Journal of Fruit and Ornamental Plant Research vol. 12, 2004 Special ed.

USE OF NATURAL ZEOLITE (CLINOPTILOLITE) IN AGRICULTURE

Ersin Polat[1], Mehmet Karaca[2], Halil Demir[1] and A. Naci Onus[1]

[1]Akdeniz University, Faculty of Agriculture, Department of Horticulture
07059 Antalya, TURKEY
[2]Akdeniz University, Faculty of Agriculture, Department of Field Crops
07059 Antalya, TURKEY

(Received May 6, 2004/Accepted August 26, 2004)

A B S T R A C T

Zeolites have been increasingly used in various application areas such as industry, agriculture, environmental protection, and even medicine. Although, there are no certain figures on the total amount of these minerals the world, some countries e.g. Cuba, USA, Russia, Japan, Italy, South Africa, Hungary and Bulgaria, have important reserves and production potentials. According to reports of 2001, the total consumption of zeolites was 3.5 million tons of which 18% came from their natural resources and the rest from synthetics. More than forty naturally occurring zeolites were reported by different research groups, and clinoptilolite, erionite, chabazite, heulandite, mordenite, stilbit and philipsite are the most well-known. The most common for agricultural applications is clinoptilolite since it has high absorption, cation exchange, catalysis and dehydration capacities. Zeolites are, therefore, used as a promoter for better plant growth by improving the value of fertilizers; retaining valuable nitrogen and improving the quality of resulting manures and sludge. They can also be used as a molecular sieve or filter medium.

Key words: zeolites, clinoptilolite, application areas, plant growing, agriculture

INTRODUCTION

Identification of zeolite as a mineral goes back to 1756, when a Swedish mineralogist, Fredrich Cronstet, began collecting some well-formed crystals from a copper mine in Sweden. They were named “Zeolite” from the Greek words meaning “boiling stones”, that is, because of ability to froth when heated to about 200°C. After their discovery, zeolites were considered as minerals found in volcanic rocks for a period of two hundred years. Fortunately in 1950s, they were rediscovered and reported to exist on all the continents (Anonymous, 2004a). In the world, their commercial production and use started in 1960s, but in Turkey they were first discovered in 1971.

To date, more than forty types of zeolites have been reported by different research groups. Among these minerals, analcime (sometimes known as analcite), clinoptilolite, erionit, chabazite, mordenite, and philipsite are well known (Doğan, 2003). Also, more than 150 zeolites have been synthesized. Some of the common synthetics are zeolites A, X, Y, and ZMS-5. Those naturally occurring and synthetic minerals are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties. Extensive research is very important to assure that the source of natural zeolites can provide their sufficient quantity with uniform characters and unique properties (cation exchange capacity, pH and B content) for application and commercial processing. Research is under progress to enhance the use of zeolites (Kütük et al., 1996). There are many minerals that show similar cage-like framework structures or have similar properties and/or are associated with zeolites, but actually are not them. Therefore, zeolites without well defined chemical characteristics may cause severe problems in their application (Kocakuşak et al., 2001).

Zeolites have many important tasks such as ion exchange, filtering, odour removal, chemical sieve, water softener and gas absorption. Therefore, apart of agriculture, numerous examples of their application are cement and brick production, stabilization of soil, building materials, paint components with anti-corrosive property, defluorination of industrial wastes, desulphurization of flue gas, methylene blue and mercury removal, copper recovery from wastes, fixation of phosphates, chlorinated phenol removal and neutralization of acid wastes, clean-up of sewerage, and both heavy metal, and ammonium ion removal (Kocakusak et al., 2001).

Table 1. Physical characteristics of some naturally occurring zeolites (after Doğan, 2003)

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

STRUCTURE OF ZEOLITE

Zeolites are composed of pores and corner-sharing aluminosilicate (AlO_4 and SiO_4) tetrahedrons, joined into 3-dimensional frameworks. The pore structure is characterized by cages approximately 12Å in diameter, which are interlinked through channels about 8Å in diameter, composed of rings of 12 linked tetrahedrons (Kaduk and Faber, 1995). 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.

