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Review/Overview Article

Zeolitic farming

KULASEKARAN RAMESH[1], ASHIS K. BISWAS[2] AND ASHOK K. PATRA[3]

ICAR-Indian Institute of Soil Science, Nabibagh, Berasia Road, Bhopal, Madhya Pradesh 462 038

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ABSTRACT

Farming with natural rocks and minerals was an age-old practice. Intensive agriculture with imbalanced fertilizer usage has led to a decline in soil quality and so, restoring this soil degradation needs urgent attention. In this context, farming with natural minerals (zeolites) has drawn attention. Zeolites are natural aluminosilicates present as rocks in different parts of the world. However, they are also inherently present in Vertisols mixed with soils. Exclusive use of zeolites has gained a new momentum in the recent past owing to multitude of benefits accrued from them. Japanese farmers were pioneering workers on zeolite usage to manage soil moisture and reaction. Their ion-exchange capacity is helpful for plant nutrition as well as soil amendment; besides the recent research on zeolite-herbicides interactions is encouraging. Although considerable research on zeolites in agriculture has been advanced, further research need to be carried out for their efficient utilization in farming.

Key words: Ion exchange, Soil amendment, Slow release nutrients, Zeolites

Farming with natural rocks and minerals is an age-old practice for food production since stone ages. The intensive production practices concomitant with imbalanced fertilizer-management practices have led to declining quality and/ or quantity of the soil resource base in several parts of the world. To ensure feeding the teeming billions, soil-resource degradation is the key issue which needs urgent attention. Indian soils are either inherently low fertile, as evident from Royal Commission on Agriculture (1928) reports, and in the recent past they were made less fertile due to mismatch between nutrient removal and replenishment (Jones *et al.,* 2013). It is in this context, the farming with natural minerals, particularly zeolites, have assumed great significance. Zeolites are aluminosilicates, specifically tectosilicates exhibiting an open three-dimensional structure. Although significance of zeolites in farming is not a new issue, e.g. Vertisols inherently contain a lot of zeolites, (Pal, 2003), exclusive use of zeolites has gained new momentum owing to the multitude of benefits accrued from their application in the recent past. Pioneering work on zeolitic farming was initiated in Japan during 1960s. Japanese farmers have used them over years to control the moisture content and to increase the *p*H of acidic volcanic soils. The reduction in ammonia losses by volatilization and the increased efficiency of N utilization when urea is used together with aluminosilicates was demonstrated in both greenhouse and field experiments (Bernardi *et al.* 2014).

[1]**Corresponding author Email:** raamechek@yahoo.co.in
[1]Senior Scientist, [2]Principal Scientist & Head, [3]Director, ICAR-Indian Institute of Soil Science, Bhopal, Madhya Pradesh 462 038

Origin, nature and properties

Alex Fredrik Cronstedt (1756), a Swedish mineralogist, first identified zeolites in a copper mine in Sweden which refer to '*boiling stones*' in Greek. Zeolites are three-dimensional, microporous, inorganic crystalline minerals which can accommodate neutral molecules in the pore spaces and mobile cations (Kar, 2001) needed to balance the electrostatic charge of the framework of silica and alumina tetrahedra and containing water (Hemingway and Robie, 1984). In spite of a long history, their commercial mining and use for farming took root only in 1960s (Polat *et al.,* 2004).

Different connections of SiO_4 and AlO_4 tetrahedra lead to the formation of three-dimensional framework with pores and voids of molecular dimension. The pores and interconnected voids are occupied by cations and water molecules. The internal surface area of these channels is making zeolites as an effective ion exchanger besides, the Si:Al ratio. Vividly, the charge imbalance due to the presence of aluminium in the zeolite framework drives it which induces potential acidic sites. 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. They contain micropores of molecular dimensions of <1 nm (Pérez-Ramírez, 2012) and the Scanning Electron Mircroscope (SEM) microimages of zeolites indicated the crystals with cuboid structure (Fig.1) for a potassium zeolite (Ramesh *et al*., 2014a), while tubular (Fig.2) for a natural Indian zeolite (Ramesh *et al*., 2014b) from Rajasthan. However, the samples of clinoptilolite zeolite contained amorphous foliated crystals (Fig.3), and in particular layered structure parting into thin sheets and sparsely distributed fibre bundles (Ramesh *et al.,* 2015a).

