UNIVERSITI PUTRA MALAYSIA

AMENDING FORMULATED COMPOUND FERTILIZERS WITH ZEOLITE TO IMPROVE MAIZE (Zea mays L.) GROWTH AND NUTRIENT USE EFFICIENCY

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By

MAGDALINA LIJA ANAK WELSON BLUE

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

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DEDICATION

I would like to dedicate this thesis to my parent, my siblings and people who are important in my life

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

AMENDING OF FORMULATED COMPOUND FERTILIZERS WITH ZEOLITE TO IMPROVE MAIZE (*Zea mays* L.) GROWTH AND NUTRIENT USE EFFICIENCY

By

MAGDALINA LIJA ANAK WELSON BLUE

April 2013

Chairman : Ahmed Osumanu Haruna, PhD

Faculty : Faculty of Agriculture and Food Sciences, Bintulu

Excessive use and poor utilization of fertilizers can cause air, soil and water pollution. These problems could be minimized by amending compound fertilizers with clinoptilolite zeolite. Objectives of this study were to: (i) determine the effect of amending NPK fertilizers with different rates of clinoptilolite zeolite on NH_3 volatilization, soil exchangeable NH_4^+, and available NO_3^-, and (ii) determine the effect of NPK fertilizers amending with different rates of clinoptilolite zeolite on maize (*Zea mays* L.) dry matter production, nutrient uptake, and nutrient use efficiency. An ammonia (NH_3) volatilization study was conducted using a closed-dynamic air flow system. Seven treatments evaluated in ammonia volatilization experiment were: 250 g soil only (T1), 250 g soil + 3.28 g ammonium nitrate (AN) without additive (T2), 44.6 g 5:3:2 formulated compound containing 31.77 g zeolite (T3), 44.6 g 5:5:5 formulated compound fertilizer containing 26.36 g zeolite (T4), 37.17 g 6:6:6 formulated compound fertilizer containing 18.92 g zeolite (T5), 22.30

g 10:10:10 formulated compound fertilizer containing 4.06 g zeolite (T6), and 14.87 g 15:15:15 commercial fertilizer (T7). Ammonia loss over 12 days was daily recorded following standard procedure. Soil pH, exchangeable NH_4^+ and available NO_3^- at the end of this incubation study were determined using standard procedures. The mixture of the formulated compound fertilizers with clinoptilolite zeolite and T7 were significantly reduced NH_3 volatilization. This was possible because of the temporary retention of NH_4^+ by clinoptilolite zeolite in the formulated compound fertilizers *via* sorption reaction. Application of commercial compound fertilizer had superior effect on soil exchangeable NH_4^+ among treatments, while available NO_3^- had similar effect for treatments containing clinoptilolite zeolite and T7. This was probably due to the source of the fertilizers used. Ammonia volatilization experiment was demonstrated that amending N, P, and K compound fertilizers with clinoptilolite zeolite could minimize NH_3 loss as commercial compound fertilizer (T7). A pot experiment by cultivate Masmadu maize variety as test crop was carried out in a greenhouse as further test to examine treatments effect on growth. The objective of this pot experiment was to observe the effect of the compound fertilizers amended with different rates of clinoptilolite zeolite on maize dry matter, nutrient uptake and fertilizer nutrient use efficiency. Treatments for pot experiment evaluated were: 7 kg soil only (T1), 44.6 g 5:3:2 formulated fertilizer containing 31.77 g zeolite (T2), 44.6 g 5:5:5 formulated compound fertilizer containing 26.36 g zeolite (T3), 37.17 g 6:6:6 formulated compound fertilizer containing 18.92 g zeolite (T4), 22.30 g 10:10:10 formulated compound fertilizer containing 4.06 g zeolite (T5), and 14.87 g 15:15:15 commercial fertilizer (T6). Selected soil

