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Arun C Kanagalabavi
Ph.D. Research Scholer,
Department of Soil Science,
KSNUAHS Shivamogga,
Karnataka, India

Dayanand Patil
Research Scholar, ICAR-
National Dairy Research
Institute, Southern Regional
Station, Bengaluru,
Karnataka, India

Prem Kumar B
Ph.D. Research Scholer,
ICAR-IARI, New Delhi and
Asst. Manager, NABARD,
Raipur, Chhattisgarh, India

Priyanka H R
M.Sc. Agriculture, Department
of Soil Science, KSNUAHS
Shivamogga, Karnataka, India

Ahalya M S
M.Sc. Agriculture, Department
of Soil Science, KSNUAHS
Shivamogga, Karnataka, India

Corresponding Author:
Arun C Kanagalabavi
Ph.D. Research Scholer,
Department of Soil Science,
KSNUAHS Shivamogga,
Karnataka, India

Zeolite in agriculture: An amendment in improving physical and chemical properties of soil

Arun C Kanagalabavi, Dayanand Patil, Prem Kumar B, Priyanka HR and Ahalya MS

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Abstract

Zeolites are hydrated aluminosilicate minerals composed of interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4), possessing a unique three-dimensional crystalline structure. They are classified into natural and synthetic forms. Zeolites are widely utilized in agriculture due to their exceptional cation-exchange capacity, high porosity and ability to retain nutrients and water. Key applications include enhancing nutrient use efficiency, improving soil physical and chemical properties, increasing water use efficiency, boosting crop yields, enhancing organic manure efficiency and mitigating heavy metal contamination in soils. Zeolites function as slow-release carriers of nitrogen, phosphorus and potassium, reducing nutrient losses to the environment and enhancing fertilizer efficiency. Their selective ammonium retention ability aids in nitrogen management, while their structural properties improve soil conditions, particularly in arid, sandy or nutrient-poor soils. Zeolites also enhance water retention without compromising aeration, leading to improved water use efficiency. Additionally, zeolites facilitate controlled release of herbicides and pesticides, minimizing environmental risks. Zeolites play a pivotal role in heavy metal remediation by immobilizing toxic ions thus mitigating their phyto-availability.

Keywords: Zeolites, cation-exchange, water retention, nutrient efficiency, soil improvement, heavy metal remediation, and slow-release.

Introduction

Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4). In simpler words, they're solids with a relatively open, three-dimensional crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them (Mineralogist community). Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules.

There are about 40 naturally occurring zeolites, forming in both volcanic and sedimentary rocks; according to the US Geological Survey, the most commonly mined forms include chabazite, clinoptilolite and mordenite. Dozens more artificial, synthetic zeolites (around 150) have been designed for specific purposes, the best known of which are zeolite A (commonly used as a laundry detergent), zeolites X and Y (two different types of faujasites used for catalytic cracking), and the petroleum catalyst ZSM-5 (a branded name for pentasil-zeolite).

History and origin of zeolites

Zeolite, first identified in 1756 by Swedish mineralogist Alex Fredrik Cronstedt, derives its name from Greek words meaning "boiling stones" due to its frothing when heated. Natural zeolites form over thousands to millions of years in volcanic rocks and shallow marine basins, reacting with alkaline groundwater. These zeolites are often impure, contaminated by other minerals and metals,

limiting their use in applications requiring high purity. In the 1960s, Japanese researchers explored zeolite's potential in agriculture, utilizing its porosity and cation-exchange capacity. Japanese farmers used zeolite to control soil moisture and increase pH in acidic volcanic soils. Its ion-exchange properties make it an effective carrier and releaser of nutrients, contributing to its agricultural applications.

