In Press, Pre-Proof Version

The Effect of Zeolite on the Hydraulic Parameters of Soil and Simulation of Water Flow Using HYDRUS-2D

M. Shadan[1], J. Behmanesh[1]*, S. Besharat[1], and N. Azad[1]

Abstract

Zeolites are recommended to utilize in agricultural sector due to their water holding and cation exchange capacity. Effect of zeolite on the hydraulic parameters of sandy loam soil was investigated and HYDRUS-2D was used to simulate the movement of water in the soil. Data needed were collected by conducting laboratory experiments. The studied treatments included four levels (zero, 5, 10, and 15 gr kg^{-1} of soil) to determine the effect of zeolite on hydraulic parameters including saturation moisture (θ_s) residual moisture (θ_r), shape parameter (n), point Check air permeability (α) and saturated hydraulic conductivity (K_s) of the soil. Four rounds of irrigation were done based on readily soil moisture and the soil moisture values before and after irrigation were measured using the Wet sensor in the depth and radial directions and recorded for 45 days. The initial value of hydraulic parameters including θ_s, θ_r, α, n and K_s were determined using Rosetta. Results showed that with increasing in the amount of zeolite, the parameters θ_s, θ_r and n increased and the value of α decreased, which indicated a decrease in the rate of water discharge from the soil. While the values of K_s tended to decrease. In fact, the mixing zeolite with soil causes to hold more water because of micro-pore structure of zeolites. The HYDRUS-2D model with the efficiency coefficient (EF), which shows the quality and how to fit the observed and estimated data, varied between 0.82 and 0.97, which shows the high efficiency of model in simulating humidity.

Keywords: Advance curve, Pot, Soil texture, Water holding capacity.

1-Introduction

Hydraulic properties of soil play an important role in the water cycle. They are used as fundamental information in the design of irrigation and drainage systems, hydrological issues, and soil quality assessment. These properties can be measured or estimated using different direct and inverse methods. However, direct measurement of these properties is difficult, costly, and time-consuming. Moreover, due to their high spatial and temporal variability, a large number of samples are required for accurate characterization (Asgarzadeh et al., 2014). The HYDRUS-2D

[1] Department of Water Engineering, Faculty of Agriculture, Urmia University, Urmia, Islamic Republic of Iran.
*Corresponding author; e-mail: j.behmanesh@urmia.ac.ir

model, developed by Šimůnek and colleagues (Šimůnek et al., 1999), is a Windows-based model for analyzing water flow, solute transport, and heat transfer under two-dimensional conditions. It is capable of estimating the hydraulic properties of soil and/or solute transport parameters using an inverse solution approach. The model uses the linear finite element Galerkin method for the numerical solution of governing equations and the Levenberg-Marquardt method for parameter optimization (Marquardt, 1963).

The HYDRUS model has been used in numerous laboratory and field studies to simulate soil moisture and hydraulic properties (Siyal and Skaggs, 2009). Several studies have investigated the effect of zeolite on soil hydraulic parameters (Colombani et al., 2014; Soudejani et al., 2020), among which some researchers have used the HYDRUS model to simulate the effect of zeolite on soil moisture (Li et al., 2021; Ibrahim and Alghamdi, 2021; Colombani et al., 2015).

In a study conducted by Colombani et al (2014), they examined changes in flow parameters and salt transport resulting from adding zeolite to silty-loamy soil. They reported that zeolites enriched with NH_4^+ increased water retention capacity in silty-loamy soils, thus limiting water and salt losses. Additionally, another study conducted by Ibrahim and Alghamdi (2021) investigated the effect of particle size of natural clinoptilolite zeolite (CZ) on moisture content (WC) and hydraulic properties of sandy loam soil and simulated it using the HYDRUS-1D model. They reported that available water content and soil water storage were increased by 3.6-14.7% and 6.8-10.5% respectively. The changes in infiltration rate and hydraulic conductivity were statistically significant, with a reduction of 25.6% and 19.3% compared to the control, only for the smallest CZ particle size. Their results demonstrated that the HYDRUS-1D model accurately simulated soil moisture content and water retention capacity. Their results also showed that the use of CZ in the form of nano-sized particles increased water retention capacity and reduced hydraulic conductivity in soils with a light texture, thus improving water use efficiency and aiding water conservation in dry areas.

In sandy soils, the addition of organic matter can alter the physical and chemical properties by reducing large pores, water, and nutrient leaching rates (Blanco-Canqui and Lal 2009), thereby increasing water holding capacity. Therefore, improving soil structure and texture increases water availability, nutrient availability, and crop yield (Samreen et al. 2017).

One of the commonly used mineral materials for improving the physical properties of soil, particularly increasing soil moisture retention capacity, is zeolite. Zeolites are natural or synthetic mineral compounds with a three-dimensional crystal structure with an open and highly porous network, which results in a large internal surface area (several hundred square meters per gram) and cation exchange capacity (McGilloway et al., 2003). The most widely used zeolite in Iran for agricultural purposes, especially for amending sandy soils due to nutrient leaching, is clinoptilolite. Among all aluminosilicate groups, clinoptilolite has the highest silica content, which gives it the highest absorption capacity among different types of natural zeolites (Reid et al., 2021; Samolej and Chalupnik, 2021). Due to the high ion exchange capacity of clinoptilolite and its strong affinity for absorption, it has received much attention in agriculture (Jha and Hayashi, 2009). These materials are highly hydrophilic and provide water and dissolved nutrient availability to plant roots easily when needed (Tohidi-Moghadam et al., 2009). Considering their properties, the use of zeolites with diverse applications is rapidly increasing in various fields (Sangeetha and Baskar, 2016). Several industrial applications, such as chemical, optical, and microelectronics industries, have been documented (Jarosz et al., 2022), and their use for environmental protection purposes has been reported (Belviso, 2020).

In recent years, zeolites have been widely used in agriculture, which is currently the main consumer of zeolite production worldwide (Szatanik-Kloc et al., 2021). They have been used as soil conditioners due to their impact on the chemical and physical properties of soil (Belviso et al., 2022). Generally, zeolites can alter the total porosity, pore size distribution, pore channel connectivity, and soil compaction with varying effects depending on the soil composition, nature of the zeolite, water properties, and even experimental conditions (Sepaskhah and Yousefi, 2007). Several articles have discussed the effects of zeolites on soil permeability (Szerement et al., 2014), saturated hydraulic conductivity (Jakkula et al., 2018), soil water content, and water holding capacity (Ravali et al., 2020).

They increase soil permeability, saturated hydraulic conductivity, water retention capacity, aeration, and many other factors (Jakkuld and Wani, 2018). In light-textured soils, such as sandy soils and loamy soils, the addition of zeolite usually has the effect of increasing the soil moisture characteristic curve and water retention capacity while reducing saturated hydraulic conductivity (Ks) and permeability (Colombani et al., 2015). In heavy-textured soils (such as clayey and silty-clayey soils), zeolites may have very different effects (Jarosz et al., 2022).

In another study Gholizadeh and Sepaskhah (2013), the effects of applying calcium-potassium zeolite on saturated hydraulic conductivity and water infiltration equation in soils with different irrigation salinities were investigated under laboratory conditions. The results showed that in all treatments with the same amount of zeolite and salinity, the final saturated hydraulic conductivity decreased as the soil texture became heavier. Additionally, in a specific soil texture and salinity, the application of zeolite up to a certain limit increased the saturated hydraulic conductivity. However, the optimal zeolite application rate varies for different soil textures (Szatanik et al., 2021). In another research Torkashvand and Shadparvar (2013), it was reported that the use of 10 grams of zeolite per kilogram of soil could retain a maximum of 8.4% of available moisture capacity and delay the wilting point in loamy sandy soils in Iran.

Razmi and Sepaskhah (2012) examined the effect of zeolite on saturated hydraulic conductivity and crack behavior in expanding silty clayey soils. Their results showed a significant increase in saturated hydraulic conductivity with the application of 8 grams of zeolite per kilogram of soil. According to studies conducted by Abedi-Koupai and Sohrabi (2004), using 8 grams of zeolite per kilogram of soil increased the volumetric moisture percentage by 3.5 to 8.4 times in sandy soil, 2.2 times in loamy soil, and 1.1 to 9.1 times in clayey soil compared to the control. In each soil texture and at each application level, adding moisture absorbers distanced the soil moisture characteristic curve from the control, indicating a significant difference in volumetric moisture percentage at each suction point of the curve compared to the control. In clayey and loamy soils, this difference increased the water retention in these textures. Furthermore, previous results have shown that the addition of different zeolite rates to soils has variable effects on their porosity, structure, and hydraulic properties (Pal et al., 2006).

