

Effects of zeolite application on nitrate and ammonium retention of a loamy soil under saturated conditions

A. R. Sepaskhah^{A,B} and F. Yousefi^A

^AIrrigation Department, Shiraz University, Shiraz, Islamic Republic of Iran.

^BCorresponding author. Email: sepa@shirazu.ac.ir

Abstract. Nitrogen (N) loss from irrigated cropland, especially in rice paddies, results in low N-use efficiency and groundwater contamination. Soil conditions that increase ammonium and nitrate ion retention alleviate these problems. Clinoptilolite, a naturally occurring zeolite with high-exchange capacity, may be used to absorb ammonium and retard excess leaching of nitrate. The objectives of this research were to determine the effects of different rates of Ca–K-zeolite application (0, 2, 4, and 8 g/kg soil) on pore water velocity and leaching of ammonium and nitrate applied as ammonium nitrate fertiliser to a loam soil at a rate of 350 kg N/ha under saturated conditions similar to that of a rice paddy. The results indicate that Ca–K-zeolite applications of 4 and 8 g/kg soil increase the pore water velocity by 35% and 74%, respectively. The maximum relative concentration (c/c_0) for the nitrate breakthrough curve occurring at pore volume of about 0.5 was reduced by 15% with a zeolite application rate of 8 g/kg soil. When applying 40 cm of leaching water, leached nitrate was 75% and 63% of total applied nitrate at the soil surface with zeolite applications of 4 and 8 g/kg soil, respectively. Due to the high ion exchange capacity of zeolite, the application of zeolite at 2 g/kg soil is enough to increase the exchange sites in the soil in order to absorb the applied ammonium and prevent its leaching by the inflow water. The maximum ammonium concentration in the breakthrough curve for the zeolite application rate of 2 g/kg soil was reduced by 43% compared with the control treatment. The relationship between the hydrodynamic dispersion coefficient (D) for nitrate and pore water velocity (v) was not linear and it was correlated with squared pore water velocity. The coefficient of the relationship between D and v^2 was dependent on the zeolite application rate and linearly increased with this rate.

Additional keywords: nitrate displacement, ammonium displacement, nitrate diffusion coefficient, mean pore radius.

Introduction

Nitrogen (N) loss from irrigated cropland, particularly sandy soils, due to net repulsion of nitrate (NO_3^-) from negatively charged soil particle surfaces, contributes significantly to nitrate contamination in surface and groundwater and increases N application requirements to crops. Therefore, N-use efficiency is low in crop production (Vlek and Byrnes 1986; Pirmoradian *et al.* 2004). Farmers try to mitigate this problem in several ways, i.e. split nitrogen application, utilisation of slow release fertilisers, and incorporation of soil amendments that increase ammonium and nitrate ion retention. Because of its high exchange capacity, clinoptilolite, a naturally occurring zeolite, has often been used as an inexpensive cation exchanger to control ammonium (NH_4^+) release (Allen *et al.* 1993, 1996). Even so, nitrification of NH_4^+ still contributes to groundwater NO_3^- contamination.

To retard the movement of anionic species, minerals with high affinity for anions are needed. It has been found that surfactant-modified zeolite (SMZ), an inexpensive anion exchanger used as a fertiliser carrier to control nitrate release, can fulfill this requirement (Li and Bowman 2002). The surfactant molecules form bi-layers on zeolite surfaces and the zeolite reverses its surface charge, resulting in a higher affinity for negative charged anions. When a mixture of soluble NO_3^- and zeolite is

leached, the effluent NO_3^- concentration is quickly decreased to <0.2 mM with <2 pore volume of water used. In contrast, the effluent NO_3^- concentration remains >0.3 mM when NO_3^- loaded SMZ is flushed with >50 pore volumes of water (Li and Bowman 2002).

Zeolite tuffs are widely distributed in huge deposits in different regions of the Islamic Republic of Iran (Kazemian 2002). Clinoptilolite tuffs with a zeolite content of 75–95% are the most abundant natural zeolites (Kazemian 2002). Although there are a few active zeolite mines providing several types of natural and modified zeolite products for agricultural use and soil amendments, rare official reports are published to the present day on their use.

