

Untersuchung natürlicher Zeolithgesteine auf ihre Eignung zur Abwasserreinigung

Vom Fachbereich Chemie der Carl von Ossietzky Universität Oldenburg
zur Erlangung des Grades eines Doktors der Naturwissenschaften
(Dr. rer. nat.)
angenommene

Dissertation

Von
Zaid Ali Al Rashdan
aus
Deir Abu Said/Jordanien

Investigation of Natural Zeolitic Tuffs on their Ability for Sewage Cleaning Purposes

Department of Chemistry
Carl von Ossietzky Universität Oldenburg
Dissertation submitted in partial fulfillment of the requierements for Ph.D. of
natural science

Zaid Ali Al Rashdan

Erstreferent: Prof. Dr. Dieter Schuller
Korreferent: apl. Prof. Dr. Axel Brehm

Tag der Disputation: 31.05.2000

List of Tables

Table. B.1 Water resources in Jordan in Million m ³ . (adopted from National environmental strategy for Jordan, 1991).	1
Table B.2. Water uses in Jordanian Million m ³ . (adopted from National environmental strategy for Jordan, 1991).	1
Table 1.1 The relationship between Si/Al ratio and cation exchange capacity of some natural zeolites; after Colella (1996), * Data calculated from unit-cell formula; (after Mumpton (1984).	6
Table (3.1): Chemical compositions (% weight) of brownish and reddish zeolitic tuffs using x-ray fluorescence analytical method *.	30
Table (3.2): Mineralogical composition of Jordanian zeolitic tuffs (% weight)*.	31
Table 3.3 Cation exchange capacity (CEC) evaluated from the mineral component of both zeolitic tuffs.	35
Table 3.4a and b. Cation exchange capacity evaluated from the amount of cations extracted during the regeneration process with different types of salt solutions.	35
Table 3.5 Determination of cation exchange capacity (meq/g) according to different equilibrium reactions.	36
Table 3.6: Represents packed bed density and the attrition resistances of zeolitic tuff sizes.	41
Table 3.7: Surface areas (m ² /g) for different grain size fractions of zeolitic tuffs.	42
Table 4.1 Concentration of plant nutrients in the manure.	43
Table 4.2: Chemical analysis of tap water used for the extraction of NH ₄ ⁺ .	44
Table 4.3 Comparison between the released amount of NH ₄ ⁺ and the total nitrogen.	46
Table 4.4 Cations adsorption / desorption (negative values) from / on the NH ₄ ⁺ - form zeolitic tuffs, (all values are in mg/l).	48
Table 4.5. Extracted amount of cations (mg/kg) from zeolitic tuffs after shaking in distilled water.	55
Table 5.1 Heavy metal solutions with different types of counter ions.	63
Table 5.2 Concentration of ions containing solutions percolated with different flow rate velocities.	65
Table 5.3 Ion concentrations of the different percolation cycles of solutions	53
Table 5.4 Total adsorption capacities of zeolitic tuffs for heavy metal ions (mg/g).	67
Table 5.5 Desorbed amounts of cations in the equilibrium reaction (mg/g).	68
Table 5.6 Adsorption-desorption kinetics on the zeolitic tuffs.	72
Table 5.8 Selectivity of zeolitic tuffs for heavy metal ions.	97

