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The Effects of Natural Zeolite on Ions Adsorption and Reducing Solution Electrical Conductivity I) Na and K Solutions

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ABSTRACT

Natural zeolites are crystalline alominosilicate minerals with three dimensions. In general, three important factors, structure, texture, chemical composition as well as economic value of natural and synthetic zeolites have made them as valuable materials. Zeolites as catalysts in oil and petrochemical industries, fire distinguishing industries and agricultural industries are just some of their applications. Zeolites are also valuable as soil fertilizer, soil moisture holder, municipals as well as industrials wastewater treatment, harmful and toxic chemicals eliminator metals and gases adsorptive. Zeolites are very effective minerals to decrease the risk of toxic cations as well as anions. In a series of experiments different mixtures of soil with zeolite were prepared using 0, 0.5, 1, 5, 10 and 100 percent of zeolite by weight. The constant amounts of mixtures were treated with constant volumes of solutions containing NaCl, $NaNO_3$, KCl and KNO_3. The electrical conductivity of each solution was 0, 5, 10, 15 and 20 dS/m. All samples were replicated two times and each batch of experiment was containing 60 samples with total number of 240 samples for the whole experiment. Mixtures of soil with zeolite were treated with different salt solutions and were shake for two hours prior to analysis. All suspensions were filtered and their electrical conductivity was measured at constant temperature. The results showed that electrical conductivity of filtered solutions was lower in mixtures containing zeolite compared to soil. Also the electrical conductivity of the filtered solutions was considerably lower in K solutions compared to Na. It concluded that zeolite could probably reduce the electrical conductivity of soil solutions by adsorption of ions from the primary solutions and it seems that zeolite would tend to adsorb more K ions compared to Na ions from the solutions resulting lower electrical conductivity of K containing compared to Na containing solutions.

Keywords: Zeolite, Cations, Soil, Electrical conductivity, Adsorption

INTRODUCTION

Zeolites are crystalline alumino silicate minerals. They are generally formed in nature when water of high pH and high salt content interacts with volcanic ash causing a rapid crystal formation. The framework of zeolites is open and contains channels and cavities in which cations and water molecules are located. The channel structure of zeolites is responsible for their function as a molecular sieve, but is also important for selective cation exchange. The selectivity for different ions is determined by several factors such as the size and state of solvation of the ions, the charge and geometry of the framework, the number of cation sites available for occupation inside the framework, and the temperature (Dyer, 1988).

Natural zeolites have been used for a long time to improve soil quality. Farmers add the zeolites to the soil to control soil pH and to improve ammonium retention (Dwyer and Dyer, 1984). Natural zeolites are also used in wastewater treatment to remove ammonium ions and heavy metals (Zamzow et al., 1990). Weber et al. (1984) investigated the effect of a natural zeolite (clinoptilolite) on heavy metal uptake by plants from an agricultural field. They did not observe a reduction in heavy-metal uptake in sorghum even at an addition rate of approximately 6.5%. Other studies concerning the addition of natural zeolites to soil also show little or no effect on the availability of metals (Mineyev et al., 1990; Chlopecka and Adriano, 1996; Chlopecka and Adriano' 1997; Baydina, 1996).

In situ immobilization of metals in contaminated soils is a technique to improve soil quality. Zeolites are potentially useful additives to bind metals. In a research, free ionic concentration of Cd and Zn strongly decreased after the addition of zeolites, which might explain the reduction in metal uptake observed in plant growth experiments. Pretreatment of zeolites with acid (to prevent a pH increase) or Ca (to coagulate organic matter) suppressed the dispersion of organic matter, but also decreased the metal binding capacity of the zeolites due to competition of protons or Ca. (Oste et al, 2001). Similar results were also found by Garau (2007).

Li et al (2000) reported that zeolites have also large cation exchange capacities, which enable them to be modified by cationic surfactant to enhance their sorption of organic and anionic contaminants. In this study, the influence of quaternary ammonium surfactants on sorption of five metal cations (Cs^+, Sr^{2+}, La^{3+}, Pb^{2+}, and Zn^{2+}) onto a clinoptilolite zeolite was investigated. Generally, the metal cation sorption capacity and affinity for the zeolite decreased, indicating that presorbed cationic surfactants blocked sorption sites for metal cations, as the surfactant loading on the zeolite increased.

