Nanoporous zeolites in farming: current status and issues ahead

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In many parts of the world food security is being affected due to declining quality and/or quantity of the soil resource base and climate change. Climate change summits are being held worldwide to prevent crop failures. Notwithstanding this fact, one of the root biophysical causes of falling per capita food grain production is reported to be soil resource degradation. In order to reverse this trend of soil base degradation, it is necessary to either expand the land base under cultivation or to intensify crop production per unit of land. Soils are either inherently low fertile or made less fertile due to the removal of nutrients without adequate replenishment by intensive farming. It is in this context that the farming with nanoporous zeolites assume significance.

Keywords: Farming, food security, nanoporous zeolites, soil degradation.

Origin, nature and properties

ZEOLITES are crystalline aluminosilicates with a general formula $M_xD_y[Al_{(x+2y)}+2_ySi_{n-(x+2y)}O_{2n}]mH_2O$, where x is the number of monovalent cations, y the number of bivalent cations, n the cation valence and m the number of water molecules in the formula. They are among the most common minerals in sedimentary rocks and are reported to be especially common in tuffaceous rocks. They have been found in rocks of diverse age, lithology and geologic setting and are valuable indicators of the depositional and post-depositional (diagenetic) environments of the host rocks[1]. They are tectosilicates exhibiting an open, three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedra and containing water[2].

Identification of zeolites as a mineral goes back to 1756, when a Swedish mineralogist, Alex Fredrik Cronstedt, collected some crystals from a copper mine in Sweden. Zeolites mean 'boiling stones' in Greek, because of their ability to froth when heated to about 200°C. Thereafter, zeolites were considered as a mineral found in volcanic rocks for a period of 200 years. Their commercial production and use started in the 1960s (ref. 3).

Different combinations of SiO_4^{4-} and $Al(OH)_6^{3-}$ tetrahedra lead to the formation of a three-dimensional framework with pores and voids of molecular dimension. Shape, dimensions and linkage of zeolite pores and voids are the key characteristics of zeolite materials. The pores and interconnected voids are occupied by cations and water molecules. The structure of each zeolite mineral is complex, but they all have large open 'channels' in the crystal structure that provide a large void space for the adsorption and exchange of cations. The internal surface area of these channels is reported to reach as much as several hundred square metres per gram of zeolite, making zeolite an extremely effective ion exchanger. Cations can be changed by ion exchange and water can be removed reversibly by application of heat. The mineral has a three-dimensional crystal lattice, with loosely bound cations, capable of hydrating and dehydrating without altering the crystal structure. Other useful chemical and physical properties include: high void volume (~ 50%), low density (2.1–2.2 g/cm^3), excellent molecular sieve properties and high cation exchange capacity (CEC) of 150–250 cmol/kg.

The kinetics of ion-exchange process in zeolites has been extensively studied. Two processes have been identified, viz. particle diffusion and film diffusion. Diffusion within the zeolite (particle diffusion) and diffusion transport through the liquid film surrounding the particle (film diffusion) have been assumed to be the most important steps in the ion-exchange process. The preference of a zeolite for a particular cation in a multicomponent system depends on various factors, viz. Si/Al ratio of the zeolite, the exchangeable cation of the starting zeolite (co-ions), the hydration ratio of the co-ion and the in-going ions as well as the temperature and three-dimensional framework of zeolite. Therefore, these features should be analysed for a better understanding of the multi-component ion-exchange mechanism[4].

The cationic interchange capacity of zeolites is two to three times greater than other types of minerals found in soils. The application of zeolites to the soil increases their cation exchange capacity, and as a result, it increases the nutrient retention capacity. Furthermore, the addition of zeolites usually increases pH levels[5]. There is a wide variation in the cation-exchange capacity of zeolites because of the differing nature of various zeolite cage

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structures, natural structural defects, adsorbed ions and their associated minerals[6].

Thus, zeolites are natural materials with the ability to exchange ions, absorb gases and vapours, act as molecular-scale sieves and catalyse reactions owing to fixed pore size and active sites in the crystal lattice.

Classification

More than 50 different species of this mineral group have been identified[7]. Zeolites have been classified on the basis of their morphological characteristics, crystal structure, chemical composition, effective pore diameter and natural occurrence.

Zeolites are classified on the basis of silica : alumina ratio as follows: (i) Low Si : Al ratio, between 1 and 1.5 – zeolite A; (ii) Intermediate Si : Al ratio, between 2 and 5 – zeolite Y; (iii) High Si : Al ratio from 10 to several thousands – erionite, mordenite.

