Scientific Reviews & Chemical Communications

Scientific Reviews and Chemical Communications
ISSN: 2277-2669

Review | Vol 8 Iss 1

Zeolites: Potential soil amendments for improving nutrient and water use efficiency and agriculture productivity

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Received: February 23, 2018; **Accepted:** May 07, 2018; **Published:** May 10, 2018

Abstract

The fertilizer use in developing countries has shown a steady increase over the last few decades, and the use and manufacture of N fertilizers contributes to about 60% of the total release of reactive N. Higher farm subsidies and lower N fertilizer prices have further increased N inputs. Inappropriate fertilization patterns and excessive use of N fertilizer have resulted in considerable N losses through ammonia NH_3 volatilization and NO_2 leaching. This has meant that NUE has been as low as ~35%. An efficient crop nutrient management is important practice and thus, new designer or smart N fertilizers technologies are needed to support the increasing demand and avoid the low nitrogen use efficiency (NUE). The ammonia nitrogen volatilization and nitrate leaching can be reduced or prevented by the use of zeolite carrier material applications which have N in their framework and act as slow/controlled release fertilizers. These materials will reduce ammonia volatization and nitrate leaching and at the same time increase crop yield. Zeolites are also known for their water holding capacity and in drylands they are the most suitable fertilizers to prolong moisture levels in severe drought like conditions. In addition to macronutrients, micronutrients can also be introduced into zeolites which can supplement nutrient deficient soils. Thus, zeolites along with increasing yield can also increase the nutrient and water use efficiency of drylands.

Keywords: Zeolites; Nutrient use efficiency; Water holding capacity; Soil conditioners; Crop yield

Introduction

Zeolites were first introduced by a Swedish mineralogist, A.F. Cronstedt in 1756, with the discovery of the mineral Stilbite [1]. By heating with a blowpipe flames this mineral lost water. He called this mineral “zeolite” from the Greek ‘zeo’, to boil and ‘lithos’, stone [2]. Since their discovery, zeolites are one of the most abundant minerals on earth which have been recognized as a separate group of minerals. After the discovery of zeolites work was carried out on ion exchange, hydration and dehydration. Zeolites are alumino-silicate minerals which have a molecular sieve action due to their open channel network, and are composed of TO_4 tetrahedra linked with oxygen sharing the negative charge created by the presence of AlO_2^- which is balanced by cations that neutralize the charge deficiency. These cations include: the alkaline (Na^+, K^+, Rb^+, Cs^+), the alkaline earth (Mg^{2+}, Ca^{2+}) cations, NH_4^+, H_3O^+ (H^+), TMA^+ (Tetramethylammonium) and other nitrogen containing organic cation, and the rare earth and noble metal ions [2]. After the discovery of zeolites, work was carried out to study their physical and chemical properties. In 1930 “Molecular sieve” was a term introduced for materials that exhibited selective adsorption properties [3]. These materials contain other elements in addition to, or in lieu of, silicon and aluminum. In the

Citation: Jakkula VS, Wani SP. Zeolites: Potential soil amendments for improving nutrient and water use efficiency and agriculture productivity. Sci Revs Chem Commun. 2018;8(1):119.

past limited classes of zeolites were known, however work by researchers on different classes of zeolites paved way for silicates, metallosilicates, metalloaluminates, $AlPO_4$s and silico-and metalloaluminophosphates.

It is simple to compare adsorptive and catalytically properties of zeolites by describing them in terms of their pore openings and channel systems. A need to relate and compare structural properties of a large number of zeolite structures has led to development of secondary building units (SBU). These units are also used in efforts to understand formation of individual structures from complex mixtures used in the synthesis [2]. As the individual tetrahedral TO_4 unit is the basic building unit of a zeolite, a secondary building unit (SBU) consists of selected geometrical groupings of those tetrahedrons. Pore size and channel system play a vital role within a zeolite framework. Instead of visualizing zeolites in terms of interconnection of voids by these 8, 10, and 12 ring pore openings; the structure can be viewed in terms of one, two or three dimensional tubes or channels. For some zeolites "channels" are very short, similar to portholes or windows connecting large cavities within the structure [2].

