Summary

This study deals with the application of Jordanian natural zeolites in the removal of heavy metal ions and plant nutrients from polluted waters. The material used was brownish and reddish zeolitic tuffs.

Both materials were found to be very different from each other in their chemical and mineralogical compositions. The predominant zeolitic minerals found in the reddish zeolitic tuff were Phillipsite, Chabazite, and Harmotome. The brownish zeolitic tuff was found to contain Phillipsite and Harmotome, however instead of Chabazite, Faujasite was found.

The obtained values of cation exchange capacities for both materials varied greatly depending on the method used (batch system or ion exchange column) as well as the applied regenerate. The reddish tuff has a significantly higher value of cation exchange capacity (2.96 meq/g) than the brownish tuff (1.84 meq/g).

The results adsorption capacity were obtained from the water absorption process, which was performed using a gas stream of H_2O and NH_3 on the zeolitic tuff beds. It was found that the brownish tuff had a higher capacity for H_2O adsorption in all regeneration types (thermal treatment, acidic treatment with diluted acidic solutions at different pH values and in their Ca-; K- or Na forms). When thermal regeneration was performed, the highest values of water absorption recorded were 9% for the brownish tuff and 7% for the reddish tuff, at temperature ranging from 150 to 250°C. The acidic treatment had little to no effect on the water absorption of the tuffs. However, a significant effect was observed on the adsorption capacity to NH_3. Chemical regeneration had a similar effect on the adsorption capacity of NH_3 for both tuff types.

The untreated sample of reddish zeolitic tuff showed a very high capacity for ammonium adsorption (46g/kg) from an ammonium standard solution in comparison to the brownish tuff (20g/kg). In contrast, the adsorption capacities for NH_4^+ were highly decreased when the zeolitic tuff was agitated with a manure. The low values of NH_4^+ absorbed were due to the presence of high concentrations of counter Ca^{2+}, K^+, Na^+ and Mg^{2+} ions and the suspended organics.

Furthermore, phosphorus was also removed from the manure. The amount removed was dependent on the type of tuff added and consequently the amount of $CaCO_3$ present in the tuff; a higher amount was removed (723 mg/kg) by the brownish tuff.

The ammonium ions, which were absorbed were then extracted from the tuffs using tap or distilled water. The reddish tuff had an elution percentage of 87% while that of the brownish tuff was 76%. The first released the NH_4^+ ions more slowly than the latter.

Similar results were obtained for the extraction process of ammonium ions, which were absorbed from the manure. It was found that when a greater amount of the tuffs was used, a slower extraction process was achieved. As well, when distilled water was used, an amount of NH_4^+ was extracted, means that the ion exchange reaction occurred between NH_4^+ ions and some extracted ions from the tuffs. In contrast, the amount of phosphate extracted from the tuffs was not affected by the weight of zeolitic tuffs used, but a significant difference was observed when the distilled water (pH 5.5) was used.

The evaluation of zeolitic tuffs for the removal efficiency of Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} from simple and complex solutions was done in a batch reactor and in an ion exchange column. In these tests, both zeolitic tuffs were used in their untreated forms as well as in their Ca-, K- and Na-forms.

In batch systems, the 1-0.315mm sample of untreated brownish tuff removed ions more efficiently from simple solutions containing only one type of ions (Cd^{2+}; Cu^{2+}; Ni^{2+} and Zn^{2+}) than the reddish tuff. In contrast, Pb^{2+} ions were highly absorbed by both tuffs (145-150mg/g). Clearly the removal process of Pb^{2+}as well as Cd^{2+} and Zn^{2+} on the brownish tuff is not only by means of the ion exchange and an absorption on the surface of the tuff particles. On the other hand the total amount of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} absorbed by reddish tuff was lower than the total adsorption capacity of this tuff. This might indicate that not all the ions were able to find sites on the zeolite mineral at which they could be exchanged.

The effects of counter (Ca^{2+} and Na^{+}) ions had on the removal of metal ions are as follows:

1. The Pb^{2+} and Cu^{2+} ions absorbed were not affected by the presence of counter ion and were not dependent on the type of regeneration form used.
2. The amount of Zn^{2+}, Cd^{2+} and Ni^{2+} absorbed was highly dependent on the regenerated-form of tuff used and was not affected by the presence of Ca^{2+} or Na^{+} ions.

The adsorption capacity of both zeolitic tuffs using ion exchange method was highly affected by the flow rate of effluent solution. A higher efficiency for the removal metal ions was obtained when a flow rate of 400 ml/hr rather than 600 ml/hr was used.

The results obtained from the test of both zeolitic tuffs in the different forms of regeneration in column process indicated that the brownish zeolitic tuff in Na-form had an especially high efficiency for removing metal ions. Furthermore, its capacity for the adsorption of metal ions was increased by repeating the regeneration-exhaustion processes using the same zeolitic tuff bed. The extracted metal ions from the zeolitic tuffs are highly variable and dependent on the regeneration solution used ($CaCl_2$, KNO_3 or $NaNO_3$) as well as the previously used form of zeolitic tuff. In general, more metal ions were removed from the Na-form of brownish zeolitic tuff, and this amount it was further increased by a second cycle of regeneration. There was only one exception, Cu^{2+}, which was not exchanged from the tuff. The cause of this might be that it was already removed by the tuff through precipitation on the surface of tuffs particles or within the zeolite structures themselves.