In 1997, the Subcommittee on Zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names had recommended nomenclature for zeolite minerals[8]. The report suggested that zeolite species are not to be distinguished solely on the Si : Al ratio, except for heulandite (Si : Al < 4.0) and clinoptilolite (Si : Al ≥ 4.0). Dehydration, partial hydration and over hydration are not sufficient grounds for the recognition of separate species of zeolites.

Flanigen[9] has classified zeolites based on pore diameter. (i) Small-pore zeolites (8 rings) with free pore diameter 0.3–0.45 nm. (ii) Medium-pore zeolites (10 rings) with free pore diameter 0.45–0.6 nm. (iii) Large-pore zeolites (12 rings) with free pore diameter 0.6–0.8 nm. (iv) Extra large-pore zeolites (14 rings) with free pore diameter 0.8–1.0 nm.

Agricultural applications

Zeolites are important materials with broad applications in refineries as catalysts, sorption and separation processes, and also in agriculture and environmental engineering. Some significant uses of zeolites are discussed here, but their importance is growing day-by-day. Today, synthetic zeolites are mainly being used widely in petroleum refining and chemical process industries as selective adsorbents, catalysts and ion exchangers. However, the importance of zeolites has been realized in a greater extent in the agriculture sector.

Most of the initial research on the use of zeolites in agriculture took place in the 1960s in Japan. A brief review of the literature points out that Japanese farmers have used zeolite rocks over the years to control moisture content and increase the pH of acidic volcanic soils. Ion-exchange properties of zeolites can be utilized in agriculture because of their large porosity and high cation-exchange capacity. They can be used both as carriers of nutrients and as a medium to free nutrients.

The current growing awareness of the phenomenon and availability of inexpensive natural zeolites in the world has aroused considerable commercial interest. The reason zeolites are now attracting attention lies in the honeycomb structure of cavities and minute channels in different directions, which works at the cellular level trapping heavy metals and concomitant toxins in the soils and/or water.

The evolution in zeolite materials with improved or novel properties has strongly influenced the expansion of their applications and has provided new flexibility in the design of products and processes[10].

Zeolites are becoming the subject of investigation in various agricultural issues.

Input use efficiency

As a carrier of nutrients: It has been verified that, when mixed with nitrogen, phosphorus and potassium compounds, zeolite enhances the action of such compounds as slow release fertilizers, both in horticultural and extensive crops[11,12]. Natural zeolites have high tendency of ammonium selective properties[13]. The main use of zeolites in agriculture is in nitrogen capture, storage and slow release. It has been shown that zeolites, with their specific selectivity for ammonium (NH_4^+), can take up this specific cation from either farmyard manure, composts or ammonium-bearing fertilizers, thereby reducing losses of nitrogen to the environment. There is a new possibility, which is the addition of zeolite to the organic substrate[14]. Natural zeolites, due to their structure and properties (inert and non-toxic) can be used as a slowly releasing carrier of fertilizers[15]. It is possible to obtain an increase in the efficiency of nitrogen fertilizers in forage crops when nitrogenated clinoptilolites (Table 1) are used in comparison to urea[16].

Improving organic manure (farmyard manure/poultry) efficiency: It has been reported that zeolites, with their specific selectivity for ammonium (NH_4^+), can take up this specific cation from either farmyard manure, composts or ammonium-bearing fertilizers, thereby reducing loss of nitrogen to the environment. Ammonium-charged zeolites have also been tested successfully for their ability to increase the solubilization of phosphate minerals. Rodríguez *et al.*[17] confirmed that zeolite mixed with manure increases the effectiveness of organic fertilizers on meadowland soils. Most of the manure–ammonia sequestered in the zeolite is unavailable to nitrifying bacteria because of the small (4–5 Å) pore size of the crystal lattice structure[18]. Experiments by Leggo[14] revealed that zeolite incorporated with poultry manure served as an effective fertilizer and soil conditioner. Chuprova *et al.*[19] found the beneficial effect of zeolite fertilizers on mobile humus substances of Chernozem and on biological productivity of maize.

