



# Enhancing nitrogen availability from urea using clinoptilolite zeolite



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## ABSTRACT

The high costs of nitrogen fertilizers have necessitated best-developed practices to optimize nitrogen fertilizers use whilst minimizing nitrate losses. Ammonium adsorption inhibits loss of nitrogen in the form of nitrate thereby increasing nitrogen availability for crops. Due to the negatively charged properties of nitrate, it moves freely in the soil solution and not adsorbed onto soil particle surfaces. In this study, clinoptilolite zeolite was used in soil leaching and ammonium adsorption and desorption studies to determine: (i) soil total nitrogen availability, exchangeable ammonium, and available nitrate, and (ii) the capacity of clinoptilolite zeolite to adsorb and desorb ammonium from different rates of urea. Different rates of urea amended with clinoptilolite zeolite significantly reduced ammonium and nitrate release from urea compared with urea alone. Clinoptilolite zeolite enhanced retention of soil total nitrogen, exchangeable ammonium, and available nitrate due to the high cation exchange capacity of the mineral to adsorb ammonium, thus, improving nitrogen availability through temporary retention on the exchange sites of the clinoptilolite zeolite. The availability of nitrogen can be enhanced if urea is amended with clinoptilolite zeolite.

## 1. Introduction

Plant available nitrogen (N) is positively influenced by N fertilization, mineralization of soil organic matter, and biological N fixation whereas nitrate ( $\text{NO}_3^-$ ) leaching, immobilization, crop uptake and removal, denitrification, volatilization, soil run-off, and erosion have negative effects on N availability (Hofman and Van Cleemput, 2004). The relative importance of these processes depends on soil pH, topsoil texture, aeration, water supply and temperature, type, amount, placement and timing of N fertilizers, available carbon, crop residue management, tillage, soil compaction, and irrigation (Di and Cameron, 2002). The increased cost of N fertilizers and concerns about the adverse environmental impacts of N losses had prompted great interest in fine-tuning N fertilizer management. The need for the efficient management of N fertilizers is to match application source, rate, timing, and method to supply on-farm sources of N (e.g. chemical fertilizers or organic amendments) to meet crop requirement.

Ammonium ( $\text{NH}_4^+$ ) adsorption is the process by which  $\text{NH}_4^+$  is attached to the negative charged surfaces of mineral such as clinoptilolite zeolite (Daković et al., 2007). Ammonium adsorption is a beneficial process that improves N availability because the  $\text{NH}_4^+$  remain available to crops besides being protected from losses due to

leaching, runoff, and volatilization (Hatfield and Prueger, 2004). Desorption is the opposite of adsorption and it occurs when adsorbed nutrients are released from the surfaces of for example, soil organic matter or inorganic minerals such as clinoptilolite zeolite (Ashman and Puri, 2002).

Because of the size of  $\text{NH}_4^+$ , it is able to penetrate the internal spaces that lie between individual 2:1 clay minerals in minerals such as vermiculite, illite, and some forms of montmorillonite. Once held within the clay structure,  $\text{NH}_4^+$  becomes available to crops. Both 2:1 and 1:1 clay minerals are made up of layers of silica and aluminium hydroxide. The silica layer consists of a series of silicon and oxygen atoms, in the ratio of 1:4, forming small pyramid-shaped structures known as silica tetrahedral (Ashman and Puri, 2002). In contrast to  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  is a negatively-charged anion, thus it is repelled by negatively charged soil colloids. Nitrate salts are highly soluble, move with soil water, and easily leached through soils (Brady and Weil, 2010). Leaching of  $\text{NO}_3^-$  represents a loss of crop available N from soils. According to Di and Cameron (2002), the two fundamental factors which determine the amount of  $\text{NO}_3^-$  leached from soils to groundwater are the amounts required by crop uptake and drainage volume. High  $\text{NO}_3^-$  leaching loss occurs when there is high amount of  $\text{NO}_3^-$  in soils' profile in conjunction with or followed by a high drainage volume

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(Di and Cameron, 2002).

Inhibiting the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  could minimize N loss. However, it is not possible to completely prevent the movement of some  $\text{NO}_3^-$  to water supplies, but good management practices can keep losses within acceptable limits (Lamb et al., 2014). Highly weathered soils have low N holding capacities because most or all of the minerals with significant negative charges are lost through weathering. Due to low N retention capacity and high permeability of these soils, heavy rainfall causes rapid  $\text{NO}_3^-$  leaching from N fertilizers (Renck and Lehmann, 2004). The use of clinoptilolite zeolite in agriculture has shown that both soil and plant can benefit from clinoptilolite zeolite additions (Ahmed et al., 2009; Latifah et al., 2017) because of the high ion-exchange and large adsorptive affinity of this mineral for water and  $\text{NH}_4^+$  (Polat et al., 2004).

Zeolites are a group of highly crystalline hydrated aluminosilicates minerals, which when dehydrated, develop a porous structure with minimum pore diameters of between 0.3 and 1 nm. All zeolites are considered molecular sieve materials that can selectively absorb molecules based on their sizes (Peres-Caballero et al., 2008). This characteristic enables zeolite to retain cations such as  $\text{NH}_4^+$  (Inglezakis et al., 2002). Gradual desorption of adsorbed  $\text{NH}_4^+$  on the surface zeolites ensures slow-release N fertilizers for optimum plant uptake (Gruener et al., 2003; McGilloway et al., 2003; Rehakova et al., 2004).

For  $\text{NH}_4^+$  removal from water and wastes, ion exchange using zeolites was reported to be the most effective and low-cost material (Sprynsky, 2009). Ammonium ions are removed from aqueous solutions using zeolites by exchanging with cations or by adsorption in pores of aluminosilicate groups. Based on this rationale, it was hypothesized that the use of clinoptilolite zeolite could enhance N availability through  $\text{NH}_4^+$  retention following application of urea. In this study, an attempt was made to optimize the use of urea by reducing urea by 25% and 50% of the standard recommended urea for *Zea mays* L. To this end, soil leaching and  $\text{NH}_4^+$  adsorption and desorption studies were carried out to determine the: (i) availability of soil total N, exchangeable  $\text{NH}_4^+$ , and available  $\text{NO}_3^-$ , and (ii) capacity of clinoptilolite zeolite to adsorb and desorb  $\text{NH}_4^+$  from different rates of urea.