chemical properties after planting were analyzed following standard methods. Dry weight, nutrient concentration, nutrient uptake and nutrient use efficiency at 65 DAP were also measured. Formulated compound fertilizers with zeolite increase soil pH compared to soil alone (T1) and commercial compound fertilizer (T6). Application of the formulated compound fertilizers were significantly similar effect on total N, exchangeable NH_4^+ and NO_3^- availability in soil to commercial compound fertilizer. T6 significantly increased plant height, while total dry weight of treatments with clinoptilolite zeolite was similar to T6. Nitrogen and K concentrations in all parts of maize were statistically similar for treatments with clinoptilolite zeolite and T6, while commercial compound fertilizer had better P concentration. Formulated compound fertilizer and commercial compound fertilizer were had similar Ca concentration in all parts of maize except stems. Mg concentration was greater in maize roots when T6 was applied, while treatments with clinoptilolite zeolite had better Mg concentration in stems and leaves compared to T6. T2, T3, T4 and T5 cause lower uptake of N and P compared to T6. Application of T3, T4, and T5 had statistically similar K uptake to T6 application. Application of T6 was significantly increased N and P use efficiency, while, T2 significantly increased K use efficiency. T2 had high K use efficiency because it had lower rate K applied. A field study for at least three cropping cycles is needed to confirm the findings of this study.

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

MEMINDA FORMULASI BAJA KOMPAUN DENGAN ZEOLIT UNTUK MENINGKATKAN PERTUMBUHAN JAGUNG (*Zea mays* L.) DAN KECEKAPAN PENGGUNAAN NUTRIEN

Oleh

MAGDALINA LIJA ANAK WELSON BLUE

April 2013

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Penggunaan baja sebatian berlebihan serta pengurusan yang lemah boleh menyebabkan pencemaran udara, tanah dan air. Masalah ini boleh dikurangkan dengan meminda baja sebatian dengan zeolit klinoptilolit. Objektif kajian ini adalah untuk: (i) menentukan kesan meminda baja NPK pada kadar zeolit klinoptilolit yang berbeza terhadap pemeruapan NH_3, tukarganti NH_4^+, dan NO_3^- tersedia, dan (ii) menentukan kesan baja NPK dipinda dengan kadar zeolit klinoptilolit yang berbeza terhadap berat, pengambialn nutrien dan kecekapan penggunaan nutrien pokok jagung (*Zea mays* L.). Kajian pemeruapan ammonia (NH_3) telah dijalankan menggunakan sistem aliran udara tertutup dinamik. Tujuh rawatan yang telah dinilai dalam eksperimen pemeruapan ammonia adalah: 250 g tanah sahaja (T1), 250 g + 3.28 g AN tanpa aditif (T2), 44.6 g 5:3:2 baja yang diformulasi mengandungi 31.77 g zeolit (T3), 44.6 g 5:5:5 baja yang diformulasi mengandungi 26.36 g zeolit (T4), 37.17 g 6:6:6 baja yang diformulasi mengandungi 18.92 g zeolit

(T5), 22.30 g 10:10:10 baja yang diformulasi mengandungi 4.06 g zeolit (T6), dan 14.87 g 15:15:15 baja komersial (T7). Kehilangan ammonia telah direkod setiap hari menggunakan kaedah piawai. pH tanah, tukarganti NH_4^+ dan NO_3^- tersedia di akhir kajian inkubasi ini telah ditentukan menggunakan kaedah piawai. Campuran baja sebatian yang diformulasi dengan zeolit klinotilolit dan T7 telah mengurangkan pemeruapan NH_3 secara beerti. Ini adalah mungkin disebabkan pemegangan sementara NH_4^+ oleh zeolit klinoptilolit dalam baja sebatian yang diformulasi melalui reaksi penyerapan. Aplikasi baja sebatian komersial mempunyai kesan yang baik terhadap tukarganti NH_4^+ di kalangan rawatan, manakala NO_3^- tersedia mempunyai kesan yang sama untuk rawatan mengandungi klinoptilolit zeolit dan T7. Ini mungkin disebabkan sumber baja yang digunakan. Eksperimen pemeruapan ammonia telah membuktikan bahawa meminda baja N, P, dan K dengan zeloit klinoptilolit boleh mengurangkan kehilangan ammonia seperti baja sebatian komercial (T7). Eksperimen di dalam pasu dengan mengunakan varieti jagung Masmadu sebagai tumbuhan uji telah dijalankan di rumah hijau sebagai kajian lanjutan untuk menyelidik kesan rawatan terhadap pertumbuhan. Objektif eksperimen pasu ini adalah untuk memerhati kesan pindaan baja sebatian dengan zeolit klinoptilolit pada kadar berbeza terhadap berat kering, pengambilan nutrien dan kecekapan penggunaan nutrien baja oleh pokok jagung. Rawatan yang dinilai untuk ekperimen pasu ini ialah: 7 kg tanah sahaja (T1), 44.6 g 5:3:2 baja yang diformulasi mengandungi 31.77 g zeolit (T2), 44.6 g 5:5:5 baja yang diformulasi mengandungi 26.36 g zeolit (T3), 37.17 g 6:6:6 baja yang diformulasi mengandungi 18.92 g zeolit (T4), 22.30 g 10:10:10 baja yang diformulasi

