REMEDIATION OF METAL CONTAMINATED SOIL USING COCONUT TREE SAWDUST, EGGSHELL AND SUGARCANE BAGASSE AS AMENDMENT AGENTS

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ABSTRACT

This research aimed to evaluate the potential of coconut tree sawdust (CTS), eggshell (ES) and sugarcane bagasse (SB) to immobilise metals in contaminated soil. This research is divided into three parts, namely characterisation studies, adsorption studies and pot experiments. The characterisation studies of amendment agents were performed using Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) Spectrometer and Fourier Transform Infrared (FTIR) Spectrometer. The characterisation studies were conducted to identify the effects of metal ion binding on the surface morphology of the amendment agents, to confirm the presence of functional groups in the amendment agents and to elucidate the possible binding mechanism. The SEM images showed that the surface morphology of the amendment agents changed significantly following interaction with metal. Meanwhile, the EDX spectra confirmed the presence of metal on the surface of the amendment agents after adsorption process. The FTIR spectra confirmed that amine, carbonate, carbonyl, carboxyl and hydroxyl are the active sites for the amendment agents. The adsorption studies were carried out to evaluate the ability of the amendment agents to bind metal ion. Two experimental parameters were examined in this study, namely solution pH and initial metal concentration. The Freundlich constant (n) and separation factor (R_L) values suggest that the adsorption of Cu(II), Pb(II) and Zn(II) ions onto amendment agents was favourable. The effectiveness of amendment agents to immobilise metals in soil was further evaluated in two sets of pot experiment using water spinach (*Ipomoea aquatica*). The pot experiments were carried out for 8 weeks at three rates of application, namely 0, 1 and 3% (w/w). The results show that the accumulation of metals in the plant tissues and bioavailability of metals in soil decreased following treatment. In conclusion, remediation of contaminated soil using CTS, ES and SB could reduce soil metal contamination and increase biomass yield of water spinach. Overall, the utilisation of low-cost materials such as coconut tree sawdust, eggshell and sugarcane bagasse could be suggested to restore soil contamination as well as to reduce the operational cost of soil remediation.

PEMULIHAN TANAH TERCEMAR OLEH LOGAM MENGGUNAKAN HABUK KAYU POKOK KELAPA, KULIT TELUR DAN HAMPAS TEBU SEBAGAI EJEN PEMINDAAN

