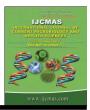


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Case Study

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Zeolite: A Soil Conditioner

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ABSTRACT

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. In this context, farming with zeolites has drawn attention. Zeolites are natural aluminosilicates present in rocks in different part of the world. Use of zeolite has gained a momentum in the recent past owing to multitude of benefits accrued from them. Clinoptilolite Zeolites are useful in agriculture because of their large porosity, cation exchange capacity and selectivity for ammonium and potassium cations. They can be used both as carriers of nutrients and as a medium to free nutrients. (C, Sangeetha and P, Baskar, 2016). Natural zeolites has been reported to be used extensively as amendments for sandy soils. Zeolitic amendment is an effective way to improve soil condition in arid and semiarid environments (Yasuda et al., 1998). It was also found that application of soil amendments such as Clinoptilolite zeolite with composted manure improves soil physical properties such as soil CEC. Inorganic and organic fertilizer along with Clinoptilolit Zeolite showed the best N, P and K uptake in plant tissues because of less leaching of these nutrients and helps to retain nutrients in root zone by enhancing nutrient absorption. (Ahmed, 2010). Zeolites could be used as an effective additive to control the odour as they could adsorb the volatile substances like acetic acid, butanoic acid, isovaleric acid, indole and enhances effectiveness of the manure (Leggo, 2000). Zeolite acts as a superior substrate or carrier for the nutrients or acts as a slow-release source of nutrients to plants assuring higher yields. The nano-sized zeolite is capable of retaining Zn and releasing slowly into the soil solution, which may serve as a slow release Zn fertilizer and improve use efficiency by crops (Yuvaraj et al., 2018). The effect of zeolite and its combination with chemical fertilizer (NPK) and organic fertilizers (sugarcane filter cake) showed improved soil quality and increased sugarcane yield as compared to control (without fertilization) (Cairo et al., 2017). Although considerable research has been advanced, further research needs to be carried out for their efficient utilization in farming.

Keywords

Food, Security, Zeolite, Fertilizer

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Introduction

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 has led to declining quality and/or quantity of the soil resource base and climate change. To feed the growing population, soil degradation is the key issue which needs urgent attention. (C, Sangeetha and P, Baskar, 2016).

As agriculturalists the world over increase their effort to expand crop and animal production, more and more attention is being paid to various mineral materials as soil amendments and as dietary supplements in animal husbandry. The close relationship between the agricutural and geological sciences is not new and crop production depends on the existence and maintenance of fertile soil of clays and other soil constituents. In the animal sciences, the addition of crushed limestone to chicken feed to strengthen egg shells is well known, as is the use of bentonite as a binding agent in pelletized animal feed stuffs. Recently, one group of minerals has emerged as having considerable potential in a wide variety of agricultural processes. This group of minerals is the zeolite group. The ion-exchange, dehydrationunique rehydration, and ad-sorption properties of zeolite materials promise to contribute significantly to many years of agricultural and aquacultural technology.

Most of the initial research on the use of zeolites in agriculture took place in the 1960s in Japan, Japanese farmers have used zeolite rock for years to control the moisture content and malodor of animal wastes and to increase the pH of acidic volcanic soils. The addition of small amounts of the Zeolites such as clinoptilolite and mordenite to the normal protein diet of pigs, chickens, and ruminants

gave noticeable increases in the body weight and general "health" of the animals. The use of zeolites in rations also appeared to reduce odor and associated pollution problems and to provide a means of regulating the viscosity and nitrogen retentivity of animal manure. These same zeolites were also found to increase the ammonium content of rice paddy soils when added with normal fertilizers.

Although most of these were preliminary results and often published in rather obscure journals or reports from local experiment stations, they did suggest that zeolites could act as traps or reservoirs for nitrogen both in the body and in the soil. The growing awareness of such phenomena and of the availability of inexpensive natural zeolites in the Western United States and in geologically similar parts of the world has aroused considerable commercial interest. Zeolites are fast becoming the subject of serious investigation in dozens of agricultural laboratories both here and abroad. In this context, farming with natural zeolites has assumed to be great significance. (Rhodes, C., 2010)

Zeolites of India

Natural zeolite minerals in India were reported inamygdaloidal vesicles in the Deccan lava flows. Since the 1970s, the state of Maharashtra has provided zeolites thathave come out of the enormous lava flows called the Deccan Traps were reported way back in the 18th century itself, regarding their formation and distributionin the lava flows. These minerals do not occur everywhere in the Western Deccan Traps, but are restricted localities around certain (Bombay), Vadodara (Baroda), Pune (Poona), Heulandites (most popular and Nasik. Zeolites of the world) zone was found in the highlands of plateauin 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 km² situated betweenlatitudes 0° and 20°S and longitude 70° and 84° E ofthe central Indian basin contained zeolites. In addition to Maharashtra, zeolite occursas filling in the amygdularcavites in deccantrapbasalts of Gujarat, Madhya Pradesh and Karnataka too (Ramesh *et al.*, 2015).

Etymology, nature and properties

Identification of zeolitesas 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.

Different combinations of SiO₄ and Al (OH)₃⁶⁻ tetrahedral 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 watermolecules. 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 exchange. 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/ cm³), excellent molecular sieve properties and high cation exchange capacity (CEC) of 150–250 cmol/kg), cation selectivity, specifically for cations likeammonium, potassium, cesium, etc.

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 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 multicomponent ion exchange mechanism.

Structure of Zeolite

Zeolites are composed of pores and corner sharing aluminosilicate (AlO₄ and SiO₄) tetrahedrons, joined into three dimensional frameworks. The pore structure characterized by cages approximately 12Å in diameter, which are interlinked through channels about 8Å in diameter, composed of rings of 12 linked tetrahedrons. The pores are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites have large vacant spaces or cages within and resemble

honeycomb or cage like structures. The presence of aluminium results in a negative charge, which is balanced by positively charged cations. The general empirical formula, which represents a zeolite chemical structure, is shown below: M2nO.Al2O3.xSiO2.yH2O

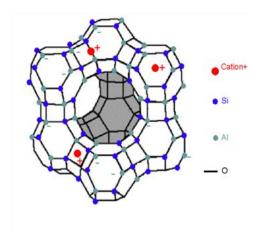


Fig.1 Zeolite chemical structure

M represents any alkali or alkaline earth cation, n the valence of the cation, x varies between 2 and 10, and y varies between 2 and 7, with structural cations comprising Si, Al and Fe³⁺, and exchangeable cations K, Na and Ca (Sheppard and Mumpton,1981); (Hemingway and Robie,1984). Tetrahedral AlO_4^{-5} and SiO_4^{-4} bound by oxygen atoms to form tectosilicatescalled Zeolites.

Application of natural zeolites is based on other chemical properties

Cation exchange

The ability to exchange inherent cations for other cations on a basis of ion selectivity. High CEC for heavy metal cations that can be removed from liquid effluents through the process of ion-exchange. These cations include Pb, Hg, Cd, Co, Zn, Cu, Ag, Mg, Fe, Al, Cr and others.