CLINOPTILOLITE

Clinoptilolite originally received its Greek name, meaning "*oblique feather stone*" because it was thought to be the monoclinic phase of the mineral ptilolite (as in "*oblique ptilolite*") but it was later found the earlier named mineral was mordenite; consequently the name ptilolite, is no longer in use. Clinoptilolite, one of the most useful naturally occurring zeolites, is applied as a chemical sieve, feed and food additive, as well as gas and odour absorber. Suitability for such applications is due to its large amount of pore spaces, a high resistance to extreme temperatures and chemically neutral basic structure. Clinoptilolite can easily absorb ammonia and other toxic gases from air and water and thus can be used in filters, both for health reasons and odour removal.

The properties such as high absorption level, ion exchange capacity, catalysis, dehydration activity and easily shapeable features make clinoptilolite important in plant production. Pure or composite clinoptilolite added to soil improves its physical and chemical characteristics (Anonymous, 2004a).

PRODUCTION OF ZEOLITES IN THE WORLD

Although, there are no certain figures on the total amount of zeolites in the world, it is well known that they are present on all the continents with varying mineral contents and kinds. According to reports of 2001, the total consumption of zeolites was 3.5 million tons of which 18% came from natural resources and the rests from synthetics such as A, X, Y, and ZMS-5 (Öz et al., 2003). Clinoptilolite and chabazite are most commonly consumed. The use of natural zeolites has been continuously increasing over last years. Such countries as Cuba, USA., Russia, Japan, Italy, South Africa, Hungary and

Bulgaria have important resources of these minerals and production potentials (Anonymous, 2004a).

Also, Turkey has substantial zeolite resources, estimated to be approximately 50 billion tons, mainly consisted of clinoptilite ores. In this country, zeolite production in 2002 was 25 000 tons of which 80% was used internally and the rest exported to the USA, France, Italy, Israel, and United Kingdom. According to the General Directorate of Mineral Research and Exploration, Turkey, resources of clinoptilolite in the Manisa-Gördes region are estimated at 2 billion tones (Anonymous, 2004a).

APPLICATION OF CLINOPTILOLITE IN AGRICULTURE

Fertilizer efficiency

Clinoptilolite in agriculture improves the efficiency of used fertilizers, thus promotes better plant growth and consequently enhances the yield. For instance, Torii (1978) reported that the application of zeolite at the rate of 4-8 tons/acre increased apple yield by 13-38%. This mineral used in the amount of 2 to 8 kg/tree, can contribute to a better new orchard establishment. Zeolites are used successfully in the cultivation of a wide variety of crops including cereals, vegetables, grapes and other fruits (Burriesci et al., 1984; Anonymous, 2004ab).

Zeolites added to fertilizers help to retain nutrients and, therefore, improving the long term soil quality by enhancing its absorption ability. It concerns the most important plant nutrients such as nitrogen (N) and potassium (K), and also calcium, magnesium and micro-elements. Zeolite can retain these nutrients in the root zone to be used by plants when required. Consequently this leads to the more efficient use of N and K fertilizers by reducing their rates for the same yield, by prolonging their activity or finally by producing higher yields. Large losses of fertilizers which move out of the root zone (leaching) often happen in sandy soils, which lose their capability to retain high nutrient levels (Flanigen and Mumpton, 1981; Mumpton, 1981). Therefore an application of zeolites will enhance the plant growth and development by reducing the loss of nutrients (Anonymous, 2004a).

Gas absorption

Natural zeolites can absorb CO, CO_2, SO_2, H_2S, NH_3, HCHO, Ar, O_2, N_2, H_2O, He, H_2, Kr, Xe, CH_3OH and many other gases and can thus be used to collect them or control odours. Therefore, those minerals are being used in intensive animal husbandry sheds, significantly reducing the content of ammonia and H_2S, which cause undesirable odours. NH_4^+ absorbed zeolite becomes a natural enriched slow release fertilizer. High ammonia absorption capacity makes it a very effective natural way to control high levels of this gas generated in fish farms. It can be used in the filtration systems or simply be broadcast over the water surface as it is totally harmless to water life (Anonymous, 2004a). Additionally, food crops growing in soil containing high amounts of Pb, Cd, and Cu can be protected by the absorption ability of zeolites. Also, research showed that S^{90} uptake by plants was significantly reduced.