Simulating soil moisture using the HYDRUS model in potted crops is a very suitable and novel research field. Crops are commonly grown in pots, but so far no research has been conducted on estimating soil hydraulic parameters using the HYDRUS-2D software in different zeolite treatments in potted experiments. Therefore, the purpose of this research was to investigate the effects of using different amounts of zeolite on soil hydraulic parameters in a light soil texture and to simulate the water flow of the soil treated with zeolite using HYDRUS-2D.

2. Materials and Methods

2.1. Site description

Experimental studies were conducted using 10 kg plastic pots (length of pot 25cm, top and down diameters 22 and 18cm respectively). It is mentioned that the whole of pot had not filled with soil. The height of soil in the pot was 22cm and the top radius of the filled soil approximately was 11cm and by creating a hole in the bottom of the pot, a structure similar to a lysimetric was created. Then, by placing a container with a lid under the pots and using a graduated container, the amount of outgoing water after each irrigation was measured (Figure 1). The pot floor was filled with a layer of 2 cm coarse sand as drainage. Then, the pots were placed on a platform 20 cm above the ground. Clinoptilolite zeolite was added and mixed at four levels (without zeolite, 5, 10 and 15 grams of zeolite per kilogram of soil). The bulk density of the soil was determined using the cylinder method (Balk and Hartg, 1986), and the soil texture was determined using the hydrometer method (Klute, 1986) and electrical conductivity (EC) and acidity (pH) using an EC meter and pH meter and The moisture content at the field capacity point and wilting point were measured by pressure plates (Black et al., 1965). The physical and chemical characteristics of the soil are shown in Table 1.

The zeolite used in this study was clinoptilolite type zeolite obtained from the hot water zeolite mine in Semnan province. The zeolite was crushed using a rod mill and sieved to a particle size of 0.075-0.180 mm using a sieve. The properties of the zeolite used are shown in Table 2. Irrigation time was also determined based on soil moisture in the control pot and using equation 1:

$$D = \frac{(\theta_{fc} - \theta_{pwp})}{100} D_{rz} \times \text{MAD} \qquad (1)$$

Where, θ_{fc} moisture content of field capacity (L^3L^{-3}), θ_{pwp} moisture at wilting point (L^3L^{-3}), D readily soil moisture (L), D_{rz} depth of the pot (L) and MAD optimal or accessible water content for the witness. The investigations showed that the readily soil moisture was about 50 percent of available water content. After 14-day, the soil moisture was receiving to this water content and this subject was the reason of selecting 14-day irrigation frequency. The same amount of irrigation water was used for all treatments. Since any crop was not cultivated, then with the same amount of irrigation water the mentioned effect can better compare in the different treatments.

Figure 1. Schematic view of the pot in the laboratory.

Table 1. Physical properties of the experimental soils.

Depth (cm)	Texture	Sand	Silt	Clay	Bulk density	pH	EC
			%		(g/cm^3)	-	(ds/m)
0-30	Sandy loam	66	19	15	1.43	7.67	0.850

Table 2. Chemical analysis of zeolite used.

LOI*	CaO	Na_2O	Al_2O_3	SiO_2	P_2O_5	TiO_2	MnO	Fe_2O_3	Cl	CEC
			(%)						ppm	(meq gr^{-1})
10-12	0.6	3.8	11	68.5	0.01	0.03	0.04	0.2-0.9	1600	2.6

In this study, the HYDRUS 2D model was used to simulate soil moisture based on the numerical solution of the Richards equation (Simunek et al., 2006). Due to the high symmetry of the right and left halves of the soil moisture profile under realistic conditions, the simulation of the moisture profile was only performed for the right half and then compared with actual conditions. In this research, to define the two-dimensional simulation environment in the HYDRUS model, a pot with a top width of 11 cm, a bottom width of 9 cm, and a height of 22 cm was defined.

The irrigation cycle was 14 days as the average irrigation interval based on (the readily soil moisture was about 50 percent of available water content) in total 4 stages of irrigation, and in each irrigation cycle, a variable water height was established on the top of the pots for irrigation.

2.2. Modeling soil moisture distribution using the HYDRUS-2D model

The HYDRUS-2D model is a simulation model that simulates water and solute flow in one, two, or three dimensions under saturated and unsaturated conditions. This model simulates the two and three-dimensional movement of water in soil using the numerical solution of Richard's equation. In this study, the two-dimensional form of the model was used, which assumes homogeneity and uniformity, and the two-dimensional movement is presented as equation 2 (Celia et al., 1990).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\frac{\partial h}{\partial x}\right] + \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] \quad (2)$$

Where: θ is the volumetric soil moisture content (L^3L^{-3}), h is the water pressure in the soil (L), x and z are the horizontal and vertical coordinates (L), t is the time (T), K(h) is the unsaturated hydraulic conductivity of the soil (LT^{-1}). Considering the water movement assumption in the initial part of the software, the geometry includes a pot length of 22 centimeters, a vertical soil column, and one soil layer. The selected model for the hydraulic properties of the soil is the Van Genuchten-Mualem model. The hydraulic characteristics of the soil were obtained using the Van Genuchten relationship (Van Genuchten, 1990), which is described as follows:

$$\theta(h)=\begin{cases}\theta_r + \frac{\theta_s+\theta_r}{(1+\alpha h^n)^m} & h < 0 \\ \theta_s & h \geq 0\end{cases} \quad (3)$$

$$K(h)= K_s S_e^{\,l}\left[1-(1-S_e^{\,1/m})^m\right]^2 \quad (4)$$

Where:

$$S_e = \frac{\theta(h)-\theta_r}{\theta_s-\theta_r} \qquad , m=1-\frac{1}{n} \qquad , n>1$$

In these relationships, there are independent hydraulic parameters θ_r, θ_s, K_s, α, and n, which represent residual moisture ($L^3\ L^{-3}$), saturation moisture ($L^3\ L^{-3}$), saturated hydraulic conductivity of soil (LT^{-1}), inverse of air entry suction (L^{-1}), and pore size distribution index (-), respectively. The relative saturation S_e and l in the hydraulic conductivity function represent the parameters for the pore connectivity and tortuosity, respectively, which were estimated as 0.5 for most soils (Mualem, 1976). It is necessary to accurately determine these parameters for solving the Richards equation numerically in HYDRUS 2D. The initial value parameters were estimated for hydraulic conductivity, K_s, residual moisture, θ_r, and saturation moisture, θ_s, in Van Genuchten form, using the information of soil mechanical analysis (soil texture) and bulk density measurement in Rosetta model.

The simulation in the HYDRUS model is conducted by numerically solving the governing equations for water flow based on the appropriate selection of values for the parameters in these equations, as well as the determination of the appropriate initial and boundary conditions (Crevoisier *et al.,* 2008). Generally, the calibration process of the model was applied to the calibration of soil hydraulic parameters (Van Genuchten-Mualem parameters). For calibration of soil hydraulic parameters, including saturated hydraulic conductivity (K_s), shape parameters (n and α), residual moisture (θ_r), and saturation moisture (θ_s) were used.

In order to measure the amount of pots evaporation in laboratory conditions, the simplest form of the water balance equation. In this research, the amount of irrigation water and drained water from the pots were measured and used in the equation 5, (Hillel, 2004).

$$E_s = I - \sum(\Delta\theta)\, d - D \quad (5)$$

Where, E_s is the evaporation from the soil surface (mm), I is the amount of irrigation water (mm), $\Delta\theta$ is the moisture changes in the soil profile (mm), d is the depth of the moisture layer (mm) and D is the depth of the drained water (mm).

Due to any crop was not cultivated, transpiration was considered to be zero.

