



UNIVERSITI PUTRA MALAYSIA

**NITROGEN AND POTASSIUM EXCHANGE IN AN ACID TROPICAL
SOIL INCORPORATED WITH SYNTHETIC AND NATURAL ZEOLITES**

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By

ZUBAIDAH ILIAS

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
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Generally, soils in the tropics are highly weathered, acidic and low in fertility status. High precipitation and low soil cation exchange capacity (CEC) require large amounts of fertilization and liming to ameliorate and increase the potential of these soils. Leaching losses of NH_4^+ and K^+ are extremely large in tropical soils. Zeolites are natural clay silicates that have high affinity and ability to adsorb NH_4^+ and K^+ . They are able to release these ions gradually. A study was carried out in three parts. Experiment I was conducted to determine the chemical characteristics of natural and synthetic zeolites. The result of this study suggested that the materials used were zeolites and therefore can be used for further experiment. Experiment II was conducted to determine the adsorption characteristics of NH_4^+ and K^+ by the natural and synthetic zeolites. The result showed that treatment with synthetic Zeolite A (ZA), and natural zeolite (namely Clinop I, from Malang, Indonesia and Clinop II from Sweetwater County, Wyoming, USA) reduced leaching of K^+ and NH_4^+ . The zeolites treatments increased 2-3 times higher the CEC of the soils after 20 days of incubation. Natural zeolites treatments were



better than the synthetic zeolite in retaining exchangeable cation. Experiment III was conducted to evaluate the efficacy of NH_4^+ and K^+ retained in the soil using corn (var. Putra J-58) as a test crop planted for 56 days. The results showed there were significant differences between the zeolites treatment and the control for K and N concentration in the plant tissue. The application of K^+ and NH_4^+ saturated zeolites increased the soil CEC about 2-3 times higher. However, there was no significant difference in dry matter yield and root weight. This study showed that zeolite can be used as a soil amendment to overcome low CEC soils and leaching losses of NH_4^+ and K^+ on highly weathered soils.

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

**TUKARGANTI AMMONIUM DAN POTASIMUM BAGI TANAH TROPIKA
BERASID MENGGUNAKAN ZEOLIT SINTETIK DAN SEMULAJADI**

Oleh

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Pengerusi : Dr. Syed Omar Syed Rastan

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Kebanyakan tanah tropika mengalami luluhawa yang tinggi, berasid dan status kesuburan tanah yang rendah. Hujan yang tinggi dan kadar pertukaran kation (KPK) yang rendah memerlukan pembajaan dan pengapuran yang banyak bagi mengatasi dan meningkatkan potensi tanah ini. Larutlesap NH_4^+ dan K^+ adalah tinggi di kawasan tropika. Zeolit adalah sejenis mineral lempung yang mempunyai keupayaan untuk menjerap kation terutamanya NH_4^+ dan K^+ , dan membebaskannya dengan perlahan. Kajian terbahagi kepada tiga bahagian. Eksperimen I dilakukan untuk mengenalpasti zeolite sintetik dan semulajadi berdasarkan ciri-ciri kimianya. Keputusan mendapati bahawa bahan yang dikaji adalah zeolit dan boleh digunakan untuk kajian seterusnya. Eksperimen II dilakukan untuk membandingkan daya jerapan NH_4^+ dan K^+ oleh zeolite sintetik dan semulajadi. Keputusan menunjukkan rawatan dengan zeolit sintetik zeolit A (ZA), dan zeolit semulajadi (Clinop I dari Malang, Indonesia (Mlg) dan Clinop II dari Sweetwater County, Wyoming, USA) mengurangkan larutlesap K^+ dan NH_4^+ . Rawatan zeolit meningkatkan kadar KPK 2-3 lebih tinggi selepas 20 hari rawatan. Zeolit

