UNIVERSITI PUTRA MALAYSIA

ALLEVIATING SOIL ACIDITY, ALUMINIUM AND IRON TOXICITY IN AN ACID SULFATE SOIL USING LIME AND BIO- ORGANIC FERTILIZER TO INCREASE RICE YIELD

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By

ALIA FARHANA BINTI JAMALUDIN

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

September 2016

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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September 2016

Chairman : Prof. Shamshuddin Jusop, PhD
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Rice (*Oryza sativa*) is a staple food for over half of the world's population. The production of rice should be increased because growth in rice production has been slower than the population growth. With no room for area expansion, improving the fertility of marginal soils (such as acid sulfate soils) is one of the ways to increase rice production and maintain food security in Malaysia. Acid sulfate soils are known to contain pyrite (FeS_2) which upon oxidation results in the production of high amount of acidity (pH <3.5), aluminium (Al) and iron (Fe) which significantly affect rice growth. In order to increase the rice production, the infertility of acid sufate soils need to be alleviated first.

A laboratory experiment was conducted to investigate the effects of pH, Al and/or Fe on rice root morphology and explain how rice growing under such conditions can withstand the stresses. Two rice varieties, MR219 and MR 253 were grown under various pH (3, 4, 5, 6 and 7), Al and/or Fe stress (0, 20, 40, 60, 80 and 100 µM) conditions. After 14 days, rice root length and surface area were determined using a root scanner while the organic acids released by the roots of rice were determined by high performance liquid chromatography (HPLC). Results showed that the root length decreased with increasing Al and/or Fe concentration. On the contrary, the root length increased as the pH of the solution increased. This phenomenon was in part related to the exudation of oxalic, citric and malic acids by the rice roots. It was observed that the amount of organic acids released increased with increasing Al and/or Fe concentrations in the solution culture. It is believed that these organic acids were responsible for chelating some of the Al and/or Fe in the solution, rendering them unavailable for their uptake by rice. Organic acids were also secreted at very low solution pH. With this tolerant mechanism, the rice planted on acid sulfate soil can continue to produce yield but less than 3t/ha/season compared to the average national rice production, 4.7 t/ha/season (DOA Paddy Statistic, 2012).

Another study was conducted in a glasshouse to determine the effects of ground magnesium limestone in combination with bio-organic fertilizer application on the chemical properties of the soils and rice yield. Three rice seedlings were transplanted in pots which were previously amended with 0, 2, 4, 6 and 8 t/ha GML with or without bio-organic fertilizer. Rice varieties MR 219 and MR 253 were grown for two seasons in the same pots. Without applying the amendments, rice grown on the soils was affected severely by the high acidity, Fe and Al toxicity. Results showed that the critical pH for the two rice varieties was 6. The critical Al^{3+} activities for MR 219 and MR 253 were 4.23 µM and 5.53 µM, respectively. The infertility of acid sulfate soils in Malaysia can be ameliorated by applying 2 t GML/ha in combination with 0.25 t/ha of bio-organic fertilizer. At this rate of GML and bio-organic application, the soil pH increased to 5 and resulted in the concomitant reduction of Al^{3+} activity that would be translated into improved rice growth. The ameliorative effects of amendments had at least lasted for 2 seasons, indicating that this agronomic intervention is sustainable in the long run. The growth of rice was improved further by the presence of organic matter in the bio-organic fertilizer that inactivated Fe and/or Al present in the acidic water via chelation.

