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ZINC UPTAKE BY LOWLAND AND UPLAND RICE GROWN IN TROPICAL SOIL AMENDED WITH BURNED RICE HUSK AND ZEOLITES

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By

BABAK KHAYYAMBASHI

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

December 2014

DEDICATION

I'd dedicate each pages of this thesis to:

My wife who is My Journey Mate in Life and gave me the courage

my lovely daugther who is my Promising Future

My mother who support me to spread my wings and fly

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: Associate Professor Anuar Abd Rahim, PhD
Faculty : Agriculture

There has been a dramatic increase in rice consumption over the past decade and therefore, one of the main considerations is enhancement of the quantity and quality of rice production at present. Application of soil amendments is an important method to improve rice yield. Although physicochemical properties of soil can be improved with soil amendments, Zn availability for plants will be declined due to the adsorption process. Zinc is an essential element for human and plant but too low or high concentrations can be problematic for human health and plant growth. Addition of soil amendment is a practice to restore physical, biological and chemical properties of soils. In Kedah and Perlis states of Peninsular Malaysia the application of burned rice husk into soils is common, but very little is known about the composition, quality and its effects on Zn availability for paddy plants. Therefore, this study was conducted to investigate the mechanisms of Zn sorption by burned rice husk and zeolite, to assess the concentrations of Zn, Fe and P in different parts of the submerged (var. 219) and upland rice (var. Tenom), and to evaluate the potential of burned rice husk and zeolite in reducing Zn uptake by paddy plants.

The mineralogical composition of the zeolite samples were investigated by X-ray diffraction, and FT-IR spectra were used to elucidate the functional groups of the coco peat and burned rice husk. The detailed profiling of the elements presented on a particular surface was determined by SEM-EDX method. Specific surface area, total pore volume and pore diameter of all materials were determined by BET and BJH methods. A sorption study on Zn by organic (burned rice husk and coco peat) and inorganic (Iranian and Chinese zeolites) soil amendments were conducted to select the best adsorbent of Zn from each categories of amendments. The sorption data was fitted to the Langmuir and Freundlich adsorption models. The influence of acidity on Zn sorption by the selected adsorbents was also investigated at pH 5 and 7. A greenhouse experiment was conducted at Universiti Putra Malaysia during August and December 2012 using the selected adsorbents. A factorial randomized complete block design (RCBD) experiment was used with two soil amendments (Iranian zeolite (5% w/w) and BRH (2% w/w)) and five Zn rates (0, 2.5, 5, 10 and 20 mg kg^{-1}) with 3 replications to determine the effects of the treatments on Zn uptake by MR219 (submerged) and Tenom (upland) paddy plant varieties in Kangar soil series.

The data indicated that Iranian and Chinese zeolites contained 93.21 %, 58.83 % clinoptilolite-Na, respectively, but high amounts of tridymite (28.04 %) was also

found in the Chinese zeolite. The results showed that the predominant functional groups on BRH were silicate and sulphonate groups while the amino, C-H, carboxylic (C=O), C=C, N-H, CH_2 and C-O-H functional groups were the dominant in the coco peat. The Zn sorption isotherm data for both Iranian zeolite and Chinese zeolite were better fitted to the Langmuir model while for both coco peat and burned rice husk the Freundlich model fitted the sorption data better. It was found that the q_{max} of the Iranian zeolite was higher than the Chinese zeolite, and the affinity of burned rice husk for Zn adsorption was higher than coco peat. Hence, the burned rice husk and Iranian zeolite, which had higher adsorption rate of Zn, were selected for the subsequent experiment to evaluate their potentials in reducing Zn uptake by rice. The q_{max} value of Zn sorption was higher at pH 5 than 7 for both the Iranian zeolite and burned rice husk. However, the affinity of adsorption (K_L) was the same for the Iranian zeolite at both pHs while for the burned rice husk it was higher at pH 7.

