

## Review

# The role of natural and synthetic zeolites as soil amendments for mitigating the negative impacts of abiotic stresses to improve agricultural resilience

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## ABSTRACT

Plants are exposed to different types of biotic and abiotic stresses that reduce growth and yield. The review presents the negative effects posed by salinity, water scarcity and phytotoxic metals to the agriculture sector and underscores the protective role of natural and synthetic zeolites to improve the unfavourable growth environment. Furthermore, based on extensive literature review, zeolites (specifically natural zeolites) possess extraordinary adsorption capacity, highly functional nutrient and water holding and releasing characteristics. The enhanced and selective nutrient retention capacity of zeolites enables lower nutrient loss from soil, thereby minimizing the issue of water pollution through the leaching of excessive nutrients. The adsorption potential of zeolites against  $\text{Na}^+$ ,  $\text{Cl}^-$  and various phytotoxic metals in soils improve the growth environment for the plants. Specifically, the addition of zeolites to soil facilitates improvements in water availability and better plant growth parameters: chlorophyll content, total protein concentration, and increased activity of antioxidant defense; eventually mitigating the unfavourable effects of environmental stresses such as extreme temperatures, drought or salinity. Natural zeolites, particularly clinoptilolite, were shown to be better in alleviating plant stresses such as salinity in comparison to synthetic zeolites; handling salt load of up to 100 mM of NaCl. Interestingly, zeolites can be used in combination with other substances such as compost, biochar or calcium-based materials to reduce salinity. The greater availability of hydrophilic active sites in zeolites enhances their water sorption strength, restricting the formation of liquid film required for growth of pathogens; delivering effective desiccant-like effects to protect the plants from several pathogens. In general, zeolite applications can be used as buffering agents to improve plant growth and to deliver better biological resilience during different unfavourable growth conditions.

## 1. Introduction

The exponential increase in population emanates to greater demand for food as well as higher production of food to meet the needs of communities (Alexandratos and Bruinsma, 2012; Baghbani-Arani et al., 2017; Razzaq et al., 2021; Singh et al., 2023). Plants are exposed to different kinds of stresses which results in growth reduction and having lower crops yield. Agricultural stresses have been classified as biotic and abiotic stress (Gull et al., 2019; Suzuki et al., 2014). Biotic stress involves growth reduction caused by several pathogens like fungi, bacteria,

nematodes, allelopathy and herbivores, to the plants. Salinity, floods, drought, heat, cold, radiation, and toxic metals are examples of abiotic stresses encountered by the plants (Berens et al., 2019; Liu et al., 2012; Song et al., 2022; Wu et al., 2023; Yuan et al., 2014; He et al., 2023). Globally, the loss in agricultural crops are caused by these biotic and abiotic stresses (González Guzmán et al., 2022; Gull et al., 2019). Therefore, the application of inorganic chemical fertilizers, investments of heavy equipment and high water usage, are becoming crucial necessities of the conventional agricultural sector to meet food and nutritional requirements of the increasing population (Abbott et al.,

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2018; Mondal et al., 2021). But these rigorous agricultural activities have resulted in the degradation of soil nutritional quality, phytotoxic metal adulteration, mixing of unused fertilizer with water resources, ultimately leading towards declines in soil health, crop production and food availability (Liu et al., 2012; Ming and Mumpton, 1989; Shaghaleh et al., 2024; Singh et al., 2023; Yang et al., 2018). Plants generally have evolved and developed effective mechanisms to tolerate stresses; further agronomic support from improved soil water availability, better soil physio-chemical characteristics and the use of chelating substances to immobilize phytotoxic metals, can further enhance plant growth, yield and resilience to unfavourable conditions (Abbott et al., 2018; Ahanger et al., 2016; Sani et al., 2023; Wong et al., 2020). The conventional agricultural practices mostly involve the use of nitrogen-based inorganic fertilizers and the biological availability of nitrogen for utilization by plants is often lesser; attributed to physio-chemical-related immobilization within the rhizosphere, leaching, denitrification and evaporative losses of nitrogen (Hosono et al., 2013; Peña-Haro et al., 2010; Wang et al., 2020, Wang et al., 2022). Also, the release of nitrate from soil to water resources via nitrogen fertilizers application, deteriorate the ground water quality, causing adverse effects on human health such as blue baby syndrome, gastro-intestinal disorders and emission of nitrous oxide gas via denitrification (Aschebrook-Kilfoy et al., 2013; Wang et al., 2022). Hence, zeolites prevent water pollution by minimizing the use of nitrogen fertilizers, giving rise to better practices in environmental sustainability. Another nutrient in fertilizer is phosphate, which can also cause eutrophication of water resources (Caspersen and Ganrot, 2018; Delkash et al., 2014). The retention of soil nutrients is an important challenge to improve the soil nutritional quality and crop productivity. As nutrients help to activate biochemical pathways and components of defense system in plants, therefore nutrient retention and availability within the rhizosphere contribute to improving resilience to drought, salinity and heat stress in crops (Ahanger et al., 2016; Alam, 1999; de Bang et al., 2021; El-Ramady et al., 2018) Hence, the modification of soil with organic compounds has got much attention for long term improvement in physical and chemical properties of soil (Abbott et al., 2018; Chowdhury et al., 2024; Mahabadi et al., 2007; Sani et al., 2023; Sani and Yong, 2022; Wong et al., 2020). In this context, zeolites emerge as potential soil ameliorating agents, possess superior nutrient and water capturing capacity, cation exchange potential, and better water capture from seepages (Jha and Singh, 2016; Sarkar and Naidu, 2015). Zeolites have remarkable role in agriculture, medicinal and environmental protection fields (Polat et al., 2004). Zeolites have shown to increase the photosynthesis rate in plants (De Smedt et al., 2017). Zeolites are good fertilizers as well as functioning as chelating substances; they decrease

the rapid release of nutrients from fertilizer to provide consistent availability of nutrients throughout the growth phases (Perez-Caballero et al., 2008). Several researchers have affirmed the potential of zeolites in improving the agricultural and horticultural plants quality and yield (Chen et al., 2017; Ghanbari and Ariaifar, 2013; Nur Aainaa et al., 2018; Shahsavari et al., 2014). Furthermore, natural zeolites also exhibit adsorption potential against toxic metals such as cadmium, arsenic, lead, nickel along with other soil contaminants, preventing soil pollution (Kazemian & Malah, 2006). Zeolites prevent downstream water pollution issues by improving the nitrogen use efficiency of inorganic-based fertilizers, giving rise to environmental sustainability as well. Interestingly, zeolites have further functionality and serving as plant protection substances. They can be utilized as particle films to cope with several crop diseases and pests. With their small particle size, zeolites were able to reduce heat stress and fungal diseases in plants (De Smedt et al., 2015). Zeolites play a key role to protect the plants against drought, salinity and temperature stresses, ultimately help to improve plant growth and yield (Babaousmail et al., 2022; Rahimi et al., 2021; Sayed et al., 2010). The various types of stresses encountered by plants are shown in Fig. 1.

## 2. Zeolites

Zeolites were discovered in 1756 by Fredrich Cronstedt, a Swedish mineralogist (Polat et al., 2004). The term zeolite originated from Greek word meaning “boiling stones” as they effervesce by heating around 200°C. Zeolites have been reported as minerals located in volcanic and sedimentary rocks for around 200 years. In 1960s, they have been produced commercially around the globe (Polat et al., 2004). Zeolites are composed of aluminosilicates tetrahedral units interlinked into three-dimensional cage like structure (Munir et al., 2024; Nakhli et al., 2017). The zeolite’s empirical formula is  $M_{2n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ . M represents the alkali or alkaline earth cation, n represents the charge of cation. The value of x in zeolite formula ranges between 2 and 10 and y value is between 2 to 7, having structural cations comprised of  $Si^{2+}$ ,  $Al^{3+}$  and  $Fe^{3+}$  and  $K^+$ ,  $Na^+$  and  $Ca^{2+}$  as interchangeable cations (Hemingway and Robie, 1984). In zeolites, negative charge present on aluminum ions is counterpoised by cations ( $Na^+$ ,  $K^+$  and  $Ca^{2+}$ ) positive charge. Interestingly, zeolites have more than 50 structural configurations or forms. Clinoptilolite, erionite, chabazite and mordenite are a few examples of naturally occurring zeolites. There are more than 150 types of synthetic zeolites; including zeolite ZSM-5, X, Y and the type A zeolites (Król, 2020). The distinctive properties of zeolite include ion-exchange, adsorption, filtration and catalysis.