The third study was a field trial. The field experiment was conducted in Kemasin-Semerak, Kelantan to determine the effects of applying ground magnesium limestone (GML) with or without bio-organic fertilizer on the properties of an acid sulfate soils and rice yield. In this study, the soil was treated with GML and/or bio-organic fertilizer using Randomized Complete Block Design, with 4 replications. The pH of the untreated soil was 3.78, while the exchangeable Al and extractable Fe were 2.82 $cmol_c$/kg and 211.01 mg/kg, respectively. As a result, the grain yield of rice was only 2.12 t/ha because rice was significantly affected by Al and Fe toxicity as well as acidity. Al toxicity inhibits the root elongation, while Fe toxicity forms a coating area on the root surface. Both phenomena disrupted the plant from taking the available nutrients in the soil solution and eventually reduce the yield. This study showed that the infertility of acid sulfate soils in Malaysia can be ameliorated for sustainable rice production by applying 2 t GML/ha in combination with 0.25 t bio-organic fertilizer/ha. At this rate of applying the amendments, soil pH increased up to 5.25. At this pH, the Al and Fe started to form their inert hydroxides. The yield of rice was found to increase from 2.12 t/ha to 3.99 t/ha. The addition of bio-organic fertilizer supplied NPK and contained microbes that could fix N, which helped increase the rice growth and eventually its yield.

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

PENAMBAHBAIKAN KEASIDAN TANAH , KETOKSIKAN ALUMINIUM DAN FERUM DI DALAM TANAH ASID SULFAT DENGAN MENGGUNAKAN KAPUR DAN BAJA BIO-ORGANIK UNTUK MENINGKATKAN HASIL PENGELUARAN PADI.

Oleh

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Padi (Oryza sativa) merupakan makanan ruji bagi lebih separuh daripada penduduk dunia. Pengeluaran padi perlu ditingkatkan kerana kadar pertumbuhan dalam pengeluaran padi adalah lebih perlahan berbanding pertumbuhan penduduk. Disebabkan tiada ruang untuk meluaskan kawasan penanaman, meningkatkan kesuburan tanah bermasalah (seperti tanah asid sulfat) adalah salah satu cara terbaik untuk meningkatkan pengeluaran padi dan mengekalkan keselamatan makanan di Malaysia. Tanah asid sulfat yang diketahui mengandungi pyrite (FeS_2) yang sekiranya teroksida, ia akan menghasilkan kadar keasidan (pH <3.5), serta melepaskan aluminium (Al) dan ferum (Fe) yang tinggi dalam tanah, memberi kesan yang ketara kepada pertumbuhan padi. Dalam usaha untuk meningkatkan pengeluaran padi, ketidaksuburan tanah sulfat asid perlu diperbaiki dahulu.

Eksperimen makmal telah dijalankan untuk mengkaji kesan pH, Al dan / atau Fe pada morfologi akar padi serta menjelaskan bagaimana padi mampu bertahan di dalam larutan tanah yang bermasalah. Dua jenis varieti padi digunakan, MR219 dan MR 253, yang dicambah di dalam larutan yang pelbagai pH (3, 4, 5, 6 dan 7) serta pelbagai kepekatan Al dan/atau Fe (0, 20, 40, 60, 80 and 100 µM). Selepas 14 hari, panjang akar padi dan luas permukaannya ditentukan menggunakan *root scanner* manakala asid organik yang dikeluarkan oleh akar padi ditentukan oleh *High Performance Liquid Chromatography* (HPLC). Hasil kajian menunjukkan bahawa panjang akar menurun dengan peningkatan kepekatan Al dan/atau Fe di dalam larutan. Sebaliknya, panjang akar meningkat apabila pH larutan meningkat. Fenomena ini mungkin sebahagiannya berkaitan dengan rembesan asid oksalik, sitrik dan malic oleh akar padi. Keputusan kajian menunjukkan bahawa jumlah asid organik yang dirembes oleh akar padi meningkat dengan peningkatan kepekatan Al dan/atau Fe dalam larutan. Ini kerana asid organik bertanggungjawab mengikat sebahagian daripada Al dan/atau Fe di dalam larutan, menjadikan kedua unsur tersebut tidak tersedia untuk diserap oleh akar padi. Asid organik juga dirembeskan pada pH larutan yang sangat rendah. Dengan

mekanisme toleransi, padi yang ditanam di atas tanah asid sulfat boleh terus mengeluarkan hasil tetapi hanya kurang daripada 3 tan/ha/musim berbanding dengan purata pengeluaran padi negara, 4.7 tan/ha/musim