In the green house study, the aerial dry biomass of both MR219 and Tenom were highest in soil amended with burned rice husk. There was no significant different in aerial dry biomass of both MR219 and Tenom planted in soils amended with Iranian zeolite and the control. However, the difference in Zn uptake by MR219 in the burned rice husk and Iranian zeolite amended soil was not significant. The increase in Zn rate increased the Zn in Y leaf of MR219 in all the treatments. The increase in the Zn rate decreased the concentration of Fe only in Y leaf, and similar trend was also observed for P concentration in Y leaf, leaf and stem. In general, Zn uptake by MR219 in zeolite and burned rice husk amended soils was lower than in the control plot at all Zn rates. The increasing Zn rate increased the Zn concentration in the Y leaf, leaf and stem of Tenom variety planted in the the control plot but in the amended plots, Zn concentration increased only in the leaf with the increasing Zn rate. The increase in the Zn rate decreased the concentration of P only in the leaf. The uptake of Zn by Tenom variety was lower in the amended soils than the control and the zeolite was better than the burned rice husk in reducing the Zn uptake by the Tenom variety.

In conclusion soil amendment can be used to reduce Zn uptake by paddy plants. In addition, soil amendments can also increased the aerial dry biomass of the paddy plants. Burned rice husk was better than the Iranian zeolite in reducing Zn uptake and increasing aerial dry biomass of the paddy plants

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGAMBILAN ZINK (ZN) OLEH PADI SAWAH DAN PADI HUMA DI TANAH YANG DILETAK DANGAN SEKAM PADI BAKAR DAN ZEOILITES

Oleh

BABAK KHAYYAMBASHI

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Terdapat peningkatan dramatik dalam penggunaan beras sepanjang dekad yang lalu dan dengan itu, salah satu pertimbangan utama dalam penanaman padi adalah peningkatan kuantiti dan kualiti beras pada masa ini. Penambahan agen pembaikan tanah adalah satu kaedah penting untuk meningkatkan hasil padi. Walaupun ciri-ciri fizikal-kimia tanah dipertingkatkan dengan pembaikan tanah, tetapi kekurangan ketersediaan Zn untuk tumbuhan tetap berlaku disebabkan oleh proses penjerapan. Zn adalah elemen penting untuk manusia dan tumbuhan tetapi kandungan yang terlalu rendah atau tinggi boleh menjadi masalah untuk kesihatan manusia dan pertumbuhan tumbuhan. Penambahan agen pembaikan tanah merupakan amalan untuk memulihkan sifat fizikal, biologi dan kimia tanah. Di Kedah dan Perlis, negeri-negeri di Semenanjung Malaysia, walaupun penggunaan sekam padi yang dibakar pada sawah padi adalah cara konvensional, namun hanya sedikit maklumatnya terdapat mengenai komposisi, kualiti dan kesannya terhadap adanya Zn untuk tanaman padi. Oleh itu, kajian ini dijalankan untuk mengkaji mekanisme penyerapan Zn oleh sekam padi terbakar dan ‘zeolite’. Objektif seterusnya adalah untuk menilai kepekatan Zn, Fe dan P di bahagian-bahagian yang berbeza daripada padi sawah (var. MR219) dan padi huma (var. Tenom), dan untuk menilai potensi dan sekam padi terbakar (BRH) dengan ‘zeolite’ dalam mengurangkan pengambilan Zn oleh beras.

