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The Effects of Natural Zeolite on Ions Adsorption and Reducing Solution Electrical Conductivity II) Cl and NO_3 Solutions

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ABSTRACT

Zeolites can change soil solution compositions due to having high capacity of adsorption as well as water holding capacity. Zeolite are able to decrease fertilizer losses and their leaching from the soil and also able to adsorb the environmental pollutants such as heavy metals and toxic elements from the wastewaters. Some soil solutions are rich of different metals as well as anions which may potentially be harmful for the organisms and the environment. Natural zeolites such as clinoptilolite, analcime, laumomtite, phillipsite, mordenite are crystalline alominosilicate minerals and are 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 NO_3^- solutions compared to Cl^-. 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 NO_3^- ions compared to Cl^- ions from the solutions resulting lower electrical conductivity of NO_3^- containing compared to Cl^- containing solutions.

Keywords: Zeolite, Anions, Soil, Adsorption, Electrical conductivity.

INTRODUCTION

Zeolite is a naturally occurring crystal formed from volcanic ash over 300 million years ago. This crystalline compound has a cage-like, honeycomb structure, which is negatively charged and therefore attracts and captures harmful substances. Britannica Concise Encyclopedia explain zeolites as any member of a family of hydrated aluminosilicate minerals that have a framework structure enclosing interconnected cavities occupied by large metal cations (positively charged ions) generally sodium, potassium, magnesium, calcium, and barium and water molecules. The ease of movement of ions and water within the framework allows reversible dehydration and cation exchange, properties that are exploited in water softeners and molecular sieves for pollution control, among other uses (Britannica Concise Encyclopedia, 2008).

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential (Wikipedia, 2008).

Although many researchers have reported relatively high Cation adsorption capacity for zeolites (Mineyev et al, 1990; Zamzown et al,1990; Weber et al, 1982; Li et al, 2000; Oste et al, 2001), there are some reports on the adsorption of anions by zeolites (Zhang et al, 2006; Sullivan et al, 2003; Yousofi and Sepaskhah, 2005).

Zhang et al (2006) investigated the potential of using surfactant (hexadecyltrimethylammonium)-modified zeolite (SMZ) as an inexpensive sorbent for removing perchlorate (ClO_4^-) from contaminated waters in the presence of competing anions. They found, in batch systems, the presence of 10 m*M* OH^- (i.e., pH 12), CO_3^{2-}, Cl^-, or SO_4^{2-} had little effect on the sorption of ClO_4^- by SMZ, indicating that the sorption of ClO_4^- by SMZ was very selective. The presence of 10 m*M* NO_3^-, however, reduced the sorption of ClO_4^- at low initial concentrations. The maximum sorption capacity for ClO_4^- by the SMZ remained relatively constant (40–47 mmol kg^{-1}), in the absence or presence of the competing ions. In flow-through systems, ClO_4^- broke through the SMZ columns much later than other anions present in an artificial ground water. The affinity of the anions for SMZ followed the sequence of $ClO_4^- >> NO_3^- > SO_4^{2-} > Cl^-$. The exchange of ClO_4^- with NO_3^- corroborated results of the batch tests where NO_3^- was shown to compete with ClO_4^- sorption on the zeolite surfaces. In a similar work, Yousofi and Sepaskhah (2005) found that application of 2, 4 and 8 gKg^{-1} zeolite to the soil, were decreased the amounts of NO_3^- leached down out of the soil columns to 87.7%, 74.7% and 63%, compared to 95% for control, respectively, indicating clear evidence for zeolite to adsorb NO_3^- anions.

Reviewing the literatures shows that new types of soil amendments are being considered to reduce the leaching losses of N fertilizers. One such potential soil amendment is clinoptilolite, which is a natural zeolite (Weber et al, 1982). Clinoptilolite zeolite has a high CEC (160 cmol kg^{-1}), a large affinity for NH^+_4 ions and water molecules that may reduce N leaching on sand based putting greens. In an experiment, the impact of CZ amendment of sand putting greens on N leaching was determined. The lysimeter method was used to determine NO_3^- and NH^+_4 leaching potential and fertilizer N use efficiency. The results showed that sand plus zeolite had a lowered concentration of NO^-_3 and NH^+_4 in leachate while doubling the water retention capacity and increasing CEC 200 fold. The greatest reduction of N leaching was found from lysimeters amended with zeolite at the highest N rate. Nitrate and NH^+_4 leaching were 86 and 99% lower, respectively, than the unamended sand lysimeters. The N fertilizer use efficiency was improved by 16 to 22% with the addition of zeolite to sand, depending on N application rate. Amendment of sandy rooting media with clinoptilolite promoted better fertilizer N uptake efficiency and reduced N leaching from a highly leachable soil (Huang and Petrovic, 1992). Similar results were also found by others (Weber et al, 1982).