mengandungi 4.06 g zeolit (T5), dan 14.87 g 15:15:15 baja komersial (T6). Sifat kimia terpilih tanah selepas penanaman dianalisis mengikuti kaedah piawai. Berat kering, kepekatan nutrien, pengambilan nutrien dan kecekapan penggunaan nutrien juga ditentukan. Baja sebatian dengan zeolit telah meningkatkan pH tanah berbanding tanah sahaja (T1) dan baja sebatian komersial (T6). Aplikasi baja sebatian yang diformulasi tidak memberikan perbezaan beerti terhadap jumlah N, tukarganti NH_4^+ dan ketersediaan NO_3^- dalam tanah seperti T6. T6 telah berjaya meningkatkan dengan ketinggian tumbuhan secara beerti, manakala pengeluaran bahan kering bagi rawatan mengandungi zeolit klinoptilolit adalah sama dengan T6. Kepekatan nitrogen, dan K dalam semua bahagian jagung adalah sama secara statistik bagi rawatan mempunyai zeolit klinoptilolit dan T6, manakala baja sebatian komersial mempunyai kepekatan P lebih baik. Baja yang diformulasi dan baja sebatian komersial mempunyai kepekatan Ca yang sama di semua bahagia pokok jagung kecuali stem. Kepekatan Mg di dalam akar jagung adalah tinggi apabila pokok telah diberi T6, manakala rawatan dengan zeolit klinoptilolit mempunyai kepekatan Mg lebih baik di dalam stem dan daun berbanding T6. T2, T3, T4, dan T5 menyebabkan pengambilan N dan P rendah berbanding T6. Aplikasi T3, T4 dan T5 mempunyai pengambilan K yang sama dengan T6 secara statistik. Aplikasi T6 telah meningkatkan kecekapan penggunaan N dan P secara bererti manakala, T2 telah meningkat kecekapan penggunaan K secara bererti. T2 mempunyai kecekapan penggunaan K yang tinggi kerana ia megandungi kadar K yang rendah. Satu kajian lapangan sekurang-kurangnya tiga kitaran tanaman diperlukan untuk mengesahkan penemuan kajian ini.

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I certify that a Thesis Examination Committee has met on 12 April 2013 to conduct the final examination of Magdalina Lija Anak Welson Blue on her thesis entitled "Amending of Formulated Compound Fertilizers with Zeolite to Improve Maize (*Zea mays* L.) Growth and Nutrient Use Efficiency" 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 Master of Science.

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

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DECLARATION

I declare that the thesis is my original work except for quotation and citation which have been duly acknowledged. I also declared that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MAGDALINA LIJA ANAK WELSON BLUE

Date: 12 April 2013

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LIST OF ABBREVIATIONS

%	Percentage
°C	Degree Celcius
AAS	Atomic absorption spectrometer
AN	Ammonium Nitrate
ANOVA	Analysis of variance
Ca	Calcium
$CaCO_3$	Calcium carbonate
CEC	Cation exchange capacity
CsCl	Caesium chloride
DAP	Day after planting
DNMRT	Duncan new multiple range test
DW	Dry weight
ERP	Egypt rock phosphate
g	Gram
h	Hour
H_2SO_4	Sulphuric acid
ha	Hectare
HCl	Hydrochloric acid
HNO_3	Nitric acid
K	Potassium
K_2SO_4	Potassium sulphate
KCl	Potassium chloride