In this experiment, the soil moisture in the treatments was daily measured at center of the pods at a vertical distance of 5 cm using the Wet sensor (Delta-T, made in England). This sensor was portable and can be moved from one pot to another Figure 2. Based on Figure 2, the soil profile was considered as a checkered grid and these readings were recorded at a horizontal interval of 11cm and a vertical interval of 5cm after each irrigation for 45 days.The initial conditions for water distribution in the soil were determined by the moisture content present in the soil before irrigation at multiple points, using a Wet sensor device, measured in the laboratory before the experiment for the soil layer (0 to 22 cm), and their averages were used in the model. Initial and boundary conditions for water flow: The initial conditions for water distribution in the soil were determined by the moisture content present in the soil before irrigation at multiple points, using a Wet sensor instrument, measured in the laboratory before the experiment for the soil layer (0 to 22 cm), and their averages were used in the model. The upper boundary condition during irrigation was considered as a variable water head. The end of the model was considered as a free drainage boundary condition because this type of boundary condition is used for most soil columns in laboratory conditions and for cases where they are in contact with air from below and have zero pressure Figure 2.

Figure 2. A representation of a physical model.

2.3. Performance Evaluation Indices of Models

In this research, 80% of the measured data were used for model coefficient calibration and 20% of the data were used for validation. For evaluating the efficiency of model validation and credibility of the model, evaluation indices such as Efficiency coefficient of the model (EF), the normalized root mean square error (NRMSE), coefficient of residual mass (CRM) and the coefficient of determination (R^2) were used for simulated and observed soil moisture values (Adeboye and Alatise, 2007; Loague and Green).

$$EF = 1 - \frac{\sum_i^n (P_i - O_i)^2}{\sum_i^n (O_i - \bar{O})^2} \quad (6)$$

$$NRMSE = \frac{RMSE}{\bar{O}} 100 \quad (7)$$

$$CRM = 1 - \left[\frac{\sum_{i=1}^n P_i}{\sum_{i=1}^n O_i}\right] \quad (8)$$

$$R^2 = 1 - \frac{\sum_i^n (P_i - O_i)^2}{\sum_i^n (O_i - O_i)^2} \quad (9)$$

In these relationships: RMSE stands for Root Mean Square Error, P_i represents simulated values, O_i represents observed values, $\bar{O}$ represents the average observed values, $\overline{(Pi)}$ represents the average measured values, and n represents the number of samples being examined. The negative value of EF indicates that the average of the measured values has a better estimate than the predicted values. The simulation is considered excellent with NRMSE less than 10%, as good if NRMSE is greater than 10 and less than 20%, fair if NRMSE is greater than 20 and less than 30%, and poor if NRMSE is greater than 30% (Bannayan and Hoogenboom 2009). The values of the CRM index show the ability of the model to estimate the values compared to the measured values.

The negative CRM values indicate the tendency of the model to overestimate the measurements, the closer the CRM value is to zero, the better the simulation effect will be (Jamieson et al., 1991). R^2 index expresses the simulation process and the closer it is to one, the more accurate the simulation process is. If all measured and simulated data are identical, CRM and NRMSE are zero and EF is unit (Loague and Green, 1991).

3. Results and Discussion

The application of zeolite in light soil increases the number of fine pores in the soil, leading to a decrease in k_s compared to the treatment without zeolite. Clearly, in light soils, the use of zeolite to reduce the amount of k_s is desirable because it reduces water transfer capacity in the soil, resulting in less vertical infiltration and water loss. The results of this study were consistent with the studies conducted by Jakkula et al., 2018. Similar results were also observed by Gholizadeh and Sepaskhah, 2013 and Szatanik-Kloc et al., 2021.

Regarding the values of soil hydraulic parameters, the percentage of θ_s increased with increasing zeolite content, with the highest value recorded at 60.1% cm³/cm³ in the treatment with 15 grams of zeolite per kilogram of soil (Table 3). Due to the fine and porous nature of zeolite, the weight moisture content has also increased. Since light soils have a limited capacity to store and retain moisture, adding a superabsorbent (zeolite) to the soil not only increases the water retention capacity in the soil but also reduces the evaporation rate of water from the soil. Additionally, θ_r increased with the application of zeolite in loamy soil due to increased water retention caused by the presence of zeolite in the soil. These results are consistent with the studies conducted by Comegna et al., 2023. Due to its porous structure, zeolite can increase the capillary porosity of the soil, and by absorbing water into itself, it can increase the amount of water holding capacity in sandy soils, because of this, θ_s has increased. The increase of zeolite has led to the increase of delicate pores in the soil, which reduces the amount of k_s as the pores become smaller. Similar results were also observed by Jabro, 1992 and Sepaskhah and Yousefi, 2007.

Table 3. Hydraulic parameters of soil and some of the model HYDRUS validations in the model calibration phase.

Zeolite application (g kg^{-1})	$\boldsymbol{\theta_r}$ (cm^{3}cm^{-3})	$\boldsymbol{\theta_s}$ (cm^{3}cm^{-3})	$\boldsymbol{\alpha}$ (m^{-1})	n -	K_s (cm/day)
0	0.0543	0.5	0.16	1.7	120.43
5	0.063	0.523	0.13	1.84	112.56
10	0.067	0.543	0.09	2.08	90.87
15	0.07	0.601	0.083	2.58	75.80

3.2. Investigation of the effect of zeolite on moisture retention characteristics

Factors affecting the shape of the curve, the model coefficients, or the function of the moisture retention curve also have an impact. Among them, the coefficients α (air-entry suction) and n (slope of the moisture retention curve) are included in the van Genuchten curve (Van Genuchten et al., 1991). The shape coefficients indicate the rate of moisture discharge from the curves under the influence of gravity or evaporation energy. Based on the results of investigating the effect of zeolite on the van Genuchten model coefficients, parameter α decreased with the increase of application of zeolite in sandy loam soil (Table 3). This is due to the changes resulting from increased water holding capacity and delay in losing gravitational and non-gravitational water, in which zeolite's positive effect on creating finer porosity and increased water retention becomes evident. A decrease in this parameter indicates an increase in fine defects and an increase in fine defects can alleviate the problem of water retention in light soils. It also indicates the superiority of matric potential over gravitational potential, which is why the water infiltration rate in the soil is low at the beginning of entry into the soil, which is consistent with studies (Shaddox, 2004).

The results obtained from Table 3 show that θ_s and θ_r percentages differ depending on the treatment, where the highest saturation and residual moisture percentages belong to the treatment with 15 grams of zeolite per kilogram of soil. With the addition of moisture absorbents, the moisture characteristic curve of each treatment deviates from the previous treatment, indicating a significant difference in volumetric moisture content among different zeolite treatments. With the increase in zeolite application, this deviation distance between the moisture characteristic curves increases, resulting in increased water retention in these treatments. This study's results align with research by (Abedi Koupai and Sohrab, 2004). Due to its porous structure, zeolite can increase the porosity of the soil structure and also increase moisture retention in sandy soils by absorbing water. Water retention in higher suction is due to zeolite absorption, leading to an increase in the amount of usable water in light-textured soils. In general, it was observed that as the percentage of zeolite in the soil increased, the characteristic moisture curves shifted upwards. This effect is evident in all different zeolite and soil treatments, which is consistent with the results of a study by Comegna et al., 2023.

The values of calibration coefficients for soil hydraulic parameters in the four mentioned treatments are presented in Table 4. As it is clear in this table, the amount of NRMSE error in the simulation of water flow in the soil in the two stages of validation and calibration, respectively, in the treatments of not using zeolite in the range (16.5-20.11 percent) and for 5 gram of zeolite is in the range of (13.68-13.90 percent), based on this statistic, the volume water content modeling by HYDRUS is average. For the treatments of 10 grams of zeolite (6.97-6.59 percent) and 15 grams of zeolite (8.31-6.69 percent), based on this statistic, the volume water content modeling by software is less than 10 percent in consideration.

The high R^2 value of the results shows the power of HYDRUS -2D software in estimating soil moisture in different soil treatments. The value of CRM statistic was obtained for the two stages of validation and calibration for the treatment of 5 and 10 grams of negative zeolite, which showed that the software tends to overestimate. For the two control treatments and 15 grams of zeolite, the positive value showed that the software tends to underestimate and predicts the water content more than the measured values. The efficiency value of the EF model, which indicates the quality and how to fit the observed and estimated data, varied between 0.82 and 0.97. In other researches, the RMSE error value in the simulation of soil moisture changes has been reported in the range of 0.015-0.017, 0.011-045, and 0.028-0.033 cubic cm (Simunek *et al.*, 2012; Ibrahim and Alghamdi, 2021). The low values of ME error in the table show the appropriate performance of the model. In another research, (Soudejani *et al.*, 2020) stated that HYDRUS-1D numerical model with average RMSE and NRMSE from 0.013 to 0.032 cubic cm/cubic cm and 0.076 to 0.195, respectively. They were changing. The coefficient of determination values varied from 0.57 to 0.92. (Nazari *et al.*, 2021; Sun et al., 2023) have also stated the high accuracy of HYDRUS simulation in modeling soil moisture changes.

