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Influences of clinoptilolite and surfactant-modified clinoptilolite zeolite on nitrate leaching and plant growth

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ABSTRACT

The increasing demands for environmental protection and sustainable food production require an increase in the use of natural and non-toxic materials for agriculture. In this study, the feasibility of using surfactant-modified zeolite (SMZ) in comparison with zeolite clinoptilolite (Cp) application to reduce nitrate leaching and enhance crop growth was investigated. The effects of size (millimeter and nanometer) and application rate (20 g kg^{-1} and 60 g kg^{-1}) of Cp and SMZ on nitrate leaching and crop response were also evaluated. Using soil lysimeters, it was determined that the maximum and mean nitrate concentration in the leachate of SMZ-amended soil were significantly ($p < 0.05$) lower than those of Cp-amended soil. The amount of NO_3-N leached from SMZ- and Cp-amended lysimeters at the higher application rate (60 g kg^{-1}) was approximately 26% and 22% lower, respectively, than that from the control system. The mean grain yield, grain nitrogen content, stover dry matter, and N uptake were significantly greater in Cp-amended than SMZ-amended lysimeters. There was no significant effect due to the particle size of the two soil amendments. The results implicitly suggest that plants may have a better response if Cp is used as a fertilizer carrier rather than SMZ when applied at a rate of 60 g kg^{-1}.

1. Introduction

Nitrogen, a constituent of chlorophyll, proteins and many other molecules, is vital for plant growth and therefore its availability influences the yields and quality of arable and horticultural plants. As nitrogen is most often the limiting nutrient in plant growth, N fertilizers are used to overcome this limitation and increase crop yields [1]. While N effectively stimulates plant growth and is an extremely valuable nutrient, it is the major nutrient of concern in water pollution. About 40–70% of the nitrogen applied in normal fertilizers is lost to the environment and cannot be absorbed by plants, which causes not only large economic and resource losses, but also responsible for serious environmental pollution [2]. Numerous studies have documented the adverse effects of high NO_3 levels in humans, most notably methemoglobinemia [3], stomach cancer [4], and non-Hodgkin's Lymphoma [5].

The development of new products that would 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. Natural zeolites are a group of aluminosilicate minerals that are receiving attention in the field of agriculture, as their physical and chemical properties make them potentially suitable soil amendments and/or carriers of plant nutrients [6,7]. One natural-occurring zeolite in particular, clinoptilolite (Cp), is often used in agricultural production [6] due to its high cation exchange capacity (CEC) and high affinity for NH_4^+ [8,9]. Several reports have demonstrated that increased N use efficiency occurs in zeolite-amended soils [9,10]. Although zeolite tuffs are widely distributed in huge deposits in different regions of Iran [11], there are a few reports about the application of natural Iranian zeolite as a soil amendment.

If the N in applied fertilizers is in an anionic form such as nitrate, due to the net repulsion between the anions and soil surfaces, it will be excluded from the soil surfaces and is easily leached [12,13]. Due to the low retention of nitrate by soil surfaces, an elevated amount of applied fertilizer is therefore required for plants to grow well. However, the increased dose will exert greater impact on environmental water quality, causing elevated nitrate concentrations in groundwater [14]. Thus, it is of great interest to use inexpensive soil amendments that can increase fertilizer efficiency and decrease nitrate leaching.

The cation-exchange properties of natural zeolites can be exploited to modify their surface chemistries such that other classes of compounds, particularly anions and non-polar organics, will also be retained. The quaternary amine hexadecyltrimethylammonium (HDTMA) is a long-chain cationic surfactant that possesses a permanent positive charge [15]. The maximum loading of HDTMA is about 200% of the zeolites external cation exchange capacity (ECEC). At the HDTMA sorption maximum, the surfactant molecules

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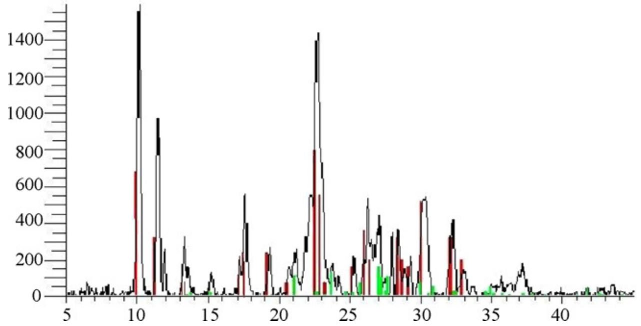

Fig. 1. The XRD pattern of zeolite (🟥 : clinoptilolite (83%), 🟩 : orthoclase (17%)).

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 [16]. 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 [16–18]. 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 [18–20].

The objective of this study was to investigate the feasibility of using Iranian Cp and SMZ as soil amendments to reduce nitrate leaching from soil. Using soil lysimeters, the response of corn was examined to evaluate and compare the application of SMZ and Cp. The effects of size and application rate of Cp and SMZ on nitrate leaching and crop characteristics were also evaluated.

2. Material and methods

2.1. Zeolite

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 (Fig. 1). The total elemental analysis was performed by fluorescence spectroscopy using a Spectro X-Lab 2000 X-Ray instrument. The zeolite had the following chemical composition (mass%) $SiO_2 = 65.90$, $Al_2O_3 = 11.20$, $Na_2O = 2.10$, $K_2O = 2.31$, $CaO = 3.20$, $Fe_2O_3 = 1.25$, $MgO = 0.52$, LOI = 11.89, and $SiO_2/Al_2O_3 = 5.9$.

