

# Use of Zeolite and Surfactant Modified Zeolite as Ion Exchangers to Control Nitrate Leaching

R. Malekian, J. Abedi-Koupai, S. S. Eslamian

**Abstract**—Nitrogen loss from irrigated cropland, particularly sandy soils, significantly contributes to nitrate ( $\text{NO}_3^-$ ) levels in surface and groundwaters. Thus, it is of great interest to use inexpensive natural products that can increase the fertilizer efficiency and decrease nitrate leaching. In this study, the ability of natural Iranian zeolite clinoptilolite (Cp) and surfactant modified zeolite clinoptilolite (SMZ) to remove  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively, from aqueous solutions was determined. The feasibility of using Cp and SMZ as soil amendment to reduce nitrate leaching from soil using lysimeters was also investigated. Zeolite showed 10.23% to 88.42%  $\text{NH}_4^+$  removal efficiency over a wide range of initial  $\text{NH}_4^+$  concentrations. Nitrate removal efficiency by SMZ was 32.26% to 82.26%. Field study results showed that Cp and SMZ significantly ( $p < 0.05$ ) reduced leachate  $\text{NO}_3^-$ -N concentration compared to control. There was no significant difference between maximum and mean leachate  $\text{NO}_3^-$ -N concentration of SMZ lysimeters and those of Cp lysimeters.

**Keywords**— Ammonium removal, Leaching, Nitrate removal, Surfactant modified zeolite

## I. INTRODUCTION

NITROGEN leaching from agricultural land is a contributor of nitrate ( $\text{NO}_3^-$ ) contamination of surface and groundwaters. This is a growing concern, especially as population growth is causing urbanization of former agricultural/horticultural lands. In semiarid and arid regions, especially areas with sandy soils, the potential of  $\text{NO}_3^-$  leaching increases due to frequent irrigations, which are needed to sustain plant growth.  $\text{NO}_3^-$  leaching is because negatively charged nitrate normally does not have much affinity for soil particle surface, and thus, does not readily sorb on soils [1]. Numerous studies have documented the adverse effects of high  $\text{NO}_3^-$  levels in humans, most notably methemoglobinemia [2], stomach cancer [3], and non-Hodgkin's Lymphoma [4]. The development of new natural products that would decrease nitrate leaching, improve fertilizer use efficiency, and increase crop yield and at the same time not pollute our environment is a challenge for agronomists and soil chemists throughout the world. Zeolites are crystalline hydrated aluminosilicates with a framework

structure containing pores occupied by water and by alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites show special importance in agriculture and aquaculture [5]. Although natural raw zeolites, with their negative charge framework, have already been used as cation exchanger, they are obviously unable to use as an anion exchanger. However, the removal of anions was made possible on SMZ, prepared through the sorption of cationic surfactant, such as hexadecyltrimethylammonium (HDTMA), on the zeolite surface [6]. The maximum loading of HDTMA is about 200% of the zeolites external cation exchange capacity (ECEC). At the HDTMA sorption maximum, the surfactant molecules form bilayers on zeolite surfaces with the lower layer held by electrostatic interactions between the negatively-charged zeolite surface and the positively-charged surfactant head groups, while the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers [7]. Under the surfactant bilayer configuration, the zeolite reverses its surface charge, resulting in a higher affinity, sorption, and retention of negatively-charged anionic contaminants that is attributed to surface anion exchange [7, 8]. The use of surfactant-modified zeolite (SMZ), which represents a type of inexpensive anion exchanger, to remove anionic contaminants from water has been studied extensively [9, 10].

The objective of this study was to investigate the ammonium exchange on natural Iranian zeolite clinoptilolite (Cp) and nitrate exchange on natural Iranian SMZ through batch experiment. The feasibility of using Cp and SMZ as soil amendments to reduce nitrate leaching from soil was also investigated through field experiment.

## II. EXPERIMENTAL METHODS

The natural zeolite used in this study originated from Semnan province, Iran. Mineral identification using X-ray diffraction showed that the zeolite consisted mainly of clinoptilolite. The zeolite had the following chemical composition (in %)  $\text{SiO}_2 = 65.90$ ,  $\text{Al}_2\text{O}_3 = 11.20$ ,  $\text{Na}_2\text{O} = 2.10$ ,  $\text{K}_2\text{O} = 2.31$ ,  $\text{CaO} = 3.20$ ,  $\text{Fe}_2\text{O}_3 = 1.25$ ,  $\text{MgO} = 0.52$ ,  $\text{LOI} = 11.89$ , and  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.9$ . The particle size of zeolite was between 0.2 and 0.8 mm. The cation exchange capacity (CEC) of the zeolite was  $140 \text{ cmol kg}^{-1}$  as determined by the 1 M  $\text{NH}_4\text{OAc}$  saturation method [11]. The ECEC of the zeolite was determined to be  $70 \text{ mmol kg}^{-1}$  using the method of Ming and Dixon [12].