Improving nitrogen use efficiency: Nitrogen dynamics in the soil–air–water system is of interest in farming for its rational use. Higher nitrogen efficiency is an essential factor for reducing environmental contamination. Surface and groundwater contamination as a result of nitrogen fertilization have been demonstrated in Argentina[20,21]. The development of a slow nitrogen-release system to be used as fertilization technology could simultaneously contribute to the reduction in contamination and improvement of crop yields. Use of soluble N fertilizers is one of the major causes for groundwater contamination. Nitrogen liberation dynamics of the occluded form (in zeolites) is much slower than for the ionic form[16]. The nitrogen molecules are retained by electrostatic attraction, and modifications of molecular angles, and single and double bonds occur in it[22]. There are reports of urea-impregnated zeolite chips, which can be used as slow-release nitrogen fertilizers. Li[23] demonstrated the feasibility of using surfactant-modified zeolite (SMZ) using hexa decyltrimethylammonium as fertilizer carrier to control nitrate release, and concluded that SMZ is a good sorbent for nitrate, whereas slow release of nitrate is achievable. These dual properties suggest that SMZ has potential as fertilizer carrier to control the release of nitrate and other anions. Ammonium (NH_4^+) occupying the internal channels of clinoptilolite should be slowly set free, allowing progressive absorption by the crop, which results in a higher dry matter production of crops[16]. Pores in the clinoptilolite framework are small enough for small cations like ammonium and potassium to enter, but too large for nitrifying bacteria to enter. This means that once ammonium is held internally on the cation exchange sites within the clinoptilolite, it is not likely to be leached out easily as water passes through. It is more likely that it will move out slowly and be taken up in small amounts by the turfgrass plant, similar to the way a slow-release fertilizer works. Nitrification (conversion of ammonium to nitrate) was substantially reduced[24]. Not only does clinoptilolite improve nitrogen fertilization efficiencies, it also reduces nitrate leaching by inhibiting the nitrification of ammonium to nitrate[25].

Table 1. Total nitrogen content in the aerial plant parts of *Lolium multiflorum*[16]

Type of fertilizer (doses of N kg/ha)	N content (per mg of aerial part)
Clinoptilolite–NH_4 (0)	8.1
Clinoptilolite-NH_4 (60)	20.2
Clinoptilolite-NH_4 (120)	31.9
Clinoptilolite-NH_4 (180)	40.5
Clinoptilolite-urea (0)	8.1
Clinoptilolite-urea (60)	14.9
Clinoptilolite-urea (120)	24.0
Clinoptilolite-urea (180)	27.5
Urea (0)	8.1
Urea (60)	20.5
Urea (120)	28.0
Urea (180)	35.3

Improving phosphorus use efficiency: Zeolites have been used to control release of fertilizer components. Ammonium-charged zeolites have shown their ability to increase the solubilization of phosphate minerals, leading to improved phosphorus uptake and yield of crops. Studies conducted to examine solubility and cation-exchange in mixtures of rock phosphate and NH_4^+ and K-saturated clinoptilolite revealed that mixtures of zeolite and phosphate rock have the potential to provide slow-release fertilization of plants in synthetic soils by dissolution and ion-exchange reactions[26]. The power-function equation has been found to describe the transport kinetics of the nutrient release process in these systems[27]. Investigation conducted to study the effects of potassium and ammonium-saturated clinoptilolite on P availability in Ferrosols revealed that it can increase P solubility while providing K and NH_4^+ to the soil, a concurrent positive effect for plant growth[28].

Improving herbicide use efficiency: Controlled release of inputs is being employed extensively in agriculture to deliver active substances like pesticides, herbicides and fertilizer material. Porous materials with well-ordered structures are attractive candidates for storage and release of organic guest molecules. Controlled release of paraquat using zeolite has been reported recently from USA[29].

As an input in farming

As a fertilizer: Zeolites in soils exchange sodium and potassium cations for NH_4^+. After the second and third year of zeolite action in the soil, the mineral is an effective nitrogenous fertilizer. A combination of zeolite and natural fertilizer was found to be effective for improving crop growth. The use of NH_4^+–phillipsite tuff offers an alternate option to the widely used soluble NH_4-fertilizers in agriculture[12]. The high potential of zeolitic minerals as nitrogen fertilizers has been demonstrated; their use would diminish environmental problems and increase fertilizer efficiency[16]. Studies using natural zeolites have demonstrated significant improvements in fertilizer efficiency for zeolites compared to soluble salts (clinoptilolite is 7–9 times more efficient than KNO_3)[30]. Zeolites increase ion-exchange sites in soils in addition to offering absorption sites for small molecules, due to their porous structure[31].