The particle size of zeolite was between 0.2 and 0.8 mm. To obtain nanosized mineral particles the mineral was ground in a jet mill. The particle size was determined using a particle size analyzer and the average size was 800 nm. The CECs of the millimeter- and nanometer-sized particles of Cp were 140 and 165 cmol kg^{-1}, respectively, as determined by the 1 M NH_4OAc saturation method [21]. The ECECs of the millimeter- and nanometer-sized Cp were determined to be 70 and 115 mmol kg^{-1}, respectively, using the method of Ming and Dixon [22].

2.2. 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 millimeter-sized zeolite and 180 ml of 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 [23]. The same procedure was used for nanometer-sized zeolite modification, but the HDTMA concentration used was 77 mM.

2.3. Site description

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 and plant characteristics 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 1.

The experiment was a randomized complete block experimental design using a complete factorial arrangement of treatments. The treatments consisted of two soil amendment types of Cp (Z) and SMZ (S), two soil amendment sizes of millimeter (M) and nanometer (N), and two soil amendment rates of 20 g kg^{-1}, which is equivalent to 9 ton ha^{-1} (a), and 60 g kg^{-1}, which is equivalent to 27 ton ha^{-1} (b). Each treatment was performed in triplicate and three unamended soil lysimeters were used as a control (C). The soil amendments were broadcast applied to the soil surface of the lysimeters and incorporated to a depth of 3 cm prior to the planting of crops.

In this study, maize was selected over other crops in view of its rapid growth cycle, responsiveness to changes in nutrient availability, and short harvest intervals. 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 [24] 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 L 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^{-1}. 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_3-N concentration in the irrigation water averaged 3.4 mg L^{-1} (Table 2), which resulted in 25 kg additional N ha^{-1} applied with the irrigation water. This application rate of N (fertilizer and irrigation water) was very close to the recommended N rate for corn based on soil test results [25].

Table 1
Initial soil characteristics of the experimental lysimeters.

Characteristic	0–30 cm	30–60 cm
pH	7.6	7.8
Electrical conductivity (dS m^{-1})	0.99	0.83
Cation exchange capacity (cmol kg^{-1})	6.8	6.8
NO_3-N (mg kg^{-1})	42	28
NH_4-N (mg kg^{-1})	32	25
K (mg kg^{-1})	382.8	316.1
P (mg kg^{-1})	29.8	27.2
Total nitrogen (%)	0.1	0.1
Organic matter (%)	1.03	0.9

Table 2
Characteristics of the irrigation water.

Characteristic	Value
No. of samples	3
pH	8.3 ± 0.1
Electrical conductivity (dS m^{-1})	0.43 ± 0.2
Ca (mg L^{-1})	52 ± 8.72
Mg (mg L^{-1})	10.8 ± 1.56
Na (mg L^{-1})	10.5 ± 7.4
K (mg L^{-1})	2.1 ± 0.5
NO_3-N (mg L^{-1})	3.4 ± 0.2
Cl (mg L^{-1})	106.5 ± 1.5
SO_4 (mg L^{-1})	1.5 ± 0.5

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

2.4. Data collection

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 for NO_3^- [26].

Soil water samples were also collected typically during the growing season. At each of the 27 experimental lysimeters, two ceramic soil–water suction samplers (Irrometer, Model SSAT) with a 1.5 cm diameter were installed vertically at depths of 15 and 50 cm. A 50 kPa vacuum was applied to each soil water sampler 24 h after irrigation to collect soil solution samples for NO_3 concentration determination. The soil solution was extracted from each soil water sampler using a syringe 24 h after vacuum application. The NO_3 content in the soil solution was determined by the steam distillation procedure [26].

At the end of the study, soil samples were collected for each lysimeter at depths of 0–30 and 30–60 cm. At each soil depth, three samples were collected, blended, air-dried, and then passed through a 2 mm sieve. Ammonium and nitrate in soil were extracted with 2 M KCl and their concentrations were determined by the steam distillation procedure [26].

The leaf area index (LAI) was measured with a portable leaf area meter four times: 36, 54, and 85 DAP and at harvest. After the corn was harvested on 14 October, 2009, the total grain and stover biomass were measured. The total nitrogen content of stover and grain were also determined using the Kjeldahl procedure [27].

2.5. Data analysis

All analyses were performed using SAS statistical analysis software [28]. Separation of the means was performed using LSD at $p < 0.05$.

3. Results and discussion

3.1. Nitrate leaching

The mean NO_3-N concentration in the leachate of the lysimeters during the growing season showed a similar trend for the different treatments (Fig. 2). Regardless of the first NO_3-N leaching event, maximum NO_3-N leaching occurred after fertilizer application. However, both of the soil amendments lowered the NO_3-N concentration in the leachate and the reduction was greater at the higher amendment application rate (Fig. 2).