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#### A. Surfactant modification

HDTMA bromide (Merck) was used for zeolite surface modification. The zeolite was modified by HDTMA to 200% of the ECEC. In a 250-ml centrifuge bottle, 60 g of raw zeolite and 180 ml of a 47 mM HDTMA solution were mixed on a reciprocal shaker for 24 h at 150 rpm at 25 °C. The mixture was then centrifuged at 5000 rpm for 20 min and the supernatant was removed. The mineral was then washed with two portions of distilled water and allowed to air dry [13].

#### B. Batch ammonium exchange

The NH<sub>4</sub><sup>+</sup> removal procedure by Iranian zeolite was as follows. To prepare working solutions, an ammonium chloride stock solution was prepared by dissolving the appropriate amount of NH<sub>4</sub>Cl in a 0.03 M NaCl solution. Then the appropriate amount of NH<sub>4</sub>Cl stock solution was added to a 0.03 M NaCl solution to obtain NH<sub>4</sub><sup>+</sup> ion concentrations of between 90 and 3610 mg L<sup>-1</sup>. For each 50-ml centrifuge tube, 1 g zeolite and 30 ml of working solution was mixed at 25 ± 1 °C for 2 h at 200 rpm. The mixtures were then centrifuged and the NH<sub>4</sub><sup>+</sup> was analyzed by a steam distillation procedure [14]. The amount of NH<sub>4</sub> exchanged was calculated from the difference between the initial and equilibrium concentrations. All samples were prepared in triplicate. The NH<sub>4</sub><sup>+</sup> exchanged on zeolite was calculated using the equation [15]:

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

Where  $q_e$  is the NH<sub>4</sub><sup>+</sup> exchanged on zeolite (mg g<sup>-1</sup>), M is the clinoptilolite mass (g),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of NH<sub>4</sub><sup>+</sup> in solution (mg L<sup>-1</sup>), respectively, and V is the volume of the solution (L). The removal efficiency was evaluated according to:

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where E is the ammonium removal efficiency expressed in %.

#### C. Batch nitrate exchange

To each 40-ml centrifuge tube, 2.5 g of SMZ and 25 ml of 2, 4, 6, 8, 12, 16, or 20 mM KNO<sub>3</sub> solution were mixed for 24 h at 150 rpm. The mixtures were then centrifuged the nitrate solution concentration analyzed by the steam distillation procedure [14]. The amount of nitrate exchanged was calculated from the difference between the initial and equilibrium concentrations. All samples were prepared in triplicate. The NO<sub>3</sub><sup>-</sup> exchanged on SMZ and removal efficiency was calculated using (1) and (2), respectively. Where  $q_e$  is the NO<sub>3</sub><sup>-</sup> exchanged on SMZ (mmol kg<sup>-1</sup>), M is the SMZ mass (kg),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of NO<sub>3</sub><sup>-</sup> in solution (mmol L<sup>-1</sup>), respectively.

#### D. Ammonium release

The NH<sub>4</sub><sup>+</sup>-loaded zeolite was used for release studies, which were conducted as a function of release time. For each 50-ml centrifuge tube, 1 g of NH<sub>4</sub><sup>+</sup>-loaded zeolite and 30 ml of

releasing solution with ionic strengths of 0.03 were mixed for varying amounts of time (10, 30, 60, 90, 150, 200, and 300 min) at 25 ± 1 °C and 200 rpm, followed by centrifugation. All samples were prepared in triplicate. The supernatant was analyzed for released NH<sub>4</sub><sup>+</sup> at each time of agitation using a steam distillation procedure [14].

