UNIVERSITI PUTRA MALAYSIA

ASSESMENT OF SELECTED INDUSTRIAL BYPRODUCTS TO REDUCE UPTAKE OF HEAVY METALS BY SWEET CORN (ZEA MAYS, L) FROM SEWAGE SLUDGE AMENDED SOIL

NUR HANANI MANSOR

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NUR HANANI MANSOR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Agricultural Science

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DEDICATION

This thesis is dedicated specially to:

My lovely husband:

Fauzan Mohd. Jakarni

My parents:

Mansor Mohd. Lazim

&

Zaniah Hashim

My parents-in-law:

Mohd. Jakarni Mohd. Said

&

Bedah Ishak

To my brothers and sisters

&

All family members and friends

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Agricultural Science

ASSESSMENT OF SELECTED INDUSTRIAL BYPRODUCTS TO REDUCE UPTAKE OF HEAVY METALS BY SWEET CORN (*Zea mays, L*) FROM SEWAGE SLUDGE AMENDED SOIL

By

NUR HANANI MANSOR

January 2007

Chairman : Associate Professor Che Fauziah Ishak, PhD

Faculty : Agriculture

In-situ fixation or inactivation of metals using soil amendments has been proposed for the remediation of polluted soils. This approach is based on the ability of some materials to precipitate or adsorb and eventually fix heavy metals. Drinking water treatment residue (WTR), coal fly ash (CFA) and red gypsum (RG) were used as soil amendments to treat the soil which has been applied with sewage sludge. Thus, the general objective of this study was to assess if WTR, CFA and RG can be utilized as soil amendments to immobilize heavy metals in contaminated soils and also the effects of these amendments on plant growth.

The first study, which involved three different industrial byproducts (WTR, CFA and RG) were collected from Puncak Niaga Sdn. Bhd in Sabak Bernam Selangor, Sultan Salahuddin Abdul Aziz electric generating power station in Kapar, Selangor, and titanium dioxide industry in Telok Kalang, Terengganu, respectively. A necessary

first step before utilization of these byproducts is to evaluate whether these byproducts are suitable for use on agricultural land. Therefore, the samples were air dried and their chemical, physical, mineralogical and morphological properties were determined. All the byproducts have pH value greater than 7, which can influence in lowering free metal ion activities in soil. The acid neutralizing capacity (ANC), expressed as % calcium carbonate equivalents are 0.50, 0.50 and 1.79 for WTR, CFA and RG, respectively. The cation exchange capacity (CEC) of these byproducts is very low (< 10 $cmol.kg^{-1}$) which indicate the lower ability of these byproducts to retain or adsorb cationic ions. The levels of heavy metals in all byproducts are still below the allowable levels for land application of waste.

The second study was a laboratory incubation study of Bungor Series soil treated with sewage sludge and amended with byproducts (WTR, CFA and RG) for soil solution and soil fractionation study. This study was done to determine pH and heavy metals availability from soil solution and to determine the forms of heavy metals from soil fractionation of sewage sludge amended soil treated with WTR, CFA and RG, respectively. The treatments which were selected for the soil solution and soil fractionation were as follows and the data reported are average values of four replicates. Soil solution study; T1 – soil + 0% byproducts + 5 % sewage sludge, T2 – soil + 2.5% byproducts + 5 % sewage sludge, T3 – soil + 5% byproducts + 5% sewage sludge, T4 – soil + 10% byproducts + 5% sewage sludge, T5 – soil + 20% byproducts + 5% sewage sludge, and T6– soil + 40% byproducts + 5% sewage sludge; Soil fractionation study: T1 – soil + 0% byproducts + 5% sewage sludge, T2 – soil + 2.5% byproducts + 5% sewage sludge and T6 – soil + 40% byproducts + 5% sewage sludge. Pots were arranged in a complete randomized design (CRD).

