UNIVERSITI PUTRA MALAYSIA

ALLEVIATION OF SOIL ACIDITY AND ALUMINUM TOXICITY IN ULTISOL USING BIOCHAR FOR MAIZE CULTIVATION

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By

MAHAMOUD ABDILLAHI RABILEH

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

February 2014

DEDICATION

TO MY BELOVED PARENTS AND FAMILY

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

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February 2014

Chairman: Professor Shamshuddin Jusop, PhD
Faculty : Agriculture

Phytotoxicity of Al ion (Al^{3+}) and low pH stress are the main two important factors limiting maize production under tropical acid soils in Malaysia. Acid soils in Malaysia are often acidic, account about 72% of the country that was classified under Ultisols and Oxisols. Maize production under these highly weathered soils is not favourable due to aluminium (Al), and manganese (Mn) toxicities accompanied by calcium (Ca) and magnesium (Mg) deficiencies. Al is the main component that contributes to soil acidity. Al saturation in an Ultisol is high (> 60%), which limits maize growth. High Al concentration in acid soils restricts root growth by inhibiting cell elongation and cell division and subsequently reduce crop yield. The addition of biochar to agricultural soils has recently received much attention due to the apparent benefits to correct soil acidity. Studies were carried out to investigate the effectiveness of biochar and ground magnesium limestone (GML) as acid soil ameliorants.

Three experiments were conducted: experiment 1) and 2) were carried out in the laboratory, while experiment 3) was conducted in a glasshouse.

The first experiment, conducted in the laboratory, was to investigate the effects of different concentration of Al and/or pH on maize root seedling growth and organic acid release. The result showed that increasing Al concentration in the solution had significantly decreased the root length and root surface area; similarly, low pH decreased both root length and root surface area. It was found that root of maize seedling released oxalic acid when exposed to high concentrations of Al and low pH values; however, it can to some extent reduced the effects of Al^{3+} toxicity by secreting this organic acids. Al concentration and pH value, corresponding to 90 % relative root growth of maize seedling were 20 µM and 6, respectively.

The second study was also conducted in the laboratory in batch adsorption experiment. The aim of this experiment was to examine the ability of EFB-biochar for the removal of Al from aqueous solutions. The effects of pH, contact time, adsorbent dosage and initial Al concentration on the adsorption process were investigated. The optimum pH for adsorption was found to be 4. Adsorption of Al ion reached its equilibrium concentration at highest removal percentage within 120 minutes of contact time. The experiments also showed that the highest removal rate was 80% at solution pH 4, contact time 120 minutes and initial concentration of 10 mg L^{-1} when adsorbent dose was 5 g L^{-1}. The results generally showed that EFB-biochar could be considered as a potential adsorbent for Al removal from aqueous solutions.

The third experiment was conducted in a glasshouse to determine the effects of empty fruit bunch based-biochar and/or ground magnesium limestone (GML) on the soil chemical properties and the growth of maize. Biochar was applied at 0, 5, 10 and 20 t ha^{-1} either in the absence or presence of 2 t GML ha^{-1}. Maize was planted as a test crop. The experiment was arranged in complete randomized block design with four replications. At the end of experiment (50 days), the soil solution in the poly bags was sampled using rhizon soil moisture sampler. Agronomic observations were determined, including height, root growth, dry matter weight (root, leaf and shoot) and nutrient concentration in the maize tissues.

The results showed that soil pH, exchangeable bases, basic cations in soil solution, CEC, total C were increased with increasing rate of biochar and/or GML application. It was also found that biochar application had alleviated soil acidity. Applying biochar at the rate of 10 t ha^{-1} increased soil solution pH from 4.32 to 5.17. The increase in pH was due to the alkalinity existing in the EFB-biochar. Soils treated at this rate of biochar have less Al^{3+} activities resulting from Al being complexed by the EFB-biochar and/or precipitation of Al as Al-hydroxides when soil pH increased, rendering it inactive and therefore unavailable to the maize. Application of biochar alone or in combination with GML had significantly improved maize growth, shown by the increase in maize height, dry matter weight of roots and shoots. However, biochar application in combination with GML is not cost-effective and farmers cannot afford. Relative maize dry matter weight increased linearly with increasing soil solution pH, while it decreased as Al^{3+} and Mn^{2+} activities increased. This study showed that the critical Al^{3+} activity for maize grown on an Ultisol under tropical condition was 11 µM (about 22 µM in terms of concentration). A good crop of maize can be grown on Ultisols in Malaysia provided that the adverse effects of soil acidity are alleviated. This can be achieved by EFB-biochar applied at 5-10 t ha^{-1}.

