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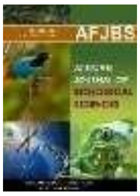

Assessing The Impact of Nano zeolites On Different Fruit Crops

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ABSTRACT

Zeolites are natural substances consisting of pores, corners and there is a three-dimensional network of aluminosilicate tetrahedrons. Therefore, it is necessary to manage the physical and chemical characteristics of the soil in order to increase the effectiveness of nutrient use along with implementation of environment friendly techniques. Zeolites are useful in improving the chemical and physical characteristics of soils. They have a significant impact on specific surface area, internal void structure, and moisture holding ability. These characteristics of zeolites may therefore improve the effectiveness of using nutrients and water. Additionally, they reduce the possibility of environmental degradation brought on by nitrate leaching compounds, nitrous oxide emissions, and NH_3 emissions. Thus, the use of zeolite is advantageous for providing balanced does of NPK fertilizer. The soil can be improved by farming with naturally occurring fertilizers. Restoring soil degradation requires immediate attention because intensive agriculture and unbalanced fertilizer usage.

Keywords: Zeolite, water holding capacity, phytotoxicity, leaching, cation exchange capacity

INTRODUCTION

The significant use of agrochemicals throughout the last few decades, has increased agricultural production but also endangered the health of people and the soil, disrupting food supplies as a result agricultural yield is decreased (Prashar et al., 2016). Currently, fertilizer helps to improve 50% of all agricultural productivity, but at the same time, adding more fertilizer does not always ensure increased crop yield. Moreover, increasing soil fertility and like practices require excessive use of nutrients like N, P, K, Ca, Mg, Fe, Zn, and B in turn they increase the risk of contaminating the soil (Zulfiqar et al., 2019). Due to the large size of the nutrients in chemical fertilizers, crops only absorb up to half of application since the nutrients are not readily accessible (Chugh et al., 2021). When chemical fertilizers are applied through spraying or drizzling over plants, the nutritional needs of the plant and soil are often overlooked. Non-targeted conventional fertilizer application methods result in less supply of nutrient reaching to the plant, with substantial losses through leaching and spillage from agricultural fields into soil and water bodies. Besides this, traditional fertilizers pose various kind of drawbacks, including financial losses, environmental harm, disrupted microflora, altered ground food webs causing gene mutations, ecosystem ecology changes, reduced nitrogen fixation, and increased pathogens and pests, impacting soil fauna and flora (Acharya et al., 2020).

Nanotechnology in agriculture remains in the demand nowadays as compared to medical and other engineered applications. Nanoparticles have the potential to serve as carriers and have advantages over conventional agrochemicals due to their large surface area, gradual release of nutrients, solubility and dispersion of micronutrients, and lower rate of nutrient loss (Acharya et al., 2020). Nanoparticles like zeolites are highly effective at adsorbing N, P, K, and S nutrients from precursor solutions because of porous shape. Rather than providing simple nutrients, they offer slower release nutrients in addition to their transportation. Bacakova et al., (2018) have also observed that adding zeolite to soil improves the efficiency with which micronutrients are used.

Naturally occurring zeolites include clinoptilolite, analcime, chabazite (CHA), erionite, mordenite (MOR), sodalite (SOD), Lind type A (LTA) etc. and their bulk density, pore diameters, and ion exchange characteristics may vary (Krol et al., 2020). While on the other hand, artificial zeolites can be produced utilizing a variety of techniques (like hydrothermal treatment, template-free synthesis, and template assistance), with the benefit that their physiochemical characteristics altered (Bernardi et al., 2016). Nano zeolite (NZ) may increase nutritional absorption. Additionally, nano zeolite delivers nutrients more gradually than conventional fertilizer and greatly reduces nutrient leakage (Mikhak et al., 2017).

NANOZEOLITES

Zeolites are hydrated crystals of alumina silicates containing alkali and alkaline earth cations and often referred as molecular sieves (Schwanke et al., 2017). Their three-dimensional structure defines a network of interconnecting pores and channels within them. Axel Fredrik Cronsted, a Swedish mineralogist, first used the term "zeolite" in 1756 after seeing that when heated it, the substance created steam from the water after absorption. Based on this, he termed it as "zeolite," derived from the Greek words "zeo" for "to boil" and "lithos" for "stone."