Soil salinity is a major abiotic factor limiting crop production but an amendment with synthetic zeolite may mitigate effects of salinity stress on plants. In a research, 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).

Other researchers have also reported other ions such as Arsenic (Sullivan et al, 2003), Chromate, CO^{2-}_3 and HCO^-_3 (Li, 1996) on surfactant-modified zeolites. Zeolites have also been shown to have the potential to control NH_3. Because of their properties it is also expected that zeolites could effectively adsorb NH_3 and odor (Cai et al, 2006) Zeolite adsorption of ethylene and other gases for use in the purification of natural gas has also been well characterized (Peiser and Suslow. 1998).The poultry manure was treated with various amendments which included two natural zeolites, clay, $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, and $Al_2(SO_4)_3$. The zeolite amendments were proposed to be the most suitable for reducing NH_3 losses during composting of poultry manure (Kithome et al, 1997).

The object of this study was to investigate the effects of natural zeolite on solution electrical conductivity and some selected anions sorption 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 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 NO_3^- salts with Cl^- salts revealed that there were differences between NO_3^- and Cl^- in terms of zeolite effects. 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 1). The corresponding data for $NaNO_3$ solutions were 0%, 3%, 25%, 20% and 8%, respectively, compared to the control (Figure 2). Mean pooled data for salinity levels also 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 (Figure 3). At the same conditions for pooled data, the corresponding values for NaCl showed that zeolite decreased the electrical conductivity by 0%, 9%, 12%, 2% and 17%, respectively showing greater decrease in electrical conductivity in NO_3^- salts compared toCl^-(Figure 3). Since all the conditions in the experiment were the same, and also both salts were contained Na as their cations, the differences between these salts could be due to the difference between their anions which are NO_3^- and Cl^-.

Other data for NO_3^- and Cl^- salts in potassium solutions were also showed similar but much stronger results compared to which were already found for sodium solutions (Figures 4 and 5). As an example, in KNO_3 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 47%, 54%, 52%, 53% and 65%, respectively, compared to the control with no added zeolite (Figure 4) while the corresponding data for KCl solutions were only 2%, 19%, 5%, 10% and 33%, respectively (Figure 5). 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 KNO_3 solutions, decreased the electrical conductivity by 13%, 33%, 31%, 49% and 52%, respectively, compared to the control (Figure 6). The corresponding data for KCl salt were only 2%, 14%, 2%, 4% and 8%, respectively (Figure 6), indicating much greater effects of zeolite in NO_3^- solutions compared to Cl^-, even if pooled data are examined. Again, similar to sodium salts, since all the conditions in the experiment were the same, and also both salts were contained K as their cations, the differences between these salts could be due to the difference between their anions which are NO_3^- and Cl^-

Although there are plenty reports to reveal high cation adsorption capacity for zeolites (Mineyev et al, 1990; Zamzown et al,1990; Weber et al, 1982; Li et al, 2000; Oste et al, 2001), however, the affinity of zeolite to adsorb some anions were also been reported (Zhang et al, 2006; Sullivan et al, 2003; Yousofi and Sepaskhah, 2005). The findings in this research were in agreement with other findings who have also reported NO_3 adsorption by zeolites (Huang and Petrovic, 1992, Yousofi and Sepaskhah, 2005). They found that application of 2, 4 and 8 gKg^{-1} zeolite to the soil, were decreased the amounts of NO_3^- leached down out of the soil columns to 87.7%, 74.7% and 63%, compared to 95% for control, respectively (Yousofi and Sepaskhah, 2005), and also, the greatest reduction of N leaching was found from lysimeters amended with zeolite at the highest N rate where nitrate and NH^+_4 leaching were 86 and 99% lower, respectively, than the unamended sand lysimeters (Huang and Petrovic, 1992), indicating clear evidence of NO_3^- adsorption by zeolite.