Adsorption and related molecular sieving

The adsorption process is fully reversible and of purely physical nature. The adsorption on molecular sieves is therefore dependent on the following physical molecular properties: Size and Shape: molecules or ions larger than the pore opening of the zeolite cannot be adsorbed, smaller molecules or ions can. Molecular Polarity: due the charge on outer and inner zeolitic surface particle, molecules with large polarity can be adsorbed preferentially under identical conditions.

Dehydration and rehydration

Biological activity

Natural zeolite has been shown to exhibit diverse biological activities and has been used successfully for the treatment in medical therapy, promotes better plant growth by improving the value of fertilizer, helps preventing the plant from burning, that can be caused by over use of fertilizer, by trapping and slowly releasing valuable nutrients. As additive in concentrated animal growing facilities improve feed conversion, reduce airborne ammonia up to 80%, act as a mycotoxin binder, and improve bone density, it can be used in general odour elimination for all animal odours.

Surface modification of natural zeolite

Modifying the surface of Zeolites with longchain quaternary amines allowed it to adsorb benzene, toluene, and xylene in the presence of water. Surface modified natural zeolites remove toxic compounds from animal food. Natural zeolite can be treated further with additional amine to produce anion exchangers capable of taking up chromate, arsenate, selenate, and other metal oxyanions from aqueous solutions.

Classification

More than 50 different species of thismineral group have been identified. 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 thousand 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. 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 e" 4.0). Dehydration, partial hydration and over hydration are not sufficient grounds for the recognition of separate species of zeolites.Later, Flanigen (2001) 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 largepore zeolites (14 rings) with free pore diameter 0.8–1.0 nm.

How Zeolites Forms

Natural zeolites are produced by the forces of volcanism (Figure 2), and are often associated with mountainous regions, e.g. the Caucasus and the Balkans, while there are also deposits found in the Himalayas and in Switzerland, and in the U.S. around the Gulf of Mexico (including Cuba), which has a volcanic history. When molten magma, the force of which pushes up mountains, can escape through a volcanic vent, the volcanic rocks (solidified lava) and ash layers that are produced may transform (crystallize) into a zeolite if they come into contact and reaction with alkalineysaline lake or ground-waters. Beds of zeolites may be hundreds of meters thic. Zeolites have also crystallized in postenvironments over periods depositional ranging from thousands to millions of years in shallow marine basins, and are found in some ocean sediments. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential. (Frederick A. Mumpton, Chapter VIII)

Natural Zeolites – Uses:

Petrochemical industry
Nuclear Industry
Medical-medicine
Heating and refrigerator
Detergent
Construction
Petroleum Refinery
Animal Welfare
Wastewater treatment
Pozzolanic Material in Cement and
Concrete Composites
Zeolites in Food Processing Industries
Zeoponic system
Air Separation and Pollution Control

Aquaculture / Fisheries Agriculture as a soil conditioner

How NZ act as a Soil Conditioner

Improving soil physical properties and chemical properties
As a Soil Amendments
Nitrogen management
Phosphorus management
Organic manure handling and management
Slow release of herbicides
Slow release of nutrient
Soil Microbial population
Plant growth

Details Results and Discussion of Experiment described below

Improving soil physical properties and chemical 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 water needed for irrigation. Amendment of sand with zeolite increases available water to the plants by 50%

Case Study 1

The study was plotted in the sugarcane growing areas of the northern coast of Villa Clara province. Different zeolite levels and combinations with organic fertilizers were applied in Vertisols (Table 3). The

Experiment was set up as a randomized complete block design with 9 treatments and 4 replications. The individual plot sizes were 10×9.6 m. Sugarcane variety Ja 60-5 was used and was planted in furrows at 1.60 m row spacing. Organic fertilizer (sugarcane filter cake-SFC), and natural mineral (zeolite-Z) and chemical fertilization (nitrogenphosphorus-potassium-NPK) were applied. The treatments were: T1- control (without application of fertilizer), T2- Z 7.5 t ha⁻¹, T3-Z 15 t ha⁻¹, T4- Z 7.5 t ha⁻¹ +100 kg ha⁻¹, T5- $Z 15 t ha^{-1} + N 100 kg ha^{-1}, T6- Z 7.5 t ha^{-1} +$ SFC 22.5 t ha⁻¹, T7- Z 3 t ha⁻¹ + SFC 18 t ha⁻¹, T8- Z 7.5 t ha^{-1} + NPK (100-60-200 kg ha^{-1}), T9- Z 7.5 t ha^{-1} + NPK (100-60-200 kg ha^{-1} 1). Significant effects on organic matter and structure were observed. Treatment, Z 7.5 t ha⁻¹ + SFC 22.5 t ha⁻¹ (T6) showed the best result, where 3 of the indicators (organic matter, water-stable aggregates and degree of soil aggregation) reached the highest values. (Pedro Cairo, 2017)

Fig.6shows the soil water regime by comparing the control treatment (T1) with the soil treated with Z 7.5 t ha⁻¹ + SFC 22.5 t ha⁻¹ (T6), when sampling moisture is carried up from a meter deep after 25 mm of rainfall.

In control treatment, water accumulated on the surface, remaining much drier in depth, due to the limited speed of water infiltration. However, treatment of soil with zeolite guarantees the uptake of rainwater in depth, due to the structural changes (Table 3), which is synonymous with a better use of rainwater and subsequent supply of assimilable water to plants. In the natural soils, all the detained superfluous water is lost by evaporation surface area which may be decisive in cane yield. The results show that the effect of the zeolite and its combination with organic fertilizer not only has its influence on the topsoil but also in depth. (Pedro Cairo, 2017).

Case Study 2

A field study was carried out at the Share Farm of Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia (latitude 3° 30'N, longitude 113°09′E). The study area is a humid tropic with yearly average oflow and high temperatures of 23°C and 34°C, respectively. A field study was carried out from 10th April 2014 to 21st June 2014 for first planting cycle and 25thJuneto 27th August 2014 for second planting cycle of Zea mays L. These planting periods were considered short term because compost and clinoptilolite zeolite were applied before planting. Longterm effects involve repeated or regular application of amendments for many years. The experimental plots were arranged in a randomized complete block design (RCBD) with three blocks (replications). Thai Super Sweet hybrid F1 variety was used as the test crop. Treatments evaluated in the field study were:

- (i) Soil only (control) (T0)
- (ii) 7.40 g urea + 5 g TSP + 3.80 g MOP (T1)
- (iii) 7.40 g urea + 5 g TSP + 3.80 g MOP + 192 g clinoptilolite zeolite (T2)
- (iv) 5.55 g urea + 3.75 g TSP + 2.85 g MOP + 385 g compost + 192 g clinoptilolite zeolite (T3)
- (v) 3.70 g urea + 2.50 g TSP + 1.90 g MOP + 577 g compost + 192 g clinoptilolite zeolite (T4)

From the Fig.7 & 8 it can be said that the treatments with rice straw compost and clinoptilolite zeolite (T2, T3, and T4) significantly improved soil total organic C and organic matter (Figure 4) because they increased total N, exchangeable NH4 +, and available NO3 –. Increase in soil N facilitates decomposition of composts to release more C and humus.(Omar *et al.*, 2018)

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 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 Taiwan for this purpose. Zeolitic amendment is an effective way to improve soil condition in an arid and semiarid environment. 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. Zeolites increase the water-retention capacity of the soils.