## 2. Material and methods

### 2.1. Characterization of soil selected physical and chemical properties

The soil used in this study was Ultisols, *Typic Paleudults* (Bekenu Series). This soil is fine loamy, siliceous, isohyperthermic, red-yellow to yellow. It has an argillic horizon with fine sandy clay loam textures. The structure is generally weak medium to coarse sub angular blocky. It is friable in nature (Paramanathan, 2000). It was collected at 0–20 cm depth from an uncultivated area at Universiti Putra Malaysia Bintulu Campus Sarawak, Malaysia. The soil was air dried and ground to pass a 2 mm sieve for initial characterization. Soil texture and bulk density were determined using the method described by Tan (2005). Soil CEC was determined using the leaching method (Tan, 2005) followed by steam distillation (Bremner, 1965).

Soil pH was determined in a ratio of 1:2 (soil: distilled water suspension) using a pH meter. Total C, N, and organic matter of the soil were determined using Leco CHNS Analyzer (LECO Truspec Micro Elemental Analyzer CHNS, New York). The method of Keeney and Nelson (1982) was used to extract exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$  after which their contents were determined using steam distillation. Soil available P was extracted using the double acid method (Tan, 2005) followed by the molybdenum blue method (Murphy and Riley, 1962). Exchangeable cations were extracted using the leaching method (Tan, 2005) after which their contents were determined using Atomic Absorption Spectrophotometry (Analyst 800, Perkin Elmer, Norwalk, USA). The texture of the soil was sandy loam with a bulk density of  $1.51 \text{ g cm}^{-3}$ . These physical properties are consistent with

**Table 1**

Selected chemical properties of Bekenu Series. S.E. is standard error. Standard data range reported by Paramanathan (2000). CEC is cation exchange capacity. nd is not determined.

Property	Value obtained	Standard data range
	Mean $\pm$ S.E	
CEC ( $\text{cmol}_c \text{ kg}^{-1}$ )	$7.43 \pm 0.15$	8.0–24
pH <sub>water</sub>	$4.66 \pm 0.10$	4.6
Exchangeable calcium ( $\text{cmol}_c \text{ kg}^{-1}$ )	$1.41 \pm 0.05$	0.01
Exchangeable magnesium ( $\text{cmol}_c \text{ kg}^{-1}$ )	$1.53 \pm 0.05$	0.21
Exchangeable potassium ( $\text{cmol}_c \text{ kg}^{-1}$ )	$0.60 \pm 0.02$	0.19
Total nitrogen (%)	$0.15 \pm 0.01$	0.04–0.17
Organic matter (%)	$2.06 \pm 0.10$	nd
Total carbon (%)	$1.20 \pm 0.60$	0.57–2.51
Available phosphorus ( $\text{mg kg}^{-1}$ )	$4.16 \pm 0.13$	nd
Exchangeable ammonium ( $\text{mg kg}^{-1}$ )	$19.85 \pm 0.68$	nd
Available nitrate ( $\text{mg kg}^{-1}$ )	$5.16 \pm 0.09$	nd

those reported in Soil Survey Staff (2014). The selected chemical properties of the soil are summarized in Table 1. The soil pH, total N, and total C are also consistent with those reported by Paramanathan (2000) for Bekenu series whereas exchangeable Ca, Mg, and K are higher than the reported values of Paramanathan (2000).

### 2.2. Chemical properties of clinoptilolite zeolite

The clinoptilolite zeolite used in this study was in powder form (sieved to pass 250  $\mu\text{m}$ ). Total N of the clinoptilolite zeolite was determined using Kjeldahl method (Bremner, 1965). The exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$  of the clinoptilolite zeolite were determined using the method described by Keeney and Nelson (1982). The pH of the clinoptilolite zeolite was determined in a ratio of 1:2 (clinoptilolite zeolite:distilled water suspension) using a pH meter. The CEC of the clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). This method was used to avoid underestimation of the CEC of the clinoptilolite zeolite as the CsCl method does not lead to entrapment of  $\text{NH}_4^+$  in the channels of the clinoptilolite zeolite. The exchangeable K, Ca, and Mg of the clinoptilolite zeolite were extracted using the method of Ming and Dixon (1986). Thereafter, contents were determined using Atomic Absorption Spectrophotometry (Analyst 800, Perkin Elmer, Norwalk, USA).

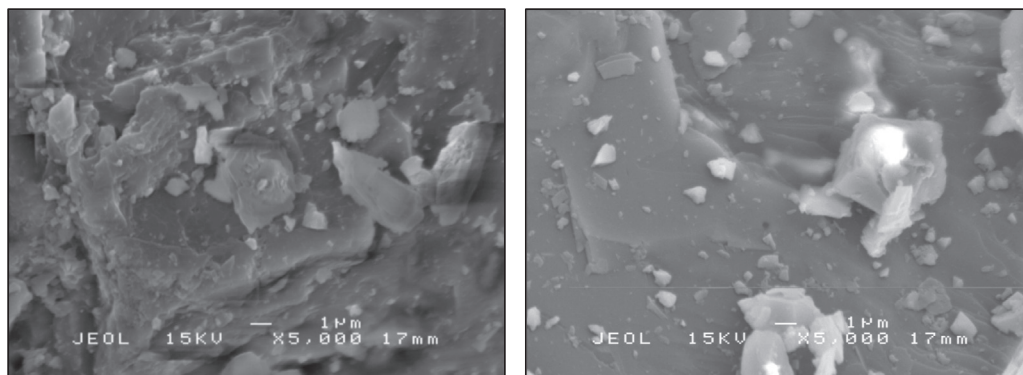
The chemical properties of the clinoptilolite zeolite used in this study are summarized in Table 2. The CEC of the clinoptilolite zeolite was lower ( $100 \text{ cmol}_c \text{ kg}^{-1}$ ) than the value obtained from the supplier of clinoptilolite zeolite ( $160 \text{ cmol}_c \text{ kg}^{-1}$ ), however the value obtained in this study is within the standard range (Table 2). Ming and Dixon (1986) reported a range of clinoptilolite zeolite CEC as  $100\text{--}300 \text{ cmol}_c \text{ kg}^{-1}$ . This range depends on the amount of  $\text{Al}^{3+}$  that replaces  $\text{Si}^{4+}$  in the clinoptilolite zeolite structure (Ming and Dixon, 1986). The pH, total N, Ca, Mg, and K of the clinoptilolite zeolite were lower than those obtained from the supplier of this mineral (Table 2).