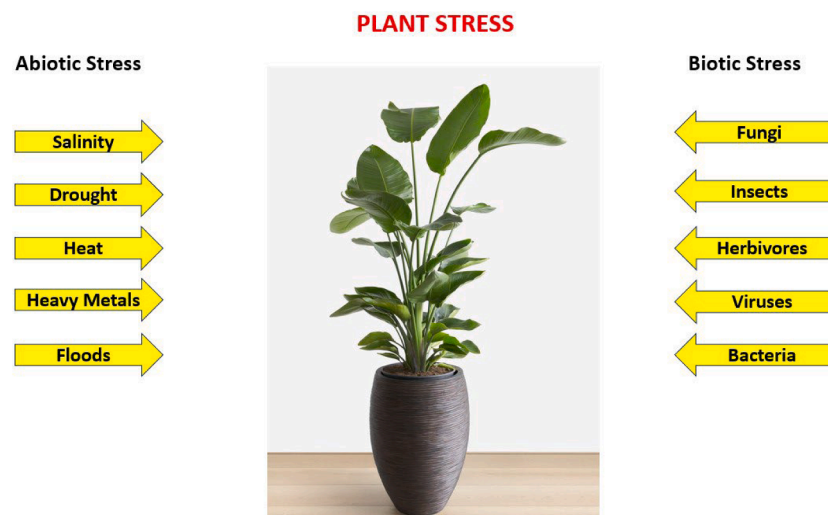


Fig. 1. The various abiotic and biotic stresses affecting plants growing at unfavourable conditions

Zeolites can be classified into low or high silica zeolite depending upon Si/Al (silica to aluminum) content. The higher Si/Al content is responsible for increased thermal stability, high acid resistivity, more hydrophobicity and reduced affinity for polar compounds (Szerement et al., 2021). Zeolites can be appropriately utilized for agronomic practices as slow release fertilizers, mitigating substances for polluted soil and for condition of soil, owing to their internal crystal structure and unique characteristics (Ming and Allen, 2001). Additionally, zeolites are bounteous geographically, cheap and easily available, they can be applied in management of practical field leading to sustainable agriculture (Farzad et al., 2007). The distinctive characteristics of zeolites could vary based on their natural or synthetic source of materials used for production (Noviello et al., 2021; Restiawaty et al., 2024).

### 2.1. Natural zeolites

Natural zeolites mostly originate from volcanoes from pyrogenic rocks either extracted in crystalline forms or in granular forms in sedimentary rocks. Interestingly, zeolites are also abundant at bottom of ocean sediments, but these reserves are not easily accessible to humans (Noviello et al., 2021). The reaction of volcanic ash with basic lakes water could result in zeolites formation under natural circumstances (Krol, 2020). Natural zeolites are predominantly found across the globe and their deposits are widespread in Asia, Europe, Africa, Australia, New Zealand and United States. Among naturally occurring zeolites, chabazite, clinoptilolite, mordenite and erionite possess interesting characteristics and have the potential for commercial utilization (U.S. Geological Survey, 2021). The crystalline honeycomb framework of these minerals with minute cavities allows them to lose or gain water. They have been also considered as pozzolanic substances and employed as significant fraction of clay or tuff (Ahmadi et al., 2010). As natural zeolites are selective against phytotoxic metals and ammonium ions, these materials have been utilized in agronomy and ecological conservation projects (Velarde et al., 2024). The most advantageous zeolite existing in nature is clinoptilolite owing to its application as feed supplement, molecular sieve and gas sorbent (Akyalcin et al., 2024). The excessive number of pore gaps, extreme temperature resistance and basic chemical framework is attributed towards large application of clinoptilolite. Pristine or composite clinoptilolite has been employed to enhance the physio-chemical properties of soil (Pirzad et al., 2014). Although natural zeolites are readily available, and their formation is not expensive; however, these natural zeolites have certain limitations to be used widely in the various industry. For example, in clinoptilolite, diameter of cavities is very small and measures around 0.30–4 nm, restricting the adsorption of huge organic and gaseous molecules. Also, the natural zeolites exhibit mild adsorption potential and the negative charge on the surface of zeolite allowing them to adsorb cations only (Restiawaty et al., 2024). In natural zeolites, Si/Al content cannot be

varied, and is responsible for determining several physio-chemical zeolite characteristics. Adsorption, ion exchange and catalytic characteristics of zeolite are associated with hydrophilicity and hydrophobicity of zeolite. The hydrophobicity can be increased by enhancing Si/Al ratio as Si-O-Si moiety is non-polar. Hydrophilic zeolites possess low Si/Al content and are involved in ion-exchange mechanism. As natural zeolite's Si/Al content is fixed, so their utilization is limited and needs to be modified (Munir et al., 2024). Zeolites exhibiting increased Si/Al content are also more thermo-stable. Furthermore, the geological reserves of natural zeolites are un-replenishable source; and the formation of zeolites exhibiting distinctive characteristics in laboratory involves many complex steps (Krol et al., 2020). The simple structure of a zeolite is shown in Fig. 2.

### 2.2. Synthetic zeolites

Around one hundred and fifty types of zeolites have been fabricated synthetically from natural precursors or synthetic silicates via hydrothermal process (Kordala et al., 2024). The laboratory preparation of zeolites involves specialized equipment, energy input, requirements for high temperature, high pressure and the availability of purified substrates. Thus, the synthetic production of zeolites is considered to be expensive in comparison to harvesting natural zeolites; therefore, researchers are looking for cheaper and readily assessable sources of zeolites to minimize the production cost (de Carvalho et al., 2024). Several natural silica sources such as clay minerals including kaoline, halosite and volcanic glasses have been employed for fabrication of zeolites. Furthermore, the waste substances of aluminosilicates such as rice husk or fly ash have also been utilized to fabricate zeolite artificially (Krol et al., 2020).

The fabrication of zeolites via the hydrothermal process started in 1950s for the first time. The precursor materials of aluminosilicates are heated for hours or days by spiking with basic solution having pH > 8.5 till final product is achieved. Hydrothermal process is frequently employed protocol and involves temperature conditions ranging from 80 to 350°C (Kordala et al., 2024). Other processes such as dissolution, condensation and crystallization occur in the autoclaves at increased pressure and require optimum control of reaction conditions for suitable product (Kastanaki et al., 2024). Molten salt process, fusion method, alkali activation, microwave assisted synthesis and dialysis process are examples of other routes for synthetic zeolite (Kordala et al., 2024). A new ionothermal process has also been formulated to fabricate zeolite maintaining optimum pressure in open containers. This process utilizes ionic liquids, consisting of ions and exhibiting melting temperature under 100°C. Ionic liquids have trivial vapour pressure, more chemically and thermally stable, enhanced ionic conductivity and catalytic properties, so employed in fabrication of organic, inorganic and biocatalysts. The pioneer zeolite synthesized ionothermally was AEL zeolite in 2004

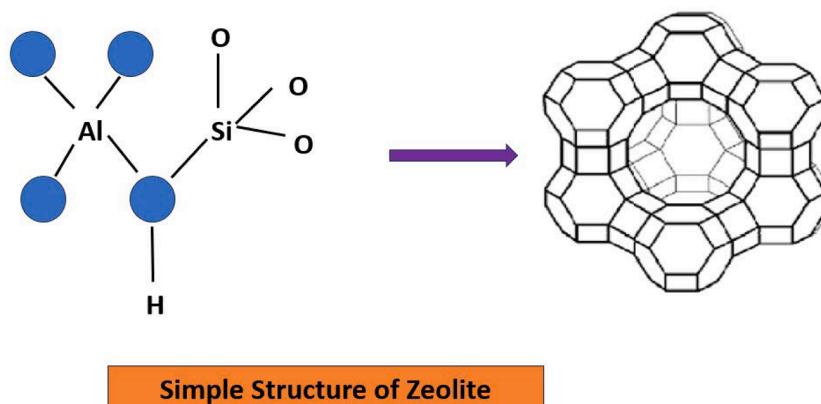


Fig. 2. The simplified structure of a zeolite exhibiting Al, Si and hydrogen bonding.

(Cai et al., 2008). Recently, effective strategies were developed to formulate NaP synthetic zeolites hydrothermally by utilizing natural zeolite clinoptilolite. This process turned out to be an economically-feasible protocol as it used natural mineral as the precursor of aluminosilicates (Moreno-Torres et al., 2024).

Zeolite-A, zeolite-X, zeolite-Y, zeolite L, zeolite N-A, zeolite P, zeolite ZSM-5, zeolite O and zeolite ZK-4 are few examples of synthetic zeolites with interestingly properties to mitigate soil and water pollution (Kordala et al., 2024; Markovska and Irena, 2009).

### 3. Role of zeolites in agriculture

#### 3.1. Effects on soil properties

The physical characteristics of soil include bulk density, aeration, porosity of soil, water retention potential and particle density (Bittelli et al., 2015). Generally, zeolite can alter soil porosity, pore size dispersal, pore connectivity and tortuosity, depending on structure and quality of soil, zeolite type of zeolite and also on reaction conditions. Researchers have reported the zeolite impacts on infiltration rate of soil (rate at which water enters to soil), hydraulic conductance (ease at which water proceed through soil pores), water proportion, water detention potential and management of fertilizers leaching in soil (Comegna et al., 2023; Prisa et al., 2023). The bulk density of soil is the important feature which impacts the stability of topsoil. The amendment of soil with zeolite minimizes the bulk density, which changes the water holding potential and porosity of soil/ (Mondal et al., 2021). The water content of soil is important for growth of plant, control of temperature of soil as well as activity of soil microbes (Bittelli et al., 2015). Zeolites, either natural or synthetic, are well-known for their water holding potential and have been considered as an effective amendment to enhance water availability under critical conditions of drought in drylands.

