Zeolites and Their Potential Uses in Agriculture

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Abstract

Zeolites are natural crystalline aluminosilicates. They are among the most common minerals present in sedimentary rocks. Zeolites occur in rocks of diverse age, lithology, and geologic setting, and represent valuable indicators of the depositional and postdepositional (*diagenetic*) environments of the host rocks. It was reported that, of the 40 naturally occurring zeolites studied by research groups, the most well-known ones are clinoptilolite, erionite, chabazite, heulandite, mordenite, stilbite, and phillipsite. Structurally, zeolites are tectosilicates exhibiting an open three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedral units. Pores and voids are the key characteristics of zeolite

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materials. The pores and interconnected voids are occupied by cations and water molecules. The internal surface area of these channels are reported to reach as much as several hundred square meters per gram of zeolite, making zeolites an extremely effective ion exchangers. The Si/Al ratio is an important characteristic of zeolites. The charge imbalance due to the presence of aluminum in the zeolite framework determines the ion-exchange property of zeolites and is expected to induce potential acidic sites. The Si/Al ratio is inversely proportional to the cation content, however directly proportional to the thermal stability. Cations can be exchanged by ion exchange and water can be removed reversibly by application of heat. The unique physical and chemical properties of zeolites, coupled with their abundance in sedimentary deposits and in rocks derived from volcanic parent materials, have made them useful in many agricultural applications. 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 has pointed out that Japanese farmers have used zeolite rock over years to control the moisture content and to 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 as both carriers of nutrients and a medium to free nutrients. Zeolites are important materials with very broad applications in agriculture and environmental engineering. Zeolite incorporation in soil was found to increase crop yields and to promote nutrient use efficiency. Other possible uses being investigated include applications as a carrier of slow-release fertilizers, insecticides, fungicides, and herbicides, and as a trap for heavy metals in soils.

With the population pressure on the land resources increasing, world food security is dwindling due to declining quality and/or quantity of the soil resource base. One of the fundamental root causes for falling per capita food grain production is supposed to be the soil resource degradation resulting from depletion of nutrient reserves, declining soil organic carbon stocks, heavy metal contamination etc. Most agricultural soils are either inherently low in fertility or made less fertile due to the continuous removal of nutrients without adequate replenishment. Coupled with low native soil fertility is the problem of low use efficiency of inputs, particularly chemical fertilizers and water. Owing to nutrient losses through various loss mechanisms, the use efficiency of applied nutrients continues to be low in most tropical agroecosystems. It is in this context that the use of zeolites in agriculture/soil fertility management assumes greater significance.

Zeolites are crystalline aluminosilicates. 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 postdepositional (*diagenetic*) environments of the host rocks. 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. Different connection of SiO_4 and AlO_4 tetrahedra leads to the formation of 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 with cations and water molecules. The internal surface area of these channels is reported to reach as much as several hundred square meters per gram of zeolite, making zeolites an extremely effective ion exchangers. Cations can be changed by ion exchange and water can be removed reversibly by application of heat. Other useful chemical and physical properties include high void volume, low density, excellent molecular sieve properties, and high cation–exchange capacity. Although both clays and zeolites are alumino-silicate materials, they are dissimilar in structure. While clays can easily break down into tiny particles or soil colloids, zeolites have three-dimensional rigid crystalline structures that have much greater control over molecule movement. This means special care must be taken in testing to provide enough time for the ion exchange to occur (Shaw and Andrews, 2001). The unique physical and chemical properties of zeolites, coupled with their abundance in sedimentary deposits and in rocks derived from volcanic parent materials, have made them useful in many agricultural applications.

1. Origin and History of Zeolites

Identification of zeolite as a mineral goes back to 1756, when a Swedish mineralogist, Alex Fredrik Cronstedt, collected some crystals from a copper mine in Sweden. He found that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material zeolite, from the Greek words meaning "*boiling stones*," because of ability to froth when heated to about 200°C. Following Cronstedt's findings, zeolites were considered as minerals found in volcanic rocks for a period of 200 years. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in postdepositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, etc. For this reason,

naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

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 has pointed out that Japanese farmers have used zeolite rock over years to control the moisture content and to 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 as both carriers of nutrients and a medium to free nutrients.