Classification of zeolites

More than 50 different species of this mineral group have been identified and still more to be identified. Zeolites have been classified on the basis of their morphological characteristics, crystal structure, chemical composition, effective pore diameter, natural occurrence, *etc.*, in the year 1997, the subcommittee on zeolites of the International Mineralogical Association Commission on New Minerals and Mineral Names has recommended nomenclature for zeolite minerals. The report suggested that zeolite species are not to be distinguished solely on the ratio of Si to Al, except for heulandite and clinoptilolite (Si:Al 4.0). Dehydration, partial hydration and over-hydration are not sufficient grounds for the recognition of separate species of zeolites. The Si/Al ratio is an important characteristic of zeolites. The charge imbalance due to the presence of aluminum in the zeolite framework determines the ion-exchange characters of zeolites and is expected to induce potential acidic sites. The Si/Al ratio is inversely proportional to the cation content, however directly proportional to the thermal stability. The surface selectivity changes from hydrophilic to hydrophobic when the ratio increases. Silica molecular sieves (silicalite-1) have a neutral framework; are hydrophobic in nature, and have no ion exchange or catalytic properties.

Zeolites are classified on the basis of silica/alumina ratio as follows:

1. Zeolites with low Si/Al ratio (1.0 to 1.5)
2. Zeolites with intermediate Si/Al ratio (2 to 5)
3. Zeolites with high Si/Al ratio (10 to several thousands)

As the Si to Al ratio continues to increase, the catalytic activity often tends to pass through a maximum because of two opposing effects: increasing effectiveness of each acid center on the one hand, and decreasing number of acid centers on the other. The aluminous zeolites are excellent desiccants whereas the most siliceous zeolites tend to be organophilic nonpolar sorbents (Barrer, 1986) ^[5]. Flanigen (1980) ^[14] considered that “low silica” zeolites or aluminum-rich zeolites contain the maximum number of cation-exchange sites balancing the framework aluminum, and thus the highest cation contents; “intermediate silica” zeolites exhibit a common characteristic in terms of improved stability over the “low silica” zeolites and “high silica” zeolites representing heterogeneous hydrophilic surfaces within a porous crystal. The surface of the high silica zeolites approaches a more homogeneous characteristic with an organophilic hydrophobic selectivity and exchange capacities. Flanigen (2001) ^[13] has classified zeolites based on pore diameter, namely, small-pore zeolites, medium-pore zeolites, large-pore zeolites, and extra-large-pore zeolites:

- a) Small-pore zeolites (8-rings) with free pore diameter of 0.3-0.45 nm
- b) Medium-pore zeolites (10-rings) with free pore diameter of 0.45-0.6 nm
- c) Large-pore zeolites (12-rings) with free pore diameter of 0.6-0.8 nm
- d) Extra-large-pore zeolites (14-rings) with free pore diameter of 0.8-1.0 nm.