A study conducted on *Solanum lycopersicum* Mill. seedling revealed that the modification of soil with 30 % clinoptilolite zeolite resulted improved soil water holding potential up to 260 % entire plant growth and physiological output (Méndez Argüello et al., 2018). As zeolites alter the pore size dispersal of soil, wilting point (where no water is assessable) and field capacity (soil water content after excess water drainage) of soil can also be modified under zeolite addition. The administration of synthetic zeolite to loamy soil changes wilting point from 26 to 46 % and field capacity from 41 % to 59 % (Belviso et al., 2022). In another study, natural zeolite and bentonite enhanced water capturing potential, field capacity and moisture content in sandy soil (Hassan et al., 2013). Similarly, natural zeolite clinoptilolite enhanced water content by 3.6–14.7 % in loamy soil owing to increase in microporosity of soil (Ibrahim et al., 2021). Zeolite modified soil resulted in an increase in water holding potential from 0.4 to 1.8 % under conditions of drought and in normal conditions, water holding capacity of soil increased from 5 to 15 % in comparison to non-modified soil. The zeolites used in the study was natural zeolites; known as mordenites and have sizes of less than 0.25mm (He and Huang, 2001). Another study involving the application of 5 kg m<sup>-2</sup> clinoptilolite zeolite to sand dune soil revealed that soil salt and water content has been increased to 1.4 and 20 % respectively. The amount of cations such as sodium, potassium, magnesium and calcium has been increased with the increase in soil salinity (Abideen et al., 2014; Shoukat et al., 2020). The study affirmed that zeolites enhanced the cation exchange potential as well as quantity of cations on soil surface, which can be released at the cost of salts present in saline water (Inglezakis et al., 2012). Hence, a lowered salinity environment on test plants was effectively delivered by reduced salt accretion in the soil subsurface. The greater pore volume of zeolite is responsible for increased water holding capacity in their framework (Mondal et al., 2021). The amendment of silty clay soil with 8 g kg<sup>-1</sup> zeolite enhanced the hydraulic conductivity. The ease of transportation of water within soil, employed to design irrigation system is called hydraulic conductivity (Gholizadeh-Sarabi and Sepaskhah, 2013). Loamy

and sandy soils showed increased water detention and minimum infiltration speed and hydraulic conductance by amending with zeolite. The rate of infiltration and hydraulic conductivity was effectively declined by up to 26 and 19 %; during the exposure of loamy soil to clinoptilolite zeolites (Ibrahim et al., 2021). The rate of infiltration was conversely associated with zeolite administration reflecting the increased soil water retention and lowering the leaching of salt and nutrients. The micro-porous structure of zeolites generally reduces the permeation of water into the soil matrices (Comegna et al., 2023). In another research, synthetic zeolites (even with a small amount added) affected the hydraulic and transport characteristics of the test soil by altering the pore size distribution. The alteration of macroporous soil region towards the microporous is considered advantageous as it resulted in reduced mobility of nutrients, water and pesticides. Zeolite addition also decreased crack areas in silty soils. Specifically, the test soil modified with zeolites of up to 8 g kg<sup>-1</sup> revealed reduction in crack depth up to 50 % in dry and muddled soil (Razmi and Sepaskhah, 2012). Lime-zeolite addition to clay soil enhanced its properties of swelling, compressive strength and plasticity. The index of plasticity declined to 9.4 % by adding zeolites; and the swelling can be completely eliminated by incorporating zeolites. Moving forward, this unique property may help to replace conventional stabilizing substances with minerals to improve various structures such as pavements (Khajeh et al., 2023). In another study, zeolite application to soil increased the water availability for plant usage by up to 50 % (Ramesh et al., 2010).

A study was conducted to examine the effects of four natural clinoptilolite on Bermuda grass “Tifdwarf”; grown on sandy soil modified with 8.5 % zeolite. The quantity of transpiration water in sand has been found to increase from 1 to 16 %, with the addition of zeolite; demonstrating the increase in water content of the modified soil (Wehtje et al., 2003). Natural zeolite enhanced the ventilation porosity and water holding strength of chernozem (black fertile soil). Soil porosity has been enhanced by adding 10 % zeolite and water holding strength by 20 % addition of zeolite to soil (Ma et al., 2018). The combination of micro-spherical zeolites with sodium alginate and gelatin was interesting; the resultant property was a soil booster with effective water retention and antimicrobial potential (Lu et al., 2023).

#### 3.2. Effects on the nutrient holding capacity

The nutrient holding capacity of soil can be enhanced by addition of zeolites as soil physical, chemical and biological characteristics are affected by zeolitic minerals. Zeolites show increased sorption selectivity against ammonium ions (NH<sub>4</sub><sup>+</sup>) owing to their enhanced cation exchange potential. The positive charge of NH<sub>4</sub><sup>+</sup> and zeolite’s negative charge sites has been responsible for electrostatic interactions facilitating NH<sub>4</sub><sup>+</sup> adsorption by zeolite (Englert and Rubio, 2005). This high attraction of zeolites for ammonium ions have been utilized to retain and release NH<sub>4</sub><sup>+</sup> in soil. The Si/Al ratio of zeolite, their pore size, pH, contact time, cations of zeolite and percentage of other ionic substances present in soil/water has been found accountable for detainment of ammonium ions by zeolite (Sarkar and Naidu, 2015; Wang et al., 2022). Zeolites exist in diverse forms due to the variation in zeolite framework or natural flaws in their structure and cation exchange potential of a few natural zeolites have been found three times more as compared to other soil minerals (Kazemian et al., 2012; Malekian et al., 2011; Ramesh et al., 2015). Hence, the recognition of the effective adsorption characteristics in several forms of zeolites is paramount to understanding how these interesting compounds minimize the NH<sub>4</sub><sup>+</sup> loss and improving nitrogen retention in soil.

The combined applications of zeolite and fertilizers to soil minimizes the nitrogen percolation, decline in release of greenhouse gases and inhibits the discharge of nutrients into soil (Behzadfar et al., 2017). Researchers have found reduction in loss of ammonia by using fertilizers along with zeolite in comparison to utilization of pristine fertilizers (Palanivell et al., 2016). In order to enhance the nitrogen use efficiency



(NUE) in agro practices and to decrease the loss of nitrogen via leaching, physicochemical characteristics of zeolites such as superior cation exchange potential has been utilized (Sarkar and Naidu, 2015). Nitrogen percolation and nitrogen use efficiency (NUE) are interlinked to each other as lowering groundwater leaching of ammonium ions via addition of zeolite will result in enhancement of NUE (Ming and Allen, 2001). One of the naturally present zeolites having increased permeability for ammonium ions is Clinoptilolite. In a study, experiment has been performed on Clinoptilolite column loaded with pulse of urea and ammonium nitrate solution. The results depicted the leaching of minute amount of ammonium ions/ nitrogen up to 3 % from Clinoptilolite column as compared to sand column in which leaching was found to be 17 %. Hence, an overall reduction of 82 % in leaching was observed (Piñón-Villarreal et al., 2013). In another experiment, columns filled with 2 and 8 g kg<sup>-1</sup> of Clinoptilolite, pulse loaded with solution of ammonium nitrate showed reduction in ammonium/ nitrogen leaching up to 43 % and 50 % correspondingly (Sepaskhah and Yousefi, 2007). The biological transformation of soil ammonium ions to nitrate (NO<sub>3</sub><sup>-</sup>) can also be prevented by zeolite via phenomenon of nitrification. This conversion can lead towards nitrate water pollution. Natural zeolites like Clinoptilolite having reduced pore sizes in crystal framework can easily accommodate ammonium cations. The microbes undergoing the conversion of ammonium to nitrate ions are not accessible to zeolite pores. Hence, when ammonium ions are adsorbed and retained by zeolite voids, nitrifying microbes cannot access ammonium ions, ultimately preventing the phenomenon of nitrification (Baerlocher et al., 2007). The reduction in nitrogen percolation particularly in aerated soils was achieved by inhibiting the nitrification mechanism by zeolites (Gholamhoseini et al., 2012). The addition of 10 % (w w<sup>-1</sup>) clinoptilolite tuff to sand in which source of nitrogen was supplied by ammonium sulphate, reduction in leaching of NO<sub>3</sub><sup>-</sup> from clinoptilolite modified sand has been found to be 86 % than un-modified sand. The decrease in NH<sub>4</sub><sup>+</sup> leaching came out to be 99 % (Nakhli et al., 2017).

The availability of soil nutrients has been increased by the application of zeolite along with other substances to soil, which in turn increases the growth of plant as well (Colombani et al., 2015; Lim et al., 2016). It was reported that the modification of soil by fly ash along with clinoptilolite increased the amount of nitrogen in soil in comparison to individual application of fly ash or clinoptilolite. Thus, enhanced nutrient retention resulted in lesser loss of nutrients, thereby minimizing the water pollution by nutrient leaching (Lim et al., 2016). Hence, zeolites possess an extraordinary potential to prevent nitrate water pollution also by minimizing the biological transformation of soil ammonium ions to nitrate (NO<sub>3</sub><sup>-</sup>), in addition to improved nutrient retention by plants.

