UNIVERSITI PUTRA MALAYSIA

AVAILABILITY AND PHYTOREMEDIATION OF ZINC AND COPPER IN TWO MALAYSIAN SOILS TREATED WITH SEWAGE SLUDGE

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By

AISHAH RAMADAN MOHAMED BINADAM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

July 2017
DEDICATION

To the soul of my father “may Allah forgive him and grant him his highest paradise”. To my beloved mother and my siblings with love and eternal appreciation.
Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman : Professor Shamshuddin Jusop, PhD
Faculty : Agriculture

The disposal of municipal sewage sludge face serious challenges. Currently, over 3.2 \( \times 10^6 \) metric tons of domestic sewage sludge in Malaysia are in need of safe disposal. Phytoremediation provides an efficient soil remediation solution since it uses plants to remove contaminants. A glasshouse experiment were conducted to assess the potential of four plant species (\textit{Jatropha curcas}, \textit{Hibiscus cannabinus}, \textit{Acacia mangium} and \textit{Syzigium cumini}) to the phytoremediation of excess Zn and Cu in Oxisol and in Ultisol amended by different rates of sewage sludge: 0, 5 and 10% v/v.

The results showed that the addition of 10% sewage sludge enhanced the nutritional status of the Oxisol and Ultisol, shown by the increase in soil pH from 5.36±0.01 to 5.84±0.02 in the Oxisol, and from 4.77±0.02 to 5.37±0.01 in the Ultisol, the CEC increased from 8.00±0.57 to 9.39±0.01 cmol\(_c\) kg\(^{-1}\) in Oxisol and from 10.33±0.01 to 11.22±0.06 cmol\(_c\) kg\(^{-1}\), available P increased from 10.70±0.05 mg kg\(^{-1}\) to 24.00±0.02 mg kg\(^{-1}\), in Oxisol and from 10.90±0.05 mg kg\(^{-1}\) to 26.80±0.01 mg kg\(^{-1}\) in Ultisol.

Among the four plants examined, it was found that \textit{J. curcas} and \textit{H. cannabinus} were capable of accumulating more Zn and Cu than those of the \textit{A. mangium} and \textit{S. cumini}, which was shown by their high translocation factor (TF>1). \textit{H. cannabinus} had the highest TF value of Zn (2.43±0.02), while \textit{J. curcas} had the highest TF value of Cu (1.52±0.02).

Fractionation of metals showed that the Zn and Cu existed in the residual form, while the sludge application into the soils tended to shift the forms of Zn and Cu away from residual fraction to water soluble and exchangeable fractions that might be more available for plant uptake.
A leaching study was conducted to determine movement of Zn and Cu in the tested soils. The results showed that the application of 10% sewage sludge seemed to increase the concentration of Zn and Cu in the leachates of the soils, the maximum concentration of Zn in the leachates from the Ultisol was 82.35±0.45 mg L⁻¹ which was higher than that of the Oxisol 62.91 ±0.25 mg L⁻¹. For Cu, it was 8.69±0.15 mg L⁻¹ in the leachates of the Ultisol which was lower than that of the Oxisol of 11.67±0.05 mg L⁻¹. The downward movement of Zn and Cu in the soil columns after the leaching process was different among the metals, whereby Zn had a lower concentration (1.12±0.03 mg kg⁻¹) compared that to Cu (5.6±0.07 mg kg⁻¹) in the both soils, especially for the 0-5 cm layer.

The results adsorption study showed that the sewage sludge application had significant effect on the processes of adsorption-desorption of Zn and Cu. This is shown by the systematic change of the distribution coefficients (K_d). Comparison between K_d values for both soils indicated the following selectivity of metals; Cu (K_d= 3.42) > Zn (K_d=2.82). It is clear that Zn adsorption was lower than that of Cu. The adsorption isotherms of Zn and Cu of both soils were well fitted to linear Freundlich and Langmuir equations (R² = 0.96 - 0.99).

This study suggests that sewage sludge possessed the ability to improve the fertility of highly weathered soils. However, the presence of Zn and Cu is a negative side effect of using sewage sludge. The excess Zn and Cu in treated soils can be successfully removed by phytoremediators, such as *J. curcas* and *H. cannabinus*. 
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KETERSEDIAAN DAN FITOREMEDIASI ZINK DAN KUPRUM DALAM DUA JENIS TANAH MALAYSIA YANG DIRAWAT DENGAN SISA KUMBahan

Oleh

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Pelupusan sisa kumbahan adalah suatu proses yang amat mencabar. Di Malaysia, lebih 3.2 juta tan metrik sisa kumbahan domestik perlu dilupuskan dengan selamat. Fitoremediasi merupakan suatu penyelesaian untuk pemulihan tanah yang efisien kerana ianya menggunakan tumbuhan untuk mengelurkan bahan pencemaran dari tanah. Satu kajian rumah kaca telah dijalankan bertujuan menilai potensi empat spesies tumbuhan (*Jatropha curcas, Hibiscus cannabinus, Acacia mangium* and *Syzigium cumini*) untuk fitoremediasi kandungan Zn dan Cu yang berlebihan dalam tanah Oxisol dan Ultisol yang diletakkan dengan sisa kumbahan pada kadar yang berbeza, iaitu pada kepekatan 0, 5 dan 10% i.p./i.p.