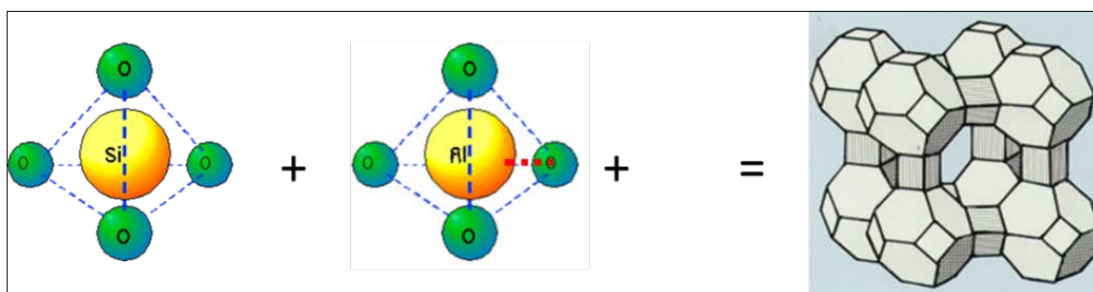


Fig 1: basic zeolite structure

Structure and chemical composition of zeolites

Zeolites are a volcanogenic sedimentary mineral composed primarily of aluminosilicates. The mineral has a three-dimensional crystal lattice, with loosely bound cations, capable of hydrating and dehydrating without altering the crystal structure (Holmes, 1994) ^[45]. Zeolites are generally formed in nature when water of high pH and high salt content interacts with volcanic ash causing a rapid crystal formation (Oste *et al.*, 2002) ^[46]. The structure of zeolite can be split into two regions: columns of fused rings that expand with temperature and the inter column regions that tend to contract on heating. These competing changes combine to produce a material that contracts parallel to the crystallographic “a” and “b” axes and expands in the “c”

direction (Villaescusa *et al.*, 2001) ^[40]. In the structure of natural zeolite, the water and cations can be reversibly removed or replaced by other cations. The maximum size of any ionic species that can enter the pores of a zeolite is a function of the dimensions of the channels. These are defined by the ring size of the aperture. “8-Ring” structure refers to a closed loop that is built from 8 tetrahedral coordinated silicon (or aluminum) atoms with equivalent oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical.

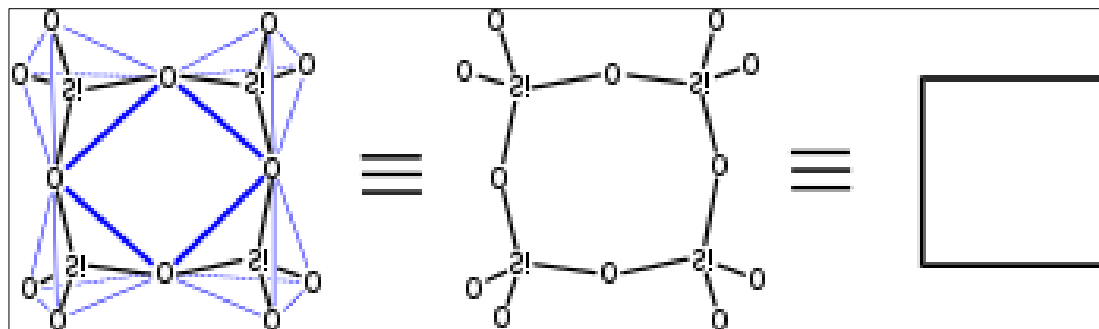


Fig 2: Three ways to represent the oxygen 4-membered ring structure of silicate compounds

Table 1: Characterization of zeolite for physical and chemical properties

Zeolite characterization	
Parameters	Values
MWHC (%)	89.50
pH (1: 2.5)	7.41
EC (dS m ⁻¹)	0.61
N (%)	0.14
P (%)	0.18
K (%)	0.77
Ca (%)	1.24
Mg (%)	0.19
S (%)	0.28
Fe (%)	22.91
Mn (%)	0.92
Cu (mg kg ⁻¹)	0.79
Zn (mg kg ⁻¹)	0.94
B (mg kg ⁻¹)	nil
Si (%)	33.60
Na (%)	12.50
CEC (Cmol (p+) kg ⁻¹)	184
Bulk density (g cc ⁻¹)	0.54
Porosity (%)	66.24
Particle density (g cc ⁻¹)	0.64

Mumpton (1960)^[30] suggested a compositional gap between the mineral heulandite (Si/Al ratio 2.75-3.25) and clinoptilolite (Si/Al ratio 4.25-5.25), clinoptilolite being temperature-stable to above 600 °C. Recent zeolite research has focused on widening the scope of synthetic procedures, on further exploiting zeolites in commercial processes, and on applying modern characterization techniques to unraveling the complexities of zeolite structural properties. Recent zeolite research has focused on widening the scope of synthetic procedures, on further exploiting zeolites in commercial processes, and on applying modern characterization techniques to unraveling the complexities of zeolite structural properties (Newsam, 1986)^[31]. The higher the average ionic potential of the extra-framework cations, the larger the hydration capacity of the clinoptilolite. This trend may be attributed to the small size as well as the efficient water-cation packing of high field strength cations in the zeolite structure (Yang *et al.* 2001)^[43].