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

PEMULIHAN KEASIDAN TANAH DAN KETOKSIDAN ALUMINUM DI TANAH ULTISOLS DENGAN BIOCHAR UNTUK TANAMAN JAGUNG

Oleh

MAHAMOUD ABDILLAHI RABILEH

Februari 2014

Chairman: Professor Shamshuddin Jusop
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Jagung ditanam secara global dan tanaman ini menduduki tempat ketiga dalam pengeluaran bijian sedunia selepas tanaman padi dan gandum. Ketoksidan oleh ion Al dan gangguan pH yang rendah merupakan dua faktor yang penting yang mengehadkan pengeluaran jagung dalam tanah asid tropika di Malaysia dimana lebih kurang 72% daripada tanah-tanah di Malaysia digolongkan bawah kumpulan óUltisolsô dan óOxisolsô. Ketoksidan unsur Al dan Mn serta kekurangan unsur Ca dan Mg merupakan faktor-faktor yang menyebabkan pengurangan hasil tanaman jagung di tanah terluluhawa yang tinggi. Unsur Al merupakan komponen utama yang menyumbang kepada keasidan tanah. Unsur Al di tanah óUltisolsô adalah tinggi (> 60%) adalah antara faktor yang mengehadkan tumbuh-besaran pokok jagung. Kepekatan unsur Al yang tinggi mengganggu pertumbahan akar melalui penyekatan dalam pemanjangan dan pembahagian dalam sel akar dan seterusnya mengurangken hasil tanaman. óBiocharô yang dihasilkan daripada buah tandan sawit kosong adalah sejenis ócharcoalô yang stabil disebabkan struktur molekul óbiocharô yang kukuh dari segi kimia dan biologi, maka sifat ini menjadikan óbiocharô dapat menyimpan karbon untuk tempoh yang lebih panjang. Selain itu, permukaan óbiocharô mengandungi beberapa kumpulan bahan kimia yang aktif seperti ï CH, OH dan C=0 , maka óbiocharô mempunyai potensi yang tinggi untuk menyerap unsur Al dan Mn dalam tanah asid. Penambahan óbiocharô dalam tanah pertanian telah menerima perhatian disebabkan kelebihannya untuk mengurangkan keasidan tanah. Beberapa kajian telah dilakukan untuk menentukan keberkesanan óbiocharô dan batu kapur Mg sebagai bahan pemulihan tanah asid. Tiga eksperimen telah dijalankan dimana eksperimen (1) dan (2) dilakukan di makmal manakala eksperimen (3) djalankan di rumah kaca. Eksperimen (1) yang djalankan di makmal adalah untuk menentukan kesan daripada kepekatan Al dengan/atau pH yang berlainan terhadap akar anak pokok jagung dan perlepasan asid organik. Keputusan yang diperolehi menunjukkan kepekatan unsur Al dalam larutan yang semakin meningkat telah mengurangkan panjang dan luas permukaan akar, keadaan yang sama berlaku dengan unit pH yang semakin menurun dalam larutan. Akar anak pokok jagung membebaskan asid óoxalicô apabila terdedah kepada kepekatan unsur Al yang tinggi atau keasidan larutan yang tinggi. Namun begitu, akar anak pokok jagung dapat mengurangkan kesan daripada ketoksidan unsur Al dengan merembeskan asid organik. Kepekatan unsur Al pada 20 mM dan pH larutan pada unit 6.0 masing-masing menyumbang kepada pertumbuhan relatif 90% pada akar anak pokok jagung. Kajian

kedua juga dilakukan di makmal di bawah eksperimen penyerapan secara kumpulan dengan tujuan utama bagi eksperimen ini adalah untuk menentukan keupayaan óbiocharô buah tandan sawit kosong untuk menyingkirkan unsur Al daripada larutan. Kesan pH pada masa penyerapan ini telah dikaji dan pH optima yang didapati adalah unit 4.0. Penyerapan unsur Al telah mencapai kepekatan sama paras dengan penyingkiran yang tertinggi pada masa bertindak 120 minit. Eksperimen ini juga menunjukkan kadar penyingkiran yang tertinggi adalah 80% atau pada dos penyerapan 5 gL^{-1} dengan masa bertindak 120 minit dan kepekalan awal 10 mg L^{-1} .