**Table 2**

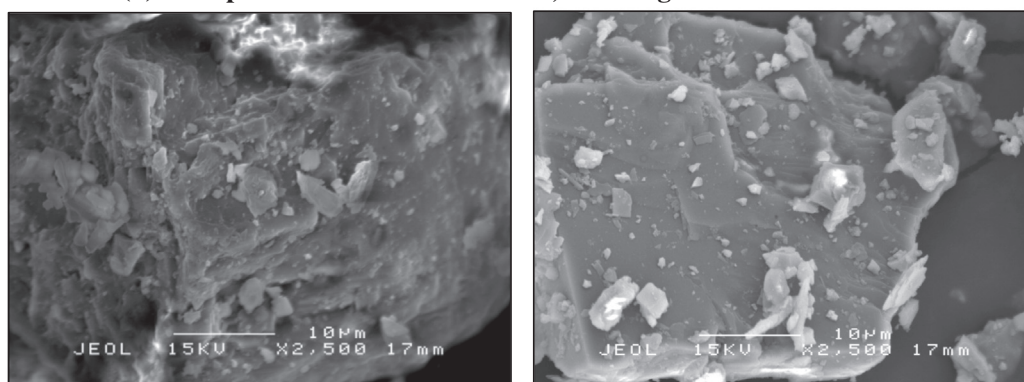
Selected chemical properties of clinoptilolite zeolite. S.E. is standard error. Data were obtained from Luxurious Empire Sdn. Bhd. Kulai Jaya, Malaysia.

Property	Present study (Mean $\pm$ S.E.)	Reference
pH	$6.80 \pm 0.03$	8–9
CEC ( $\text{cmol}_c \text{ kg}^{-1}$ )	$100 \pm 0.35$	160
Total nitrogen (%)	$1.18 \pm 0.04$	1.36
Calcium ( $\text{mg kg}^{-1}$ )	$18,400 \pm 19.09$	25,600
Magnesium ( $\text{mg kg}^{-1}$ )	$11,200 \pm 4.48$	15,000
Potassium ( $\text{mg kg}^{-1}$ )	$14,850 \pm 10.17$	22,600
Sodium ( $\text{mg kg}^{-1}$ )	$17,184 \pm 5.43$	17,600
Ammonium ( $\text{mg kg}^{-1}$ )	$12.60 \pm 0.43$	nd
Nitrate ( $\text{mg kg}^{-1}$ )	$11.58 \pm 0.18$	nd

### a) Clinoptilolite zeolite surfaces at 5,000x magnification under SEM



### (b) Clinoptilolite zeolite surfaces at 2,500x magnification under SEM



### c) Clinoptilolite zeolite surfaces at 1,000x magnification under SEM

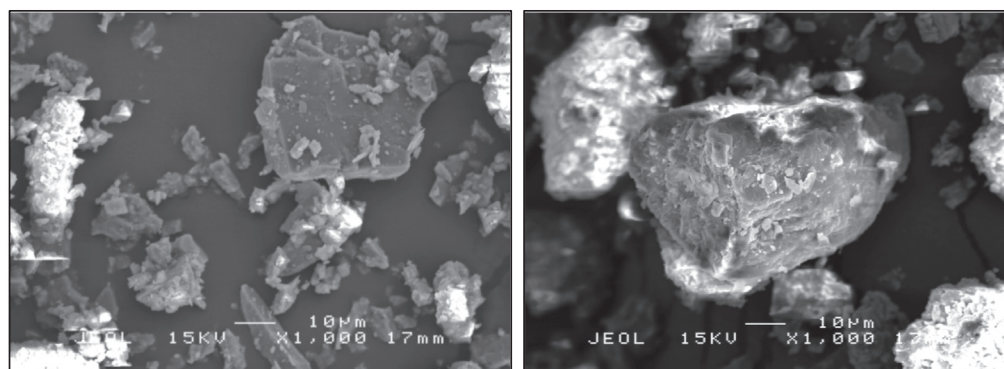


Fig. 1. Surface morphology of clinoptilolite zeolite using Scanning Electron Microscopy.

Microanalysis through Scanning Electron Microscopy-attached with Energy Dispersive X-ray Spectroscopy analysis (SEM-EDX JEOL JSM-6400) was carried out to analyze surface morphology and elemental composition of clinoptilolite zeolite.

#### 2.3. Soil leaching experiment

Leaching experiment was carried out for 30 days in the Soil Science Laboratory of Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia. The treatments evaluated in this experiment were:

- (i) Soil only (T0)
- (ii) Soil + 130 kg ha<sup>-1</sup> urea without additives (U1)

- (iii) Soil + 130 kg ha<sup>-1</sup> urea + 0.192 kg ha<sup>-1</sup> clinoptilolite zeolite (U1Z)
- (iv) Soil + 97.5 kg ha<sup>-1</sup> urea + 0.192 kg ha<sup>-1</sup> clinoptilolite zeolite (U2Z)
- (v) Soil + 65 kg ha<sup>-1</sup> urea + 0.192 kg ha<sup>-1</sup> clinoptilolite zeolite (U3Z)