List of Tables

List of Figures

Figure. 1.1 Primary building unit of SiO ₄ and AlO ₄ . Tetrahedra.	3
Figure 1.2. The main secondary building units (SBUs) of zeolite.	4
Figure (3.1): Distribution of grain size fraction of 100g. brownish or reddish zeolitic tuffs after wet sieving for 15 min. (the average of 10 samples).	26
Figure 3.2: Adsorption apparatus for the elimination of ammonia from the atmosphere.	28
Figure (3.3): Identification of zeolite minerals by scanning electron microscopy.	31
Figure 3.4a and b : Eluted cations (mg/g) from the zeolitic tuff during the regeneration process with salt solutions using the batch system.	33
Figure (3.5): The eluted cations (mg/g) from 20 g. zeolitic tuff (R and B represent Reddish and Brownish zeolitic tuffs respectively).	34
Figure 3.6: Weight loss (%) of zeolitic tuffs related to thermal treatment.	37
Figure 3.7: Water gain (%) of zeolitic tuffs related after the thermal treatment.	37
Figure 3.7.1 Ammonia adsorption on the zeolitic tuffs in their different forms of regeneration.	38
Figure 3.7.2a and b Humidity adsorption by the zeolitic tuffs in a different forms of regeneration.	39
Figure 3.8. Represents the pore opening of different zeolite minerals as well as other cations and H ₂ O and NH ₃ .	40
Figure 4.1 The kinetic of NH ₄ ⁺ released from the previously treated zeolitic tuffs with an ammonium standard solution.	46
Figure 4.2a, b and c Cations adsorbed from the tap water used in relation to ammonium ions extraction from the zeolitic tuffs.	47
Figure 4.3a and b Adsorbed amount of ammonium in relation to the addition amount of zeolitic tuffs and the contact time.	49
Figure 4.4a and b Adsorption-desorption amount (in mg) of counter cations.	50
Figure 4.5a and b The amount of phosphor eliminated from the manure.	52
Figure 4.6a and b Amount of NH ₄ ⁺ ions desorbed from the pretreated zeolitic tuffs with the manure.	
Figure 4.7a and b The dissolution properties of phosphor from pre-treated zeolitic tuffs.	56
Figures 4.8a-d Adsorbed/desorbed cations (mg) from the pretreated tuffs.	57
Figure 5.1 Laboratory scale ion exchange column apparatus.	64

List of Figures

Figure 5.2a and b Worked exchange capacity of Jordanian zeolitic tuff for heavy metal ions.	68
Figure 5.2c Ions uptake from solutions using NaA zeolite and the Jordanian zeolitic tuffs in Na-form.	70
Figure 5.3a Effect of regeneration type on the total adsorption capacity of zeolitic tuffs.	71
Figure 5.3 b Desorbed cations (mg/g) from the different forms of zeolitic tuffs.	72
Figures 5.4 a-e Worked exchange capacities for heavy metals as an effect of the neutralisation type.	73
Figure 5.5 Counter ions effect on the adsorption capacity.	76
Figure 5.6 Amount of Ca^{2+} or Na^+ absorbed on the zeolitic tuffs.	77
Figure 5.7 a-c Desorbed amounts of cations (mg/g) in the equilibrium reaction.	78
Figure 5.8 a. Lead breakthrough curves on Jordanian zeolitic tuffs.	80
Figure 5.8 b. Elution curves of Ca^{2+} and Mg^{2+} from the zeolitic tuffs.	81
Figure 5.8 c. Elution curves of Na^+ and K^+ from the zeolitic tuffs.	81
Figure 5.9a Cd^{2+} breakthrough curves and the outgoing of Na^+ ion.	82
Figure 5.9 b Absorbed amount of Cd^{2+} and desorbd amount of cations from zeolitic tuffs.	83
Figure 5.10 a. Cu^{2+} breakthrough curve on Jordanian zeolitic tuffs.	84
Figure 5.10 b Extracted cations from the treated zeolitic tuffs with Cu^{2+} containing solution.	85
Figure 5.11 a. Breakthrough curves of Ni^{2+} on Zeolitic tuffs.	86
Figure 5.11b. Cations eluted from untreated Jordanian zeolitic tuffs after treated with a solution containing Ni^{2+} .	87
Figure 5.12a. Breakthrough curves of Zn^{2+} on the Jordanian zeolitic tuffs.	88
Figure 5.12b. Eluted sequence of cations from zeolitic tuffs pretreated with Zn^{2+} solutions.	89
Figures 5.13 a-e Breakthrough curves of heavy metal ions on natural form Jordanian zeolitic tuffs.	90
Figures 5.14 Absorbed percent of heavy metals during the processes with different flow rates.	93
Figure 5.15 Total desorbed cations from the zeolitic tuff beds (mg/g).	93
Figures 5.16a and b. Extracted cations during the equilibrium process.	94
Figure 5.17 a and b. Formation of mass transfer zone in the zeolitic tuff beds.	95