Pepper *et al.* (1982) applied a clinoptilolite type of zeolite at a rate of 8% to a sandy soil and indicated a decrease in NO_3^- and NH_4^+ leaching and an increase in the N-use efficiency of turf grass. Application of 8 t/ha of zeolite along with 60 kg/ha of N as urea to a light-textured soil increased the rice yield, whereas its effect was not pronounced in the heavy-textured soil (Kawoosi and Rahimi 2000). However, no data were shown on the amounts of nitrate leaching for different application rates of zeolite in the light-textured soil, and the water table was high in their experimental field. Um and Jung (1988) indicated that application of zeolite in pots with drainage for

rice growth reduced deep percolation, and leaching of nitrogen and potassium.

For better management of fertiliser application and controlling nitrate leaching, especially under flooded irrigation of paddy fields, the application of zeolite may be helpful. Knowledge of the rate at which nitrate moves with percolating water from the soil surface to groundwater under zeolite application is important, in order to determine the potential of zeolite for decreasing nitrate leaching and enhancing the N-use efficiency of crops.

According to Eberl (2002), application of a mixture of zeolite and urea fertiliser to soil resulted in less nitrate leaching by different mechanisms such as: (i) placement of urea in pores of zeolite crystals, (ii) decrease in transformation of urea to nitrate by nitrification, and (iii) decrease in the nitrification process by ammonium adsorption on zeolite. Further, zeolite application to loess soil with low infiltration resulted in enhancement of water infiltration by 50% (Xiubin and Zhanbin 2001). According to Ferguson and Pepper (1987) and Xiubin and Zhanbin (2001), although water infiltration increases, nitrate leaching may be inhibited. This discrepancy requires further investigation. In addition, the values of the hydrodynamic dispersion coefficient may be varied by different application rates of zeolite.

The objectives of this research were to determine the effects of different rates of zeolite application on pore water velocity, the hydrodynamic dispersion coefficient, and leaching of ammonium and nitrate applied as ammonium nitrate fertiliser to a loam soil under saturated conditions, such as that of a paddy field.

Methods and materials

The experiment studying applied ammonium and nitrate leaching under saturated condition was conducted in soil columns. A loam soil from 0 to 0.20 m was re-packed in PVC tubes with internal diameter 0.11 m and height 0.30 m, with bulk density of 1.23 g/cm³ after soil settlement. The bottom of the column was sealed with plastic screen with mesh number 40. The experimental soil contained 40% sand, 47% silt, 13% clay, and 2.2% organic matter with pH 7.9, electrical conductivity (EC) of saturation extract 0.45 dS/m, and cation exchange capacity (CEC) 56 cmol/kg clay. Loam soil was used for its high nitrate-leaching ability, which is found in some of the paddy fields in the study area.

Before re-packing the soil in the column, it was passed through a 2-mm screen and mixed with Ca-K-zeolite (clinoptilolite) at application rates of 0, 2, 4, and 8 g/kg soil (equivalent to 0, 5, 10, and 20 t/ha). Each zeolite application treatment was replicated 3 times. The saturated water extract of the zeolite had a pH 7.47 and an EC 5.81 dS/m. The CEC of zeolite was about 140 cmol/kg. Most (99%) of the zeolite particles were <2.0 mm in diameter and the diameter of the 50% of zeolite particles (D₅₀) was about 0.6 mm.

The soil column was immersed in a water bucket to be saturated from the bottom. After saturation, the soil column was placed on a tripod. A solution of ammonium nitrate with 2290 mg N/L (equivalent to 350 kg N/ha) was uniformly added to the saturated soil surface. Farmers usually use a high application rate of N for paddy fields in the region with heavy-textured

soil (about 200 kg N/ha). In the present investigation with loam soil of higher leaching ability for nitrate, a higher rate of nitrogen application was used. Immediately after penetration of ammonium nitrate solution into the soil, tap water was connected to the soil column to hold a constant 0.5 cm water height on the soil surface. The tap water had similar chemical properties and salinity level to the irrigation water used in the region. The concentrations of nitrate N and ammonium N in the tap water were 4.4 and 0.1 mg/L, respectively. The effluent from bottom of the soil column was collected in a beaker and its volume was measured at different time intervals. Samples from the effluent (50 cm³) were used for determining NO₃⁻ by spectrophotometer as described by American Public Health Association (1992). The ratio of effluent NO₃⁻ concentration to the surface added nitrate solution (6.61 g/L) was calculated as c/c_0 , and the cumulative effluent volume was calculated as pore volume (1 pore volume is 1390.5 cm³ for the experimental column). The relationship between c/c_0 and pore volume was drawn as a breakthrough curve. Samples from the effluent were also used to determine ammonium by the colourimetric method using a special filter for ammonia as described by American Public Health Association (1992).