Lower salinity when NO_3^- salts are used could be explained by preference of NO_3^- adsorption compared to Cl^- by zeolite. Although the equilibrated solution samples were not analysed for NO_3^- and Cl^- concentrations in this stage, however, significant lower electrical conductivity in NO_3^- solutions compared to Cl^- in the presence of both sodium as well as potassium cations, supported the idea that more adsorption of NO_3^- has been probably occurred compared to Cl^- using zeolite. Although it may not be the only reason to explain this response, but anions competition for adsorption on zeolite could be an explanation. Other workers were also found similar results that NO_3^- was shown to compete with ClO_4^- sorption on the zeolite surfaces (Zhang et al, 2006). They also showed that the affinity of the anions for zeolite followed the sequence of $ClO_4^- >> NO_3^- > SO_4^{2-} > Cl^-$, indicating greater affinity of NO_3^- for adsorption compared to Cl^- (Zhang et al, 2006)

The results of this research suggested that zeolite is an effective soil amendment in order to improve soil salinity in both NO_3^- as well as Cl^- solutions. However the data suggested stronger effect of zeolite in NO_3^- solutions compared to Cl^- to decrease the solution electrical conductivity. Since NO_3^- could be leached down easily in soils especially in sandy textures, zeolites would be useful materials to prevent the loss of N fertilizers in soil and to supply good source of N to the roots.

REFERENCES

Ahmed Al-Busaidi; Tahei Yamamoto; Mitsuhiro Inoue; A. Egrinya Eneji; Yasushi Mori; Muhammad Irshad. 2008 .Effects of Zeolite on Soil Nutrients and Growth of Barley Following Irrigation with

Saline Water. Journal of Plant Nutrition, Volume 31, Issue 7 July 2008, pages 1159 – 1173.

Britannica Concise Encyclopedia. 2008. Available Online at: http://www.Britannica.com.

Cai, Lingshuang; Jacek A. Koziel, Yi Liang, Anh Thu Nguyen, and Hongwei Xin. 2006 .Evaluation of Zeolite for Control of Odorants Emissions from Simulated Poultry Manure Storage. J. Environ. Qual. 36: 184-193.

Huang, Z. T. and A. M. Petrovic. 1992 . Clinoptilolite Zeolite Influence on Nitrate Leaching and Nitrogen Use Efficiency in Simulated Sand Based Golf Greens. J. Environ. Qual. 23: 1190-1194.

Kithome, M.; J. W. Paul, and A. A. Bomke. 1997 .Reducing Nitrogen Losses during Simulated Composting of Poultry Manure using Adsorbents or Chemical Amendments. J. Environ. Qual. 28: 194-201.

Li, Zhaohui, Daniel Alessi, and Lori Allen. 2000. Influence of Quaternary Ammonium on Sorption of Selected Metal Cations onto Clinoptilolite Zeolite. J. Environ. Qual. 31: 1106-1114.

Li, Zhaohui. 1996. Chromate Extraction from Surfactant-Modified Zeolite Surfaces. 1996 . J. Environ. Qual. 27: 240-242.

Mineyev, V.G., A.V. Kochetavkin, and N. Van Bo. 1990. Use of natural zeolites to prevent heavy metal pollution of soils and plants. Sov. Soil Sci. 22:72–79.

Oste, Leonard A., Theo M. Lexmond, and Willem H. Van Riemsdijk. 2001. Metal Immobilization in Soils Using Synthetic Zeolites. J. Environ. Qual. 31: 813-821.

Peiser, G. and T.V. Suslow. 1998 .Factors Affecting ethylene adsorption by zeolite: The last word (from us). Perishables Handling Quarterly Issue No. 95 Page 17.

Rowell, D. 1994. Soil science: methods and applications. Longman Scientific and Technical, p.350.

Sullivan, Enid J.; Robert S. Bowman, and Irene A. Legiec. 2003. Sorption of Arsenic from Soil-Washing Leachate by Surfactant-Modified Zeolite. J. Environ. Qual. 32: 2387-2391.

Weber, M.A., K.A. Barbarick, and D.G. Westfall. 1984. Application of clinoptilolite to soil amended with municipal sludge. p. 263–271. *In* W.G. Pond and F.A. Mumpton (ed.) Zeo-agriculture, use of natural zeolites in agriculture and aquaculture. 1st ed. Westview Press, Boulder, CO.

Weber, M. A., K. A. Barbarick, and D. G. Westfall. 1982 . Ammonium Adsorption by a Zeolite in a Static and a Dynamic System. J. Environ. Qual. 12: 549-552.

Wikipedia . 2008. Available Online at: http://www.wikipedia.org.

Yousofi and Sepaskhah, 2005. The effects of zeolite on nitrate and ammonium retention in saturated soil. The 9th Soil Science Congress of Iran, August, 2005,Tehran (in Farsi).

