UNIVERSITI PUTRA MALAYSIA

REDUCING SOIL ACIDITY IN ULTISOLS AND OXISOLS USING RED GYPSUM AND BIOCHAR IN MALAYSIA

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By

TALHA IBRAHIM ZANNAH

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

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DEDICATION

This thesis is dedicated to my parents and family affiliates.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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Chairman : Professor Shamshuddin Jusop, PhD
Faculty : Agriculture

The accruing benefits from RG, rich in Ca and S, produced in over 400,000 tonnes, yearly in Malaysia, can impact positively on the overall growth of crops by providing a readily soluble form of calcium, which is a principal problem in the Malaysian tropical soils. Biochar has 4.49 million ha under oil palm plantation, this connotes huge amount produced yearly. The pursuits to boost food production, the maize grown on these soils which have been below optimal yield are unsatisfactory due to the acid infertility. Therefore, the underlying hypothesis was that red gypsum and/or biochar application can impact positively or negatively on soil chemical properties and productivity of maize crop. The studied soils are representative of Peninsular Malaysia Ultisols and Oxisols comprising four Series, two from each taxonomic class. A series of experiments were conducted in laboratory, greenhouse and in the field to determine i) the effects of sulphate adsorption on pH and the charge properties of Ultisols and Oxisols ii) Al and Mn toxicity in the soils using red gypsum in combination with biochar and iii) the effects of red gypsum application on the growth of maize. Sulphate adsorption capacities differ among soil studied due to variation in physical and chemical properties. Four t ha^{-1} RG incorporation significantly ($P < 0.05$) increased sulphate adsorption from 22 to 456, 38 to 526, 28 to 474, 70 to 516 mg kg^{-1} in Bungor, Kuala Brang, Segamat and Kuantan Series respectively, raising soil pH from 4.5 to 5.2 and 4.9 to 5.5 with significant reduction in the activities of Al and Mn in the soil solution from 9.3 to 1.0 and 10.1 to 2.0 µM in Segamat and Kuantan Series, lowering PZC by 0.6 digits in Kuantan Series. Five t ha^{-1} biochar application significantly increased the sulphate adsorption from 22 to 138, 38 to 170, 28 to 358, 70 to 180 mg kg^{-1}, raising pH from 4.4 to 4.9, 3.9 to 4.5, 4.5 to 5.3 and 4.9 to 5.7 in Bungor, Kuala Brang, Segamat and Kuantan Series respectively, lowering the PZC by 0.2 to 0.3 digits in Bungor, Kuala Brang and Segamat Series, with significantly decreased Al and Mn activities in all the soil studied. The 3 t ha^{-1} RG + 2 t ha^{-1} biochar incorporation significantly ($P < 0.05$) increased sulphate adsorption from 22 to 458, 38 to 494, 28 to 494, 70 to 542 mg kg^{-1} in Bungor, Kuala Brang, Segamat and Kuantan Series respectively, significantly, raising pH from 3.9 to 4.6, 4.5 to 5.4 to 5.8 in Kuala Brang, Segamat and Kuantan Series due to significant reduction in Al activity, lowering the PZC by 0.6 digits in Kuala Brang and Segamat Series. Calcium levels increased significantly due to respective application of 4, 5 and 3 + 2 t ha^{-1} RG, biochar and RG + biochar. Both RG and biochar playing a substantial role in reducing toxicities of Al and Mn. The mechanism for the adsorbed sulphates involves both specific and non-specific adsorption processes. Incorporation of red gypsum and/or biochar into the acid soils improved maize growth. The red gypsum treated soils had significantly increased the biomass of the maize crop, which ranged from 17 to 45 g $plant^{-1}$ in the greenhouse experiment, in Kuala Brang and Kuantan Series. This had contributed 66 and 78 % to the growth of maize crop. The RG and biochar had significant effects on maize growth (761 to 1309 g $plot^{-1}$) as an amendment under field condition on Bungor Series. In addition to the discrete soil characteristics in terms of nutrient supply, the biomass in the RG amended soils was significantly positively related to available P, exchangeable Ca, Mg and K but negatively related to soil exchangeable Al and Mn ($P < 0:05$). The reduction in acidity by red gypsum was due to increased exchangeable Ca contents.