The preference of a zeolite for one particular cation depends on factors like Si:Al ratio, the exchangeable cation of the zeolite, temperature and the framework and they should be analyzed to understand the ion-exchange mechanism (Barros *et al.,* 2003). Although their cationic-interchange capacity is 2 to 3 times greater than other types of minerals found in soils, there is a wide variation among zeolites because of the differing nature of various zeolite-cage structures, natural structural defects, adsorbed ions and their associated minerals (Mondale *et al*., 1995). Makungwe (2014) found an increase of 0.10 cmol/kg and 0.11 cmol/kg in ACRISOL and ALISOL, respectively, for every gram of zeolite added to a kilogram soil. A similar phenomenon was noted by Ozbahce *et al.* (2015) at Turkey, besides, an increase in soil pH (Ming and Boettinger, 2001) too. Thus in short, zeolites are natural/synthetic materials work as nano-adsorbents (Chauhan and Talib, 2012) with the ability to exchange ions, act as molecular-scale sieves and catalyze reactions owing to pore textural properties and active sites in the crystal lattice.

Zeolites of India

Natural zeolite minerals in India were reported in amygdaloidal vesicles in the Deccan lava flows. Since the 1970s, the state of Maharashtra has provided zeolites that have come out of the enormous lava flows called the Deccan Traps were reported way back in the 18^{th} century itself (Dana, 1854), regarding their formation and distribution in the lava flows. These minerals do not occur everywhere in the Western Deccan Traps, but are restricted to certain localities around Mumbai (Bombay), Vadodara (Baroda), Pune (Poona), and Nasik (Sukheswala *et al*., 1974). Heulandites (most popular zeolites of the world) zone was found in the highlands of plateau in the region around Pune (Maharashtra), which is the top-most region up to the highest point Kalsubai. In this region, around 30% of the rock is occupied by zeolites (Phadke, 1984). An area of 4.2 million km^2 situated between latitudes 0^o and 20^oS and longitude 70^o and 84^o E of the central Indian basin contained zeolites (Iyer and Sudhagar, 1995). In addition to Maharashtra, zeolite occurs as filling in the amygdular cavites in deccan trap basalts of Gujarat, Madhya Pradesh and Karnataka too (GSI, 2011).

Classification

More than 80 different species of zeolites have been identified and still more to be identified. Zeolites have been classified on the basis of their morphological characteristics, crystal structure, chemical composition and effective pore diameter etc. According to silica : alumina ratio, they are classified as Low (between 1 and 1.5), Intermediate (2–5) and high (>10). Later, Flanigen (2001) utilizing pore diameter made 4 groups, viz. small-pore (8-rings) with free pore diameter of 0.3–0.45 nm, medium-pore (10-rings) with free pore diameter 0.45–0.6 nm, large-pore (12-rings) with free pore diameter 0.6–0.8 nm and extra-large-pore (14-rings) with free pore diameter of 0.8–1.0 nm.

Field applications

Since in many parts of the world, zeolites are available at low cost and with evolution of new zeolites containing novel properties has provided new flexibility in the design of products and processes (Flanigen, 1980). This led to considerable rise in commercial utility. They are becoming the subject of interesting investigation in various agricul-

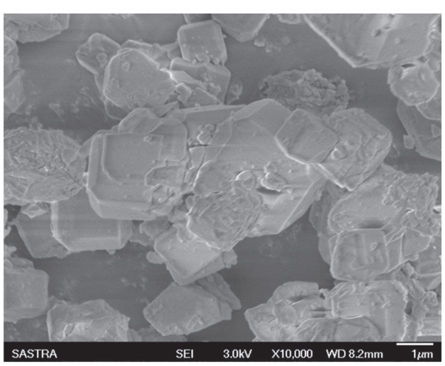

Fig. 1. Cuboid

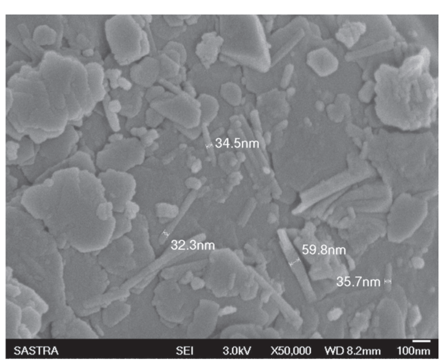

Fig. 2. Tubular

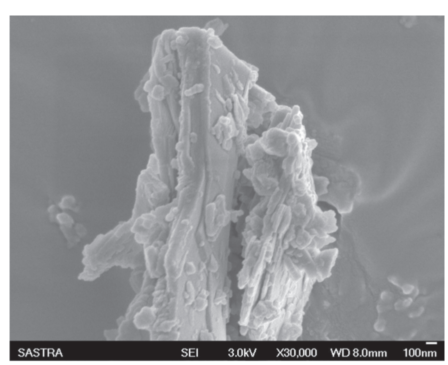

Fig. 3. Foliated crystals

tural issues (Ramesh *et al*., 2010a, 2011; Ramesh, 2013) particularly the ion-exchange properties, as they can serve the dual role of carrier and dispenser of plant nutrients. Among the natural zeolites, clinoptilolite (Ramesh *et al.,* 2015b) is most commonly used in agriculture. As they play an important role in modifying the physics, chemistry and biology of soils (Pal *et al.,* 2013), its application at Iran along with plant residues in soil have shown even positive effects on improving carbon pools and increasing carbon sequestration (Aminiyan and Akhgar, 2014). They can capture zinc (Ramesh *et al.,* 2012) and ammonia diffused in wastewater too (Markou *et al.,* 2014).