Table 4. Statistical evaluation of the simulation of water content inside the soil columns by the HYDRUS-2D model.

Zeolite application (g kg^{-1})	NRMSE (%)	R^2	CRM	EF
Validation				
0	16.5	0.83	0.01	0.97
5	13.68	0.89	-0.06	0.82
10	6.97	0.95	-0.01	0.94
15	8.31	0.95	0.01	0.89
Calibration				
0	20.11	0.85	0.03	0.95
5	13.90	0.88	-0.05	0.83
10	6.59	0.95	-0.02	0.94
15	6.69	0.95	0.10	0.92

The graphs presented in Figure 3 show the output of the model in comparison with the volumetric water content values measured in different zeolite treatments at a depth of 0 to 5 cm (moisture measured with Wet sensor) during a period of 45 days. In the treatment of 15 grams of zeolite, it can be seen that at a depth of 0-5 cm in (four rounds of irrigation), the amount of saturated moisture was 23% more than the control. After 14 days of irrigation, the amount of moisture was 30% higher than the control, which indicates the high absorbability of zeolite due to its high specific surface area.

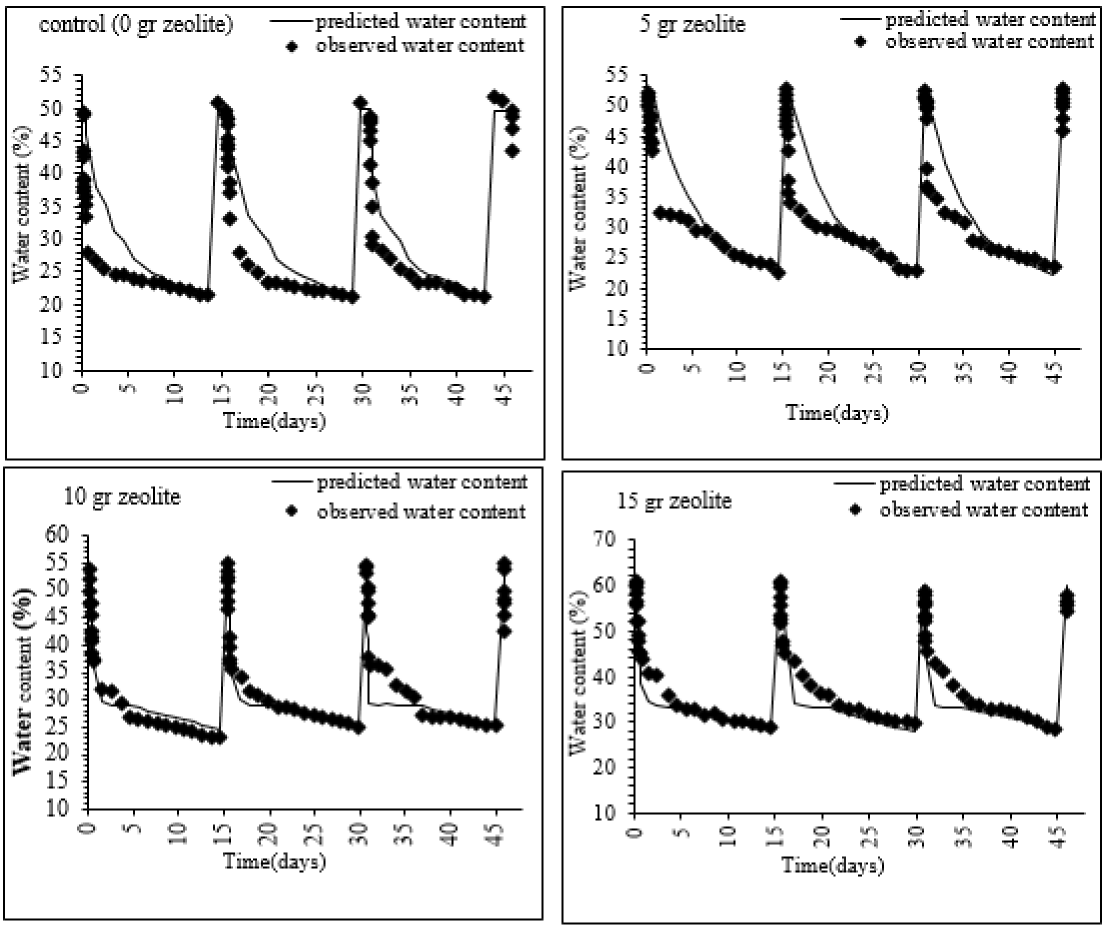

Figure 3. Comparison of measured and simulated changes in soil moisture using HYDRUS-2D in the depth (0 to 5 cm from the soil surface) in different zeolite treatments, where the circles indicate measured data and the solid line indicates estimated by the HYDRUS-2D model.

The comparison of the calibration and validation results obtained from the Hydrus model with the water content values measured in the laboratory is shown in Figures 4 and 5. The high R^2 of the results shows the power of HYDRUS -2D software in estimating soil moisture in different soil treatments. Also, the slope of the 1:1 line is close to one, indicating that the model does not overestimate or underestimate. Other factors affecting the difference between the measured and modeled values can be caused by the errors in the water content measurement by the Wet sensor and the accuracy of the device itself. As the figures 4 and 5 show, in the treatment of 15 and 10 grams of zeolite per kilogram of soil, it has high accuracy and the simulated and measured values show a very high agreement.

The reason for the increase in water content after irrigation in zeolite treatments indicates that, unlike clay minerals, in zeolites, the structural framework is large enough and this feature creates the unique properties of zeolites, they can easily move within the network. and without changing the structure of the zeolite network.

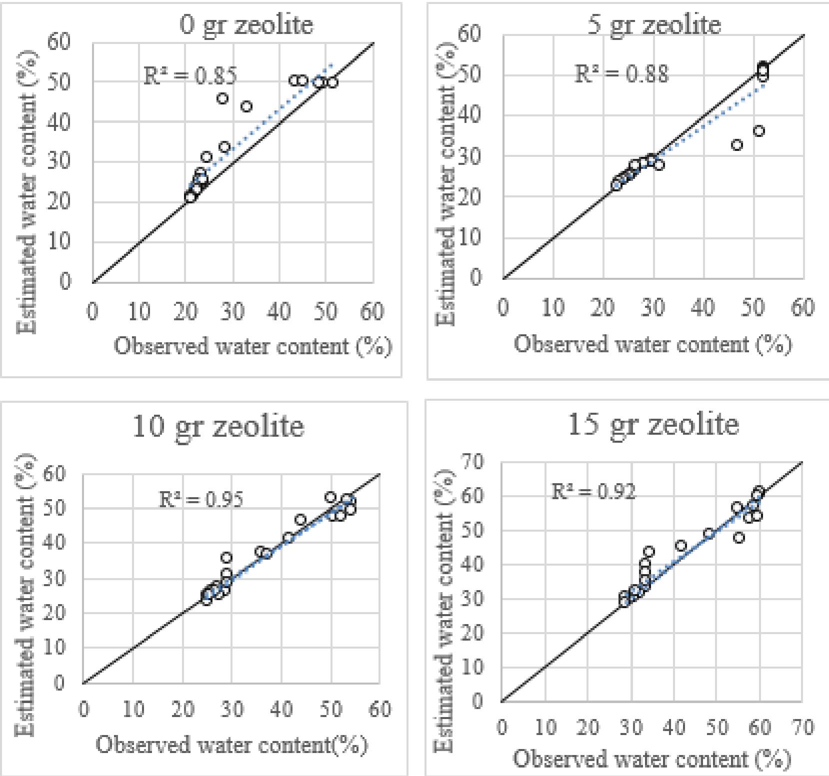

Figure 4. Observed and measured values for Calibration of water contentin different treatments at a depth of (0 to 5 cm).