#### E. Nitrate release

Batch release experiments were conducted as function of release time. To each 40-ml centrifuge tube, 2.5 g of nitrate-loaded SMZ and 25 ml of releasing solution with ionic strengths of 0.03 were mixed for varying amounts of time (1/4, 1/2, 3/4, 1, 2, 8, and 16 h) at 25 ± 1 °C and 200 rpm. The mixtures were then centrifuged at 5000 rpm for 20 min and the supernatant was analyzed for released NO<sub>3</sub><sup>-</sup> at each time of agitation using a steam distillation procedure [14]. All samples were prepared in triplicate.

#### F. Field experiment

This study was conducted at Isfahan University of Technology, north east of Isfahan in the central part of Iran during July-October, 2009. In the study area the mean annual temperature, rainfall, and humidity are 17 °C, 134 mm, and 38%, respectively.

The effect of Cp and SMZ on nitrate leaching was performed in lysimeters. Each lysimeter was 50 cm in diameter, 90 cm in depth, and had a drain pipe at the bottom. The soil texture at the experimental site was sandy loam with 18% clay, 25.5% silt, and 56.5% sand. Several characteristics of the soil used in the lysimeters at the beginning of the study are listed in Table I.

TABLE I

INITIAL SOIL CHARACTERISTICS OF THE EXPERIMENTAL LYSIMETERS		
Characteristic	0-30 cm	30-60 cm
pH	7.6	7.8
Electrical conductivity (dS m <sup>-1</sup> )	0.99	0.83
Cation exchange capacity (cmol kg <sup>-1</sup> )	6.8	6.8
NO <sub>3</sub> -N (mg kg <sup>-1</sup> )	42	28
NH <sub>4</sub> -N (mg kg <sup>-1</sup> )	32	25
K (mg kg <sup>-1</sup> )	382.8	316.1
P (mg kg <sup>-1</sup> )	29.8	27.2
Total nitrogen (%)	0.1	0.1
Organic matter (%)	1.03	0.90

The treatments consisted of Cp and SMZ. Each treatment was performed in triplicate and three unamended soil lysimeters were used as a control. The soil amendments were broadcast applied to the soil surface of the lysimeters at rate of 60 gr kg<sup>-1</sup> (equivalent to 27 ton ha<sup>-1</sup>) and incorporated to a depth of 3 cm prior to the planting of crops. Three seeds of maize single cross 704 were planted 4 cm deep in each lysimeter and after 22 days, corn in each lysimeter was thinned to one plant. The lysimeters were surface irrigated and was scheduled with 2-day intervals based on cumulative evapotranspiration replenishment using the maize evapotranspiration, which was estimated using the FAO-56 [16] Penman-Monteith reference evapotranspiration equation as a function of crop development stage. During each

irrigation event, 15% more water was applied to allow for drainage.

Water was delivered into each lysimeter through individual 16 mm pipes that were branched from 10 liter boxes connected to the main dividing box reservoir. The dividing box was placed at a height of 1 m in order to ensure the identical irrigation discharge for all lysimeters. The volume of water applied to each box was measured using flow meters. N fertilizer was applied via irrigation water (fertigation) at rate of 150 kg N ha<sup>-1</sup>. Half of this amount was applied two times during the crop cycle, at 17 and 49 days after planting (DAP). The N source was ammonium nitrate. The NO<sub>3</sub>-N concentration in the irrigation water averaged 3.4 mg l<sup>-1</sup> (Table II), which resulted in 25 kg additional N ha<sup>-1</sup> applied with the irrigation water.

The leached solution from each lysimeter was collected weekly by opening the drainage valve located at the end of drainage pipe. The accumulated drainage from each lysimeter was measured and the drainage valve remained closed until the next outflow measurement. The drainage samples were filtered and immediately frozen at -20 °C until they were subjected to analysis by the steam distillation procedure [14] for NO<sub>3</sub><sup>-</sup>.

TABLE II

CHARACTERISTICS OF THE IRRIGATION WATER

Characteristic	Value
No. of samples	3
pH	8.3 ± 0.1
Electrical conductivity (dS m <sup>-1</sup> )	0.43 ± 0.2
Ca (mg L <sup>-1</sup> )	52 ± 8.72
Mg (mg L <sup>-1</sup> )	10.8 ± 1.56
Na (mg L <sup>-1</sup> )	10.5 ± 7.4
K (mg L <sup>-1</sup> )	2.1 ± 0.5
NO <sub>3</sub> -N (mg L <sup>-1</sup> )	3.4 ± 0.2
Cl (mg L <sup>-1</sup> )	106.5 ± 1.5
SO <sub>4</sub> (mg L <sup>-1</sup> )	1.5 ± 0.5

The data are presented as the mean ± standard deviation for three samples taken at different times during the irrigation period.