According to Coombs *et al.* (1997) "a zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four oxygen atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H_2O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about $400°C$ and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra."

2. Classification of Zeolites

More than 50 different species of this mineral group have been identified and still more to be identified. Zeolites have been classified on the basis of their morphological characteristics, crystal structure, chemical composition, effective pore diameter, natural occurrence, etc. In the year 1997, the subcommittee on zeolites of the International Mineralogical Association Commission on New Minerals and Mineral Names has recommended nomenclature for zeolite minerals. The report suggested that zeolite species are not to be distinguished solely on the ratio of Si to Al, 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 (Coombs *et al.*, 1997).

The Si/Al ratio is an important characteristic of zeolites. The charge imbalance due to the presence of aluminum in the zeolite framework determines the ion-exchange characters of zeolites and is expected to induce potential acidic sites. The Si/Al ratio is inversely proportional to the cation content, however directly proportional to the thermal stability. The surface selectivity changes from hydrophilic to hydrophobic when the ratio increases. Silica molecular sieves (silicalite-1) have a neutral

framework; are hydrophobic in nature, and have no ion-exchange or cata-lytic properties.

Zeolites are classified on the basis of silica:alumina ratio as follows:

1. Zeolites with low Si:Al ratio (1.0 to 1.5)
2. Zeolites with intermediate Si:Al ratio (2 to 5)
3. Zeolites with high Si:Al ratio (10 to several thousands).

As the Si to Al ratio continues to increase, the catalytic activity often tends to pass through a maximum because of two opposing effects: increasing effectiveness of each acid center on the one hand, and decreasing number of acid centers on the other. The aluminous zeolites are excellent desiccants whereas the most siliceous zeolites tend to be organophilic nonpolar sorbents (Barrer, 1986). Flanigen (1980) considered that "low silica" zeolites or aluminum-rich zeolites contain the maximum number of cation-exchange sites balancing the framework aluminum, and thus the highest cation contents; "intermediate silica" zeolites exhibit a common characteristic in terms of improved stability over the "low silica" zeolites and "high silica" zeolites representing heterogeneous hydrophilic surfaces within a porous crystal. The surface of the high silica zeolites approaches a more homogeneous characteristic with an organophilic—hydrophobic selectivity and exchange capacities Flanigen (2001) has classified zeolites based on pore diameter, namely ,small-pore zeolites, medium-pore zeolites, large-pore zeolites, and extra-large-pore zeolites:

a. Small-pore zeolites (8-rings) with free pore diameter of 0.3—0.45 nm
b. Medium-pore zeolites (10-rings) with free pore diameter of 0.45—0.6 nm
c. Large-pore zeolites (12-rings) with free pore diameter of 0.6—0.8 nm
d. Extra-large-pore zeolites (14-rings) with free pore diameter of 0.8—1.0 nm.

3. STRUCTURE AND NOMENCLATURE OF ZEOLITES

Zeolites are a volcanogenic sedimentary mineral composed primarily of aluminosilicates. The mineral has a three-dimensional crystal lattice, with loosely bound cations, capable of hydrating and dehydrating without altering the crystal structure (Holmes, 1994). Zeolites are generally formed in nature when water of high pH and high salt content interacts with volcanic ash causing a rapid crystal formation (Oste et al., 2002). The structure of zeolite can be split into two regions: columns of fused rings that expand with temperature and the inter column regions that tend to contract on heating. These competing changes combine to produce a material that contracts parallel to the crystallographic "a" and "b" axes and expands in the "c" direction (Villaescusa et al., 2001). In the

structure of natural zeolite, the water and cations can be reversibly removed or replaced by other cations (Rehakova et al., 2004).

The maximum size of any ionic species that can enter the pores of a zeolite is a function of the dimensions of the channels. These are defined by the ring size of the aperture. "8-Ring" structure refers to a closed loop that is built from 8 tetrahedral coordinated silicon (or aluminum) atoms with equivalent oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical (Beitollah and Sadr, 2009).