As shown in Fig. 2, the NO_3-N concentrations in the leachate of the unamended soil lysimeters (control) were between 13 and 42 mg L^{-1} during the growing season, with all samples exceeding the federal drinking water standard of 10 mg NO_3-N L^{-1} [29]. This concentration range is consistent with a previous study by Nyamangara et al. [30] who reported NO_3-N concentrations as high as 22.5 mg L^{-1} below the corn root zone in lysimeters that received ammonium nitrate fertilizer. In addition, Gheysari et al. [31] reported a minimum and maximum NO_3-N concentration value of 10.38 and 31.15 mg L^{-1}, respectively, at a 60 cm depth in a silage maize field which received 200 kg ha^{-1} of urea. The application of Cp reduced the leachate NO_3-N concentration compared to control and was most significant in the lysimeters that received the higher application rate (Fig. 2). During the growing season, the NO_3-N concentrations in leachate of the lysimeters amended with the lower rate of Cp were between 11.6 and 38 mg L^{-1} whereas the higher rate of Cp reduced the leachate NO_3-N concentration range to 7–25 mg NO_3-N L^{-1}. Approximately 64% and 61% of the ZNb and ZMb samples, respectively, exceeded the EPA limit of 10 mg NO_3-N L^{-1} [29]. This result may be attributed to the increasing CEC of the soil Cp mixtures in the soil surface and the high affinity and selectivity of natural zeolite for NH_4^+ and therefore decreasing its availability to nitrifying bacteria [32]. In the ZMb and ZNb treatments, the calculated soil surface CECs were 14.8 and 16 cmol kg^{-1}, respectively, while the ZMa and ZNa CECs were 9.5 and 9.9 cmol kg^{-1}, respectively.

In agricultural soil, the nitrification of NH_4^+ to NO_3^- can result in the loss of N through the leaching of NO_3^- [33]. MacKown

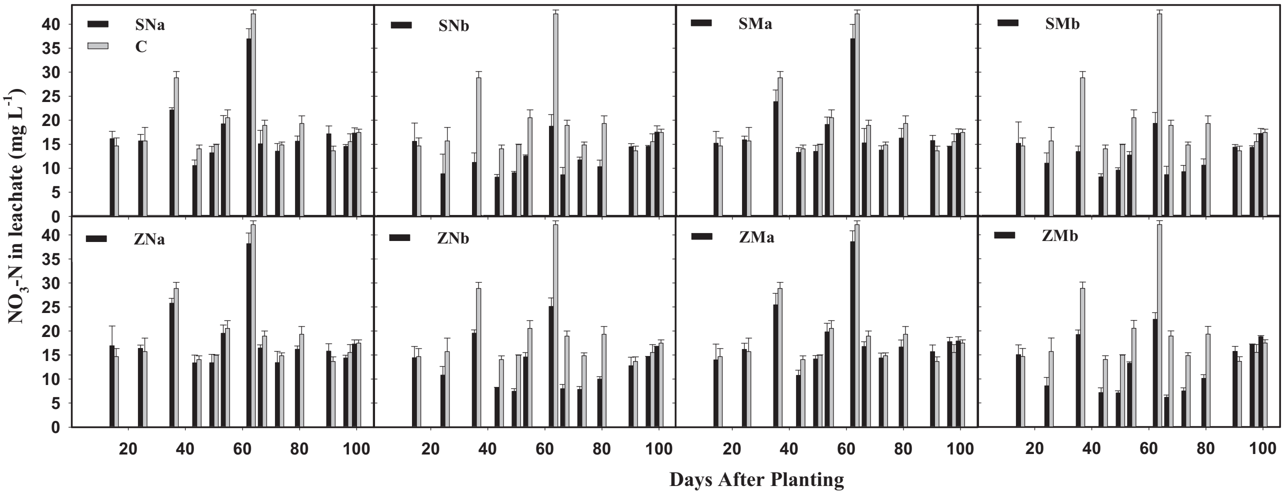

Fig. 2. NO_3-N concentration in leachate for different soil amendment types (S: surfactant-modified zeolite; Z: zeolite clinoptilolite; C: unamended soil control), sizes (M: millimeter; N: nanometer), and rates (a: 20 g kg^{-1}; b: 60 g kg^{-1}).

Table 3
Effect of soil amendment type, size, and application rate on the maximum and mean NO_3-N concentration of leachate and the total amount of NO_3-N leached.

Treatment	NO_3-N concentration in leachate (mg L^{-1})		N leached (kg ha^{-1})
	Maximum	Mean	
Amendment type			
Cp	31.07a*	17.15a	15.60a
SMZ	28.00b	16.63b	15.00a
Amendment size			
Millimeter	29.33a	16.95a	15.42a
Nanometer	29.75a	16.84a	15.19a
Application rate (g kg^{-1})			
20	37.67a	19.05a	16.83a
60	21.41b	14.74b	13.80b

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

[34] found through an incubation experiment that by using a rate equivalent to 30 ton ha^{-1} of NH_4-exchanged clinoptilolite, nitrification decreased in Rositas loamy sand and Gila silty clay loam by 11% and 4%, respectively. MacKown and Tucker [9] also demonstrated that the application of 12.5, 25, or 50 g kg^{-1} Cp significantly reduced NH_4^+ leaching compared to the $(NH_4)_2SO_4$ control. NO_3^- leaching was not measured in this study because N-serve was added to the soil. Huang and Petrovic [35] also reported that the NO_3-N concentration in leachate from unamended lysimeters increased dramatically, whereas the concentration in leachate from clinoptilolite zeolite-amended sand lysimeters did not exceed 10 mg NO_3-N L^{-1}.