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.

Case Study3

An experiment was carried out at Share Farm of University Putra Malaysia of Bintulu Campus, Sarawak in Maize plant with organic, inorganic and Zeolites, where soil chemical properties were studied.

From the above table 4 it can be says that the addition of chemical fertilizer and compost along with Clinoptilolite zeolite affect different natural processes in the soil where compost enhances the organic matter percentage of soil. Increase in soil pH increases the availability of soil nutrients for the maize plant. (Ahmed, 2010)

Case Study 4

The experiment was conducted on sandy loam soil during the 2008 and 2009 growing seasons at the research farm of TarbiatModares University, Tehran, Iran (358410N, 518190E and 1215 masl). The region is characterized as semi-arid, with mean annual precipitation of 298 mm, which mostly falls during the autumn and winter month in Sunflower crop with 4 treatment combination which is given in Table 5.

From the above table it can be says that Irrigation water productivity describes the quantitative relation between plant growth and water consumption. It is defined as dry matter produced (kg) per unit of water consumption (m3). It is shows that in both years, the F5 treatment hadgreater IWP than the F1 treatment. In other words, water useefficiency increased during limited water conditions. For the F1treatment, IWP was due to increased water percolationand evaporation. In integrated treatments with zeolite (F3, F4and F5), application of manure increased soil water retentioncapacity. This effect is due to hydrophiliccomponents of manure, such as polysaccharides. Furthermore, improved growth and development of plants and increased dry matter production by prolonging N availability. Thus, the higher IWP in integrated treatments with zeolite can beexplained by two separate processes: increased water retentiondue to manure application and better plant growth and

developmentdue to the presence of zeolite.(Majid *et al.*, 2013)

Case Study5

A field study was carried out at the Share Farm of Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia (latitude 3° 30′N, longitude 113°09'E). The study area is a humid tropic with yearly average of low and high temperatures of 23°C and 34°C, respectively. A field study was carried out from 10th April 2014 to 21st June 2014 for first planting cycle and 25th Juneto 27th August 2014 for second planting cycle of Zea mays L. These planting periods were considered short term because compost and clinoptilolite zeolite were applied before planting. Long-term effects involve repeated or regular application of amendments for many years. The experimental plots were arranged in a randomized complete block design (RCBD) with three blocks (replications). Thai Super Sweet hybrid F1 variety was used as the test crop. Treatments evaluated in the field study were

- (i) Soil only (control) (T₀)
- (ii) $7.40 \text{ g urea} + 5 \text{ g TSP} + 3.80 \text{ g MOP} (T_1)$
- (iii) 7.40 g urea + 5 g TSP + 3.80 g MOP + 192 g clinoptilolite zeolite (T₂)
- (iv) 5.55 g urea + 3.75 g TSP + 2.85 g MOP + 385 g compost + 192 g clinoptilolite zeolite (T₃)
- (v)3.70 g urea + 2.50 g TSP + 1.90 g MOP + 577 g compost + 192 g clinoptilolite zeolite (T₄)

It might be due to the Soil CEC significantly improved with T_2 , T_3 , and T_4 (Table 5) because of the inherent CEC of the ricestraw compost and clinoptilolite zeolite. Composts improve soil CEC because of the affinity of their humic acids and fulvic acids for positively charged multivalent ions such as K^+ , Ca^{2+} , and Mg^{2+} . The negatively charged

aluminosilicates of the clinoptilolite zeolite are also responsible for theimproved soil CEC. The treatments with rice straw compost and clinoptilolitezeolite (T₂, T₃, and T₄) increased soil pH (Table 5) because of the relatively high Ca and Mg of the amendments. Soil incubation and leaching experiments had shown that rice strawcompost and clinoptilolite zeolite can mitigate soil acidity. (Omar *et al.*, 2018)

Nitrogen management

Although nitrogen is regarded as king pin in agriculture and widely used in all crops and cropping system, its use efficiency is just 30-40% only. Urea impregnated zeolite chips have also been developed, found increased nitrogen-use efficiency in rice owing to application of zeolites and ensured good retention of soil-exchangeable cations, available P and NO₃ within the soil in maize at Malaysia (*Rabai et al.*, 2013).

Case Study6

An experiment was carried out at Share Farm of University Putra Malaysia of Bintulu Campus, Sarawak in Maize plant with organic, inorganic and Zeolites, where soil chemical properties were studied.

From the above result it can be seen that Treatments with zeolite showed the best N, P and K uptake in plant tissues because of less leaching of these nutrients. Zeolites help to retain nutrients in root zone and, therefore, improving the long term soil quality by enhancing nutrient absorption (Ahmed *et al.*, 2010).

Case Study7

The experiment was conducted on sandy loam soil during the 2008 and 2009 growing seasons at the research farm of

TarbiatModares University, Tehran, Iran (358410N, 518190E and 1215 masl). The region is characterized as semi-arid, with mean annual precipitation of 298 mm, which mostly falls during the autumn and winter month in Sunflower crop with 4 treatment combination which is given in Table 8.

Both year it can be seen that the treatment F5 shows the lowest nitrogen leaching as compare to treatment F1, it might be due to the not only cattle manure responsible for improved the soil condition but zeolite has the potential role to reduced the nitrogent leaching by capturing the nitrogen in its honeycomb structure and made available to plant.(Majid *et al.*, 2013)

Case Study8

This study was conducted from December 2013 to March 2014 at the greenhouse of ShahidChamran University of Ahvaz, Iran, in a completely randomized design, with a factorial arrangement of treatments in three replications. The treatments consisted of Z0 (control): 100 kg ha-1 urea fertilizer; Z1: 0.5 g kg- 1 raw zeolite + 100 kg ha-1 urea fertilizer; Z2: 1 g kg-1 raw zeolite + 100 kg ha-1 urea fertilizer; Z3: 0.5 g kg-1 NH4 +zeolite + 80 kg ha-1urea fertilizer; and Z4: 1 g kg- 1 NH4 +-zeolite + 60 kg ha-1 urea fertilizer, all of which were applied to two types of soil with clay loam and sandy loam textures. The steps of the study included the of NH4 +-zeolites in preparation laboratory, cultivation wheat in the greenhouse and finally the collection of drainage waters followed by the analysis of the yield of wheat and nitrogen leaching in the different treatments.