Organic manure handling and management

Handling organic and animal manure is a recurrent problem, besides severe loss of valuable nutrients through leaching and volatilization, particularly for nitrogen. Release of volatile compounds from various animal manures is a deterrent for their usage in farming. Zeolites could be used as an effective additive to control the odour (Sharadqah and Al-Dwairi, 2010), as they could adsorb the volatile substances (Rodríguez *et al.,* 1994) like acetic acid, butanoic acid, isovaleric acid, indole, and skatole (Cai *et al*., 2007) and enhances effectiveness of the manure (Leggo, 2000). Surface application of zeolite has potential for mitigating feedyard manure NH_3 losses thereby reducing losses of nitrogen to the environment, but specific zeolite properties influenced its effectiveness (Waldrip *et al.,* 2014). Nitrifying bacteria could not use the manure-ammonia in the zeolite due to small pore size (Mumpton, 1999). Ramesh and Islam (2012) have found reduced loss of ammonium from zeolite mixed with cow manure at Ohio, USA. Mature compost with good agronomic properties was produced by co-composting chicken slurry and paddy husk using zeolite and urea as additives by Latifah *et al.* (2015).

Nitrogen management

Although nitrogen is regarded as kingpin in agriculture and widely used in all crops and cropping systems, its use efficiency is just 30–40% only. As surface and groundwater contamination have been reported in some countries (Costa, 1997), its rational use is necessary to enhance nitrogen-use efficiency and reducing environmental contamination (Patra *et al.,* 1996). MacKown and Tucker (1985) noticed decreased nitrification and leaching losses by about 11% due to NH_4-clinoptilolite application. Free urease was found to be adsorbed on the outer surface of zeolite by cation-exchange reaction, and more than 70% of urease was adsorbed within 30 min (Choi and Park, 1988). A reduction in soil urease activity with zeolite was also noticed by Ramesh *et al*. (2010 b,c). Urea-impregnated zeolite chips have also been developed elsewhere. Kavoosi (2007) found increased nitrogen-use efficiency in rice owing to application of zeolites and ensured good retention of soil-exchangeable cations, available P, and NO_3 - within the soil in maize at Malaysia (Rabai *et al*., 2013). There is a possibility of surfactant-modified zeolite as a good sorbent for nitrate (Li, 2003), besides retaining large quantities of ammonium ion, interfere with the process of nitrification (Perrin *et al*., 1998). Zeolites with fertilizers in Cocoa enhanced fruiting (Sánchez-Mora *et al*., 2013), reduced nitrate and ammonium leaching (Moradzadeh *et al*., 2014) and so Clinoptilolite with 75% fertilizers to maize was equally good to that of 100% fertilizers alone at Malaysia *(Aainaa et al., 2015).*

Slow release of nutrients

When mixed with major nutrients, zeolites with their specific selectivity for ammonium (Kithome *et al*., 1998), can take up this specific cation from ammonium-bearing sources and acted as a slow release fertilizer in several crops (Dwairi, 1998a) since the supply of bases from them could prevent the soils from losing their productivity (Bhattacharya *et al.,* 1999). The adsorbed ammonium ion after the second and third year of zeolite application in the soil behaved as an effective nitrogenous fertilizer and improved crop growth (Dwairi, 1998b). The main use of zeolites is for nitrogen capture, storage and slow release, as they adsorb molecules at relatively low pressure (Kamarudin *et al.,* 2003) and is considered as nano-enhanced green application (Lavicoli *et al.,* 2014).

There is a new possibility, which is the addition of zeolite to the organic substrate (Leggo, 2000). Zeolite as coating material has shown the potential to increase water absorption and water retention of NPK fertilizer and to retard N, P, and K release from the fertilizer in a sandy soil in Indonesia (Sulakhudin and Sunarminto, 2011). Zeolite applied with urea reduced the ammonia volatilization by 8%. Concentrated zeolite used as a sand-soil amendment also increased at least 10% of soil-water retention and 15% of available water capacity (Bernardi *et al*., 2013).

