THE EFFECTIVENESS OF DURIAN TREE SAWDUST, COCONUT COIR AND OIL PALM EMPTY FRUIT BUNCH FOR THE REMEDIATION OF METAL CONTAMINATED SOIL

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ABSTRACT

This study investigates the effectiveness of durian tree sawdust (DTS), coconut coir (CC) and oil palm empty fruit bunch (EFB) as amendment agents for the remediation of metal contaminated soil. Three main aspects namely characterisation, adsorption and pot experiment were studied. The characterisation study was carried out using Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) Spectrometer and Fourier Transformed Infrared (FTIR) Spectrometer. The influence of two experimental parameters, namely solution pH and initial metal concentration on adsorption process was assessed in batch experiment. The adsorption behaviour of Cu(II), Pb(II) and Zn(II) onto DTS, CC and EFB was evaluated using the Langmuir and Freundlich equilibrium isotherm models. Two sets of pot experiment were carried out for 8 weeks at three rates of application, namely 0, 1 and 3% (w/w) to evaluate the ability of amendment agents to immobilise metals in contaminated soil. Water spinach (*Ipomoea aquatica*) was used as an indicator in order to assess the effects of amendment agents' application on metal uptake by plant. The surface morphology of amendment agents changed significantly following interaction with metal. The complexation between metal ions and binding sites of the amendment agents was the main mechanism for adsorption process. The separation factor (R_L) and Freundlich constant (n) values suggest that the adsorption process was favourable. The biomass yield of water spinach increased following application of amendment agents. The bioavailability of metal in contaminated soil and accumulation of metal in the plant tissues reduced following treatment. A pronounced effect was obtained for soil treated with coconut coir. Overall, durian tree sawdust, coconut coir and oil palm empty fruit bunch can be utilised as low-cost materials to immobilise metals in contaminated soil. This method could be suggested as an alternative to expensive soil remediation techniques.

KEBERKESANAN HABUK KAYU POKOK DURIAN, SABUT KELAPA DAN TANDAN KOSONG BUAH KELAPA SAWIT UNTUK PEMULIHAN TANAH TERCEMAR OLEH LOGAM

ABSTRAK

Kajian ini menyiasat keberkesanan habuk kayu pokok durian (DTS), sabut kelapa (CC) dan tandan kosong buah kelapa sawit (EFB) sebagai ejen-ejen pemindaan untuk pemulihan tanah tercemar oleh logam. Tiga aspek utama iaitu pencirian, penjerapan dan eksperimen pasu telah dikaji. Kajian pencirian telah dilakukan menggunakan Mikroskop Elektron Pengimbas (SEM), Spektrometer Penyebaran Tenaga Sinar-X (EDX) dan Spektrometer Inframerah Transformasi Fourier (FTIR). Pengaruh dua parameter eksperimen, iaitu pH larutan dan kepekatan awal logam ke atas proses penjerapan telah dinilai dalam eksperimen berkelompok. Kelakuan penjerapan Cu(II), Pb(II) dan Zn(II) ke atas DTS, CC dan EFB telah dinilai menggunakan model keseimbangan isoterma Langmuir dan Freundlich. Dua set eksperimen pasu telah dijalankan selama 8 minggu pada tiga kadar penggunaan, iaitu 0, 1 dan 3% (w/w) untuk menilai keupayaan ejen-ejen pemindaan untuk menyahgerak logam-logam dalam tanah yang tercemar. Kangkung (*Ipomoea aquatica*) telah digunakan sebagai penunjuk dalam kajian ini bagi menilai kesan penggunaan ejen pemindaan terhadap pengambilan logam oleh tumbuhan. Morfologi permukaan ejen-ejen pemindaan berubah dengan ketara selepas interaksi dengan logam. Pengkompleksan antara ion-ion logam dan tapak-tapak pengikatan ejen-ejen pemindaan adalah mekanisma utama bagi proses penjerapan. Nilai-nilai faktor pemisahan (R_L) dan pemalar Freundlich (n) mencadangkan bahawa proses penjerapan adalah baik. Hasil biojisim kangkung meningkat selepas penggunaan ejen pemindaan. Bioketersediaan logam dalam tanah tercemar dan pengumpulan logam dalam tisu-tisu tumbuhan berkurangan selepas rawatan. Kesan yang ketara telah diperolehi bagi tanah yang dirawat dengan sabut kelapa. Secara keseluruhannya, habuk kayu pokok durian, sabut kelapa dan tandan kosong buah kelapa sawit boleh digunakan sebagai bahan kos rendah untuk menyahgerak logam-logam dalam tanah tercemar. Kaedah ini boleh dicadangkan sebagai satu pilihan kepada teknik-teknik pemulihan tanah yang mahal.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration Factor
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
CC	Coconut coir
CEC	Cation Exchange Capacity
DOA	Department of Agriculture Malaysia
DOE	Department of Environment Malaysia
DPR	Department of Petroleum Resource of Nigeria
DTPA	Diethylenetriaminepentaacetic acid
DTS	Durian Tree Sawdust
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
EFB	Oil Palm Empty Fruit Bunch
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agricultural Organisation
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of Detection
LOQ	Limit of Quantification
MTC	Malaysian Timber Council

SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leaching Procedure
TF	Translocation Factor
USDA	United States Department of Agriculture
USEPA	United States Environment Protection Agency
WHO	World Health Organisation

CHAPTER 1

INTRODUCTION

1.1 Soil

Soil is a biogeochemical complex that covers around 80% of the earth's crust (vanLoon & Duffy, 2011). It is a part of geosphere, which interact with lithosphere, atmosphere and hydrosphere. United States Department of Agriculture (USDA) defined soils as a natural body that consists of solid fraction (mixture of inorganic materials and organic matter), liquid and gases that gives it the loose texture (1999). Soil is formed from the chemical and physical weathering process of larger materials called coarse or mineral fragments to smaller particles of sand, silt and clay (Pierzynski, Sims, & Vance, 2000). The sizes of the soil particles usually classify using the diameter as given in Table 1.1. The composition and arrangement of soil's solid fraction will affect the movement of liquids and gases in the soils.

Table 1.1

The size classification of soil particles according to the USDA system.

Soil Particles[a]	Diameter (mm)[a]	Comparison[b]
	Coarse fragments	
Stones	>254	Greater than 10 in.
Cobbles	75-254	3 to 10 in.
Gravel	2-75	0.08 to 3 in.
	Soil particles	
Sand	2.0-0.05	
Very coarse	2.0-1.0	Thickness of a nickel
Coarse	1.0-0.5	Size of pencil lead
Medium	0.5-0.25	Salt crystal
Fine	0.25-0.10	Flat side of a book page
Very fine	0.10-0.05	Nearly invisible to the eye
Silt	0.05-0.002	
Coarse	0.05-0.02	Root hair
Medium	0.02-0.01	Nematode
Fine	0.01-0.002	Fungi
Clay	<0.002	
Coarse	0.002-0.0002	Bacteria
Fine	<0.0002	Viruses

Source: a - USDA, 1975; b - Pierzynski et al., 2000.

Generally, solid fraction in soils compromised of 5% of organic matter and 95% of inorganic materials (Manahan, 2005). However, the constituents in the soil also depend on the type of soil; for example, the peat and forest soils contain higher amount of organic matter than most soils. The soil organic matters are comprised of plants and microorganisms biomass in the various decay states (vanLoon & Duffy, 2011). It can undergo chemical reaction, and influence the soil's infiltration rate, water-holding capacity and aggregate stability. Other than that, the liquid portion of soil (soil solution) contains dissolved matter from soil chemical process and interchange with hydrosphere and biosphere. On the other hand, the gases in soil are results from direct contact with the atmosphere and the respiration process of organic matter decay by microorganism (van der Perk, 2006).

The soil plays an important role as environment agent. It provides the physical support, water and essential nutrients for plants, foods for living organism and acts as gene reservoir (Bolan & Duraisamy, 2003; USDA, 1999). In addition, it acts as a key link in global carbon, nitrogen, phosphorus and sulphur cycles and regulation of water in the ecosystem. The chemical process in soil can affect the nature and amount of element released to hydrosphere and atmosphere. Soil also can act as source and sink for various contaminants that can affect living organism (Bolan & Duraisamy, 2003). For example, the inorganic materials in soil can acts as natural filter adsorbing toxic substances in soil (van der Perck, 2006).

1.2 Soil Contamination by Heavy Metals

1.2.1 Pollutants vs. contaminants

Pollution and contamination are the two terms that often used synonymously in the environmental studies. However, contamination is frequently used by researcher in the perspective of soil and land (Alloway, 2013). The contaminant or pollutant is defined as substances (natural or man-made) that are harmful and poisonous to human being and ecosystem which result from anthropogenic activities (Manahan, 2005). The present of contaminant in environment can modify the chemical, physical, biological and radiological integrity of soil and water by killing species, change their growth rate, disturbed food chain and affect human health (Manahan, 2005).