For a given means within each column of each section followed by the same letter are not significantly different ($p \le 0.05$)

Mean comparison of grain yield and total N in shoots of the wheat plants influenced by zeolite treatments and soil texture is shown in Table 9. Nitrogen uptake by plants in soils treated with Z0(only N fertilizer) and Z4 (NH4 +-enriched zeolite) was significantly higher than those of Z2 (raw zeolite), because an amount of N was absorbed by the raw zeolites and was unavailable for plants, thus reducing the percentage of N uptake in the growing plants. Application of materials with properties of zeolite probably causes a slow and controlled N release. Although these properties reduce the plant nitrogen uptake, they can prevent the loss of nitrogen from soil.(Mehrab et al., 2018)

Phosphorus management

CZ properties, such as it being alkaline and having negative charges, can be used to improve P availability through amelioration of soil pH, reduction of soil acidity, soil exchangeable Al, and soil exchangeable Fe.In addition, CZ incorporation into fertilization programs may trigger induceexchange dissolution mechanisms that release P through uptake of nutrients by the plant. Phosphorus release demonstrated exchange-induced dissolution system is as NH₄⁺ + H₂PO₄⁻ This will result in less P being fixed by metal oxy-hydroxides.

Case Study9

A field experiment was conducted at Universiti Putra Malaysia Bintulu Sarawak Campus (latitude 03° 21.516' N and longitude 113° 094.181' E). The climate is humid tropical with an annual precipitation of 4042 mm, and the average monthly precipitation is 336.85 mm, and the relative humidity is highest and lowest 85.6%. The the temperatures are 32.1°C and 23.6°C, respectively.

The test crop used was Zea mays L. F1 hybrid. Five seeds were sown in each planting hole and were thinned to one at seven days after seeding. The recommended rates of the fertilizers were: urea (130 kg ha⁻¹), Egypt rock phosphate (ERP) (214 kg ha⁻¹), Christmas Island rock phosphate (CIRP) (200 kg ha¹), triple superphosphate (TSP) (130 kg ha⁻¹), and muriate of potash (MOP) (67 kg ha⁻¹) 1). These rates were reduced to per plant basis and were equivalent to 4.85 g urea plant⁻¹, 7.95 g ERP plant⁻¹, 7.42 g CIRP plant⁻¹, 4.84 g TSP plant⁻¹, and 2.47 g MOP plant⁻¹ from existing standard fertilizer the recommendation. Half the fertilizer was applied at 10 days after seeding (DAS) and the remainder at 28 DAS. This method of fertilization was used to determine the maize plants' response to treatments. Weeding was done manually with hoe to keep the plots free from weeds.

From the table it was found that relative to control, significant P availability is noted in all P fertilizer treatments regardless of the rate and type of P fertilizer applied. The addition of CZ to the treatments with 75% fertilizers rate (T2, E2, and C2) showed comparable total P and available P with the recommended rate in both the first and second planting cycles. Inclusion of CZ in these treatments mitigated soil pH besides reducing Al, and soil acidity. Hence, resulting in lesser amount of P being fixed to the soil colloid and metal ion oxyhydroxides. Although lesser amounts of P fertilizers were applied. Moreover, the comparable soil total P, exchangeable P, and soil exchangeable Ca contents obtained was possible due to enhanced dissolution of the **PRs** as induce-exchange affected bv mechanism of the CZ mediated by maize plant uptake.(Hasbullah et al., 2018)

Case Study10

A field study was carried out at the Share

Farm of Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia (latitude 3° 30'N, longitude 113°09′E). The study area is a humid tropic with yearly average of low and high temperatures of 23°C and 34°C, respectively. A field study was carried out from 10th April 2014 to 21st June 2014 for first planting cycle and 25th Juneto 27th August 2014 for second planting cycle of Zea mays L. These planting periods were considered short term because compost and clinoptilolite zeolite were applied before planting. Long-term effects involve repeated or regular application of amendments for many years. The experimental plots were arranged in a randomized complete block design (RCBD) with three blocks (replications). Thai Super Sweet hybrid F1 variety was used as the test crop.

Plots with chemical fertilizers, rice straw compost, and clinoptilolite zeolite (T2, T3, and T4) showed higher contents and uptake of P than the plots without fertilizer (T0) and chemical fertilizers (T1). Timely retention of available P might have enhanced the Zea mays L. growth and development. Coapplication of rice straw compost and chemical fertilizers increased soil microbial biomass C and activity and resulted in increased availability of P. Confirmed that soil available P following compost application contributes to P uptake. As observed in this study, amending compound fertilizers with clinoptilolite zeolite is also important because the approach ensures retention of soil N, P, K, Ca, and Mg to sustain vegetative growth until reproductive and kernel development of Zea mays L.

Organic manure handling and management

Zeolites could be used as an effective additive to control the odour (Sharadeqah and Al-Dwairi, 2010), as they could adsorb the volatile substances (Rodriguez et al., 1994) like acetic acid. butanoic acid. isovalericacid,indole, skatole (Caiet al., 2007) and enhances effectiveness of the manure (Leggo, 2000). Surface application of zeolite has potential for mitigating farmyard manure NH3 losses thereby reducing losses of nitrogen to the environment, but specific zeolite properties influenced its effectiveness (Waldripet 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 Latifahet al., (2015).

Slow release of herbicides

The most hydrophobic solids such as zeolite 'ZSM 5' were found to adsorb atrazine betterwhen organics were present (Botteroet thecompartmentalized al., 1994) in intracrystalline void space of zeolites(Corma and Garcia, 2004). This was brought a considerableattention on soil clay minerals for slow-release formulation of herbicides. Zeolite (ZSM-5) was found to accommodateherbicide paraquat the microstructure with restrictedmobility (Walcarius and Mouchotte, 2004).This wasfollowed by surface by Zhang modification of paraquat etal., (2006). Humic acid zeolites were also found to besorbents for phenylurea herbicides (Capassoet al., 2007). Clinoptilolitic tuff was considered as a suitable material forremoving atrazine from soil (Salvestrine et al., 2010) andwater (Jamilet al., 2011) too. Later an enhanced activity ofzeolite- loaded catalysts on herbicide isoproturon was foundto be synergistic effect of increased visible light absorptionand the high porous nature of facilitating theadsorption zeolite of

recalcitrant molecules (Reddy *et al.*, 2012). This was followed by Bakhiary*et al.*, (2013) with 2,4-Dherbicide showed gradual temporal release pattern and keptthe active ingredient in the upper 5 cm soil layer (Shirvani*et al.*, 2014).

Slow release of nutrient

Zeolite as coating material has shown the potential to increase water absorption and water retention of NPK fertilizers and to retard N,P and K release from the fertilizers in a sandy soil in Indonesia (Sulakhudin and Sunarminto, 2011).