Mumpton (1960) suggested a compositional gap between the minerals heulandite (Si/AI ratio 2.75−3.25) and clinoptilolite (Si/A1 ratio 4.25−5.25), clinoptilolite being temperature-stable to above 600°C. Recent zeolite research has focused on widening the scope of synthetic procedures, on further exploiting zeolites in commercial processes, and on applying modern characterization techniques to unraveling the complexities of zeolite structural properties. Recent zeolite research has focused on widening the scope of synthetic procedures, on further exploiting zeolites in commercial processes, and on applying modern characterization techniques to unraveling the complexities of zeolite structural properties (Newsam, 1986). 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 (Yang et al. 2001).

4. PHYSICAL AND CHEMICAL PROPERTIES OF ZEOLITES

Two major processes have been identified as kinetics of ion–exchange process in zeolites, namely, particle diffusion and film diffusion. Zeolites are one of the greatest cationic interchangers and their cationic interchange capacity is two to three times greater than other types of minerals found in soils. Zeolites are potential adsorbents due to the ability of their microporous structures to adsorb molecules at relatively low pressure (Kamarudin et al., 2003). There is a wide variation in the cation-exchange capacity of zeolites because of the differing nature of various zeolite cage structures, natural structural defects, adsorbed ions and their associated minerals. Thus in short, zeolites are natural materials with the ability to exchange ions, absorb gases and vapors, act as molecular-scale sieves, and catalyze reactions owing to fixed pore sizes and active sites in the crystal

Table 1 Chemical composition of clinoptilolite/zeolites

Zeolite origin/place	Elemental composition (%)							CEC[*]	SiO_2 to Al_2O_3 ratio
	SiO_2	CaO	K_2O	Al_2O_3	Na_2O	Fe_2O_3	MgO		
Indonesia (Idrus et al., 2008)	72.00	3.3−4.50	0.7−1.0	9−11	1.1−1.5	1.60	08−1.2		6.55
Hungary clinoptilolite (Kallo, 1993)	69.50	1.83	4.44	11.65	0.44	1.06	0.59		5.97
Parnaíba Basin, Brazilian (Monte et al., 2009)	64.7	3.10	0.97	12.7	0.80	3.30	1.50		5.09
Turkish clinoptilolite—Gördes (Gedik and Imamoglu, 2006)	74.36	1.95	4.07	11.87	0.59	1.03	0.85	—	6.26
Turkish clinoptilolite—Bigadiç (Gedik and Imamoglu, 2006)	72.76	4.16	3.13	11.93	0.10	1.26	1.26	—	6.09
Mühlbachová and Šimon (2003)	66.6	5.00	3.84	12.30	0.19	1.89	1.40	—	5.41
Argentina clinoptilolite (Millán et al., 2008)	62.7	0.40	1.20	12.50	6.40	0.60	0.60	175	5.02
Oregon clinoptilolite (MacKown and Tucker, 1985)	59.8	4.94	0.15	12.17	0.11	0.89	0.89	—	4.91
Iran zeolite (Khodaeijoghan et al., 2010)	65.0	2.30	3.00	12.02	1.08	1.50	0.10	200	5.41
Indian zeolite (Gadekar et al., 2008)	56.7	4.30	—	13.23	0.48	1.12	—	—	4.29
Agoura clinoptilolite (Wise et al., 1969)	69.2	1.09	3.13	11.76	2.63	0.30	0.39	—	5.88
Slovakian clinoptilolite (Pawelczyk and Popowicz, 2006)		65−71	2.70−5.20	2.2−3.4	11.50 −13.10	—	—	—	—	4.8−5.4

(Continued)

Table 1 (*Continued*)

Zeolite origin/place	Elemental composition (%)							CEC[*]	SiO$_2$ to Al$_2$O$_3$ ratio
	SiO$_2$	CaO	K$_2$O	Al$_2$O$_3$	Na$_2$O	Fe$_2$O$_3$	MgO		
Japanese clinoptilolite (Minato and Morimoto, 2006)	61.8	1.67	3.01	12.60	2.20	1.86	1.02	148	4.90
Neapolitan Yellow Tuff (Buondonno *et al.*, 2006)	52.15	2.35	7.54	18.56	3.30	0.20	0.20	212	2.81
Turkey clinoptilolite (Çağın *et al.*, 2006)	78.31	4.23	3.37	11.44	0.26	1.93	0.48	—	6.85
Beli plast deposit, Eastern Rhodopes, Bulgaria (Chakalov *et al.*, 2006)	—	—	—	—	—	—	—	125	—