1.2.2 Sources of heavy metals in soil

Heavy metals are normally refers to the group of element in the periodic table that have metallic properties (metals and metalloids) and often linked with contamination and potential toxicity (Vamerali, Bandiera, & Mosca, 2010). The heavy metals have relatively high atomic mass and density greater than 5 g/cm^3 (Manahan, 2005). About ten major elements made up around 99% of the total mass of the earth's crust. They are aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg), oxygen (O), phosphorus (P), potassium (K), silicon (Si), sodium (Na) and titanium (Ti). The remaining elements known as trace elements, which constitute about 1% of the earth's crust mass (Alloway, 2013).

Heavy metals that commonly found in soil are arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), mercury (Hg), nickel (Ni), silver (Ag) and zinc (Zn). Table 1.2 shows the mean concentration of heavy metals found in the soils. Historically, human has used some heavy metals such as Ag, Cu, Pb and Sn for years. For example, Cu has been utilised since 6000 years ago in production of brass and bronze, electrical equipment, plumbing pipes and pigments (Alloway,2013).

Table 1.2

The mean concentration of heavy metal in soils for world and different countries (mg/kg).

Element	Worldwide data[a]	Agricultural soils of Sweden[b]	Agricultural soils of Japan[c]	US soils data[d]
Ag	0.1	0.11	0.1	-
As	4.7	3.8	-	7.2
Cd	1.1	0.17	0.33	<0.01-41
Cr	42	22	58	54
Cu	14	17	48	25
Hg	0.1	0.043	-	0.09
Mo	1.8	0.58	1.3	0.97
Ni	18	13	26	19
Pb	25	18	24	19
Sn	-	1.8	2.4	1.3
Zn	62	65	89	60

Source: a - Kabata-Pendias & Mukherjee, 2007; b - Eriksson, 2001; c - Takeda, Kimura, & Yamasaki, 2004; d - Burt, Wilson, Mays, & Lee, 2003.

The heavy metals present in the contaminated soils can originate from natural occurring and also as the result of anthropogenic activities. In perspective of natural occurring, minerals ore of soil parent materials weathered and released these elements in soluble forms. The formation of acid rain has caused the soil to become acidic and cause significant changes in solubility and oxidation-reduction rates of minerals (Alloway, 2013; Park et al., 2011).

Briefly, soil contamination by anthropogenic activities can occur either by localised or diffuse source (Vamerali et al., 2010). The contaminations from localised source arise from identified point of discharge (Pierzynski et al., 2000). It is frequently associated with abandoned industrial plant, accidental leakage of contaminants and improper waste disposal (Vamerali et al., 2010). On the other hand, diffuse source contamination commonly will affect large areas. This contamination generally come from various and indirect sources (Pierzynski et al., 2000). The main pathways for diffuse contamination are by atmospheric deposition, flowing water and soil erosion (Vamerali et al., 2010). The particles containing metals emitted to the atmosphere and transfer to the soil and water by bulk deposition (Alloway, 2013).

Throughout the history, mining and smelting are the major contributors for heavy metal contamination in soils. The mining activity will produce waste ore, tailings and slag that contained high concentration of heavy metal. For instance, the mining activities carried out in the former mining sites located in La Unión, Murcia, Spain since Roman times has caused soil contaminated due to the accumulation of metalliferous mine wastes (Clemente, Paredes, & Bernal, 2007). It was reported that the concentration of Pb found in the soil was 3235 mg/kg. Table 1.3 displays the statistical data of world mine production of several metals and metalloids in 1994, 2004 and 2010. The data showed that Cu was the element most mined since 1994, followed by Zn and Pb. The productions of these elements keep increasing over the years. Therefore, the massive production of these elements will continue to impact the environmental quality of soil.

Table 1.3

The world mine production of heavy metals and metalloids (tonnes).

Element	1994	2004	2010
As	43,000	37,500	54,500
Ag	13,900	19,500	22,200
Cd	18,100	17,200	22,000
Cu	9,430,000	14,500,000	16,200,000
Hg	1,760	1,750	1,960
Ni	906,000	1,400,000	1,550,000
Sb	106,000	112,000	135,000
Pb	2,800,000	3,150,000	4,100,000
Zn	6,810,000	9,100,000	12,000,000

Source: Alloway, 2013.

Smelting activities have contaminated the area in and around the smelter due to atmospheric deposition of heavy metals. The airborne emission from smelter normally contained high amount of As, Cd, Cu, Pb and Zn, and these toxic metals will be dispersed over the surrounding areas (Janoš, Vávrová, Herzogová, & Pilařová, 2010). For example, lead smelter located in the North of France had emitted around

18.4 tonnes of Pb, 26.2 tonnes of Zn and 823 kg of Cd in 2001 (Pruvot, Douay, Hervé, & Waterlot, 2006).

