

ZEOLITES IN AGRONOMY

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Abstract

Green Approach is an approach that protects human and environmental health by replacing hazardous chemicals, processes, and products with safer processes and safer alternatives. Mineral fertilizers applied to agricultural crops have great potency to improve yield but they have adverse effect on environment and cause air, water and soil pollution when applied at large scale. Zeolites are most appropriate in agricultural uses due to their unique structure and properties like ion exchange and adsorption. Application of zeolites as fertilizers improves quality and yield of crops and reduces the harmful and negative effects. Zeolites improve the nutrients holding capacity and act as water moderator. These promote plant growth, improve the efficiency and value of fertilizer & increase the yield. Zeolites can retain important plant nutrients like nitrogen (N), potassium (K), and calcium (Ca), magnesium (Mg) in the root zone to be used by plants when required. This leads more efficient use of N and K fertilizers by reducing their application rates for same yield. These zeolite samples can be characterized by FTIR, XRD, N₂ adsorption, TGA & DSC and SEM.

Keywords: *Zeolites, Green chemistry, ion exchange capacity, Heavy metals, Soil remediation.*

INTRODUCTION

Fertilizers are used for proper and healthy growth of plants but with this they are very harmful for environment. Fertilizers are substance, which can be synthetic or organic and can be added to the soil in order to increase the supply of essential nutrients that boost the growth of plants and vegetation in that soil. With the rapid increase in population globally, the demand of food and agricultural yield has been rising tremendously. To increase the production at high level almost 40-60% of agricultural crops are grown with the use of different types of fertilizers. More than 50% people

feed on crops that are grown as a result of using synthetic fertilizers. Excess use of fertilizers increases the amount of harmful chemicals in soil by leaching process.(B.Wiedenfeld,2003) Zeolites are being used as fertilizers in agriculture for past many years, due to the microporous structure .(Jakkula 2005)

Zeolites are micro porous hydrated aluminosilicate mineral that contain different metal ions in its cavities. Their framework composed of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral in which corner share to form different open structures. These tetrahedrons link together to form cages connected by pore opening of different sizes. The pore size ranges from 0.3 – 1 nm. A general formula for zeolite may be written as $M_{x/n} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where M is the charge balance cation, n is the charge on cation, x is generally ≥ 2 , and y is number of water molecules in the voids of zeolites. (G.Gottardi, 1986)

Natural Zeolites are formed as a result of chemical reaction of volcanic ash and alkali water. Synthetic zeolites are produced in lab by different methods according to need. About 50 natural zeolites are known and 150 have been synthesized. Zeolites are largely distributed in Deccan traps of India. (R.N.Sukheswala et al, 1974)

Ion exchange process in zeolite is reversible. Due to this property zeolite behaves as a filter for dust, toxin removal and as catalyst in many chemical reactions. Zeolites are very efficient and cost effective minerals with high usability in many fields. To study the properties of zeolites and applicability, its characterization is most important. (R. Malekian et al, 2011)

METHODS USED FOR THE ZEOLITE CHARACTERIZATION

Zeolite characterization and –application are strongly related. Not all zeolite properties are of the same importance for every application. (J.C.H.van Hooff et al 1991) Individual analysis techniques probe only a particular aspect of the material and, consequently, a combination of methods is necessary to give a balanced description of the zeolite.(A.Jentys et al 2001)

As zeolite may be modified or exchanged with some particular ions for better growth of crops, different methods of characterization are again applied. Particle size may be analysed for comparing efficiency of zeolite with different particle size, which can be analyzed with particle size analyser. Different experimental methods like Infrared

Spectroscopy (IR), X-Ray diffraction (XRD), Nitrogen adsorption, DTA, TGA, DSC, SEM-EDAX, AFM and ICP/MS are used to identify the structural group, crystal structure, acidity, binding sites and trace elements in zeolites. N₂ Adsorption is used to determine the pore sizes of zeolites. (R.Panek et al, 2014; Marian Holub et al, 2016).