In the soil solution study, a rhizon soil moisture sampler was used to extract the soil solution from the Bungor Series soil incubated in a pot. Laboratory incubation was carried out for 70 days and soil solution was collected at day 1 till day 70 at a regular interval of once a week for pH and heavy metals determination. Soil fractionation study was done at the end of 70 days of incubation to determine forms of heavy metals (Zn,Cu,Cd,Ni,Pb,) using TI (0%), T2 (2.5%) and T6 (40%) treatments which represent the control, the lower and the highest rate of application of industrial byproducts, respectively. Heavy metals were analyzed according to six operationally defined fractions which are water soluble, exchangeable, carbonate bound, Fe-Mn oxides bound, organically bound and residual forms. The concentration of water soluble heavy metals especially Zn in the soil solution for WTR, CFA and RG are lower compared to the control. The lowering of water soluble heavy metals were probably due to the addition of different rates of the byproducts which caused changes in the pH of the soil solutions.

For soil fractionation study, forms of fractionations of WTR treatments showed that the dominant fraction of water soluble Ni and Cd were in residual fractions, whereas water soluble Zn in the Fe-Mn form, Cu in organic form and RG in exchangeable form, respectively. Fractionation of CFA treatments showed the dominant form for water soluble heavy metals (Cu, Ni and Cd) are in the residual forms with the exceptions of Zn and Pb. Zn is dominant in the Fe-Mn form and Pb is dominant in the exchangeable form, respectively. Fractionation of CFA treatments showed the dominant form for water soluble heavy metals (Cu, Ni and Cd) are in the residual forms with the exceptions of Zn and Pb. Zn is dominant in the Fe-Mn form and Pb is dominant in the exchangeable form, respectively. In general, only water soluble and exchangeable fractions are mobile and can be taken up by plants. Others are considered immobile fractions. Therefore, this probably explains that even though the concentration of heavy metals in soil treated with byproducts were high, they are not available for plant uptake.

The third study was a glasshouse study on the reduction of heavy metal uptake by corn in soil amended with sewage sludge and treated with WTR, CFA and RG. This study is to determine the optimum WTR, CFA and RG applications rates that can improve plant growth and reduce heavy metals uptake by corn in glasshouse study. Sweet corn was used as a test crop. Pots were arranged in a complete randomized design (CRD). The treatments which were selected for the glasshouse study were as follows; P1 – soil + 0% byproducts + 5 % sewage sludge, P2 – soil + 2.5% byproducts + 5 % sewage sludge, P3 – soil + 5% byproducts + 5 % sewage sludge, P4 – soil + 10% byproducts + 5 % sewage sludge and P5 – soil + 20% byproducts + 5 % sewage sludge. Forms of heavy metals was also determined in a glasshouse study using treatment; P1 – soil + 0% byproducts + 5 % sewage sludge, P2 – soil + 2.5% byproducts + 5 % sewage sludge and P5 – soil + 40% byproducts + 5 % sewage sludge.

The suitable rates for plant growth by using byproducts as a soil amendment are up to 10% usage of WTR, 5% usage of CFA and 2.5% usage of RG, respectively. In particular, the main purpose of using these byproducts is not to supply nutrient or increase corn yield, but instead to reduce heavy metals uptake by the corn plant. However, for WTR, there is an added benefit where usage of 2.5% WTR can increase the corn weight. Based on the application of WTR, CFA and RG treatment, only Zn and Cu, Zn and Cd, and Zn and Cu concentrations in corn uptake have shown significant reduction, respectively, as compared to the control treatment. Comparison of macronutrients in soil with nutrient sufficiency range (NSR) for corn shows that concentration of N and K is insufficient for corn growth in all byproducts treatments. Therefore additional K (140 kg/ha) was added to all treatments because visual K deficiency was detected. Even though visual N deficiency was not detected, additional N should be added since N was also found low compared to the adequate level for corn growth.

Land applications of WTR, CFA and RG can be recommended as soil amendments because of their cost effectiveness in heavy metals retention in the soil through changes in soil pH. However for WTR, P deficiency in plant has to be monitored because of WTR ability to adsorb and/or precipitate P. Before applying CFA, it has to be weathered or lagooned to remove excess B. From the incubation study, results indicate the possibility of using these byproducts to reduce heavy metals concentration in soil solution especially water soluble Zn. From the glasshouse study, results show that by using industrial byproducts, certain heavy metals uptake by corn can be reduced such as Zn and Cu in WTR and RG, and Zn and Cd in CFA, respectively. The usage of byproducts at suitable rates (WTR up to 10% usage, CFA up to 5% usage and RG up to 2.5% usage) show no significant effect compared to the control treatment. The glasshouse study also depicts the additional benefit, whereby, 2.5% of WTR can increased corn weight.