Binary exchange reactions (Ca^{2+}–K^+, Ca^{2+}–NH_4^+, and K^+–NH_4^+) were also conducted on two soils and with combinations of these soils with bentonite or zeolite added. Binary exchanges were used to predict ternary exchanges (Ca^{++} - K^+ - NH_4^+). The results showed that K^+ and NH_4^+ were preferred over Ca^{2+}, and K^+ was preferred over NH_4^+ in all soils and soils with amendments. Generally, the addition of bentonite did not change cation selectivity over the native soils, whereas the addition of zeolite did. Although additions of bentonite or zeolite may not help increase the NH_4^+ selectivity of a liner material, increases in the overall cation exchange capacity (CEC) of a soil will ultimately decrease the amount of soil needed to adsorb downward-moving NH_4^+ (DeSutter, and Pierzynski, 2004). Other workers were also found similar results (Weber et al, 1982; Fishman and Mumpton, 1977).

Other studies were conducted to quantify apatite and phillipsite (zeolite) sequestration of selected metal contaminants. The results revealed that zeolite was more effective than apatite at sorbing aqueous

Ba^{2+}. Zeolite additions significantly enhanced plant growth and reduced Cd, Pb, and Zn concentrations in all analyzed tissues (grain, leaves, and roots). Sequential extractions of the soil indicated that the Cd, Pb, and Zn were much more strongly sorbed onto the amended soil, making the contaminants less phytoavailable (Knox et al, 2002).

Other finding revealed that zeolite could be useful to decrease negative effects of high salinity. Soil salinity is a major abiotic factor limiting crop production but an amendment with zeolite may mitigate effects of salinity stress on plants. The objective of the study was to determine the effects of zeolite on soil properties and growth of barley irrigated with diluted seawater. Barley was raised on a sand dune soil treated with calcium type zeolite at the rate of 1 and 5% and irrigated every alternate day with seawater diluted to electrical conductivity (EC) levels of 3 and 16 dS m^{-1}. Irrigation with 16 dS m^{-1} saline water significantly suppressed plant height by 25%, leaf area by 44% and dry weight by 60%. However, a substantial increase in plant biomass of salt stressed barley was observed in zeolite-amended treatments. The application of zeolite also enhanced water and salt holding capacity of soil. Post-harvest soil analysis showed high concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}) due to saline water especially in the upper soil layer but concentrations were lower in soils treated with zeolite. Zeolite application at 5% increased Ca^{2+} concentration in salt stressed plants; concentrations of trace elements were also increased by 19% for iron (Fe^{2+}) and 10% for manganese (Mn^{2+}). The overall results indicated that soil amendment with zeolite could effectively ameliorate salinity stress and improve nutrient balance in a sandy soil (Al-Busaidi et al, 2008).

The object of this study was to investigate the effects of natural zeolite on solution electrical conductivity and some selected metal adsorption under the condition of this experiment.

MATERIALS and METHODS

In a series of experiments different mixtures of soil with zeolite were prepared using 0, 0.5, 1, 5, 10 and 100 percent of zeolite by weight. The constant amounts of mixtures were treated with constant volumes of solutions containing NaCl, $NaNO_3$, KCl and KNO_3, separately. The saline solutions were prepared using different concentrations of each salt to make the final electrical conductivity of each solution as 0, 5, 10, 15 and 20 dS/m (Rowell, 1994). All samples were replicated two times and each batch of experiment was containing 60 samples with total number of 240 samples for the whole experiment. Mixtures of soil with zeolite based on the ratio of 0, 0.5, 1, 5, 10 and 100 percent of zeolite by weight (equal to 0, 0.1, 0.2, 1, 2, and 20 grams of zeolite per 20 grams of soil-zeolite mixtures, respectively) were treated with different salt solutions and were shake for two hours prior to analysis. All suspensions were filtered and their electrical conductivity was measured at constant temperature. The concentrations of Na and K ions were also determined in the equilibrated solutions using flame photometry method (Page, 1982). The data processing and graphs were performed using Excel computer program.