ABSTRAK

Kajian ini bertujuan untuk menilai potensi habuk kayu pokok kelapa (CTS), kulit telur (ES) dan hampas tebu (SB) bagi menyahgerak logam-logam di dalam tanah yang tercemar. Penyelidikan ini dibahagikan kepada tiga bahagian, iaitu kajian pencirian, kajian penjerapan dan eksperimen pasu. Kajian pencirian bagi ejen pemindaan dilakukan menggunakan Mikroskop Pengimbas Elektron (SEM), Spektrometer Penyebaran Tenaga Sinar-X (EDX) dan Spektrometer Inframerah Transformasi Fourier (FTIR). Kajian pencirian telah dijalankan untuk menentukan kesan pengikatan ion logam terhadap morfologi permukaan ejen pemindaan, untuk mengesahkan kehadiran kumpulan berfungsi dalam ejen pemindaan dan untuk menjelaskan mekanisme pengikatan yang mungkin berlaku. Imej SEM menunjukkan bahawa morfologi permukaan ejen pemindaan berubah dengan ketara selepas interaksi dengan logam. Sementara itu, spektra EDX mengesahkan kehadiran logam pada permukaan ejen pemindaan selepas proses penjerapan. Spektra FTIR mengesahkan bahawa amina, karbonat, karbonil, karboksil dan hidroksil adalah tapak-tapak aktif untuk ejen pemindaan. Kajian penjerapan telah dijalankan untuk menilai keupayaan ejen pemindaan untuk mengikat ion logam. Dua parameter eksperimen telah dikaji dalam kajian ini, iaitu pH larutan dan kepekatan awal logam. Nilai-nilai pemalar Freundlich (n) dan faktor pemisahan (R_L) mencadangkan bahawa penjerapan ion-ion Cu(II), Pb(II) dan Zn(II) ke atas ejen pemindaan adalah baik. Keberkesanan ejen pemindaan untuk menyahgerak logam-logam di dalam tanah telah selanjutnya dinilai dalam dua siri eksperimen pasu menggunakan kangkung (*Ipomoea aquatica*). Eksperimen pasu telah dijalankan selama 8 minggu pada tiga kadar penggunaan, iaitu 0, 1 dan 3% (w/w). Dapatan menunjukkan pengumpulan logam-logam dalam tisu tumbuhan dan kebiosediaan logam-logam dalam tanah berkurangan selepas rawatan. Kesimpulannya, pemulihan tanah yang tercemar menggunakan CTS, ES dan SB dapat mengurangkan pencemaran logam dalam tanah dan meningkatkan hasil biojisim kangkung. Secara keseluruhannya, penggunaan bahan-bahan kos rendah seperti habuk kayu pokok kelapa, kulit telur dan hampas tebu boleh dicadangkan untuk pemulihan pencemaran tanah di samping dapat mengurangkan kos operasi pemulihan tanah.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
AMT	Acid mine tailings
ASTM	American Society for Test Material
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration factor
BET	Braunauer-Emmet-Teller
BJH	Barret Joyner Halenda
$Ca(NO_3)_2$	Calcium nitrate
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
$CdCl_2$	Cadmium chloride
CH_3COONH_4	Ammonium acetate
CTS	Coconut tree sawdust
$Cu(NO_3)_2$	Copper (II) nitrate
DNA	Deoxyribonucleic acid
DOE	Department of Environment
DTPA	Diethylenetriaminepentaacetic acid
EDDS	Ethylenediamine-N,N'-disuccinic acid
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
ES	Eggshell
FAOSTAT	Food and Agricultural Organisation Statistic

FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
HNO_3	Nitric acid
JRC EU	Joint Research Centre of the European Commission
KNO_3	Pottasium nitrate
LOD	Limit of Detection
LOQ	Limit of Quantification
MEP	Ministry of Environment Protection
$MgCO_3$	Magnesium carbonate
MOA	Ministry of Agricultural
MSW	Municipal solid waste
NaCN	Sodium cyanide
NaOH	Sodium hydroxide
NH_4OAc	Ammonium acetate
NTA	Nitrilotriacetic acid
$Pb(NO_3)_2$	Lead (II)nitrate
PFA	Prevention of Food Adulteration
SB	Sugarcane bagasse
SEM	Scanning Electron Microscope
TCLP	Toxicity characteristics leaching procedure
TF	Translocation factor
USDA	United States Department of Agricultural
USEPA	United States Environment Protection Agency
USGS	United States Geological Survey
WHO	World Health Organisation

$Zn(NO_3)_2$	Zinc (II) nitrate

CHAPTER 1

INTRODUCTION

1.1 Research Background

Soil can be described as a dynamic system that can be found on the upper land surface between air and rock. It is consists of 95% inorganic and 5% organic materials and is formed from weathering of the parent material (Davies, 1994; Hohl & Varma, 2010; Mirsal, 2008). According to United State Department of Agriculture (USDA, 2010), soil can be defined as a natural body consists of solid, liquid and gasses that can be identified from the parent material. Soil is divided to the individual size groups of mineral particles, namely sand (2.0-0.02 mm), silt (0.05-0.002 mm) and clay (<0.002 mm) (McDaniel, Falen, & Fosberg, 2012; USDA, 1987). The total land area including ice-covered surface, deserts and rocky surface of the world is around 130,575,895 km^2 (Osman, 2014). Soil covers approximately 80% of the earth's crust (Manahan, 2005).