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

PENILAIAN BEBERAPA BAHAN SAMPINGAN INDUSTRI TERPILIH UNTUK MENGURANGKAN PENGAMBILAN LOGAM BERAT OLEH JAGUNG MANIS (*Zea mays, L*) DALAM TANAH YANG TELAH DIRAWAT DENGAN ENAP CEMAR KUMBAHAN

Oleh

NUR HANANI MANSOR

Jun 2007

Pengerusi : Profesor Madya Che Fauziah Ishak, PhD

Fakulti : Pertanian

Pengikatan in-situ ataupun penyahaktifan logam berat dengan menggunakan bahan pembaik pulih tanah telah dikenalpasti untuk memulihkan tanah yang telah tercemar. Kaedah ini adalah berdasarkan kepada keupayaan sesetengah bahan untuk menjalankan proses pemendakan atau penjerapan, dan seterusnya mengurangkan ketersediaan logam berat dalam tanah pada tumbuhan. Sisa rawatan air minuman (WTR), debu arang batu (CFA) dan gipsum merah (RG) telah digunakan sebagai bahan pembaik pulih tanah untuk merawat tanah yang telah dicampur dengan sisa enap cemar kumbahan. Oleh itu, objektif umum bagi kajian ini adalah untuk menilai sama ada WTR, CFA dan RG dapat digunakan sebagai bahan pembaik pulih tanah untuk memegunkan logam berat di dalam tanah yang tercemar dan juga menghalang pengambilan logam berat oleh tumbuhan.

Dalam kajian pertama, yang melibatkan tiga jenis bahan sampingan industri iaitu WTR, CFA dan RG dimana ianya telah diambil dari pelbagai tempat yang berbeza. Langkah pertama yang perlu dilakukan sebelum bahan sampingan industri ini dapat digunakan adalah dengan menilai sama ada bahan sampingan ini sesuai untuk kegunaan tanah, khususnya, pertanian. Oleh yang demikian, sampel-sampel yang diambil telah dikering udara dan sifat-sifat kima, fizik, mineralogi dan morfologi sampael telah ditentukan. Kesemua bahan sampingan ini mempunyai nilai pH melebihi 7, di mana ianya boleh memberi kesan terhadap pengurangan aktiviti pengionan logam berat di dalam tanah. Kapasiti peneutralan asid (ANC) yang diwakili dengan peratus persamaan kalsium karbonat untuk WTR, CFA dan RG ialah 0.50%, 0.50% dan 1.79%. Keupayaan kadar pertukaran kation (KPK) untuk semua bahan sampingan ini adalah sangat rendah (<10 $cmol.kg^{-1}$), dimana ianya menggambarkan keupayaan bahan sampingan ini menyimpan dan menjerap ion kationik. Paras logam berat bagi kesemua bahan sampingan ini adalah masih dibawah paras yang dibenarkan bagi sisa yang digunakan untuk tanah pertanian.