List of Figures

Figure 5.18 Percent of heavy metals absorbed in relation to the type of regeneration.	96
Figure 5.19a-c The effect of regeneration-exhaustion processes on the adsorption capacity.	98
Figure 5.20a and b Total absorbed/desorbed amount of heavy metal ions (mg/g).	100
Figure 5.21a and b Microphotographs of cations distribution in Na-form zeolitic tuffs after the 3ed percolation treatment..	101
Figures 5.22 Lead elution curves from the zeolitic tuff beds..	102
Figure 5.23 Elution curves of cadmium from the zeolitic tuff beds..	103
Figure 5.24 Elution curves of copper from the zeolitic tuff beds.	104
Figure 5.25 Elution curves of nickel from the zeolitic tuff beds.	105
Figure 5.26 Elution curves of zinc from the zeolitic tuff beds.	105
Figures 5.27a and b Regeneration efficiencies of exhausted zeolitic tuffs.	106
Figure 5.28a and b. Breakthrough curves of metal ions for both beds of zeolitic tuffs in Na-form.	108
Figure 5.29 .Breakthrough curves of counter ions on zeolitic tuffs in Na-form.	109

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

Summary

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.

Zusammenfassung

Zusammenfassung

Diese Arbeit beschäftigt sich mit der Untersuchung der Möglichkeiten in Jordanien vorkommende natürliche Zeolithe für die Entfernung von Nährstoff- und Schwermetallionen aus belastetem Wasser zu verwenden.

Bei den Untersuchungen wurden zwei zeolithhaltige Gesteinssorten verwendet, die als Braune- und Rote-Zeolithe bezeichnet werden. Als Ergebnis stellte sich heraus, daß beide Gemische sehr unterschiedliche Eigenschaften haben.

Die dominanten Zeolithmineralien, die in der Korngrößenfraktion 1-0,315 mm der roten Zeolithe gefunden wurden, sind: Phillipsite, Chabazite und Harmotome. Bei Analyse der gleichen Korngrößenfraktion der braunen Zeolithe stellten sich als die dominanten Zeolithmineralien Phillipsite, Faujasite und Harmotom dar.

Die Ergebnisse der Bestimmung der gesamten Ionenaustauschkapazität zeigen relativ große Schwankungen. Diese Unterschiede hängen von verschiedenen Randbedingungen ab: Die Methode (Batch-Reaktor oder Ionenaustauschsäule) mit der die Analyse durchgeführt wird, hat ebenso Einfluß wie die Wahl der verwendeten Salzlösung. Die Ergebnisse der Kationaustauschkapazitätsversuche zeigen, daß die roten Zeolithe (2,96 meq/g) eine merkbar höhere Kapazität als die braunen Zeolithe (1,84 meq/g) haben.

Die Ergebnisse der Zeolithadsorptionskapazität wurden in einem Versuch erzielt, bei dem auf Ionenaustauschsäulen aus einem Luftstrom Wasserdampf und Ammoniak adsorbiert worden waren. Braune Zeolithe besitzen eine höhere Absorptionskapazität für Wasserdampf als die roten Zeolithe. Die größte Adsorptionskapazität wird bei den braunen Zeolithen nach thermischer Aktivierung durch Aufheizen auf eine Temperatur von 150°-250°C erreicht.

Die mit verdünnten Säurelösungen behandelten Zeolithproben zeigten keine veränderte Absorptionskapazität für H₂O, jedoch für NH₃. Die Wirkung der chemischen Behandlung auf die beiden Zeolithe ergab folgendes: Die höchste Absorptionskapazität für NH₃ zeigte die Ca-Form der beiden Zeolith-Arten. Die Absorptionskapazität der chemisch behandelten roten Zeolithe für H₂O wurde nicht wesentlich verändert, bei den braunen Zeolithen wurde bei Verwendung der Ca-Form die höchste Menge an absorbiertem H₂O erreicht.

