Ammonium and Potassium Exchange in Acid Tropical Soil Treated with Zeolites

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ABSTRACT
High precipitation and low soil cation exchange capacity (CEC) of highly weathered acidic tropical soils require large amounts and many rounds of fertilization to increase the potential of these soils from leaching losses of soil ammonium (NH$_4^+$) and potassium (K$^+$). This study was conducted to evaluate the exchange properties of natural and synthetic zeolites on soil NH$_4^+$ and K$^+$. A Bungor Series soil (Typic Pahudults) was taken from a depth of 0 to 5 cm for this leaching experiment. Each soil treatment was added either with equal amounts of NH$_4^+$ or K$^+$ and treated with and without zeolites. The treated soil was then leached with deionised water for 20 days and the soil leachate was collected at 5-day interval, to analyze for NH$_4^+$ and K$^+$ concentration. The results of this study showed that all types of zeolites were able to reduce substantial leaching losses of soil NH$_4^+$ and K$^+$. The natural zeolites were better than the synthetic zeolites in retaining these cations. The study has demonstrated that zeolites could be used as an effective soil amendment to reduce leaching losses of soil NH$_4^+$ and K$^+$ in acid tropical soils with low CEC.

Keywords: zeolites, clinoptilolite, acid soil, ammonium, potassium

INTRODUCTION
Soils in the tropics are generally highly weathered and have low fertility status. In Peninsular Malaysia, more than two-thirds of the total land area are covered by acid soils of which Ultisols and Oxisols are the most abundant (IBSARAM 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 problems of nitrogen (N) deficiency (Pushparajah 1977).

Conventionally, organic matter is added to soil to help retain nutrients due to their high CEC (Wallace 1994). Nitrogen applied as NH$_4^+$ is retained on the surface of the clay exchange site. However, when desorbed quickly, it is converted microbially to NO$_3^-$. Nitrate is subsequently subjected to leaching (Ferguson et al. 1986). Excessive NO$_3^-$ production may lead to 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 in 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 NO$_3^-$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 CEC of more than 200 cmol, 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). MacKnown and Tucker (1985) showed that clinoptilolite (a zeolite variety) 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. The study was conducted to evaluate the exchange properties of natural and synthetic zeolites on NH$_4^+$ and K$^+$ in acid tropical soils.

**MATERIALS AND METHODS**

*The Soils*

Bungor Series soil (Typic Paleudults) was selected for the leaching experiment. The soil was sampled in the field at a depth of 0-15 cm (topsoil). It was then air-dried, ground and sieved through a 2.00-mm mesh and carefully repacked into a leaching column. The leaching tube was made of glass of 4-cm diameter and 15.5-cm length (*Fig. 1*). Ninety gram of the soil was mixed with 30 g of acid washed sand (AWS) to allow for easier water infiltration in the leaching
tube. Soil leachate was collected at 5-day intervals to determine NH$_4^+$ and K$^+$ ions.

Method of Saturating Zeolites with NH$_4^+$ and K$^+$

The synthetic and natural zeolite samples were weighed (15 g) and placed into 100 mL centrifuge tubes. The samples were washed five times with 1 M chloride solution (pH 7) (NH$_4$Cl for NH$_4$-saturated zeolite) or KCl (for K$^+$-saturated zeolite) and centrifuged at 10,000 rpm for 15 minutes. The samples were then washed five times with distilled water, 95% ethanol and acetone to remove excess chloride. The samples were dialysed with AgNO$_3$ to remove excess interstitial salts. The saturated samples were then oven-dried at 45°C for 24 hours (Ming et al. 1991). Later, the samples were tested for cation exchange capacity.

![Diagram](image)

*Fig. 1: A diagrammatic representation of the leaching column*

Treatments

The soil in the leaching tube was amended with four treatments and each treatment was replicated 3 times in a completely randomized design. The treatments are given in Table 1. Three types of zeolites were used in this study: the synthetic zeolite from rice husk (zeolite A); the natural zeolite from Malang, Indonesia (Clinop I); and natural zeolite from Sweetwater Country, Wyoming, U.S.A. (Clinop II).

The treatments were incorporated either with NH$_4^+$ or K$^+$ saturated zeolites to the amount of 10% based on the weight of soil mixed. The amount of exchangeable K in Zeolite A, Clinop I and Clinop II were 148 cmol$_c$.kg$^{-1}$, 132 cmol$_c$.kg$^{-1}$ and 165 cmol$_c$.kg$^{-1}$, respectively. The amount of exchangeable NH$_4^+$ in saturated-Zeolite A, Clinop I and Clinop II were 144 cmol$_c$.kg$^{-1}$, 125 cmol$_c$.kg$^{-1}$
TABLE 1
Potassium and ammonium saturated zeolites