It was also observed that the application of SMZ reduced the NO_3-N concentration in leachates compared to the control samples (Fig. 2). In the lysimeters amended with the lower rate of SMZ, the leachate NO_3-N concentrations were between 12.2 and 37 mg L^{-1} during the growing season, whereas those in the leachate of the lysimeters amended with the higher rate of SMZ were between 7.8 and 19 mg NO_3-N L^{-1}. Approximately 67% and 72% of the SNb and SMb samples, respectively, exceeded the EPA limit of 10 mg NO_3-N L^{-1} [29] (Fig. 2). Although nitrate does not readily adsorb onto soils due to a lack of significant positive charges in many soils, SMZ can easily adsorb nitrate due to HDTMA bilayer formation [16]. Due to this characteristic, SMZ is capable of adsorbing up to 80 mmol kg^{-1} of nitrate [12], which may explain the observed reduction of NO_3-N in the leachate of lysimeters amended with SMZ.

The analysis of variance for comparisons between the maximum NO_3-N concentration in leachate (63 DAP) revealed that the maximum nitrate concentration in leachate of SMZ-amended soil (28.00 mg NO_3-N L^{-1}) was significantly lower ($p < 0.05$) than that of Cp-amended soil (31.07 mg NO_3-N L^{-1}) (Table 3). This suggests that the application of modified zeolite to agricultural soil would be more effective than unmodified zeolite for the reduction of nitrate leaching. The analysis of variance also showed that the maximum NO_3-N concentration in the leachate at the higher rate of soil amendment application was significantly lower than that of the lower application rate (Table 3). The results obtained from analysis of variance for the mean leachate nitrate concentration during the growing season were identical to those for the maximum nitrate concentration of leachate (Table 3).

Although adsorbents with a smaller particle size have a greater specific surface area and therefore a greater theoretical capacity for external surface adsorption [36], there was no significant effect of the amendment size on the leachate NO_3-N concentration for either SMZ or Cp (Table 3). This result may be attributed to the fact that the particle size also affects desorption of NH4+ and NO_3^- by Cp and SMZ, respectively, and as the particle size of Cp or SMZ decreases more N is released [37].

The total amount of NO_3-N leached during the study in the control lysimeters was 18 kg ha^{-1}. Soil amendments reduced the amount of NO_3-N leached compared to the control, whereas there was no significant difference ($p < 0.05$) between the control and the soil amended at the lower application rate (Fig. 3). The total amount of NO_3-N leached from the SMZ and Cp-amended lysimeters at the higher rate was approximately 26% and 22% lower, respectively, than that from the control.

Although SMZ application significantly reduced the mean NO_3-N concentration of leachate compared to the zeolite, the amount of NO_3-N leached from the lysimeters was unaffected by the amendment type (Table 3). This is likely due to the difference between adsorption and desorption of NH_4^+ and NO_3^- by Cp and SMZ, respectively, during the study period. The adsorption and desorption of NH_4^+ on Cp are due to cation exchange and diffusion [38], whereas the adsorption and desorption of nitrate on SMZ surfaces are attributed to surface anion exchange [16]. In addition, the amount of nitrate leached is also affected by the leachate volume. Although there was no significant difference ($p < 0.05$) between the mean volume leachate of the treatments during each sampling time point, the leachate volume did differ during the study due to differences in plant uptake, evapotranspiration, and irrigation (data not shown). The application rate of soil amendments had a significant effect ($p < 0.05$) on the amount of NO_3-N leached (Table 3). The application of soil amendment at a higher rate significantly reduced the amount of NO_3-N leachate (13.8 kg ha^{-1}) compared to the lower rate (16.83 kg ha^{-1}).

3.2. *Corn growth and nitrogen uptake*

The effect of the application of Cp and SMZ on the growth and nitrogen uptake by corn was also examined. Soil amended with Cp and SMZ reduced nitrogen losses and provided more N for corn growth compared to the control (Table 4). The corn grain yield, grain nitrogen content, stover dry matter, and plant nitrogen uptake also increased in soil-amended lysimeters compared to the control, but were only significant for the higher application rate of soil amendments (Table 4). Despite the statistical significance, the differences were relatively small; they may be more dramatic in coarse-textured soils and with a lower rate of fertilizer application.

The NO_3-N concentration in the soil water extracted by ceramic caps at 43 and 77 DAP showed that the concentration in the first soil layer (at a soil depth of 20 cm) was greater in soil-amended lysimeters compared to the control, whereas the control had a higher

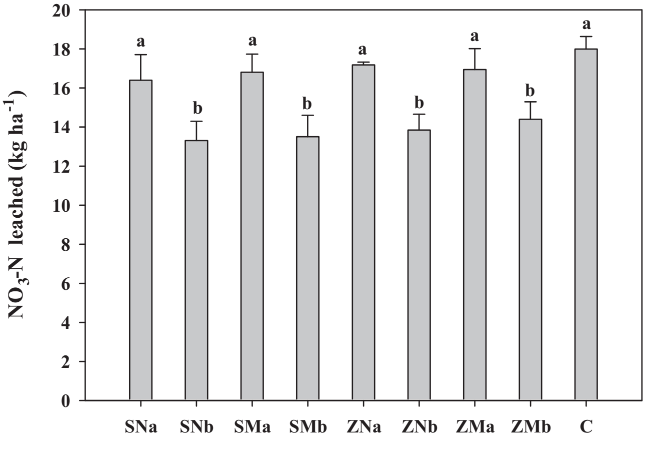

Fig. 3. The amount of NO_3-N leached for different soil amendment type (S: surfactant-modified zeolite; Z: zeolite clinoptilolite; C: unamended soil control), size (M: millimeter; N: nanometer), and rate (a: 20 g kg^{-1}; b: 60 g kg^{-1}). Different letters above the columns indicate significant difference at $p < 0.05$.