RESULTS and DISCUSSIONS

The results showed that, generally, application of zeolite to the soil significantly decreased the electrical conductivity of the equilibrated solutions in the mixtures of soil-zeolite (Figures 1 to 6). However, comparing the results of Na salts with K salts revealed that there were differences between K and Na salts in terms of zeolite effects. For example, in EC equal to 20 dSm^{-1}, application of zeolite by the rates of 0.1, 0.2, 1, 2 and 20 grams per 20 grams mixtures in $NaNO_3$ solutions, decreased the electrical conductivity by 0%, 3%, 25%, 20% and 8%, respectively, compared to the control treatment (no zeolite added to the soil) (Figure 1). At the same conditions, the corresponding data for KNO_3 showed that, zeolite decreased the electrical conductivity by 47%, 54%, 52%, 53% and 65%, respectively (Figure 2), showing greater decrease in electrical conductivity in K salts compared to Na.

Although, the magnitudes of zeolite effects are found to be different between different levels of salinity in terms of decreasing electrical conductivity (Figures 1 and 2), however, mean pooled data for salinity levels showed that application of zeolite by the rate of 0.1, 0.2, 1, 2 and 20 grams per 20 grams mixtures in $NaNO_3$ solutions, decreased the electrical conductivity by 2%, 6%, 15%,18% and 16%, respectively, compared to the control. The corresponding data for KNO_3 salt were 13%, 33%, 31%, 49% and 52%, respectively (Figure 3), showing greater effects of zeolite in K solutions compared to Na even if pooled data are examined.

Other data for K and Na salts in chloride solutions were also showed relatively similar results which were already found for nitrate solutions (Figures 4 and 5). However, the data showed some disintegrates specially at the lower levels of salt concentrations. Most of data at the higher levels of salinity (such as EC equals to 15 and 20 dSm^{-1}) were found similar trends to the previous nitrate solutions data. As an example, in NaCl solutions and EC equal to 20 dSm-1, application of zeolite by the rates of 0.1, 0.2, 1, 2 and 20 grams per 20 grams mixtures, decreased the electrical conductivity by 2%, 0%, 16%, 2% and 23%, respectively, compared to the control with no added zeolite (Figure 4) while the corresponding data for KCl solutions were found to be 2%, 19%, 5%, 10% and 33%, respectively (Figure 5). However, again if mean pooled data are considered for salinity levels, the effects of zeolite to decrease salinity would be stronger in K solutions compared to Na solutions (Figure 6).

Greater decrease in salinity when K salts are used could be explained by preference of K adsorption compared to Na by zeolite. The results from analysing equilibrated solutions for K and Na also supported the evidence as K concentrations were found to be lowered in the solutions after mixing with zeolite, compared to Na concentrations, indicating more adsorption of K compared to Na (data were not shown here). Although no any clear reason is mentioned for this process in the literatures, but smaller hydrated K ions compared to Na could be one the reason which would influence the adsorption phenomena to adsorb more K over Na. However other workers have also reported the preference of K adsorption over NH_4^+ by zeolite in soil (DeSutter, and Pierzynski, 2004).

In overall, the results from the experiment suggested that zeolite is an effective additive in order to improve soil salinity in both K as well as Na solutions. However the data suggested stronger effect of zeolite in K solutions compared to Na. Since zeolite has relatively large capacity to adsorb cations from the soil solutions (Li et al, 2000), decrease salinity is expected due to application of zeolite to the soil. This would be important properties since in additions of salinity control it could be used as a good source of plant nutrients (Dwyer and Dyer, 1984).