Komposisi mineralogi sampel ‘zeolite’ telah diuji oleh pembelauan sinar-X, manakala spektrum FT-IR telah digunakan untuk menerangkan kumpulan berfungsi yang terlibat dalam penyerapan pada media gambut dan sekam padi terbakar. Penamaan unsur terperinci yang dikemukakan pada permukaan tertentu telah ditentukan oleh kaedah SEM-EDX. Luas permukaan tertentu, jumlah isi-padu liang dan garis pusat liang pada semua bahan telah ditentukan oleh kaedah BET dan BJH. Kajian penyerapan Zn telah menggunakan bahan organik (sekam padi terbakar dan media gambut) dan bukan organik, (zeolite daripada Iran dan China) dijalankn untuk menentukan penjerap terbaik daripada setiap kategori agen pembaikan. Data daripada eksperimen tersebut disesuaikn dengan mengunakan model penjerapan Langmuir dan Freundlich. Pengaruh asid terhadap penjerapan Zn oleh penjerap terpilih juga disiasat pada pH 5 dan 7. Eksperimen rumah hijau telah dijalankan di Universiti Putra Malaysia pada bulan Ogos dan Disember 2012. Rekabentuk eksperimen ini adalah susunan blok secara penuh rawak. Eksperimen ini yang terdiri daripada 3 faktor, iaitu dua agen pembaikan tanah [‘zeolite’ Iran (5% w / w) dan sekam padi terbakar (2% w / w)], lima kadar Zn (0, 2.5, 5, 10 dan 20 mg kg^{-1}) dan

dua jenis padi (padi sawah-MR219) dan padi tanah tinggi-Tenom) menggunakan tanah siri Kangar. Terdapat 3 replikasi bagi setiap rawatan dalam eksperimen ini.

Data menunjukkan bahawa "zeolite" Iran dan China yang terkandung 93,21%, 58,83% clinoptilolite-Na, masing-masing, tetapi jumlah yang tinggi tridymite (28,04%) juga terdapat dalam 'zeolite' Cina. Hasil kajian menunjukkan bahawa kumpulan berfungsi utama di BRH adalah kumpulan silikat dan "sulphonate"; manakala kumpulan amino (C-H), kumpulan karboksilik (C=O), C=C, N-H, CH_2, dan C-O-H ialah kumpulan berfungsi dominan dalam media gambut. Data serapan zeolite sesuai dimasukkan dalam model penjerapan Langmuir manakala data sekam padi lebih sesuai menggunakan model Freundlich. Data Zn serapan isoterma untuk kedua-dua 'zeolit' Iran dan 'zeolite' China diguna lebih baik untuk model Langmuir; manakala untuk kedua-dua media gambut dan sekam padi terbakar, model Freundlich yang lebih sesuai untuk data penyerapan. Data juga menunjukkan q_{max} 'zeolite' Iran adalah lebih tinggi daripada 'zeolite' China, dan hubungan sekam padi terbakar bagi Zn penjerapan adalah lebih tinggi daripada media gambut. Oleh itu, kombinasi sekam padi terbakar dan 'zeolite' Iran, yang mempunyai kadar penjerapan Zn yang lebih tinggi, telah dipilih untuk ujikaji seterusnya, iaitu menilai daya potensi dalam mengurangkan pengambilan Zn oleh beras. Hasil kajian menunjukkan bahawa nilai q_{max} lebih tinggi pada pH 5 daripada 7 untuk kedua-dua 'zeolite' Iran dan sekam padi terbakar. Hasil penjerapan di kedua-dua pH adalah sama untuk 'zeolite' Iran, manakala lebih tinggi pada pH 7 daripada 5 untuk sekam padi terbakar.

Dalam kajian rumah hijau, dalam kedua-dua keadaan, biomass kering beras dalam tanah yang dirawat dengan sekam padi terbakar adalah lebih tinggi daripada rawatan 'zeolite' Iran dan rawatan kawalan. Tiada perubahan ketara dalam perubahan biomas kering bagi kedua-dua MR219 dan Tenom yang ditanam dengan Zeolite Iran dan juga kawalan. Walaubagaimanapun perubahan pengambilan Zn oleh MR219 dalam tanah yang ditambah sekam padi dan Zeolite Iran tidak menunjukan perubahan ketara. Peningkatan kadar Zn meningkatkan kadar Zn dalam daun Y didalam kesemua rawatan terhadap MR219. Peningkatan kadar Zn hanya menurunkan kadar Fe didalam daun Y, tetapi kondisi yang sama juga didapati terhadap kepekatan P didalam daun Y, daun dan juga batang. Pada umumnya pengambilan Zn oleh MR219 didalam tanah yang ditambah zeolite dan sekam padi adalah lebih rendah daripada plot kawalan dalam kesemua kadar rawatan. Terdapat corak peralihan Zn yang berbeza dalam daun-Y, daun dan batang padi huma (var. Tenom) dalam plot kawalan yang dirawat dengan 'zeolite' dan sekam padi terbakar. Kandungan Zn hanya meningkat didalam daun dengan peningkatan kadar Zn. Peningkatan kadar Zn hanya menurunkan kepekatan P hanya didaun. Pengambilan Zn oleh varieti Tenom adalah lebih rendah didalam tanah yang ditambah agen pembaikan berbanding plot kawalan. Zeolite juga adalah lebih baik daripada sekam padi dalam mengurangkan pengambilan Zn bagi varieti Tenom.