Water absorption

Zeolites may hold water up to 60% of their weight due to a high porosity of the crystalline structure. Water molecules in the pores could be easily evaporated or reabsorbed without damage to such structures (Kocakuşak et al., 2001). Zeolites assure a permanent water reservoir, providing prolonged moisture during dry periods; they also promote a rapid re-wetting and improve the lateral spread of water into the root zone during irrigation. This results in a saving in the quantity of water needed for irrigation. Furthermore, high absorption capacity makes zeolites a carrier of agricultural pesticides.

Ion exchange

Zeolite with a negative charge provides an ideal trap for positive cations such as sodium, potassium; barium and calcium, and positively charged groups such as water and ammonia. Both carbonate and nitrate ions are attracted by the negative charge within zeolites. Therefore, alkali and soil alkali metallic cations are attracted in the same way and water can be absorbed by zeolites (Mumpton, 1999). Absorbed cations are relatively mobile due to their weak attraction, and can be replaced using the standard ion exchange techniques, making zeolites good ion exchangers.

Animal feed additive

It is already known that the addition of clinoptilolite to the diet of pig, poultry and cattle, improves their weight gain and increases feed conversion ratios. Clinoptilolite acts as a mycotoxin binder, absorbing toxins which can be dangerous to animals. It also helps to control aflatoxins in animal feed, thus lowering mortality from digestive stress and reducing the need for antibiotics. It also absorbs other toxins produced in the feed by moulds and microscopic parasites and enhances food absorption by animals.

Soil amendment

Unlike other soil amendments (e.g. lime) zeolite does not break down over time but remains in the soil to improve nutrient retention. Therefore, its addition to soil will significantly reduce water and fertilizer costs by retaining beneficial nutrients in the root zone. The porous structure of natural zeolite helps to keep the soil aerated and moist as well as active for a long time. Zeolite is not acidic but marginally alkaline and its use with fertilizers can help buffer soil pH levels, thus reducing the need for lime application. This mineral is therefore very beneficial in the construction of golf courses and sport fields where the resulting irrigation and maintenance costs can be very substantial.

CONCLUSION

The most common zeolite for agricultural applications is clinoptilolite due to its relatively high absorption rate, cation exchange, catalysis and dehydration capacities. Zeolites are, therefore, used to promote better plant growth by improving the value of fertilizers. They retain valuable nitrogen and improve the quality of the resulting manures and sludge and can also be used as a molecular sieve or filter medium. When applying zeolites to agricultural production, one should assure that their natural source is of uniform characters and unique properties such as cation exchange capacity, pH and B content.

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WYKORZYSTANIE NATURALNEGO ZEOLITU (KLINOPTYLOLITU) W ROLNICTWIE

Ersin Polat, Mehmet Karaca, Halil Demir i A.Naci Onus

STRESZCZENIE

Zeolity są coraz częściej stosowane w różnych dziedzinach, takich jak przemysł, rolnictwo, ochrona środowiska, a nawet w medycynie. Chociaż nie ma danych na temat całkowitych zasobów tych minerałów na świecie, wiadomo, że są one obfite w niektórych krajach, jak Kuba, USA, Rosja, Japonia, Włochy, Republika Południowej Afryki, Węgry i Bułgaria. Doniesienia z roku 2002 wskazują, że roczne wykorzystanie zeolitów osiągnęło 3,5 milionów ton, z czego 18% z ich pochodziło z naturalnych zasobów, a reszta to produkt syntetyczny. Wśród ponad 40 typów zeolitów występujących w naturalnych złożach i stwierdzonych przez wiele zespołów badawczych, najbardziej znane to: klinoptylolit, erionit, chabazyt, heulandyt, mordenit, stylbit i filipsyt.

W rolnictwie najczęściej wykorzystywanym zeolitem jest klinoptylolit, z uwagi na jego wysokie właściwości adsorpcyjne i odwadniające, wymianę kationową i działanie katalityczne. Dlatego też stosowanie tego minerału wpływa korzystnie na wzrost roślin przez polepszenie właściwości nawozów, zatrzymywanie azotu w strefie korzeniowej oraz poprawę jakości uzyskiwanego obornika i szlamu. Zeolity mogą również pełnić funkcję sita molekularnego lub środka filtracyjnego.

Słowa kluczowe: zeolity, klinoptylolit, stosowanie, wzrost roślin, rolnictwo