The volume of cumulative effluent was divided by the soil column area and plotted as a function of elapsed time. The slope of this linear relationship is considered as soil water flux. The mean pore water velocity was calculated by dividing soil water flux by soil porosity (0.53).

The parameters were statistically analysed and the mean values in different treatments were statistically compared by least square difference method (Steel *et al.* 1997).

Theoretical analysis

The leaching of NO₃⁻ was assumed to be described by the 1-dimensional advection–dispersion equation as follows:

$$\partial c / \partial t = D (\partial^2 c / \partial x^2) - v (\partial c / \partial x) \quad (1)$$

where c is the NO₃⁻ concentration in effluent at the bottom of the soil column (mg/L), t is the time (s), D is the combined chemical diffusion and hydrodynamic dispersion coefficient (cm²/s), x is the depth (cm), and v is the average pore-water velocity over the area (cm/s). The general solution to Eqn 1 subjected to the initial condition of zero concentration and the boundary condition of an arbitrary concentration imposed at the soil surface (c_0) can be expressed by the following equation as described by Jury and Sposito (1985):

$$c/c_0 = L / \left[2(\pi D t^3)^{1/2} \right] \exp \left[-(L - vt)^2 / (4Dt) \right] \quad (2)$$

where L is the reference depth of direct extraction (column length) in cm. Taking the derivative of Eqn 2 and equating it to zero results in the following equation for determining the combined diffusion and hydrodynamic dispersion coefficient (D):

$$(c/c_0)_{\max} = v^{0.5} / \left[2(\pi D/L)^{0.5} \right] \quad (3)$$

where $(c/c_0)_{\max}$ is the maximum amount of c/c_0 in the breakthrough curve. Considering a new derivation of the Taylor-Aris theory of solute dispersion in a capillary (Gupta and Bhattacharya 1983), the relationship between diffusion

Table 1. Mean pore water velocity at different zeolite application rates
Means followed by the same letters are not significantly different at $P = 0.05$ by l.s.d. test

Zeolite application rates (g/kg)	Mean pore water velocity (cm/min)
0	0.23a
2	0.25ab
4	0.31b
8	0.40c

coefficient of NO_3^- in soil and hydrodynamic dispersion is as follows:

$$D = r_0^2 v^2 / (48 D_s) \quad (4)$$

where D_s is the diffusion coefficient of NO_3^- in soil (cm^2/s), and r_0 is the mean soil pore radius (cm).

Determination of mean soil pore radius

A soil column with a diameter of 0.02 and a height of 0.30 m was used. The bottom of this soil column was immersed in a Petri dish filled with 95% ethyl alcohol to be absorbed by the soil column. The rate of alcohol rise in the soil column was measured. Then, the relationship between the rate of capillary rise of alcohol and the inverse of the capillary rise was determined by linear regression analysis. The maximum capillary rise was estimated by substituting the rate of capillary rise equal to zero in this linear equation. The maximum capillary rise was used in the capillary rise equation to estimate the mean soil pore radius (r_0) as follows (Letey *et al.* 1962):

$$h = 2\gamma\cos\alpha / (\rho G r_0) \quad (5)$$

where h is the maximum capillary rise (cm); γ is the surface tension of ethyl alcohol (dyne/cm); α is the soil contact angle assumed to be zero for ethyl alcohol; ρ is the density of ethyl alcohol (g/cm^3); and G is the acceleration due to gravity (cm/s^2).