Zamzow, M.J., R. Eichbaum, K.R. Sandgren, and D.E. Shanks. 1990. Removal of heavy metals and other cations from wastewater using zeolites. Separ. Sci. Technol. 25:1555–1569.

Zhang, Pengfei.; David M. Avudzega, and Robert S. Bowman. 2006 . Removal of Perchlorate from Contaminated Waters Using Surfactant-Modified Zeolite. J. Environ. Qual. 36: 1069-1075.

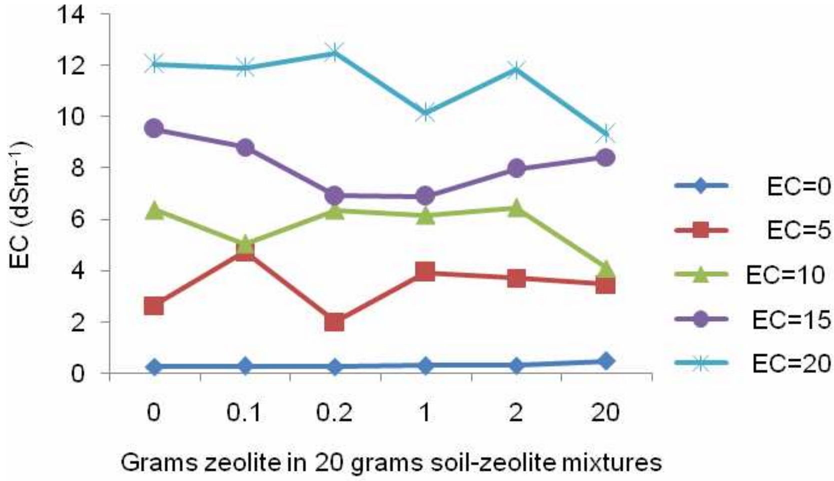

Figure 1. The effects of zeolite on electrical conductivity of soil using NaCl

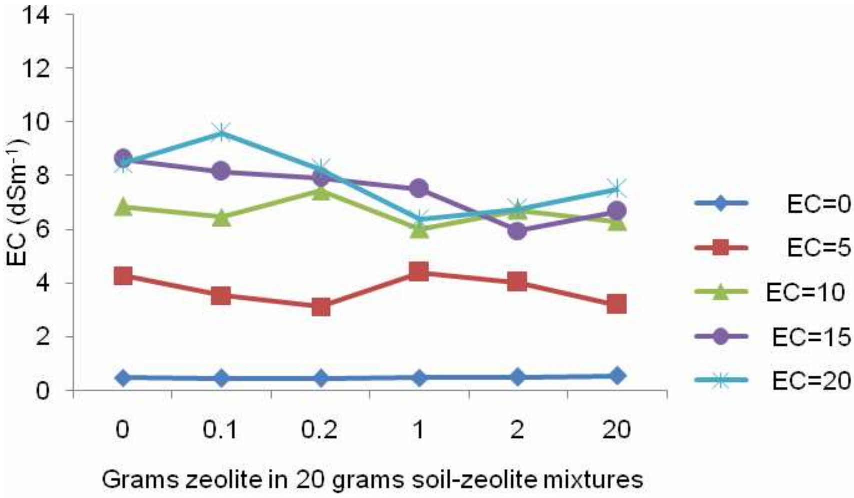

Figure 2. The effects of zeolite on electrical conductivity of soil using $NaNO_3$

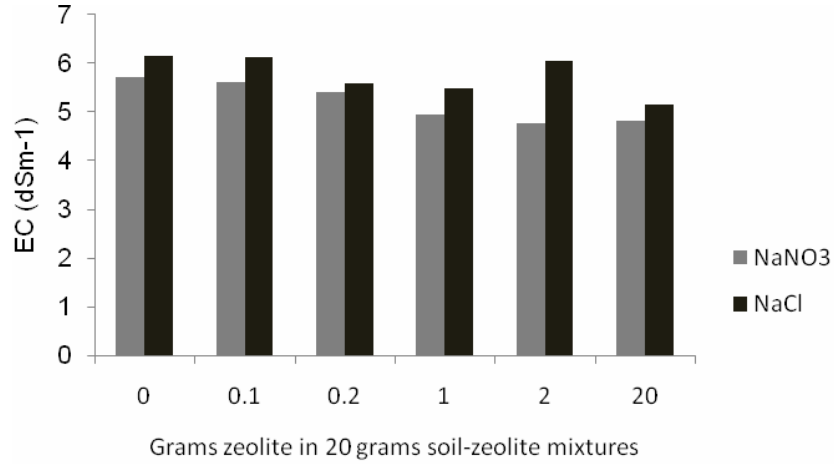

Figure 3. The effects of zeolite on electrical conductivity (pooled mean values for NO_3 and Cl in sodium solutions)