Die unbehandelte rote Zeolithprobe (1-0,315mm) zeigte, im Vergleich zum braunen Zeolith (20g/kg), eine höhere Absorptionskapazität für NH₄⁺ (46g/kg) nachdem sie mit einer Ammoniumstandardlösung behandelt worden war. Diese Kapazität sank auf Mengen bis zu 2,2g/kg für die roten Zeolithe und 1g/kg für die braunen Zeolithe nachdem beide Zeolithe mit Gülle behandelt worden waren. Diese niedrige Kapazität ergibt sich wegen der hohen Konzentrationen von Fremdkationen (Ca²⁺, K⁺, Na⁺ und Mg²⁺) und wahrscheinlich auch der gelösten und suspendierten Organika. Mit der Adsorption von NH₄⁺ aus der Gülle mit Hilfe von den Zeolithen wurde ebenfalls Phosphor aus der Gülle entfernt. Die Elimination des Phosphors stieg an bei Verwendung einer größeren Menge der Zeolithe. Es war zu bemerken, daß bei der Verwendung von braunen Zeolithen eine höhere adsorbierte Menge an Phosphat (723mg/kg) erreicht wurde. Der Grund hierfür ist, daß der braune Zeolith einen hohen Prozentsatz an CaCO₃ als Begleitmineral enthält.

Mit Hilfe von Leitungswasser oder bidestilliertem Wasser wurde das vorher aus der Standardlösung oder aus der Gülle absorbierte NH₄⁺ eluiert. Als Ergebnis kam heraus, daß aus den roten Zeolithen eine höhere Menge Ammonium (87%), im Vergleich mit den braunen Zeolithen (76%), eluiert wurde. Außerdem erfolgte die Elution des Ammonium aus den roten Zeolithen langsamer, was charakteristisch für diese ist. Die gleichen Ergebnisse wurden bei Untersuchung der Elution des vorher aus der Gülle absorbierten Ammoniums an den Zeolithen gefunden. Benutzt man eine große Menge an Zeolithen für den Elutionsprozeß,

Zusammenfassung

desto besser und langsamer sind die Elutionsverhältnisse für das Ammonium. Bei Verwendung von bidestilliertem Wasser bei der Elution wurde viel Ammonium aus den Zeolithen desorbiert, obwohl dieses Wasser keine Kationen enthielt.

Die Menge des im Elutionsprozeß wieder gelösten Phosphors ist unabhängig von der eingesetzten Zeolithmenge; es scheint jedoch, daß der pH-Wert der Lösung entscheidende Wirkung bei der Elution besitzt.

Die Adsorptionskapazität von natürlichen jordanischen Zeolithen für Schwermetallionen aus einfachen und komplexen Lösungen war Gegenstand der weiteren Untersuchungen. Die Versuche wurden in Batchreaktoren und in Ionenaustauschsäulen durchgeführt. Für die Versuche wurden Zeolithe in verschiedenen Formen verwendet: unbehandelte Formen und Zeolithe in ihren Ca-, K- und Na-Formen

Im Batchreaktorsystem zeigte sich für die Korngrößenfraktion 1-0,315mm der unbehandelten braunen Zeolithe eine höhere Effektivität bei der Entfernung von Cd^{2+} , Cu^{2+} , Ni^{2+} und Zn^{2+} Ionen aus jeweils nur ein Salz enthaltenden Lösungen als für die gleiche Korngrößenfraktion der roten Zeolithe.

Im Gegensatz dazu wurden Pb^{2+} -Ionen von beiden Zeolith-Arten praktisch gleich stark adsorbiert (145-150mg/g). Die Entfernung von Pb^{2+} , Cd^{2+} und Zn^{2+} aus wässrigen Lösungen durch den braunen Zeolithen geschieht nicht nur durch Ionenaustausch sondern auch durch Adsorption an äußeren Oberflächen des Zeolithrohstoffes. Auf der anderen Seite war die Gesamtabsorption von Cd^{2+} , Cu^{2+} , Ni^{2+} und Zn^{2+} beim roten Zeolith geringer als die gesamte Adsorptionskapazität dieses Stoffes. Ähnliche Ergebnisse wurden auch bei der Absorption von Cu^{2+} und Ni^{2+} durch die braunen Zeolithe beobachtet. Es könnte sein, daß nicht alle Ionen in der Lage waren an den Zeolithmineralien Austauschplätze zu finden.