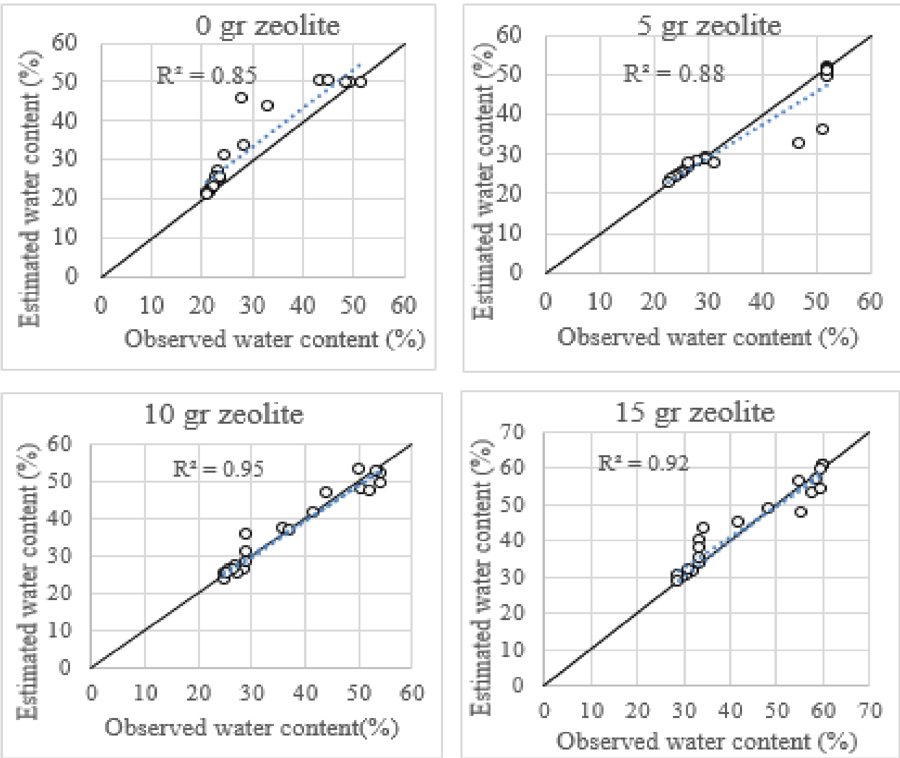

Figure 5. Observed and measured values for validation of water content in different treatments at a depth of (0 to 5 cm).

In figure 6, 7 and 8, the front of the water content in the treatments of not using zeolite, 5, 10 and 15 grams of zeolite in the period of 0.016, 1.1 and 14 days are presented. The changes of the front of moisture advance in three time periods were presented to show the effect of zeolite on the three critical periods of moisture changes, (i.e. after irrigation, one day after irrigation, and 14 days after irrigation) on the water holding capacity in the soil.

According to Figure 6, at the time of 0.016 days, the moisture front day in the treatment of 15 grams of zeolite is less than other treatments, the reason can be attributed to the fine particles and pores of zeolite, which has caused changes in gravitational and non-gravitational water loss. It also shows the superiority of the buoyant potential over the gravitational potential, that is why the speed of the advancing front is slower at the beginning of entering the soil, which was consistent with the studies (Shaddox, 2004; Al-Busaidi et al., 2008).

According to Figure 6, at the time of 0.016 days, the moisture front in the treatment of 15 grams of zeolite is less than other treatments, the reason can be attributed to the fine particles and pores of zeolite (Shaddox, 2004). The progress of the moisture front in the treatment of not using zeolite is more than other treatments, because zeolite, due to its micro pore structure and porosity, reduces infiltration at the beginning of entering the soil. (Ibrahim and Alghamdi, 2021) was consistent. Figure 8 shows the progress of moisture after 14 days in different treatments. The distribution of the moisture profile after 14 days of irrigation in the treatment of 15 grams of zeolite was different from other treatments. After 14 days, this shows that with the increase in the irrigation time, the moisture front has increased in the zeolite treatment, which is the opposite of the treatment without zeolite. One of the reasons can be that zeolite is very hydrophilic, which, while having the speed and capacity to absorb water, easily absorbs water when needed and dehydrates when needed, and the three-dimensional network structure of zeolite can absorb the water molecule inside itself for a long time. Due to its porous structure, zeolite can increase water retention by absorbing water into itself, especially in sandy soils. Also, the open skeleton of zeolites has channels and holes containing cations and water molecules. The pores of zeolite are connected and form long wide channels with different sizes depending on the type of mineral. These channels allow ions and water molecules to easily move in and out of the structure. The results of this research were consistent with the research (Ibrahim and Alghamdi, 2021; Shaddox, 2004).

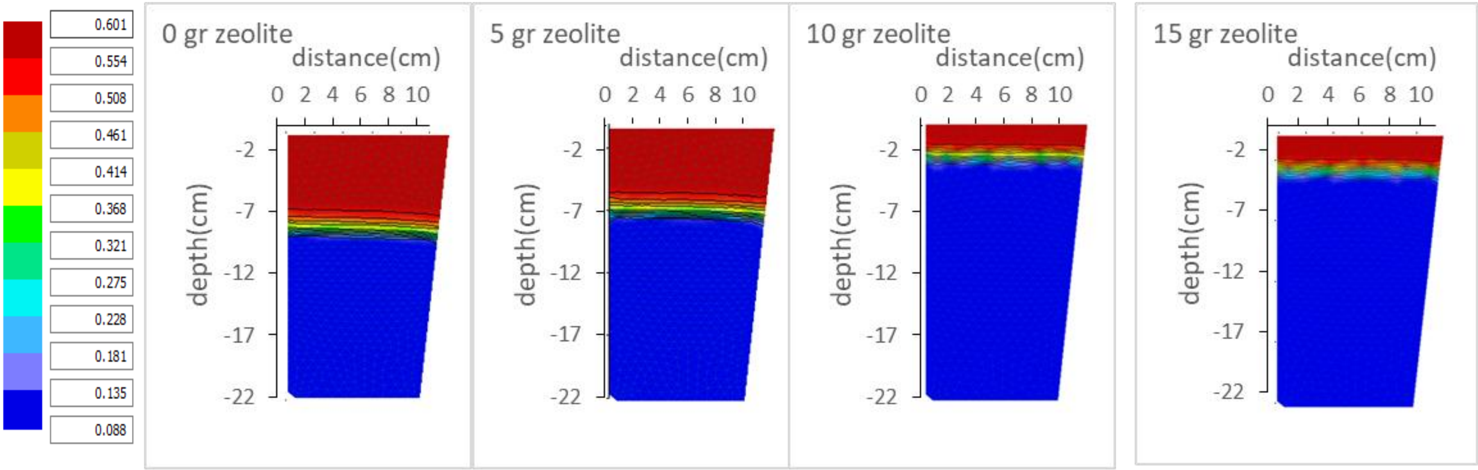

Figure 6. Spatial soil moisture distribution at time 0.16 day.

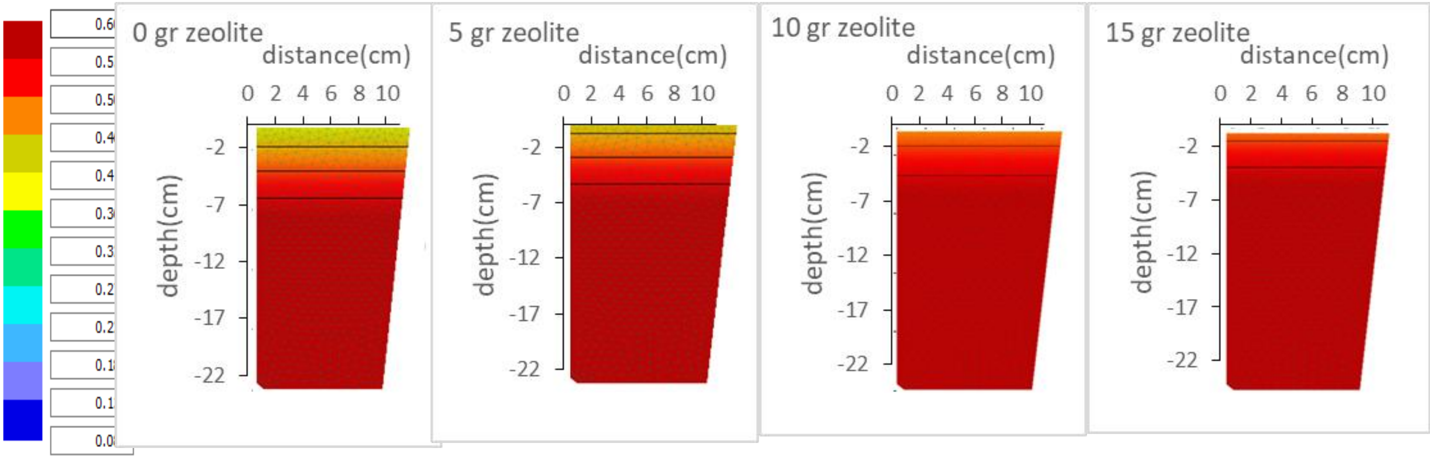

Figure 7. Spatial soil moisture distribution at time 1.1 day.