Soil is a part of nature that has a fundamental role for survival of living organism and environment (Bech, Abreu, Chon, & Roca, 2014; Kabata-Pendias & Mukherjee, 2007). Soil also helps to generate human food, fuel and fiber (Blanco-Canqui & Lal, 2008). On the other hand, the function of soil for living organism and environment is irreplaceable. The function of soil include: (1) medium for plant growth (2) water recycle, (3) place for degradation organic compound, (4) source of nutrient and (5) place for living organism(s) (Abrahams, 2002; Dighton, 2014; Fränzle, 2010; Nortcliff, 2002).

On a spatial basis, the main sources of heavy metal in the soil are lithogenic and input from anthropogenic activities (Dudal, 2005; Oves, Khan, Zaidi, & Ahmad, 2012). The lithogenic source is the rock or unconsolidated drift material (parent material), while the anthropogenic source include mining, industry, agriculture, atmospheric deposition and waste disposal (Alloway, 2013a; Hooda, 2010; Wuana & Okieimen, 2011). The deployment of metal in the soil is depends on the source of metal around sites. For example, in the urban soil, traffic emissions, utility network pipes, discharging of human and industrial wastes, weathering building and pavement surface are the major source of heavy metal in the soil (Meuser, 2010). Meanwhile, the application of fertiliser and inorganic pesticide in the agricultural activities has attributed to elevated contamination of heavy metals in soil (Su, Jiang, & Zhang, 2014).

Heavy metal can be divided into essential (required), possible essential and non-essential elements (Kabata-Pendias & Mukherjee, 2007). For example, all higher plants need seven micronutrients and nine macronutrients for normal growth and health. The seven micronutrients are boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn). Meanwhile, the nine macronutrients include calcium (Ca), carbon (C), hydrogen (H), oxygen (O), magnesium (Mg), nitrogen (N), phosphorus (P), potassium (K), and sulfur (S) (Schulin, Johnson, & Frossard, 2010). Other than that, some plants also reported need nickel (Ni) as an essential element (Appenroth, 2010). For human, zinc plays several fundamental functions in metabolic process, mainly in proteins, carbohydrates and deoxyribonucleic acid (DNA). Zinc also has roles for growth, development, and reproduction (Kabata-Pendias & Mukherjee, 2007).

The deficiency and excess of heavy metals in the living organism may lead several health risks (Avci & Deveci, 2013; Singh et al., 2011). For example, the deficiency of iron in the human body can cause anemia (Kabata-Pendias & Mukherjee, 2007). Meanwhile high level of Cr(VI) can cause harmful effects such as lung tumors, chronic bronchitis, kidney damage and dermatitis (Agency for Toxic Substances and Disease Registry [ATSDR], 2012). The effects of toxicity of heavy metals for living organisms are greatly influenced by their physical and chemical characteristics, availability and the nature of living organisms (Wang, Shi, Lin, Chen, & Chen, 2007). For example, Wong and Bradshaw (1982) reported that the order of toxicity of seedlings of rye grass was Cu > Ni > Mn > Pb > Cd > Al > Hg > Cr > Fe. A study on the effect of 10 heavy metals in the duckweed *Lemna minor* L. clone on the basis of E_rC_{50} was investigated by Naumann, Eberius, and Appenroth (2007) and reported the order of phytotoxicity of metals was Ag > Cd > Hg > Tl > Cu > Ni > Zn > Co > Cr(VI) > As(II) > As(V).

Contamination of soil by heavy metal is a worldwide problem in these past years. For example, The Joint Research Centre of the European Commission (JRC EU, 2014) reported that 35% of the total contaminant in the European soil is heavy metals. They also estimated that 342,000 sites have been identified as contaminated in 2011. Meanwhile, according to United States Environmental Protection Agency (USEPA, 2012) about 22.38 million of tonnes of heavy metals were generated from municipal solid waste (MSW) in the USA in 2012. In China, Ministry of Environmental Protection of the People's Republic of China (MEP, 2009) reported that of 78,950 soil samples analysed, 8,757 samples were contaminated. Department of Environment of Malaysia has reported that about 103,944 metric tonnes heavy metal sludge was generated in Malaysia in 2013. (Department of Environment of Malaysia [DOE Malaysia], 2014).