Der Einsatz von Fremdionen (Ca^{2+} und Na^+) hat folgende Effekte:

- Die Adsorption von Pb^{2+} - und Cu^{2+} -Ionen wurde nicht durch die Fremdionen (Ca^{2+} , Na^+ , ...) beeinflußt, sondern war abhängig vom verwendeten Regenerationstypus.
- Die Gesamtadsorption von Zn^{2+} , Cd^{2+} und Ni^{2+} war stark abhängig vom verwendeten Regenerationstypus und wurde ebenfalls nicht durch Ca^{2+} oder Na^+ Ionen in der Lösung beeinflußt.

Die Fließgeschwindigkeit der Lösung beeinflußte die Adsorptionskapazität der Zeolithe in den Ionenaustauschsäulen. Die Durchbruchskurven sind zu höheren Durchsatzvolumina verschoben, wenn eine Durchflußrate von 400ml/Stunde anstelle von 600ml/Stunde gewählt wird. Gleichzeitig wurde eine höhere Effizienz bei der Entfernung der Schwermetallionen beobachtet.

Aus den Ergebnissen für die beiden verwendeten Zeolitharten in ihren regenerierten Formen in den Ionenaustauschsäulen, kann man erkennen, daß die braunen Zeolithe in der Na-Form eine besonders hohe Adsorptionskapazität für Schwermetallionen aus der Lösung besitzen. Des Weiteren stieg ihre Adsorptionskapazität für Schwermetallionen durch Wiederholung des Regeneration-Elutions-Prozesses in der gleichen Ionenaustauschsäule an.

Die Menge der aus den Zeolithen extrahierten Schwermetallionen ist sehr variabel und hängt sowohl stark von der Art der benutzten Regenerationslösung als auch von der vorher verwendeten Zeolithform (Ca-, K- oder Na-Form) ab. Im allgemeinen wurden von der Na-Form der braunen Zeolithe mehr Schwermetallionen adsorbiert und dann auch wieder desorbiert. Die Menge an umgesetzten Schwermetallionen stieg durch einen zweiten Regenerationszyklus noch an. Eine Ausnahme bildete das Cu^{2+} -Ion, welches aus den Zeolithmineralien weitgehend nicht wieder desorbiert wurde. Der Grund hierfür könnte sein, daß das Kupfer durch Fällung an der äußeren Oberfläche des Zeolithrohstoffes oder innerhalb der Zeolithstruktur entfernt worden war.

Background

Background

B1 Water Problem in Jordan

Water supply reservoirs in Jordan (ground and surface water) will soon be exhausted and it is expected to suffer from water shortage in the near future, (Bannayan, 1991; National environment strategy for Jordan, 1991), (Tables 1.1 and 1.2.)

Table. B.1 Water resources in Jordan in Million m³. (adopted from National environmental strategy for Jordan, 1991).

Year Resources	1985		1989		1995		2005	
	Available	Consumed	Available	Consumed	Available	Consumed	Available	Consumed
Renewable ground water.	280	313	280	375	280	359	280	390
Non Renewable ground water	118	25	118	56	118	118	118	118
Surface water	466	466	500	500	594	594	755	755
Treated waste water	20	20	32	32	60	60	60	60
Total	884	824	930	963	1052	1131	1213	1323

Table B.2. Water uses in Jordanian Million m³. (adopted from National environmental strategy for Jordan, 1991).

Water uses	1985	1989	1995	2005
Domestically and industrial uses	200	242	254	301
Agricultural uses	624	721	877	1067
Total	824	963	1131	1368

The growing water consumption has exceeded all resources of the country for domestic, irrigation and industrial purposes, this is mainly as a consequence of its geographic climate (semiarid area); the high population growth rate (3,5%); continuously upgrading in the living standard; and increasing in agricultural and industrial uses.