Exchanged zeolite has a significant effect on nutrient release, therefore percolation reactor may be used for a comparison of slow release tendency for adsorbent and fertilizer (A.Manikandan,2014) S,Preetha have observed that nanosized zeolite fortified with nutrients behaves as long lasting behaves as long lasting fertilizer.(S.Preetha,2014)

Infrared Spectroscopy is used in identifying major structural groups present in zeolites . The characterization of zeolites by FTIR technique is based on the presence of bands in three regions. Especially mid IR region [4000 – 200 cm⁻¹] is used for the determination of zeolite structure type and groups. A higher one corresponds to the OH stretching modes (3650 – 3450 cm⁻¹) with an additional band at 1620 – 1640 cm⁻¹ (Lewis sites). (Marian Holub et al, 2016). Finger printing region of zeolites ranges from 1500 – 400 c⁻¹ in infrared spectroscopy. (K.S.Prasad et al, 2007)

Pore size and structures plays an important role in defining applicability of zeolites in different areas. Nitrogen adsorption/desorption is commonly used to characterise the pore structures, the pore size distribution and surface area of pores in the zeolites. (M. A. A.Musa et al, 2011)

SEM is a powerful tool for morphological studies of zeolites. It gives a complete knowledge of surface structure and distribution of particle size. Using SEM, different images of zeolites are taken with the help of different signals which are produced by various energy sources like Backscattered secondary and auger electrons and X-Ray fluorescence photons etc. These energy sources produce different images of surface which give a broad idea of morphology and distribution of particles. Energy dispersive X-Ray spectroscopy provides elemental information of the zeolites. (F.A.Mumpton et al, 1976)

APPLICATIONS OF ZEOLITE:

Soil Amendment

Zeolite is a natural super porous mineral (part of a group of hydrated aluminosilicates). It carries a negative charge balanced by freely moving cations with positive charges, which provide an ideal trap for positive cations like nitrogen rich ammonium and potassium, which are then released when demanded by plants. (H. Ghorbani et al, 2008) .It can hold nutrients in the root zone for plants to use when required. This leads to more efficient use of N and K fertilizers - either less fertilizer for the same yield or the same amount of fertilizer lasting longer and producing higher yields. An additional benefit of zeolite application is that unlike other soil amendments (gypsum and lime) it does not break down over time but remains in the soil to help improve nutrient and water retention permanently. With subsequent applications the zeolite will further improve the soil's ability to retain nutrients and produce improved yields. (W. Shia et al, 2009).

Fertilization Efficiency

Zeolites have a very open framework with a network of pores giving it a large surface area for trapping and exchanging valuable nutrients. Natural zeolite clinoptilolite saturated with ammonia has been used as a fertilizer. Clinoptilolite itself has special physical and chemical properties, which improve soil fertility, develop property of slow release of fertilizer and also affect buffer capacity of soil. Enrichment of soil by clinoptilolite does not influence soil properties. (H.Kusa,) Modified zeolitic concentrate has been used to increase the yield and similar results have been obtained as obtained by other commercial products. (M.B.M.Monte, 2009). Not only Clinoptilolite improves nitrogen fertilization efficiency of soil. Zeolites also reduce the leaching of nitrates by inhibiting the nitrification of ammonia to nitrate (Perrin et al., 1998). A.K.Bansiwal have investigated that surfactant modified zeolite behaves as a better carrier for fertilizer and also help in slow release of nutrients. In his experiment zeolite A was modified by using hexadecyltrimethyl ammonium bromide which is a cationic surfactant followed by treatment with fertilizer. It was observed that after modification capacity to retain anion increases and tendency of slow release of nutrient also developed in it. (A.K.Bansiwal, 2006).