semulajadi adalah lebih baik dari zeolite sintetik dalam memegang kation tukarganti. Eksperimen III dilakukan untuk menilai keberkesanan NH_4^+ dan K^+ pada pokok jagung (var Putra J-58) yang ditanam selama 56 hari. Keputusan mendapati bahawa terdapat perbezaan yang bermakna antara rawatan zeolit dan kawalan dari segi kepekatan K dan N dalam tisu daun. Penggunaan zeolit tepu K^+ dan NH_4^+ meningkatkan KPK sehingga 2-3 kali ganda. Walaubagaimanapun, tidak terdapat perbezaan yang bermakna pada berat kering pokok dan akar. Kajian ini mendapati bahawa Zeolit boleh digunapakai sebagai peminda tanah dalam mengatasi masalah KPK tanah, mengurangkan larutlesap NH_4^+ dan K^+ pada tanah terluluhawa.

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TABLES OF CONTENTS

	Page
ABSTRACT.....	2
ABSTRAK	4
ACKNOWLEDGEMENTS.....	6
APPROVAL SHEETS.....	7
DECLARATION FORM	9
TABLES OF CONTENTS	10
LIST OF TABLES	13
LIST OF FIGURES	14

CHAPTERS

1. INTRODUCTION	16
II LITERATURE REVIEW	19
Natural Zeolites	19
Crystalline Synthetic Zeolites	20
Early Observation	21
Classification and Nomenclature	21
Synthetic Zeolites	21
Zeolites A	22
Chemical and Physical Characteristic of Zeolite A	22
Mineral Zeolites	25
Clinoptilolites	25
Clinoptilolites In Agriculture	27
Zeolites In Controlling Leaching Losses	28
Acid Soils	30
Nitrogen Dilemma	31
Losses of Nitrogen	32
Potassium in Soil	34
III MINERALOGY AND CHEMICAL PROPERTIES OF NATURAL AND SYNTHETIC ZEOLITES	
Introduction	36
Materials and methods	36
Location of experimental site and treatments	36
Synthesis zeolite A	37
Natural zeolites	39
X-Ray Diffraction	39
Fourier Transform Infrared Spectroscopy Measurement	41
Nitrogen Adsorption Measurement	42



Determining of Cation Exchange Capacity of Zeolites	44
Results and Discussion	44
Initial Chemical Properties of Zeolites	44
CEC, pH and Exchangeable Cations of zeolites	45
The Infrared Spectrum of Zeolite A and Natural Zeolites.....	47
Zeolites A	47
Clinoptilolites	48
X-Ray Diffraction of zeolites	50
Nitrogen adsorption	53
Conclusion	54
IV THE EFFECTS OF NH₄⁺ AND K⁺ SATURATED ZEOLITES ON AN ACID SOILS	55
Introduction	55
Materials and methods	56
Method of saturating zeolites with NH ₄ and K	57
Treatments	58
Leachate collection	59
Analysis of NH ₄ , K and basic cation in the soils	60
Result and Discussion	60
The effect of K- and NH ₄ -saturated zeolites on the soils	60
The effect of zeolite application on soluble and exchangeable Ca, Mg and Na	66
The effect of zeolite incubation on soil acidity and CEC	70
Conclusion.....	72
V EVALUATION OF THE RESIDUAL EFFECTS OF NH₄⁺ AND K⁺ SATURATED ZEOLITES ON CORN GROWTH	
Introduction	73
Materials and methods	74
Experimental site, treatments and design	74
Experimental parameters	75
Extraction of exchangeable ammonium	76
Basic cations and cation exchange capacity	77
Soil pH	77
Nutrient tissue analysis	78
Results and Discussion	78
The effect of K saturated zeolite on plant tissue	78
The effect of NH ₄ - saturated zeolite on plant tissue	80
The effect of NH ₄ and K- saturated zeolite on soil pH and soil CEC	82
The effect of NH ₄ and K- saturated zeolite on plant and root dry matter yield	84
Conclusion	86

VI CONCLUSION AND SUGGESTION	87
BIBLIOGRAPHY	88
APPENDICES	
Appendix A – Raw material	98
Appendix B – Calculation	104
Appendix C	106
BIODATA OF THE AUTHOR	107