Zeolites applications in agriculture

Enhancing nutrient use efficiency

There are several reports in the literature showing that the addition of zeolite to the source of N can improve the

nitrogen use efficiency. Surface-modified zeolites offer a great promise as anion carriers for slow release of nutrients. The high potential of zeolites as nitrogen fertilizers has been demonstrated. Their use would diminish environmental problems and increase fertilizer efficiency. It has been verified that when mixed with nitrogen, phosphorus, and potassium compounds, zeolite enhances the action of such compounds as slow-release fertilizers, both in horticultural and extensive crops. Natural zeolites have high tendency of ammonium selective properties. The main use of zeolites in agriculture is for nitrogen capture, storage, and slow release. It has been shown that zeolites, with their specific selectivity for ammonium (NH₄⁺), can take up this specific cation from either farmyard manure, composts, or ammonium-bearing fertilizers, thereby reducing losses of nitrogen to the environment. There is a new possibility, which is the addition of zeolite to the organic substrate. Natural zeolites, due to their structure and properties, inert and nontoxic material can be used as a slowly releasing carrier of fertilizer. It is possible to obtain an increase in the efficiency of nitrogen fertilizer in forage crops when nitrogenated clinoptilolites are used in comparison with the use of urea. Ferguson and Pepper (1987)^[12] suggested that the effects of zeolite on N uptake and plant growth would vary with soil

type, and that maximum benefit would be expected on course-textured low cation-exchange capacity soils.

Improving soil physico-chemical properties

Natural zeolites are extensively used to improve soil physical environment, particularly in sandy and clay poor soils. Application of zeolite to the tune of one-fifth of the soil weight was found to be the best medium for tomato plants. Emphasized that zeolites were commonly used as soil conditioners. Demonstrated that zeolite application at soybean planting time encouraged the initiation of vegetative phenology on allophonic soil. Zeolite has an effect to mitigate the salt damage to plants and that the leaching of CaCl_2 substitutes adsorbed Na in zeolite for Ca. Substituted zeolite gives high productivity to sand. Zeolite amendment is an effective way to improve soil condition in an arid and semiarid environment. Application of natural zeolite increased the available nitrogen, phosphorus, calcium, and magnesium of the medium. A study by Wiedenfeld (2003) [41] concluded that the slight effect of zeolite application observed in a study suggests that its potential benefit might be realized only under poorer conditions where the needs for improvement in nutrient retention and moisture holding capacity are greater. Farmers add the zeolites to the soil to control soil pH and to improve ammonium retention (Dwyer and Dyer, 1984) [10]. The CEC of soil may be increased by using zeolites as soil amendments.

Improving water use efficiency

Zeolites possess high water holding capacities without reducing air filled pore space (Huang and Petrovic, 1994) [18]. The results of field studies clearly showed that zeolites act as soil amendments for crop production improve available water to the plants (Olczyk, 2005) [32]. Zeolite increased the water use efficiency of strawberry plants (Abdi *et al.*, 2006) [1].

Improving crop yields

Addition of clinoptilolite increased yields of barley, potato, clover, and wheat after adding 15-ton ha^{-1} in a sandy loam soil. Pierla *et al.* (1984) [34] found that in the field, the zeolite clinoptilolite reduced corn yields, while in the greenhouse this material appeared to act as a slow-release fertilizer increasing the growth of radish after three successive harvests. Bouzo *et al.* (1994) [47] found increased productivity of sugar cane with utilization of 6-ton ha^{-1} of zeolite in an Oxisol. Carrion *et al.* (1994) [8] observed that the application of 150 kg ha^{-1} of urea coated with 5-10% of zeolite increased productivity of rice and tomato crops. Wiedenfeld (2003) [41] found that zeolite application did not affect cabbage yields, but pepper yields showed a quadratic response to zeolite application rate, primarily as an initial decrease than an increase in fruit size as rate increased. Highest green herbage yield of Alfalfa was obtained by Turk *et al.* (2006) [38] when 20 per cent zeolite 180 per cent soil was used.