Keputusan ini secara umumnya menunjukkan óbiocharô buah tandan sawit kosong mempunyai potensi sebagai bahan penyerapan bagi penyingkiran unsur Al daripada larutan. Eksperimen ketiga dilakukan di rumah kaca bagi menentukan kesan daripada óbiocharô buah tandan sawit kosong dengan/atau batu kapur Mg ke atas sifat kimia tanah dan pertumbuhan pokok jagung sebanyak 0, 5, 10 dan 20 t óbiocharô ha^{-1} diberikan bersama 0 atau 2 t GML ha^{-1} . Pokok jagung ditanam sebagai tanaman ujian dalam eksperimen ini. Rekabentuk bagi eksperimen ini adalah óRandomized Complete Block Designô dengan empat replikasi. Pada hari ke-50, larutan tanah dalam polibeg telah diambil dengan menggunakan órhizon soil moisture samplerô. Data-data agronomi seperti ketinggian tanaman, pertumbujan akar, berat kering (akar, daun dan batang) dan kepekatan nutrien dalam daun pokok jagung telah diambil. Keputusan yang diperolehi menunjukkan pH tanah, kation penukargantian, kation asas dalam larutan tanah, kapasiti penukargantian kation dan jumlah karbon telah meningkat selaras dengan peningkatan kadar óbiocharô dengan/atau GML dalam rawatan. Selain itu, pemberian óbiocharô telah mengurangkan keasidan tanah dimana 10 t óbiocharô ha^{-1} telah meningkatkan pH larutan tanah dari unit 4.32 ke 5.11. Keadaan ini berlaku disebabkan unsur kealkalian yang wujud dalam óbiocharô buah tandan sawit kosong. Tanah yang dirawat dengan kadar 10 t óbiocharô ha^{-1} juga mengalami pengurangan dalam aktiviti ion Al^{3+} yang kemungkinan besar disebabkan penggabungan ion Al^{3+} dengan óbiocharô dengan/atau proses hidrolisis unsur Al yang menjadikan ion Al^{3+} tidak bertindak dengan akar pokok jagung bila keasidan tanah meningkat. Rawatan óbiocharô sahaja atau bergabung dengan GML telah meningkatkan pertumbuhan pokok jagung secara ketara, seperti ketinggian pokok jagurg, berat jisim kering akar dan batang. Walaubagaimanapun, rawatan gabungan antara óbiocharô dengan GML adalah tidak ekonomik dan petani tidak mampu untuk memberi rawatan ini. Berat jisim bering relatit pokok jagung meningkat secara terus dengan penambahan unit pH larutan tanah, pada masa yang sama menurum selaras dengan peningkatan dalam aktiviti ion Al^{3+} dan Mn^{2+}. Kajian ini juga menunjukkan paras kritikal bagi pertumbuhan pokok jagung di tanah tropika óUltisolsô bagi aktiviti ion Al^{3+} adalah 11 µM (lebih kurang kepekatan (22 µM), sama seperti keputusan daripada eksperiman di makmal. Tanaman jagung dapat dibesarkan dengan baik di tanah óUltisolsô di Malaysia sekiranya keasidan tanah dapat dipulihkan. Usaha ini akan tercapai dengan pemberian 5-10 t óbiocharô buah tandan sawit kosong dalam sehektar tanah.

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IN THE NAME OF ALLAH, THE MOST GRACIOUS, THE MOST MERCIFUL
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I certify that a thesis Examination Committee has met on 6 February 2014 to conduct the final examination of Mahamoud Abdillahi Rabileh on his thesis entitled ñAlleviation of soil acidity and aluminium toxicity in Ultisol using biochar for maize cultivation ò in accordance with Unversities and Unversitity Colleges Act 1971 and the Constitution of the Unversiti 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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Date:

DECLARATION

Declaration by Graduate Student

I hereby confirm that:

- this thesis is my original work
- quotations, illustrations and citations have been duly referenced
- the thesis has not been submitted previously or concurrently for any other degree at any institutions
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia
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Signature: é é é é é é é é é é é Date: 6th February 2014

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- Supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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ANUAR ABD RAHIM, PhD
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TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