Case Study 11

A laboratory study was undertaken at the Department of Nano Science & Technology, Tamil Nadu Agricultural University, Coimbatore. During the experimentation, synthesis, characterization, Zn release pattern and Zn fractionation pattern were studied in nano-size zeolite fortified with or without Zn.

Nano-zeolite showed leaching of Zn in three stages (Figure 9). Zn levels decrease sharply in the first 220 hr and stabilize thereafter. The result also showed that from 300 to 500 hr it follows second stage. In this stage, it supplies 1.5 ppm of Zn. The next stage falls from 500 hr and it supplies 1.1 ppm of Zn and this condition is static even after 1,000 hr. This may be due to the fact that, the zeolite not only increases nutrient retention but also achieves the slow release process of nutrient for gradually releasing the nutrient to the plant so as to reduce environmental nutrient losses of the soil by means of the ion exchange ability. Therefore, the natural environmental materials of the diatomite and the zeolite are mixed was the plant growth medium for agriculture to increase crop yields. The data suggest that the nano-zeolite based fertilizers supply Zn for an extended

period of up to 40 days, while such release ceased to exist within 10–12 days. The trend of Zn release pattern can be exploited in the development of nano-fertilizer that ensures sustainable plant development besides environmental safety.(Yuvaraj and Subramanian, 2018)

Soil microbial properties

In this trial four treatments with four replicates eachwere set up in a randomized, complete block design.The minimum experimental unit was a plot of 28 m2, divided into two equal subplots. In one of these, samplingsof soil and plants were made throughout the growing season, while the other was reserved for thefinal harvest. The treatments tested and doses applied to the soil were: 1) the MC treatment was a basal dressingwith manure compost at a dose of 38 t ha-1; 2) the MCZ treatment was identical to MC, but also zeolitewas simultaneously applied at a dose of 90 t ha-1 (3%);3) the MF treatment was a conventional mineral fertilization, serving as an assay control, and consisted of abasal dressing using an NPK complex (8-24-8) which was added to the soil at the recommended dose (0.35 tha-1) for the barley crop; 4) the ZL treatment consisted f a basal dressing with zeolite supplemented withleonardite at a dose of 75 t ha-1. The topdressing dosewas divided into two halves, applying the first in thetillering phase of barley and the second in the extensionstage. The top-dressing dose applied was 90 Nfertilizer units (NFU), using calcium and ammoniumnitrate (27%). The topdressing dose of the tested organictreatments (MC, MCZ, and ZL) was equivalent o a quarter of that applied in the conventional mineraltreatment (MF).

In general a decrease in soil enzyme activity, except for soil urease activity (URA), was observedduring the barley cultivation,

regardlessof the basal dressing used (Figure 3). Forsoil β-glucosidase activity (BGA), significant differences were not observed between treatments.Soil alkaline phosphatase activity(APA) showed significant differences betweenthe treatment involving amendment with compostand that involving compost supplemented with zeolite, being higher in the former. While the cellobiohydrolase activity (CBH) was found significantlyhigher in treatments MC and MCZ thanin MF and ZL respectively. Similar values of ureaseactivity (URA) were measured in MC, MCZ, and MF cultivation, during the barley being significantlyhigher than that of ZL.(José Luise et al., 2017)

Plant Yield and Yield Attributing Characteristic

Case Study 12

An experiment was carried out at Share Farm of University Putra Malaysia of Bintulu Campus, Sarawak in Maize plant with organic, inorganic and Zeolites, where soil chemical properties were studied.

The Highest Cob weight (kg/ha) and Grain/cob was observed in T4 (Table 13) as compared to the other treatment and which was significantly at par with Treatment T1, T2 and T3 but significantly different with T0. This Might be due to the incorporation of Zeolite along with compost manure.(Ahmed *et al.*, 2010)

Case Study13

The experiment was plotted in the sugarcane growing areas of the northern coast of Villa Clara province. Different zeolite levels and combinations with organic fertilizers were applied in Vertisols (Table 14). The Experiment was set up as a randomized

complete block design with 9 treatments and 4 replications. The individual plot sizes were 10×9.6 m. Sugarcane variety Ja 60-5 was used and was planted in furrows at 1.60 m row spacing. Organic fertilizer (sugarcane filter cake-SFC), and natural mineral (zeolite-Z) and chemical fertilization (nitrogenphosphorus-potassium-NPK) were applied. The treatments were: T1- control (without application of fertilizer), T2- Z 7.5 t ha⁻¹, T3-Z 15 t ha⁻¹, T4- Z 7.5 t ha⁻¹ +100 kg ha⁻¹, T5- $Z 15 t ha^{-1} + N 100 kg ha^{-1}, T6- Z 7.5 t ha^{-1} +$ SFC 22.5 t ha⁻¹, T7- Z 3 t ha⁻¹ + SFC 18 t ha⁻¹, T8- Z 7.5 t ha^{-1} + NPK (100-60-200 kg ha^{-1}), T9- Z 7.5 t ha⁻¹ + NPK (100-60-200 kg ha⁻¹ 1). Significant effects on organic matter and structure were observed. Treatment, Z 7.5 t ha^{-1} + SFC 22.5 t ha^{-1} (T6) showed the best result, where 3 of the indicators (organic matter, water-stable aggregates and degree of soil aggregation) reached the highest values. (Pedro Cairo, 2017)

Crop yield considered in these studies, had an extraordinary value for selecting quality indicators and determining soil quality. Hence, integration of natural minerals and organic amendments is suitable for Vertisols with high clay contents and improves physical soil properties. Application of Zeolite along with organic manure helps in improving cane yield and cane sucrose yield. The highest value observed in treatment **Z** 7.5 t ha⁻¹+SFC(22.5 t ha⁻¹)(table 14) as compared to other treatment and statistically found highly significant with other treatment. (Pedro Cairo, 2017)

Wastewater treatment

Zeolites may be used for removingammonia from wastewater. Clinoptilolite is effective for selective removal of NH_4 + cations from wastewater.

Table.1 Physical characteristics of some naturally occuring Zeolites (Dogan, 2003)

Zeolite	Porosity [%]	Bulk density [g/cm ³]	Ion exchange capacity [meq/g]	Specific gravity [g/cm ³]	Heat stability	Cations
Analcime	18	1.85	4.54	2.24-2.29	High	Na
Chabezite	47	1.45	3.84	2.05-2.10	High	Ca, Na
Clinoptilolite	34	1.15	2.16	2.15-2.25	High	Na, K, Ca
Erionite	35	1.51	3.12	2.02-2.08	High	K, Na, Ca
Heulandite	39	1.69	2.91	2.18-2.20	Low	Ca
Mordenite	28	1.70	4.29	2.12-2.15	High	Na, Ca
Philipsite	31	1.58	3.31	2.15-2.20	Moderate	K, Na

 Table.2 Natural Zeolites - Typical formulae of some zeolites (chemical composition)