Table 4
Mean grain yield and nitrogen content (NC), stover dry matter and nitrogen content (NC), leaf area index maximum (LAI_{max}), nitrogen uptake (NU), and ratio of N uptake to applied N fertilizer (RUF) for different soil amendment types (S: surfactant-modified zeolite; Z: zeolite clinoptilolite; C: unamended control soil), size (M: millimeter; N: nanometer), and application rate (a: 20 g kg^{-1}; b: 60 g kg^{-1}).

Treatment	Grain		Stover		LAI_{max}	N uptake (kg ha^{-1})	RUF (%)
	Yield (kg ha^{-1})	NC (%)	Dry matter (kg ha^{-1})	NC (%)			
SNa	5634.20c*	1.540c	9398.52c	0.530a	3.36a	136.63c	78.07c
SNb	5687.53b	1.573b	10196.07b	0.533a	3.37a	143.95b	82.27b
SMa	5633.67c	1.540c	9401.50c	0.527a	3.37a	136.40c	77.95c
SMb	5690.44b	1.576b	10217.87b	0.527a	3.38a	143.59b	82.05b
ZNa	5634.00c	1.540c	9400.57c	0.527a	3.33a	136.43c	77.96c
ZNb	5924.20a	1.600a	10389.27a	0.537a	3.40a	150.68a	86.10a
ZMa	5633.93c	1.540c	9387.27c	0.527a	3.34a	136.20c	77.83c
ZMb	5890.30a	1.596a	10333.63ab	0.537a	3.36a	149.51a	85.43a
C	5631.43c	1.527c	9393.97c	0.527a	3.33a	135.44c	77.40c

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

NO_3-N concentration in the second soil layer (at a soil depth of 50 cm) (Fig. 4). This suggests that nitrate remains at the soil surface due to the association with soil amendments, but it is leached from the soil surface in the control. These results are likely due to the fact that Cp and SMZ are cation [36,39] and anion exchangers [19,40], respectively. They are capable of adsorbing nitrogen in the forms of NH_4^+ (by Cp) and NO_3^- (by SMZ) and then release it the manner of a slow-releasing fertilizer [12,37]. Therefore, plant roots in soil amended with Cp or SMZ were likely exposed to more nitrogen compared to control.

The mean grain yield, grain nitrogen content, stover dry matter, and N uptake were significantly greater ($p < 0.05$) in Cp-amended lysimeters compared to those in SMZ-amended lysimeters (Table 5). It is considered that this was likely due to the effect of the proportion of NH_4^+ and NO_3^- in the soil solution on corn growth. Previous studies have shown that the combination of NH_4^+ and NO_3^- appears more ideal for corn growth than NO_3^- alone [41,42], and the same is true for wheat [43] and some horticultural crops [44]. The ammonium added to the soil through the application of fertilizer may have been nitrified or volatilized before being taken up by plants. In contrast, Cp has the capacity to adsorb the NH_4^+ present in fertilizer [33], which can then be released by Cp and taken up by plants before it is nitrified. This result implicitly suggests that plants may have a better response if Cp is used as a fertilizer carrier rather than SMZ.

Although there were no significant differences between the mean plant growth characteristics of the two soil amendment sizes, the application rate had a significant effect on grain yield, grain N concentration, stover dry matter, and N uptake (Table 5). However, the leaf area index and stover nitrogen content were not affected by the soil amendment application (Table 5). There was also no significant difference between plant growth characteristics of the lower rate application of Cp and SMZ and those of the control (Table 4).

The ratio of N uptake to the applied N fertilizer (RUF) was 77.4% for the control (Table 4). Previous studies have reported a RUF values, ranging from 50–66% [45], 68% [35], and 21–71% [1]. The application of soil amendments increased the mean RUF to 81.83% and 80.08% for Cp and SMZ, respectively (Table 5). This result is consistent with the improved fertilizer N uptake efficiency reported in sandy rooting media amended with clinoptilolite [35]. A significant difference between the RUF of the higher rate of soil amendment application and that of the lower rate of application was also observed. Application of SMZ and Cp at a higher rate resulted in an increase in RUF of approximately 5% and 10%, respectively.

3.3. Inorganic nitrogen content in soil

At the end of the study, the mean NO_3-N and NH_4-N concentrations of the two soil layers for all of the treatments were determined (Fig. 5). As can be seen in the figure, the mean NO_3-N concentrations of soil from lysimeters amended at a higher rate in both layers are clearly different from those of soil amended at a lower rate and the unamended soil lysimeters (control). At a higher application rate of soil amendments, the NO_3-N concentration in the first soil layer (0–30 cm) was significantly greater than that of the second layer. It is therefore suggested that the application of Cp or SMZ at a higher rate retained NO_3-N in the first layer due to their cation and ion exchange properties, respectively. Since 50–60% of the total water uptake occurs from the first 30 cm soil depth [46], the application of soil amendments at a higher rate results in increased nitrogen availability for plants at this soil depth. For the lower application rate of soil amendment and unamended soil (control), NO_3-N leaching