LIST OF TABLES

Tables		Page
1	The types of vibration FTIR spectroscopy measurement	42
2	The exchangeable chemical properties of zeolites and the bungor series soil	45
3	The strong peak of x-ray powder data for synthetic and natural zeolite	51
4	The surface area, total pore volume and average pore size of zeolite A and Clinoptilolites	53
5	The CEC of saturated zeolite of NH ₄ and K	59



LIST OF FIGURES

Figures	Page
1. The truncated octahedron (a) and (b) the array of truncated octahedron in the framework of zeolite A	24
2. A diagram of the section of zeolite A	24
3. Schematic diagram synthesis of zeolite A	38
4. The infrared spectrum for (a) Zeolite A	48
(b) Clinop I	49
(c) Clinop II	49
5. The x-ray diffractogram of sample used in the experiment: (a) Zeolite A	51
(b) Clinop I	52
(c) Clinop II	52
6. Photograph showing (A) zeolite A (B) Clinop I (C) Clinop II	56
7. A diagram of leaching column	57
8. Effect of zeolite application on soil leachate K at 5-days interval	61
9. Effect of zeolite application on soil exchangeable K after 20-days treatment	62
10. The change of soil leachate NH_4 with time of affected by zeolite application	65
11. Effect of zeolite application on soil exchangeable NH_4 after 20 days treatment	65
12. Effect of zeolite application on soil leachate Ca at 5-days interval	67
13. Effect of zeolite application on soil exchangeable Ca after 20 days treatment	67
14. Effect of zeolite application on soil leachate Mg at 5-days interval ...	68
15. Effect of zeolite application on soil exchangeable Mg after 20 days treatment	68

16.	Effect of zeolite application on soil leachate Na at 5-days interval ...	69
17.	Effect of zeolite application on soil exchangeable Na after 20 days treatment	69
18.	Effect of zeolite application on soil pH	70
19.	Effect of zeolite application on soil cation exchange capacity after 20-days treatments	71
20.	K concentration in plant tissue in soil treated with K- saturated zeolite and K fertilizer	79
21.	The soil exchangeable K at harvest	80
22.	The effect of treatment on NH ₄ concentration in the plant tissue	81
23.	The effect of treatment on exchangeable NH ₄	82
24.	The effect of treatment on pH	83
25.	The effect of treatment on CEC	84
26.	The effect of K-saturated zeolite on dry matter root (DMR) and dry matter yield (DMY)	85
27.	The effect of N-saturated zeolite on dry matter root (DMR) and dry matter yield (DMY)	85



CHAPTER 1

INTRODUCTION

Soils in the tropics are generally highly weathered and have low fertility status. In Peninsular Malaysia, more than two third of the total land area is covered by acid soils of which Ultisols and Oxisols are the most abundant (IBSRAM, 1985). Ultisols and Oxisols are soils with low pH, cation exchange capacity and basic cations contents (Tessen and Shamshuddin, 1983). Ninety three percent of tropical soils have problem of nitrogen (N) deficiency (Pushparajah, 1977). Generally, the level of N needed in the soil for plant growth is 0.20% (Sanchez et al., 1995), but the N level in most acid soils is below this value. Soils are acidic because of leaching of basic cations due to heavy precipitation, production of carbon dioxide from humus decomposition and root respiration and oxidation of ammonium fertilizers (Marschner, 1986). Below pH 5, aluminium (Al) becomes the main factor in controlling the soil solution pH (Sumner, 1995). In general, acid soil are limed with either calcitic or dolomitic limestone. Hue (1992) has shown that soil acidity can also be corrected with addition of organic residue.