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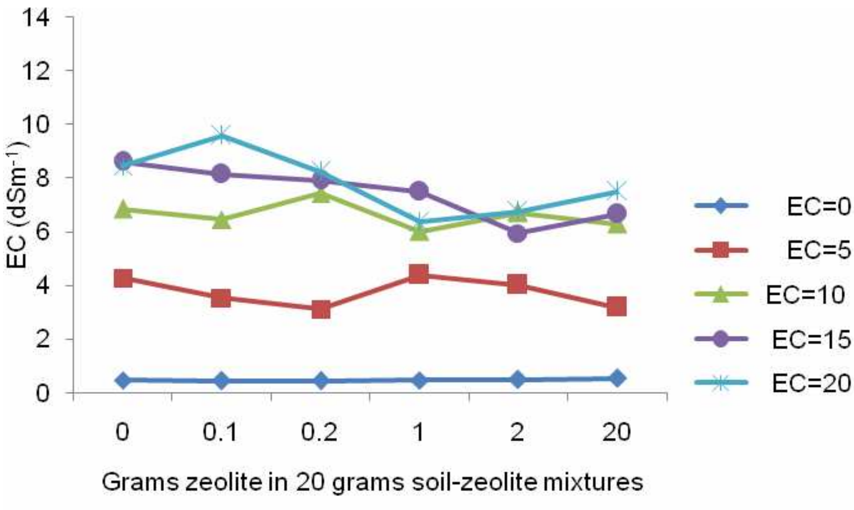

Figure 1. The effects of zeolite on electrical conductivity of soil using $NaNO_3$

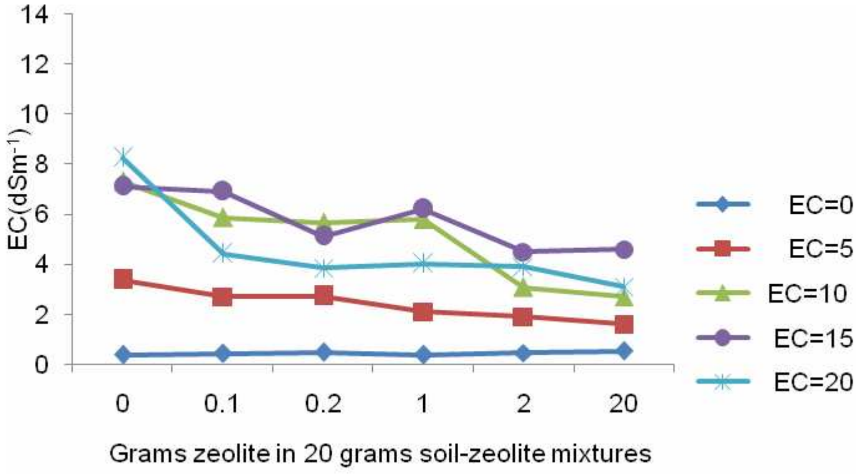

Figure 2. The effects of zeolite on electrical conductivity of soil using KNO_3

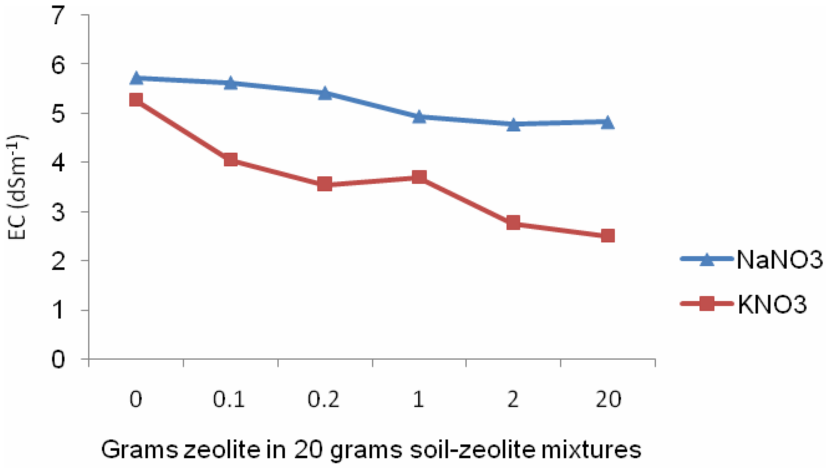

Figure 3. The effects of zeolite on electrical conductivity (pooled mean values for Na and K in nitrate solutions)