### III. RESULTS AND DISCUSSION

#### A. NH<sub>4</sub><sup>+</sup> removal

The amounts of ammonium removed by natural Iranian Cp from aqueous solutions at different initial NH<sub>4</sub><sup>+</sup> concentrations were determined (Fig. 1 (a)). All the data reported are the average values derived from triplicate samples. Based on this analysis, the initial NH<sub>4</sub><sup>+</sup> concentration was found to be an important factor for NH<sub>4</sub><sup>+</sup> removal by Cp. As the initial concentration of NH<sub>4</sub><sup>+</sup> increased, the removal efficiency of NH<sub>4</sub><sup>+</sup> ion decreased (Fig. 1 (a)). This result may be attributed to the ion-exchanger tending to become saturated, resulting in an increase in the driving force required for further exchange of NH<sub>4</sub><sup>+</sup> ions onto the zeolite [17]. The Iranian zeolite showed 10.23% to 88.42% NH<sub>4</sub><sup>+</sup> removal efficiency over a wide range of initial NH<sub>4</sub><sup>+</sup> concentrations (90 to 3620 mg L<sup>-1</sup>).

The Langmuir isotherm model was used in order to fit the exchange equilibrium data. The Langmuir isotherm is given by the following equation:

$$q_e = \frac{bq_m C_e}{(1 + bC_e)} \quad (3)$$

Where  $q_e$  is the ammonium exchanged at equilibrium (mg NH<sub>4</sub><sup>+</sup>/g) and  $C_e$  is the ammonium equilibrium concentration in solution (mg NH<sub>4</sub><sup>+</sup>/L).  $q_m$  is ammonium exchange capacity (mg g<sup>-1</sup>) and  $b$  is Langmuir exchange coefficient. The experimental data of NH<sub>4</sub><sup>+</sup> exchange are well fitted by this model (R<sup>2</sup>=0.999). The maximum NH<sub>4</sub><sup>+</sup> exchange capacity by the Cp at equilibrium was 11.31 mgNH<sub>4</sub><sup>+</sup>/g ( $q_m$ ) (Fig. 1 (b)). The comparison of the NH<sub>4</sub><sup>+</sup> exchange capacity of previously reported some of the other natural zeolite [18, 19] with capacity of the present sample indicates that natural Iranian zeolite exhibits a reasonable exchange capacity for NH<sub>4</sub><sup>+</sup>.

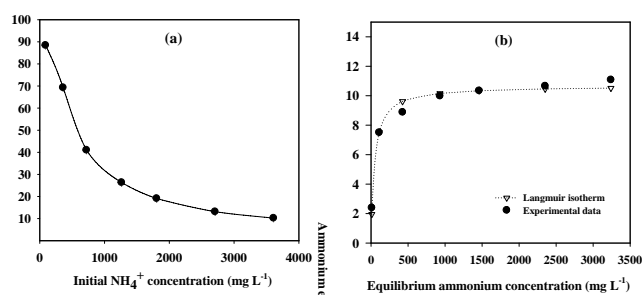


Fig. 1. NH<sub>4</sub><sup>+</sup> removal efficiency (a) and NH<sub>4</sub><sup>+</sup> exchange isotherm (b) by Iranian zeolite clinoptilolite.

#### B. NO<sub>3</sub><sup>-</sup> removal

Fig. 2 (a) displays the NO<sub>3</sub><sup>-</sup> removal with different initial nitrate concentrations by SMZ. Clearly, the SMZ sample used here appears efficient for nitrate uptake. This contrasts strongly with the behavior of the raw Cp material, which displays, as expected, no affinity to nitrate due to lack of significant positive charges. The Iranian SMZ showed 32.26% to 82.26% NO<sub>3</sub><sup>-</sup> removal efficiency over a wide range of initial NO<sub>3</sub><sup>-</sup> concentrations (124 to 1240 mg L<sup>-1</sup>) (Fig. 2 (a)). The exchange of nitrate can be well described by the Langmuir isotherm (R<sup>2</sup>=0.988), leading to a calculating nitrate exchange capacity ( $q_m$ ) of 71.91 mmol kg<sup>-1</sup> (Fig. 2 (b)) and a Langmuir coefficient ( $b$ ) of 0.592 mM<sup>-1</sup>.