The rates of urea (MARDI, 1993) and clinoptilolite zeolite (Najafinezhad et al., 2014) used were based on the standard fertilizer recommendation for *Zea mays* L. cultivation. The N requirements of the test crop are 60 kg N (130 kg ha<sup>-1</sup> urea). Urea was applied based on per plant requirement which was 7.40 g. The amounts of urea applied in U2Z and U3Z were reduced by 25% and 50%, respectively of the



standard recommendation (U1). The mixture was then filled in leaching tubes and leached with distilled water and thereafter, the leachates were collected at three days interval based on a five year rainfall data obtained from the [Sarawak Meteorological Department, Malaysia \(2013\)](#). Afterwards, the leachates were analyzed for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  using the method of [Keeney and Nelson \(1982\)](#) whereas the pH of the leachates were determined using a digital pH meter (Seven Easy Mettler Toledo). The volume of the distilled water used was based on rainy days over 30 days. The volume of the distilled water used every three days in the leaching experiment was 32 mL. The soil samples at 30 days of the leaching experiment were analyzed for total N, exchangeable  $\text{NH}_4^+$ , and available  $\text{NO}_3^-$  using standard procedures ([Bremner, 1965](#); [Keeney and Nelson, 1982](#)).

#### 2.4. Ammonium adsorption and desorption study

The effects of clinoptilolite zeolite on  $\text{NH}_4^+$  adsorption and desorption from the different rates of urea were conducted in different concentrations of  $\text{NH}_4\text{Cl}$ -NaCl isonormal solution. A 4 g of each treatment was weighed and added with 40 mL of isonormal  $\text{NH}_4\text{Cl}$ -NaCl solution (0, 18, 180, 450, and 900  $\text{mg kg}^{-1}$  of  $\text{NH}_4\text{-N}$ ). These solutions were used to maintain a constant ionic strength in the mixture ([Bernal and Lopez-Real, 1993](#)). The mixture was shaken for 17 h on an orbital shaker at 150 revolutions per minute (rpm). At 17 h of equilibration, the mixture was centrifuged at 16211 RCF (relative centrifugal force) (i.e., 10,000 rpm) for 15 min, and the supernatant solution was analyzed for  $\text{NH}_4^+$  using steam distillation ([Stevenson, 1996](#)). The amounts of  $\text{NH}_4^+$  adsorbed were determined by the difference between amount of the  $\text{NH}_4^+$  initially added and those remaining in the supernatant solutions. Ammonium adsorbed in the solution was fitted to Langmuir equation ([Ünlü and Ersoz, 2006](#)):

$$x = abC/(1 + aC)$$

where:  $x$  is the total amount of  $\text{NH}_4^+$  adsorbed ( $\text{mg kg}^{-1}$ )

$a$  is the constant related to the binding strength ( $\text{mg kg}^{-1}$ )

$b$  is a sorption maximum  $C$  is the  $\text{NH}_4^+$  concentration remaining in solution after the 17 h equilibrium ( $\text{mg kg}^{-1}$ )

The remaining supernatant solutions were washed thoroughly with 20 mL of ethanol followed by 20 mL of distilled water. The samples were further extracted with 40 mL of 2 M KCl by agitating the samples for 17 h followed by centrifugation at 16211 RCF for 15 min. The supernatant was analyzed for desorbed  $\text{NH}_4^+$  using steam distillation ([Stevenson, 1996](#)).

#### 2.5. Experimental design and statistical analysis

The experimental design of the soil leaching experiment was completely randomized design (CRD) with three replications. Analysis of variance (ANOVA) was used to detect treatment effects whereas Tukey's test was used to compare treatment means at  $P \leq 0.05$ . The Statistical Analysis System version 9.2 was used for the statistical tests.

### 3. Results and discussion

#### 3.1. Surface morphology and elemental composition of clinoptilolite zeolite

Surface morphological characteristics of the clinoptilolite zeolite showed crystals with well-defined shapes. The particle size of the clinoptilolite zeolite ranged between 1 and 10  $\mu\text{m}$ , magnified at 5,000 $\times$ , 2,500 $\times$ , and 1,000 $\times$  magnifications ([Fig. 1](#)). The well-defined shapes and particle sizes of the clinoptilolite zeolite were confirmed with elemental composition microanalysis which is indicated by marked points (spectra) or sharp peaks ([Fig. 2](#)). According to [Shoumkova and Stoyanova \(2013\)](#), well-defined shaped crystals with sharp peaks indicate good crystallinity. The peaks suggest the presence of amorphous particles that might be consistent with some silicate