Conventionally, organic matter are added to soil to help retain nutrients and water (Wallace, 1994). Nitrogen applied as NH_4^+ is retained on the surface of clay exchange site, however, when desorbed quickly is converted microbially to NO_3^- . Nitrate is subsequently subjected to leaching (Ferguson et al., 1986). Excessive NO_3^- production may lead to an environmental pollution, if not properly controlled (Gaines and Gaines, 1994). High precipitation is one of the major factors that intensifies this problem. If 2-5 cm of

precipitation per day is experienced within 10 days of fertilizer application, a large proportion (up to 50% or more) of the applied nitrogen and potassium is lost through leaching (Chew and Pushparajah, 1995). Since organic amendments decompose in the soil with time, their beneficial effects of retaining nutrients in soils is limited.

Leaching, denitrification and volatilization losses of N fertilizers are serious problems in agriculture (Perrin et al., 1998). One way of reducing these losses is to increase ammonium ion (NH_4^+) retention in soil by adding appropriate soil amendments. The retained NH_4^+ helps reduce nitrification and subsequently reduces leaching and denitrification of NO_3^- . Nitrogen leaching from agricultural land is a major contributor of nitrate (NO_3^-) contamination in surface and groundwater (Lichtenberg and Shapiro, 1997). Addition of organic matter such as peat has a retentive effect on leaching of $\text{NO}_3\text{-N}$, but is not sustainable in acid soils (Gaines and Gaines, 1994). One of the potential natural soil amendments that carries permanent negative charge that is sustainable in soil is zeolites (Weber et al., 1983).

Zeolites are natural clay-silicate mineral (tectosilicates) with a high degree of internal tunneling and cation exchange capacity. Zeolites are available as sand-size particles, with good drainage and water holding characteristics, and a cation exchange capacity of more than $200 \text{ cmol}_c \text{ kg}^{-1}$ (Ferguson et al., 1986). Thus, zeolites have desirable physical properties associated with sand and favorable chemical characteristics associated with clay. Zeolites have high affinities for NH_4^+ and K^+ (Breck, 1974; Southard and Kolesar, 1978), where the former is physically protected from nitrifying bacteria (Ferguson,

1984). MacKown and Tucker (1985) showed that clinoptilolite - zeolite effectively enhanced the retention of NH_4^+ and reduced the amount of NH_4^+ leached. This characteristic enables zeolites to be a potential soil amendment for retaining soil NH_4^+ and K from being leached.

This study was conducted to:

1. To determine the chemical characteristics of natural and synthetic zeolites.
2. To compare the exchange properties of natural and synthetic zeolites on NH_4^+ and K, and
3. To evaluate the residual effect of synthetic and natural zeolites on sweet corn.

CHAPTER II

REVIEW OF LITERATURE

Natural Zeolites

Natural zeolites are formed through geological processes. Zeolites are crystalline, hydrated aluminosilicates of cations that possess infinite, three-dimensional crystal structures with fully cross-linked open framework structures made up of corner-sharing SiO_4 and AlO_4 tetrahedra (Breck, 1974; Vaughan, 1978). Zeolites are able to hydrate reversibly and exchange some of their constituent cations (Ming and Mumpton, 1989), making them useful molecular sieves. Total world demand of natural zeolites is currently between 2.5 million tonnes per year and is growing rapidly. US demand for zeolites is forecast to reach 250,000 tonnes per year by 2000 and double again by 2005 (Silverstate zeolite, 2000).

The representative empirical formula of a zeolite is: $\text{M}_2/n\text{O}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_3\cdot y\text{H}_2\text{O}$, where M represents the exchangeable cation of valence n; M is generally in-group II ions or I although other metals, non-metals and organic cations may also balance the negative charge created by the presence of Al in the structure (Breck, 1974).

These unique zeolite crystals with a honeycomb-like structure of pores and channels are extremely small in size ranging from 2.5 to 5.0 Å (Breck, 1974; Shaw, 1994). The crystalline pores are so small, only one gram of material has an equivalent surface area of 40



m² (Shaw, 1994). The surface area make zeolites highly effective ion exchangers (Breck, 1974; Mumpton, 1984). Because the ions are bound loosely to the crystal, they can be replaced by other ions that enter the structure. This ion exchange property of zeolites coupled with unique properties of their porous structure accounts for the interesting and potentially important usefulness of zeolites in agriculture (Parham, 1989).