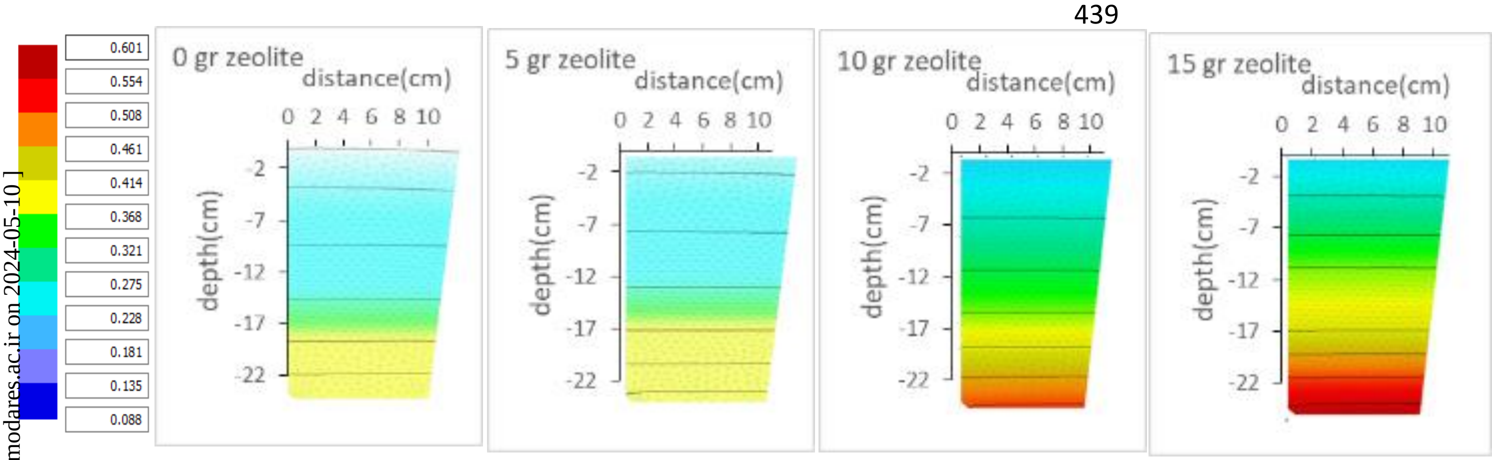

Figure 8. Spatial soil moisture distribution at time 14 day.

In Figure 9, the amount water holding capacity by different zeolite treatments at depths of 2,7, 10, and 15 cm from the soil surface in 0.01, 1.1, and 14 days are presented.

According to this figure 9, in the period of 1.1 days, the water holding capacity at a depth of 10-15 cm in the treatment of 15 grams of zeolite per kilogram of soil is more than other treatments. The highest and lowest moisture content was related to the treatment of 15 grams of zeolite and 0 grams of zeolite per kilogram of soil, which values are 87.2 and 70.9 mm, respectively. While increasing the water holding capacity in light soils, zeolite can increase the irrigation intervals by quickly absorbing water and keeping it. For a time 14 days at a depth of 10-15 cm, the moisture kept in the treatment of 15 grams of zeolite is more than zero grams of zeolite. The present results were consistent with studies (Bernardi et al., 2013). Zeolites, by rapidly absorbing water and preserving it, in the case of soil irrigation, also increase the irrigation intervals, and the amount of this increase depends on the amount of zeolite consumption and the physical conditions of the soil (Zangui Nasab et al., 2012). The results of the present study were consistent with studies (Xiubin and Zhanbin, 2001; Szerement et al., 2014; Colombani et al., 2014). (Xiubin and Zhanbin, 2001) stated that the soil mixed with zeolite increased the moisture retention rate by 30-50% and increased the soil moisture by 1.8-0.4% in drought conditions and 15-5% in normal conditions.

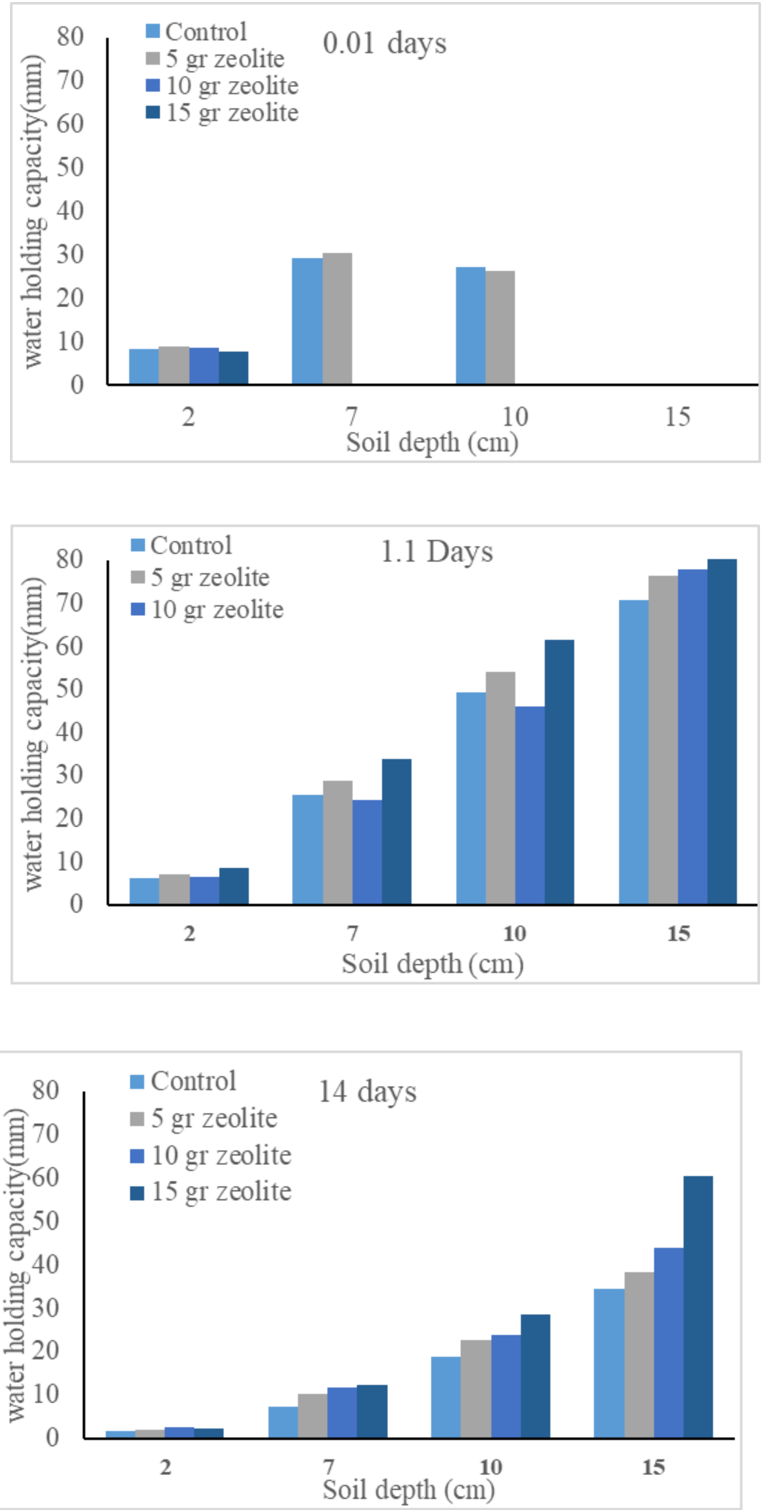

Figure 9. Represents the water holding capacity depths for the durations of 0.01, 1.1, and 14 days in different zeolite treatments.