Zeolites can enhance the efficiency of nutrient use by increasing the accessibility of P from phosphate rocks, and the consumption of NH_4 , N and NO_3 , reduce loss by leaching of K^+ and also act as a slow releaser of fertilizer without harming the

environment. (M.Mahesh et al,2018)

The Results of the study by Jiang et al showed that the zeolite, applied to the poor soils, improved their chemical and physical properties, decreasing the salt concentration in the salinized soils with increasing in fertilizer efficiency (C. Jiang, 1993)

The effect of Ca-K clinoptilolite on available potassium in salinized soil and its subsequent effect were studied by Zhou and others .The results showed that the content of available potassium in soil increased with clinoptilolite application increase. (E. Zhou, 1999)

Reduction Of Volatilization And Leaching Losses

With the current high price of ammonium fertilizers zeolite can be used to extend their efficiency and performance. Blending fertilizer with zeolite can produce the same yield from less fertilizer applied because of the reduction of volatilization and leaching losses. It is particularly suitable for banding under drip irrigation planting where it will assist water infiltration, distribution and retention. When fertigation is practiced it will actively hold the nutrients in the root zone. (A.M. Torkashvand, 2012). Earlier studies showed that the Zeolites could be used as artificial soil. The Agricultural cultivation with the artificial soil containing zeolite is known as zeoponics (Mumpton, 1999).

The ammonia nitrogen volatilization and nitrate leaching can be reduced or prevented by the use of zeolite carrier material applications which have N in their framework and act as slow/controlled release fertilizers. These materials will reduce ammonia volatilization and nitrate leaching and at the same time increase crop yield.

Nitrogen is an important nutrient for the growth and development of plant as it improves biomass production and increases photosynthetic rate. Urea is a rich source of nitrogen but N-use efficiency of urea may be decreased sometimes. There are many factors, which may be responsible for it. One of the main causes is that, as urea is applied on soil surface, therefore loss of nitrogen may take place by volatilization of ammonia to atmosphere. Using zeolite as an additive in fertilizer may reduce these losses. Zeolites have high cation exchange capacity, they help to decrease N_2

concentration in soil solution through cation exchange. It was also observed that when urea is applied with zeolites volatilization of ammonia is also reduced which increases silage corn dry matter production (A.C.C. Bernardi, 2011). A study shows that the application of zeolite has a significant effect on essential oil yield and medicinal peppermint. (Ghanbari and Ariaifar, 2013)

B. Kwakye has worked on the activity of zeolite exchanged with ammonium. It was observed by him that addition of ammonium exchanged zeolite LTX(NH₄-LTX) increases pH, total nitrogen content, potassium and sodium content and water retention capacity of soil. It also leads a significance increase in fresh weight, dry weight, plant height, stem thickness, stem elongation, no. of leaves, leave area as investigated for maize and okro plants.(B.Kwaye,2013)

It has been also observed that zeolite doped with potassium proved fertilizer for K releaser in growing oats and wheat. It also help to increase transfer factor of K significantly. Transfer factor is then measure of metal quantity which pass from soil to root tissue and transferred to other parts of plant. (C.Orha, 2015)

Zeolite also promoted the formation of soil aggregate that increase in soil porosity and decreasing soil bulk density and improving the output of crops (X.Huo et al., 1991)

More Efficient Use Of Water

Zeolite assists water infiltration and retention in the soil due to its very porous properties and the capillary suction it exerts. Acting as a natural wetting agent, it is an excellent amendment for non-wetting sands and to assist water distribution through soils. Due to this property Zeolite has been also proved an important tool in cultivation of invasive species in many areas of southwest U.S. It was difficult to grow these species there due to unavailability of water. In such conditions clinoptilolite behaved as a wicking material which helped to draw water through capillary action from shallow ground water table up to the root zone of plants as a result of which plants became able to reduce dependence on surface water or precipitation. (B.Tanzy,2006) . Leaching of different forms of nitrogen in the soil can be controlled by the use of zeolites. It can maintain the water balance of the soil , increases the soil water retention capacity and decreases the percolation by holding more water in its pores. (Colombani et al., 2015).

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