Kesimpulannya, agen penambahbaikan tanah boleh digunakan untuk mengurangkan pengambilan Zn oleh pokok padi. Disamping itu, agen penambahbaikan tanah juga boleh meningkatkan biomas kering pokok padi. Sekam padi adalah lebih sesuai daripada Zeolite Iran dalam mengurangkan pengambilan Zn dan juga meningkatkn biomas kering pokok padi.

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I certify that a Thesis Examination Committee has met on 9 september 2014 to conduct the final examination of Babak Khayyambashi on his thesis entitled "Zinc uptake by lowland and upland rice grown in tropical soil amended with burned rice husk and zeolites" 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 relevant degree of Doctor of Philosophy.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
BET	Brunauer, Emmett, Teller
BJH	Barrett, Joyner, Halenda
BRH	Burned Rice Husk
CEC	Cation Exchangeable Capacity
CP	Coco Peat
DAT	Days After Transplanting
DNMRT	Duncan New Multiple Range Test
D.W.	Aerial Dry Biomass Weight
EDX	Energy Dispersive X-ray
SEM	Scanning Electron Microscope
SOM	Soil Organic Matter
Tris	(hydroxymethyl) aminomethane
XRD	X-Ray Diffraction

CHAPTER ONE

INTROUCTION

Rice is the most important staple food of most world's population and 90% of Asians in the word (IRRI, 2004; Srivastava and Mohanty, 2012). Increase in rice production can be sustainably achieved by efficient and good agricultural practices, water and nutrient inputs.

One of the most economical ways to ameliorate the yield is improving physical and chemical characteristics of soil by using inexpensive minerals and organic amendments in rice cultivated soils (Bolan and Duraisamy, 2003). Soil amendment has effect on plant growth rate by increasing cation exchange capacity (CEC) and improves the efficiency of fertilizer. With regard to the source of these materials, they are classified to organic and inorganic. Inorganic soil amendment is included mineral material such as natural zeolites while inorganic is included animal or plant source material such as rice husk, coco peat, coco fibre and burned rice husk (Alloway, 2013).The advantage of the use of organic or inorganic soil amendment, such as zeolite/agricultural by-product, is reduction of nutrients loss in soil. They are providing an ideal trap for positive cations like ammonium and potassium which are released when demanded by plants. On the other hand, the disadvantage of them is sorption and fixation of micronutrient such as zinc refer to their physical and chemical properties, surface area, ion exchange capacity and sorption/desorption phenomena (Barquist, 2009). It is prevented or decreased absorption of micronutrient by plants (Imtiaz et al., 2010).

Human and plant need zinc as an essential element in proper amount, but low or high concentration of zinc can make problem for human health and plant growth (Kabata-Pendias, 2010). Zinc has great roles in plant metabolic systems. Its action as a component of range of enzymes, such as peptides, proteinases, phosphor hydrolases and dehydrogenases is remarkable. Some reports indicated that the metabolism of carbohydrates, proteins, phosphates, and also auxins, RNA, and ribosome formations are associated with the functions of zinc in plants (Takkar and Walker, 1993; Sharma, 2006). It is confirmed that zinc stabilizes cell components and affects systems of microorganisms and permeability of their membranes. There is some evidence that Zn has been stimulated the resistance of plants to dry and hot weather and, also to fungal and bacterial diseases. This might be due to the positive effects of zinc on protein levels, abscisic acid and chlorophyll content as observed in bean seedlings (Zengin, 2006).