This review is an overview of application of zeolites in various fields with emphasis on their use in agriculture as effective soil conditioners, their influence on cation exchange capacity, their soil nutrient interactions and their impact on soil properties, nutrient and water use efficiency and crop yield. Most of the research carried out on zeolites relates to irrigated and temperate conditions. It is therefore envisaged that through this review an understanding of zeolites for drylands and semi-arid tropical climatic conditions is established, which will then pave way for synthesizing these materials as slow/controlled release fertilizers to minimize the use of urea in developing countries and also as effective macro/micro nutrient carriers for enriching degraded soils of drylands.

Applications of Zeolites

Zeolites have numerous applications i.e. in catalysis, in gas adsorption, industrial gas separation, water treatment (wastewater and drinking water), agriculture, and metal immobilization in soils, ion exchange, aquaculture, odour control, and desiccation and as phosphate substitutes in detergents. Zeolites have various applications, based on their cost and ion exchange behavior the main areas where zeolites are widely used are in detergents; in ammonia/ammonium removal from wastewater effluent; in radioactive isotope removal from spent pile effluent and in agriculture. By far the most important of these is in detergents, where zeolites are employed as water softeners, partially replacing tri-polyphosphate builders [4]. The annual turnover of Zeolite A for this purpose alone in the U.S is several billions of dollars. The adsorption capacity of various zeolites i.e. Mordenite, Chabazite, Clinoptilolite, Ferrierite and Phillipsite, have been tested for ammonia over methane in the gasification procedure and demonstrated that Phillipsite would not adsorb CO, CO_2 and CH_4 in a gasification stream [5] but at 25^0C, Phillipsite adsorbs NH_3 rapidly. Synthetic zeolites are potentially useful additives to bind heavy metals, study by Lewis et al. [6] showed that out of the many zeolites i.e. Zeolite A, Mordenite, Faujasite, Zeolite X, Zeolite P; Zeolite A has the highest capacity to bind heavy metals such as cadmium and zinc. Zeolite A has the highest binding capacity between pH 5 and 6.5 and was stable pH>5.5 [6].

Many authors have studied the possibilities of separation of ammonium ions from drinking water and from wastewaters by zeolites [7-9]. The application of synthetic Phillipsite prepared by hydrothermal alteration of power plant ashes, when compared to a natural Slovakian Clinoptilolite, showed that the former significantly reduced the concentration of ammonium ions in wastewaters [10]. Various systems are proposed for removal of pollutants including heavy metals and radioactive ions from industrial effluents, in Denver, Colorado (USA) natural zeolites are used for removal of ammonium in potable water systems. Na^+ present in wastewater can also be removed using natural zeolites, thereby allowing this water to be used for agricultural applications. In a study by [11], it was observed that only 14.3% of the exchangeable Na^+ adsorption capacity i.e. 22.04 mEq/100 g Na^+ was for natural zeolite. In order to increase the adsorption capacity, zeolites were treated with $NH_4C_2H_3O_2$ at 1 M concentration which increased the adsorption capacity to 41.08 mEq/g. This increase represents 26.6 % of the theoretical exchangeable capacity of zeolite material. Since synthetic zeolites were first used commercially, they have found many uses in adsorbent and catalytic applications based on their unique physical structure. As adsorbents, zeolites have wider applications in chemical, petroleum and natural gas operations. They are used to dry and purify gaseous and liquid streams along with wide use in drying and purifying both gaseous and liquid streams along with separating olefins from paraffin's, oxygen from air and Para xylene from mixed xylenes.

Work has been carried out in introducing metals into zeolite framework, which serves as both oxidation and reduction catalysts due to the chemical reactions take place within the internal cavities. In principle the high internal surface area allows high reactivity and the cation exchange capacity of zeolites permits facile introduction of acidic or transitional metal catalytic function [12]. Some examples of catalysis uses are: titanium ZSM-5 in the production of caprolactum, and copper zeolites in NO_X decomposition. Zeolites are widely used in catalysis and are improved heterogeneous catalysts as compared to amorphous catalysts. Because of the shape selectivity zeolites are used in cracking and alkylation processes i.e. in hydrocracking, toluene alkylation, and methanol dehydration. Due to the ban on production and use of chlorofluorocarbons (CFCs) and Halons, which resulted in ozone depletion, there is a greater need for safe disposal of these banned materials and/or their conversion into alternative materials, which are environmentally acceptable. Development of zeolite-based catalysts can act as potential agents for dehalogenation processes for environmental protection [12].