Another essential plant nutrient is phosphorous, which exist mainly in the form of phosphate (PO<sub>4</sub><sup>3-</sup>) in soil (Lambers, 2022). Phosphate ions carry negative charge, which bind easily to soil matrix (Gholamhoseini et al., 2012; Shi et al., 2019). The various adsorption and fixation processes results in the fixation of phosphate ions in soil matrices (Lambers, 2022; Moharami and Jalali, 2014). The continuous application of high amount of phosphates in fertilizers for cultivation results in the saturation of soil adsorption sites; often resulting in leaching of phosphates in surface run off and causing environmental issues in waterbodies and ground water (Sharpley et al., 2007; Sun et al., 2023). As zeolites possess negative charge on its surface and do not exhibit anion exchange potential. Hence, it has no role in phosphate leaching, when mixed to soil (Elliot and Zhang, 2005). The experiment has been conducted on soil modified with natural zeolite clinoptilolite, which is added at the rate of 10 % (w w<sup>-1</sup>) along with ammonium phosphate solution. The results showed that the sorption of phosphate in modified soil is same as in un modified soil (Nakhli et al., 2017). The utilization of slow release fertilizers (SRF) is a potent method to lessen the nutrients uptake rate by roots of plants and nutrients release rate by fertilizers (Ni et al., 2010). But, the use of zeolites as slow-release fertilizers is restricted to positively charged nutrients like potassium (K<sup>+</sup>)

or ammonium (NH<sub>4</sub><sup>+</sup>), which can be loaded on sites of zeolite. So, the un-modified zeolite is unable to load anionic nutrients like phosphate. But phosphate can be released slowly and controllable manner by using combined zeolite and mineral dissolution (Chesworth et al., 1987). The ion exchange process enables apprehension of dissolved cations by zeolites, increasing dissolution and cations for ion exchange has been provided by mineral dissolution. Thus, ion exchange and dissolution processes operate each other (Omekeh et al., 2015).

Zeolites possess extraordinary selectivity for potassium ions (K<sup>+</sup>) as compared to sodium, calcium and magnesium ions, making it hard to eliminate potassium from exchange sites, expediting maximum sorption of potassium ions by roots of plants via ion exchange within zeolite and root (Rivero and Rodríguez-Fuentes, 1988). Hence, K<sup>+</sup> loss via surface run off and leaching of ground water may be declined though supplementation of zeolite as SRF (Ming and Allen, 2001). Zeolite capped fertilizers demonstrated effective water holding capacity and lowered the rate of nutrients release by fertilizers to the soil. Furthermore, zeolites, especially chabazite and bentonite, also exhibited adsorption capacity for iron and zinc micronutrients (Yuvaraj and Subramanian, 2018). The high concentrations of zinc, manganese and copper were observed in leaves of beans by increasing the addition of zeolites to soil (dosage of around 90 kg ha<sup>-1</sup>). Hence, the maximum availability of macro- and micronutrients in soil can be improved with the addition of zeolites (Hazrati et al., 2017). The functional roles of zeolites in plants are highlighted in Fig. 3.

### 3.3. Gradual herbicides release by zeolite

As zeolites exhibit high porosity and possess unique honey comb-like structure, they possess extraordinary capacity to store and release herbicides gradually. ZSM 5 zeolite, a synthetic type of zeolite having high hydrophobicity due to high silica percentage as compared to alumina, possess 5 Angstroms (Å) pore diameter has the potential to adsorb class of herbicides called triazine. ZSM 5 binds to triazine in its intracrystalline space and release it gradually (Corma and Garcia, 2004). The phenylurea group of herbicides have been adsorbed by aggregates of humic acid-zeolite (Sangeetha and Baskar, 2016). However, atrazine has been released from soil or water by Clinoptilolite zeolites (Salvestrini et al., 2010). The effectivity of herbicide to manage the weed floras has been increased by gradual release of herbicide due to zeolites, resulting in weed free crops. A prolonged detention time of zeolite aided herbicide on leaves of weed improves the effectivity of herbicidal mechanism of

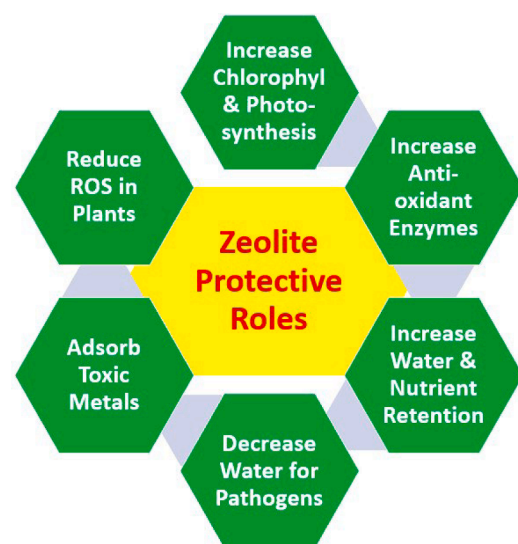


Fig. 3. The protective roles of zeolites in plants to ameliorate biotic and abiotic stresses

action (Shirvani et al., 2014). Selected zeolites suitable for improving the physio-chemical properties of soil are listed in Table 1.

#### 4. The potential of zeolites to improve resilience to abiotic stress

##### 4.1. Salinity stress

The high amount of salt ions either in water sources employed for plants cultivation having electrical conductivity level  $> 1.0$  mS/cm or in soil extracts having EC level  $> 2$  mS/cm, represents one of the extensive global abiotic stresses in agriculture sector called as salt stress (Ondrasek et al., 2022). Salinity is one of the paramount obstacles to viable agriculture worldwide, adversely impacting the crop growth via disruption of biochemical, structural and physiological functions of plants (Arif et al., 2020). Salinity is adversely affecting greater than 6 % of land worldwide (Mahmoud et al., 2019). In nature, the salinity stress is caused by a sodium salt, primarily sodium chloride (Negahban et al., 2014; Wu et al., 2023; He et al., 2023). It has been revealed that salinity stress along with adverse ecological imputations will turn more

**Table 1**  
The roles of selected zeolites in improving physio-chemical properties of soil and soil nutrient acquisition.

Zeolite type	Soil properties	Zeolite effects	References
Mordenite	Water holding potential	Water holding capacity increased from 0.4 to 1.8 %	(He and Huang, 2001)
clinoptilolite and vermiculite	Salt & water holding potential	Cation's increase, soil salt and water content increase 1.4 and 20 %	(Inglezakis et al., 2012)
Clinoptilolite	Hydraulic conductivity	Reduction in crack depth up to 50 % in soil	(Razmi and Sepaskhah, 2012)
Clinoptilolite	Water holding potential	water availability to plant increases up to 50 %	(Ramesh et al., 2010)
Clinoptilolite	Water holding potential	Water content increase from 1 to 16 %	(Wehtje et al., 2003)
Chilean natural zeolite	Nutrient holding potential	NH <sub>4</sub> <sup>+</sup> adsorption	(Englert and Rubio, 2005)
Clinoptilolite and fertilizers	Nutrient holding potential	Reduction in nitrogen percolation	(Behzadfar et al., 2017)
Clinoptilolite	Nutrient holding potential	Reduction in loss of ammonia	(Palanivell et al., 2016)
Clinoptilolite	Nutrient holding potential	Reduction of ammonium ions/ nitrogen leaching up to 82 %	(Piñón-Villarreal et al., 2013)
Clinoptilolite	Nutrient holding potential	NH <sub>4</sub> <sup>+</sup> adsorption, Decreased conversion of ammonium ions to nitrate (NO <sub>3</sub> <sup>-</sup> )	(Baerlocher et al., 2007)
Clinoptilolite	Nutrient holding potential	Reduction in NH <sub>4</sub> <sup>+</sup> leaching to 99 %	(Nakhli et al., 2017)
Clinoptilolite with fly ash	Nutrient holding potential	Reduction in loss of nutrients	(Lim et al., 2016)
Zeolite as SRF	Nutrient detention	Maximum sorption of potassium ions by roots of plants. Reduction in K <sup>+</sup> loss	(Ming and Allen, 2001)
Chabazite & Bentonite	Nutrient detention	High adsorption for iron and zinc micronutrients	(Yuvaraj and Subramanian, 2018)
ZSM 5 Zeolite	Gradual herbicides release	Adsorption of herbicide triazine	(Corma and Garcia, 2004)
Humic acid-Zeolite	Gradual herbicides release	Adsorption of phenylurea group of herbicides	(Sangeetha and Baskar, 2016)

ensorious owing to rapid global warming. For example, the recurring drought stress associated with elevated air temperatures, high sea level and the enhanced propensity of low-quality grey water (Ondrasek et al., 2022). The immoderate amount of salt in water or soil negatively impacts the cultivation of crops. The enhanced accretion of Na<sup>+</sup> and effluence of Ca<sup>+</sup> and K<sup>+</sup> from cytosol have been responsible for negative impacts of salinity, resulting in cellular homeostasis imbalance and deficiency of nutrients (Kamran et al., 2019). Salinity stress has also been linked to the induction of osmotic load in plants, suppressed rate of photosynthesis, pigments hydrolysis and disproportion in uptake of nutrients and absorption of water (Mahmoud et al., 2019; He et al., 2023). Salinity also actuates the plant cells death via excessive generation of reactive oxygen species and initiation of oxidative stress in plants. The disruption of DNA and proteins, degradation of membranes, peroxidation of lipids, are the negative impacts of reactive oxygen species (Das and Roychoudhury, 2014). The impacts of salt stress on plants have been mentioned in the Fig. 4 below.