[*] CEC, cation-exchange capacity (cmol (p$^+$) kg^{-1}).

lattice. The size of clinoptilolite channels controls the size of the molecules or ions that can pass through them and therefore a zeolite like clinoptilolite can act as a chemical sieve allowing some ions to pass through while blocking others (Mumpton, 1999). Their internal areas mostly fall in the range of $400-850 \text{ m}^2 \text{ g}^{-1}$ for zeolites (Barrer, 1986). Zeolites vary widely in their chemical composition, particularly with respect to contents of SiO_2, CaO, K_2O, Al_2O_3, Na_2O, and Fe_2O_3 as shown in Table 1.

Dixon and Ming (1987) outlined the techniques for separation of clinoptilolites from soil by combining the low specific gravity and fine particle-size characteristics of clinoptilolite in soils. Clinoptilolite was separated from the silt fractions of the chemically treated and untreated samples using a heavy liquid.

5. Major Natural Zeolites of Agricultural Importance

Of more than 48 natural zeolites species known, clinoptilolite is the most abundant in soils and sediments. Among the natural zeolites, clinoptilolite (Abadzic and Ryan 2001). is most commonly used in agricultural practices as a soil amendment and for promoting nitrogen retention in soils (He *et al.*, 2002; MacKown and Tucker, 1985; Nus and Brauen, 1991; Polat *et al.*, 2004; Wehtje *et al.*, 2003). Clinoptilolite is a member of the heulandite group of natural zeolites, a temperature-stable heulandite seems to be the most abundant zeolite in soils over a wide variety of pH conditions, from slightly acidic to strongly alkaline (Ming and Dixon, 1986b). They are the most well-known and one of the most useful zeolites. Extensive deposits of clinoptilolite are found in Western United States, Bulgaria, Hungary, Japan, Australia, and Iran (Mumpton, 1999). Clinoptilolite has a high cationic interchange capacity and a great affinity for NH_4^+ ions (Inglezakis, 2004).

It was reported by Polat *et al.* (2004) that, of the 40 naturally occurring zeolites studied by research groups, the most well-known ones are clinoptilolite, erionite, chabazite, heulandite, mordenite, stilbite, and phillipsite.

6. Zeolite Nutrient Interactions

Some of the characteristics of zeolites that potentially make them desirable for improving the properties of soils are a large internal porosity that results in water retention, a uniform particle-size distribution that allows them to be easily incorporated, and high cation-exchange capacity that retains nutrients (Ok *et al.*, 2003). The addition of zeolite has

improved the nutrient status of sand-based root zones, especially selective retention of NH_4^+ and K^+ ions (Nus and Brauen, 1991; Petrovic, 1993).

6.1. Soil urease adsorption

Urease adsorption on zeolite and the various properties of adsorbed urease were investigated to find out the influence of zeolite on activity and properties of urease by Choi and Park (1988). Free urease in solution was adsorbed on zeolite until maximum adsorption, and the amount of maximum adsorption was 11.3 mg urease/100 mg zeolite at pH 7.0. It is apparent that free urease was adsorbed on the outer surface of zeolite by cation-exchange reaction, and more than 70% of urease was adsorbed within 30 min. The activity of adsorbed urease decreased by 89.6%, whereas Km value increased to 34.4 mM, which is higher than that of free urease. The optimum pH of adsorbed urease widened 6.5—7.0, compared to that of free urease 7.0. Results of Bernanrdi et al. (2010) have shown the potential for urea and zeolite to improve the efficiency of nitrogen use, since the use of the mineral provided similar effects to the treatments with lower volatility losses and were inferior only to those sources that do not exhibit volatility losses and to that with urease inhibitor. Addition of zeolite to soil reduced soil urease activity through urease adsorption on the zeolite (Ramesh et al., 2010b) 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, $R^2 = 0.95$ (Ramesh et al., 2010c).