4. Conclusions

We investigated the effect of clinoptilolite on soil hydraulic parameters and soil moisture retention in a sandy loam soil. Experiments showed that sandy loam soil after adding zeolite showed a change in its hydraulic parameters, which is proportional to the level of zeolite. With the use of 15 grams of zeolite, the hydraulic parameters θs, θr and n were higher than the control, respectively. In fact, by adding zeolite into light soil, it leads an increase in fine pores in the soil, which increases the moisture content of the soil. Small pores cause gradually to change the pores from macro-pores to micro-pores and the value of K_s decreased by compared with control treatment. Therefore, the addition of zeolite to light soil led to the water holding capacity in the soil after 14 days of irrigation that the porous structure of zeolite causes water to be kept tightly inside the cavities of the aluminosilicate layer. HYDRUS-2D model was able to simulate soil moisture under specified initial and boundary conditions. Based on the obtained results, EF it was found that the HYDRUS-2D model has a high ability to estimate the moisture content of soil mixed with zeolite and is able to estimate high moisture conditions in soil mixed with zeolite with high accuracy. The study of laboratory conditions shows significant results in the properties of soil hydraulic parameters due to the addition of zeolite, which shows that the addition of zeolite to the soil guarantees several benefits in terms of improving the physical and hydraulic properties. In addition to reducing k_s, it increases the efficiency of water consumption and helps to reduce the amount of water used for irrigation. Due to the cheap price of zeolite in the country, this material can be used especially in light soils to increase the amount of water holding capacity and increase the watering intervals of plants in pots.

References

1. Abedi Kupai, J., and Sohrab, F. (2004). Effect of zeolite and bentonite minerals on soil hydraulic properties. Researches. In Twelfth Iranian Conference on Crystallography and Mineralogy, Shahid Chamran University, Ahvaz (pp. 562-567).
2. Adeboye, O. B., and Alatise, M. O. (2007). Performance of probability distributions and plotting positions in estimating the flood of river Osun at Apoje Sub-basin, Nigeria. Agricultural Engineering International: CIGR Journal.
3. Asgarzadeh, H., Mosaddeghi, M. R., Dexter, A. R., Mahboubi, A. A., and Neyshabouri, M. R. (2014). Determination of soil available water for plants: consistency between laboratory and field measurements. Geoderma, 226, 8-20. doi :10.1016/j.geoderma.2014.02.020.
4. Bannayan, M., and Hoogenboom, G. (2009). “Using pattern recognition for estimating cultivar coefficients of a crop simulation model.” Field Crops Research, 111 (3), 290-302.

doi:10.1016/j.fcr.2009.01.007.

5. Belviso, C. (2020). Zeolite for potential toxic metal uptake from contaminated soil: A brief review. Processes, 8(7), 820.doi:10.3390/pr8070820.
6. Belviso, C., Satriani, A., Lovelli, S., Comegna, A., Coppola, A., Dragonetti, G., and Rivelli, A. R. (2022). Impact of zeolite from coal fly ash on soil hydrophysical properties and plant growth. Agriculture, 12(3), 356. doi:10.3390/agriculture12030356.
7. Bernardi, A., Olivera, P., Melo Monte, M., Polidoro, J.C., and Barros, F.S. (2010). Brazilian sedimentary zeolite is used in agriculture. World Congress of Soil Science, Australia.
8. Blake, G. R., and Hartge, K. H. (1986). Bulk density. Methods of soil analysis: Part 1 Physical and mineralogical methods, 5, 363-375. doi:10.2136/sssabookser5.1.2ed.c13.
9. Blanco-Canqui, H., and Lal, R. (2009). Crop residue removal impacts soil productivity and environmental quality. Critical reviews in plant science, 28(3), 139-163. doi/10.1080/07352680902776507.
10. Celia, M. A., Bouloutas, E. T., and Zarba, R. L. (1990). A general mass- conservative numerical solution for the unsaturated flow equation. Water resources research, 26(7), 1483-1496. doi.org/10.1029/WR026i007p01483.
11. Colombani, N., Mastrocicco, M., Di Giuseppe, D., Faccini, B., and Coltorti, M. (2015). Batch and column experiments on nutrient leaching in soils amended with Italian natural zeolites. Catena, 127, 64-71. doi:10.1016/j.catena.2014.12.022.
12. Colombani, N., Mastrocicco, M., Di Giuseppe, D., Faccini, B., and Coltorti, M. (2014). Variation of the hydraulic properties and solute transport mechanisms in a silty-clay soil amended with natural zeolites. Catena, 123, 195-204. doi: 10.1016/j.catena.2014.08.003.
13. Comegna, A., Belviso, C., Rivelli, A. R., Coppola, A., Dragonetti, G., Sobhani, A., and Lovelli, S. (2023). Analysis of critical water flow and solute transport parameters in different soils mixed with a synthetic zeolite. Catena, 228, 107150. doi.:10.1016/j.catena.2023.107150.
14. Crevoisier, D., Popova, Z., Mailhol, J. C., and Ruelle, P. (2008). Assessment and simulation of water and nitrogen transfer under furrow irrigation. Agricultural water management, 95(4), 354-366. doi: 10.1016/j.agwat.2007.10.021
15. Fujimaki, H., Ando, Y., Cui, Y., and Inoue, M. (2008). Parameter estimation of a root water uptake model under salinity stress. Vadose Zone Journal, 7(1), 31-38. doi: 10.2136/vzj2007.0025.
16. Fan, J., Wu, L., Zhang, F., Xiang, Y., and Zheng, J. (2016). Climate change effects on reference crop evapotranspiration across different climatic zones of China during 1956–2015. Journal of Hydrology, 542, 923-937. doi: 10.2136/vzj2007.0025.

17. Ghazavi, R., Omidvar, E., and Jeyhoni, H. (2019). Investigating the effect of zeolite on the coefficients of soil moisture curve models in two sandy and loamy texture. Journal of Water and Soil Science, 23(3).

18. Gholizadeh-Sarabi, S.,and Sepaskhah, A. R. (2013). Effect of zeolite and saline water application on saturated hydraulic conductivity and infiltration in different soil textures. Archives of Agronomy and Soil Science, 59(5), 753-764.doi:10.1080/03650340.2012.675626.

19. Ibrahim, H. M., and Alghamdi, A. G. (2021). Effect of the particle size of clinoptilolite zeolite on water content and soil water storage in loamy sand soil. Water, 13(5), 607. doi:10.3390/w13050607

20. Jakkula, V. S., and Wani, S. P. (2018). Zeolites: Potential soil amendments for improving nutrient and water use efficiency and agriculture productivity. Scientific Reviews and Chemical Communications, 8(1), 1-15

21. Jarosz, R., Szerement, J., Gondek, K., and Mierzwa-Hersztek, M. (2022). The use of zeolites as an addition to fertilizers–A review. Catena, 213, 106125. doi: 10.1016/j.catena.2022.106125.

22. Jamieson, P. D., Porter, J. R., and Wilson, D. R. (1991). A test of the computer simulation model on wheat crops grown in New Zealand. Field Crops Research, 27, 337–350. doi:10.1016/0378-4290(91)90040-3.

23. Jabro, J. D. (1992). Estimation of saturated hydraulic conductivity of soils from particle size distribution and bulk density data. Transactions of the ASAE, 35(2), 557-560. doi: 10.13031/2013.28633) @1992.

24. Jha, V. K., and Hayashi, S. (2009). Modification on natural clinoptilolite zeolite for its NH4+ retention capacity. Journal of Hazardous Materials, 169(1-3), 29-35. doi: 10.1016/j.jhazmat.2009.03.052.

25. Hillel, D. (2004). Introduction to environmental soil physic. Elserier Science, San Diego, California.

26. Khorami, M., Alizadeh., A, and Ansari, H. (2013). Simulation of water movement and moisture redistribution in soil in drip irrigation by Hydrus 2D/3D model. Water and Soil, 27(4), 692-702.

27. Li, J., Liu, Z., Jiang, C., Li, Y., Li, H., and Xia, J. (2021). Optimization design of key parameters for bioretention cells with mixed filter media via HYDRUS-1D model and regression analysis. Ecological Engineering, 164, 106206. doi:10.1016/j.ecoleng.2021.106206.

28. Loague K. and Green R.E., (1991). Statistical and graphical methods for evaluating solute transport models: overview and application. J. Contam. Hydrol., 7, 51-73. doi.org/10.1016/0169-7722(91)90038-3.

29. Marquardt, D. W. (1963). An algorithm for least-squares estimation of nonlinear parameters. Journal of the society for Industrial and Applied Mathematics, 11(2), 431-441.doi:10.1137/0111030.