Results and discussion

Soil pore volume velocity

The mean soil pore volume velocities at different rates of zeolite application are shown in Table 1. The zeolite application rate of 2 g/kg soil was not effective in enhancing the pore water velocity. However, the higher rates of application (4 and 8 g/kg soil) significantly increased pore water velocity by 35% and 74%,

Table 2. Mean values of maximum c/c_0 and the pore volumes for the occurrence of $(c/c_0)_{\max}$ for different zeolite application rates
Means followed by the same letters are not significantly different at $P = 0.05$ by l.s.d. test

Zeolite appl. rate (g/kg)	Mean nitrate c_{\max} (mg/L)	Mean nitrate $(c/c_0)_{\max}$	Mean pore volume for $(c/c_0)_{\max}$	Mean maximum NH_4^+ (mg/L)
0	817.0a	0.235	0.49	0.40a
2	801.3a	0.227	0.51	0.23b
4	787.5a	0.224	0.49	0.20b
8	712.1b	0.200	0.56	0.20b

respectively. The effect of application rate 8 g/kg soil was greater than of 2 and 4 g/kg. Similar results have been reported by Xiubin and Zhanbin (2001). They applied mardinite-type zeolite to a

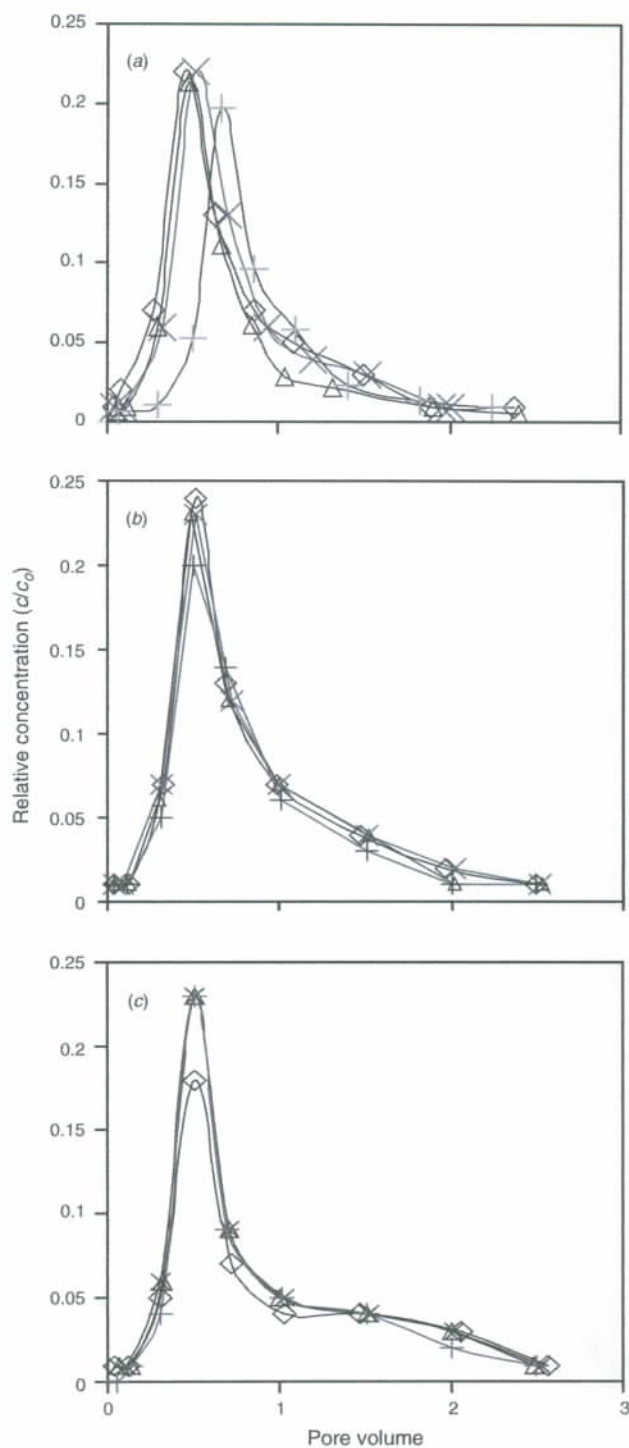


Fig. 1. Breakthrough curves for nitrate at different replications and zeolite application rates: (a) first replication, (b) second replication, (c) third replication; \diamond , 0 g/kg; \times , 2 g/kg; Δ , 4 g/kg; $+$, 8 g/kg.