6.2. Nitrate leaching

Huang and Petrovic (1994) advocated the application of zeolites in order to reduce the leaching of nitrates in golf courses located on sandy soils. Amendment of clinoptilolite zeolite to sandy soils has been reported to lower nitrogen concentration in the leachate and to increase moisture and nutrients in the soil due to increased soil surface area and cation-exchange capacity (He et al., 2002). MacKown and Tucker (1985) found that zeolite applications decreased nitrification and leaching losses, NH_4-clinoptilolite decreased nitrification by about 11%. The decrease resulted from retention of NH_4^+ by clinoptilolite in places where nitrifying bacteria could not oxidize NH_4^+.

6.3. Ammonium trapping

The small internal tunnels of clinoptilolite zeolite as an example have been found to physically protect ammonium ions from too much nitrification by microorganisms (Ferguson and Pepper, 1987). Composting experiments have shown that by incorporating clinoptilolitic tuff with animal waste,

ammonia can be retained by the zeolite (Witter and Lopez-Real, 1988). The slow retention and liberation capacity of NH_4^+ ions that have been incorporated in the channels forming crystalline structure is generally attributed to zeolites, and particularly clinoptilolites (Allen *et al.*, 1996; Kithome *et al.*, 1998; MacKown and Tucker, 1985; Lewis *et al.*, 1984). The availability of internal space volume is another interesting characteristic of zeolites for separation/purification applications (Kamarudin *et al.*, 2003). Zeolite may initially immobilize NH_4^+-N in the soil when it is applied, reducing N availability to the crop and resulting in the negative effects on growth (Wiedenfeld, 2003). Besides retaining large quantities of ammonium ion, these minerals also interfere with the process of nitrification (Bartz and Jones, 1983; Fergunson and Pepper, 1987). Zeolites have reduced ammonia emissions from animal manures (Amon *et al.*, 1997). Zeolite reduced total ammonia loss by 16% (Witter and Kirchmann, 1989). Ahmed et al. (2002) have found that zeolite mixtures significantly reduced NH_3 loss by between 32 and 61% compared with straight urea (46% N) and zeolite (0.75 and 1 g kg^{-1} of soil).

6.4. Rock phosphate dissolution

A glasshouse study undertaken by Pickering *et al.* (2002) who showed that clinoptilolite in combination with rock phosphate significantly enhanced uptake of hosphorus by sunflowers. The zeolite/rock phosphate combination possibly 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. The experiment clearly demonstrated greatly enhanced plant uptake of P from rock phosphate when applied in combination with NH_4-zeolite, though the P uptake was lower than that from the soluble P source. The zeolite/RP system offers the considerable advantage of P release in response to plant demand and is unique in this regard. Studies on ion-exchange kinetics are very important for the development of technologies of the natural zeolite utilization (Yuan et al. 2008).

7. AGRICULTURAL APPLICATIONS

Zeolites are important materials with very broad applications in refineries as catalysts, sorption and separation processes, and also in agriculture and environmental engineering. Olczyk (2005) found that incorporation of zeolite in soil increased tomato yield but had no positive effect on sweet corn. Other possible uses being investigated include applications as a carrier of slow-release fertilizers, insecticides, fungicides, and herbicides, and as a

trap for heavy metals in soils (Ming and Dixon, 1986). Zeolites are reported to have potential applications in many ways in agriculture (Ramesh et al., 2010a).