In Jordan many wastewater treatment plants have been built including: stabilisation ponds, trickling filters, activated sludge, mechanical oxidation ponds, rotating biological contactor (RBC), and combination of activated sludge and trickling filter (Ghraibeh and Rwaifi, 1989). More than 50% of wastewater is treated by stabilisation ponds, this is the

Background

most natural wastewater treatment technique, because of low energy consumption, effectively and economically participle treatment process. The suitability of a pond's performance in Jordan is due to the availability of land with appropriate climatic factors (Temperature, sufficient of sunshine, wind, and low rainfall), (Gharaibeh and Rwaifi, 1989). Low pathogens and fecal organisms with nutrient rich effluents (Ammonium and Phosphor) can be obtained in this process (WHO, 1971).

However, the pollution of ground- and surface-water bodies with nitrate, ammonium, phosphate and heavy metals has increased. These contaminants originate from an incomplete treatment of domestic or industrial wastewater treatment plants or as a result of the treatment system itself (such as stabilisation ponds). This leads to polluted water reservoirs and as a resulting restricted and unsafe reuse for human beings. Eraifej and Abu-Jaber (1999) found that, a very high concentrations of nitrate has been observed in shallow ground water aquifers in NE Jordan (Mafraq area). They suggested the main pollution sources by nitrate are resulted from the effluents of Khirbet al Samra, but also the garbage dump in Akaider area and due to the agricultural activities in the area might be to have a big role on the pollution of the ground water aquifers.

From another environmental point of view, the solubility and leach-ability of ammonium and phosphor compounds from their fertiliser containing materials, are generally the principle sources for eutrophication phenomena, e.g. the King Talal dam in North Jordan (Salameh, 1987). Toxicity to fish and aquatic life from nitrate follows as a consequence and this leads to restricted uses of water reservoirs for man. Thus there is a great need for the use of environmentally friendly fertilisers (Slow release fertiliser technique).

B2 Aim of study.

This study concerns with uses of a low priced locally natural occurring zeolitic tuffs (brownish and reddish zeolitic tuffs) in environmental conservation, as ion exchangers and/or adsorbents, for the following main topics:

1. Characterisation of Jordanian zeolitic tuffs for their mineralogical- and chemical compositions, their cation exchange capacity (CEC), their thermal and acid resistance, their adsorption capacity and other technical properties..
2. Evaluation of Jordanian zeolitic tuffs as slow releasing fertiliser for ammonium and phosphor.
3. The selectivity of Jordanian zeolitic tuff for heavy metal ions (Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) from wastewaters.

Acknowledgement

I am very indebted to Prof. Dr. Dieter Schuller, the Head of Eco-chemistry and Environmental analysis research group at Oldenburg university who gave me the chance to research on interaction-effects between Zeolites and ions in aqueous solutions under his supervision; his intensive supervisions, meaningful suggestions and strong discussions encouraged me during this research.

I thank to Prof. Dr. Frank Rößner and Dr. Axel Brehm from Technische Chemie I and II research groups for their suggestions and discussions. Special thanks also are due to Prof. Dr. Sameh Gharaibeh, the department of Earth and Environmental Science –Yarmouk university, Jordan for his special encouragement and advice's to me during the research time. Thanks are also due to Prof. Dr. I. Dwairi for supplying the zeolite sample (brownish zeolitic tuff).

I thank also all the Professors Carmine Colella, Michele Pansini and Alan Deyer who sent me a very important publication concerning my research. Special thanks are due to Prof. Dr. Reinhard Fischer and his work group at Bremen University, who helped me by the mineralogical analysis of zeolite samples using x-ray diffraction method.

Special thanks are due to the members of the research group Ökochemie und Umweltanalytik at Oldenburg university. I express a great thank and appreciation to Barbara Schroeter- Schuller, Bettina Behrens, Norbert Werner, Walter Harms and Sharif Notash for their helping and encouragement to complete this research.