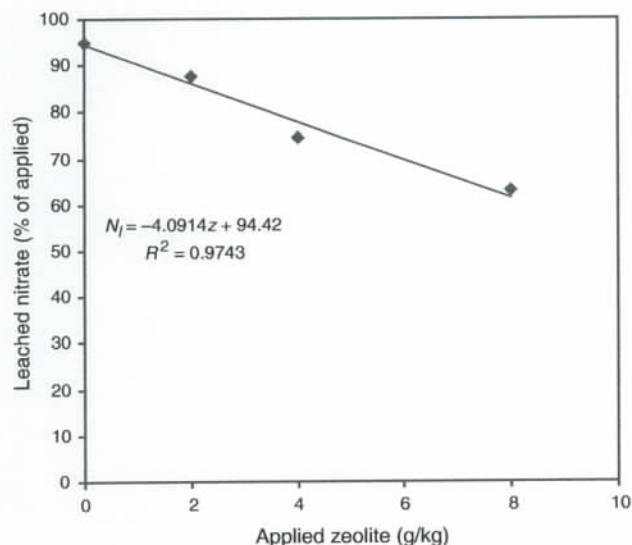


Fig. 2. Relationship between leached nitrate N_l as a percent of applied and applied zeolite z .

very fine calcareous soil and increased the infiltration rate and reduced the surface runoff by 50% on steep slopes.

Nitrate displacement

The maximum concentrations of nitrate in the effluent were statistically analysed and their mean values compared by least square difference procedure. The results are shown in Table 2. It is indicated that the c_{max} was significantly reduced at zeolite application rate of 8 g/kg of soil by about 15%.

The breakthrough curves for different zeolite application rates are shown in Fig. 1. The maximum values of c/c_0 and their corresponding pore volumes are presented in Table 2. The values of $(c/c_0)_{max}$ occurred at pore volume of about 0.5 and were <0.25 . The breakthrough curves are not completely bell shape and show a tail on the right-hand side as the pore volume increases. This indicates that although the soil column was re-packed, the soil was still somewhat structured causing the late arrival of solute. This is attributed to the gradual release of the solute to the flow channel by diffusion after the pulse has passed through the column. This solute initially was removed from the flow channels by transverse diffusion into the stagnant regions of the soil while the pulse was passing through the column (Jury *et al.* 1991, p. 228).

The maximum value of $(c/c_0)_{max}$ occurred in pore volume of about 0.5. According to theoretical interpretation, it should occur at pore volume of 1.0 for non absorbent ions, i.e. nitrate. This is due to the fact that water velocity is maximum in the middle of pores; therefore, the $(c/c_0)_{max}$ reaches the bottom of the soil column faster with lower a value than 1.0 for pore volume. However, anion exclusion occurs when negatively charged surfaces are present. Anions are repelled from such surfaces and accumulate in the centre of pores. Because water flow velocity is maximum in the centre of pores, the average anion movement will be faster than the average water movement (Leij and van Genuchten 2002).