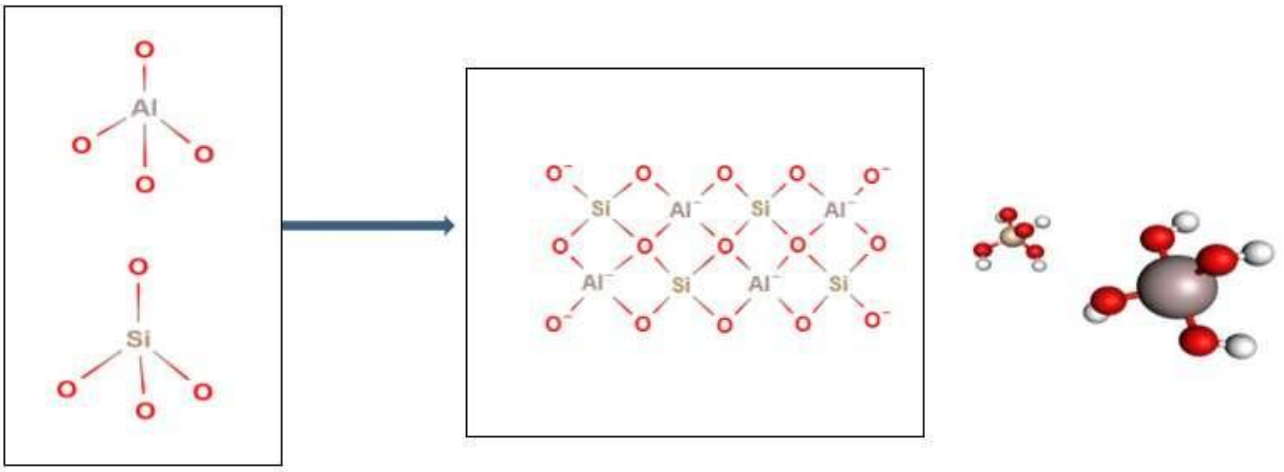
Nano zeolites are the nano sized particles having size of 50-100 nm. Nano zeolites exhibit improved absorption and repulsion kinetics and a greater specific surface area. The main goal of creating nano zeolite material is to have smaller particle sizes in order to have a greater degree of surface conductivity, especially for catalysis and absorption processes (Kianfar et al, 2019). Nanoporous zeolite is becoming popular in agriculture since it improves crop fertilizers efficiency and lessens the environmental degradation caused by them. Thirunavukkarasu et al., (2014) reported that the mesoporous structure with high surface area and nutrients loading capacity of nonporous zeolite were employed to increase the nutrient retention capacity of soil. Compared to conventional zeolites, nano-zeolites are more suited to the adsorption of pollutants (Chmielewská et al., 2021).

STRUCTURE OF ZEOLITES

Zeolite has a structure that resembles a honeycomb formed by aluminosilicate (AlO_4 and SiO_4) tetrahedrons linked into three-dimensional frameworks (Nakhli et al., 2017). The cages in the zeolite's porous structure have a diameter of about 12Å and are connected by channels with a diameter of 8Å and totally there are 12 tetrahedron rings (Sangeetha et al., 2016). Based upon the minerals type, pores are connected to create long, wide channels that make it simple for molecules to enter and exit. Cations that have positive charges counterbalance the aluminium ions' negative charges in the zeolite structure. A zeolite structure is described by the generic empirical formula $M^{2n}O. Al_2O_3. xSiO_2. yH_2O$. Any alkali or alkaline natured cation, is denoted by M (Fig.1).

Valency of cation is represented by n, and the ranges of x and y are 2 to 7 and 2 to 10, respectively. Structural cations include Si^{2+}, Al^{3+}, and Fe^{3+}, while exchangeable cations include K^+, Na^+, and Ca^{2+}. Zeolites exhibit high cation exchange capacity (CEC) exceeding typical soils (100-200 cmol (+) kg).

Moreover; they possess notable properties such as water storage capability and efficient ion adsorption on an expansive surface area (Stylianou et al., 2015).



A. Tetrahedral structures of Silicon and Aluminium

B. Natural Zeolite

C. 3D tetrahedron structure of Si and Al

Fig.1 Structure of Zeolites

Warm temperatures cause the ring columns to expand, and melt, and the interior portions of the columns to contract. In some regions, this is how temperature affects the structure of nano-zeolites (Kianfar et al., 2019). The structure of nano zeolites has the ability to replace or reverse the water and cations by the other cation. Nano zeolites comprises of eight rings that relates to a small ring, consists of eight cross-linked silicon and aluminum tetrahedrons with balanced oxygen atoms. Nano zeolites are generally known for having a crystalline structure with high empty spaces, low density, and a high degree of hydration during drainage time.

CHARACTERIZATION OF ZEOLITES

Characterization of zeolites is essential for understanding their structure, properties, and performance in various aspects. Several techniques are commonly used to characterize zeolite materials a following:

Sr.no.	Characters	Description
I.	X-ray diffraction (XRD)	XRD is a powerful tool for determining the crystal structure and purity of zeolites (Prodinger et al., 2020). By analyzing the diffraction pattern of X-rays scattered by the zeolite. It becomes easy to identify the specific zeolite framework type and determine the degree of crystallinity.
I.	Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)	It helps to provide high-resolution image of zeolite particles and allows visualizing their morphology, particle size distribution, and surface features. Such techniques are mandatory for understanding the physical characteristics of zeolites (Wan et al., 2018).
I.	Fourier-transform infrared spectroscopy (FTIR)	FTIR spectroscopy is an important technique, used to analyze the chemical composition and functional groups present in zeolites (Ma et al., 2021). It provides information about the bonding environment of atoms within the zeolite structure.
.	Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)	Used to determine the thermal stability, dehydration behavior, and phase transitions of zeolites under controlled temperature and atmosphere conditions (Paula et al., 2019).

METHODS OF SYNTHESIS OF NANOZEOLITES

The synthesis of zeolites involves the creation of these crystalline materials through controlled chemical reactions (Fig. 2). Zeolites can be made using a variety of techniques, each with unique benefits and drawbacks. Typical synthesis techniques include the following:

Hydrothermal synthesis: For synthesis, this is the most used approach. Alkali metal hydroxides or other sources of alkali ions are combined with silica and alumina, and the combination is heated to high pressures in an autoclave (Fang et al., 2022). Zeolite crystals are created as the consequence of the combination going through a crystallization process.

Sol-gel synthesis: The process involves the hydrolysis and polycondensation of silicon and aluminum alkoxides in a precursor solution, which is then used to create zeolites. Zeolite crystals are created by heating the gel via a sequence of processes that eliminate the organic components and solvent (Li et al., 2019).