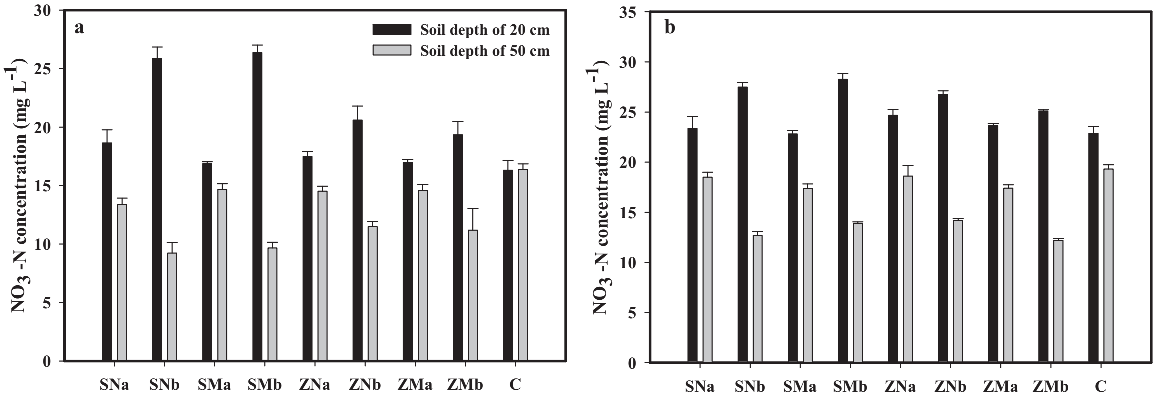

Fig. 4. NO_3-N concentration of soil solutions at a soil depth of 20 and 50 cm below the soil surface for different soil amendment type (S: surfactant-modified zeolite; Z: zeolite clinoptilolite; C: unamended control soil), size (M: millimeter; N: nanometer), and rate (a: 20 g kg^{-1}; b: 60 g kg^{-1}) at 43 DAP (a) and 77 DAP (b).

Table 5
Effect of soil amendment type, size, and application rate on grain yield and nitrogen content (NC), stover dry matter and nitrogen content (NC), leaf area index maximum (LAI_{max}), nitrogen uptake (NU), and ratio of N uptake to applied N fertilizer (RUF).

Treatment	Grain		Stover		LAI_{max}	NU (kg ha^{-1})	RUF (%)
	Yield (kg ha^{-1})	NC (%)	Dry matter (kg ha^{-1})	NC (%)			
Amendment type							
Cp	5770.61a*	1.60a	9877.68a	0.53a	3.36a	143.20a	81.83a
SMZ	5661.46b	1.56b	9803.49b	0.53a	3.37a	140.15b	80.08b
Amendment size							
Millimeter	5712.09a	1.56a	9835.07a	0.53a	3.36a	141.92a	80.81a
Nanometer	5719.98a	1.56a	9846.10a	0.53a	3.36a	141.43a	81.10a
Application rate (g kg^{-1})							
20	5633.95b	1.54b	9396.96b	0.53a	3.35a	136.42b	77.95b
60	5798.12a	1.59a	10284.21a	0.53a	3.38a	146.93a	83.96a

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

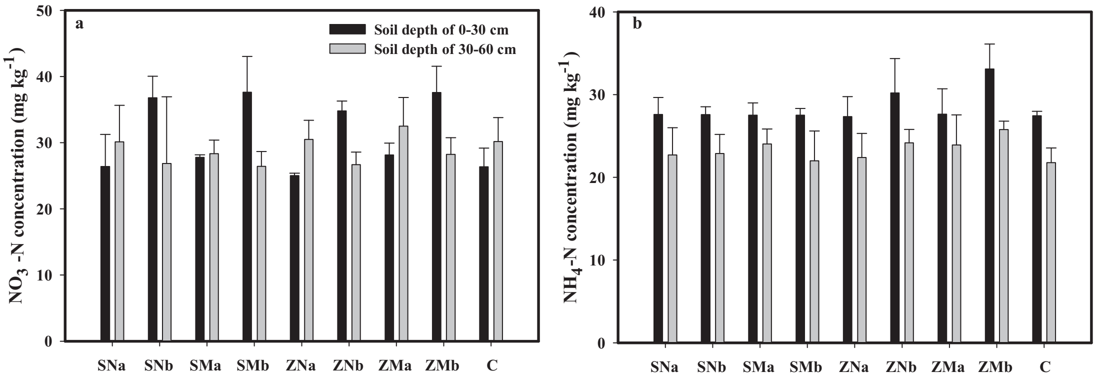

Fig. 5. NO_3-N (a) and NH_4-N (b) concentrations of soil for different soil amendment type (S: surfactant-modified zeolite; Z: zeolite clinoptilolite; C: unamended control soil), size (M: millimeter; N: nanometer), and rate (a: 20 g kg^{-1}; b: 60 g kg^{-1}) at the end of the study.

from the first soil layer resulted in a higher NO_3-N concentration in the second layer (Fig. 5). The leaching of N to lower soil layers would not only result in the reduction of available nutrients for crops, but could also contaminate water (NO_3-N) and air (N_2O) [47].

With respect to the NH_4-N concentration, the application of Cp at a higher rate (ZMb and ZNb) resulted in a greater mean NH_4-N concentration in the first soil layer at the completion of the experiment (Fig. 5). This may have been due to the retention of NH_4^+ by Cp in sites where nitrifying bacteria could not oxidize the NH_4^+. Interestingly, the NH_4-N concentration in the ZMb lysimeter was slightly greater than that observed for ZNb (Fig. 5). This result implies that the release of NH_4^+ from Cp particles of larger size was slower than smaller-sized particles, which was most likely due to an increase in diffusion path length. Perrin et al. [37] reported that as the NH_4^+-loaded Cp size decreased, less N urea was generally recovered.