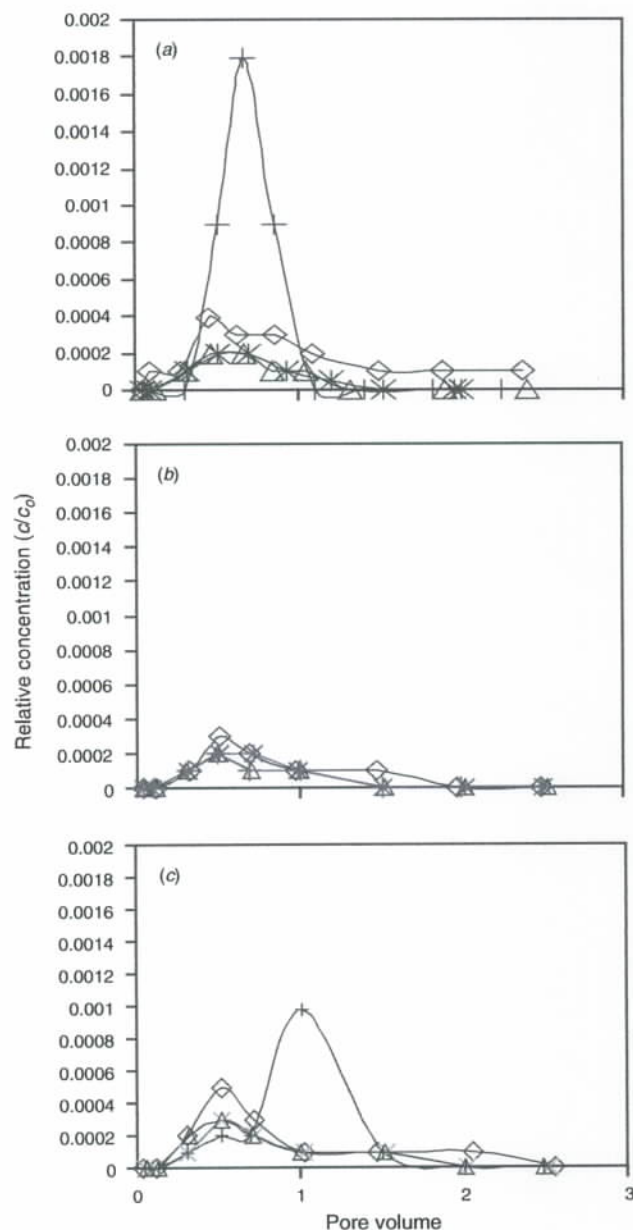


Fig. 3. Breakthrough curves for ammonium at different replications and zeolite application rates: (a) first replication, (b) second replication, (c) third replication; \diamond , 0 g/kg; \times , 2 g/kg; Δ , 4 g/kg; $+$, 8 g/kg.

The values of $(c/c_0)_{max}$ for zeolite application rate of 8 g/kg soil were decreased by 15% compared with the control treatment, indicating that some portion of the applied N was held in the soil by application of zeolite and was not leached by water. This shows that by increasing the zeolite application rate the leached nitrate was decreased.

In general, after passing 40 cm of water, the area under the breakthrough curves for different zeolite application rates was determined and the results were compared with the amount of applied nitrate to the soil surface. The ratio of total amount of

leached nitrate to applied nitrate was correlated with the applied zeolite (Fig. 2). The percentage of leached nitrate decreased with an increase in zeolite application rate according to the following equation:

$$N_l = -4.09z + 94.4, R^2 = 0.97 \quad (6)$$

where N_l is the percentage of leached nitrate and z is the zeolite application rate in g/kg. A decrease in nitrate leaching results in a decrease in groundwater pollution, economic use of N, and increased availability of N for crop growth. With zeolite application of 10 g/kg soil, the leached nitrate is reduced to 50%.

Ammonium displacement

Breakthrough curves for different zeolite application rates are shown in Fig. 3 and the maximum concentrations of ammonium in the effluent in Table 2. The maximum concentration of NH_4^+ was significantly reduced by zeolite application rate of 2 g/kg soil compared with the control and there was no difference in the values of $(\text{NH}_4^+)_{\text{max}}$ for other zeolite application rates. This indicates that zeolite application of 2 g/kg soil adequately increased the exchange sites in the soil to absorb the applied NH_4^+ and prevent its leaching by the inflow water. The value of maximum NH_4^+ concentration in the breakthrough curve for the zeolite application rate of 2 g/kg soil was reduced by 43% compared with the control treatment.

Zeolite effect on hydrodynamic dispersion of nitrate

The values of pore water velocity (v) and $(c/c_o)_{\text{max}}$ for nitrate were used in Eqn 3 to calculate the hydrodynamic dispersion (D). The results showed that the values of D increased at higher pore water velocity due to zeolite application. However, this relationship is not linear like the one presented by Jury *et al.* (1991), since the linear relationship resulted in a negative

intercept, i.e. the diffusion coefficient of nitrate should be negative and the dispersivity is 0.004 cm, a very small value, which is not physically sound.