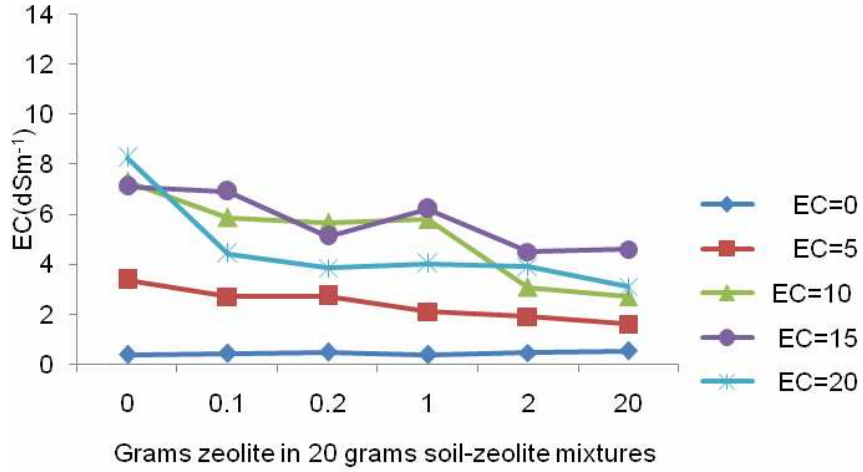

Figure 4. The effects of zeolite on electrical conductivity of soil using KNO_3

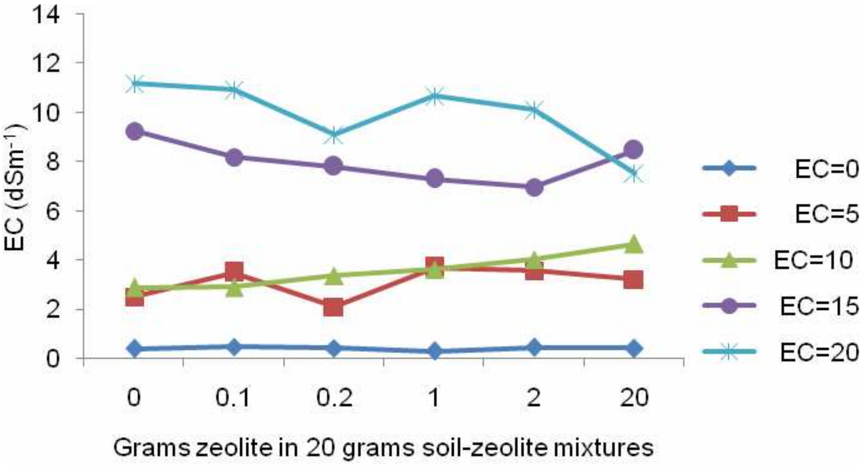

Figure 5. The effects of zeolite on electrical conductivity of soil using KCl

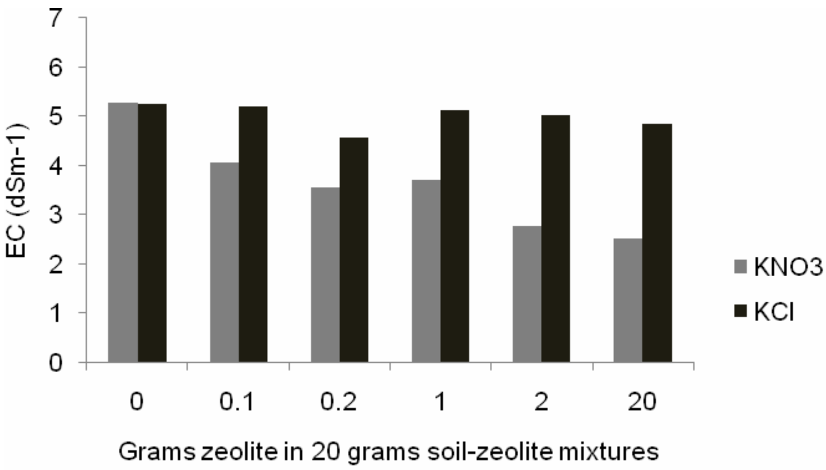

Figure 6. The effects of zeolite on electrical conductivity (pooled mean values for NO_3 and Cl in potassium solutions)