LIST OF ABBREVIATIONS

AA	Auto ïanalyzer
AAS	Automic absorption spectrophotometer
Al	Aluminum
ANOVA	Analysis of variance
BET	Brunauer Emmett Teller
CEC	Cation exchange capacity
DAS	Days after sowing
DMW	Dry Matter Weight
EFBB	Empty fruit bunch-biochar
FTIR	Fourier Transform Infrared Spectroscopy
GML	Ground magnesium limestone
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
Nm	nano molar
RRL	Relative Root Length
SNK	Student Newman Keuls
SAS	Statistical Analysis System
SEM	Scanning Electron Microscope
µM	micro molar

CHAPTER 1

INTRODUCTION

1.1 Background

Acid soils occupy about 30% or 3,950 million ha of the world's ice free land area (Von Uexkull and Mutert, 1995). According to Fageria and Baliger, (2008), Ultisols occupied about 1347 million ha in a global land area which is equivalent to 9.3% of the worldôs total land area. The areas that have high potential for agricultural development are partly located in tropical regions where the soils are acidic and have low fertility states. These highly weathered soils are taxonomically classified as Ultisols. Ultisols are the first major reliable soils to be used for agricultural production in tropical areas, particularly Malaysia. Ultisols are mostly acidic in nature which are considered as highly weathered soils in Malaysia. It is also found in Thailand, Indonesia, Columbia, Brazil, Ecuador, Nigeria, Republic of Congo, and Cameroon and being used extensively for agricultural production.

The main characteristics of Ultisols, are acid soils with low native fertility that have been formed under forest vegetation (Shamshuddin and Fauziah, 2010). Soil pH less than 5 is very common for Malaysian Ultisols. It is well known that Ultisols are dominated by kaolinite and oxides of Fe and Al in the clay fraction. Thus, the soils are low in cation exchange capacity (CEC). These together with the low pH and low basic cations make the soils existing under natural conditions less productive (Shamshuddin and Fauziah, 2010). However, this soil infertility can be ameliorated effectively by applying lime, organic matter and other amendments.

Other major problems in Ultisols are acidity and elemental toxicities, mostly aluminum and manganese. Soil aluminum (Al), in exchangeable and soluble forms represents one of the main limiting factors associated with soil acidification. Lime is usually used to ameliorate acid soils and to alleviate aluminum toxicity, so increase crop yields (Adams, 1984). Al ions released from the clay due to reactions of protons with solid phase is the principal cause for the occurrence of acid reaction in a soil (Yu, 1997). The solubility of Al in acidic soils is important in predicting the amount of Al toxicity, amendment needed to detoxify Al and the rate at which a soil will acidify in the absence of amelioration (Ritchie, 1995). Aluminum (Al^{3+}) and hydrogen (H^{+}) ion dominance in the soil exchangeable complex causes acidity which limits crop yield and utilization of many essential nutrients by plants (Chintala et al., 2012).

Currently, the main agricultural crops of Malaysia are rubber, oil palm and cocoa. These plantation crops are, to a large extent, grown on Ultisols. These soils have occasionally been used for intercroping with maize during immature period of rubber and oil palm replanting, but yields were reported to be low due to poor soils fertility, including Al toxicity and subsoils Ca and/or Mg deficiencies (Shamshuddin et al., 1991). These factors are constraints to crop production. Under acid conditions, maize growth is below optimal and yield is unsatisfactory. The most common symptoms of Al toxicity are stunted root system with short, thick, stubby root that show little branching or growth of lateral roots. The root tips and lateral roots often turn brown. In most crops, plant size is restricted and yield is low. Plants suffering from Al toxicity showed restricted root system, which may affect the capacity for mineral nutrient acquisition and increase the risk of water stress (Rout et al., 2001). Maize is the world's third most important food crop after wheat and rice. It is mainly used for animal feed, human food and many unique industrials and commercial products in many parts of the world. In Malaysia, it is mainly used as animal feed. The country imports grain maize for feed amounting to millions of Ringgit. To meet these requirements, grain maize production should be increased by way of using proper fertilizer and other inputs.

Liming to remediate acidic soils has a longer history than the use of any other forms of soil amendments (McLean, 1971).

There has been increased interest on alternative liming agents with multiple benefits such as pyrolytic biochars which can be used to improve soil fertility and to store carbon (C) in the soil (Nguyen and Lehmann, 2009).