Kg	Kilogram
L	Liter
Mg	Magnesium
MgO	Magnesium oxide
min	Minute
mL	Mililiter
MOP	Muriate of potash
N	Nitrogen
NH_3	NH3
NH_4^+	Ammonium
NH_4OAc	Ammonium acetate
NO_3^-	Nitrate
NUE	Nutrient use efficiency
OM	Organic matter
P	Phosphorus
SAS	Statistical analysis system
UV	Ultra violet

CHAPTER 1

INTRODUCTION

Malaysia has 4.06 million hectares of agricultural land distributed in the country (Mattassan, 2008; Murad *et al.*, 2009). The agricultural sector is important as it contributes to the Malaysian economy (Murad *et al.*, 2009). According to Matassan (2008), some of the Malaysian soils are highly leached, infertile, and acidic. Crops in general require sufficient nutrients in soil to sustain performance and yield. The high demand for fertilizers to sustain high crop yield annually contribute to the high cost of their use in agriculture.USDA (2010) reported that fertilizer prices in 2010 were $517 per ton anhydrous ammonia, $421 per ton urea, $245 per ton liquid N (28%), $447 per ton DAP, and $495 per ton potash. Malaysia spent about RM9.17 billion for 4.16 million ton of imported mineral fertilizers (Sabri, 2009).

Since fertilizers are usually the highest variable costs item in crop production budget, it is essential to improve nutrient use efficiency of fertilizers. In 2006, Malaysia produced about 1.1 million ton of granular and compacted fertilizers (Shaddick, 2007). Blending of straight fertilizers can reduce fertilizer application costs and time for nutrients distribution (McCauley *et al.*, 2009). Compound fertilizers can be defined as a fertilizer that has a declarable content of at least two of plant nutrients obtained chemically or by blending (UNIDO and IFDC, 1998).

Maize like other crops requires sufficient amount of nutrients for optimum growth and development. Nitrogen, P, and K fertilizers amended with clinoptilolite zeolite may improve soil nutrients retention to sustain maize growth because zeolites contain essential nutrients such as Ca, K, and Mg that could improve growth and development of plants. Zeolite based fertilizers have several advantages namely, they are prepared based on a non-toxic natural material and easily applied at the beginning of the vegetation period yet supplies an even fertilizing effect throughout the whole period of plant growth and development (Rehakova *et al.*, 2004).

Zeolites have high CEC, high water holding capacity, and high adsorption capacity (Mumpton, 1999). Clinoptilolite zeolite decreases NH_3 volatilization by retaining NH_3 in its pore structure. In general, N loss and NO_3^- leached from agricultural soils occur through NH_3 volatilization and denitrification, respectively (He *et al.*, 2002). Zeolites improve nutrient use efficiency by increasing Ca^{2+} exchange from phosphate rock during dissolution of P. Moreover, the utilization of NH_4^+ and NO_3^- as well as reducing losses *via* cations exchange reaction, for instance Ca^{2+} and K^+ (Ghorbani and Babaei, 2008). Bernardi *et al.* (2012) reported that concentrated zeolite enriched with N, P and K was an adequate slow-release source of nutrients for plants. Zeolites also improves soil water holding capacity and its availability to plants (Xiubin and Zhanbin, 2001; Bernardi *et al.*, 2008).

In recent times, studies are focused on NH_3 volatilization from urea and direct application of zeolites (Ahmed *et al.*, 2006a, 2008a; Shamsuddin *et al.*, 2009; Latifah *et al.*, 2010). Currently, there is dearth of information on nutrient use efficiency *via* mixing ammonium nitrate (AN), Egypt rock phosphate (ERP), and muriate of potash (MOP) with clinoptilolite zeolite. These kinds of compound fertilizers with clinoptilolite zeolite may not only improve retention of nutrients but they will also aid in slow-release of nutrients for optimum plant uptake and utilization. Therefore, the objectives of this study were to: (1) determine the effect of amending NPK fertilizers with different rates of clinoptilolite zeolite on NH_3 volatilization, soil exchangeable NH_4^+, and available NO_3^-, and (2) determine the effect of NPK fertilizers amending with different rates of clinoptilolite zeolite on maize (*Zea mays* L.) dry matter production, nutrient uptake, and nutrient use efficiency.

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LIST OF PUBLICATIONS

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