In agriculture zeolites have numerous applications, as slow release fertilizers, as heavy metal removers, as soil conditioners, and as increasing the nutrient and water use efficiency along with increasing crop yield. Soils throughout the world have been contaminated with heavy metals (i.e. Cu, Cd, Pb and Zn) and with radionuclides (i.e., 134Cs, 137Cs and 90Sr). Studies have shown that zeolites are widely used in heavy metal uptake. There was a significant decrease in metal uptake by plants grown in zeolite amended soils [13]. In barren soils, contaminated with heavy metals zeolite addition completely eliminated metal phytotoxicity and allowed establishment of vegetation [14,15]. The simple concept of use of zeolites in metal contaminated soils shows that soils get alkalized and may help to reduce metal mobility and phytotoxicity. All of these depend upon zeolites ion exchange capability.

Use of zeolites in agriculture

Nitrate contamination of both underground and surface waters results from nitrogen loss from irrigated cropland, particularly sandy soils. Increase in crop yield and decrease in nitrate pollution of water systems can be achieved by addition of zeolites (both natural and synthetic) as a fertilizer amendment to soil, thereby saving the cost for future improvement. Zeolites have been used since 1960s, with the use of natural zeolites for plant growth being first reported in Japan [16]. Soil macro nutrients i.e. nitrogen, phosphorus and potassium could be supplied to plants in the form of ammonium (NH_4^+) and

Phosphate (P) exchanged zeolites [17-19]. The zeolites can act as a macro nutrient supplement. One of the most important applications of zeolites in agriculture is the slow/controlled-release fertilizer aspect. Slow release is a term that is interchangeable with delayed-release, controlled-release, controlled-availability, slow acting and metered-release [20]. The widespread abundance Clinoptilolite, Chabazite, Phillipsite and Mordenite in nature and their selectivity for certain cations (i.e. NH_4^+ and K^+) makes them suitable for slow-release fertilizer aspects.

Study by Jakkula et al. [21] has shown that Linde type F is one such zeolite which has a very high affinity towards NH_4^+. The synthesized Linde type F (LTF) which is a synthetic form of edingtonite (EDI) was ion exchanged with NH_4NO_3 and introduced as a soil amendment to look at growth of maize plant (Zea mays). The selectivity and affinity of Linde type F for NH_4^+ was higher, which resulted in lower plant growth. In a study to assess the Cd uptake of two test crops wheat and spinach, [22] found that slow-release synthetic zeolite-bound Zinc and Copper fertilizers may help to reduce Cd accumulation in edible parts of crops. Most of the previous studies carried out on the slow/controlled release fertilizer aspects of zeolites were focused on natural Clinoptilolite and to a certain extent on natural Phillipsite. Zeolites when applied with conventional fertilizers aids in an increase in seed germination and an overall increase in yield of spinach (*Spinaciaoleracea*) [23]. Zeolite also have an effect on yields of plums (*Prunuspersica*) and vines (*Vitisvinifera*), in a study in southern Italy by [24] it was found that on adding zeolites to traditional fertilizers there is an increase in fruit size and yield. Jordanian zeolite tuffs have been used for various applications. Studies on strawberries (*Fraganiaxananassa*) [25] showed by adding Jordanian Chabazite-Phillipsite tuff-soil mixture in 2:5 ratio increased crop yield ($\leq$ 72%) and plant height and decreased mortality. Although zeolites have been used since ages still there is huge scope for these materials to penetrate into agriculture as slow release fertilizers, soil conditioners and drought proof materials. Research done in the past focused on natural zeolites, current research is looking at both natural and synthetic zeolites for improving soil properties and increasing crop yield. The main focus of research is to develop zeolites which are eco-friendly, cost effective and potential fertilizer substitutes for increasing crop yield and reducing nitrate leaching.