Kajian kedua merupakan kajian inkubasi di makmal bagi tanah Siri Bungor yang telah dirawat dengan sisa enap cemar kumbahan dan dibaik pulih dengan sisa sampingan industri (WTR, CFA dan RG) untuk kajian larutan tanah dan kajian pembahagian bentuk dalam sistem tanah. Kajian ini adalah untuk mengenal pasti pH dan juga keupayaan logam berat dalam larutan tanah dan mengenalpasti bentuk logam berat dalam tanah telah dirawat dengan sisa enap cemar kumbahan dan dibaik pulih dengan sisa sampingan industri (WTR, CFA dan RG). Rawatan yang dijalankan untuk kajian larutan tanah dan kajian pembahagian bentuk tanah adalah seperti berikut dan setiap data yang diperolehi adalah purata nilai rawatan yang diulang sebanyak empat kali. Untuk kajian larutan tanah, rawatan yang dilakukan ialah T1 – tanah + 0% bahan sampingan industri + 5 % enap cemar kumbahan, T2 – tanah + 2.5% bahan sampingan industri + 5 % enap cemar kumbahan, T3 – tanah + 5% bahan sampingan industri + 5 % enap cemar kumbahan, T4 – tanah + 10% bahan sampingan industri + 5 % enap cemar kumbahan, T5 – tanah + 20% bahan sampingan industri + 5 % enap cemar kumbahan dan T6– tanah + 40% bahan sampingan industri + 5 % enap cemar kumbahan. Bagi kajian pembahagian bentuk tanah pula, rawatan yang digunakan T1 – tanah + 0% bahan sampingan industri + 5 % enap cemar kumbahan, T2 – tanah + 2.5% bahan sampingan industri + 5 % enap cemar kumbahan, dan T6 – tanah + 40% bahan sampingan industri + 5 % enap cemar kumbahan. Semua rawatan disusun dalam bentuk rekabentuk rawak lengkap.

Bagi kajian larutan tanah, penguji contoh kelembapan tanah ’rhizon’ telah digunakan untuk mengekstrak larutan tanah daripada tanah Siri Bungor dari eksperimen berpasu. Inkubasi makmal telah dijalankan selama 70 hari, dan air larutan tanah diambil dari hari pertama hingga hari tujuh puluh, dalam tempoh satu minggu sekali. Kajian pembahagian bentuk tanah telah dijalankan pada hari terakhir inkubasi untuk mengenalpasti bentuk logam berat (Zn, Cu, Ni, Cd dan Pb) bagi rawatan T1 - 0% (rawatan kawalan), T2 - 2.5% (rawatan terendah) dan T3 - 40% (rawatan tertinggi) sisa sampingan industri. Logam berat dibahagikan kepada beberapa bentuk iaitu larut air, tukar ganti, bentuk karbonat, bentuk Fe-Mn oksida, bentuk organik dan bentuk sisa baki. Kepekatan larutan logam berat (Zn, Cu, Ni, Cd and Pb) dalam larutan tanah bagi WTR, CFA dan RG adalah rendah jika dibandingkan dengan rawatan kawalan. Faktor pengurangan larutan logam berat dalam tanah adalah disebabkan penggunaan kadar sisa sampingan industri yang berbeza dan ianya menyebabkan perubahan pH dalam larutan tanah. Pembahagian bentuk sisa bahan sampingan bagi logam berat (Zn, Cu dan Ni) menunjukkan dominasi dalam bentuk sisa baki. Selain daripada itu, Cd dan Pb masing-masing menunjukkan dominasi dalam bentuk organik dan bentuk Fe-Mn oksida.

Kajian ketiga ialah kajian yang dijalankan di rumah kaca dimana ianya untuk melihat pengurangan logam berat dalam tanah yang di rawat dengan enap cemar kumbahan dan di baik pulih dengan sisa sampingan industri. Kajian ini bertujuan untuk menentukan kadar penggunaan optimum bagi WTR, CFA dan RG yang dapat meningkatkan pertumbuhan tanaman dan mengurangkan pengambilan logam berat oleh jagung di dalam kajian rumah kaca. Jagung manis telah digunakan sebagai tanaman ujian. Semua pasu disusun dalam reka bentuk rawak lengkap. Rawatan yang dijalankan untuk kajian di rumah kaca adalah seperti berikut dan setiap data yang diperolehi adalah purata nilai rawatan yang diulang sebanyak empat kali. Rawatan yang dilakukan ialah P1 – tanah + 0% bahan sampingan industri + 5 % enap cemar kumbahan, P2 – tanah + 2.5% bahan sampingan industri + 5 % enap cemar kumbahan, P3 – tanah + 5% bahan sampingan industri + 5 % enap cemar kumbahan, P4 – tanah + 10% bahan sampingan industri + 5 % enap cemar kumbahan dan P5 –

tanah + 20% bahan sampingan industri + 5 % enap cemar kumbahan. Selain daripada itu, kajian pembahagian bentuk tanah juga dilakukan yang digunakan adalah P1 – tanah + 0% bahan sampingan industri + 5 % enap cemar kumbahan, P2 – tanah + 2.5% bahan sampingan industri + 5 % enap cemar kumbahan dan P5 – tanah + 20% bahan sampingan industri + 5 % enap cemar kumbahan.