Little information is available on the liming potential of biochars produced from slow pyrolytic processes using palm oil feedstocks and their associated reaction mechanisms to reduce soil acidity. The ameliorating effect of biochars on acidic soil was assumed to be consistent with their composition and properties which depend on biomass feedstock type and pyrolytic conditions.

The current study draws attention on the effect of empty fruit bunch-based biochar applied to a low-nutrient acidic sandy clay soil, which contain high amount of Al and Mn. Biochar is the solid product material produced during a process known as pyrolysis from the thermo-conversion of biomass under little or no oxygen for use in soils as an amendment (Gaskin et al., 2008; Lehmann and Joseph, 2009). Biochar is produced from a variety of biomass residues (feedstocks) and under different pyrolytic conditions, and thus has varying nutrient contents.

Although many studies have been conducted on the application of biochar to soils, up until now, limited scientific studies have been carried out on Malaysian acid soils. For the current study, a sandy clay, acidic soil known as Bungor series was selected as it represents common problematic soils in Peninsular Malaysia. These soils are typically leached, infertile, with poor nutrient content. Therefore, they meet the requirements for soils that would potentially benefit from biochar amendment. Biochar derived from palm oil empty fruit bunch produced at 350 °C by slow pyrolysis was chosen as the principal type of biochar as it is readily available on the Malaysian market. Lastly, sweet corn was selected as a test crop as it is widely cultivated in Malaysia.

1.2 Research Objectives

The fundamental aims of this research were to investigate the problematic soil acidity, mainly Al^{3+}, H^{+} and Mn^{2+} toxicities and their effects on maize growth in both laboratory and glasshouse study, and to alleviate these elemental toxicities by using empty fruit bunch-based biochar (EFB). Specifically, the objectives were:

1) To determine the effects of high aluminum concentration and low pH on early growth of maize root seedling and release of organic acid anions by the roots under these abiotic stress;

2) To study the effectiveness of EFB-based biochar on removing aluminum toxicity from aqueous solution using batch adsorption technique; and

3) To determine the potential of EFB-biochar and ground magnesium limestone to induce changes on selected chemical properties of Ultisols such as soil pH, exchangeable aluminum, manganese toxicity and cation exchange capacity as well as plant growth performance under maize cultivation.

1.3 Thesis Structure

The thesis is divided into six chapters with reference and appendices attached: general introduction, a review of the literature, three experimental research chapters, and general conclusion.

Chapter 1, Introduction, give a general overview of the whole thesis. It explains about Ultisol in the tropics, its chemical and mineralogical properties and why maize yield is low. It also elaborates previous ways to ameliorate soil infertility by using GML. EFB-based biochar a by-product of palm oil was discussed deeply in this chapter and proposed to apply in acid mineral soil as an alternative to GML. Following a review of the literature (Chapter 2) that describes the previous investigations carried out on the implications of biochar amendment in soil chemistry and crop growth. It also explains the widespread of acid soils in the world and factors caused the acid soils. The respective three objectives of this study that addressed the above were discussed in chapter 3, 4 and 5. Each individual experiment of chapter 3, 4 and 5 is organized with an abstract, introduction, materials and methods, results and discussion and conclusions.

Chapter 3 is based on the investigation of morphological approaches of aluminum and proton toxicities on early growth seedling of Mas Madu maize cultivar. In this chapter, it was aimed to investigate the negative impact of Al toxicity and low pH stress in maize root morphology and to observe how maize seedling can defend somewhat against this abiotic stress by way of secreting organic acid from their roots. Chapter 4 was also conducted under laboratory experiments and addresses the second objective of the study through an investigation of EFB-biochar on removing Al from the aqueous solution, because this thesis is concerned about alleviation of soil acidity and Al toxicity. Thus, it is essential to perform such this adsorption studies to see the capability of EFB-biochar on removal Al toxicity from its aqueous solution. Methodology, describes the experimental design for Al sorption onto EFB-biochar. The results and discussions, presents the experimental results and these results were discussed in light of the previous findings. Chapter 5 concerns greenhouse study using EFB-biochar with the presence and/or the absence of 2 t ground magnesium limestone ha^{-1} (2 t GML ha^{-1}) to improve the productivity of the Ultisol for maize production and to observe the ameliorating effects of biochar and/or GML application on soil solution chemical properties acidity and Al toxicity detoxification.

Lastly, chapter 6 gives brief conclusions and provides a comprehensive summary from the research. Recommendations and future research are also highlighted.

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