Improving herbicide use efficiency

Controlled release of inputs is being employed extensively in agriculture to deliver active substances like pesticides and herbicides. Porous materials with well-ordered structures are attractive candidates for storage and release of organic guest molecules. Controlled release of paraquat using zeolite has

been reported by Zhang *et al.* (2006) [44]. The release of paraquat from zeolites can occur only via ion-exchange because of charge neutrality of the zeolite.

Enhanced organic manure efficiency

It has been reported that zeolites, with their specific selectivity for ammonium (NH_4^{+1}), can take up this specific cation from either farmyard manure, composts, or ammonium-bearing fertilizers, thereby reducing losses of nitrogen to the environment. Ammonium-charged zeolites have also been tested successfully for their ability to increase the solubilization of phosphate minerals. Rodriguez *et al.* (1994) [48] confirmed that zeolite mixed with manure increases the effectiveness of organic fertilizers on meadowland soils. Most of the manure-ammonia sequestered in the zeolite is unavailable to nitrifying bacteria because of the small pore size of the crystal lattice structure (Mumpton, 1999) [49]. Experiments of Leggo (2000) [23] revealed that zeolite incorporated with poultry manure served as an effective fertilizer and soil conditioner. Chuprova *et al.* (2004) [9] found the beneficial effect of zeolite fertilizers on mobile humus substances of Chernozem and on biological productivity of maize. Natural zeolites are able to bind humic acid through the action of the surface extra-framework cations and that this ability was markedly enhanced if the zeolitic material was enriched by divalent cations, especially Ca^{2+} .

Remediation of heavy metal contaminated soils

Reducing the plant availability of heavy metals (Cd, Pb, Cr, Zn, Cu, *etc.*) in soils is critical for optimizing agricultural production in areas with heavy metal contaminated soils. Phyto availability of heavy metals correlates best with their concentrations in soil solution rather with their total content in soil. The removal of heavy metals in polluted areas is very difficult because they persist in soils for very long periods. However, the fixation of heavy metals in a nonavailable form could be a useful method for soils that are already contaminated by heavy metals. Heavy metal Phyto availability may be reduced if the metals are sorbed or precipitated from the soil solution. One of the ways to heavy metal immobilization may be the application of zeolites. Zeolites in general have large cation-exchange capacity and expectedly attract positive-charged ions and, therefore, are widely used for sequestration of cationic pollutants like heavy metals (Kumar *et al.*, 2007) [21]. Natural and artificial zeolites increase ion-exchange sites in soils in addition to offering absorption sites for small molecules, due to their porous structure. Consequently, zeolites are able to retain heavy metals in soil.

Wastewater treatment

A promising alternative option to remove specific contaminants from aqueous solution could be the use of low-cost sorbent materials. Among the different minerals, which possess sorbent properties, zeolites appear to be one of the most promising sorbents for this purpose. Different kinds of natural zeolites are most frequently suggested as ammonium exchangers for wastewater treatment applications. It is well known that aluminosilicate molecular sieves (zeolites) are considered the best sorbents which are used in technological processes of division and deep clearing of liquid and gas mixtures due to their chemical nature and particularities of their porous structure.

Clinoptilolite is known for its ability to remove ammonium from polluted waters.