Zeolite	Typical Unit-Cell Formula	Cations
Analcime	Na ₁₆ (Al ₁₆ Si ₃₂ O ₉₆).16H ₂ O	Na
Chabazite	(Na ₂ Ca) ₆ (Al ₁₂ Si ₂₄ O ₇₂).40H ₂ O	Ca, Na
Clinoptilolite	(Na ₄ K ₄)(Al ₈ Si ₄₀ O ₉₆).24H ₂ O	Na, K ,Ca
Erionite	(Na ₂ Ca ₆ K) ₉ (Al ₉ Si ₂₇ O ₂₇).27H ₂ O	K, Na, Ca
Heulandite	Ca ₄ (Al ₈ Si ₂₈ O ₇₂).24H ₂ O	Ca
Mordenite	Na ₈ (Al ₈ Si ₄₀ O ₉₆).24H ₂ O	Na, Ca
Phillipsite	$(Na_2K)_{10}(Al_{10}Si_{22}O_{62}).20H_2O$	K, Na

Table.3 Influence of zeolite and sugarcane filter cake on organic matter, soil aggregate and

Sl. No.	Treatments	OM%	WSA%	DSA%	log 10k
1	Control	2.29 g	64.18 e	54.03 e	1.84 f
2	Z 7.5 t ha-1	3.43 cd	68.58 d	57.24 d	2.01 de
3	Z 15 t ha-1	3.57 b	69.38 c	60.65 c	2.05 c
4	Z 7.5 t ha-1+ N(100 kg ha-1)	3.46 c	68.58 d	57.24 d	2.13 a
5	Z 15 t ha-1+ N(100 kg ha-1)	3.52 b	69.38 c	60.65 c	2.05 c
6	Z 7.5 t ha-1+SFC(22.5 t ha-1)	3.71 a	71.04 a	65.57 a	2.09 b
7	Z 3 t ha-1+SFC(18 t ha-1)	3.40 de	69.67 b	62.62 b	2.14 a
8	Z 7.5 t ha-1+NPK(100-60-200 kg ha-	3.37 e	68.58 d	57.24 d	2.00 e
	1)				
9	Z 15 t ha ⁻¹ +NPK(100-60-200 kg ha ⁻¹)	3.24 f	69.38 c	60. 65 c	2.04cd
	$EE = \pm$	0.06	0.27	0.49	0.01

Table.4 Effects of Clinoptilolite Zeolite along with other organic and inorganic fertilizers on selected chemical characteristics of soil at 72 days after planting of Maize

Treatment	$\mathbf{P}^{\mathbf{H}}$	Total N	Available P	Exchangeable	Exchangeable
	Water	(%)	(mg kg ⁻¹)	K ⁺ (cmol kg ⁻¹)	NH_4^+
					(mg kg ⁻¹)
Soil only (T ₁)	5.72 ^b	0.18^{b}	0.004^{a}	5.96 ^b	47.60 ^b
	±	± 0.04	± 0.002	± 0.39	± 2.80
	0.26				
7.4 g Urea + 5.0 g TSP + 3.8 g	5.82 ^{ab}	0.45^{a}	0.003^{a}	10.07^{a}	534.67 ^a
$MOP(T_2)$	±	± 0.03	± 0.0003	± 0.64	± 43.47
	0.11				
7.4 g Urea + 5.0 g TSP + 3.8 g	6.22 ^{ab}	0.39^{a}	0.002^{a}	11.89 ^a	709.33 ^a
MOP + 192 g Clinoptilolite (T ₃)	±	± 0.04	± 0.001	± 0.44	± 18.67
	0.148				
5.55g Urea + 3.75 g TSP + 2.85	6.48 ^a	0.41 ^a	0.002^{a}	11.77 ^a	601.33 ^a
g MOP + 192 g Clinoptilolite +	±	± 0.02	± 0.001	± 0.14	± 45.63
192 g Compost (T ₄)	0.15				
3.70 g urea + 2.50 g TSP + 1.90	6.15 ^{ab}	0.44^{a}	0.004^{a}	11.05 ^a	624.00 ^a
g MOP + 192 g Clinoptilolite	±	± 0.03	± 0.002	± 0.75	± 48.00
Zeolite + 385 g Compost (T ₅)	0.08				

Table.5 Mean comparison of interaction effects of fertilizer treatments on DMY of Sunflower, IWP and CEC of soil

Year	Fertilizer treatments	Dry matter yield Sunflower (kg ha ¹)	Irrigation Water Productivity (kg m ³)	Cation exchange capacity) (meq 100 g soil 1)
2008- 2009	F1: 130 kg/ ha N as urea	4660 d	0.50 c	7.0 c
2002	F2: 80 kg/ ha N as urea + 50 kg/ ha N as cattle manure	5040 с	0.53 bc	8.2 b
	F3: 80 kg /ha N as urea + 50 kg/ ha N as cattle manure plus 7% zeolite,	4980 с	0.55 ab	8.2 b
	F4: 80 kg /ha N as urea + 50 kg/ ha N as cattle manure plus 14 % zeolite	5520 b	0.55 ab	8.4 ab
	F5:80 kg /ha N as urea + 50 kg/ ha N as cattle manure plus 21% zeolite	5830 a	0.57 a	8.7 a

Table.6 Soilcation exchange capacity and pH at 72 DAS of Maize

Treatment	CEC (cmol _c kg ⁻¹) (S.E.)	pH (S.E.)
First cycle		
$\mathbf{T_0}$	$7.92^{d}(0.32)$	4.25° (0.14)
T_1	18.02° (0.42)	$5.68^{b} (0.08)$
T_2	22.55 ^b (0.66)	6.22 ^a (0.14
T_3	26.14 ^a (0.47)	6.48 ^a (0.14)
T_4	24.15 ^{ab} (0.60)	$6.12^{ab} (0.07)$
Second Cycle		
T_0	7.35° (0.13)	$4.10^{c} (0.08)$
T_1	17.42 ^b (0.25)	5.54 ^b (0.14)
T_2	24.11 ^a (0.34)	6.31 ^a (0.14)
T_3	25.81 ^a (0.55)	6.43 ^a (0.14)
T_4	24.22 ^a (0.44)	6.46 ^a (0.07)

Table.7 Effects of Clinoptilolitesalongwith other organic and inorganic fertilizer treatments on Nutrient uptake in maize plant

Treatment	Total Uptake, (g plant ⁻¹)			
	N	P	K	
T ₀ : Soil only	$0.11^{\rm b} \pm 5.41$	$0.03^{d} \pm 1.44$	$0.05^{\rm b} \pm 2.77$	
T ₁ : 7.4 g Urea + 5.0 g TSP + 3.8 g MOP	$1.77^{a} \pm 22.31$	$0.67^{c} \pm 3.45$	$1.76^{a} \pm 10$	
T ₂ : 7.4 g Urea + 5.0 g TSP + 3.8 g MOP +	$2.06^{a} \pm 7.36$	$1.01^{ab} \pm 2.22$	$2.05^{a} \pm 3.58$	
192 g Clinoptilolite				
T ₃ : 5.55g Urea + 3.75 g TSP + 2.85 g MOP	$2.17^{a} \pm 22.02$	$0.92^{\rm b} \pm 4.42$	$2.09^{a} \pm 6.34$	
+ 192 g Clinoptilolite + 192 g Compost				
T ₄ : 3.70 g urea + 2.50 g TSP + 1.90 g MOP	$2.18^{a} \pm 15.79$	$1.17^{a} \pm 7.86$	$2.13^{a} \pm 9.49$	
+ 192 g +Clinoptilolite+ 385 g Compost				