Soil contamination by heavy metals is of great concern due to the short- and long-term effects. These include, human health risk, phytotoxicity, soil fertility, and destabilise of environment (Osman, 2014; USDA, 2000). The metal contaminated soil can affect human health through two pathways, namely direct link and indirect link (Abrahams, 2002). The direct links include inhalation, ingestion, skin contact and dermal absorption. In addition, the direct link in children can be through oral pathway, by putting the soil into their mouths when they are playing around the contaminated soil. Meanwhile, the atmosphere, hydrosphere, biosphere, and food are indirect links that the metal contaminated soil could be ingested in into the human body.

In Malaysia, Department of Environment has reported that the method of waste disposal was sanitary landfill, reuse and recover. For example, 107,958 metric tonnes of heavy metal sludge from industry were disposed into sanitary landfill (DOE Malaysia, 2014). The disposal of heavy metal sludge into sanitary landfill may cause new problem such as soil, water and air pollution. Unlike organic contaminants that can be degraded by soil biota, chemical and physical process, heavy metals are not degradable and therefore they will persist in the soil (Amaral & dos Santos Rodrigues, 2005). The term of remediation refers to the treatment of metal contaminated soil from harmful condition to an acceptable condition (Martin & Ruby, 2004). In recent years, several techniques such as electro-kinetic, leaching, ion exchange, solidification and phytoremediation have been developed to remediate soil contamination by heavy metals. The remediation can be carried out by applying treatment in place (*in situ*/on site) or out place (*ex situ*/off site) (Pierzynski, Sims, & Vance, 2000). The soil remediation techniques can be divided into four classes as follow (Mirsal, 2008):

1. Chemical and physical methods: ion exchange, oxidation and reduction.
2. Biological methods: aerobic bioremediation and anaerobic bioremediation.
3. Fixation methods: stabilisation and immobilisation.
4. Thermal destruction methods: incineration and thermal desorption.

In remediation process these techniques can be run as a single technique or combination of two or more techniques.

In general, *in situ* remediation is significant to: (1) reduce the leaching, (2) reduce the bioavailability of metal to living organism and (3) reestablish vegetation (Martin and Ruby, 2004). Stabilisation is a soil remediation technique to reduce the harmful effect of metals, which converts contaminants into the least soluble and mobile form (Lee, Lee, Choi, & Kim, 2009; Kumpiene, Lagerkvist, & Maurice, 2008;

USEPA, 2005). Stabilisation technique has many advantages such as time- and cost-effective, easy to apply and simple procedure (Lee et al., 2009).

The use of waste-based materials such as red mud, lime, manure and wood ash has been examined as potential amendments for remediation of heavy metal in soil (USEPA, 2007). Coconut tree sawdust and sugarcane bagasse are plant-based materials that might contain several organic compounds and functional groups (Akkaya & Güzel, 2013). Meanwhile, eggshell is a shell-based material that known consists of carbonate (Schaafsma et al., 2000). The functional groups (include carbonate) are known to favour metal ion binding (Duan, Zhao, Yu, Zhang, & Xu, 2013).

Coconut tree sawdust, eggshell and sugarcane bagasse are waste-based materials that are abundantly available in Malaysia, Indonesia and Thailand. For example, Malaysia has 3,680 of senile coconut tree in 2006 (Arancon, 2009). Currently the plantation area of coconut tree was estimated at 98,533 hectares (Ministry of Agricultural Malaysia [MOA Malaysia], 2014). In 2010, the agricultural land used for sugarcane plantation in Peninsular Malaysia was 7,865 hectares (MOA Malaysia, 2014). The total production of egg in Malaysia was reported to be 554,000 tonnes in 2010 (Food and Agricultural Organisation Statistic [FAOSTAT], 2013)

1.2 Research Aim and Objectives

1.2.1 Aim

To evaluate the potential of coconut tree sawdust (CTS), eggshell (ES), and sugarcane bagasse (SB) as amendment agents for the remediation of metal contaminated soil.