Improving soil physico-chemical and microbial properties: Natural zeolites are extensively used to improve soil physical environment, particularly in sandy and clay poor soils (Abdi et al., 2006). Application of zeolite to the tune of one-fifth of the soil weight was found to be the best medium for tomato plants (Markovic et al., 1995; Unlu et al., 2004). Bansiwal et al. (2006) emphasized that zeolites were commonly used as soil conditioners. Khan et al. (2008) demonstrated that zeolite application at soybean planting time encouraged the initiation of vegetative phenology on allophanic soil. Zeolite has an effect to mitigate the salt damage to plants and that the leaching of $CaCl_2$ substitutes adsorbed Na in zeolite for Ca. Substituted zeolite gives high productivity to sand. Zeolite amendment is an effective way to improve soil condition in an arid and semiarid environment (Yasuda et al., 1998). Application of natural zeolite increased the available nitrogen, phosphorus, calcium, and magnesium of the medium (Abdi et al., 2006). A study by Wiedenfeld (2003) concluded that the slight effect of zeolite application observed in a study suggests that its potential benefit might be realized only under poorer conditions where the needs for improvement in nutrient retention and moisture holding capacity are greater. Farmers add the zeolites to the soil to control soil pH and to improve ammonium retention (Dwyer and Dyer, 1984). The CEC of soil may be increased by using zeolites as soil amendments (DeSutter and Pierzynski, 2005). Chander and Joergensen (2002) found an increase in soil microbial biomass and incorporation of added ^{14}C into microbial biomass after zeolite amendment. The microbial populations could respond to zeolite amendment in different ways (Mühlbachová and Šimon, 2003). Kočí (1997), while studying the possible toxic effects of water extracts of some cation zeolite forms on some water organisms, concluded that zeolites were not usually toxic to organisms.

Enhancing nitrogen use efficiency: There are several reports in the literature showing that the addition of zeolite to the source of N can improve the nitrogen use efficiency (Gruener et al., 2003; McGilloway et al., 2003; Ming and Mumpton, 1989; Rehakova et al., 2004). Surface-modified zeolites offer a great promise as anion carriers for slow release of nutrients (Bansiwal et al., 2006) The high potential of zeolites as nitrogen fertilizers has been demonstrated. Their use would diminish environmental problems and increase fertilizer efficiency (Millán et al., 2008). 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 (Dwairi, 1998a, 1998b). Natural zeolites have high tendency of ammonium selective properties (Kithome et al., 1998). The main use of zeolites in agriculture

is for 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 (Legge, 2000). Natural zeolites, due to their structure and properties, inert and nontoxic material can be used as a slowly releasing carrier of fertilizer (Reháková et al., 2004). It is possible to obtain an increase in the efficiency of nitrogen fertilizer in forage crops when nitrogenated clinoptilolites are used in comparison with the use of urea (Millán et al., 2008). Ferguson and Pepper (1987) suggested that the effects of zeolite on N uptake and plant growth would vary with soil type, and that maximum benefit would be expected on coarse-textured low cation-exchange capacity soils.

The development of a slow nitrogen release system to be used as fertilization technology could simultaneously contribute to the reduction of contamination and the 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) are much slower than for the ionic one (Millán et al., 2008). The nitrogen molecules are retained by electrostatic attraction, and modifications of molecular angles and single and double bonds occur in it (Costa, 2000). There are reports of urea-impregnated zeolite chips, which can be used as slow-release nitrogen fertilizers. Li (2003) demonstrated the feasibility of using surfactant-modified zeolite (SMZ) using hexa decyltrimethyl-ammonium as fertilizer carrier to control nitrate release and concluded that SMZ is a good sorbent for nitrate, while slow release of nitrate is achievable. These dual properties suggest that SMZ has a great potential as fertilizer carriers to control the release of nitrate and other anions. Ammonium (NH_4^+) occupying the internal channels of clinoptilolite should be slowly set free, allowing the progressive absorption by the crop which results in a higher dry matter production of crops (Millán et al., 2008).Tiny pores in the clinoptilolite framework are large enough for small cations like ammonium and potassium to enter, but too small for nitrifying bacteria to enter. This means that once ammonium is held internally on the cation-exchange sites within 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 (Petrovic, 1990). Not only does clinoptilolite improve nitrogen fertilization efficiencies, it also reduces nitrate leaching by inhibiting the nitrification of ammonium to nitrate (Perrin et al., 1998). Several reports have suggested that increased N use efficiency occurs on zeolite

amended soils (Ferguson and Pepper, 1987; Ferguson *et al.*, 1986; MacKown and Tucker, 1985). Kavoosi (2007) found increased nitrogen use efficiency in rice due to application of zeolites.