a. K-saturated zeolites

<table>
<thead>
<tr>
<th>Labels</th>
<th>Soil Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Bungor soil (90 g) + 12 g K-saturated (zeolite A) + AWS* (30 g)</td>
</tr>
<tr>
<td>Clinop I</td>
<td>Bungor soil (90 g) + 12 g K-saturated (Clinop I) + AWS* (30 g)</td>
</tr>
<tr>
<td>Clinop II</td>
<td>Bungor soil (90 g) + 12 g K-saturated (Clinop II) + AWS* (30 g) + 1.852 g KCl (rate equivalent of K in Clinop II)</td>
</tr>
<tr>
<td>Control</td>
<td>Bungor soil (90 g) + 1.852 g KCl (rate equivalent of K in Clinop II) + AWS* (30 g)</td>
</tr>
</tbody>
</table>

b. NH₄⁺-saturated zeolites

<table>
<thead>
<tr>
<th>Labels</th>
<th>Soil Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Bungor soil (90 g) + 12 g NH₄⁺-saturated (zeolite A) + AWS* (30 g)</td>
</tr>
<tr>
<td>Clinop I</td>
<td>Bungor soil (90 g) + 12 g NH₄⁺-saturated (Clinop I) + AWS* (30 g)</td>
</tr>
<tr>
<td>Clinop II</td>
<td>Bungor soil (90 g) + 12 g NH₄⁺-saturated (Clinop II) + AWS* (30 g) + 1.33 g NH₄Cl (rate equivalent of N in Clinop II)</td>
</tr>
<tr>
<td>Control</td>
<td>Bungor soil (90 g) + 1.33 g NH₄Cl (rate equivalent of N in Clinop II) + AWS* (30 g)</td>
</tr>
</tbody>
</table>

* AWS: acid wash sand

TABLE 2
Cation exchange capacity of saturated zeolites of NH₄ and K

<table>
<thead>
<tr>
<th>Type of Zeolites</th>
<th>CEC (Saturated zeolite)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₄⁺ (cmol, kg⁻¹)</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>144</td>
</tr>
<tr>
<td>Clinop I</td>
<td>125</td>
</tr>
<tr>
<td>Clinop II</td>
<td>156</td>
</tr>
</tbody>
</table>
and 156 cmol·kg⁻¹, respectively (Table 2). However, the amount of exchangeable NH₄⁺ was lower than exchangeable K due to selectivity of cation in zeolites.

**Leachate Collection**

The treated soil columns were then watered daily. Distilled water was used at a rate of 30 mL per pore volume. The total pore volume used was three times or equal to 90 mL of water. The excess water was leached through the outlet at the bottom of the leaching column. The total volume of soil leachate was collected and subsequently measured using a measuring cylinder at 5-day intervals. The average leachate volume was 90-100 mL, depending on the soil treatment. Clinop II leached the highest amount of leachate and zeolite A the lowest. The concentration NH₄⁺ and K⁺ in the leachate was then analyzed once at 5-day intervals.

**Analyses of NH₄⁺, K⁺**

After 20 days of incubation, the soils were collected for chemical analysis. Half of the total soil samples in the measuring cylinder was taken, air-dried, ground and then passed through a 2.0-mm sieve. The sample was then analyzed for available N (extracted with 2 M KCl, then distilled) (Keeney and Nelson 1982), K (extracted with 1 M NH₄OAc), pH_water (1:2.5), and CEC (Ming et al. 1991) using 0.2M CsCl.

**RESULTS AND DISCUSSION**

**The Effect of NH₄⁺ and K⁺ Saturated Zeolites on the Soils**

The concentration of K in the leachate decreased in the soil sample treated with zeolites throughout the incubation period (20 days). In the control (K applied was equivalent to the amount of K in zeolite saturated-K), large amounts of added K (5152 μg mL⁻¹) were lost during the first day of leaching. This was followed by K-saturated zeolite A, K-saturated Clinop I and K-saturated Clinop II (Fig. 2). The loss of K in the treatments with natural zeolites was relatively small.

The quantities of K in the control were low after 5 days of incubation. This was probably due to the large amounts of K lost during the first day of leaching. Therefore, only limited K was available in the control. K-saturated Zeolite A leached high amounts of K on the first day (2000 μg mL⁻¹) with the amount gradually decreased until 10 days of incubation. The quantities of K leached after the 5-day intervals were about constant for both the natural zeolites. The trend of K leaching in natural zeolite samples was different
from those of the control and Zeolite-A (Synthetic Zeolite). The amount of K leached in the natural zeolites was relatively slow and decreased with time.

The result of K leached was related to the amount of K retained in the soil after the experimental period (Fig. 3). The result showed that the natural zeolites especially Clinop II retained the highest amount of K (8883.7 µg Kg\textsuperscript{-1}) and Clinop I (4976.7 µg Kg\textsuperscript{-1}). However, the available K in the control treatment soil was only 142.3 µg Kg\textsuperscript{-1} about 1.6% of the exchangeable K of the Clinop II treatment. Allen \textit{et al.} (1993) and Allen \textit{et al.} (1995a) reported similar results.