A great and special thanks for my friends in germany, Christina Blaich, Wenzel Norzel, Lars Eckmeier, Jörn Anderes and Tharwat- and Anke- Dar Seif and all others who provide me by their helps. I am very grateful for the DAAD (Deutscher Akademischer Austauschdienst) for the financial support during the study period in Germany (1995-2000).

Finally a great thank for my mother, sisters and brothers to whom this work will be dedicated.

To My Parents, Sisters and Brothers

Table of Contents

Table of Contents

List of Tables	I
List of Figures	II
Summary (in English)	V
Summary (in German)	IX
Background	1
B1 Water Problem in Jordan	1
B2 Aim of study	2
Chapter 1. Natural Zeolite: Introduction and Properties.	3
1.1 Introduction	3
1.2 Zeolite Structures	3
1.3 Formation and Occurrence of zeolite minerals	5
1.4 Properties of natural zeolite	5
1.4.1 Cation-Exchange Capacity (CEC)	5
1.4.2 Adsorption Property	6
1.4.3 Extensive Properties	7
1.5 Uses of Natural Zeolite	7
1.6 Jordanian Natural Zeolite	8
Chapter 2. Aqua-Environmental System Pollution with Heavy Metals and Plant Nutrients.	9
2.1 Heavy metals (Lead, Cadmium, Copper, Nickel and Zink)	9
2.1.1 Environmental and health risks	9
2.1.2 Treatment methods	10
2.1.2.1 Chemical precipitation	11
2.1.2.2 Ion exchange method	11
2.1.3 Applications of natural zeolite for the removal of heavy metals from wastewater (Previous work)	12
2.1 Plant nutrients (Ammonium and Phosphor)	15
2.2.1 Resources	15
2.2.2 Environmental pollution and health risks	16
2.2.3 Removal processes of Ammonium and Phosphor	17
2.2.3.1 Ammonium	17
2.2.3.1.1 Nitrification-de-nitrification	17

Table of Contents

2.2.3.1.2	Breakpoint chlorination	18
2.2.3.1.3	Air stripping	18
2.2.3.1.4	Ion exchange	18
2.2.3.1.4.1	Natural zeolite (Previous work)	18
2.2.3.2	Phosphorus Removal	21
2.2.4	Alternative environmental friendly fertiliser materials	22
Chapter 3. Jordanian Zeolitic tuffs: Chemistry, Mineralogy and Physical Characteristics.		25
3.1	Materials	25
3.2	Methods	26
3.3	Results and discussion	29
3.2.1	Chemical Analysis	29
3.2.2	Mineralogy	30
3.2.3	Total Cation Exchange Capacity (CEC)	32
3.2.3.1	Batch experiment.	32
3.2.3.2	Ion exchange column	34
3.2.4	Thermal Stability	36
3.2.5	Adsorption Capacity	38
3.2.6	Extensive Properties	41
3.2.6.1	Packed bed density and wet attrition resistance	41
3.2.6.2	Surface area	41
Chapter 4. Evaluation of Zeolitic Tuffs as Slow release Fertiliser		43
4.1	Material	43
4.2	Methods	43
4.2.1	Exhaustion process	43
4.2.1.1	Standard solution.	44
4.2.1.2	Animal manure	44
4.2.2	Released process	44
4.3	Results and Discussion	45
4.3.1	Standard solution	45
4.3.1.1	Nitrogen Exchange Capacities of Zeolite	45
4.3.1.2	Release Properties	45
4.3.2	Animal Manure	48
4.3.2.1	Plant nutrient loading capacities of zeolitic tuffs	48