4. Conclusion

In this study, the effect of using Iranian Cp and SMZ as soil amendments for the reduction of nitrate leaching from soil was examined. It was revealed that nitrogen leaching and corn growth were influenced by the application of either Cp or SMZ at a rate of 60 g kg^{-1}. The results provide evidence that both amendments can reduce N leaching while sustaining plant growth and increasing the ratio of N uptake to applied N fertilizer. It was also demonstrated that corn grown in soil amended with Cp assimilated significantly more N than corn grown in soil amended with SMZ. Therefore, these results implicitly suggest that plants may have a better response if Cp is used as a fertilizer carrier rather than SMZ. No significant effects in N leached and plant growth due to soil amendment size was observed. Also the application of Cp and SMZ at rate of 20 g kg^{-1} was not effective for reducing N leaching and enhancing plant growth, which should be taken into consideration when amending soil with zeolite.

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References

[1] M. Jalali, Nitrates leaching from agricultural land in Hamadan, western Iran, Agric. Ecosyst. Environ. 110 (3–4) (2005) 210–218.
[2] L. Wu, M.Z. Liu, Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, Carbohydr. Polym. 72 (2) (2008) 240–247.
[3] L. Fewtrell, Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion, Environ. Health Perspect. 112 (14) (2004) 1371–1374.
[4] H. Kirchmann, A.E.J. Johnston, L.F. Bergstrom, Possibilities for reducing nitrate leaching from agricultural land, Ambio 31 (5) (2002) 404–408.
[5] B.A. Kilfoy, M.H. Ward, T.Z. Zheng, T.R. Holford, P. Boyle, P. Zhao, M. Dai, B. Leaderer, Y.W. Zhang, Risk of non-Hodgkin lymphoma and nitrate and nitrite from the diet in Connecticut women, Cancer Cause Control 21 (6) (2010) 889–896.
[6] M. Rehakova, S. Cuvanova, M. Dzivak, J. Rimar, Z. Gaval'ova, Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type, Curr. Opin. Solid State Mater. Sci. 8 (6) (2004) 397–404.
[7] R.L. McGilloway, R.W. Weaver, D.W. Ming, J.E. Gruener, Nitrification in a zeoponic substrate, Plant Soil 256 (2) (2003) 371–378.
[8] V.K. Jha, S. Hayashi, Modification on natural clinoptilolite zeolite for its NH_4^+ retention capacity, J. Hazard. Mater. 169 (1–3) (2009) 29–35.
[9] C.T. MacKown, T.C. Tucker, Ammonium nitrogen movement in a coarse-textured soil amended with zeolite, Soil Sci. Soc. Am. J. 49 (1) (1985) 235–238.
[10] G.A. Ferguson, I.L. Pepper, Ammonium retention in sand amended with clinoptilolite, Soil Sci. Soc. Am. J. 51 (1) (1987) 231–234.
[11] H. Kazemian, Zeolite science in Iran: a brief review, in: Zeolite 02, 6th International Conference Occurrence, Properties and Utilization of Natural Zeolite, 2002, pp. 162–163.
[12] Z. Li, Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release, Microporous Mesoporous Mater. 61 (1–3) (2003) 181–188.

[13] C.S. Li, N. Farahbakhshazad, D.B. Jaynes, D.L. Dinnes, W. Salas, D. McLaughlin, Modeling nitrate leaching with a biogeochemical model modified based on observations in a row-crop field in Iowa, Ecol. Model. 196 (1–2) (2006) 116–130.

[14] G.J. Kraft, W. Stites, D.J. Mechenich, Impacts of irrigated vegetable agriculture on a humid north-central US sand plain aquifer, Ground Water 37 (4) (1999) 572–580.

[15] R.S. Bowman, Applications of surfactant-modified zeolites to environmental remediation, Microporous Mesoporous Mater. 61 (1–3) (2003) 43–56.

[16] Z.H. Li, R.S. Bowman, Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite, Environ. Sci. Technol. 31 (8) (1997) 2407–2412.

[17] A.I.P. Cordoves, M.G. Valdes, J.C.T. Fernandez, G.P. Luis, J.A. Garcia-Calzon, M.E.D. Garcia, Characterization of the binding site affinity distribution of a surfactant-modified clinoptilolite, Microporous Mesoporous Mater. 109 (1–3) (2008) 38–48.

[18] P.F. Zhang, D.M. Avudzega, R.S. Bowman, Removal of perchlorate from contaminated waters using surfactant-modified zeolite, J. Environ. Qual. 36 (4) (2007) 1069–1075.

[19] R.S. Bowman, G.M. Haggerty, R.G. Huddleston, D. Neel, M. Flynn, Sorption of nonpolar organics, inorganic cations, and inorganic anions by surfactant-modified zeolites, Chapter 5, in: D.A. Sabatini, R.C. Knox, J.H. Harwell (Eds.), Surfactant-enhanced Subsurface Remediation, Proc. of the ACS Symposium series 594, American Chemical Society, Washington, DC, 1995, pp. 54–64.

[20] P. Chutia, S. Kato, T. Kojima, S. Satokawa, Adsorption of As(V) on surfactant-modified natural zeolites, J. Hazard. Mater. 162 (1) (2009) 204–211.

[21] H.D. Chapman, Cation exchange capacity, in: C.A. Black (Ed.), Method of Soil Analysis, SSSA, Madison, 1965, pp. 891–901.