Salt stress negatively affect the plant height, fresh and dry weight of roots, dry weight of plant, length of stalk and number of leaves. A study performed on Chinese cabbage under saline environment revealed that the saline load suppressed the height of plant up to 23 %, leaves ratio up to 22 %, length of stalk 32 %, dry weight of plant 131 %, fresh and dry mass of roots up to 165 % and 170 % respectively (Romadhan et al., 2022). Salt stress generally reduces plant growth (Ghoreishiasl et al., 2017; Wu et al., 2023; He et al., 2023). A wide variety of precautionary and retrieval strategies have been revealed to combat salt stress in crops or to enhance salinity resistance in plants. For instance, transfer of halophytic traits to glycophytes to enhance their salt resistance, as halophytes can tolerate salt while glycophytes are sensitive to salinity. Another strategy is propagation and genetic scheme which involves choosing and creating salt resistant prototype. Genetic alteration of plant varieties also propagates salt tolerance in plants. For example, rice variety Pusa Basmati 1 has been transformed genetically via AmSOD gene utilizing gene transfer tool microprojectile bombardment. The results of this study showed that progenies were not only salt-tolerant but also revealed enhanced productivity (Sarangi et al., 2019). Modification of plant genome is another approach to induce salt resistance in plants via genome modifying tools such as CRISPR/Cas9 tool. For example, CRISPR/Cas tool has been employed in a study to edit genome of rice imparting it salt resistance. The gene modification targets SOS gene involved in signaling mechanism which shields the plant from saline stress (Farhat et al., 2019). These techniques remained the attention of researcher for prolonged period of time and turned out to be successful as well to combat salinity load in plants. However, these approaches present several limitations as the strategies rely on high throughput technology and protocols are time consuming. Other constraints include uncertain genetic gain and divergent interactions between genotype and surroundings (Sarangi et al., 2019). Conventionally, leaching is also employed to reduce salt stress, but it has been found unsuitable and costly approach under certain scenarios (Negahban et al., 2014). The remediation of negative effects of salinity on crops can be achieved economically via application of natural modifications to growth medium like zeolites, which are abundant in volcanic rocks globally (Tsintskaladze et al., 2016).

##### 4.1.1. The plausible mechanisms of zeolites in regulating salinity tolerance

Zeolites, particularly the natural zeolites have crystal-like nanoporous substance with distinctive physio-chemical characteristics encompassing orifices or cavities, behaving as molecular sifter (Munir et al., 2024). The negative charge on natural zeolite is stabilized by positively charged cations, providing a suitable allurements for positively charged ammonium ions or potassium ions, so they may be discharged when needed by plants. As zeolite possesses open infrastructure having crisscross arrangement of pores, providing it huge surface area for confining and interchanging essential nutrients (Munir et al., 2024). The adsorption potential of zeolite against sodium and chloride ions

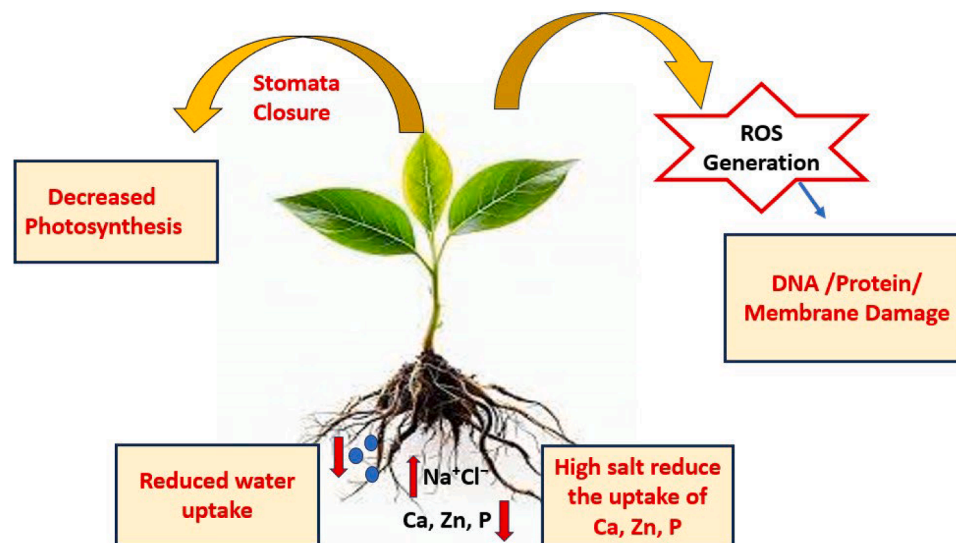


Fig. 4. The effects of elevated salt (NaCl) levels on various physiological parameters in plants

entrapped them in cavities, eventually allowing zeolite to enhance soil characteristics. The adsorption of sodium ions by zeolite inhibits its uptake to plant shoots, eventually reducing salinity. The cation exchange potential of zeolite allows the exchange of soil  $\text{Na}^+$  ions with zeolite  $\text{Ca}^{+2}$  ions, which are essential for plants cellular actions and structural stability. As natural zeolite is mild basic in nature, its application with fertilizers can maintain pH of soil, eliminating the lime requirement to neutralize acidity of soil (Noori et al., 2006).

#### 4.1.2. Zeolite potential in improving salinity tolerance

The distinctive characteristics of zeolite such as enhanced cation exchange potential, cost-effectiveness and structural stability endorsed zeolite as successful agents against salt or water stress in plants (Bybordi et al., 2016; Ippolito et al., 2011). The porous structure of zeolite can encompass large diversity of cations like sodium, potassium, calcium and magnesium. Due to slackly bound nature of these positively charged ions, they can be interchanged with other ions present in solution (Bybordi et al., 2016). For example, in a study conducted on ryegrass (*Lolium perenne* L.), the amendment of soil with ordinary and potassium rich zeolite under saline stress, resulted in reduction of sodium concentration. It has been observed that sodium amount has been declined up to 44.36 % in plant shoots and 21.31 % in plant roots by both kinds of zeolites. Furthermore, zeolites amendment of soil resulted in an increase in water and chlorophyll content, total proteins concentration and increased activity of peroxidase (POD) and superoxide dismutase (SOD) enzymes, eventually mitigating the harmful impacts of salinity (Rahimi et al., 2021). The weight of the plant has been enhanced by using natural and synthetic zeolite modified soil to cultivate *Raphanus sativus* L. It was confirmed in results that total dry weight, air fresh weight and total fresh weight has been increased in plant grown on saline soil. The effectivity of natural zeolite clinoptilolite was greater than synthetic zeolite to prevent salinity (Noori et al., 2007).

The potential of zeolites in reducing salinity stress was conducted for many species. For example, the barley plants were irrigated with 16 dS  $\text{m}^{-1}$  saline water, which reduced the leaf area of up to 44 %, height of plant up to 25 % and 60 % dry weight of plant; conversely, zeolite amendment restored the biomass in salinity stressed barley. The levels of nutrients were also restored in zeolite modified soil such as iron (19 %) and manganese (10 %) (Al-Busaidi et al., 2008). In another study, the effects of salt stress (50 mM, 100 mM, and 150 mM NaCl.) on lettuce were alleviated (up to 15%) using zeolite modified soil (Babaousmail et al., 2022). The research conducted on *Ixora coccinea* L. and *Poa pratensis* plants grown in zeolite medium also confirmed the reduction in

salt stress (de Sousa et al., 2023; Negahban et al., 2014). The *Poa pratensis* plants were grown in variable concentrations of zeolites such as 5 %, 10 % and 15 % along with sand. Plants were supplied with 0.24, 3.4 and 6.4 dS. $\text{m}^{-1}$  saline water regularly for six months. The application of 15 % zeolites resulted in the reduction of sodium or potassium leaching; and enhanced quality of turf and sodium absorption ratio (Negahban et al., 2014). In another research performed on saline stressed wheat plants, the application of zeolite delivered an increase in plant biomass, increased size of seeds of up to 58.8 %, and seed number of up to 57.5 %. The quality of soil was improved and especially for the retention of nutrients by zeolites. From the various findings, zeolites can be used to mitigate the negative effects of 100 to 150 mM salt concentration in soil (Ma et al., 2023). As salinity stress reduces the length of root and shoot along with reduction in their dry weight, pot experiments on rosemary plant have been performed using zeolite and chitosan application. Zeolites were added to soil in concentrations of 0, 4 and 8 g  $\text{kg}^{-1}$  and salt concentration applied was 0, 50 and 100 mM. The growth of plants exposed to salinity without the addition of zeolite declined with respect to root/shoot length and their dry weight along with reduction in photosynthetic pigments and oil productivity. The addition of zeolite reversed the negative impacts of salt stress on productivity and the overall growth as shown in Fig. 4. In comparison to plants grown without zeolite amendments, the treated plants showed suppressed amount of salt in root and shoot (Helay et al., 2018). In another study, the effects of zeolites in alleviating salt stress was in lettuce plants. The study also employed yeast and salicylic acid to investigate their effects on salinity stress mitigation. Plants were exposed to 0 mM, 50 mM, 100 mM and 150 mM salt amount. The results demonstrated that applying 0.5 % zeolite to the test plants enhanced its growth under saline stress of 0 and 50 mM, but failed to improve under higher saline (100 mM and 150 mM) treatments (Babaousmail et al., 2022). Zeolite addition (3.2g/10 kg soil) to salinized soil; the treatment was favourable for these Chinese cabbages with improved stalk length (up to 39 %), leaf dry weight of (23 %), and fresh and dry biomass of up to 172 % and 133 % respectively (Romadhan et al., 2022) (Fig. 5).