Satu kajian di dalam rumah kaca telah dijalankan untuk mengkaji kesan aplikasi *ground magnesium limestone* (GML) dengan atau tanpa baja bio-organik terhadap sifat-sifat kimia tanah dan hasil padi. Tiga biji benih padi dipindahkan di dalam pasu yang sebelum ini telah dicampur dengan 0, 2, 4, 6 dan 8 tan/ha GML dengan atau tanpa baja bio-organik. Padi varieti MR 219 dan MR 253 digunakan untuk eksperimen ini dan ditanam selama dua musim dalam pasu yang sama. Tanpa sebarang aplikasi GML dan baja bio-organik, tumbesaran padi yang ditanam di atas tanah asid sulfat terjejas teruk disebabkan oleh keasidan serta kepekatan Fe dan Al yang tinggi. Hasil kajian menunjukkan bahawa pH kritikal bagi kedua-dua jenis beras adalah 6. Manakala, paras aktiviti kritikal bagi Al^{3+} untuk MR 219 dan MR 253 masing-masing adalah 4.23 dan 5.53 mikromolar. Ketidaksuburan tanah asid sulfat di Malaysia boleh ditambahbaik dengan menggunakan 2 tan GML/ha dicampur dengan 0.25 t / ha baja bio-organik. Pada kadar aplikasi GML dan baja bio-organik ini, pH tanah meningkat kepada 5 dan mengakibatkan pengurangan aktiviti Al di dalam larutan tanah yang kemudian diterjemahkan kepada pertumbuhan padi yang baik. Kesan aplikasi GML dan baja bio-organik ini tahan sekurang-kurangnya selama 2 musim. Pertumbuhan padi dapat dipertingkatkan lagi dengan kehadiran bahan organik dalam baja bio-organik yang dapat mengikat Fe dan Al yang hadir di dalam air berasid.

Kajian ketiga ialah kajian lapangan. Percubaan lapangan dijalankan di sawah padi di Semerak-Kemasin, Kelantan untuk mengkaji kesan aplikasi GML dengan atau tanpa baja bio-organik di tanah asid sulfat untuk meningkatkan hasil padi. Dalam kajian ini, tanah telah dirawat dengan GML dengan atau tanpa baja bio-organik menggunakan susunan RCBD, dengan 4 ulangan. pH tanah yang tidak dirawat adalah 3.78, manakala kepekatan Al dan Fe masing-masing adalah 2.82 $cmol_c$/kg dan 211.01 mg/kg. Akibatnya, hasil padi yang diperolehi hanya 2.12 tan/ha kerana padi terjejas oleh ketoksikan Al dan Fe serta keasidan tanah. Ketoksikan Al menghalang pemanjangan akar manakala ketosikan Fe membentuk satu lapisan pada permukaan akar. Kedua-dua fenomena ini mengganggu akar tumbuhan daripada mengambil nutrien dalam larutan tanah dan menurunkan hasil padi. Kajian ini menunjukkan bahawa ketidaksuburan tanah asid sulfat di Malaysia boleh diperbaiki dengan menggunakan 2 t GML / ha dengan kombinasi 0.25 tan baja bio-organik/ha. Pada kadar aplikasi ini, pH tanah meningkat sehingga 5. Pada pH ini, Al dan Fe mula membentuk hidroksida. Hasil padi yang diperolehi meningkat dari 2.12 t/ha kepada 3.99 tan/ha. Aplikasi baja bio-organik bukan sahaja membekalkan NPK tetapi juga mengandungi mikrob yang boleh mengikat N dari udara dan dibekalkan kepada padi bagi memperbaiki pertumbuhan padi serta meningkatkan hasil

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ACKNOWLEDGEMENT

Praise to the Allah Almighty for His Blessings granting me the opportunity of doing PhD as well as giving me good health, strength and inspiration to progress and complete this thesis writing. My deepest gratitude goes to Prof. Dr. Shamshuddin Jusop for his guidance, sharing knowledge and constructive suggestions throughout the conduct of this project. I will always admire your kindness and punctuality in reviewing all my manuscripts during my PhD journey.