Ionothermal synthesis: Ionic liquids are used in this process as templates and solvents for the production of zeolites (Li et al., 2022). In addition to acting as a medium for zeolite crystallization, the ionic liquids direct the structure of the zeolite crystals, affecting their size and shape.

Dry gel conversion: Zeolites can also be produced by heating precursors or amorphous aluminosilicate gel under controlled conditions (Feliczak et al., 2018). To create zeolite crystals, this process entails dehydrating and crystallizing the precursor components.

Template-directed synthesis: This method controls the creation of zeolite crystals with precise sizes and shapes by using organic molecules or surfactants as templates (Chen et al., 2020). The final zeolite structure is then obtained by removing the templates.

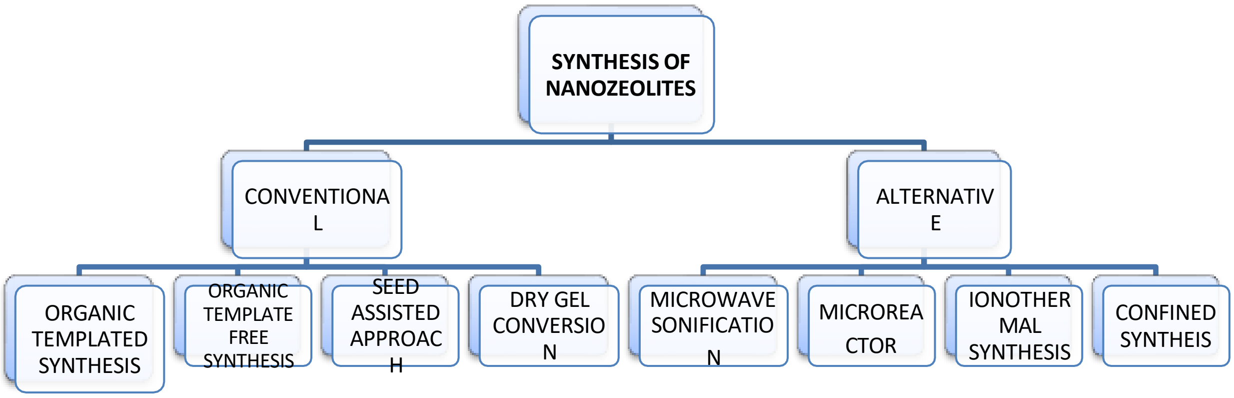


Fig.2. Synthesis of Nano zeolites

ROLE OF ZEOLITES AS FERTILIZER CARRIER

Incorporating zeolites or other additives into the soil has a number of benefits, such as maintaining the purity of water sources and assuring an adequate supply of nutrients. The agricultural environment becomes healthier as a result of these positive consequences. Use of zeolites can be accomplished by foliar or soil application. Such materials are injected into the plants either through the roots or the foliar spray. Surface and shape of a zeolite particle are key factors in influencing its biocompatibility (Jakkula et al., 2018). They (zeolites) serve as organic natural soil conditioners that improve the physical and chemical characteristics of soil, such as cation exchange capacity, water-holding capacity, and infiltration rate. Additionally, it has been claimed that zeolite-based soil amendments increase soil's capacity to retain water, which can lower the amount of water requirements (Jarosz et al., 2022).

By altering the chemical, physical and biological factors that regulate the dynamics of the nutrients in soil, zeolites help the soil to retain more nutrients. For instance, the high cationic exchange characteristics of zeolites cause them to have higher NH^{4+} sorption selectivity because of the electrostatic interaction between the positively charged NH^{4+} and negatively charged zeolite structural sites. Natural zeolites are said to have a cation exchange capacity that is two to three times greater than most other minerals (Mihok et al., 2020). Furthermore, Vogelsang et al., (2023) suggested that zeolites have a distinct selectivity for specific cations, including sulphate (SO_4^{2-}), ammonium (NH_4^{2-}), phosphorus (P), potassium (K^+), and zinc (Zn^{2+}). Zeolites' selectivity enables them to take up from composts, fertilizers, and farmyard manure, possibly lowering nitrogen losses (Maharani et al., 2018).

Zeolites are utilized as slow-releasing carriers for fertilizers, pesticides, and other chemicals that stimulate plant growth and increase soil fertility along with biological activity. Simply by mixing, above mentioned substances can be added to porous zeolites to produce the desired results. The best conditions were found in a chemical reactor that ran continuously and used to test; how well slow-release fertilizer (SRF) is supplied plants with sufficient nutrients. Due to their uses as a solid medium and fertilizer material, the majority of investigations have focused on naturally occurring clinoptilolite zeolites.

Groundwater contamination caused by excessive use of water-soluble fertilizers can be prevented by utilizing fertilizer with surfactant modifications. The addition of surfactants boosts the capacity of anionic sorption, which helps in removal of cations and organic molecules (Gorre et al., 2016). The main variables that affect zeolites' ability to adsorb are temperature, mass, particle size (lower size results in a bigger surface area), contact time (which is directly related to the amount adsorbed), and the concentration of cations in the solution at first. The capacity of zeolites for adsorption can be increased through modifications using strong acids. Zeolite application also led to an increase in urease activity, which decreased fertilizer nutrient release (Eroglu et al., 2017).