According to Eqn 4, the relationships between D and v^2 for different zeolite application rates are shown in Fig. 4. The relationship between hydrodynamic dispersion coefficient (D) for nitrate and pore water velocity (v) was not linear, and D was correlated with squared pore water velocity. The coefficient of the relationship between D and v^2 (a) was dependent on the zeolite application rate and linearly increased with this rate as follows:

$$a = 1.137 + 0.218z, R^2 = 0.97 \quad (7)$$

where a is the coefficient of the relationship between D and v^2 and z is the zeolite application rate in g/kg soil. The slopes of these relationships are the values of $r_o^2/(48D_s)$. The mean radius of pores is 1.71×10^{-3} cm for the soil used in this study (A. R. Sepaskhah, unpublished data). Therefore, using this value in the slope of $D = 1.2717v^2$, i.e. 1.2717, the value of D_s equal to 4.8×10^{-8} cm²/s is obtained. It may be assumed that D_s is invariable in zeolite-treated soils, so the value of the mean pore radius of treated soil may be affected by zeolite application rates. Using the slopes of relationships between D and v^2 for different zeolite application rates (Fig. 4) and the value of D_s , the mean pore radius of treated soil with different zeolite application rates were estimated. These values were 1.84×10^{-3} , 2.09×10^{-3} and 2.61×10^{-3} cm for zeolite application rates of 2, 4, and 8 g/kg soil, respectively. The mean pore radius was increased with the application rates of zeolite according to the following equation:

$$r_o = 16.6 + 1.16z, R^2 = 0.986 \quad (8)$$

where r_o is the mean pore radius of soil in μm and z is the zeolite application rate in g/kg soil.

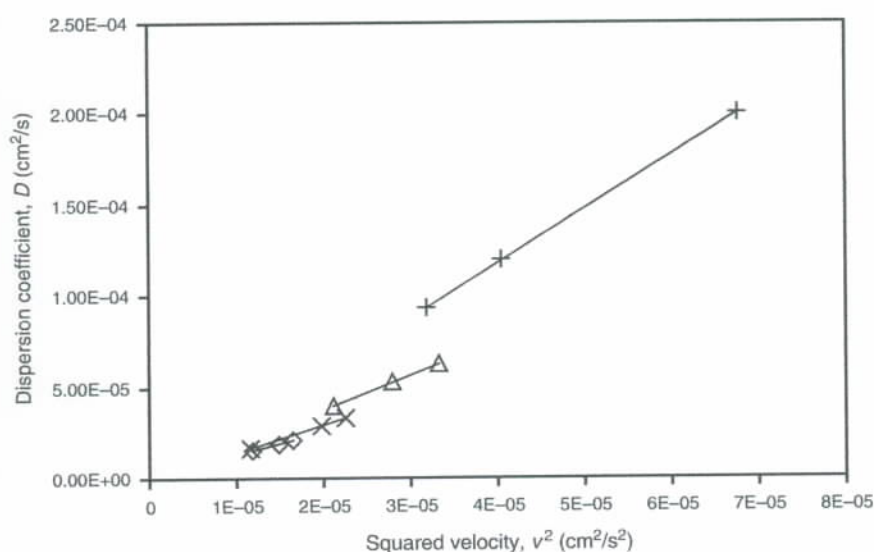


Fig. 4. Relationship between hydrodynamic dispersion coefficient and squared pore water velocity at different zeolite application rates: \diamond , 0 g/kg; \times , 2 g/kg; Δ , 4 g/kg; $+$, 8 g/kg.

Conclusions

It is concluded that Ca-K-zeolite application of 4 and 8 g/kg soil increases the pore water velocity by 35% and 74%, respectively. The maximum relative concentration (c/c_0) for nitrate breakthrough curve occurring at pore volume of about 0.5 is reduced by 15% because of zeolite application rate of 8 g/kg soil. By applying 40 cm of leaching water, the leached nitrate is 75% and 63% of the total applied nitrate at the soil surface using zeolite at 4 and 8 g/kg soil, respectively. Since zeolite has a high ion exchange capacity, it is shown that the application of zeolite at 2 g/kg soil is sufficient to increase the exchange sites in soil in order to absorb the applied NH_4^+ and inhibit its leaching by the inflow water. The value of maximum NH_4^+ concentration in the breakthrough curve for the zeolite application rate of 2 g/kg soil is reduced by 43% compared with the control treatment. The relationship between hydrodynamic dispersion coefficient (D) for nitrate and pore water velocity (v) is not linear and it is correlated with squared pore water velocity. The coefficient of the relationship between D and v^2 is dependent on the zeolite application rate and linearly increases with this rate.