I would like to express sincere thanks and appreciation to my co-supervisors, Prof. Dr. Che Fauziah Ishak and Assoc. Prof. Dr. Ahmad Husni Mohd. Haniff for the suggestions and comments. Also to all the staffs Mr. Alias Ishak, Mrs. Rusnah Ajis, Mrs. Zarinah Basir and Mrs. Nurashikin Salha for their generous help and assistance throughout this project. Boundless thanks to all my seniors, Enio, Syuhada, Rosilawati, Malissa, Elisa, Shazana, who always support me theoretically, practically, physically and emotionally throughout my PhD journey. Not to forget my fellow friend, Kang Seong Hun who always gives great suggestion and comments especially in statistical part.

My deepest appreciation goes to the woman who I love the most, Haslina Hassan, for continuously supporting me unconditionally. Thank you to my dad and all my family members for their love and continuous encouragement for me to complete this task. To my beloved husband, Ahmad Fikri Mohd Samsudin, I owe him a debt of thanks for his patience, understanding and encouragement. He always gave me the reason to go on. Once again, I would like to thank all the generous people for being part of this project. I could not have finished this project and report writing without them.

I certify that a Thesis Examination Committee has met on 5 September 2016 to conduct the final examination of Alia Farhana binti Jamaludin on her thesis entitled "Alleviating Soil Acidity, Aluminium and Iron Toxicity in an Acid Sulfate Soil using Lime and Bio-Organic Fertilizer to Increase Rice Yield" 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 Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

AA	Auto-analyzer
ANOVA	Analysis of variance
CEC	Cation exchange capacity
CRD	Completely Randomized Design
RCBD	Randomized Complete Blocks Design
DOA	Department of Agriculture
EC	Electrical conductivity
GML	Ground Magnesium Limestone
HPLC	High Performance Liquid Chromatography
IADP	Integrated agricultural development project
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
MARDI	Malaysian Agricultural Research and Development Institute
NASA	National Aeronautics and Space Administration
SEM	Scanning electron microscope

CHAPTER 1

INTRODUCTION

Rice (*Oryza sativa*) is a staple food for over half of the world's population. Global demand for rice is increasing by the years as more than a billion people depend on rice cultivation for their survival. Understanding the significance of rice and its economic role, the production of rice should be increased sufficiently because of the fast increasing world population. For Malaysian, rice is the most crucial diet in their daily life. Due to this, rice industry often become main attention and seriously emphasized by the government. Currently, the self-sufficiency level for rice production in Malaysia is only 71.4% while the remaining is imported from Thailand and Vietnam (Siwar et al., 2014).

In 2007, Thailand encountered flood disaster where the rice production was significantly decreased and the rice price hike up to a maximum of 30% in Bangkok. Meanwhile in Vietnam there were rice riots reported in Ho Chi Minh city. Since then, Malaysian government has announced the need to increase the rice self-sufficiency level to reach 86%. Rice planted area in Malaysia is estimated to be 672,000 ha with the national average rice production of 4 t/ha/season. However, in the urbanization era, Malaysia has lost many of the productive rice land for housing and development. In order to maintain or increase the self-sufficiency level of rice production, improving the fertility of marginal soils (such as acid sulfate soils) is one of the ways to increase rice production.

Acid sulfate soils are characterized by the presence of pyrite which upon oxidation would result in high amount of acidity (with soil pH< 3.5 at depth), aluminum (Al) and iron (Fe) (Shamshuddin et al., 2004). These soils occur throughout the globe, but are found to be abundant in the tropical region, especially along the coastal plains of Southeast Asia, such as Malaysia, Thailand, Indonesia and Vietnam because the environment is suitable for pyrite formation (Shamshuddin et al., 2014). Generally, rice growing on the untreated acid sulphate soils yield poorly due Al^{3+}, Fe^{2+} or H^{+} stress (Enio et al., 2011). There is a big challenge in using acid sulfate soils because using farmers' practice, the yield of rice obtained is < 3 t/ha/season, way below the national average yield of 4.7 t/ha/season (DOA Paddy Statistic, 2012). Thus, degraded and infertile lands such as acid sulphate soils need to be ameliorated using appropriate amendments so that the productivity of the soils increased to the level suitable for rice cultivation.