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

MENGURANGKAN KEASIDAN PADA TANAH ULTISOL DAN OXISOL MENGGUNAKAN GIPSUM MERAH DAN BIOCHAR DI MALAYSIA

Oleh

TALHA IBRAHIM ZANNAH

Januari 2017

Pengerusi : Profesor Shamshuddin Jusop, PhD
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Gipsum merah merupakan sumber produk sampingan yang kaya dengan Ca dan S. Ia mampu memberikan impak positif terhadap pertumbuhan jagung dengan membekalkan Ca dalam bentuk tersedia diambil oleh tanaman; di mana ia merupakan masalah utama bagi tanah pertanian di kawasan tropika. Terdapat lebih daripada 400, 000 biochar di ladang-ladang kelapa sawit, menunjukkan bahawa jumlah yang besar dihasilkan pada setiap tahun. Usaha meningkatkan pengeluaran hasil makanan; tanaman jagung yang diusahakan di tanah-tanah bermasalah ini memberikan hasil di bawah paras optimum, disebabkan oleh keasidan tinggi dalam tanah. Maka, hipotesis yang dicadangkan adalah apliaksi gipsum merah dan/ atau biochar boleh memberi impak positif atau negatif terhadap sifat kimia tanah dan pengeluaran hasil jagung. Tanah yang dikaji mewakili Ultisols dan Oxisols di Semenanjung Malaysia dan terdiri daripada empat siri, dua daripada setiap kelas taksonomi. Satu siri eksperimen di makmal, rumah hijau dan lapangan telah dijalankan bagi menentukan i) kesan jerapan sulfat terhadap pH dan sifat cas Ultisols dan Oxisols ii) ketoksikan Al dan Mn dalam tanah selepas aplikasi gipsum merah dan/ atau biochar dan iii) kesan aplikasi gipsum ke atas pertumbuhan jagung. Keupayaan jerapan sulfat didapati berbeza pada kesemua tanah yang dikaji akibat daripada perbezaan sifat-sifat fizikal, kimia dan cas. Aplikasi 4 t ha^{-1} gipsum ke dalam tanah meningkatkan jerapan sulfat secara bererti dengan nilai daripda 22 kepada 256, 38 kepada 536, 28 kepada 474 dan 70 kepada 516 mg kg^{-1} pada tanah Siri Bungor, Siri Kuala Brang, Siri Segamat dan Siri Kuantan, masing-masing, meningkatkan nilai pH daripada 4.5 kepada 5.2 dan 4.9 kepada 5.5 dengan penurunan signifikan terhadap aktiviti Al dan Mn dalam larutan tanah; daripada 9.3 kepada 1.0 dan 10.1 kepada 2.0 µM dalam tanah Siri Segamat dan Siri Kuantan, selain kesan

penurunan kadar titik cas sifar sebanyak 0.6 digit pada tanah Siri Kuantan. Aplikasi 5 t ha-1 biochar didapati pada jerapan sulfat dengan nilai 22 kepada 138, 38 kepada 170, 28 kepada 358 dan 70 kepada 180 mg kg-1, dengan peningkatan nilai pH 4.4 kepada 4.9, 3.9 kepada 4.5, 4.5 kepada 5.3 dan 4.9 kepada 5.7 pada tanah Siri Bungor, Kuala Brang, Segamat dan Kuantan, masing-masing, dengan penurunan kadar titik cas sifar sebanyak 0.2 hingga 0.3 digit pada tanah Siri Bungor, Kuala Brang dan Segamat, selain penurunan signifikan pada aktiviti Al dan Mn dalam kesemua tanah yang dikaji. Aplikasi 3 t ha^{-1} gypsum merah bersama 2 t ha^{-1} biochar meningkatkan ($p < 0.05$) jerapan sulfat daripada 22 kepada 458, 38 kepada 494, 28 kepada 494 dan 70 kepada 542 mg kg^{-1} dalam kesemua tanah yang dikaji, di samping meningkatkan pH daripada 3.9 kepada 4.6, 4.5 kepada 5.4 dalam tanah Siri Kuala Brang, Siri Segamat dan Siri Kuantan, serta merendahkan titik cas sifar sebanyak 0.6 digit dalam tanah Siri Kuala Brang dan Siri Segamat. Paras Ca meningkat secara signifikan selepas aplikasi 4, 5 dan 3 + 2 t ha^{-1} RG, biochar dan RG + Biochar, masing-masing. Kedua-dua RG dan biochar memaminkan peranan penting dalam pengurangkan kesan ketoksikan Al dan Mn dalam tanah. Mekanisma penjerapan sulfat melibatkan kedua-dua proses penjerapan spesifik dan tidak spesifik. Aplikasi RG dan / atau biochar ke dalam tanah berasid mampu menignkatkan pertumbuhan jagung. Tanah yang dirawat dengan RG memberi kesan signifikan terhadap berat jagung, iaitu antara 17 hingga 45 g $pokok^{-1}$ dalam eksperimen rumah hijau, pada tanah Siri Kuala Brang dan Kuantan. Ia menyumbang sebanyak 66 dan 78% terhadap pertumbuhan jagung. Aplikasi RG dan biochar memberi kesan signifikan terhadap pertumbuhan jagung (761 hingga 1309 g $plot^{-1}$) sebagai penambahbaik tanah di lapangan pada tanah Siri Bungor. Selain itu, berat jagung yang ditanam pada tanah yang dirawat dengan RG adalah berkait secara positif dengan kandungan P tersedia, Ca, Mg dan K bolehganti tetapi berkait negatif dengan Al dan Mn bolehganti dalam tanah ($P < 0.05$). Pengurangan keasidan adalah disebabkan peningkatan kandungan Ca bolehganti selepas aplikasi RG.