Phosphorus management

Zeolite/rock phosphate (Allen *et al.,* 1993) combination acted as an exchange-fertilizer, with Ca^{2+} exchanging onto the zeolite in response to plant uptake of nutrient cations (NH_4^+or K^+), enhancing the dissolution of the rock-phosphate (Pickering *et al.,* 2002). Ammonium-charged zeolites have shown their ability to increase the solubilization of phosphate minerals (Hua *et al.,* 2006) or animal bone ash (Lancellotti *et al.,* 2014) and promoted the rock-phosphate dissolution in all soil types (Mihajloviæ *et al.,* 2014) and reduced fixation in soils (Shokouhi *et al.,* 2015).

Slow/sustained release of herbicides

The most hydrophobic solids such as zeolite 'ZSM 5' were found to adsorb atrazine better when organics were present (Bottero *et al.,* 1994) in the compartmentalized intracrystalline void space of zeolites (Corma and Garcia, 2004). This has brought a considerable attention on soil clay minerals for slow-release formulation of herbicides. Zeolite (ZSM-5) was found to accommodate herbicide paraquat in the microstructure with restricted mobility (Walcarius and Mouchotte, 2004). This was followed by surface modification of paraquat by Zhang *et al.,* (2006). Humic acid zeolites were also found to be sorbents for phenylurea herbicides (Capasso *et al.,* 2007). Clinoptilolitic tuff was considered as a suitable material for removing atrazine from soil (Salvestrini *et al.,* 2010) and water (Jamil *et al.,* 2011) too. Later an enhanced activity of zeolite-loaded catalysts on herbicide isoproturon was found due to the synergistic effect of increased visible light absorption and the high porous nature of zeolite facilitating the adsorption of recalcitrant molecules (Reddy *et al*., 2012). This was followed by Bakhtiary *et al*. (2013) with 2,4-D herbicide, as the sorbed 2,4-D showed gradual temporal release pattern and kept the active ingredient in the upper 5 cm soil layer (Shirvani *et al.,* 2014).

Soil amendment and improving soil water-holding capacity

Zeolitic amendment is an effective way to improve soil condition in an arid and semi-arid environment (Yasuda *et al.,* 1998) owing to its cage-like polyhedral unit and increased water-retention capacity of soils (Pino *et al.,* 1994), and so considered as soil activator (Akbar-Basri, 2013). They are used extensively in Japan as amendments for sandy soils. It does not breakdown over time and could reduce water and fertilizer costs by retaining beneficial nutrients in the root zone. The higher the average ionic potential of the extra-framework cations, the larger would be the hydration capacity of the clinoptilolite. They may hold water more than half of their weight and hysteresis for water molecules could be observed without physical damage. This could assure a permanent water reservoir, providing prolonged moisture during dry periods. This results in a saving in the quantity of water needed for irrigation. Amendment of sand with zeolite increased the plant available water by 50% (Voroney and van Straaten, 1988) and enhanced the yield in many crops including vegetables in Russia, field crops in Japan, as constituents of golf course greens and trees in order to improve drainage and aeration, and improve compaction resistance (Wallace, 1998). This trend may be attributed to the small size as well as the efficient water-cation packing of high field strength cations in the zeolite structure (Yang *et al.,* 2001), as evident from successful canola production even under drought at Malaysia (Shahsavari *et al.,* 2014).

Way forward

The following issues have been identified for further research.

1. Identification of natural zeolites niches and estimation of the potential for commercial exploitation.
2. Characterization of the natural zeolite deposits for nutrient retention
3. Quantification of zeolite-amendment on nitrate leaching
4. Methodologies for organo-zeolitic manure/fertilizers and nutrient-release pattern
5. Understanding their physical stability in different agroecosystems
6. Ascertaining the long-term impact of zeolites on soil flora and fauna
7. Development of zeolitic herbicides to minimize the herbicidal residues
8. Economic feasibility of zeolites on cropping systems.

CONCLUSION

Ion-exchange properties of zeolites are recognized as important character for soil and plant nutrition owing to their high cation-exchange capacity. In the recent past, appreciable research has been taken up in zeolite–herbicides interactions. While most calcium and potassium zeolites are beneficial for plant growth, some reports indicated that certain zeolites with sodium as the main exchangeable cation may hinder crop growth through soil alkalinsation. Also, the zeolite erionite is reported to be harmful to human health. Therefore, the proper selection of appropriate zeolites to suit their application is indeed very important. Few important directions of zeolites utilizations have been discussed above, but the possibilities of the use of these zeolites are much broader, particularly in the development of slow-release inputs, viz. fertizers, herbicide etc. Thus, zeolites have a potential role in input management in cropping systems. The dual benefit of zeolites, viz. carrier and/or medium to free nutrients can be utilized in crop management practices. Considerable research has been advanced at global level because of its low-cost. Further research need to be carried out in future for their efficient utilization in farming.

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