Zeolites as effective soil conditioners

Zeolites are widely used as soil conditioners to improve soil physio-chemical properties [26]. The increase in soil pH and exchangeable K on adding Clinoptilolite to soils is significant, and has no influence on soil humus content and soil chemical composition [27]. Addition of zeolites to soil helps to control soil pH and improve ammonium retention. Out of the many properties of zeolites some of the prominent ones include increase in soil CEC, act as a reservoir of K^+ [28] and increase in the water-holding capacity of loamy sand soils [29]. Studies on synthetic Phillipsite and natural Clinoptilolite supplemented soils showed an increase in water holding capacity and CEC [26]. Natural zeolite-enriched soils increased water holding capacity by (18-19%) and CEC by 30-40%, whereas the synthetic zeolite enriched soils increased water-holding capacity by 25-30% and CEC by 40-50%. Zeolites once saturated with NH_4^+ can be used as effective fertilizers. Ion exchange plays an important role in introducing NH_4^+ into the framework, by exchanging for cations present in the zeolite framework. The use of conventional fertilizers used intensively by farmers for increased crop production can be replaced by ammonium exchanged zeolites which are valuable source for controlled release of N. Soils low in K can be replaced with, zeolites such as Linde type F synthesized in K form which can be used for replenishing K in these soils.

Increase of soil pollution by heavy metals is one of the main problems of modern agriculture. The increased accumulation of metals in soils is highly influenced by human activity and the related development of industry and irrational use of fertilizers. Heavy metals may persist in the soil for hundreds of years, which is associated with the risk of their inclusion in a trophic chain. The main factor determining the solubility of heavy metals in soil is low pH [30]. Another important factor that determines the retention of heavy metal ions is the sorption capacity of soils, which is determined by the number and quality of soil sorption complex. Natural and synthetic zeolites are being used among other additives to reduce the bioavailability of heavy metals in the soil [16]. Ion exchanged zeolites can be used as carriers of nutrient elements in fertilizers, and can be exploited to trap undesirable metals and prevent their uptake into the food chain. The transfer of fertilizer-added heavy metals, such as copper, cadmium, lead, and zinc, from soils to plants can be reduced by application of pulverized zeolites [31].

The use of zeolites in acidic soils causes an increase in pH that significantly affects reduction in heavy metals solubility and bioavailability for plants. Except of ion exchange reactions, the pH increase promotes the adsorption of heavy metals on the surface of zeolites and their oxides precipitation [32]. The use of zeolites significantly reduced the uptake of cadmium and lead in wheat [33]. Studies concerning the effects of various additives on a change of the solubility of lead, cadmium and zinc have shown that zeolites significantly reduced the solubility of lead and cadmium in polluted soils. Zeolites from Italy and New Zealand have been used for ammonium removal from wastewater [8,33]. After researching Turkish zeolites studies confirmed that nitrification decreased after zeolite application to soil [34]. The protection of groundwater at waste disposal sites can be achieved by using natural zeolites [4]. Another important use for natural zeolites is reduction in soil contamination risk associated with heavy metals [35] and decrease in the heavy metal content of plants [36].

Use of Clinoptilolite in Agriculture

The pronounced selectivity of Clinoptilolite for NH_4^+ and K^+ was exploited in Japan as slow-release chemical fertilizers. The high cation exchange property of Clinoptilolite towards NH_4^+ makes it particularly valuable when applied to finely texture sandy soils to restrict leaching of NH_4^+, as high retention of this ion would control its accessibility to nitrifying bacteria [37]. Other studies showed that an organo-zeolitic substrate incorporated in a composted mixture of poultry manure and Clinoptilolite-zeolite tuff is an effective fertilizer and soil conditioner [38]. Some of the soil properties which can be improved by incorporating zeolites as part of organic fertilizers are soil quality by improving soil structure, ion exchange capacity of soils, and moisture and nutrient retention. The nutrient loss to the environment can also be inhibited by application of zeolites to soil. Studies showed that nitrogen can be supplied to plants from soils amended with ion exchange form of NH_4^+- saturated Clinoptilolite [6,39]. A substantial reduction of NO_3 - leaching and increased uptake of N-fertilizer was observed on addition of 10% (w/w) Clinoptilolite to sand used in the construction of golf-course greens [40]. Studies on sweet corn (*Zea mays*) showed that amending soils with ammonium-Clinoptilolite [41], N leaching reduced considerably, while sustaining plant growth and increasing N-use efficiency, when compared to ammonium sulphate amended soils. Also sweet corn grown in soil amended with ammonium-Clinoptilolite assimilated significantly more N than sweet corn grown in soil amended with ammonium sulphate. Researchers developed a kinetics theory that, controlled release of P, NH_4^+ and K^+ can be accomplished in synthetic soil through dissolution and cation exchange reactions between phosphate rock and

Clinoptilolite [18]. On the other hand, mixing NH_4^+- saturated Clinoptilolite with phosphate rock can act as a supplement of N and P to plants [42,43].

