Chapter 6. Conclusions and Recommendations

6.1 Conclusions

1. The results obtained from the analysis of both types of zeolitic tuff show that both materials differ greatly from each other in their chemical composition, mineralogical components and other physical properties.
2. Mineral types (zeolitic and non zeolitic minerals) vary depending on the grain size fraction. Reddish zeolitic tuffs were found to contain 54% Phillipsite mineral. Other zeolite minerals were also found such as Chabazite and Harmotome. Brownish zeolitic tuffs contained a less amount of Phillipsite and Harmotome as well as Faujasite which was found in percentage ranges between 3.6% (in the grain size fraction of 1-0.315 mm) and up to 20% in the fractions of less than 0.315mm.
3. The total cation exchange capacity of natural zeolite was not easy to determine because the results depend on the method used, the ion selectivity of the zeolite minerals as well as the pretreatment method used prior to testing.
4. The analysed grain size fraction (1-0.315mm) of reddish zeolitic tuff contain a significant high amount of exchangeable K^+ ions, while the brownish zeolitic tuff (1-0.315 mm) contains Ca^{2+} as exchangeable ions.
5. The brownish zeolitic tuff had a higher thermal stability during treatment than the reddish tuff. This was concluded after measring the amount of rehydration for both reddish and brownish tuffs. For brownish zeolitic tuff it was found that the amount of water rehydrated decreased noticeably at 600°C, while for reddish zeolitic tuff the temperature was much lower (250°C).
6. The highest amount of NH_3 (gas stream) was absorbed (70mg/100g) after regeneration the brownish zeolitic tuff at temperature ranges between 200-250°C. At the same temperature, reddish zeolitic tuff tends to absorb only half the amount (30 mg/100g). In contrast, the amount of NH_3 adsorbed is highly decreased for both zeolitic tuffs by converting them to Ca; K- and Na-form.. Similar results were obtained by the regeneration method with diluted acid solutions, where the reddish zeolitic tuff is more stable in acidic environments than the brownish material. It is recommended that brownish zeolitic tuff be used after heating for the removal of NH_3 and (water) humidity from animal husbandry.
7. The technical properties document the suitability of the brownish zeolitic tuff (1-0.315mm) in ion exchange columns because of its high resistance to attrition and the low packed bed density in comparison with the same grain size of the reddish zeolitic tuff. In

addition, the reddish zeolitic tuff might also be used in an ion exchange column due to its high content of zeolitic minerals.

8. The grain size fraction (1-0.315 mm) of reddish zeolitic tuff in a non treated form is able to absorb a significantly higher amount of NH_4^+-N (46g/kg) in comparison with the brownish zeolitic tuff (20g/kg). Its capacity to absorb NH_4^+-N from animal manure was highly decreased to an amount of 2200mg/kg using reddish zeolitic tuff and 862 mg/kg using brownish zeolitic tuff. The results indicate the significant effect of counter K^+; Ca^{2+}; Na^+ and Mg^{2+} ions found in the manure.
9. The removal efficiency of NH_4^+-N ions from the manure using both zeolitic tuffs was not affected by extending the contact time. In contrast, it was affected by increasing the amount of zeolitic tuff, which indicated that the Jordanian zeolitic tuffs had a high selectivity for the removal of NH_4^+-N ions.
10. The percentage of PO_4^{3-}-P eliminated from the manure depends on the amount of zeolitic tuff used and consequently, the amount of $CaCO_3$ added. The results show that a higher amount of PO_4^{3-}-P was removed by using brownish zeolitic tuff (793 mg/kg).
11. Ammonium ions were partially extracted from the zeolitic tuffs by repeating the extraction process up to 23 times using distilled or tap water as an extraction solution. An ion exchange reaction might occur between the cations present in tap water or the cation released from the zeolitic tuff by means of attrition with the ammonium ions absorbed on the zeolitic tuffs. It is clear from the results that reddish zeolitic tuff have better properties for releasing NH_4^+-N than the brownish zeolitic tuff, which is slower in releasing these ions especially when a higher amount of reddish tuff has been applied.
12. By comparing the amount of NH_4^+-N desorbed from the tuffs and the adsorbed amount of cations from the tap water used, it was found that the ion exchange process mainly occurred by exchanging NH_4^+ ions with Ca^{2+} ions.
13. The amount of PO_4^{3-}-P extracted from the pretreated zeolitic tuffs with the manure was influenced by the amount of NH_4^+ desorbed and therefore by pH-value of the solution. It was seen that the amount of extracted phosphor was higher when using distilled water (pH 5.5-5.9) than using tap water (7.6-7.8). This demonstrates the effect of pH value on the dissolution process of PO_4^{3-} ions.
14. The grain size fraction 1-0.315 mm of Jordanian zeolitic tuffs resulted in a high exchange capacity for heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) from solutions using a batch reactor or ion exchange system.
15. The amount of Cd^{2+} (31 mg/g); Cu^{2+} (9 mg/g); Ni^{2+} (14 mg/g) and Zn^{2+} 54 mg/g) ions absorbed was achieved using the brownish zeolitic tuff in untreated form, while a less

amount of cation adsorption was obtained using the reddish zeolitic tuff: Cd^{2+} (12.2 mg/g); Cu^{2+} (2.3 mg/g); Ni^{2+} (5 mg/g) and Zn^{2+} (9 mg/g). With the one exception of Pb^{2+} ions, whose that were shown to be similarly absorbed on both zeolitic tuffs (145-150 mg/g).