A similar trend was also shown for the leaching of NH\textsubscript{4}\textsuperscript{+} (Fig. 4). However, the amount of NH\textsubscript{4}\textsuperscript{+} in the soil leachate was three times higher than the amount of K leachate in the control during the first day. This was true as NH\textsubscript{4}\textsuperscript{+} was relatively more mobile compared to K in soil (Gardiner and Miller 1998). The highest leaching rate of NH\textsubscript{4}\textsuperscript{+} was shown in the control, followed
by Zeolite A, Clinop I, and Clinop II which were 15840 µg mL⁻¹, 280 µg mL⁻¹, 192µg mL⁻¹ and 180µg mL⁻¹, respectively on the first day of leaching. Ammonium is not released from the zeolite until it is exchanged by another cation. After the exchange, each NH₄⁺ has to diffuse from interior channels to the surface of the zeolite before it is available for leaching. As a result, less NH₄⁺ was leached from soil amended with zeolite than the control (Perrin et al. 1998). The small amount of NH₄⁺ leached from zeolite was due to diffusion and exchange of cation in irrigation water and soluble salt (Semmen 1984; Allen et al. 1995a,b; Perrin et al. 1998) which limited its availability for the nitrifying bacteria (Semmen et al. 1977; Mackown 1978).

High leaching of NH₄⁺ in the control was probably due to: high NH₄⁺ applied, resulting in rapid dissolution; and low soil CEC in soil, which was 5.9 cmol c kg⁻¹, and hence adsorbed small amount of added NH₄⁺. The leaching trend differed among treatments where the rate of leaching for the NH₄⁺-saturated Clinop II was the highest and the control was the lowest. These results demonstrate that the amount of NH₄⁺ in the control was almost completely leached on the first day of incubation. The amount of NH₄⁺ released by Clinop II and Clinop I gradually leached over the 20 days of incubation. A large amount of NH₄⁺ was retained in the soils incorporated with Clinop II, Clinop I and Zeolite A- NH₄⁺ (Fig. 5). The results showed that exchangeable NH₄⁺ in Clinop II, Clinop I and Zeolite A were 7, 4.5 and 3 times higher than in the control after the 20 days incubation period. Both types of natural zeolites were effective, but Clinop II was superior in retaining soil exchangeable NH₄⁺. The high amount of NH₄⁺ retained by zeolite was probably due to its high affinity for NH₄⁺. Clinoptilolite-zeolite has a high ability to hold NH₄⁺ ions internally, where they are physically protected from
nitrifying bacteria that can convert $\text{NH}_4^+$ to $\text{NO}_3^-$ (Ferguson 1984; Ferguson et al. 1986).

This study demonstrated that zeolites were able to retain high amounts of $\text{NH}_4^+$ and K$^+$ up to 20 days of leaching under simulated heavy rain conditions (2000 mm yr$^{-1}$). Many researchers had reported the ability of zeolites to retain $\text{NH}_4^+$, to release $\text{NH}_4^+$ and to inhibit nitrification (MacKown and Tucker 1985; Barbarick et al. 1988; Perrin et al. 1998; Papadopoulus et al. 1996). K-saturated zeolites or naturally occurring K-zeolites probably could be used in areas which are K-deficient (Barbarick et al. 1988). However, because the size of the K$^+$ is similar to that of $\text{NH}_4^+$ ion, the two ions ought to compete with each other for the surface exchange sites (Bohn et al. 1985).

**The Effect of Zeolites on Soil Acidity and CEC**

The soil pH increased with the application of zeolite A after the 20-day incubation period. However, the natural zeolite treatments did not show
any significant change in soil pH from the control (Fig. 6).

The pH increase in zeolite A treatment was two times higher than that of the control or the natural zeolite. This could have been a result of the high buffering capacity of synthetic zeolite A. In a separate experiment, it was shown that the synthetic zeolite A needed higher amounts of 0.1 M HCl to change the pH (220 mL) than Clinop I, and Clinop II were 24 mL, and 46 mL, respectively. Soil amended with zeolite A increased the soil pH to 9 compared to other treatments with a pH value of below 5. In fact, liming to pH near neutrality may cause adverse effects on soil chemical properties such as an increase in phosphate fixation (Naidu et al. 1990) and other nutritional imbalance due to low soil CEC (Kamprath 1971; Pierre and Browning 1935).

Soil CEC increased with zeolite application after the 20-day incubation period. (Fig. 7). There was no significant difference between the synthetic and natural zeolites. However, a significant difference in soil CEC was observed between all zeolite treatments and the control. After 20 days of incubation, the soil CEC of the Clinop II, Clinop I and synthetic zeolite-A treated soils were 3.5, 3 and 2 times higher than the control, respectively. Addition of natural zeolites is a practical solution to increasing soil CEC which was relatively more stable compared to incorporating soil with organic matter, as the former was more resistant towards decomposition chemical weathering.

CONCLUSION
Zeolites were able to reduce leaching losses of soil NH₄⁺ and K⁺ by increasing the soil CEC and slowly releasing the nutrients as needed by the plant. The natural zeolites were better than the synthetic zeolites in retaining these cations.
The study has demonstrated that zeolites could be used as an effective soil amendments to reduce leaching losses of soil NH$_4^+$ and K$^+$ in acid tropical soils having of low CEC.

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