It is found that the value of hydrodynamic dispersion coefficient (D) depends on the zeolite application rate. Therefore, when N fertiliser is applied with zeolite to the soil, Eqn 2 is used to estimate the breakthrough curve. In this equation proper value of D should be used which varies with zeolite application rates.

Acknowledgments

This research was supported by the Shiraz University Research Council under research grant no. 83-GR-AGR 42.

References

- Allen ER, Hossner LR, Ming DW, Henninger DL (1993) Solubility and cation exchange in phosphate rock and saturated clinoptilolite mixture. *Soil Science Society of America Journal* **57**, 1368–1374.
- Allen ER, Ming DW, Hossner LR, Henninger DL (1996) Release rates of phosphorus, ammonium, and potassium in clinoptilolite-phosphate rock systems. *Soil Science Society of America Journal* **60**, 1467–1472.
- American Public Health Association (1992) 'Standard methods for examination of water and wastewater.' (American Public Health Association: Washington, DC)
- Eberl D (2002) Controlled release fertilizer using zeolite. U.S. Geological Survey Technology. URL: www.usag.gov/tch-transfer/factsheet/94-0666.html.
- Ferguson GA, Pepper IL (1987) Ammonium retention in sand amended with clinoptilolite. *Soil Science Society of America Journal* **51**, 231–234.
- Gupta K, Bhattacharya N (1983) A new derivation of the Taylor-Aris theory of solute dispersion in a capillary. *Water Resources Research* **19**, 945–951.
- Jury WA, Gardner WR, Gardner WH (1991) 'Soil physics.' (John Wiley & Sons, Inc.: New York)
- Jury WA, Sposito G (1985) Field calibration and validation of solute transport models for the unsaturated zone. *Soil Science Society of America Journal* **49**, 1331–1341.
- Kawoosi M, Rahimi M (2000) Effect of zeolite application on rice yield in light and heavy texture soils. Research Report, Rice Research Institute, Education and Research Organization, Ministry of Jihad-Agriculture, I.R. of Iran. (in Farsi).
- Kazemian H (2002) Zeolite science in Iran: a brief review. In 'Zeolite '02, 6th International Conference Occurrence, Properties and Utilization of Natural Zeolite'. Thessaloniki, Greece. (Ed. P Misaelides) pp. 162–163. (Aristotle University: Thessaloniki, Greece)
- Leij FJ, van Genuchten MTh (2002) Solute transport. In 'Soil physics companion'. (Ed. AW Warrick) pp. 189–248. (CRC Press: New York)
- Lety J, Osborn J, Pelishek RE (1962) Measurement of liquid solid contact angle in soil and sand. *Soil Science* **93**, 149–153. doi: 10.1097/00010694-196203000-00001
- Li Zh, Bowman RS (2002) Use of surfactant-modified zeolite as fertilizer carriers to control nitrate and sulfate release. In 'Zeolite '02, 6th International Conference on Occurrence, Properties and Utilization of Natural Zeolite'. Thessaloniki, Greece. (Ed. P Misaelides) pp. 204–205. (Aristotle University: Thessaloniki, Greece)
- Pepper IL, Ferguson GA, Kneebone WR (1982) Clinoptilolite zeolite: a new medium for turfgrass growth. In 'Proceedings of ASA'. Agronomy Abstract, p. 145.
- Pirmoradian N, Sepaskhah AR, Maftoun M (2004) Deficit irrigation and nitrogen effects on nitrogen-use efficiency and grain protein of rice. *Agronomie* **24**, 143–153. doi: 10.1051/agro:2004011
- Steel RG, Torrie JH, Dickie DA (1997) 'Principles and procedures of statistics: a biometrical approach.' 3rd edn (McGraw Hill: New York)
- Um MH, Jung PK (1988) Effect of zeolite application on rice yields by soil texture. *Agricultural Science Institution* **29**, 60–65.
- Vlek PLG, Byrnes BH (1986) Improving nitrogen fertilization in mechanized rice culture. *Fertilizer Research* **9**, 131–147. doi: 10.1007/BF01048699
- Xiubin H, Zhanbin H (2001) Zeolite application for enhancing water infiltration and retention in loess soil. *Resources, Conservation and Recycling* **34**, 45–52. doi: 10.1016/S0921-3449(01)00094-5

Manuscript received 29 May 2006, accepted 27 June 2007