Hasil kajian mendapati tanah Oxisol dan Ultisol yang rawat dengan sisa kumbahan pada kadar 10% menunjukkan peningkatan dari segi nutrisi tanah berdasarkan kenaikan pH dari 5.36±0.01 ke 5.84±0.02 dalam tanah Oxisol dan dari 4.77±0.02 ke 5.37±0.01 dalam tanah Ultisol. Nilai CEC tanah meningkat dari 8.00±0.57 ke 9.39±0.01 cmol c kg⁻¹ dalam tanah oxisol dan dari 10.33±0.01 ke 11.22±0.06 cmol c kg⁻¹ dalam tanah ultisol. Ketersediaan P juga meningkat dari 10.70±0.05 mg kg⁻¹ ke 24.00±0.02 mg kg⁻¹ dalam tanah Oxisol dan dari 10.90 ± 0.05 mg kg⁻¹ ke 26.80±0.01 mg kg⁻¹ dalam tanah Ultisol.

Di antara empat jenis tumbuhan yang dikaji, didapati pokok *J. curcas* dan *H. cannabinus* menunjukkan keupayaan mengumpulkan lebih banyak Zn dan Cu berbanding dengan pokok *A. mangium* dan *S. cumini*, berdasarkan kepada faktor transloksi yang tinggi (TF>1). Pokok *H. cannabinus* menunjukkan nilai TF yang paling tinggi untuk Zn (2.42±0.02), manakala *J. curcas* pula menunjukkan nilai TF yang paling tinggi untuk Cu (1.52±0.02).
Kajian komposisi logam menunjukkan Zn dan Cu wujud dalam bentuk mendakan, manakala aplikasi sisa kumbahan pada tanah menyebabkan kecenderungan penukaran Zn dan Cu daripada bentuk mendakan ke bentuk yang larut air dan dalam keadaan boleh ditukarganti dan lebih tersedia untuk tumbuhan.

Suatu kajian larutlesap telah dijalankan untuk melihat pergerakan Zn dan Cu dalam tanah yang diuji. Hasil kajian menunjukkan aplikasi sisa kumbahan pada kepekatan 10% meningkatkan kandungan Zn dan Cu dalam hasil larutlesap. Kepekatan maksimum Zn dalam hasil larutlesap tanah Ultisol adalah sebanyak 82.35±0.45 mg L\(^{-1}\) dan lebih tinggi berbanding kepekatan dalam tanah Oxisol iaitu sebanyak 62.91 ±0.25 mg L\(^{-1}\). Manakala untuk Cu pula, kepekatan dalam hasil larutlesap tanah Ultisol adalah 8.69±0.15 mg L\(^{-1}\) iaitu lebih rendah berbanding tanah Oxisol sebanyak 11.67±0.05 mg L\(^{-1}\). Pergerakan Zn dan Cu menuruni kolum tanah hasil dari proses larutlesap adalah berbeza. Kepekatan Zn adalah lebih rendah (1.12±0.03 mg kg\(^{-1}\)) berbanding kepekatan Cu (5.6±0.07 mg kg\(^{-1}\)) untuk kedua-dua jenis tanah terutamanya pada lapisan 0-5 sm.

Keputusan kajian jerapan menunjukkan aplikasi sisa kumbahan memberikan kesan yang ketara dalam proses jerapan dan pembebasan Zn dan Cu dalam tanah. Ini dibuktikan oleh perubahan yang sistematik dalam nilai pembolehubah taburan (K\(_d\)). Perbandingan antara nilai K\(_d\) untuk kedua-dua jenis tanah menunjukkan urutan pilihan logam seperti berikut: Cu (K\(_d\)= 3.42)> Zn (K\(_d\)=2.82). Jerapan Zn adalah jelas lebih rendah berbanding Cu. Isoterma jerapan untuk Zn dan Cu dalam kedua-dua jenis tanah adalah sangat menepati persamaan linear Freundlich dan Langmuir (R\(^2\) = 0.96 - 0.99).

