration, sedimentation, solvent extraction, chemical oxidation, membrane processes, lime softening, coagulation, electrochemical processes, electrocoagulation and chemical precipitation. All of these techniques have low efficiency in removal of trace concentration of pollutants in terms of chemical/biological oxidation, electrolysis, ion exchange and solvent extraction (Bhatnagar and Minocha, 2006; Zhang et al., 2012). Furthermore, coagulation and precipitation process produce large amount of sludge and need pH control. Fisal et al. (2012) mentioned that ozonation process to adsorb cationic dye from wastewater will not reduce the COD content, and research by Dang et al. (2009) found that membrane process suffer from the problem of fouling of the membrane used. As stated by Yang et al. (2009), alternative technologies to treat polluted soils and mine tailings include (1) *in-situ* metal immobilization methods, i.e. phytostabilization and *in-situ* biochemical fixation or stabilization by using soil amendments with inorganic and organic materials; and (2) metal extractions methods, i.e. washing, phytoextraction and electrokinetic remediation. Most of these methods lack in cost effectiveness, need more energy in intensive processing and low efficiency to remove some pollutants. Hence, more economical and environmental friendly with high adsorption capacity method have been introduced to possess rapid rate of removal and having low adverse effect on the polluted area.

Removal of heavy metals using agricultural wastes and its industrial by-products has been greatly studied due to the abundance of agricultural wastes in nature and its economical cost. Sud et al (2008) listed various agricultural wastes that had been used to remove or recover heavy metals from aqueous solution which include rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, *Cassia fistula* leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, cotton stalks and sugarcane bagasse. These wastes are one of the main resources for renewable energy and chemical feedstock sources. There are several thermochemical processes that convert biomass and agricultural wastes into valuable products, which known as liquefaction, gasification, combustion and pyrolysis. Between all the processes, pyrolysis is one of the thermochemical conversion processes that can be used to convert agricultural wastes into beneficial products such as biochar, bio-oil and non-condensable gas by heating the agricultural materials in the absence of oxygen (Demirbas, 2008). There are two types of pyrolysis involve in the production of biochar, namely the fast and slow pyrolysis. The fast pyrolysis yields higher amount of oil while biochar is produced at larger amount using the slow pyrolysis (Mohan et al., 2006). Pyrolysis can convert approximately half of the carbon in biomass into more recalcitrant forms (Lehmann et al., 2006); consequently the half-life of stable C in soil is estimated to be over 1000 years (Laird, 2008). Sequestration of carbon into soil can offset the CO_2 emissions, which would otherwise have entered the atmosphere through fossil fuel production, combustion, fertiliser production or composting. From an energy point of view, the production of bio-oil and gas from pyrolysis can be used as fuels which can off-set the fossil fuel usage (Lehmann et al., 2006).

Recently, application of biochar as a soil amendment has been given attention to all the researchers due to its potential as soil conditioning properties and the unique physicochemical properties. Apart from the beneficial effects of drawing CO_2 from the atmosphere, utilization of biochars to soil are also able to reduce the emissions of greenhouse gases (GHGs) and improve soil functions (Lehmann et al., 2006). Besides, the application of biochar as a soil amendment can give multiple advantages that include, increase in (1) cation exchange capacity (CEC) of soils (Glaser et al., 2002), (2) soil pH (O'Neill et al., 2009), soil nutrients (Wang et al., 2012) and crop yield (Graber et al., 2010). Biochar is also known to decrease the non-CO_2 GHG emissions from the soil (Karhu et al., 2011), since biochar also promotes the adsorption of NH_3 and NH_4^+ on biochar surfaces, hence affecting N ammonification, denitrification, nitrification and volatilization (Clough and Condron, 2010; Taghizadeh-Toosi et al., 2012).

1.2 Problem statement

Enormous waste of heavy metals introduced into the environment due to the mineral processing of hard rock metal ores and industrial mineral deposits from the gold mine tailings has brought a massive problem worldwide. Heavy metals do not degrade into harmless end products, unlike organic pollutants which the majority of the pollutants are susceptible to biological degradation. Some of the heavy metals are percolating into the groundwater and other estuaries system through runoff during precipitation. Soils contaminated with heavy metals will pose a long-term risk of increased leaching process into the groundwater and increasing plant uptake, with potentially adverse implications to the environment, including human health. Some research has found that using biosorbent is the most cost effective method to remove heavy metals in mine tailings (De Coninck and Karam, 2008; Santibañez et al., 2012; Pérez-Esteban et al., 2013; Lee et al., 2013). Furthermore, some studies showed the effectiveness of various biochars in removing heavy metals in mine tailings (Fellet et al., 2011; Islami et al., 2011; Kumar, 2013; Li et al., 2013; Kelly et al., 2014). Demirbas (2008) mentioned that the process of adsorption involves the presence of an adsorbent solid that will bind molecules by chemical binding, physical attractive forces and ion exchange. So, this research is aiming to solve the problem by using a low cost material from common agricultural wastes in Malaysia, namely as rice husk and empty fruit bunch of oil palm, and pyrolyzed both of these biomasses at three temperatures (350, 500 and 650 ^{o}C) as biochars to act as an amendments to immobilize heavy metals (As, Cu, Mn and Pb) in mine tailings.

1.3 Aims and objectives

The overall aim of this study was to evaluate the efficiency of empty fruit bunch (EFB) of oil palm and rice husk (RH) biochars pyrolyzed at different temperatures to immobilize As, Cu, Mn and Pb in mine tailings.

The following specific objectives are:

i. to investigate the physicochemical properties of EFB and RH biochars pyrolysed at 350, 500 and 650 ^{o}C
ii. to evaluate the adsorption properties of EFB and RH biochars produced at different temperatures for As, Pb, Mn and Cu by carrying out adsorption experiments
iii. to evaluate the capability of EFB and RH biochars to retain and stabilise heavy metals in mine tailings through incubation and leaching studies, respectively

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