#### 4.1.3. Combination of zeolite with other substances to reduce salinity

Zeolites have also been used in combination with nanoparticles such as titanium oxide nanoparticles to mitigate salinity stress in plants. The increase in growth and photosynthetic pigments has been observed in *Mentha piperita* L. plants, by applying zeolites with  $\text{TiO}_2$  nanoparticles under conditions of 100 mM salinity stress. The levels of potassium ions and phenols were raised by zeolite/  $\text{TiO}_2$  exposure, which corresponded



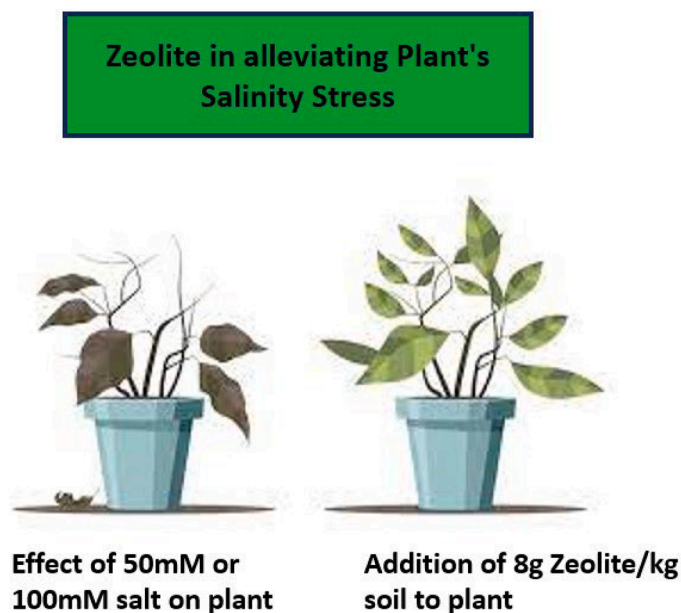


Fig. 5. The role of zeolites in ameliorating the negative effects of elevated salt levels on growth

to the enhancement of defensive substances (phenols) and osmotic regulators (potassium) in plants (Mohammadi et al., 2024). The combination of zeolites and biochar also showed crucial role in enhancing shoot length, diameter, fruit yield and quality, when applied to mango plant under salt stress conditions. The study also reported that zeolites were more effective in improving plant performance as compared to biochar (Harhash et al., 2022). Zeolites can be used with other substances to alleviate saline stress in certain species. The combined effects of zeolites, calcium and organic compounds (Ze-Ca-OC) amalgam (100mg /L) on salinity reduction was investigated in research conducted on a bread wheat variety (0, 50, 100- and 150 mM salt concentrations). The results demonstrated that the zeolite/calcium/organic compound amalgam were effective in restoring wheat growth under high saline conditions (Elsaw et al., 2023). In another study involving canola, the mixture of zeolite/calcium silicate ameliorated the negative effects of high salinity. Zeolite in combination with calcium silicate generated maximum productivity of canola oil up to 57 % in canola variety, under

moderate salt stress (Ghoreishiasl et al., 2017). It was reported that the combination of compost and zeolites, along with raised bed planting method, reduced the saline stress of up to 37 % in wheat plants and 41 % in maize plants. The productivity of wheat and maize plants were also been enhanced 16 % and 35 %, respectively (Aiad et al., 2021). In conclusion, the use of zeolites can be considered as an effective amendment to restore the growth of many species in saline soils.

#### 4.2. Drought tolerance

Drought stress is one the major challenges of agriculture sector, affecting plant growth, development and yield (Ahmadiipour et al., 2019; Zhang et al., 2022). Water shortage results in the limitation of crop cultivation worldwide (Abdelkhalik et al., 2019) The reduction in resources of water is linked with climate change, mis-management of water bodies and rainfall decrease, eventually causing adverse effects on growth and yield of plants (Besser and Hamed, 2021). Drought stress leads to dehydration in cells of plant, decrease absorption of nutrients, disturbance in hormonal production (abscisic acid, cytokinins) in plants, disruption in plant cell membrane selectivity in addition to suppression of photosynthetic rate and carbon dioxide utilization (Shehata et al., 2022). The adverse impacts of drought stress on plants have been depicted in Fig. 6

The adverse effects of water deficits in plants can be relieved by delivering effective structural, physiological and biochemical modifications (Abdelaziz et al., 2021; Ishfaq et al., 2024; Gupta et al., 2020). These alterations include collection of osmolytes to conserve water under conditions of water stress, eventually resulting in biomolecules structure stabilization (El-Mogy et al., 2022). The water use efficiency is also improved and accumulation of osmolytes in plants under drought stress is essential to increase crop yield and productivity (EL-Bauome et al., 2022; Gupta et al., 2020). In this context, multiple agricultural practices have been encouraged to enhance water use efficiency and productivity of drought stress plants such as the use of nano fertilizers, microbes, modification of soil with biochar and organic substances and better irrigation practices in soil having reduced water retention potential (Abbott et al., 2018; Ahmadian et al., 2021; Hazrati et al., 2017; Sani and Yong, 2022). The strategic amendment of soils with several nutrients, biostimulants or water retaining substances such as zeolites has been considered as favorable agent to decrease water stress in plants (Hazrati et al., 2017; Mahmoud et al., 2022; Sani et al., 2023). Zeolite amended soil resulted in improvement of soil moisture, water retention and water use efficiency, enhancing crop yield. Thus, utilization of

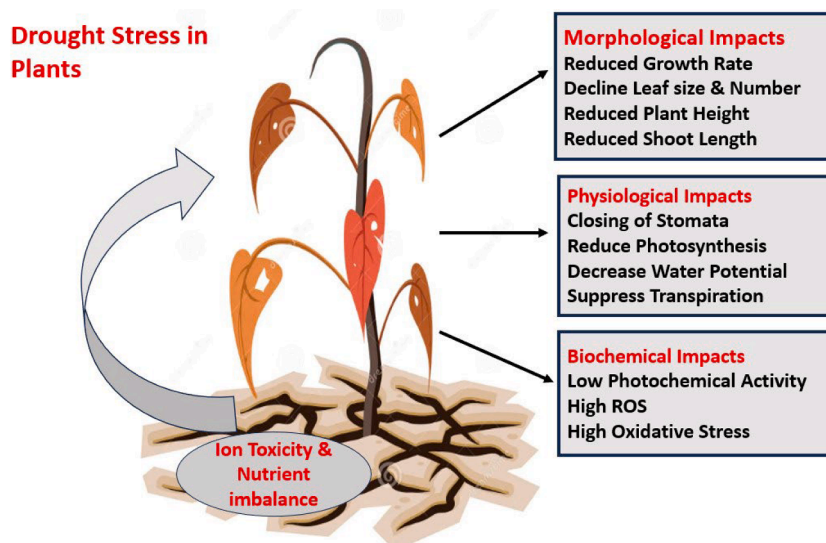


Fig. 6. The effects of water deficits on plant development and physiology in habitats with low water availability.



zeolite emerges as in-expensive and feasible method to reduce ecological stresses such as water stress in plants (Ghamarnia & Daichin, 2013; Hazrati et al., 2022). The beneficial impacts of natural zeolites on plants include improvement in nutrient amount, photosynthetic rates, plant biomass accumulation, water proportion, hormones productivity, antioxidant substances and quality and quantity of crop yield (Amirahmadi et al., 2022).

The application of zeolite along with zinc on canola plants increased the relative water proportion, oil content and productivity of plant in addition to decreasing the resistance by stomata and canopy temperature (Shahsavari & Dadrasnia, 2016). Another study conducted on *Aloe vera* under water stress environment showed that addition of 8 g of zeolite to test plants enhanced the water use efficiency and number of leaves, improving growth and yield (Hazrati et al., 2017). The addition of the calcium type of zeolites, improved the soil water retention potential and growth of barley plant. The utilization of sub surface irrigation with zeolite modification reduced water loss, stored high water in lower horizons, improved leaching of salt and helped plant to use water efficiently (Al-Busaidi et al., 2011).