Improving crop yields

Addition of clinoptilolite increased yields of barley, potato, clover, and wheat after adding 15-ton ha²¹ in a sandy loam soil. Pierla *et al.* (1984)^[34] found that in the field, the zeolite clinoptilolite reduced corn yields, while in the greenhouse this material appeared to act as a slow-release fertilizer increasing the growth of radish after three successive harvests. Bouzo *et al.* (1994)^[47] found increased productivity of sugar cane with utilization of 6-ton ha 21 of zeolite in an Oxisol. Carrion *et al.* (1994)^[8] observed that the application of 150 kg ha⁻¹ of urea coated with 5-10% of zeolite increased productivity of rice and tomato crops. Wiedenfeld (2003)^[41] found that zeolite application did not affect cabbage yields, but pepper yields showed a quadratic response to zeolite application rate, primarily as an initial decrease than an increase in fruit size as rate increased.

Highest green herbage yield of Alfalfa was obtained by Turk *et al.* (2006)^[38] when 20 per cent zeolite/180 per cent soil was used.

Application of zeolite to soil reduced cadmium (Cd) leaching in all the contaminated soils. When 15 per cent zeolite was applied, Cd concentration in the leachate decreased to below 0.1 mg L⁻¹. The higher cation exchange capacity of the zeolite/soil mixture was responsible for stabilizing Cd in these soils (Mahabadi *et al.*, 2007)^[25]. The feasibility of using ammonium and potassium loaded zeolite (NK-Z) as carriers for fertilizer and for slow release of nitrogen (N) and potassium (K) in kale (*Brassica alboglabra*) was investigated. The N and K contents in the soils were maintained at high level in NK-Z treatment compared to that in control. The results indicate that NK-Z has a greater potential as slow-release fertilizer reducing pollution by preventing leaching to the ground water (Li *et al.*, 2013)^[24].

Table 2: Chemical characteristics of natural zeolite used in the experiment (Li *et al.*, 2013)^[24]

SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	P ₂ O ₅ (%)	Moisture (%)	CEC cmol+ Kg ⁻¹
70.3	13.6	1.29	2.51	0.31	1.93	3.17	0.09	6.80	68.29

Table 3: Change in physico-chemical property of soil before and application of zeolite (Li *et al.*, 2013)^[24]

	pH			EC (dS m ⁻¹)			Av. P ₂ O ₅ (mg Kg ⁻¹)		
	CF	ZAF	ZBAF	CF	ZAF	ZBAF	CF	ZAF	ZBAF
Before	6.70	6.68	6.66	0.58	0.58	0.56	655.5	618.9	621.0
After	6.57	6.57	6.55	0.56	0.57	0.55	494.8	516.0	478.7

He *et al.* (2014) observed that soil amendment with cellulose (C), clinoptilolite zeolite (CZ) or both has a potential to reduce N losses by volatilization and leaching in calcareous sandy soils. The mechanisms responsible for the beneficial effect of amendments were involved with increased soil retention capacity for NH₄⁺ and enhanced microbial assimilation of available N in the soil. Ghazavi (2015)^[15] reported that soil treated with 10 and 20 per cent of zeolite, decreased sediment amount in outlet runoff by 23.7 per cent and 37.2 per cent respectively for 10 mm per hours of rainfall intensity and 50 per cent and 67.25 per cent for 15 mm per hours of rainfall intensity. The amount of Ca, Na and K were increased significantly in the soil treated with zeolite compared to untreated soil.

Busaidi *et al.* (2008)^[7] conducted an experiment to know the effect of zeolite on soil nutrients and growth of barley following irrigation with saline water. The overall results indicated that soil amendment with zeolite effectively ameliorate salinity stress and improves nutrient balance in a sandy soil. Application of zeolite significantly increased pH, EC and CEC with application of Zeolite @ 7.5 t ha⁻¹ followed by Zeolite @ 5 t ha⁻¹. Irrespective of zeolite levels, application of zeolite decreased bulk density and increased water holding capacity of soil. Therefore, it can be concluded that zeolite improved physico-chemical (pH, EC, CEC, OC) and physical (BD, WHC) properties of soil (Ravali *et al.*, 2020)^[36].