Table.8 Mean comparison of interaction effects of fertilizer treatments on Nitrogen leaching

Irrigation	Fertilizer treatments	N.L (kg
regimes		ha ¹)
2008 (Full	F1: 130 kg/ ha N as urea	36 a
Irrigation)	F2: 80 kg/ ha N as urea + 50 kg/ ha N	31 b
	as cattle manure	
	F3F3: 80 kg /ha N as urea + 50 kg/ ha N as cattle manure plus 7% zeolite,	28 bc
	80 kg /ha N as urea + 50 kg/ ha N as cattle manure plus 14 % zeolite	25 cd
	F5:80 kg/ha N as urea + 50 kg/ ha N as cattle manure plus 21% zeolite	22 d
2009	F1	15 a
	F2	13 a
	F3:	14 a
	F4:	11 a
	F5:	10 a

Table.9 Mean comparison of grain yield and total nitrogen in shoots of wheat plant

Treatments	Nitrogen in shoots (%)	Grains yield (kg/ha)
Contrast effect		
Clay loam		
\mathbf{Z}_0	0.77 bc	3138 a
\mathbf{Z}_1	0.72 c	2877 a
\mathbf{Z}_2	0.69 c	2845 a
\mathbf{Z}_3	0.77 bc	3092 a
\mathbf{Z}_4	0.76 bc	3834 a
Sandy Loam		
\mathbf{Z}_{0}	0.86 a	3517 a
\mathbf{Z}_1	0.76 bc	3554 a
\mathbf{Z}_2	0.74 c	3488 a
\mathbf{Z}_3	0.75 c	3584 a
\mathbf{Z}_4	0.83 ab	4225 a
Main effect		
Zeolite		
\mathbf{Z}_0	0.8 a	3328 b
\mathbf{Z}_1	0.74 bc	3338 b
\mathbf{Z}_2	0.72 c	3167 b
\mathbb{Z}_3	0.76 bc	3338 b
\mathbf{Z}_4	0.8 a	4030 a
Main effect		
Soil texture		
Clay loam	0.74 b	3157 b
Sandy loam	0.79 a	3674 a

For a given means within each column of each section followed by the same letter are not significantly different ($p \le 0.05$)

Table.10 Treatment Details of the experiment

Treatment	Urea	P fertilizer	MOP	CZ		
	(g/plant)					
$\mathbf{T_0}$	0	0	0	0		
T_1	4.85	4.84	2.47			
T_2	3.64	3.63	1.85	10.34		
$\mathbf{E_1}$	4.85	7.95	2.47			
$\mathbf{E_2}$	3.64	5.96	1.85	13.00		
C_1	4.85	7.42	2.47			
C_2	3.64	5.57	1.85	12.50		

Table.11 Selected soil physical-chemical properties of soil after sowing of maize seeds

Treatment	PF	PH		Total P (ppm)		P (ppm)
	FC	SC	FC	SC	FC	SC
$\mathbf{T_0}$	$4.43c \pm 0.01$	$4.60b \pm 0.10$	$10.36b \pm 0.46$	11.67 ± 0.23	$4.95b \pm 0.76$	$4.17c \pm 0.07$
T_1	$5.51a \pm 0.04$	$5.21a \pm 0.05$	$20.19a \pm 0.03$	$21.85a \pm 1.95$	$12.77a \pm 1.19$	$13.62a \pm 0.26$
$\mathbf{T_2}$	$5.11b \pm 0.03$	$5.43a \pm 0.00$	21.19a ±1.61	$19.93a \pm 0.69$	$7.08a \pm 0.65$	$9.36b \pm 1.31$
$\mathbf{E_1}$	$5.10a \pm 0.08$	$5.55a \pm 0.02$	$27.82a \pm 1.48$	$22.53a \pm 0.44$	$10.82b \pm 0.48$	$9.02b \pm 0.26$
$\mathbf{E_2}$	$4.88b \ a \pm 0.12$	$5.46a \pm 0.06$	$30.17a \pm 1.26$	$30.80b \pm 0.30$	$18.82a \pm 1.37$	$11.58a \pm 0.78$
$\mathbf{C_1}$	$5.34a \pm 0.06$	$5.39a \pm 0.05$	$24.01a \pm 2.05$	$25.75a \pm 0.01$	$13.05a \pm 1.05$	$12.03a \pm 1.46$
$\mathbf{C_2}$	$5.19b \pm 0.01$	$5.34a \pm 0.04$	$26.20a \pm 0.62$	$22.47a \pm 1.25$	$11.72a \pm 1.36$	$13.10a \pm 1.22$

Table.12 Effect of treatments (T0, T1, T2, T3, and T4) on phosphorus uptake of Zea mays L. above ground biomass at 72 DAS

Treatment	P uptake (mg kg ⁻¹) Mean (S.E.)
First cycle	$1046^{e} (\pm 2.90)$
T ₀ : Soil only (control)	
T ₁ : 7.40 g urea + 5 g TSP + 3.80 g MOP	$1534^{\rm d}\ (\pm 6.55)$
T ₂ : 7.40 g urea + 5 g TSP + 3.80 g MOP + 192 g clinoptilolite zeolite	3553 ^a (±6.06)
T ₃ : .55 g urea + 3.75 g TSP + 2.85 g MOP + 385 g C + 192 g CZ	$3238^{b} (\pm 9.90)$
T ₄ : 3.70 g urea + 2.50 g TSP + 1.90 g MOP + 577 g C+ 192 g CZ	$2340^{\circ} (\pm 2.08)$
Second cycle	1023 ^e (±5.78)
T_0	
T_1	$1467^{\rm d} (\pm 2.72)$
T_2	3448 ^a (±1.73)
T_3	3247 ^b (±1.76)
T_4	2427° (±3.05)

Table.13 Effects of Inorganic, Organic and NZ treatments on maize Yield and Yield attributes