Furthermore, when zeolites come into contact with certain liquids and gases, they both absorb and adsorb, release or collect moisture of certain gases and ions (Ming and Mumpton, 1989). Zeolites are able to adsorb 4.3 times of their dry weight in gases such as ammonium ions (Weber et al., 1983), over 70% in water and up to 90% of certain hydrocarbons (Shaw, 1994). Zeolites are also able to exchange cations which are positively charged (Flanigan, 1984; Ming and Mumpton, 1989).

Crystalline Synthetic Zeolites

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium and barium. Structurally, the zeolites are framework aluminosilicates which are based on extended three-dimensional network of AlO₄ and SiO₄ tetrahedral linked to each other by sharing of the oxygen (Breck, 1971).

The framework contains channel and interconnected voids, which are occupied by the cations and water molecules. The cations are quite mobile and may usually be exchanged by other cations. In many other zeolites, natural and synthetic, cation exchange or dehydration may produce structural changes in the framework. Many of the zeolites, after dehydration, are permeated by very small channel which are not interpenetrating and which causes serious diffusion blocks (Suwardi, 1994).

Early observation

Zeolites were first recognized and identified by Freiherr Axel Fredrick Cronstedt, a swedish mineralogist in 1756 (Breck, 1971) as a new group of mineral consisting of hydrated aluminosilicates of the alkali and alkaline earth. He called the mineral zeolite, which comes from two Greek words 'zein' and 'lithos' meaning "boiling stones" because they would "froth" when heated to high temperatures.

Classification And Nomenclature

Synthetic Zeolites

The characterization and identification of complex, synthetic aluminosilicates such as the zeolites, is hindered by the absence of a definitive system of chemical nomenclature. Different investigators have employed various systems of naming the synthetic zeolites, and synthetic aluminosilicates. These systems include: (1) assigning to the synthetic species the name of mineral relative and on a similarity in crystal structure by x-ray powder pattern; (2) assigning to the synthetic zeolite species a code or letter designation (Breck, 1971).

However, chemical composition and physical properties include stability, dehydration behavior, cation exchange behavior and adsorption behavior also are characteristics of zeolites.

There are more than 45 natural and 150 produced synthesized-zeolites. The 45 natural zeolites are based on their chemical composition, structure and related physical properties (Sand and Mumpton, 1978). Only eight zeolites are important in agriculture and industry for their high cation exchange capacity. Mordenite and clinoptilolite are the most important for agriculture (Fredrickson, 1985). They contain no clay and no salt making them safe to use in heavy clay soils and around salt-sensitive plants (Shaw, 1994).

Zeolite A

Local annual production of rice leaves behind about 2.4 million tonnes of husk as a waste product which is usually disposed off by burning. One of the possible commercial uses of rice husk that contains 96 – 99% SiO₂ is in synthesis of zeolite A (Hamdan et al., 1994; Ramli, 1995). The large amount of silica, freely obtained from the rice husk, provides abundant and cheap alternative of silica for many industrial uses, including the synthesis of zeolites. The reactivity of silica depends on the method of preparation and extraction from the rice husk (Hamdan and An Keat, 1993; Hamdan et al., 1993; Jusoh, 1997).

At present, zeolite A is mainly used in the manufacturing of detergent (Breck, 1974; Izumi and Tadahisa, 1986). In 1987, 375,000 tonnes of zeolite A was produced for

detergent industry. It is expected to increase to 1 million tonnes by 1999. Current data on the uses of zeolites in agricultural as cation exchanger and adsorbent properties are still limited.