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I certify that a Thesis Examination Committee has met on 16 January 2017 to conduct the final examination of Talha Ibrahim Zannah on his thesis entitled "Reducing Soil Acidity in Ultisols and Oxisols using Red Gypsum and Biochar in Malaysia" 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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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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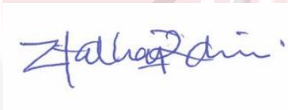

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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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LIST OF ABBREVIATIONS

MBC	Maximum Buffering Capacity
K	Bonding energy or affinity constant
B	Sulphate sorption maxima
PZC or pH0	Point zero charge
CEC	Cation Exchange Capacity
AEC	Anion Exchange Capacity
CEC_B	Basic Cation Exchange Capacity
CEC_T	Total Cation Exchange Capacity
RG	Red Gypsum
EFB	Empty Fruit Bunch
ANC	Acid Neutralizing Capacity
DDL	Diffuse Double Layer
FTIR	Fourier Transmission Infrared
XRD	X-Ray Diffraction
ICP-OES -	Inductively coupled plasma emission spectrometry
AAS	Atomic Absorption Spectrophotometer
AA	Auto Analyser
CNS	Carbon, Nitrogen and Sulphur
C:N	Carbon Nitrogen
OH	hydroxyl groups
C-C, C=O, -COO	Carboxylate groups, carbon and oxygen atoms
Si-O	Silicon and Oxygen.

CHAPTER 1

INTRODUCTION

1.1 Background

Acid Ultisols and Oxisols which occur during geological evolution, especially in areas of high rainfall due to relatively easy leaching from soils, leaving them acidic (Rengel, 2003), is one of the major causes of soil degradation. It is essential decline in soil quality or reduction in its productivity and environmental regulatory capacity (Lal, 1997), that limit crop production. It is a natural process, which can be accelerated by the activity of the living organisms or can be impeded by sound management practices. Developments of acid soils continue to increase in the tropics and worldwide, primarily because of continuous leaching by heavy rains and agricultural practices. This has become a constraint and one of the most yield-limiting factors for crop production. This trend poses a high risk of soil and environmental degradation because of harsh climate and resource-poor farmers (Lal and Stewart, 2011).

The tropical regions which cover significant portion of the world's land acreage are characterized by a large portion of the world's rapidly increasing population (Lal, 2002), projected to have a huge increase in food demand for cereals. World population is expected to increase to 8 billion by 2025 and over 9 billion by 2050 (Fageria and Baligar, 2008). It is estimated that global cereal demand (rice, wheat, and maize) will increase from 1657 million Mg in 1995 to 2436 million Mg in 2025 at the mean rate of 1.29% per year (Cassman et al., 2003). Despite the gains in global mean average crop yields, grain yields of cereals in developing countries are still low (Lal, 2007). The acid tropical soils cover a significant part of at least 48 developing countries (Narro et al., 2001), being more frequent in Ultisols and Oxisols in Malaysia.