Table 4: Impact of zeolite application on runoff and infiltrated water (Ghazavi *et al.* 2015)^[15]

Rainfall intensity (mm.hr ⁻¹)	Zeolite (%)	Time of runoff beginning (min)	Runoff			Infiltrated water			Average of Sediment (gr.lit ⁻¹)
			Time that outlet runoff reaches a constant Value (min)	Runoff amount in the first 15 min	Average of Sediment (gr.lit ⁻¹)	Time of drained water beginning (min)	Time that outlet drained water reaches a constant Value (min)	Infiltration amount in the first 15 min	
10	0	15	75	2.15	0.66	56	175	2.96	3.38
	10	20	60	0.64	0.44	76	225	1.20	1.51
	20	30	45	0.35	0.37	100	300	1.79	1.64
15	0	10	60	3.42	0.89	40	120	3.80	4.12
	10	23	45	1.71	0.67	45	165	3.10	2.08
	20	27	45	1.12	0.4	90	240	3.00	2.21

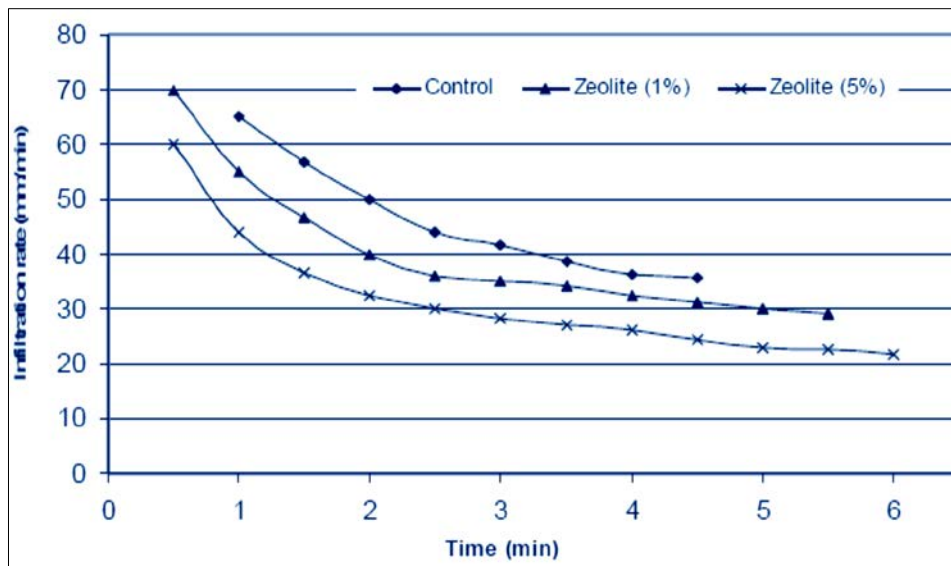


Fig 3: Infiltration rate of soil as affected by zeolite application under high salinity treatment. (Busaidi *et al.*, 2008) [7]