Use of Phillipsite in Agriculture

The exchange properties of natural Phillipsite tuff obtained from the Aritain area of Jordon were evaluated by studying the exchange properties of this zeolite in the NH_4^+-Na^+ system. The tuff has a higher selectivity for ammonium ions than sodium ions. Studies on tuff revealed that release of NH_4^+ from the saturated tuff occurs over a long period of time (630 days) [44]. These properties are favorable for using Jordanian Phillipsite tuff as a potential ammonium-based slow release fertilizer. Studies on the supply rate of P from the zeolitic fertilizer (saturated Phillipsite tuff from Tenerife) compared with KH_2PO_4 alone indicated that zeolite fertilizers supply available P after 70 days of continuous percolation, whereas P from KH_2PO_4 is exhausted after 50 days. Zeolitic fertilizers supplied available K throughout the whole experiment period [45]. Jakkula et al. [46] carried out research to study the effect of both synthetic zeolite Phillipsite and its natural counterpart on the high selectivity and affinity of these zeolites towards ammonium (NH4+) and its potential as a slow release fertilizer. Results were promising for synthetic Phillipsite which showed predominantly higher affinity towards NH_4^+. The exchange capacity of Phillipsite is around 3.5-3.6 meq.g^{-1}, which makes Phillipsite suitable for agriculture due to the presence of high levels of potassium among exchangeable cations. The use of NH_4^+-Phillipsite tuff offers an alternative option to the widely used soluble NH_4 fertilizers in agriculture.

Study was carried out in UK on synthetic and natural Phillipsite to study their effectiveness as slow release fertilizers [46]. Na-K form of Phillipsite (PHI) was synthesized and NH_4^+ was introduced into the framework. Ion exchanged synthetic zeolite was compared with its natural counterpart. In a glasshouse experiment, maize was grown in zeolite amended at different loadings. A control comprising NPK fertilizer added to soil was used for comparison. Zeolite mineral Phillipsite amended soils at various growth stages revealed the a□nity of this zeolite for NH_4^+. Results demonstrated that natural zeolite Phillipsite has lower affinity towards NH_4^+ on comparison to synthetic Phillipsite when introduced as a soil amendment. The ion exchange interactions in soil were promising for synthetic zeolite Phillipsite, with cations in soil exchanging more freely with K^+ and NH_4^+ present in the synthetic Phillipsite framework [47].

Zeoponic Substrates

Co-operative programmes between NASA and industry have developed zeoponic plant growth media and fertility systems. A zeoponic plant growth system is defined as cultivation of plants in artificial soils, which contain zeolites as a major component [20,48]. Zeoponic substrates have been used on the Russian Mir Space Station and U.S. Space Shuttles to grow various plants, including radishes, wheat and brassicas. Space gravitational biologists have considered Zeoponic substrates as preferred material for plant growth in a microgravity environment. However, the effectiveness of zeoponic substrates for plant growth in macro gravity is unclear. Between 1994-1997, Zeoponix, Inc (USA) and NASA, conducted experiments on zeoponic materials as soil amendments for plant growth, studying seed germination, root development, fruit development, fruit quality and yield. Work was carried out on horticultural species and cereal crops. According to results claimed virtually all plants tested had improved yield or quality of growth when growing in soil-less media containing 5-30%

by volume zeoponic fertilizer-amendments [49]. With rising world populations, potential improvements in crop yield indicated with zeoponic systems are of particular importance in meeting rising food demands.

Zeolite nutrient interactions in soil

Studies by Pickering et al. [50] showed that zeolites improve the use of NH_4^+-N and NO_3^--N, reducing leaching losses of exchangeable cations along with nutrient use efficiency by increasing P availability from phosphate rocks. To improve plant yield, zeolites which have a high affinity for nutrients, may be used as growth media [38]. Zeolite attracts many trace elements and macro and secondary nutrients i.e. ammonium, potassium, calcium and magnesium. In order to balance the negative charge, zeolite attracts calcium from phosphorus mineral apatite such as rock phosphate or locked up phosphorus in soil. Zeolites have affinity for majority of cation in particular ammonium and potassium. It is known that plants extract ammonium, potassium and other nutrients by active uptake from roots. When cation such as ammonium or potassium source become available either naturally or applied, zeolites get recharged and prevent free nutrients from leaching.