The chemical and physical properties of naturally occurring zeolites can be employed for applications as carriers for nutrition delivery because of their structure and characteristics (i.e., inert and non-toxic) (Yuvaraj et al., 2018). Zeolites improve the effects of substances like slow-release fertilizers in both agricultural and horticultural crops. Zeolites are primarily used in agriculture for the loading, storage, and delayed release of nutrients. The delivery of macro- and micronutrients to crops uses a variety of naturally occurring zeolites, including clinoptilolite and Phillip site.

APPLICATIONS OF ZEOLITES IN AGRICULTURE/HORTICULTURE

Zeolites are widely employed in agriculture since they are classified as "safe" for human consumption by the Food and Drug Administration (FDA) and the International Agency for Research on Cancer (IARC) (Cerri et al., 2016). Clinoptilolite, a naturally occurring zeolite belonging to the heulandite group, is the zeolite that is most frequently used in agricultural applications. It is the most common alternative in agricultural techniques due to its extensive distribution in sediments and soils to encourage retention of nitrogen and as a soil amendment.

Soil Conditioners

Zeolites are frequently employed as soil conditioners to enhance the physio-chemical qualities. They have several beneficial effects on soil parameters, including increasing soil moisture, boosting hydraulic conductivity, and enhancing yields in acidified soils as shown in Fig. 3. Zeolite is slightly alkaline but not acidic; therefore, using it with fertilizers can help in balancing soil pH levels and lessen the need to apply lime. CEC of vineyard soils was greatly improved by zeolite, altering the availability of nutrients, stimulating microbial metabolic activity (increased dehydrogenase activity), and changing the soil's organic matter (Doni et al., 2021). The nano-sized zeolite has the ability to store Zn^{2+} and release it gradually into the soil solution, making it possible to utilize it as a fertilizer with a slow release of Zn^{2+} and to increase the efficiency with which crops utilize particular ion (Yuvaraj et al., 2018). Taiwan exports of natural zeolites to help with sandy soils; this is probably a common practice in Japan (Kalita et al., 2020).

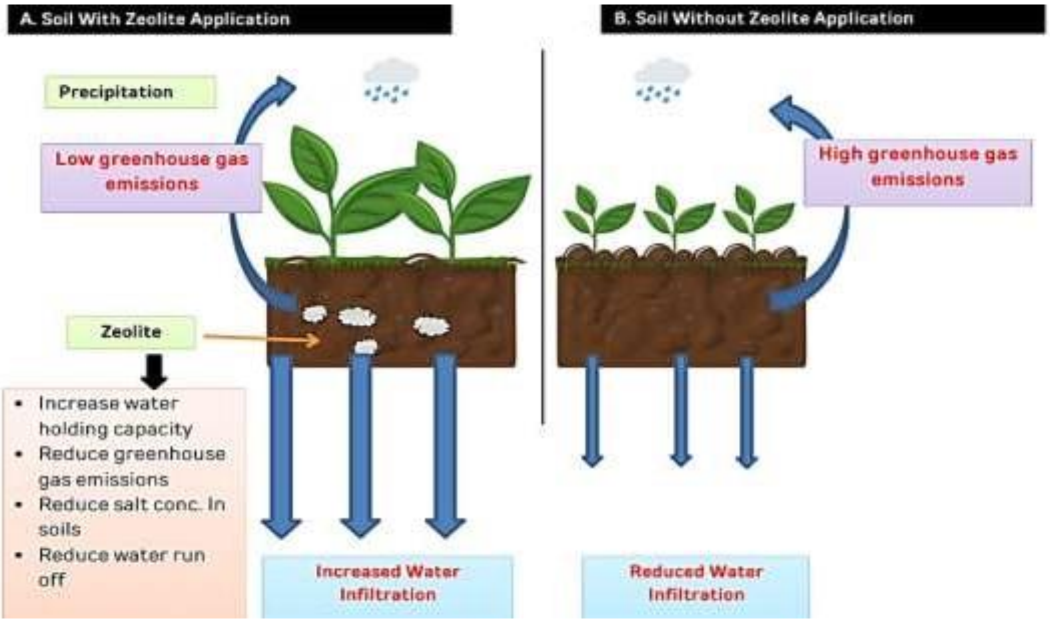


Fig. 3: Nature of soil with or without the application of zeolite

Slow release of herbicides

The use of slow-release formulations is an aspect of farmer safety and energy savings. Slow-release formulations have been demonstrated to provide the active ingredient of herbicides for a longer length of effectiveness. Zeolites ZSM-5 found to be effective in the absorption of Atrazine and Paraquat better (Williams et al., 2018). Atrazine removal from soil and water was thought to be possible with clinoptilolite tuff. Additionally, Paul et al., (2023) discovered that zeolites were slow-release carriers for the herbicide 2, 4-dichlorophenoxyacetic acid (2, 4-D).

Enhancement of photosynthetic activity in different crops

Carbon dioxide molecules can be slowly released into the biosphere by zeolites after they have been absorbed. Zeolites can be sprayed as foliar application to increase carbon dioxide levels, which result in closing of the stomata (Cataldo et al., 2021). For C_3 plants, including vines, orange trees and apple trees, this phenomenon may result in a higher rate of photosynthesis with an improvement in the rate of absorption of net carbon CO_2 (velocity of carboxylation) intake and a reduction in carbon dioxide loss by the photorespiratory system. Higher growth, more rapid development of the foliage surface and less transpiration may result from phenomena.