In view of the foregoing, the accruing benefits from waste generated in the majority of industrial production processes recycling with special relations to soil properties cannot be neglected, as these waste materials become a subject of research in different field of endeavours in recent years. A growing number of soil scientists and environmentalists are becoming interestingly alarmed over the importance of waste material recycling in resolving issues related to soil and environmental degeneration. These are of great concern for both economy as well as environmental reasons/or benefits.

Red gypsum (RG) and the empty fruit bunch (EFB) of palm oil which are typically by-products of industry and farming respectively, commonly called wastes because they are not the primary product. Such wastes are a resource that can be utilized and not just discarded. The possible dividend of such wastes include use as soil amendment/or fertilizer, thus improving soil physical, chemical and biological characteristics. Therefore, the underlying hypothesis is that, red gypsum and/or biochar application can impact on positively or negatively on soil chemical properties and hence improved productivity. Energy production from varying sources such as crop residues, and/or other organic wastes has been utilized in agriculture to varying degrees in different parts of the world (Westerman and Bicudo, 2005). The utilization of a specific waste in agriculture depends among several factors, including the characteristics of the waste such as nutrient content, availability and transportation costs, benefits to agriculture and regulatory considerations.

1.2 Justification

Red gypsum is rich in Ca, S and Fe contents (Fauziah et al., 1996; 2011; Rodriguez-Jorda et al., 2010) which can be harnessed for enhancing soil fertility. Over one million tonnes of red gypsum is produced each year (Azdarpour et al., 2014). It total accumulation in Malaysia is about 400,000 tonnes per year (Kamarudin and Zakaria, 2007). Red gypsum is 75% gypsum (Azdarpour et al., 2014) which is a calcium rich source. Therefore, proposed as a new feedstock for mineral CO_2 sequestration (Rahmani et al., 2014).

This can impact positively on overall growth of maize plants by providing a readily soluble form of calcium which is a principal problem to the Malaysian tropical soils. And biochar being carbonaceous recalcitrant product can be used as a tool to modify or improve soil productivity. In addition to it carbon sequestration potential, biochar has been shown to improve soil quality and crop yields (Brunn, 2011; Abdulrazzaq et al., 2014). The great carbon sequestration potential of biochar, together with biochar apparent ability to improve soil quality, has become a highly interesting concept in recent time. The pursuits to boost food production, the maize grown on these soils which have been below optimal yield are unsatisfactory due to the acid infertility. The maize crop have been used as test crop because is acid sensitive affecting it growth, principally due to toxicities of Al and Mn which led to nutrients deficiencies of Ca, Mg and K and thus requires great attention. This necessitates exploration and efficient management of waste from surrounding environment with a view to have effective soil, plant and water relations for sustainable agriculture.

Numerous strategies have been pursued to manage these acid soils. Adequately limed soils have been proven positive as it enhances sustainability of the cropping systems. However, there has been increased interest on alternative multiple liming agents due it multiple benefits. But it appears that, results around the world toward addressing problems of this nature or related to soil acidity heavily rely on locally sourced materials. As this acknowledges or addresses the problems of cost and practicability to the target beneficiaries and hence the dearth of information on the effects of red gypsum in combination with biochar application in reducing soil acidity in Ultisols and Oxisols necessitate the present investigation. In addition, adsorption and exchange effects of the anions such as suphate in soils are significantly less understood as compared to cations adsorption and exchange.

1.3 Research Objectives

The general objective of this study was to understand the effects of red gypsum and/or biochar application in reducing soil acidity, and the consequential soil properties on chemical and charge characteristics. The specific objectives are as follows:

1) To determine the effects of sulphate adsorption on pH and the charge properties of Ultisols and Oxisols;
2) To alleviate Al and Mn toxicity in the soils using red gypsum in combination with biochar; and
3) To determine the effects of gypsum application on the growth of maize.

1.4 Organisation of the Thesis

The thesis has been structured into seven chapters. Chapter one finds background and justification, research objectives and organisation of the thesis. Chapter two reviewed related literature. Chapter three describes general materials and methods used. Chapter four presents characterization of soils under study. Chapter five identifies sulphate adsorption characteristics of the selected soils and it effects on soil chemical properties after red gypsum and/or biochar application. Chapter six determines effects of applying red gypsum and/or biochar on maize growth after greenhouse and field studies. Chapter seven provides a general discussion, summary of the major findings. It also concludes the study and articulates recommendations and likely future research.

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