In the monsoon season (November to January), Kelantan, which has soils containing pyrite are always under submerged condition due to flooding. This pyrite was formed when the Kelantan Plains were inundated with seawater some 6,000 BP when the sea level was 3-5m above the present level (Roslan et al., 2010; Enio et al., 2011). In 1984, Malaysian government has decided to set up a project called Kemasin-Semerak Integrated Agriculture Development Project which covers about 64,000 ha and provides drainage, irrigation and flood mitigation facilities to the farmers in Kelantan.

As time goes by, the harmless undisturbed pyrite in the area had been exposed to the atmosphere and oxidized. Once oxidized, a new mineral named jarosite [$KFe_3(SO_4)_2(OH)_6$], is eventually formed, appearing as yellowish mottles in the soil profiles (Shamshuddin et al., 2004).

Jarosite is a mineral indicator in the field which shows that pyrite is oxidizing, producing sulfuric acid, accompanied by the release of high amount of Al and Fe in the soil solution. When jarosite is observed within a soil profile, the soil pH is not only low (< 3.5), but also contain toxic amounts of Al and/or Fe (Shamshuddin, 2006). According to Shamshuddin et al. (2014), water in the paddy fields of acid sulfate soil areas in Peninsular Malaysia usually contained Al concentration of > 800 µM. The high acidity, Al and Fe concentrations can create a variety of adverse impacts on agriculture.

Acid sulfate soils can be alleviated by applying lime (Rosilawati et al., 2014), organic materials (Muhrizal et al., 2003) or bio-fertilizer (Panhwar et al., 2014a; Panhwar et al., 2014b). Liming appears to be the most common approach to raise soil pH, inactivate soluble Fe^{2+} and/or Al^{3+}, thereby reducing their toxicity. Besides increasing pH, GML can supply Ca and Mg which are needed for rice growth in large amount (Ting et al., 1993; Rosilawati et al., 2014). However, the growing on acid sulfate soils is not only affected by the high acidity as well as Al and/or Fe, but also by the lack of phosphorus, calcium and magnesium (Suswanto et al., 2007; Dent, 1986). Thus, by applying lime alone is not enough to ameliorate the infertility of acid sulfate soils. A bio-organic fertilizer so named as JITU^{TM} contains some N, P, K, Mg, Ca and Si with trace elements that can be used for the above purpose. Application of GML in combination with bio-organic fertilizer can produce up to 7.5 t/ha of rice (Suswanto et al., 2007).

Rice variety MR 253 has been recommended in marginal soils, such as peat or organic soils, as it outperforms MR 219, a high yielding but non-acid tolerant variety. So far no study has been conducted to test whether MR 253 is really acid tolerant or can be grown on acid sulfate soils without problem. It is therefore worthwhile to investigate further the use of lime in combination with bio-organic fertilizer to ameliorate the infertility of acid sulfate soils in Malaysia for rice cultivation. The specific objectives of the study were:

1. To explain how rice can detoxify Al and Fe toxicity;
2. To determine the effects of applying ground magnesium limestone (GML) with or without bio-organic fertilizer on the chemical properties of an acid sulfate soil; and
3. To determine the effects of applying GML with or without bio-organic fertilizer on the yield of rice, varieties MR 219 and MR 253.

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LIST OF PUBLICATIONS

Alia, F.J., Shamshuddin, J., Fauziah, C.I., Ahmad Husni, M.H., Panhwar, Q.A. (2015). Effects of Aluminum, iron and/or low pH on rice seedlings grown in solution culture. International Journal of Agricultural Biology, 17(4): 702-710.

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Root elongation, root surface area and root organic acid secretion of rice seedlings under Al^{3+}, Fe^{2+} and H^+ stress (Proceedings of Soils 2013, Kuantan).

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