Kadar yang sesuai untuk pertumbuhan tanaman menggunakan sisa buangan industri sebagai bahan pembaik pulih tanah adalah penggunaan WTR sehingga 10%, CFA sehingga 5% dan RG penggunaan sehingga 2.5%. Secara amnya tujuan utama penggunaan sisa buangan industri ini bukanlah untuk meningkatkan berat kering jagung dan memberi nutrien tambahan kepada pertumbuhan jagung tetapi untuk mengurangkan pengambilan logam berat daripada tanah oleh jagung. Walau bagaimanapun, penggunaan WTR sehingga 2.5% dapat meningkatkan berat kering jagung. Berdasarkan penggunaan sisa buangan industri, pengambilan logam berat Zn dan Cu oleh jagung dapat dikurangkan dengan penggunaan WTR dan RG berbanding dengan rawatan kawalan. Manakala bagi penggunaan CFA, pengambilan logam berat Zn dan Cd oleh jagung dapat dikurangkan berbanding rawatan kawalan. Perbandingan kadar nutrien optimum yang diperlukan oleh jagung dengan kadar nutrien dalam tanah menunjukkan kepekatan N dan K adalah tidak mencukupi untuk pertumbuhan jagung dengan penggunaan semua rawatan sisa buangan industri. Oleh yang demikian, tambahan bagi baja K (140 kg/ha) telah dilakukan ke atas kesemua rawatan disebabkan oleh simptom kekurangan nutrien K telah dikenalpasti. Walaupun simptom kekurangan nutrien N tidak kelihatan pada tanaman jagung, baja

N juga perlu ditambah kerana nilai N dalam tanah tidak mencukupi untuk pertumbuhan jagung.

Penggunaan WTR, CFA dan RG ke atas tanah dapat dicadangkan sebagai bahan pembaik pulih tanah disebabkan oleh keberkesanan dalam mengawal logam berat dalam tanah dengan mengubah nilai pH tanah. Walau bagaimanapun, dengan penggunaan WTR, kekurangan P di dalam tumbuhan perlu dipantau disebabkan kebolehan WTR untuk menjerap nutrien P. Sebelum penggunaan CFA dapat dijalankan sebagai bahan pembaik pulih tanah, proses pengudaraan atau penglagunan perlu dilakukan untuk menyingkiran lebihan nutrien B. Daripada kajian inkubasi, hasil keputusan menunjukan kebarangkalian penggunaan sisa sampingan industri ini dapat mengurangkan kepekatan logam berat terutamanya Zn di dalam larutan tanah. Daripada kajian rumah kaca, penggunaan sisa buangan industri iaitu WTR dan RG, dapat mengurangkan pengambilan logam berat Zn dan Cu oleh jagung berbanding dengan rawatan kawalan. Manakala bagi penggunaan CFA, pengambilan logam berat Zn dan Cd oleh jagung dapat dikurangkan berbanding rawatan kawalan. Penggunaan sisa sampingan industri pada kadar yang tertentu (dengan menggunakan sehingga 10% WTR, 5% CFA dan 2.5% RG) dapat meningkatkan hasil berat kering jagung jika dibandingkan dengan penggunaan tanah yang dirawat dengan menggunakan sisa enap cemar kumbahan sahaja. Kajian rumah kaca juga menunjukkan penggunaan 2.5% WTR dapat meningkatkan berat kering jagung.

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I certify that an Examination Committee met on 19th June 2007 to conduct the final examination of Nur Hanani Mansor on her Master of Agricultural Science thesis entitled "Assessment of Selected Industrial Byproducts to Reduce Uptake of Heavy Metals by Sweet Corn (Zea mays L.) from Sewage Sludge Amended Soil" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the degree of Master of Agriculture Science

Members of the Examination Committee are as follows:

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Date: 27 September 2007

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

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Date: 15 November 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declared that it has not been previously or concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.

NUR HANANI MANSOR

Date:

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