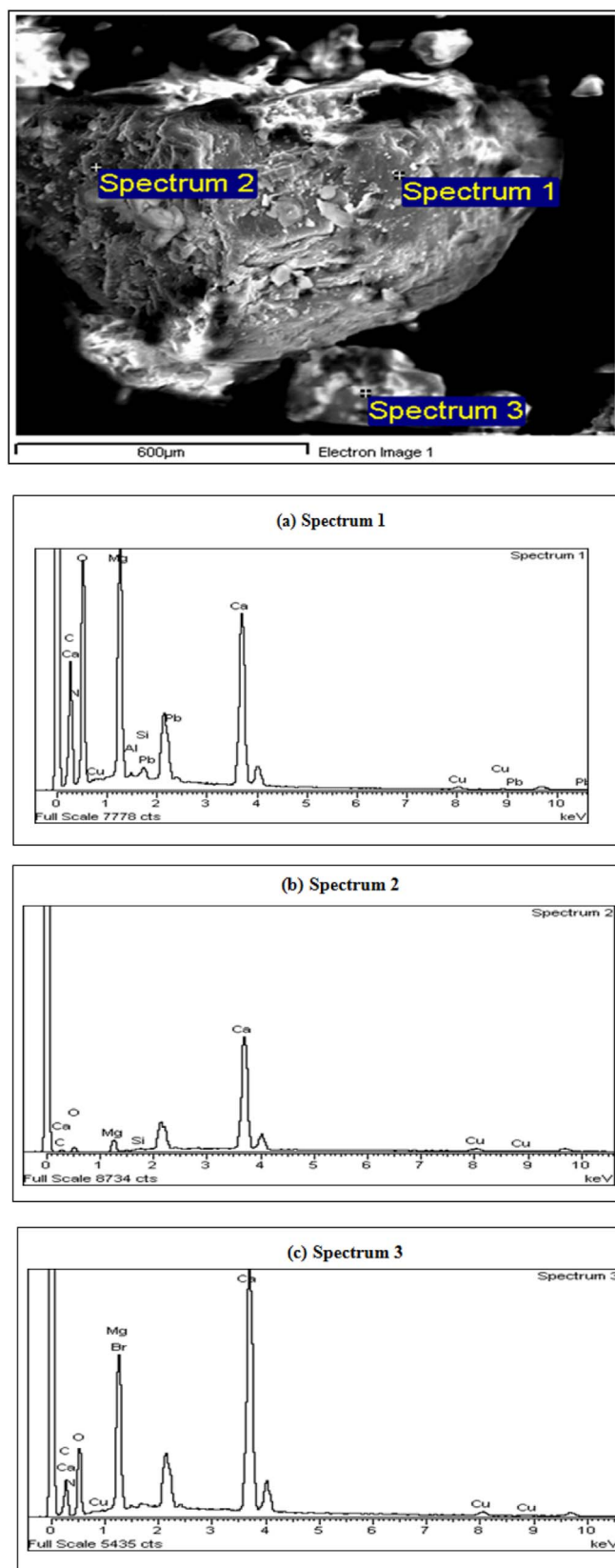


Fig. 2. Spectra of clinoptilolite zeolite under Energy Dispersive X-ray Spectroscopy (EDXS).

crystals ([Shoumkova and Stoyanova, 2013](#)).

As given in the microanalysis using Energy Dispersive X-ray Spectroscopy (EDX-S), the clinoptilolite zeolite is made up of O, Al, Fe,

**Table 3**

Elemental composition of clinoptilolite zeolite analyzed using Energy-dispersive X-ray spectroscopy. All elements were analyzed on dry weight basis.

Elements/dry weight (%)											
Spectrum	C	N	O	Mg	Al	Si	Ca	Cu	Br	Pb	Total
Spectrum 1	27.26	0.43	49.96	10.79	0.18	0.44	9.80	0.74	–	0.39	100
Spectrum 2	5.40	–	22.92	6.39	–	0.71	58.97	5.61	–	–	100
Spectrum 3	16.55	1.51	39.37	14.06	–	–	25.59	2.22	0.69	–	100

Si, Ca, Mg, K, and Na (Table 3). The relative intensity of Si was larger than that of Al and this is important for isomorphous substitution, a process by which Si is replaced by Al to define the negative charges of the clinoptilolite zeolite framework (Wingenfelder et al., 2005). The negative charges of the clinoptilolite zeolite framework are important for  $\text{NH}_4^+$  adsorption. This is demonstrated by the fact that  $\text{NH}_4^+$  adsorption begins to predominate with increased  $\text{NH}_4^+$  content in solution and abundant negative charges of zeolites for  $\text{NH}_4^+$  (Kithome et al., 1998; Jorgensen and Weatherley, 2008).

Cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  which are present in clinoptilolite zeolite (Tables 2 and 3) enable exchange sites of the clinoptilolite zeolite to attract  $\text{NH}_4^+$  and other metal cations, depending on the pH value of the solution and their concentrations (Torma et al., 2014). Calcium and Mg ions of the clinoptilolite zeolite are important cation exchangers because the cation exchange of clinoptilolite zeolite prevails when  $\text{NH}_4^+$  contents are equal or lower than the exchangeable cations contents of the clinoptilolite zeolite (Jorgensen and Weatherley, 2008).

### 3.2. Leaching of ammonium and nitrate

The mixtures amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) significantly reduced leaching of  $\text{NH}_4^+$  from urea compared with soil alone (T0) and urea alone (U1) because the clinoptilolite zeolite has high surface area for  $\text{NH}_4^+$  adsorption (Fig. 3). The lower amounts of  $\text{NO}_3^-$  leached from the treatment without clinoptilolite zeolite (U1) could be due to loss of  $\text{NH}_4^+$  (Fig. 4). The lower leaching of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the treatments amended with clinoptilolite zeolite (Figs. 3 and 4) was consistent with those of Zwingmann et al. (2009) as they also reported reduction in N leaching losses in column experiment with clinoptilolite zeolite.

The  $\text{NH}_4^+$  retention in the treatments amended with clinoptilolite zeolite was possible because of the specific selectivity of clinoptilolite zeolite for  $\text{NH}_4^+$  (Ferguson and Pepper, 1987). Because of this property, clinoptilolite zeolite has been widely used as adsorbent agent to temporary sorb  $\text{NH}_4^+$  (Kithome et al., 1998; Polat et al., 2004; Torma

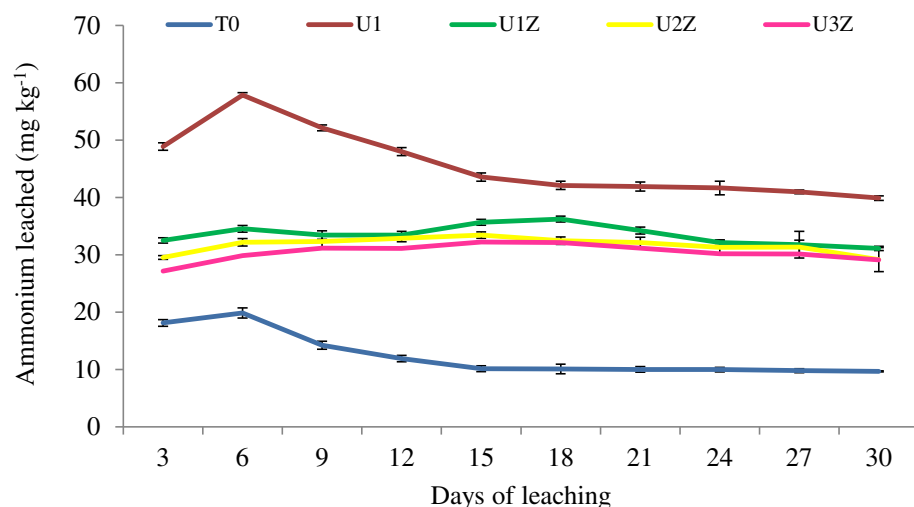
et al., 2014). Zaman et al. (2008) demonstrated the effectiveness of zeolites to remove a high amount of  $\text{NH}_4^+$  from solutions via ion exchange mediated by high permanent negative charge density and the inner channels zeolites for ion diffusion.