Nitrogen dynamics in soil−air−water systems is of great interest in agriculture for its rational use. Higher nitrogen efficiency is an essential factor for reducing environmental contamination. Surface and ground-water contamination as a result of nitrogen fertilization has been demonstrated in Argentina (Andriulo *et al.* 2000; Costa, 2000). The pronounced selectivity of clinoptilolite to NH_4 ion was exploited in slow release of chemi-cal fertilizers (Minato, 1968). Soil−clinoptilolite−nitrogen dynamics are variable, depending on the physico-chemical soil characteristics, clinoptilolite and nitrogen doses applied and crop management (Ando *et al.*, 1996; Babaririck and Pirela, 1984; Kolyagin and Karasev, 1999; Lewis *et al.*, 1984; Postnikov *et al.*, 1996). The high potential of the clinoptilolite has been demonstrated as a vehicle for nitrogen fertilizers, with the aims of decreasing negative impacts on the environment and increasing fertilizer efficiency (Millán *et al.*, 2008). Crespo (1989) showed, in a pot experiment with clinoptilolite, an increase of around 130% in N use efficiency, N uptake, and dry matter yield of *Brachiaria decumbens.*

Improving phosphorus use efficiency: Zeolites have been used to control release of fertilizer components. Ammonium-charged zeolites have been shown their ability to increase the solubilization of phosphate minerals, leading to improved phosphorus uptake and yields of crops. Studies conducted to examine solubility and cation-exchange relationships 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 (Allen *et al.*, 1993). The power-function equation has been found to describe the transport kinetics of the nutrient release process (Allen *et al.*, 1996) in these systems. Investigation conducted to study the effects of the potassium- and ammonium-saturated clinoptilolite on P availability in Ferrosols revealed that potassium- and ammonium-saturated clinoptilolite can increase P solubility while providing K and NH_4^+ to the soil, a concurrent positive effect for plant growth (Hua *et al.*, 2006).

Enhanced organic manure 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 losses 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.* (1994) 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 $(4-5 \, A°)$ pore size of the crystal lattice structure (Mumpton, 1999). Experiments of Leggo (2000) revealed that zeolite incorporated with poultry manure served as an effective fertilizer and soil conditioner. Chuprova et al. (2004) found the beneficial effect of zeolite fertilizers on mobile humus substances of Chernozem and on biological productivity of maize. Natural zeolites are able to bind humic acid through the action of the surface extra-framework cations and that this ability was markedly enhanced if the zeolitic material was enriched by divalent cations, especially Ca^{2+} (Capasso et al., 2005).

Improving herbicide use efficiency: Controlled release of inputs is being employed extensively in agriculture to deliver active substances like pesticides and herbicides. 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 by Zhang et al. (2006). The release of paraquat from zeolites can occur only via ion-exchange because of charge neutrality of the zeolite.

Improving water use efficiency: Zeolites possess high water holding capacities without reducing air filled pore space (Huang and Petrovic, 1994). The results of field studies clearly showed that zeolites act as soil amendments for crop production improve available water to the plants (Olczyk, 2005). Zeolite increased the water use efficiency of strawberry plants (Abdi et al., 2006).

Improving crop yields: Addition of clinoptilolite increased yields of barley, potato, clover, and wheat after adding $15 \, ton \, ha^{-1}$ in a sandy loam soil (Mazur et al., 1986). Pierla et al. (1984) found that in the field, the zeolite clinoptilolite reduced corn yields, while in the greenhouse this material appeared to act as a slow-release fertilizer increasing the growth of radish after three successive harvests. Bouzo et al. (1994) found increased productivity of sugar cane with utilization of $6 \, ton \, ha^{-1}$ of zeolite in an Oxisol. Carrion et al. (1994) observed that the application of $150 \, kg \, ha^{-1}$ of urea coated with $5-10\%$ of zeolite increased productivity of rice and tomato crops. Wiedenfeld (2003) found that zeolite application did not affect cabbage yields, but pepper yields showed a quadratic response to zeolite application rate, primarily as an initial decrease than an increase in fruit size as rate increased. Highest green herbage yield of Alfalfa was obtained by Turk et al. (2006) when 20% zeolite + 80% soil was used.