The improper use of inorganic pesticides, fungicides and fertilisers and also irrigation have enriched the amount of certain element in agricultural soils (Udeigwe, Eze, Teboh, & Stietiya, 2011; Zeng et al., 2011). The application of fertiliser usually associated with the accumulation of heavy metals like As, Cd, Pb and Hg in agricultural soils. For example, the use of phosphatic fertiliser increased the level of Cd in agricultural soils (Udeigwe et al., 2011).

Besides that, combustion of fossil fuel, road traffic, dumping of solid and liquid waste and paints contributed to the contamination in the urban area (Álvarez-Ayuso, Otones, Murciego, & García-Sánchez, 2013; Pierzynski et al., 2000). Military and firing range activities can also cause soil contamination from shells, bullets, bomb, mines and leaking fuel (USDA, 2000).

1.2.3 Case study on contamination of heavy metals in Malaysia

In these recent years, soil contamination by heavy metals has become worldwide environmental concern. For example, European Commission reported that 35% contaminants found in European soil were heavy metals (University of the West of England, 2013). A survey on several urban soil and dust, as well as in agricultural soils in the cities across China in 2010 found that the concentration of heavy metals such as As, Cd, Cr, Cu, Hg, Ni and Pb were higher that their background values (Wei

& Yang, 2010). Department of Environment Malaysia (DOE) revealed that 0.9% report or complaint regarding environmental issues received in 2013 was related to soil contamination (DOE, 2013).

The main contributor for environmental contamination in Asia, especially in Malaysia is through waste management sector (Agamuthu & Fauziah, 2010). Department of Environment Malaysia (DOE) has reported that about 2,965,611.65 metric tonnes of scheduled wastes have been generated in Malaysia in 2013 (DOE, 2013). Terengganu found to be the largest contributor for scheduled wastes which produced about 29.75% of total scheduled waste in Malaysia. The main wastes that are generated in Malaysia were gypsum, spent lubricating oil and heavy metals sludge. All of these waste are mostly comes from coal-fired power plant (55.10%), water treatment facilities (31.25%) and others (13.65%) (DOE, 2013).

The disposal of the wastes without proper management can cause severe impact on environment. The means for wastes disposal in Malaysia is dominated by landfill (80%) and remaining by recycling and intermediate processing (Ismail & Manaf, 2013). Ministry of Housing and Local Government Malaysia (MHLG) reported that there are about 251 officially recognised landfill in Malaysia. Among these, 150 of the landfill are still active (Ashraf, Yusoff, Yusof, & Alias, 2013, MHLG, 2013). The landfill in Malaysia can be classified to five levels. Level 0 is open dumpsite, level I is controlled tipping landfill, level II is sanitary landfill with bund and daily cover, level III is sanitary landfill with leachate recirculation system and level IV is sanitary landfill with leachate treatment facilities (Adnan, Yusoff, &

Chua, 2013). However, most landfill in Malaysia is non sanitary and open dumpsite type.

The disposal of wastes in landfill can cause negative impact on environment such as risk of explosion, odour problem and leachate of the contaminant into soil, surface water and groundwater (Agamuthu & Fauziah, 2010; Ismail & Manaf, 2013; Mohamed, Yaacob, Taha, & Samsudin, 2009). The leachate form when water makes contact with solid waste (Ashraf et al., 2013). The leachate usually contains dissolve and xenobiotic organic compound, inorganic salts, ammonia, heavy metals and other toxicants.

The leachate seepage can enhanced the level of heavy metal in soil. Adnan et al. (2013) reported that the soil in former landfill in Ampang Tenang was significantly polluted by Al, As, Cu and Pb. The amount of As and Pb in the soil found exceed safe limit values of Provincial Sediment Quality Guideline for Metals and Interim Sediment Quality Values of 5.90 mg/kg and 31.00 mg/kg, respectively. Agamuthu and Fauziah (2010) analysed the quality of soil in ex-disposal site in Kelana Jaya, Selangor. The found that the soil collected from the site still heavily contaminated by heavy metals. The highest concentration of As and Hg was 64.4 mg/kg and 11.5 mg/kg, respectively, which exceeded the Dutch Intervention value. Other than that, Rosazlin, Fauziah, Rasidah, and Rosenani (2010) reported that application of raw and composted recycle paper mill sludge will cause leaching of heavy metals into the soil after six months. The concentration of heavy metal leached into the soil was in order of Zn > Mn > Cu > Ni > Pb > As.