Chemical and Physical Properties of Zeolite A

The aluminosilicate framework of zeolite A consists of two types of polyhedral D4R and the truncated octahedron of 24 tetrahedral and β -cage with double 4 rings (Figure 1). The unit cell of zeolite A contains 24 tetrahedral 12 AlO_4 and 12 SiO_4 . When fully hydrated, there are 27 water molecules. The chemical formula is $\text{Na}_{12}\{(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}\} \cdot 27\text{H}_2\text{O}$. The electrostatics valence rule modified by Loewenstien, requires vigorous alternation of the AlO_4 and SiO_4 tetrahedral, with a Si/Al ratio of 1:1 (Breck, 1974) and not forming Al-O-Al bonds. The center of the unit cell is a large cavity with a free diameter of 11.4 Å (α -cages) and (β -cages) 6.6 Å. The shaded circle represents Al and Na^+ in site 1. There are two interconnecting, 3 dimensional channel systems, one consisting of connected (α -cages) (Breck, 1971; Ramli, 1996)(Figure 2).

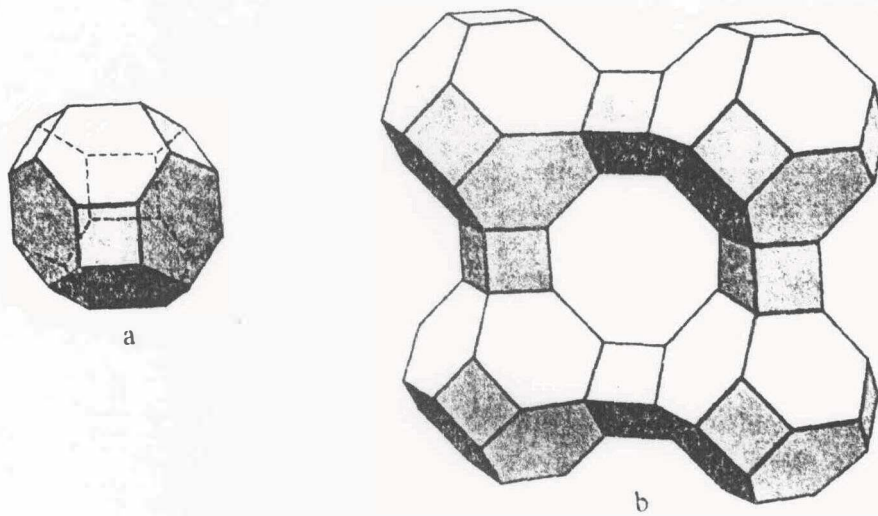


Figure 1: The truncated octahedron (a) and (b) the array of truncated octahedra in the framework of zeolite A (Breck, 1974)

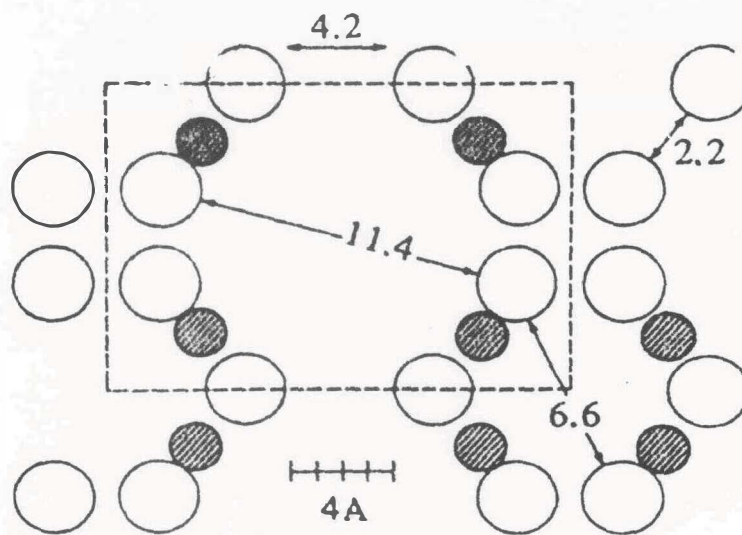


Figure 2: A diagram of the section of zeolite A (Breck, 1974)