Soil amelioration

Improving soil physical properties: Zeolites have been reported to improve the soil physical properties. They may hold water more than half of their weight due to high porosity of the crystalline structure. Water molecules in the pores could easily be evaporated or reabsorbed without damage to such structures. Zeolites assure a permanent water reservoir. Providing prolonged moisture dry periods helps plants to withstand dry spell; they also promote a rapid rewetting and improve the lateral spread of water into the root zone during irrigation. This results in saving water needed for irrigation. Amendment of sand with zeolite increases available water to the plants by 50% (ref. 32).

Remediation of contaminated soil: The application of zeolites to soil contaminated with heavy metals or radionuclides can be effective in lowering their input. This area of research is promising and needs extensive studies.

Removal of odour: Natural zeolites have been used in partial liquidation of fast and liquid wastes from animal production in agriculture and can be utilized for removing unpleasant smell in stables.

As soil amendment: Zeolites consist of cage-like polyhedral units with a high cation-exchange capacity and internal pores in crystal lattices that result in high water adsorption and nutrient retention[33]. Zeolite does not break down over time, but remains in the soil to improve nutrient retention. Therefore, its addition to the soil may significantly reduce water and fertilizer costs by retaining beneficial nutrients in the root zone. The porous structure of natural zeolite helps keep the soil aerated and moist as well as active for a long time. Natural zeolites have been reported to be used extensively in Japan as amendments for sandy soils, and small tonnages have been exported to Taiwan for this purpose. Zeolitic amendment is an effective way to improve soil condition in an arid and semi-arid environment[34]. Zeolites have been tested for use as a soil amendment on various crops, including vegetables and in greenhouses in Russia, field crops in Japan, as constituents of golf course greens and tees in order to improve drainage and aeration, to improve compaction resistance, and reduce leaching of pesticides and fertilizers from the soil[35]. Zeolites increase the water-retention capacity of the soils[36]. The higher the average ionic potential of the extra-framework cations, the larger the hydration capacity of the clinoptilolite. This trend may be attributed to the small size as well as the efficient water–cation packing of high field strength cations in the zeolite structure[37].

Buffering soil pH *levels:* Zeolite is not acidic but marginally alkaline and its use with fertilizers may help buffer soil pH levels, thus reducing the need for lime application.

Cleaning of wastewater

Wastewater treatment: Zeolites may be used for removing ammonia from wastewater. Clinoptilolite is effective for selective removal of NH_4^+ cations from wastewater. Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the harmless nature of their exchangeable ions[4].

Since most zeolites are beneficial for plant growth, it has been demonstrated that certain zeolites with sodium as the main exchangeable cation can actually decrease plant growth and yield. Also, the zeolite erionite is reported to be harmful to health. Therefore, proper selection of appropriate zeolites to suit their application is important. A few important applications of zeolites have been discussed above, but the possibilities of their usage are much broader.

Future research

The following issues have been identified for further research in soil and plant management: (1) To characterize the Bronsted and Lewis acid centres in zeolites. (Bronsted acid sites are assigned to bridging hydroxyl groups, whereas Lewis acid sites are essentially electron-acceptor centres and they can be cations or different aluminium species located in defect centres; the latter are the so-called true Lewis acid sites[38]). (2) To characterize the available zeolite deposits in each country. (3) To probe whether zeolite amendment will reduce the potential for nitrate leaching in agriculture. (4) To develop methodologies for organo-zeolitic manure/fertilizers. (5) To characterize the nutrient release pattern from organo-zeolites. (6) To probe the physical stability of zeolites in a variety of soil environments. (7) To probe the long-term impact of zeolites on soil flora and fauna. (8) To develop zeolitic herbicides to minimize herbicidal residues. (9) To carry out field testing of zeolites on soil and plant systems.

Conclusion

There is an increasing interest in the utilization of nanoporous zeolites in farming over the years because of current public concern about the adverse effects of chemical fertilizers on the agro-ecosystem. Ion-exchange properties of zeolites are recognized as important for plant nutrition due to their high cation-exchange capacity and porosity. Both ion-exchange and porosity are relevant to agronomy and soil science. The specific structure and diversity of the zeolites vary as also their application. They can be used either as carriers of nutrients and/or a medium to free the nutrients. Several applications have been identified in zeolite research and attempts are being made worldwide. Considerable research has been carried out globally to exploit the potential of zeolites in the perpetual maintenance of soil productivity. The current growing awareness of the phenomenon and availability of inexpensive natural zeolites has aroused considerable commercial interest. Also, a number of issues have been identified for future research.

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