Zeolites are being investigated for use as fertilizer enhancers and other agricultural amendments because of their unique cation-exchange properties. Zeolites serve as a slow release source of nutrients upon precharged with ammonium-nitrogen (NH_4-N), potassium (K^+), or iron (Fe^{+2}) when such precharged zeolites are used as a component of soilless media [51]. Studies on controlled release fertilizers have shown zeolite materials to have NH_4 adsorption kinetics, natural zeolites have also shown NH_4 adsorbent properties and controlled-release fertilizer properties [52]. Another use of zeolites is in P fertilization [43], ion exchanged zeolites i.e. ammonium exchanged zeolites increases solubility of soil P, enhances its uptake by the plants, and decreases its precipitation and fixation by exchanging NH_4^+ with other cations [43-45]. In addition, zeolitic tuff can be used in saline soils or when saline water is used for irrigation. In a study on absorption of four Na^+ salts [sodium chloride (NaCI), sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), and sodium sulfate (Na_2SO_4)] by a natural zeolite (clinoptilolite) from China, it was shown that the zeolite strongly absorbed Na^+ and anions and that the rate of absorption increased with time as the salt concentration increased [53]. It was concluded in that study that zeolites might be used as amendments for sodic saline alkaline soils. Urea-N losses could be minimized using zeolites as additives in the fertilizers to control the retention and release of NH_4^+ and convert it as an enhanced efficiency fertilizer (EEF). The fact that zeolite can relatively strongly fix the ammonia nitrogen leads to the reduction of nitrogen leaching.

Among the various zeolites assessed for high cation exchange capacity, clinoptilolite allows for entrapping or releasing various cations [54]. This zeolite can be used to control N loss from urea because of the small molecular size of the open-ringed structure which physically protects NH_4^+ ions against microbial nitrification [55]. Excessive use of fertilizers results in environmental pollution, studies by Mcgilloway et al. [3] have shown that adoption of zeolite i.e. clinoptilolite decreases the excessive and unbalanced use of N fertilizers in agriculture by maximizing N use efficiency and water use efficiency. Studies have shown that N use efficiency can be improved by the use of clinoptilolite zeolite and N fertilizers in conjunction with each other [2,56-58]. The increased efficiency of N utilization when urea is used together with clinoptilolite zeolite has been demonstrated by a number of researchers [59-61]. Addition of zeolite to soil reduced soil urease activity through urease adsorption on the zeolite [62] and the prediction equation followed exponential function $Y = 40.975e^{-3.6848x,}$

where Y is the soil urease activity and x is the soil: zeolite ratio, R^2=0.95 [63]. Studies by He et al. [7] showed that natural zeolite clinoptilolite amended soil increases soil surface area and cation exchange capacity which aids in lowering nitrogen concentration in the leachate and increasing moisture and nutrients in the soil.

Impact of zeolites on soil properties, nutrient and water use efficiency and crop yield

Zeolite assists water infiltration and retention in the soil and acts as a natural wetting agent due to its very porous properties and the capillary suction it exerts. It order to assist water distribution through soils, zeolites act as excellent amendment for non-wetting sands [64]. In order to achieve less fertilizer for the same yield or the same amount of fertilizer lasting longer and producing higher yields, zeolites can be used which hold nutrients in the root zone for plants to use when required which leads to more efficient use of N and K fertilizers [65,66]. Zeolites are effective carriers of herbicides, fungicides, and pesticides due to their high adsorption capacities in the dehydrated state and the high ion-exchange capacity. Zeolites can be produced from various sources and they help in absorption and retention of plant nutrients and water and supplemented micronutrients, the synthetic zeolite produced from coal ash is a beneficial soil amendment which aids in the above properties [23].