#### C. NH<sub>4</sub><sup>+</sup> release

The result of the ammonium release kinetic experiments of NH<sub>4</sub><sup>+</sup>-loaded Iranian Cp is presented in Fig. 3 (a). All the data reported are the average values derived from triplicate samples. As can be seen in this Fig., the NH<sub>4</sub><sup>+</sup> release was rapid for the first 60 min, then slower for the rest of the time. Also the NH<sub>4</sub><sup>+</sup> release process was nearly complete within 150-200 min. This result could be due to the fact that the NH<sub>4</sub><sup>+</sup> release is a diffusion-controlled process. This result has previously been observed for NH<sub>4</sub><sup>+</sup> [20] and other similar ions such as K<sup>+</sup> [21].

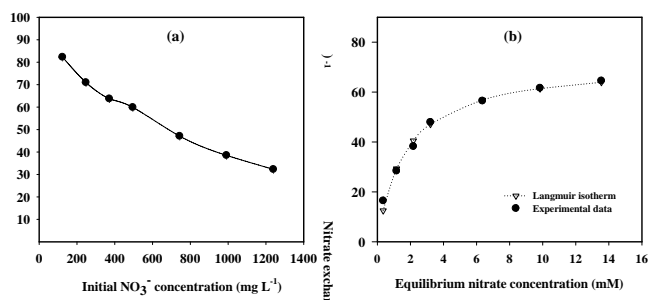


Fig. 2  $\text{NO}_3^-$  removal efficiency (a) and  $\text{NO}_3^-$  exchange isotherm (b) by Iranian surfactant modified zeolite.

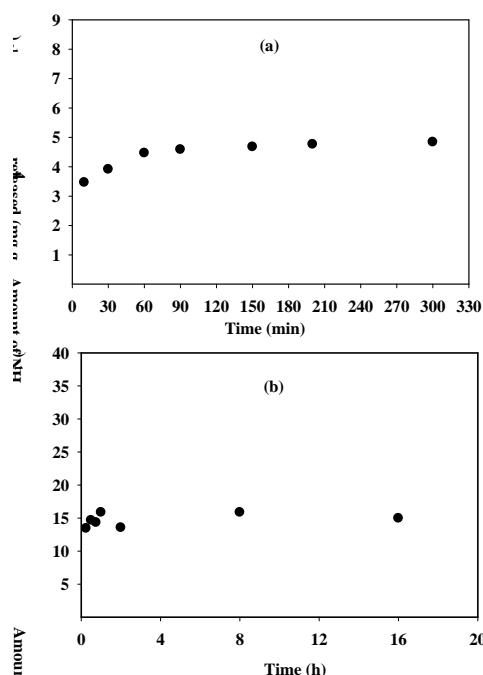


Fig. 3 Ammonium release kinetic by Cp (a) and nitrate release kinetic by SMZ (b).

#### D. $\text{NO}_3^-$ Release

The preloaded nitrate was subjected to release study from SMZ surfaces. The release kinetic of nitrate can be seen in Fig. 3 (b). All the data reported are the average values derived from triplicate samples. It seems that the  $\text{NO}_3^-$  release is somehow instantaneous, making it very difficult to fit the observed data to any release model. Release of anionic species on SMZ surfaces is attributed to surface anion exchange [22]. This result is supported by Li [1]. The mean percentage of nitrate released was 19.57. Li [1] showed that the accumulated nitrate released from SMZ increases with release repeats. The mean percentage of nitrate released after six release repeats was  $55 \pm 2$ .

#### E. Nitrate leaching

The mean  $\text{NO}_3\text{-N}$  concentration in the leachate of the treatments during the growing season is presented in Fig. 4. As shown in this Fig., the leachate  $\text{NO}_3\text{-N}$  concentration had a similar trend for treatments and control. Regardless of first

leaching event, maximum  $\text{NO}_3\text{-N}$  leaching occurred after fertilizer application (Fig. 4).