Antifungal activity and crop protection

Zeolites have the ability to reduce the environmental effects caused by plant diseases. Zeolites have been shown to have the potential to lessen the environmental impacts due to such diseases. A number of authors investigated these materials for the prevention of harmful insects (Floros et al., 2018). Zeolites are useful as a leaf-coating product against insect pests and fungi because of their unique properties. They are suitable because of their unique structure, smaller particle sizes, ability to absorb carbon dioxide (CO_2), and capacity to lessen heat stress. An effective way to manage sour rot, grey mould, and Lobesia botrana on grapevines was demonstrated in case of Vitis Vinifera L. by applying natural Italian chabazite (Calzarano et al., 2019).

Protection from heat stress and sunburn on crops

The mobility of CO_2 in relation to O_2 decreases with increasing temperature, as Rubisco's affinity for CO_2 (enzyme responsible for fixing carbon in plants). The ratio of carboxylation to oxygenation decreases as a result of rising temperature. By protecting the plant with zeolites, it is possible to lower the leaf temperature because of the growing whiteness (reflectiveness) of infrared radiation on leaves. Greer et al., (2018) found that apple trees and vines had a lower canopy temperature and a higher rate of leaf carbon assimilation with the application of zeolite.

Heavy metal traps

The increased use and release of metals from factories has resulted in a rise of metallic materials in water bodies. When humans and aquatic organisms consume water contaminated with heavy metals, it can have serious, long-term negative health impacts. Zeolites are frequently employed for the sequestration of cationic contaminants, such as heavy metal (Cd^{2+}, Pb^{2+} and Cr^{3+}) since they have high cation-exchange capacity and attract ions that are positively charged (Dasan et al., 2020).

ZEOLITES APLLICATION IN DIFFERENT FRUIT CROPS

Crop	Scientific name and Family	Variety	Nano zeolites concentration	Additional component	Results	References
Apple	Malus domestica (Rosaceae)	HRMN-99	250 ppm	Bio capsules (500 ppm) + NPL(RDF)	Used to improve the vegetative and reproductive growth.	Vats et al., (2022).
Banana	Musa paradisiaca (Musaceae)	Ambon banana	1.5g	100 ppm ethylene gas	Shelf-life can be maintained by nano zeolites for 23 days at 25 C and 85% RH.	Syamsu et al., (2016)
Papaya	Carica papaya (Caricaceae)	Sekaki	25-100%	NPK- 15:15:15 N:P:K:Mg-12:12:17:2	Application of clinoptilolite zeolite with NPK resulted in increased growth yield and NPK content in papaya leaves. Peat+clinoptilolite zeolite improved pH, P and K availability.	Choo et al., (2020)
Pineapple	A. comosus L. (Bromeliaceae)	Moris	5g,10g,14g,20g	NPK -20g, Peat- 975g	Zeolite was added at different concentrations (25-100%), which improved fruit quality, yield including growth. Additionally, application of zeolite (25%) and NPK fertilizers together resulted in a increased availability of soil ammonium.	Choo et al., (2022)
Aloe	Aloe vera L. (Asphodelaceae)	-------	0.4-8g zeolite /kg soil	-----	Zeolite treatment significantly lessens the impacts of water deficit stress and enhances plant development and production. WUE I also increased as a result of the application of zeolite.	Hazrati et al., (2017)
Mango	Mangifera indica (Anacardiaceae)	Ewaise	1-3 kg	Biochar (1-3kg)	Zeolite found to improve the shoot length, tree trunk thickness, yield, fruit quality.	Harhash et al., (2022)
Cactus pear	Opuntia ficus indica	Yellow Sulfarina, Red	Chabazite(zeolite)-20%	Peat (80-100%)	The application of zeolites (natural chabazite) ensures the possibility of reducing substrate fertilizer	Domenico et al., (2020)

	(Cactaceae)	Sanguigna, and White Muscaredda			requirements and improving irrigation. By using this method, healthier plants with better growth, higher yields, and less stress susceptibility are produced.	
Grapes	Vitis vinifera (Vitaceae)	Thompson seedless	Conc. 0%, 3%, 6%	Anthrone and thiourea (each @ 0.1%)	The best preharvest treatment for improving different quality indicators, physical structure, and stopping the spread of decay during 60-day storage period.	Huwie et al., (2021)

PHYTOTOXICITY OF ZEOLITES

In agricultural applications, the degrees of zeolite toxicity must be taken into account. Important elements that affect the application process, such as surface chemistry, size, and concentration, are critical in determining possible toxicity and other changes as shown in Fig. 4. Plants covered with particle coatings don't harm other plants, but they could be harmful to animals (Ma et al., 2016). In this case, the exact kind of zeolite that is utilized and its application rate have an impact on how well zeolites reduce the phytotoxicity of soil residues left behind by the Singer herbicide.

Moreover, Mohsin et al., (2023) indicated that zeolites have the ability to catalyze the degradation of xenobiotics present in soil residues because of herbicide applications. Metsulfuron-methyl (MSM) in aqueous solutions degrades in the presence of natural zeolites, such as the ZPS brand, according to analysis of their sorption properties, particularly in their acid-modified form (Spiridonov et al., 2021).