Kajian ini menunjukkan bahawa sisa kumbahan mempunyai keupayaan untuk meningkatkan kesuburan tanah yang terluluhawa, walaupun kehadiran Zn dan Cu merupakan kesan sampingan yang negatif dari penggunaan bahan ini. Namun, kandungan Zn dan Cu yang berlebihan dalam tanah ini boleh hapuskan melalui fitoremediasi oleh pokok J. curcas dan H. cannabinus.
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I certify that a Thesis Examination Committee has met on 21 July 2017 to conduct the final examination of Aishah Ramadan Mohamed Binadam on her thesis entitled "Availability and Phytoremediation of Zinc and Copper in Two Malaysian Soils Treated with Sewage Sludge" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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<td>5.6</td>
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<td>63</td>
</tr>
</tbody>
</table>
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6.8 Distribution of Zn and Cu in Ultisol columns: (A) Control (T1), (B) Ultisol with sewage sludge (T2), (C) Ultisol after cultivation (T3).

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7.5 Desorption of Zn and Cu from the Oxisol (A) and Ultisol (B)
**LIST OF ABBREVIATIONS, UNITS AND SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>BCF</td>
<td>Bio-concentration factor</td>
</tr>
<tr>
<td>BD</td>
<td>Bulk density</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
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<tr>
<td>F1</td>
<td>Water soluble fraction of heavy metal</td>
</tr>
<tr>
<td>F2</td>
<td>Extractable fraction of heavy metal</td>
</tr>
<tr>
<td>F3</td>
<td>Carbonate Fraction of heavy metal</td>
</tr>
<tr>
<td>F4</td>
<td>Fe-Mn Oxides Fraction of heavy metal</td>
</tr>
<tr>
<td>F5</td>
<td>Organic Fraction of heavy metal</td>
</tr>
<tr>
<td>F6</td>
<td>Residual Fraction of heavy metal</td>
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<tr>
<td>ICP</td>
<td>inductively coupled plasma spectrometry</td>
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<tr>
<td>IWK</td>
<td>Indah Water Konsortium</td>
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<tr>
<td>L</td>
<td>liter</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>mg kg⁻¹</td>
<td>Milligram per kilogram</td>
</tr>
<tr>
<td>OM</td>
<td>Organic matter</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
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<tr>
<td>PCV</td>
<td>Polyvinyl chloride</td>
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<tr>
<td>PET</td>
<td>polyethylene terephthalate container</td>
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<tr>
<td>SAS</td>
<td>Statistical Analysis System</td>
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<tr>
<td>TC</td>
<td>Total Carbon</td>
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<tr>
<td>TF</td>
<td>Transfer factor</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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</table>
CHAPTER 1

INTRODUCTION

1.1 General overview

The accruing benefits from sludge recycling generated from sewage treatment of municipal wastewater cannot be neglected because this sewage sludge has become a subject of research in different fields in recent years. A growing number of environmentalist scientists are becoming interestingly over the importance of sewage sludge recycling which is of great concern for environmental such as soil pollution. However, due to the increasing costs of chemical fertilizers; recycling sewage sludge as a fertilizer is economical option.

Increased population, a consequence of economic development and rapid urbanization has led to the production of huge amounts of sewage sludge around the world, which brings about considerable stresses on the environment and accumulation of various kinds of biological and chemical pollutants, especially on soils (Adriano, 2013). Sewage sludge has been used as an amendment to soil improvement conditions. The application of sewage sludge to tropical soils is one of the proposed methods of maintaining soil characteristics. It is also an alternative for the disposal of waste products. Sewage sludge has the potential to enhance soil productivity because it contains high organic matter (30 to 56%) and plant nutrients. Malaysian domestic sewage sludge is acidic in nature (pH 3.92 to 6.43) and it has variable chemical composition (nitrogen (N), phosphorus (P), calcium (Ca), potassium (K) and magnesium (Mg)) and heavy metals with higher concentrations of zinc (153 to 7012 mg kg\(^{-1}\)) and copper (63 to 732 mg kg\(^{-1}\)). However, environmental issues concerning contamination are increasing in heavy metals in soil which is derived from applying sewage sludge to soils (Indah Water Konsorttium, 2014). The disposal of sewage sludge from wastewater treatment plants is a problem of concern due to the challenges in disposal and the cost of disposal. However, in Malaysia, issues concerning the disposal of sewage sludge owing to the limited number of facilities of sewage sludge treatment have given rise to environmental pollution (Indah Water Konsorttium, 2014).

In the 21\(^{st}\) century, pollution control has turned out to be a big challenge because of a spectacular growth in contaminants caused from activities of human (Larue et al., 2010). Pollution of forest and agricultural soils is probably to continue and has become comparatively widespread already. Heavy metals, organic and inorganic pollutants are accumulating in soils from different resources such as transport, agricultural activities, industrial and sewage sludge (Salomons and Stigliani, 2012).