The growth and productivity of rice crop have been restored under water stress environment by the addition of 15 t ha<sup>-1</sup> zeolite. The rates of photosynthesis, leaf area index, water use efficiency, quality and yield of grain increased effectively by using zeolites, irrespective of water supply. The head rice rate has also enhanced and a decrease in rice chalkiness has also been observed, which validates the reduction in use of water in agriculture by zeolite supplementation (Zheng et al., 2018). The stress of water deficit was declined in rapeseed plant by zeolite addition of up to 15 t ha<sup>-1</sup> and selenium up to 30g L<sup>-1</sup>. The plant growth rate, total dry weight and leaf area index enhanced prominently by zeolite and selenium supplementation (Sayed et al., 2010). The potential of plants to survive under drought stress can be improved by using zeolites. The physiological and structural traits of Mallow plants, such as biomass, length of roots and shoots, stomatal conductance, and chlorophyll content, have been significantly enhanced under water deficit conditions by soil modification with 8 gm of zeolites (Ahmadi Azar et al., 2015). The other studies performed on grass pea, amaranth, fenugreek and potato plants also confirmed the effectiveness of zeolite applications for improving drought resilience in plants (Baghbani-Arani et al., 2017; Karami et al., 2020; Ozbahce et al., 2018; Pirzad and Mohammadzadeh, 2014). The negative effects of drought stress were reduced by clinoptilolite zeolite treatment in grapevines. The plant biomass, concentration of phenolic compounds and sugar were also restored in zeolite-treated grapevines under water stressed conditions (Catalado et al., 2024).

In a study, conducted on bean plants, the addition of hydrogel polymer, zeolites and glutathione enhanced the physiological properties, growth and yield of plants under conditions of simulated drought. Administration of zeolite and GSH minimized the levels of peroxidase and catalase antioxidant enzymes up to 21.8 and 15.5 % respectively under conditions of irrigation regimes. With more research, zeolites are emerging as antitranspirants and soil conditioner; working effectively as a plant "strengtheners" during water shortages in agriculture sector by improving the water use efficiency of crops (Elseedy et al., 2023). Zeolite amalgamation with salicylic acid reported favorable impacts on water stressed wheat plants. The administration of 1 mM salicylic acid and 8 g kg<sup>-1</sup> zeolite to wheat plants under conditions of water shortage ameliorated the negative effects of drought. The concentration of catalase and proteins increased up to 18 and 20 % respectively and hydrogen peroxide levels has been decreased in water stressed plants. Zeolite application also enhanced the biological properties of wheat with greater grain productivity, (Sedaghat et al., 2022). Recently, another study reported the effects of zeolites on the biological status of grapevine canopy and biochemical constituents of their leaves (Cataldo et al., 2024).

#### 4.3. Resilience to phytotoxic metals

Elevated levels of heavy metals and metalloids such as arsenic, cadmium, cobalt, copper, molybdenum, manganese, nickel and others cause negative effects to ecosystem and humans (Alloway, 2013; Kim et al., 2017; Liu et al., 2012; Nabulo et al., 2010; Tow et al., 2019; Tan et al., 2010). Interestingly, trace amounts of these metals are naturally present in soil and they are required for proper growth and development of plants (de Bang et al., 2021). As these metals and metalloids cannot be degraded, their increased concentrations cause toxicity and harmful effects on plant growth (Antoniadis & Damalidis, 2014; Li et al., 2009; Liu et al., 2009). Municipal and house-hold waste, mining and industrial practices and agriculture activities are responsible for soil contamination with heavy metals (Certini et al., 2013; Palansooriya et al., 2020; Tuovinen et al., 2016; Yang et al., 2018). Stabilization and solidification processes are mostly utilized to mitigate heavy metals contamination of soil by immobilizing them. The solubility and mobility of phytotoxic metals are known to be reduced by the technique of stabilization. Solidification involves encapsulation or adsorption of these metals to compounds or minerals having high binding affinity (Conner and Hoeffner, 1998). The mitigation of soil metal contamination by the modification with phosphates, carbonates or zeolite mineral involves process of stabilization or solidification, declining the availability and uptake of metals by plants (Chen et al., 2000; Park et al., 2011). A summary of the phytotoxic effects of heavy metals on plants is illustrated in Fig. 7.

Natural and modified zeolites have been effectively used for the stabilization of toxic metals such as lead, cadmium and nickel in contaminated soil, eventually reducing their uptake by plants. The remediation of the metals by zeolites include either an ion exchange or adsorption mechanism (Castaldi et al., 2005; Colella, 1999). The Pb pollution study demonstrated that zeolite addition improved the soil physio-chemical characteristics to facilitate better cation exchange potential by zeolites; eventually lowering the uptake of lead by rapeseed plants. The rise in soil pH was a major factor contributing to immobilizing the Pb in the Pb test soil. To lower the soil lead levels, the optimized amount of zeolites added was about 10g kg<sup>-1</sup> (Li et al., 2009). In another similar study, adequate lead suppression in plants was achieved by adding a combination of zeolites and humic acid to the test soil (Shi et al., 2009). The potential of zeolites in removing metals such as cadmium, nickel, lead and zinc was confirmed for ryegrass by using a zeolite load of 2.5 % (Contin et al., 2019). The immobilization of phytotoxic metals and lowering their uptake and organ-to-organ transfer by plants through zeolite application is considered a very important tool for growing plants in polluted and/or degraded soils. The effects of various zeolite applications on plants encountering different stresses are highlighted in Table 2.

#### 5. Zeolites in crop protection from biotic stress (pathogens)

Zeolites have emerged as the agronomic protecting substances against multiple pathogens. They can be employed as particle films to alleviate diseases and pathogens in plants. Zeolites can effectively adsorb carbon dioxide and be harnessed as a coating leaf surfaces to safeguard them from microbes (bacteria, fungi) and insects (De Smedt et al., 2015; Fontana and Campbell, 2004). The greater availability of hydrophilic active sites in zeolites enhances their water sorption potential and rendering them as highly effective desiccants (Ng and Mintova, 2008; Percival and Boyle, 2009). In addition, the coating of zeolites on the leaf surfaces produces a "water barrier fence", thereby isolating the disease inoculum from the foliar surfaces (Fontana and Campbell, 2004). In a study, zeolites protected the plants from apple scab (*Venturia inaequalis*) by the restricting liquid film. The absorption of the water condensates by zeolites restricted the water liquid film synthesis, essential for pathogens for propagule germination (Puterka et al., 2000). In another experiment conducted on tomato plants, the addition

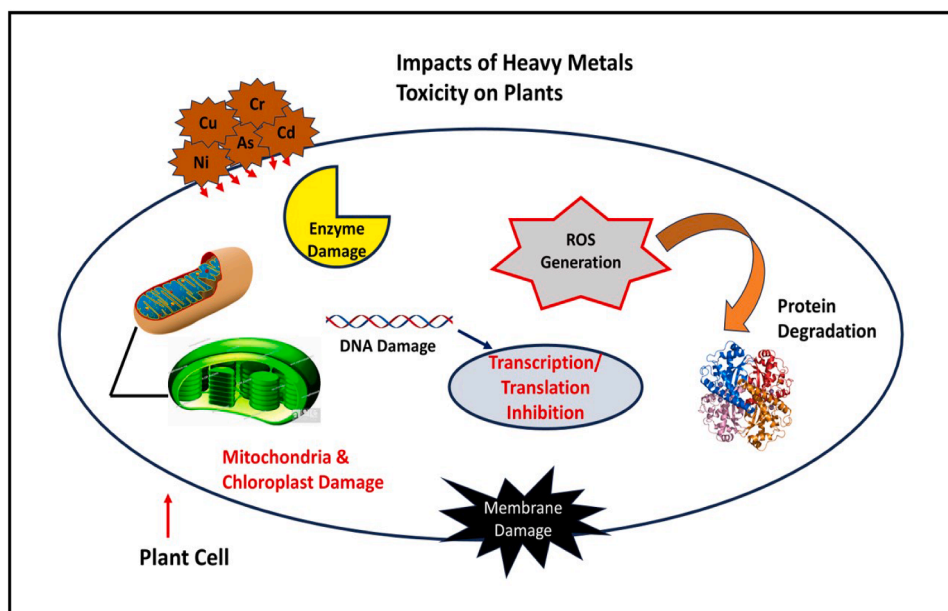


Fig. 7. The effects of high levels of heavy metals on cellular processes in plants

Table 2

Effects of various zeolites in enhancing resilience to abiotic stresses in different species