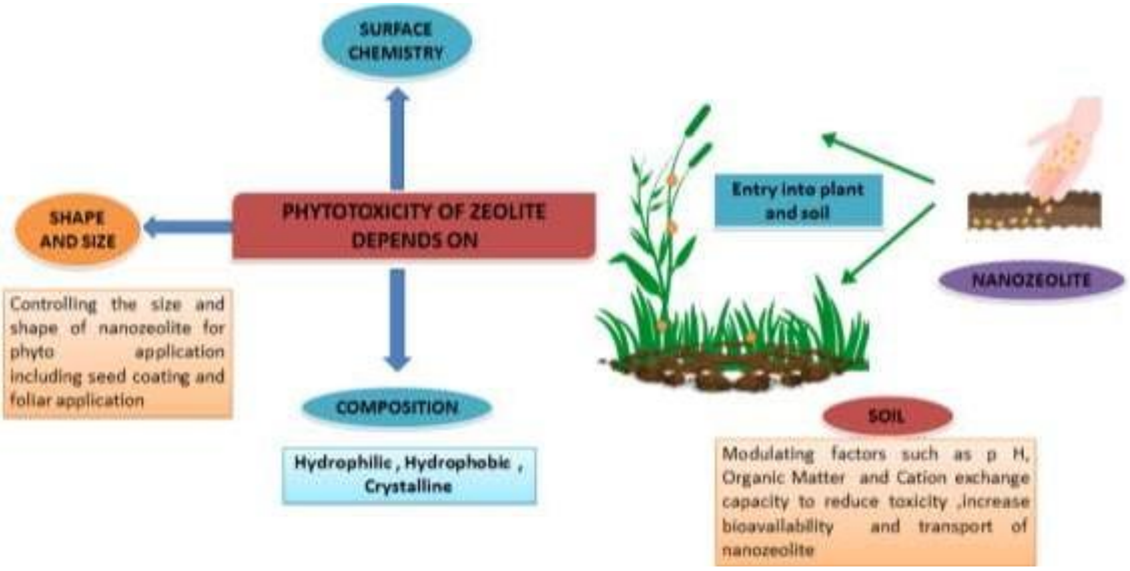


Fig. 4: Different parameters and degree of phytotoxicity of Zeolites

FUTURE SCOPE AND CHALLENGES

Zeolites have a vital role in agricultural activities, which has been thoroughly demonstrated. Still, systematic and exhaustive efforts are required for future research, including: (a) precise visualization of the available zeolite deposits in each nation, (b) assessment of zeolites' physical stability under various agro-climatic conditions, (c) development of feasible organo-zeolitic manure or fertilizer, and (d) assessment of the likelihood that a toxic surfactant substances that is loosely bound to the zeolite surface will leach, (e) evaluation of the zeolite application's long-term effects on rhizosphere microbes and fauna; (f) comprehension of the mechanisms zeolite-mediated heavy metal consolidation in contaminated soil; and (h) creation of zeolite-rich herbicides to reduce the risk threat.

Although zeolites have been investigated for a various use, such as soil enhancement and fertilizer effectiveness, there seem to be a research gap in their specialized application for increasing the post-harvest shelf life of fruit crops. While several studies have looked into the use of zeolites in fruit post-harvest storage, more study is required to completely comprehend and optimize their impact on fruit quality and shelf life. Zeolites are special materials that have qualities including a high cation exchange capacity and the capacity to absorb moisture that may help with fruit preservation. Zeolites interact with fruits on a cellular and biochemical level, and this interaction may play a role in fruit shelf-life extension. Understanding this interaction may reveal the underlying mechanisms involved. instance, zeolites can be employed as nutrient transporters to increase nutrient usage efficiency. Zeolites can be a useful tool for farmers to conserve water content, lower canopy temperature, and sustainability.

CONCLUSION

Application of zeolites is currently gaining more and more attention in the agricultural sector, especially in soil management. Zeolites, on the contrary, may be mandatory for lowering polluted discharges and for detoxification of toxic substances from plant. Recently, the interactions between zeolite and herbicides have received significant consideration. While the majority of calcium and potassium zeolites are helpful for plant growth. Several studies suggested that zeolites with sodium as the principal exchangeable cation may increase crop growth through soil alkalinization.

REFERENCES

1. Acharya, A., and Pal, P. K. (2020). Agriculture nanotechnology: Translating research outcome to field applications by influencing environmental sustainability. NanoImpact, 19, 100-232.
2. Bacakova, L., Vandrovcova, M., Kopova, I., & Jirka, I. (2018). Applications of zeolites in biotechnology and medicine-a review. Biomaterials science, 6(5), 974-989.
3. Bernardi, A. D. C., Polidoro, J. C., Monte, M. D. M., Pereira, E. I., de Oliveira, C. R., & Ramesh, K. (2016). Enhancing nutrient use efficiency using zeolites minerals: a review.
4. Cataldo, E., Salvi, L., Paoli, F., Fucile, M., Masciandaro, G., Manzi, D., ... & Mattii, G. B. (2021). Application of zeolites in agriculture and other potential uses: A review. Agronomy, 11(8), 1547.
5. Cerri, G., Farina, M., Brundu, A., Daković, A., Giunchedi, P., Gavini, E., & Rassu, G. (2016). Natural zeolites for pharmaceutical formulations: Preparation and evaluation of a clinoptilolite-based material. Microporous and Mesoporous Materials, 223, 58-67.
6. Chmielewská, E., Tylus, W., & Bujdoš, M. (2021). Study of Mono-and Bimetallic Fe and Mn Oxide-Supported Clinoptilolite for Improved Pb (II) Removal. Molecules, 26(14), 4143.
7. Choo, L. N. L. K., Ahmed, O. H., Razak, N. A., & Sekot, S. (2022). Improving Nitrogen Availability and Ananas comosus L. Merr var. Moris Productivity in a Tropical Peat Soil Using Clinoptilolite Zeolite. Agronomy, 12(11), 2750.
8. Choo, L. N. L. K., Ahmed, O. H., Talib, S. A. A., Ghani, M. Z. A., & Sekot, S. (2020). Clinoptilolite zeolite on tropical peat soils nutrient, growth, fruit quality, and yield of Carica papaya L. cv. Sekaki. Agronomy, 10(9), 1320
9. Chugh, G., Siddique, K. H., & Solaiman, Z. M. (2021). Nanobiotechnology for agriculture: smart technology for combating nutrient deficiencies with nanotoxicity challenges. Sustainability, 13(4), 1781.
10. Dasan, Y. K., Bhat, A. H., & Khan, I. (2020). Nanocellulose and nanochitin for water remediation by adsorption of heavy metals. Nanomaterials for water remediation, 2, 1-18.