### 3.3. pH of leachate

The pH of the leachate of urea alone (U1) was lower than those of the different rates of urea amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) (Fig. 5). The dissolved  $\text{NH}_3$  associated with urea without clinoptilolite zeolite (U1) might have lowered the soil pH because  $\text{NH}_3$  is highly water soluble and as it hydrolyzes to form  $\text{NH}_4^+$  ions,  $\text{H}^+$  ions are consumed to raise soil pH to 9 or higher (Walworth, 2013). However, this effect was temporary as the final pH of the soil with urea alone was lower because of the acidification caused by nitrification of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  (Walworth, 2013).

### 3.4. Soil exchangeable ammonium, available nitrate, and total nitrogen

At 30 days of leaching, the different rates of urea amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) showed higher contents of soil exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$  (Table 4) compared with the treatment urea without additives (U1) because most of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in U1 were leached (Figs. 3 and 4). These findings suggest that clinoptilolite zeolite regulated the release of  $\text{NH}_4^+$  activity following the application of urea, thus limiting the intensity of nitrification in the soil. The regulation of soil exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$  in the treatments with clinoptilolite zeolite was because the channels in clinoptilolite zeolite effectively controlled the equilibrium between the clinoptilolite zeolite,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ . The high affinity and selectivity of the clinoptilolite zeolite for  $\text{NH}_4^+$  in particular, was due to the protection of  $\text{NH}_4^+$  by this mineral from excessive leaching (Ferguson and Pepper, 1987). This is evident in the surface morphology of the clinoptilolite zeolite (Figs. 1 and 2). As reported by Liu et al. (2003), clinoptilolite zeolite has the capacity to hold up to 20–30% of its weight in  $\text{NO}_3^-$ , thus, minimizing leaching of  $\text{NO}_3^-$ . This observation is

**Fig. 3.** Ammonium leached at three-day interval over thirty days of leaching study.

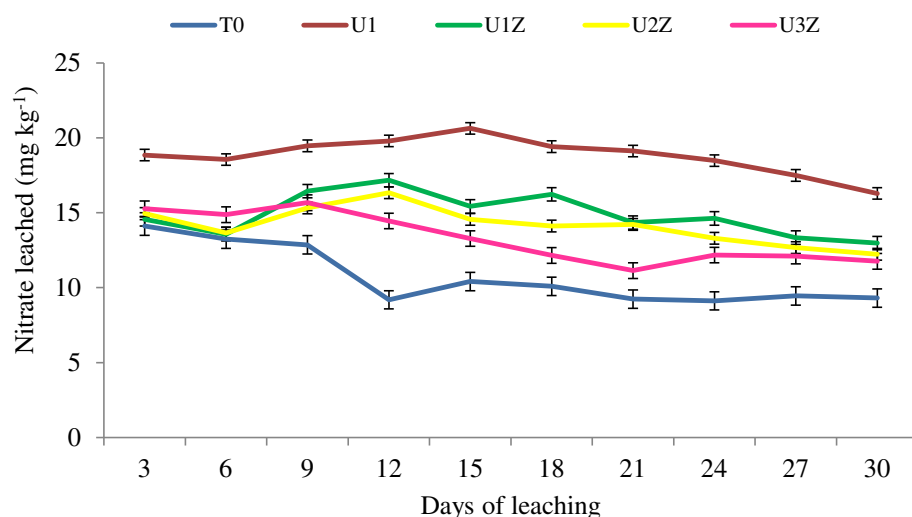


Fig. 4. Nitrate leached at three-day interval over thirty days of leaching study.

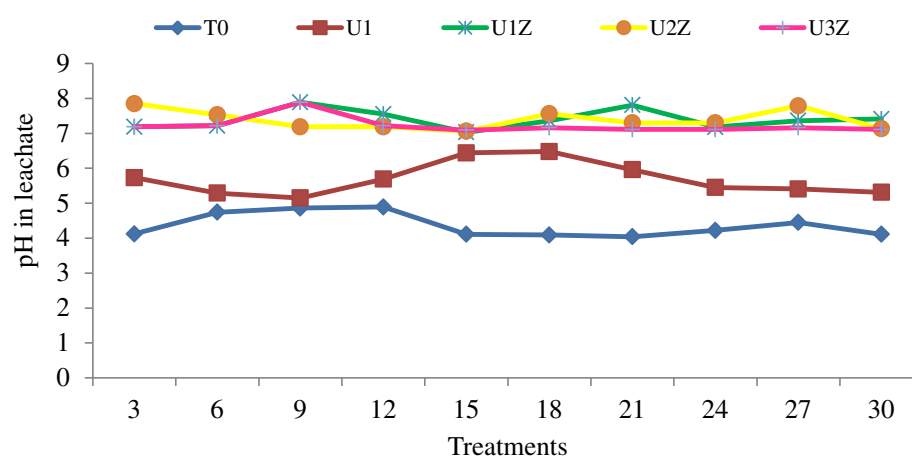


Fig. 5. pH of leachate at three-day interval over thirty days of leaching study.

Table 4

Retention of soil exchangeable ammonium, available nitrate, and total nitrogen after thirty days of leaching study. Means with same letter are not significantly different by Tukey's test at  $P \leq 0.05$ . S.E. is standard error.

Treatments	Ammonium	Nitrate $\text{mg kg}^{-1}$	Nitrogen
T0	$4.61 \pm 0.45$	$3.11 \pm 0.09$	$1233 \pm 5.66$
U1	$16.44 \pm 0.77$	$12.44 \pm 0.15$	$3519 \pm 7.88$
U1Z	$28.99 \pm 0.51$	$16.33 \pm 0.22$	$6544 \pm 9.80$
U2Z	$29.35 \pm 0.65$	$15.35 \pm 0.11$	$5566 \pm 10.45$
U3Z	$21.47 \pm 0.33$	$14.33 \pm 0.55$	$4533 \pm 9.80$

comparable to the findings of Mackdown and Tucker (1985) who also used clinoptilolite zeolite to minimize the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ .

The higher soil total N of the treatments with urea amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) in comparison to urea without clinoptilolite zeolite (U1) ensured slow release of urea-N (Table 4). The lower retention of soil total N in U1 (urea only) compared with urea amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) confirmed the loss of N through leaching. Although soil as a whole does not have electric charge, the negative charges of clay particles of soils are balanced by the positive charges of the cations of soils. Thus, the negative charges associated with clinoptilolite zeolite might have partly contributed to the retention of  $\text{NH}_4^+$ .

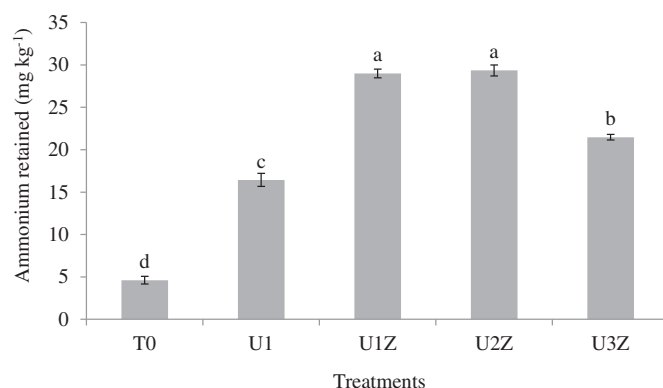


Fig. 6. Effect of treatments on the amount of ammonium adsorption under different initial concentration of isonormal solution ( $\text{NH}_4\text{Cl-NaCl}$ ).

### 3.5. Ammonium adsorption, Langmuir sorption isotherm, and ammonium desorption

The higher CEC of the clinoptilolite zeolite (Table 2) enabled higher sorption of  $\text{NH}_4^+$  in U1Z, U2Z, and U3Z compared with U1 (Fig. 6). The sorption of  $\text{NH}_4^+$  represented by “x” (total amount of  $\text{NH}_4^+$  adsorbed) in each treatment and equilibrium solution concentrations (C) were analyzed using Langmuir isotherm equation ( $R^2 > 0.82$ ) (Table 5). The higher adsorption of  $\text{NH}_4^+$  in U1Z, U2Z, and U3Z compared with U1 could be due to the aluminosilicate framework of clinoptilolite zeolite as it has high CEC, ion adsorption, and  $\text{NH}_4^+$  selective

**Table 5**

Soil pH, Langmuir parameter values, and estimates for ammonium adsorption coefficients. *a* is binding strength; *b* is a sorption maximum.

Treatments	pH	<i>a</i> (mg kg <sup>-1</sup> )	<i>b</i> (mg kg <sup>-1</sup> )	R <sup>2</sup>
T0	5.28	0.010	5.20	0.91
U1	5.56	0.030	5.70	0.97
U1Z	6.26	0.009	29.80	0.82
U2Z	6.18	0.008	22.12	0.82
U3Z	6.11	0.002	18.50	0.90

properties (Kithome et al., 1998). The highest sorption rate of  $\text{NH}_4^+$  of U1Z is related to the higher concentration of  $\text{NH}_4^+$  (Fig. 6 and Table 5). According to Franus and Wdowin (2010), increase in sorption rate of  $\text{NH}_4^+$  by clinoptilolite zeolite relates to increasing concentration of  $\text{NH}_4^+$  in solution. Cooney et al. (1999) also found that column  $\text{NH}_4^+$  removal (adsorption of  $\text{NH}_4^+$  by clinoptilolite zeolite) depends on the initial  $\text{NH}_4^+$  concentration in solution. With  $\text{NH}_4^+$  concentrations of 200 and 1000 mg  $\text{NH}_4^+$ -N L<sup>-1</sup>, Singh and Prasad (1997) reported adsorption of clinoptilolite zeolite as 15 and 31.08 mg  $\text{NH}_4^+$  g L<sup>-1</sup>, respectively.

The retention of  $\text{NH}_4^+$  using clinoptilolite zeolite was achieved through ion exchange and adsorption. At lower concentration of  $\text{NH}_4^+$ -N in solution, ion exchange dominates whereas, at higher concentration of  $\text{NH}_4^+$ -N, adsorption of  $\text{NH}_4^+$  is dominant (Liu et al., 2003). One of the important properties of clinoptilolite zeolite is its high CEC for both  $\text{NH}_4^+$  adsorption and ion exchange (Kenderilik et al., 2005). The numerous negative charges of the exchange groups of clinoptilolite zeolite are responsible for the adsorptive capacity of this mineral. The sorption ability of clinoptilolite zeolite is associated with the random dispersion of this mineral in aqueous solution. With  $\text{NH}_4^+$  as the exchanging cation, the overall mass transport is divided into processes such as diffusion of  $\text{NH}_4^+$  through solution to clinoptilolite zeolite particles or the diffusion of  $\text{NH}_4^+$  through clinoptilolite zeolite particles, a process which is accompanied by anion in solution. Other mechanisms such as chemical exchange between  $\text{NH}_4^+$  and exchangeable cations at exchange site in the interior of zeolites mineral are common (Kithome et al., 1998).

The kinetics of the cation exchange is governed either by diffusion or mass action mechanism, depending on which of the diffusion and cation exchange is the slowest (Kithome et al., 1999). According to Demir et al. (2002), only ionized form (cationic form) is removed by the ion-exchange process. Jorgensen and Weatherley (2008) demonstrated the adsorption of  $\text{NH}_4^+$  ions from aqueous solutions by clinoptilolite zeolite via exchange with cations or by adsorption in pores of alumina silicate systems. It was also reported that ion exchange prevails when the concentration of  $\text{NH}_4^+$  is equal or lower than the concentration of exchangeable cations of the clinoptilolite zeolite. After this process, adsorption dominates with increasing  $\text{NH}_4^+$  content (Jorgensen and Weatherley, 2008). The equilibrium-exchange capacity remains constant up to pH 7. However, for optimum ion-exchange operation, the pH of the aqueous solution must be at or below 7 (Demir et al., 2002).