Treatments	Cob weight (kg/ha)	Grain/ cob
T . Call and	$1.5^{\rm b} \pm 0.0003$	$242.50^{\text{b}} \pm 4.5$
T ₀ : Soil only		
T ₁ : 7.4 g Urea + 5.0 g TSP + 3.8 g MOP	$6.6^{a} \pm 0.0003$	$648.00^{a} \pm 15.59$
T ₂ : 7.4 g Urea + 5.0 g TSP + 3.8 g MOP +	$6.4^{a} \pm 0.0004$	$657.33^{a} \pm 22.43$
192 g Clinoptilolite		
T ₃ : 5.55g Urea + 3.75 g TSP + 2.85 g MOP +	$6.5^{a} \pm 0.0002$	$681.67^{a} \pm 21.67$
192 g Clinoptilolite + 192 g Compost		
T ₄ : 3.70 g urea + 2.50 g TSP + 1.90 g MOP	$6.6^{a} \pm 0.0002$	$709.00^{a} \pm 8.02$
+ 192 g +Clinoptilolite+ 385 g Compost		

Table.14 Influence of zeolite and sugarcane filter cake on sugarcane yield

Treatments	Cane yield	Sucrose yield
	(t ha ⁻¹)	(t ha ⁻¹)
Control	86.37 i	14.99 i
Z 7.5 t ha ⁻¹	89.41 h	15.31 h
Z 15 t ha ⁻¹	114.40 f	19.48 f
$Z 7.5 t ha^{-1} + N(100 kg ha^{-1})$	154.84 b	24.14 a
Z 15 t ha ⁻¹ + N(100 kg ha ⁻¹)	142.30 c	23.84 c
Z 7.5 t ha ⁻¹ +SFC(22.5 t ha ⁻¹)	162.00 a	24.42 b
Z 3 t ha ⁻¹ +SFC(18 t ha ⁻¹)	137.66 d	22.95 d
Z 7.5 t ha ⁻¹ +NPK(100-60-200 kg ha ⁻¹)	135.79 e	22.19 e
Z 15 t ha ⁻¹ +NPK(100-60-200 kg ha ⁻¹)	106.93 g	17.29 g
$\mathbf{E}\mathbf{E} = \pm$	3.90	0.58

Tukey HSD at p≤0.05. SFC (sugarcane filter cake)

Fig.2 CEC mechanism of Zeolite

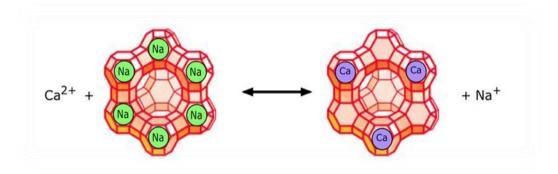


Fig.3 Adsorption and related molecular sieving mechanism of Zeolite

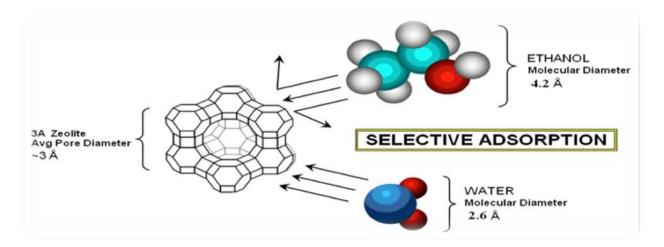


Fig.4 Rehydration and Dehydration mechanism of Zeolite

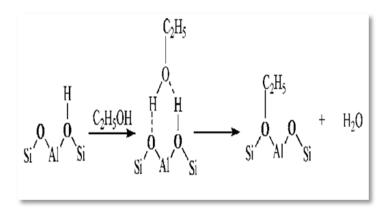


Fig.5 Natural zeolite formation

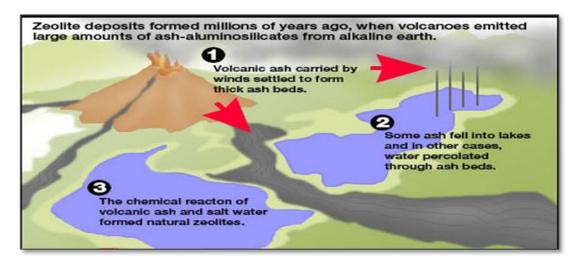
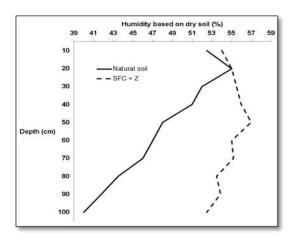


Fig.6 Soil moisture profile (25 mm of rain before sampling). Average values of sampling of the soil moisture content (Z 7.5 tha⁻¹ + SFC 22.5 t ha⁻¹)Average values of sampling of the soil moisture content (Control without fertilization)



3 3 2.5 а 2 2 1.5 1 1 % 0.5 0 0 T0 T1 T2 Т3 Τ4 T0 T1 T2 T3 T4 Organic Organic 1.23 1.67 2.68 2.73 2.66 1.23 1.67 2.68 2.73 2.66 Carbon (%) Carbon (%)

Fig.7& 8: Oragnic carbon of soil First Cycle and Second Cycle respectively

Fig.9 Slow release Zn fertilizer using nano-zeolite as carrier pattern

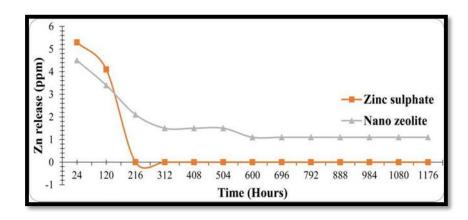
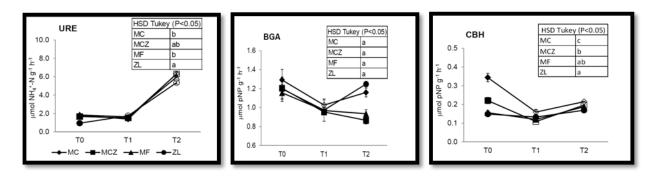


Fig.10 Effect of the enzyme activities of after applying different treatments in Barly crop



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 (Barros *et al.*, 2003). 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 1pplication is important. A few important applications of zeolites have been discussed above, but the possibilities of their usage are much broader.

Summary

There is an increasing interest in the utilization of nanoporous zeolites in farming over the years because ofcurrent public concern about the adverse effects of chemical fertilizers on the agro-ecosystem. Ionexchange 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 are being made worldwide. Considerable research has been carried out globally to exploit the potential of zeolites in perpetual maintenance 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.

It is concluded that, zeolites can be used as a potential source of soil conditioner which help in improving soil physico-chemical properties and Biological properties in one way, improving the crop production in others.

The way forwarded

The following issues have been identifiedfor further research in soil and plant management:

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 electronacceptorcentres and they can be cations or different aluminium

- species located in defect centres; the latter are the so-called true Lewis acid sites).
- To probe whether zeolite amendment will reduce the potential for nitrate leaching in agriculture.
- To characterize the available zeolite deposits in each country.
- To develop methodologies for organo-zeolitic manure/fertilizers.
- To characterize the nutrient release pattern from organo-zeolites.
- To probe the physical stability of zeolites in a variety of soil environments.
- To probe the long-term impact of zeolites on soil flora and fauna.
- To develop zeolitic herbicides to minimize herbicidal residues.
- To carry out field testing of zeolites on soil and plant systems.

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