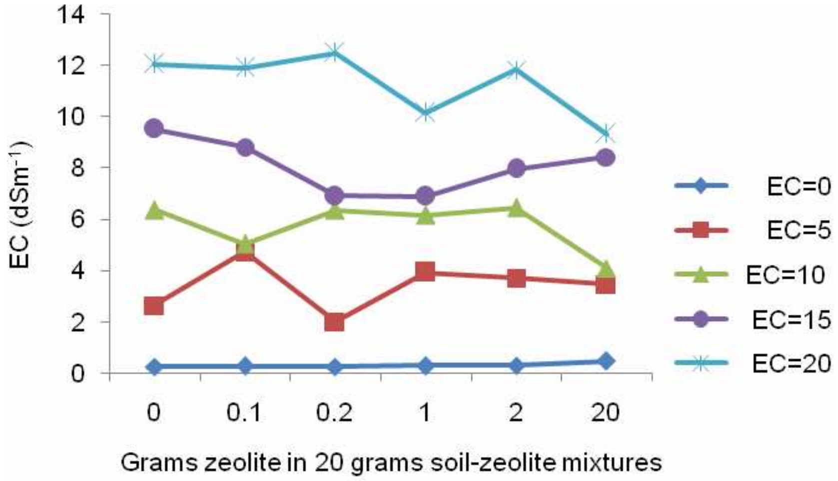

Figure 4. The effects of zeolite on electrical conductivity of soil using NaCl

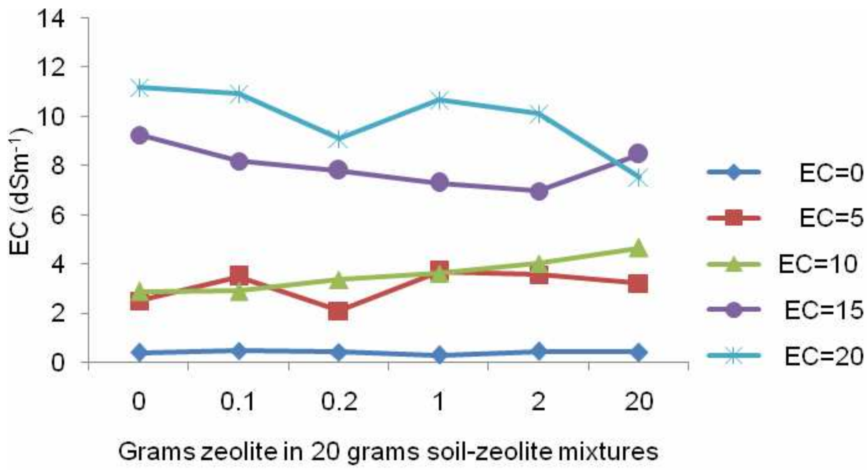

Figure 5. The effects of zeolite on electrical conductivity of soil using KCl

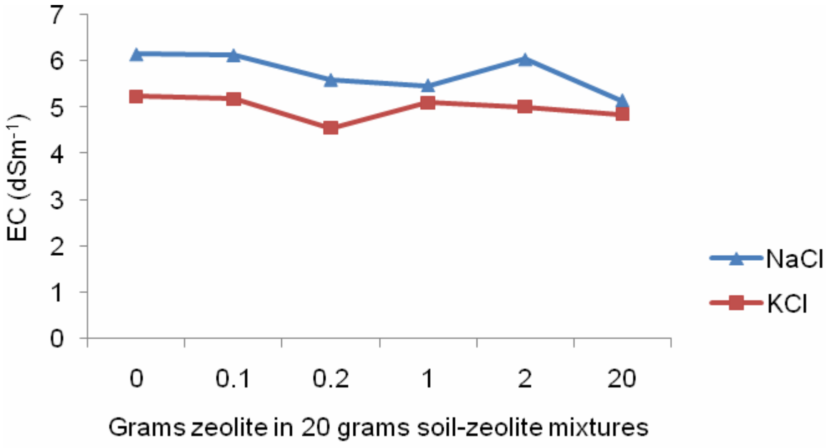

Figure 6.The effects of zeolite on electrical conductivity (pooled mean values for Na and K in chloride solutions)