Type of Zeolite	Plant types	Stress Type	Effect of Zeolite	References
Potassium rich Clinoptilolite	<i>Lolium perenne</i> <i>L.</i>	Salinity	Na <sup>+</sup> declined 44.36 % in shoots and 21.31 % in roots. Water, chlorophyll, POD, SOD increase.	(Rahimi et al., 2021)
Clinoptilolite	<i>Raphanus sativus</i> <i>L.</i>	Salinity	Total dry weight & total fresh weight of plant increase.	(Noori et al., 2007)
Synthetic Ca-type zeolite	Barley	Salinity	Iron (19 %) & manganese (10 %) increase in soil.	(Al-Busaidi et al., 2008)
Natural zeolite	lettuce	Salinity	Leaves growth enhanced by 15 %	(Babaousmail et al., 2022)
Zeolite with zinc	Canola	Drought	Water proportion, oil content and plant productivity increase.	(Shahsavari and Dadrasnia, 2016)
Natural zeolite	<i>A. vera</i>	Drought	Water use efficiency, number of leaves, plant growth increase.	(Hazrati et al., 2017)
Natural zeolite	Rice	Drought	Increase photosynthesis rate, leaf area index, water use efficiency	(Zheng et al., 2018)
Zeolite with selenium	Rapeseed	Drought	Plant growth rate, total dry weight & leaf area index increase.	(Sayed et al., 2010).
Zeolite	Mallow	Drought	Increase plant length, stomata conductance, shoot fresh weight and chlorophyll	(Ahmedi et al., 2015)
Zeolite and vermicompost	Fenugreek	Drought	Leaf area index and plant yield increase.	(Baghbani-Arani et al., 2017)
Natural zeolite	Rapeseed	(Pb) toxicity	Reduction in Pb uptake.	(Li et al., 2009)
Zeolite with humic acid	Wheat	(Pb) toxicity	Reduction in Pb uptake.	(Shi et al., 2009)
Natural zeolite	Ryegrass	Metal toxicity (Cd, Ni, Pb and Zn)	Plant biomass and nutrients increase. Cd, Ni, Pb and Zn concentration reduced.	(Contin et al., 2019)

of chabazite zeolites (up to 3-6 mm), along with useful bacteria, resulted in larger plant yield and with better fruit quality. The study also demonstrated that the addition of chabazite to the growth media protected the species from the pathogenic *Phytophthora infestans* and *Leivellula taurica*; thereby protecting the species from biotic stress (Domenico, 2020). Zeolites have also been found effective against other fungal species *Fusarium oxysporum* and *Verticillium dahlia*. The modification of soil with zeolite supports plant health and turned out to be most appropriate strategy to combat with disease causing fungi (Kefalogianni et al., 2017).

In addition to the role of zeolites as desiccants, they can be used against insects. The non-sorptive particles of zeolites detach the outer cuticle (epicuticular) of insects via erosion. The large insects' epicuticular lipid molecules cannot pass into the inner cavities of zeolites; and detaching the external cuticle of insects via the adsorption of lipid molecules on surfaces of the zeolites. The hydrophobicity of zeolites is responsible for this adsorption, resulting in quick loss of water from body of insect, causing its death via desiccation (De Smedt, 2016). The

use of zeolites was demonstrated as a preventive agent against *Tuta absoluta*, a pinworm affecting tomato plant (De Smedt, 2016). The insecticidal potential of zeolites was also confirmed for cowpeas against *Callosobruchus maculatus*. The treatment of cowpeas with 5 g m<sup>-2</sup> synthetic zeolites for 36 hours resulted in mortality of *Callosobruchus maculatus* adults of up to 100 % (Lü et al., 2017). Zeolite addition to wheat showed shielding effect against three global stored grain insects: *Sitophilus oryzae*, *Tribolium confusum* and *Oryzaephilus surinamensis*. The results also demonstrated that *Oryzaephilus surinamensis* was highly vulnerable to zeolite load (Rumbos et al., 2016). Additionally, natural zeolites also induced mortality in red flour beetle and rice weevil; when exposed to wheat of up to 21 days (Andrić et al., 2012). Natural zeolite clinoptilolite showed insecticidal effectivity against *Acanthoscelides obtectus*, adult bean weevil. Zeolite addition to dry beans also delivered 100 % mortality of *Acanthoscelides obtectus* within one day exposure (Floros et al., 2018).

The pantry pests caused reduction in yield and quality of wheat and cereal based agricultural crops. *Tribolium confusum* and *Callosobruchus*

*maculatus* has been considered as most harmful pests of wheat and cowpea respectively. The application of nano zeolite having size 40-50 nm to seeds of wheat and cowpea revealed mortality of *Tribolium confusum* after 14 days subjection, while after 3<sup>rd</sup> day exposure, mortality of *Callosobruchus maculatus* was induced. The death of insects increased with the increase in zeolite dosage and contact time (Ibrahim and Salem, 2019). Zeolites were proven effective against other pantry insects as well such as reticulate-winged trogiid (*Lepinotus reticulatus*), *Liposcelis decolor*, *Acarus siro* and *Stegobium paniceum* (Agrafioti et al., 2023). These studies confirmed the role of zeolites in protecting crops from various kinds of pathogens, eventually enhancing crop quality and quantity, leading towards cleaner agricultural production. The protective roles of selected zeolites against several pathogens are listed in Table 3.

## 6. Conclusions

There is an increasing interest in using natural and synthetic zeolites in agriculture, particularly as protective agents to combat various stresses and achieving agricultural sustainability. Many studies have reported improvements in the physiological, morphological, and biochemical features of the test plants following zeolite application to the soil. In addition, zeolites (specifically natural zeolite) possess effective adsorption capacity, nutrients and water holding potential help to improve the growth environment for plants. Zeolites provide several useful features in soil conditioning, decontamination, reducing bulk density and enhancing its porosity. In addition, zeolites facilitate the conservation of essential nutrients such as ammonium (NH<sub>4</sub><sup>+</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), potassium (K<sup>+</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>), thereby improving the growth and productivity of plants. As some zeolites exhibit high porosity and unique honeycomb like structure, they possess extraordinary capacity to store and release herbicides. The increase in water use efficiency (WUE) by zeolites supports conservation of water, reduction in crop canopy temperature, encouraging better development and yield of crops in conditions of drought and heat stresses. The activation of antioxidant enzymes by zeolites help to reduce reactive oxygen species (ROS). The adsorption of Na<sup>+</sup>, Cl<sup>-</sup> and phytotoxic metals by zeolites through cation exchange potentially immobilizes them in soil, restricting their uptake in plants. Certain zeolites have interesting agronomic biocontrol properties against multiple pathogens. These zeolites can be coated on leaf surfaces as a "shielding agent" to safeguard them from pathogenic microbes and insects. Some of the natural, synthetic and nano-zeolites can be harnessed as desiccants to reduce the availability of water for pathogens; in some cases, causing their mortality to be 100 %.

## Future perspectives

The usage of zeolites in agricultural practices have been well established by researchers, but further investigations are required to study the minimum dosage and long-term impacts of zeolites on soil properties in unfavourable environment. Both natural and synthetic zeolites have been harnessed to improve resilience to abiotic stress resilience in plants; but natural zeolites emerged to be more effective and economical solution for agriculture. For example, natural zeolite clinoptilolite performs better in alleviating abiotic stresses such as salinity in comparison to synthetic zeolites. For example, zeolites were proven effective in counterbalancing the negative effects of salt load of 100 mM concentration in plants. Based on extensive literature review, the zeolites are able to improve the quality, growth, and yield of crops by up to 50 %. Moving forward, the greater use and effectiveness of synthetic zeolites in agriculture require more research. As the excessive usage of chemical fertilizers are responsible for increases in greenhouse gases, soil acidification and water pollution, the greater use of zeolites as alternate fertilizing materials could be a promising solution towards reducing the various negative environmental issues.

**Table 3**

Protective role few zeolites on plants resistance against several pathogens to improve food security

Zeolite types	Type of Pathogen	Plant types	Effect of Zeolite	References
Z Kaolin	<i>Venturia inaequalis</i>	Apple	Restriction of liquid film, protection from fungi.	(=Puterka et al., 2000)
Chabazite	<i>Phytophthora infestans</i> & <i>Leveillula Taurica</i>	Tomato	Plant growth & yield increase, protection from fungi.	(Domenico, 2020)
Zeolite BEA, Faujasite, Linde type A	<i>Tuta absoluta</i>	Tomato	Detachment of epicuticular of insects, protection from insects.	(De Smedt, 2016)
Synthetic zeolite	<i>Callosobruchus maculatus</i>	Cowpeas	Mortality of insects.	(Lu et al., 2017)
Commercial zeolite (Zeoprofeed Land-93, Zeofeed and raw zeolite	<i>Sitophilus oryzae</i> , <i>Tribolium confusum</i> & <i>Oryzaephilus surinamensis</i>	Wheat	Protection from insects.	(Rumbos et al., 2016)
Natural zeolite dust	Red flour beetle & Rice weevil	Wheat	Mortality of insects.	(Andrić et al., 2012)
Clinoptilolite	<i>Acanthoscelides obtectus</i>	Dry beans	100 % mortality of insects.	(Floros et al., 2018)
Nano-zeolite	<i>Tribolium confusum</i> & <i>Callosobruchus maculatus</i>	Wheat & Cowpea	Mortality of insects.	(Ibrahim and Salem, 2019)
Natural zeolite	<i>Lepinotus reticulatus</i> , <i>Liposcelis decolor</i> , <i>Acarus siro</i> & <i>Stegobium paniceum</i>	Wheat	Mortality of insects.	(Agrafioti et al., 2023)
Mordenite zeolite	<i>F. oxysporum</i> & <i>V. dahlia</i>	Cotton	Protection from insects.	(Kefalogianni et al., 2017)

## CRedit authorship contribution statement

**Ayesha Javaid:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Neelma Munir:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Formal analysis, Data curation. **Zainul Abideen:** Writing – review & editing, Writing – original draft, Visualization, Software, Resources, Methodology, Funding acquisition, Conceptualization. **Zamin Shaheed Siddiqui:** Writing – review & editing, Writing – original draft, Supervision, Software. **Jean Wan Hong Yong:** Validation, Visualization, Writing – original draft, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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