Zinc deficiency was diagnosed in rice (*Oryza sativa*) on the northern Indian calcareous soils for the first time (Nene, 1966; Yoshida and Tanaka, 1969). Quijano and Kirk (2002), and also Neue *et al.* (1994) considered that zinc insufficiency is the most common nutrient disorder after disorder of nitrogen, phosphorus and potassium in lowland rice. Generally, Zn deficiency is expected in calcareous soils, sandy soils, peat soils, and soils with high phosphorus (Alloway, 2008b; Alloway, 2009). For that reason, more attention has been given to research work on calcareous soil. The submerged soils are well recognized for the lack of Zn availability to the plants (Mikkelsen and Kuo, 1977). Flooding and submergence decrease the concentration of available Zn with the changes in pH value and insoluble Zn compound formation.

Under the submerged conditions for rice cultivation, Zn is transformed into amorphous sesquioxide precipitates or franklinite; $ZnFe_2O_4$ (Sajwan and Lindsay, 1988; Alloway, 2009).

Susceptibility to Zn deficiencies is widely different among plant species and varieties. Recovered plants from zinc disorder will show significant delay in maturity and reduction in yield (Neue *et al.*, 1994; Wissuwa *et al.*, 2006; Qaisrani, 2011)

On the other hand, toleration of plant to Zn toxicity have been vastly concerned due to the long-standing use of Zn fertilizers, as well as its input from factorial and industrial pollution (Nagajyoti *et al.*, 2010) Although Zn is not considered to be highly phytotoxic, there are some reports that Zn toxicity retarded plant growth in sensitive species (Kabata-Pendias, 2010). There are some reports about phytotoxicity of Zn, especially in heavily slugged and acid soils (Baran, 2013). The zinc toxic physiology and biochemistry in plants are similar to those described for other heavy metals.

Rice breeders in Malaysia have used a different type of soil amendment to perk up root zone, promoting plant growth, increasing crop yield or promoting their quality. In Kedah and Kelantan, rice husks are used as a renewable fuel and commonly burnt in rice mills by cyclonic furnaces to operate rice dryers. Therefore burned rice husk is a combustion by-product found in large volume in major rice mills. Based on the surveys in Kedah and Kelantan, there are more than 50 mills that produced "burned rice husk" as a by-product of rice dryer process. It is estimated that about 32000 metric tonnes were produced annually in these areas and the farmer mixed them with soil (Theeba *et al.*, 2012). These materials may decrease some micronutrient availability for the plant due to their sorption behaviour when used as soil amendments.

While it seems that the focus of research carried out on the calcareous soil that amended with organic and inorganic material, use of these materials are conventional in tropical soil without enough evaluation of the effect and potential of them on Zn absorption by plants. The existing gap of knowledge in “reduction effect of amendments for uptake of Zn in tropical soil” is an extremely challenging issue for increasing the quantity and quality of rice in Malaysia.

Bearing all above factors in mind, the present study was therefore carried out to investigate sorption and desorption of zinc by organic (burned rice husk, coco peat) and inorganic (Iranian and Chinese zeolite) material to choosing high zinc absorbent material and evaluate the effect of them as a soil amendment on zinc uptake of submerged and upland rice for sustainable management of rice nutrition.

1.1 Objectives of the study

The present study was carried out with the following objectives:

1- To investigate the sorption/desorption of Zn by different sources of organic matter (coco peat, burned rice husk) and zeolite (Iranian zeolite and Chinese zeolite).

2- To elucidate the sorption mechanisms of Zn by the zeolites and organic amendments.

3- To measure the concentrations of Zn, Fe and P in different parts of the submerged and upland rice and their correlations with Zn uptake.

4- To evaluate the potential of selected soil amendments in reducing Zn uptake by submerged (variety 219) and upland (variety Tenom) rice.

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