Zeolites sorption capability and its ability towards uniform release of nutrients into the soil along with its ion-exchange ability prevents against their quick elution [67]. The controlled release unique properties of zeolites allow a gradual and controlled introduction of necessary nutrients i.e. potassium, ammonium or phosphates into the soil. Moreover, zeolites modified with Cu (II) ions can be a good source for Cu deficient soils. Zeolites have the ability to be retained in the soil for several years, therefore the stabilization of ionic exchange balance in soil for several minutes or hours can be considered as fast. The redundant ammonium ions would bind to zeolite in soil and would be gradually release into the soil solution; this will help the liquid nitrogen-based plant nutrition mechanisms.

In semi-arid India, on tropical soils in order to increase crop yield and quality, liming and balanced nutrient supply are essential. Best management practices involve balanced nutrition whereby fertilizers need to be applied as per the need of crop, excessive use of fertilizers (urea in particular) results in nitrate leaching and losses by NH_3 volatilization. In order to minimize the nitrate leaching and NH_3 volatization slow/controlled release fertilizers in the form of zeolites are need of the hour to support the increasing N demand and avoid the low N use efficiency (NUE). Use of aluminosilicates (zeolites) with nitrogenous fertilizer materials can reduce the nitrate leaching [68]. Zeolites used with urea mineral fertilizer can enhance the efficiency of this source by improving the nitrogen use through the control of retention of ammonium ion, contributing to increased N uptake and crop yields. In order to decrease the environmental impact of agriculture, zeolite utilization which maximizes the N use efficiency along with water use efficiency are key as zeolite aids in increasing water holding capacity [7], which helps in reduction of soil irrigation, because water is well retained within zeolite’s structure. The other properties of zeolites are reduction of soil acidity [69,70] and reduction of temperature oscillations. It has been reported that natural zeolites not only augment water holding capacity and soil drainage [71,72] but also increase crop water use efficiency [73].

Zeolites not only improve soil conditions but also help in increasing crop yields, in the past studies carried out on various soil types and various crops i.e., potato, maize, rice, tomato, eggplant, carrot showed crop yield increase and in some cases yield increase reached up to 60% [74]. Due to the zeolites exceptionally high ion-exchange capacity along with vegetable crops, zeolites can also be successfully used in cultivating different cereals, forage crops, vine and fruit crops [75]. In order to improve the horizontal spread of water after irrigation zeolites play an important role as their porous structure assures a permanent water reservoir in the root zone [76,77]. Zeolites make available nutrients exactly when needed thereby preventing unnecessary losses of nutrients [78]. Zeolites being source of nutrients act as excellent carriers, stabilizers and regulators of mineral fertilizers [79]. Zeolites decrease application rate of N and K fertilizers, as they themselves are carriers of N and K fertilizers thereby increasing efficacy [77].

Conclusion

Zeolites (a separate group of minerals found on earth in abundance and also could be synthesized) find a large number of potential applications in agriculture, particularly in soil management as well as wastewater treatment and heavy metal pollution removal. Nitrogen released as NH_4 after dissolution of applied chemical fertilizers or decomposition of manures and cover crops is adsorbed by zeolite. They can be used either as carriers of nutrients and/or medium to free nutrients to promote nutrient use efficiency. Zeolites are effectively used as soil ameliorants for treating salinity and have a positive effect on soil fertility, sorption properties of soil and subsequently the formation of phytomass. Also zeolites improve the efficiency of water and nutrient use of plants and decrease runoff and sediments amount by increasing the soil water holding capacity. Acting as slowly soluble fertilizers, they improve water balance and sorption characteristics of light sandy soils in particular, which is reflected in higher yield and better quality. Studies have shown that zeolites significantly adsorb NH_4 and P and minimize reactive NO_3 formation and also could be effectively used for wastewater treatment as well as cleaning of heavy metal polluted sites. Usage of zeolites increased plant growth in many research studies across the globe, and also use of zeolite is expected to reduce a third to half Urea-N fertilization. Soil fertilized or amended with organo-zeolite mixtures regulate N release and minimize reactive N (NO_3^-) formation. Research on efficient utilization of zeolites for rainfed dryland agriculture is critical in the current climate change scenario. It is hoped that continued research in enhanced ammonia supply by zeolite as carrier will result in better nitrogen fertilization management through strategies best-suited to support vegetative development of tested crops in drylands. As rainfed agriculture experiences drought year after year, use of zeolites which increases the water holding capacity of various soil types could be alternatives to conventional fertilizers. Finally, zeolites can serve as future environmentally friendly materials for both increasing crop yield and reducing agriculture input costs.

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