30. McGilloway, R. L., Weaver, R. W., Ming, D. W., and Gruener, J. E. (2003). Nitrification in a geoponic substrate. Plant and soil, 256, 371-378. doi:10.1023/A:1026174026995.

Mualem, Y. (1976). A new model for predicting the hydraulic conductivity of unsaturated porous media. Water resources research, 12(3), 513-522. doi:10.1029/WR012i003p00513

31. Nazari, E., Besharat, S., Zeinalzadeh, K., and Mohammadi, A. (2021). Measurement and simulation of the water flow and root uptake in soil under subsurface drip irrigation of apple tree. Agricultural Water Management, 255, 106972.

32. Pal, D. K., Bhattacharyya, T., Ray, S. K., Chandran, P., Srivastava, P., Durge, S. L., and Bhuse, S. R. (2006). Significance of soil modifiers (Ca-zeolites and gypsum) in naturally degraded Vertisols of Peninsular India in redefining the sodic soils. Geoderma, 136(1-2), 210-228. doi: 10.1016/j.geoderma.2006.03.020.

33. Ravali, C., Rao, K. J., Anjaiah, T., and Suresh, K. (2020). Effect of zeolite on soil physical and physico-chemical properties. Multilogic Sci, 10, 776-781.

34. Razmi, Z., and Sepaskhah, A. R. (2012). Effect of zeolite on saturated hydraulic conductivity and crack behavior of silty clay paddled soil. Archives of Agronomy and Soil Science, 58(7), 805-816.

35. Reid, G., Klebe, S., Van Zandwijk, N., and George, A. M. (2021). Asbestos and Zeolites: from A to Z via a Common Ion. Chemical research in toxicology, 34(4), 936-951. doi: 10.1021/acs.chemrestox.0c00286.

36. Samolej, K., and Chalupnik, S. (2021). Investigations on the application of different synthetic zeolites for radium removal from water. Journal of Environmental Radioactivity, 229, 106529. doi:10.1016/j.jenvrad.2021.106529.

33. Samreen, T., Shah, H. U., Ullah, S., and Javid, M. (2017). Zinc effect on the growth rate, chlorophyll, protein, and mineral contents of hydroponically grown mung bean plant (Vigna radiata). Arabian Journal of Chemistry, 10, S1802-S1807. doi:10.1016/j.arabjc.2013.07.005.

34. Sangeetha, C., and Baskar, P. (2016). Zeolite and its potential uses in agriculture: A critical review. Agricultural Reviews, 37(2), 101-108.doi: 10.18805/ar.v0iof.9627.

35. Sepaskhah, A. R., and Yousefi, F. (2007). Effects of zeolite application on nitrate and ammonium retention of a loamy soil under saturated conditions. Soil Research, 45(5), 368-373.

36. Shaddox, T. (2004). Investigation of soil amendments for use in golf course putting green construction. University of Florida..

37. Šimunek, J., Van Genuchten, M. T., and Šejna, M. (2012). HYDRUS: Model use, calibration, and validation. Transactions of the ASABE, 55(4), 1263-1274.

38. Šimůnek, J. I. R. K. A., Van Genuchten, M. T., and Šejna, M. (2006). The HYDRUS software package for simulating two-and three-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Technical manual, version, 1, 241.

39. Šimůnek, J., Šejna, M., and Van Genuchten, M. T. (1999). The HYDRUS-2D software package for simulating the two-dimensional movement of water, heat, and multiple solutes in variably-saturated media: Version 2.0. US Salinity Laboratory, Agricultural Research Service, US Department of Agriculture.

40. Siyal, A. A., and Skaggs, T. H. (2009). Measured and simulated soil wetting patterns under porous clay pipe sub-surface irrigation. Agricultural water management, 96(6), 893-904. doi.: 10.1016/j.agwat.2008.11.013

41. Soudejani, H. T., Shayannejad, M., Kazemian, H., Heidarpour, M., and Rutherford, M. (2020). Effect of co-composting municipal solid waste with Mg-modified zeolite on soil water balance components using HYDRUS-1D. Computers and Electronics in Agriculture, 176, 105637. doi:10.1016/j.compag.2020.105637.

42.Sun, L., Li, B., Yao, M., Mao, L., Zhao, M., Niu, H., ... and Wang, J. (2023). Simulation of Soil Water Movement and Root Uptake under Mulched Drip Irrigation of Greenhouse Tomatoes. Water, 15(7), 1282. doi.10.3390/w15071282.

43. Szatanik-Kloc, A., Szerement, J., Adamczuk, A., and Józefaciuk, G. (2021). Effect of low zeolite doses on plants and soil physicochemical properties. Materials, 14(10), 2617, doi.org/10.3390/ma14102617

44. Szerement, J., Ambrożewicz-Nita, A., Kędziora, K., and Piasek, J. (2014). Use of zeolite in agriculture and environmental protection. A short review. Вісник Національного університету Львівська політехніка. Теорія і практика будівництва, (781), 172-177.

45. Tohidi-Moghadam, H. R., Shirani-Rad, A. H., Nour-Mohammadi, G., Habibi, D., Modarres-Sanavy, Mashhadi-Akbar-Boojar, M., Habibi, D., Modarres-Sanavy, S. A. M., Shirani-Rad, A. H., Nour-

46. Torkashvand, A. M., and Shadparvar, V. (2013). Effect of some organic waste and zeolite on water holding capacity and PWP delay of soil. Current Biotica, 6(4), 459-465, doi:10.2136/sssaj1980.03615995004400050002x

47. Van Genuchten, M. T. (1980). A closed- form equation for predicting the hydraulic conductivity of unsaturated soils. Soil science society of America journal, 44(5), 892-898. doi:10.2136/sssaj1980.03615995004400050002x

48. Van Genuchten, M. V., Leij, F. J., and Yates, S. R. (1991). The RETC code for quantifying the hydraulic functions of unsaturated soils.

تاثیر زئولیت بر پارامترهای هیدرولیکی خاک و شبیه‌سازی جریان آب در خاک با استفاده از مدل HYDRUS -2D

م. شادان، ج. بهمنش، س. بشارت، و ن. آزاد

چکیده

زئولیت‌ها به دلیل ظرفیت بالای نگهداری آب و تبادل کاتیونی برای استفاده در بخش کشاورزی توصیه شده‌اند. در این مطالعه اثر زئولیت بر پارامترهای هیدرولیکی خاک لوم شنی بررسی شد. بدین منظور از مدل HYDRUS-2D جهت شبیه‌سازی حرکت آب در خاک استفاده شد و داده‌های مورد نیاز جهت واسنجی و صحت‌سنجی مدل با انجام آزمایشات آزمایشگاهی (گلدانی) جمع‌آوری گردید. تیمارهای مورد مطالعه شامل چهار سطح (صفر، 5 و 10 و 15 گرم زئولیت در هر کیلوگرم خاک) بود تا تاثیر زئولیت بر پارامترهای هیدرولیکی شامل رطوبت اشباع (θ_s)، رطوبت باقیمانده (θ_r) پارامتر شکل (n)، نقطه ورد هوا (α) و هدایت هیدرولیکی اشباع (K_s) خاک بررسی شود. 4 دور آبیاری براساس رطوبت سهل‌الوصل صورت گرفت و مقادیر رطوبت خاک قبل و بعد آبیاری، با استفاده از (Wet sensor) سنسور در جهت عمقی و شعاعی اندازه‌گیری و به مدت 45 روز ثبت گردید. مقدار اولیه پارامترهای هیدرولیکی θ_r،θ_s ، α ، n و K_s با استفاده از Rosetta مشخص شد. نتایج نشان داد که با افزایش مقدار زئولیت مقادیر پارامترهای θ_r، θ_s و n افزایش و مقدار α کاهش یافته که نشان‌دهنده کاهش سرعت تخلیه آب از خاک بود. در حالیکه مقادیر K_s تمایل به کاهش یافت. به‌طور کلی زئولیت به دلیل ساختار ریز منافذ به مخلوط خاک و زئولیت اجازه می‌دهد تا آب بیشتری را در خود نگه دارد. مدل HYDRUS-2D با ضریب کارایی EF که نشان دهنده کیفیت و چگونگی برازش داده‌هاي مشاهده‌اي و برآورد شده میباشد بین 0/82 تا 0/97 متغییر بود که این نشان دهنده کارایی بالاي مدل در شبیه سازي رطوبت است.