Higher costs of chemical fertilizers, higher prices of alternate disposal besides stricter guidelines on discharge of sewage sludge into water procedures have increased in application of sewage sludge in production of crop. Some studies have addressed the risks and benefits of agricultural usage of sewage sludge (Alvarenga et al., 2015).
Sewage sludge could improve the physio-chemical conditions of soil. But the most important discussion in using sewage sludge is the increase in heavy metals. Applying sewage sludge to soils must be limited by heavy metals presence as well as other pollutants (Fang et al., 2016). Soil application of sewage sludge is widely recommended in numerous countries due to its environmental advantage and economic benefits, obtained by the purposeful use of sewage sludge (Wu et al., 2012). In fact, there is limited information in the long-term impacts of sewage sludge on the structural and chemical properties of soils in the wet tropics lands (Nogueirol et al., 2013).

However, concerns were brought up on the fact that excessive and repeated addition of sewage sludge could lead to detrimental environmental risks, particularly in soils toxic metals pollution (Wu et al., 2012). It has also been claimed that heavy metal on soils has been increased due to applying sewage sludge and this would possibly present risk to humans, animals and plants (Bondarczuk et al., 2016). Most commonly found heavy metals in sewage sludge are zinc (Zn), copper (Cu), lead (Pb), nickel (Ni) and cadmium (Cd). Zinc and Cu must be carefully checked and controlled because when the sewage sludge is applied to soil.

Zinc and copper gained more attention because of their high concentrations in sewage sludge (7012 and 732 mg kg\(^{-1}\) for Zn and Cu respectively). Consequently, we chose to study Zn and Cu, which are essential to plants when in low concentrations, but toxic when in high concentrations. Yet Zn and Cu have a contrasting behavior in soils, with Cu typically found less mobile than Zn (Mehes-Smith et al., 2014).

High concentrations of heavy metals in soil lead to phytotoxic effect and led to bad development on vegetation (Wuana and Okieimen, 2011; Adriano, 2013). However, recognizing the chemical forms in which the metals are preserved in soil helps to predict their mobility to water sources (Rosazlin et al., 2006).

Consequently, remediation of soil polluted by heavy metals is needed in imperative to scale down the related hazards, create the soil obtainable for agricultural production, and improve food safety. So far different conventional remediation methods have been employed for the purpose of remediation soils. Efforts presented by various academics to clean up polluted soils are either too costly or not ecofriendly, where different type of conventional remediation methods have been used in earlier decades but limited methods have been applied successfully in practice. Presently, there is phenomenal attention in the methods of phytoremediation (Öztürk, 2016).

Phytoremediation is one of the unique methods of the remedial hopes for environment. The achievement of phytoremediation can be contingent in a high precision on the selection of the plants, agriculture conditions, land adjustments, and heavy metals movements which is soil and climate specific (Hernandez-Allica et al., 2008). Plant species grown in contaminated soils have the ability to uptake heavy metals in ions form soil solution and stored in different parts of the plant such as leaves, stems, fruits, seeds,
and roots (Tangahu et al., 2011). Plants readily assimilated metals through their roots in dissolve water and ionic forms (Bohra et al., 2015).

Soil pollution has become a major source of concern and has posed serious environmental problems within the last few years in many developed nations. Sewage sludge is one of the major sources of enrichment of heavy metals. It contains heavy metals such as Zn and Cu. Phytoremediation offers environmental friendly method to treat the polluted soil. It offers opportunities to use the biomass of plant for environmental benefits. Hence, this study is crucial in examining the ability of woody plants species as Zn and Cu accumulators for remediating Oxisol and Ultisol.

1.2 Justification

Sewage sludge applications onto soils offer multiple benefits and adverse environmental consequences. Variety pollutants, including heavy metals, are eventually transported to the environment. Thus, soil contaminants need to be cleaned up to improve environmental safety. This study was conducted to quantify the response of weathered highly soils to an increase in pollution due to sewage sludge application and to assess the ability of phytoremediation technology in remediating two Malaysian soils treated with sewage sludge.

1.3 The Objectives

This study was aimed to evaluate the efficacy of selected woody plants (Jatropha curcas, Hibiscus cannabinus, Acacia mangium and Syzigium cumini) as Zn and Cu accumulators in contaminated soils.

Considering the previous background, the specific objectives of the present study were:

i. To screen the ability of four woody plants species as heavy metals accumulators in Oxisol and Ultisol amended with sewage sludge;

ii. To elucidate the potential of two selected plants species to remediate heavy metal contaminated soils which have been treated with sewage, and to determine the availability and relative distribution of various forms of the metals in the sewage sludge and treated soils;

iii. To investigate the influence of sewage sludge on the leaching and downward movement characteristics of Zn and Cu; and

iv. To assess the adsorption and desorption of Zn and Cu for soils having different rates of sewage sludge.
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