Remediation of heavy metal contaminated soils: Reducing the plant availability of heavy metals (Cd, Pb, Cr, Zn, Cu, etc.) in soils is critical for optimizing agricultural production in areas with heavy metal contaminated soils. Phytoavailability of heavy metals correlates best with their concentrations in soil solution rather with their total content in soil (Kabata-Pendias and Brümmer, 1992). The removal of heavy metals in polluted areas is very difficult because they persist in soils for very long periods. However, the fixation of heavy metals in a nonavailable form could be

a useful method for soils that are already contaminated by heavy metals. Heavy metal phytoavailability may be reduced if the metals are sorbed or precipitated from the soil solution. One of the ways to heavy metal immobilization may be the application of zeolites. Zeolites in general have large cation-exchange capacity (Table 1) and expectedly attract positive-charged ions and, therefore, are widely used for sequestration of cationic pollutants like heavy metals (Kumar *et al.*, 2007). Natural and artificial zeolites increase ion-exchange sites in soils in addition to offering absorption sites for small molecules, due to their porous structure. Consequently, zeolites are able to retain heavy metals in soil (Mühlbachová and Šimon, 2003).

Some zeolites, for example, clinoptilolite, are stable in acid conditions up to pH 2 (Ming and Mumpton, 1989). High affinity of zeolites to heavy metals has been demonstrated (Barrer, 1978; Tsadilas, 2000). Alexander and Christos (2003) studied Pb adsorption in soil and zeolite, and reported that clinoptilolite zeolite sorbed 20−30 times more Pb than the soil. Application of zeolite leads to a decrease of Pb concentrations in soil solution retaining the metal in the solid phase, where it should be less available for plants. Calculations based on the value of maximal sorption capacity of zeolite reveal that 1% added zeolite can retain 3.6 mmol Pb kg^{-1} or 750 mg kg^{-1} soil. Advantage of zeolite for soil remediation is its high efficiency independent of soil pH in the pH range 3−5 (Alexander and Christos, 2003). Leggo *et al.* (2006) showed that organo-zeolitic−soil systems offer an opportunity to revegetate land made barren by metal pollution and as a consequence reduction of erosion and dissemination of contaminants.

Wastewater treatment: A promising alternative option to remove specific contaminants from aqueous solution could be the use of low-cost sorbent materials. Among the different minerals, which possess sorbent properties, zeolites appear to be one of the most promising sorbents for this purpose (Tashauoei *et al.*, 2010). Different kinds of natural zeolites are most frequently suggested as ammonium exchangers for wastewater treatment applications (Hedstrom, 2001). It is well known that aluminosilicate molecular sieves (zeolites) are considered the best sorbents which are used in technological processes of division and deep clearing of liquid and gas mixtures due to their chemical nature and particularities of their porous structure (Nesterenko, 2007). Clinoptilolite is known for its ability to remove ammonium from polluted waters (Rahmani and Mahvi, 2006). Matulová and Klokočníková (1994) reported 50% inhibition of algae growth after zeolite addition to water. Haggerty and Bowman (1994) reported that SMZ, a type of inexpensive anion exchanger, removes anionic contaminants from water. Results of Erdem *et al.* (2004) indicate that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

8. Researchable Issues

There exists a wide scope for zeolites use in agriculture. Rational and profitable use of these zeolites, however, requires a systematic and comprehensive research effort. The most important aspects of future research include: (a) Characterization of the available zeolite deposits in each country, (b) determining physical stability of zeolites in a variety of soil environments, (c) development of methodologies for low-cost and effective organo-zeolitic manure/fertilizers, (d) assessment of nutrient release pattern from organo-zeolites, (e) assessing long-term impact of zeolites on soil biological functions, (f) understanding mechanisms of zeolite mediated heavy metal stabilization in contaminated soil, and (g) development of zeolitic herbicides to minimize the herbicidal residues in soil—plant systems.

9. Conclusions

Over the years, there has been a growing interest in and recognition to zeolites use in agriculture because of public concerns about quality and sustainability of soil resources under intensive production systems. Zeolites find a large number of potential applications in agriculture, particularly in soil management. They can be used as either carriers of nutrients or medium to free nutrients to promote nutrient use efficiency. Zeolites are effective as soil ameliorants and in remediation of heavy metal contaminated soils. Research efforts are underway in many countries to exploit the potential of zeolites for the maintenance of soil productivity in perpetuity.

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