11. Domenico, P. (2020). Comparison between sterilized zeolite and natural zeolite in the Cactus Pear (Opuntia Ficus-Indica L. Mill.) growing. GSC Advanced Research and Reviews, 5(1), 007-014.
12. Doni, S., Gispert, M., Peruzzi, E., Macci, C., Mattii, G. B., Manzi, D. & Grazia, M. (2021). Impact of natural zeolite on chemical and biochemical properties of vineyard soils. Soil Use and Management, 37(4), 832-842.
13. Eroglu, N., Emekci, M., & Athanassiou, C. G. (2017). Applications of natural zeolites on agriculture and food production. Journal of the Science of Food and Agriculture, 97(11), 3487-3499.
14. Floros, G. D., Kokkari, A. I., Kouloussis, N. A., Kantiranis, N. A., Damos, P., Filippidis, A. A., & Koveos, D. S. (2018). Evaluation of the natural zeolite lethal effects on adults of the bean weevil under different temperatures and relative humidity regimes. Journal of economic entomology, 111(1), 482-490.
15. Gorre, K., Yenumula, S., & Himabindu, V. (2016). A Study on the Ammonium Adsorption by using Natural Heulandite and Salt Activated Heulandite. International Journal of Innovation and Applied Studies, 14(2), 483.
16. Greer, D. H. (2018). Photosynthetic responses to CO_2 at different leaf temperatures in leaves of apple trees (Malus domestica) grown in orchard conditions with different levels of soil nitrogen. Environmental and experimental botany, 155, 56-65.
17. Harhash, M. M., Ahamed, M. M., & Mosa, W. F. (2022). Mango performance is affected by the soil application of zeolite and biochar under water salinity stresses. Environmental Science and Pollution Research, 29(58), 87144-87156.
18. Hazrati, S., Tahmasebi-Sarvestani, Z., Mokhtassi-Bidgoli, A., Modarres-Sanavy, S. A. M., Mohammadi, H., & Nicola, S. (2017). Effects of zeolite and water stress on growth, yield and chemical compositions of Aloe vera L. Agricultural Water Management, 181, 66-72.
19. Huwei, S., Asghari, M., Zahedipour-Sheshglani, P., & Alizadeh, M. (2021). Modeling and optimizing the changes in physical and biochemical properties of table grapes in response to natural zeolite treatment. LWT, 141, 110-854.
20. Jakkula, V. S., & Wani, S. P. (2018). Zeolites: Potential soil amendments for improving nutrient and water use efficiency and agriculture productivity. Scientific Reviews & Chemical Communications, 8(1), 1-15.
21. Jarosz, R., Szerement, J., Gondek, K., & Mierzwa-Hersztek, M. (2022). The use of zeolites as an addition to fertilisers-A review. Catena, 213, 106-125.
22. Kalita, B., Bora, S. S., & Gogoi, B. (2020). Zeolite: a soil conditioner. International Journal of Current Microbiology and Applied Sciences, 9(1), 1184-1206.
23. Kianfar, E. (2019). Nanozeolites: synthesized, properties, applications. Journal of Sol-Gel Science and Technology, 91, 415-429.
24. Kianfar, E. (2019). Nanozeolites: synthesized, properties, applications. Journal of Sol-Gel Science and Technology, 91, 415-429.
25. Król, M. (2020). Natural vs. synthetic zeolites. Crystals, 10(7), 622.
26. Ma, Y., Zhu, M., Shabala, L., Zhou, M., & Shabala, S. (2016). Conditioning of roots with hypoxia increases aluminum and acid stress tolerance by mitigating activation of K+ efflux channels by ROS in barley: insights into cross-tolerance mechanisms. Plant and Cell Physiology, 57(1), 160-173.
27. Maharani, D. K., Dwiningsih, K., Savana, R. T., & Andika, P. M. V. (2018). Usage of zeolite and chitosan composites as slow release fertilizer. International Conference on Science and Technology (ICST 2018), 179-182.