The  $\text{NO}_3\text{-N}$  concentrations in leachate were consistently low from lysimeters where soil amendments (SMZ or Cp) were used. Concentrations from unamended lysimeters (control) were between  $12.85\text{-}42.12 \text{ mg L}^{-1}$  during the growing season. While the leachate  $\text{NO}_3\text{-N}$  concentrations were between  $7.77\text{-}19.35$  and  $6.04\text{-}22.42 \text{ mg L}^{-1}$  for the lysimeters amended with SMZ and Cp, respectively. Higher  $\text{NO}_3\text{-N}$  leaching of unamended lysimeters is probably due to high solubility of ammonium nitrate fertilizer, resulting in rapid dissolution and also low CEC in soil, which adsorbed little of the added  $\text{NH}_4^+$ . In agricultural soil, the nitrification of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  can result in the loss of N through the leaching of  $\text{NO}_3^-$ . As shown in the batch experimental results, natural Cp is a suitable ion-exchanger for  $\text{NH}_4^+$  ion removal. Application of Cp may result in exchange of  $\text{NH}_4^+$  and limited its availability to nitrifying bacteria [23-24]. Application of SMZ, however, resulted in sorption and retention of nitrate that is attributed to surfactant-bilayer formation, on which, positive charges will develop and surface anion exchange was the main sorption mechanism [7]. This result is consistent with batch experimental results.

As shown in Fig. 4, all samples of unamended lysimeters (control) exceeded the federal drinking water standard of  $10 \text{ mg NO}_3\text{-N L}^{-1}$  [25]. Whereas application of SMZ and Cp resulted in the total number of samples exceeding the EPA limit of  $10 \text{ mg NO}_3\text{-N L}^{-1}$  [25] to be 28% and 38%, respectively, lower than that of the control.

The analysis of variance for comparisons between the maximum (63 DAP) and mean (during the study period)  $\text{NO}_3\text{-N}$  concentration in leachate revealed that both maximum and mean nitrate concentrations in leachate of SMZ and Cp-amended soil were significantly lower ( $p < 0.05$ ) than that of control (Table III). There was no significant difference between maximum and mean leachate  $\text{NO}_3\text{-N}$  concentrations of lysimeters amended with SMZ and Cp (Table III).

#### IV. CONCLUSION

Results from this study showed that Iranian zeolite clinoptilolite is capable of exchanging up to  $11 \text{ mg g}^{-1}$  ammonium. Modifying of zeolite clinoptilolite using HDTMA made it capable of exchanging up to  $80 \text{ mmol kg}^{-1}$  of nitrate. Application of Iranian Cp and SMZ as soil amendments at a rate of  $60 \text{ gr kg}^{-1}$  for the reduction of nitrate leaching from soil showed that nitrogen leaching was influenced by the application of either Cp or SMZ and both amendments can reduce N leaching. The results, from the standpoint of batch and field tests, provided experimental evidences that using Cp and SMZ as ion exchangers to control nitrate leaching is feasible. It can be concluded that natural zeolite is a suitable cation-exchanger and can be an appropriate anion-exchanger under surfactant bilayer configuration. As such, it can be recommended for use in wastewater treatment and agriculture

purposes as it represents a sustainable, environmentally friendly, and affordable ion exchange material.

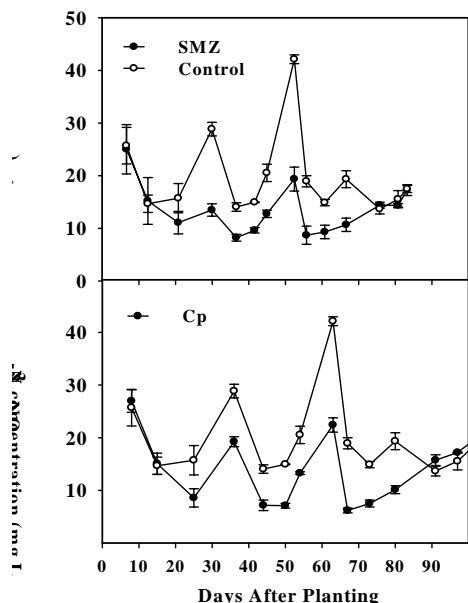


Fig. 4 NO<sub>3</sub>-N concentration in leachate for SMZ: surfactant modified zeolite, Cp: zeolite clinoptilolite, and unamended soil (control)

TABLE III  
EFFECT OF SOIL AMENDMENT TYPE ON THE MAXIMUM AND MEAN NO<sub>3</sub>-N CONCENTRATION OF LEACHATE.

Treatment	NO <sub>3</sub> -N concentration in leachate (mg L <sup>-1</sup> )	
	Maximum	Mean
Cp	22.42b*	14.94b
SMZ	19.35b	14.60b
Control	42.12a	20.01a

\* Mean value within a column followed by a different letter are significantly at p < 0.05.

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