1.2.2 Objectives

1. To study the physical and surface properties of CTS, ES, and SB following interaction with metal.
2. To evaluate the ability of CTS, ES, and SB to adsorb metal in soil solution.
3. To study the effect of CTS, ES, and SB on metal uptake by plant (*Ipomoea aquatica)*

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals and Our Life

The use of heavy metals in human activities has been started from long years ago. It has been already 6000 or so years ago since the first utilisation of copper for human needs (Alloway, 2013b). Copper is widely used for electrical equipment, construction (roofing and plumbing), industrial machinery, and alloy (Kabata-Pendias & Mukerjee, 2007). Global modernisation has changed the use of wood-material to metal-materials. For example, the use of house roofing shifted from wood originated from coconut and teak to metals based material. Other than that, almost all of the household properties are made up from metal materials. Thus, heavy metals cannot be separated from our life.

2.2 Soil Contamination by Heavy Metals

Naturally, the occurring of heavy metal in soil is derived from weathering of bedrock or overburden (metal enriched) rocks (Alloway, 2013a; Mirsal, 2008; Saxena & Misra, 2010). These materials had been usually transported by wind, water or glacial activities. Basically, the earth's crust consists of 95% ingneous rocks and 5% sedimentary rock (Thornton, 1991). Another composition of the earth's crust was described by Wedepohl (2004). They mentioned that the earth's crust is made up from 7% sedimentary rock, 27% granitic rock, 13% gneisses and mica schists, 6% amphibolites and gabbros, and 47% granulites.

Although the amount of elements in the periodic table achieved more than 100 elements, but 99% of the earth's crust made up of 10 major elements. The 10 major elements are aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), oxygen (O), potassium (K), phosphorus (P), sodium (Na), silicon (Si), and titanium (Ti). The remainders are called minor elements or better known as trace elements, including copper (Cu), lead (Pb) and zinc (Zn). Normally, the concentration of trace element in the earth's crust is less than 1000 mg/kg (Alloway, 2013a).

The range concentration of both trace elements and major elements occurs in the upper earth's crust and the common types of rocks are presented in Table 2.1. For example, the granitic rock contains the lowest magnesium compared with another rock type. Meanwhile the highest concentration of titanium is introduced by greywackes. The concentrations of Ti in greywackes are 95 times compared with limestones.

Table 2.1

The concentration of metal derived from abundant rock species (mg/kg)

Type of rock	Mg	Ti	Mn	Fe	Cu	Pb	Zn	Cd
Shales	16,000	4,600	850	48,000	45	22	95	0.13
Greywackes	13,000	38,000	750	38,000	24	14	76	0.09
Limestones	26,000	400	700	15,000	4	5	23	0.16
Granitic rocks	6,000	3,000	325	20,000	13	32	50	0.09
Gneisses, mica schists	13,000	3,870	600	33,000	23	13	65	0.20
Basaltic and gabbroric	37,000	9,700	1,390	86,000	90	3.5	100	0.20
Granulites	31,000	5,000	930	57,000	37	12.5	79	0.10
Continental crust	22,000	4,010	716	43,000	25	15	65	0.10
Oceanic Crust	45,000	9,700	1,200	70,000	81	0.5	78	0.13

Note. Adapted from Wedhepol, 2004

The range of concentration element in the soil commonly changed due to the pedogenic and anthropogenic activities (Davies, 1994). The main anthropogenic sources of trace elements inputs are from atmospheric deposition, land application of sewage sludge, land disposal of industrial by-products and wastes and agricultural activities (Hooda, 2010).

Mining and smelting activities have been regarded as major anthropogenic sources. For example, a study on two former smelter sites in Janhang, Korea by Bade, Oh, and Sik Shin (2012) found that the first soil was contaminated with Cu (440.9 ± 0.4 mmol/kg), while in the second site soil was highly contaminated with Pb (589.8 ± 25.9 mmol/kg).