The higher values of *b* (18.50 to 29.80 mg kg<sup>-1</sup>) suggest that higher  $\text{NH}_4^+$  was fixed by the clinoptilolite zeolite. In a related study, Tsitsishvili et al. (1992) reported high affinity of clinoptilolite zeolite for  $\text{NH}_4^+$ . Higher  $\text{NH}_4^+$  adsorption in U1Z, U2Z, and U3Z compared with U1 is also related to soil pH (Table 5). Soil pH is one of the important factors that regulate the adsorption capacity of clinoptilolite zeolite because the surface of clinoptilolite zeolite and ionization degree of the cations is proportional to pH level of the solution (Hui et al., 2005). The soil pHs as affected by clinoptilolite zeolite in U1Z, U2Z, and U3Z ranged from 6.11 to 6.26 (Table 5). With pH increase from 3 to 6.20, the capacity of the clinoptilolite zeolite to adsorb  $\text{NH}_4^+$  ions increased from 2.96 to 11.35 mg g<sup>-1</sup> (Korkmaz et al., 2012) because with increasing soil pH, the surface of the clinoptilolite zeolite became more negatively charged such that the affinity of the clinoptilolite zeolite for

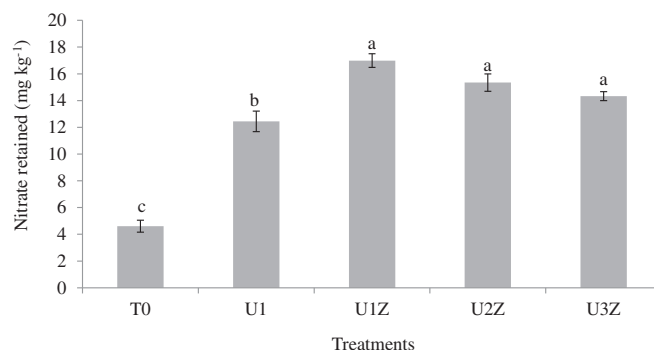


Fig. 7. Effect of treatments on the amount of ammonium desorption under different initial concentration of isonormal solution ( $\text{NH}_4\text{Cl-NaCl}$ ).

$\text{NH}_4^+$  increased (Dogan and Alkan, 2003).

The lower  $\text{NH}_4^+$  desorption in U1Z, U2Z, and U3Z compared with U1 explains the ability of clinoptilolite zeolite to improve N availability (Fig. 7). According to Johnson et al. (1983), large amounts of  $\text{NH}_4^+$  are adsorbed by clinoptilolite zeolite and gradually desorb  $\text{NH}_4^+$  ions to make them available for crop uptake. The lower adsorption of  $\text{NH}_4^+$  higher than  $\text{NH}_4^+$  desorption in U1 (without clinoptilolite zeolite) was because of the rapid release of the sorbed  $\text{NH}_4^+$  during urea hydrolysis (Kithome et al., 1998). For U1Z, U2Z, and U3Z (different rates of urea amended with clinoptilolite zeolite), the higher  $\text{NH}_4^+$  adsorption (Fig. 6) was because of the high affinity of clinoptilolite zeolite for  $\text{NH}_4^+$ . The fixation of  $\text{NH}_4^+$  by clinoptilolite zeolite explains the lower amount of  $\text{NH}_4^+$  desorbed in the soil with U1Z, U2Z, and U3Z. This observation is similar to the findings of other studies in which N loss was reduced through  $\text{NH}_4^+$  adsorption by zeolites (Bernardi et al., 2010; Ippolito et al., 2011). The fact that clinoptilolite zeolite in U1Z, U2Z, and U3Z decreased  $\text{NH}_4^+$  desorption compared with U1 (Fig. 7), further explains why the treatments with clinoptilolite zeolite increased  $\text{NH}_4^+$  ion adsorption.

According to Barbarick and Pirela (1984), fixing of N by zeolites in soils occurs because  $\text{NH}_4^+$  which are adsorbed in the small channels of zeolites are protected from being nitrified by nitrifying bacteria. This process suggests that both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  which are noted to be in equilibrium are regulated by clinoptilolite zeolite to minimize losses of those ions ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) which have been implicated in water pollution such as eutrophication. In this  $\text{NH}_4^+$  adsorption and desorption study, the stabilization of ionic exchange balance in 17 h can be considered as rapid because zeolites commonly remain in soils for more than one cropping cycle (residual effect or carry-over effect) (Palanivell et al., 2016). Therefore, clinoptilolite zeolite can be used to amend liquid nitrogen fertilizers on the basis that when zeolites are applied to soils would prevent the loss of redundant  $\text{NH}_4^+$  as these ions would be bound to zeolites in moist soils and afterwards,  $\text{NH}_4^+$  will be gradually or slowly released into the soil solution.

#### 4. Conclusions

Standard recommendation of urea with clinoptilolite zeolite as well as reduction of urea by 25% and 50% from standard recommendation but amended with clinoptilolite zeolite (U1Z, U2Z, and U3Z) significantly reduced leaching of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  compared with the existing standard recommendation of urea alone (U1). Amending different rates of urea with clinoptilolite zeolite favoured temporary retention of exchangeable  $\text{NH}_4^+$  on the exchange sites of clinoptilolite zeolite thus, improving N availability compared with urea alone. At the end of the soil leaching study, clinoptilolite zeolite also enhanced retention of soil total N, exchangeable  $\text{NH}_4^+$ , and available  $\text{NO}_3^-$  because the high CEC of the clinoptilolite zeolite enabled adsorption of  $\text{NH}_4^+$ . The availability of N from different rates of urea can be enhanced if they are amended with clinoptilolite zeolite. Thus, the



inclusion of clinoptilolite zeolite in urea (co-application of urea and clinoptilolite zeolite) use in agriculture could be a potential cost effective approach of improving soil N availability and crop productivity.

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