16. The removal process of Pb^{2+} on both tuffs as well as Cd^{2+} and Zn^{2+} on the brownish tuff could be due to a combination of the ion exchange process and the adsorption effect on the surface of tuffs particles. On the other hand, the total adsorption capacity of both tuffs was less for Cd^{2+}; Cu^{2+}; Ni^{2+} and Zn^{2+} on reddish zeolitic tuff as well as Cu^{2+} and Ni^{2+} on the brownish zeolitic tuff, which might depend on the type of occupied cations in the exchangeable sites of zeolite minerals.
17. The adsorption capacity of Pb^{2+} (37 mg/g); Cd^{2+} (12.4 mg/g) and Cu^{2+} (4.5 mg/g) was independent on the regeneration type as well as the type of zeolitic tuffs used. In contrast, the amount of Ni2+ (7.6-9.4 mg/g) and Zn2+ (19 mg/g) absorbed on the brownish tuff was significantly higher than that obtained by using the reddish tuff (3.6-4.2 and 8-10 mg/g respectively). It was found that the untreated form of brownish zeolitic tuff had a higher adsorption capacity for Zn^{2+}, Ni^{2+}, Cu^{2+} or Cd^{2+}, than in Ca-, K-, or Na-form. This might indicate the effect of unidentifiable minerals in the brownish zeolitic tuff.
18. The effect of counter Ca^{2+} or Na^{+} ions on the worked adsorption capacity of zeolitic tuffs (in the three used forms of regeneration) for metal ions was highly variable as follows:

a. Pb^{2+} and Cu^{2+} adsorption was not affected by the presence of counter ion types and was independence on the type of regeneration form used.

b. The amount of Zn^{2+} absorbed was highly dependent on the regeneration form used and was not affected by the presence of Ca^{2+} or Na^{+} ions.

c. Similar effects of the Ca^{2+} or Na^{+} were observed on the adsorption capacity of Cd^{2+} and Ni^{2+} ions.

d. The Na form of reddish zeolitic tuff showed a higher efficiency for Ca^{2+} adsorption than the brownish zeolitic tuff.

19. The flow rate velocity in an ion exchange process shows a significant effect on the adsorption capacity of zeolitic tuff for metal ions.
20. The brownish zeolitic tuff in Na-form shows an especially high efficiency for removing metal ions from solutions in an ion exchange column. The removal of ions can be increased by repeating the regeneration-exhaustion process on the same zeolitic tuff sample.
21. The previously absorbed metal ions are extracted in different percentages depending on the type of extracting solution used, the applied form of zeolitic tuff and also on the

number of regeneration-exhaustion repetitions. One exception was recognised for Cu^{2+} ions, which had the lowest extraction percentage from both zeolitic tuffs using a $CaCl_2$, KNO_3 or $NaNO_3$ regenerate. This might indicate that Cu^{2+} was eliminated by a precipitation process either on the tuff particles or within the structure of zeolite minerals themselves.

22. The amounts of heavy metal desorbed were mainly obtained from the exhausted brownish zeolitic tuffs. Furthermore this was increased by applying a second cycle of regeneration to the brownish zeolitic tuff in Na-form using a $NaNO_3$ regenerate.
23. The highest removal efficiency of heavy metal ions was achieved by use the Na-form of brownish zeolitic tuff in an ion exchange operation accompanied by the presence of high concentrations of counter NH_4^+ and Ca^{2+} ions.

6.2 Recommendations

The results obtained through these experiments are:

1. The use of the exhausted reddish zeolitic tuff with NH_4^+ as a slow release fertiliser.
2. When NH_4^+ or Ca^{2+} are the pollutants to be removed from wastewater, the reddish zeolitic tuff is more efficient than the brownish zeolitic tuff.
3. The use of brownish zeolitic tuff in Na-form for the removal of heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) from wastewater containing these pollutants.
4. The wastewater to be treated should be previously neutralised with CaO and not with NaOH, when an ion exchange column using zeolitic tuff is concerned.

Several studies should be made on some subjects mentioned in this work:

1. The zeolitic tuffs should be studied in detail for their mineralogical compositions, because some minerals were not identifiable through this study.
2. A test should be performed to show the ability of zeolite to remove NH_3 and humidity from the air in animal enclosures or barns.
3. The application of reddish zeolitic tuff as slow releasing fertiliser for ammonium in a real soil-zeolite mixture.