[22] D.W. Ming, J.B. Dixon, Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method, Clay, Clay Miner. 35 (6) (1987) 463–468.

[23] Z. Li, R. Beachner, Z. McManama, H. Hanlic, Sorption of arsenic by surfactant-modified zeolite and kaolinite, Microporous Mesoporous Mater. 105 (3) (2007) 291–297.

[24] R.G. Allen, L.S. Pereira, D. Raes, M. Smith, Crop evapotranspiration-guidelines for computing crop water requirements, FAO irrigation and drainage paper 56, Rome, Italy, 1998.

[25] M.J. Malakouti, M.N. Geybi, Determining critical levels of efficient nutrients in soil, plant and fruit in order to increase quantity and quality of strategic country's crop, second ed., Nashreh Amuzesh Keshavarzi (In Farsi), 2000.

[26] D.R. Keeney, D.W. Nelson, Nitrogen inorganic forms, in: A.L. Page (Ed.), Methods of Soil Analysis, Part 2, Agronomy vol. 9, second ed., ASA, SSSA, Madison, 1982, pp. 643–698.

[27] J.M. Bremner, C.S. Mulvaney, Nitrogen total, in: A.L. Page (Ed.), Methods of Soil Analysis, Part 2, Agronomy vol. 9, second ed., ASA, SSSA, Madison, 1982, pp. 595–624.

[28] SAS, V 8.2. SAS Institute Inc., Cary, NC 27513-2414, USA, 1987.

[29] USEPA, Quality criteria for water, EPA 440/5-86-001, 1986.

[30] J. Nyamangara, L.F. Bergstrom, M.I. Piha, K.E. Giller, Fertilizer use efficiency and nitrate leaching in a tropical sandy soil, J. Environ. Qual. 32 (2) (2003) 599–606.

[31] M. Gheysari, S.M. Mirlatifi, M. Homaee, M.E. Asadi, G. Hoogenboom, Nitrate leaching in a silage maize field under different irrigation and nitrogen fertilizer rates, Agric. Water Manage. 96 (6) (2009) 946–954.

[32] B.W. Mercer, L.L. Ames, C.J. Touhill, W.J. Van Slyke, R.B. Dean, Ammonia removal from secondary effluents by selective ion exchange, J. Water Pollut. Control Fed. 42 (2) (1970) 95–107.

[33] M.A. Weber, K.A. Barbarick, D.G. Westfall, Ammonium adsorption by a zeolite in a static and a dynamic system, J. Environ. Qual. 12 (4) (1983) 549–552.

[34] C.T. MacKown, Role of Mineral Zeolites as Soil Amendments, University of Arizona, Tuscon, 1978.

[35] Z.T. Huang, A.M. Petrovic, Clinoptilolite zeolite influence on nitrate leaching and nitrogen use efficiency in simulated sand based golf greens, J. Environ. Qual. 23 (6) (1994) 1190–1194.

[36] H. Huang, X. Xiao, B. Yan, L. Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, J. Hazard. Mater. 175 (1–3) (2010) 247–252.

[37] T.S. Perrin, D.T. Drost, J.L. Boettinger, J.M. Norton, Ammonium-loaded clinoptilolite: a slow-release nitrogen fertilizer for sweet corn, J. Plant Nutr. 21 (3) (1998) 515–530.

[38] M.J. Semmens, Cation-exchange properties of natural zeolite, in: W.G. Pond, F.A. Mumpton (Eds.), Use of Natural Zeolites in Agriculture and Aquaculture, Zeo-Agriculture, Westview Press, Boulder, Co., 1984, pp. 45–54.

[39] M. Siljeg, L. Foglar, M. Kukucka, The ground water ammonium sorption onto Croatian and Serbian clinoptilolite, J. Hazard. Mater. 178 (1–3) (2010) 572–577.

[40] J. Schick, P. Caullet, J.L. Paillaud, J. Patarin, C. Mangold-Callarec, Batch-wise nitrate removal from water on a surfactant-modified zeolite, Microporous Mesoporous Mater. 132 (3) (2010) 395–400.

[41] F.E. Below, L.E. Gentry, Effect of mixed N nutrition on nutrient accumulation, partitioning, and productivity of corn, J. Fert. Issues 4 (3) (1987) 79–85.

[42] K.L. Barber, G.M. Pierzynski, R.L. Vanderlip, Ammonium/nitrate ratio effects on dry matter partitioning and radiation use efficiency of corn, J. Plant Nutr. 17 (5) (1994) 869–882.

[43] P.A. Joseph, R. Prasad, Correlation studies on ammonium/nitrate concentrations in soil and growth and yield of wheat, J. Agron. Crop Sci. 171 (1) (1993) 26–30.

[44] L.A. Rupp, Greenhouse culture, in: D.W. James, K.F. Toppers (Eds.), Utah Fertilizer Guide, Cooperative Extension Service, Utah State University, Logan, UT, 1989.

[45] G.M. Pierzynski, J.T. Sims, G.F. Vance, Soils and Environmental Quality, second ed., CRC Press, 2000.

[46] FAO, available from: http://www.fao.org/landandwater/aglw/cropwater/wheat.stm#uptake (accessed 6/06/2010).

[47] A.F. Bouwman, Direct emission of nitrous oxide from agricultural soils, Nutr. Cycl. Agroecosyst. 46 (1) (1996) 53–70.