28. Mihok, F., Macko, J., Oriňak, A., Oriňaková, R., Kovaľ, K., Sisáková, K., ... & Kostecká, Z. (2020). Controlled nitrogen release fertilizer based on zeolite clinoptilolite: Study of preparation process and release properties using molecular dynamics. Current Research in Green and Sustainable Chemistry, 3, 100-030.
29. Mikhak, A., Sohrabi, A., Kassaee, M. Z., & Feizian, M. (2017). Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (Matricaria chamomilla L.). Industrial crops and products, 95, 444-452.
30. Mohsin, M. Z., Huang, J., Hussain, M. H., Zaman, W. Q., Liu, Z., Zhuang, Y., & Mohsin, A. (2023). Revolutionizing bioremediation: Advances in zeolite-based nanocomposites. Coordination Chemistry Reviews, 491, 215-253.
31. Nakhli, S. A. A., Delkash, M., Bakhshayesh, B. E., & Kazemian, H. (2017). Application of zeolites for sustainable agriculture: a review on water and nutrient retention. Water, Air, & Soil Pollution, 228, 1-34.
32. Paul, S. K., Xi, Y., Sanderson, P., Deb, A. K., Islam, M. R., & Naidu, R. (2023). Investigation of herbicide sorption-desorption using pristine and organoclays to explore the potential carriers for controlled release formulation. Chemosphere, 337, 139-335.
33. Prashar, P., & Shah, S. (2016). Impact of fertilizers and pesticides on soil microflora in agriculture. Sustainable Agriculture Reviews: Volume 19, 331-361.
34. Sangeetha, C., & Baskar, P. (2016). Zeolite and its potential uses in agriculture: A critical review. Agricultural Reviews, 37(2), 101-108.
35. Schwanke, A. J., Balzer, R., & Pergher, S. (2017). Microporous and mesoporous materials from natural and inexpensive sources. Handbook of ecomaterials, 1-22.
36. Spiridonov, Y. Y., Chkanikov, N. D., Khalikov, S. S., Spiridonova, I. Y., Nasakina, E. O., & Glinushkin, A. P. (2021). Studies of the effect of zeolites after acid modification on the chemical stability of sulfonylurea herbicides. In IOP Conference Series: Earth and Environmental Science , 663, 012-057.
37. Spiridonov, Y. Y., Chkanikov, N. D., Spiridonova, I. Y., Nasakina, E. O., & Glinushkin, A. P. (2021). Biological testing of zeolites as herbicide sorbents. In IOP Conference Series: Earth and Environmental Science, 663, 012-060
38. Stylianou, M. A., Inglezakis, V. J., & Loizidou, M. (2015). Comparison of Mn, Zn, and Cr removal in fluidized-and fixed-bed reactors by using clinoptilolite. Desalination and Water Treatment, 53(12), 3355-3362.
39. Syamsu, K., Warsiki, E., Yuliani, S., & Widayanti, S. M. (2016). Nano zeolite-$KMnO_4$ as ethylene adsorber in active packaging of horticulture products (Musa Paradisiaca). Int. J. Sci. Basic Appl. Res, 30, 93-103.
40. Thirunavukkarasu, M., & Subramanian, K. S. (2014). Surface modified nano-zeolite used as carrier for slow release of sulphur. Journal of Applied and Natural Science, 6(1), 19-26.
41. Vogelsang, C., & Umar, M. (2023). Municipal solid waste fly ash-derived zeolites as adsorbents for the recovery of nutrients and heavy metals—A Review. Water, 15(21), 3817.
42. Williams, C. D. (2018). Application of zeolites to environmental remediation. Urban Pollution: Science and Management, 1, 249-258.
43. Yuvaraj, M., & Subramanian, K. S. (2018). Development of slow release Zn fertilizer using nano-zeolite as carrier. Journal of plant nutrition, 41(3), 311-320.
44. Zulfiqar, F., Navarro, M., Ashraf, M., Akram, N. A., & Munné-Bosch, S. (2019). Nanofertilizer use for sustainable agriculture: Advantages and limitations. Plant Science, 289, 110-270.
45. Prodinger, S., & Derewinski, M. A. (2020). Synthetic zeolites and their characterization. In Nanoporous Materials for Molecule Separation and Conversion (pp. 65-88). Elsevier.

46. Wan, W., Su, J., Zou, X. D., & Willhammar, T. (2018). Transmission electron microscopy as an important tool for characterization of zeolite structures. Inorganic Chemistry Frontiers, 5(11), 2836-2855.
47. Ma, Y. K., Rigolet, S., Michelin, L., Paillaud, J. L., Mintova, S., Khoerunnisa, F., & Ng, E. P. (2021). Facile and fast determination of Si/Al ratio of zeolites using FTIR spectroscopy technique. Microporous and Mesoporous Materials, 311, 110-683.
48. Paula, T. P., Marques, M. F. V., & da Costa Marques, M. R. (2019). Influence of mesoporous structure ZSM-5 zeolite on the degradation of urban plastics waste. Journal of Thermal Analysis and Calorimetry, 138, 3689-3699.
49. Fang, L., Yan, S., Wu, H., Wang, M., Du, T., Wang, T., & Ren, L. (2022). Defect-Guided Synthesis of Hierarchical Sn-B-Beta Zeolite with Highly Exposed Sn Sites. Inorganic Chemistry, 61(30), 11939-11948.
50. Li, S., Li, J., Dong, M., Fan, S., Zhao, T., Wang, J., & Fan, W. (2019). Strategies to control zeolite particle morphology. Chemical Society Reviews, 48(3), 885-907.
51. Li, X., Curnow, O. J., Choi, J., & Yip, A. C. K. (2022). Recent advances in the imidazolium-based ionic liquid-templated synthesis of microporous zeolites. Materials Today Chemistry, 26, 101-133.
52. Feliczak-Guzik, A. (2018). Hierarchical zeolites: Synthesis and catalytic properties. Microporous and Mesoporous Materials, 259, 33-45.
53. Chen, L. H., Sun, M. H., Wang, Z., Yang, W., Xie, Z., & Su, B. L. (2020). Hierarchically structured zeolites: from design to application. Chemical reviews, 120(20), 11194-11294.