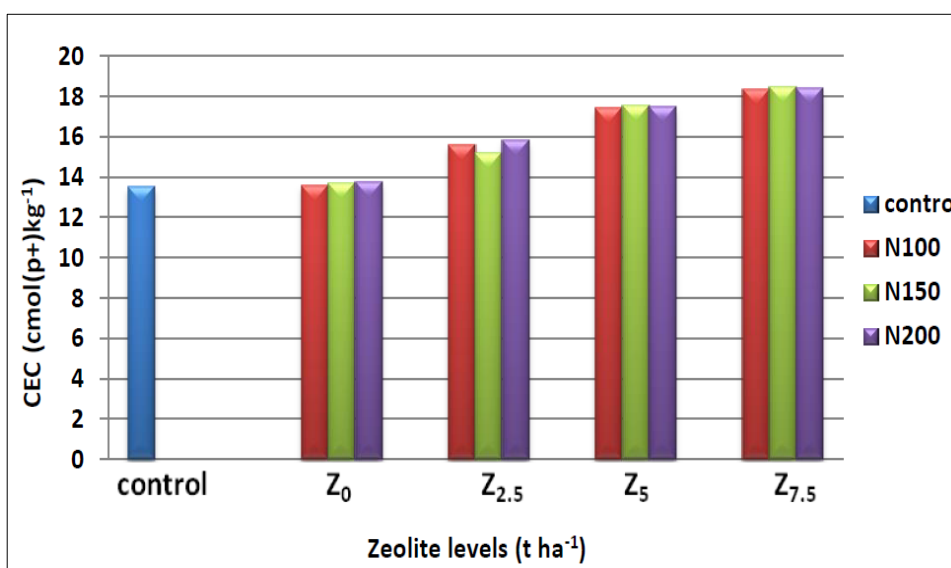


Fig 4: Effect of different levels of nitrogen (kg ha⁻¹) and zeolite (t ha⁻¹) application on Cation Exchange Capacity of soil (cmol (p+) kg⁻¹) (Ravali *et al.*, 2020) [36]

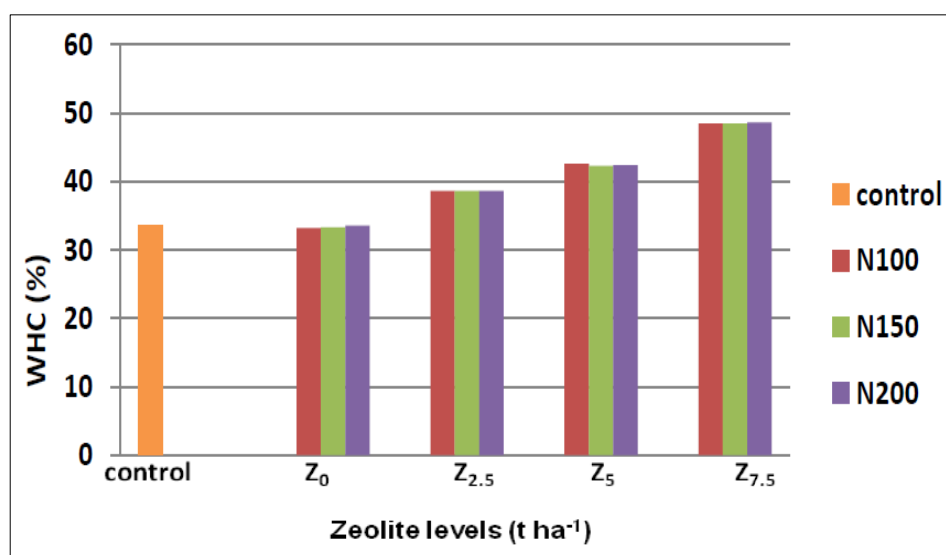


Fig 5: Effect of different levels of nitrogen (kg ha⁻¹) and zeolite (t ha⁻¹) application on water holding capacity (%) of soil (Ravali *et al.*, 2020) [36]

Conclusion

Zeolites are versatile minerals with exceptional properties, including high cation-exchange capacity, molecular sieving, water retention and porosity, making them valuable in agriculture. Their application enhances soil fertility, improves physical and chemical properties and mitigates environmental challenges like heavy metal contamination. Zeolites contribute to nutrient retention, slow-release fertilization and better water use efficiency, thus improving crop yields sustainably.

Research highlights their ability to reduce nitrogen and potassium leaching, improve soil pH, enhance cation exchange capacity (CEC) and lower bulk density. They also mitigate salinity stress, improve nutrient balance and reduce sediment runoff under high rainfall. Furthermore, zeolites act as effective carriers for fertilizers and soil conditioners in various crop systems, particularly in sandy or nutrient-deficient soils. Overall, zeolites offer a sustainable solution for enhancing soil quality, increasing crop productivity and addressing environmental concerns in modern agriculture.

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