Table of Contents

4.3.2.2 Extraction Process	53
4.3.2.2.1 Ammonium	53
4.3.2.2.2 Phosphor	55
4.3.2.2.3 Other plant nutrients	56
Chapter 5. Removal of Heavy Metals from Industrial Wastewater using Natural Zeolite	60
5.1 Introduction	60
5.1.1 Batch reactor system	60
5.1.2 Ion Exchange Process	60
5.2 Materials	61
5.2.1 Samples preparation	62
5.3 Methods	62
5.3.1 Batch system	62
5.3.1.1 Adsorption capacity of metal ions	62
5.3.1.2 Effect of regeneration form	63
5.3.1.3 Effect of counter cation types	63
5.3.2 Ion exchange column	64
5.3.2.1 Adsorption capacity	64
5.3.2.2 Effluent velocity effect on the adsorption capacity	65
5.3.2.3 Effect of regeneration type	66
5.4 Results and discussion	67
5.4.1 Batch reactor system	67
5.4.1.1 Adsorption capacity of heavy metals	67
5.4.1.2 Effect of regeneration form	70
5.4.1.3 Effect of counter cations	73
5.4.2 Ion exchange column	79
5.4.2.1 Adsorption capacity of heavy metals	79
5.4.2.1.1 Lead	79
5.4.2.1.2 Cadmium	82
5.4.2.1.3 Copper	84
5.4.2.1.4 Nickel	85
5.4.2.1.5 Zinc	87
5.4.2.2 Effect of the effluent velocity on the adsorption capacity	89
5.4.2.3 Effect of the regeneration form	96

Table of Contents

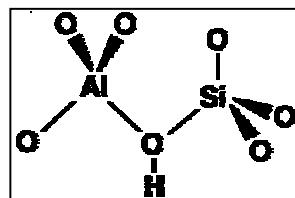
5.4.2.3.1	Regeneration efficiency of zeolitic tuff	102
5.4.2.4	Synthetic wastewater	107
Chapter 6. Conclusions and Recommendations		110
6.1	Conclusions	110
6.2	Recommendations	113
References		114
Appendices		125

Chapter 1. Natural Zeolite: Introduction and Properties.

1.1 Introduction

Natural zeolite minerals are secondary minerals and can be defined as crystalline, hydrated alumino-silicates of alkali and alkaline-earth cations that consist of infinite or finite three dimensional crystal structures of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra, which are linked together by the sharing of oxygen atoms (Mumpton, 1983, Flanigen 1983 and Gottardi, 1978), (Figure 1.1). Their structure contains channels and pores filled with a certain amount of water and exchangeable cations. This water can evaporate when heated to about 250°C (dehydration) and is regained at room temperature (re-hydration) (Gottardi, 1985), also some of cations constituent may be exchangeable from the zeolite inner cavities and pores without any major change of zeolite structure (Mumpton, 1983).

Figure. 1.1 Primary building unit of SiO_4 and AlO_4 . Tetrahedra



Zeolite minerals were first discovered in Sweden by Cronstedt in 1756, (Gottardi, 1978), who gave them their name, which comes from the Greek word meaning the “boiling stones”. Since that time, about 50 zeolite natural species have been accounted for, and in the late 1940's, work carried out on developing a synthesis zeolite under hydro-thermal conditions (temperature $< 100^\circ\text{C}$ and at normal atmospheric pressure), more than 100 species have been synthesised in the laboratory, which have no natural counterparts (Mumpton, 1978).

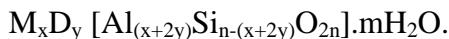
1.2 Zeolite Structures

Zeolite structure contains two types of building units namely, primary and secondary . A primary building unit (PBU) is the simpler and is illustrated in figure 1.1, a tetrahedron of (TO_4) of 4 oxygen ions surrounding a central ion of either Si^{4+} or Al^{3+} . These PBU are linked together to form a three-dimensional framework and nearly all oxygen ions are shared by two tetrahedra (Flangin, 1983; Gottardi, 1985). This arrangement reduces the oxygen: silicon ratio to 2:1, and if tetrahedra were centred by Si the chemical formula of its framework would be

Chapter 1. Natural Zeolite: Introduction and Properties.

Si_nO_{2n} , and the structure would be electrically neutral like Quartz (SiO_2). However , in zeolite structure some of the quadrivalent Si is replaced by trivalent; thus $(\text{Al}_m\text{Si}_{n-m}\text{O}_{2n})^{m-}$, giving rise to a deficiency of positive charge in the zeolite frameworks, and this is balanced by mono- and divalent cations, such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , located outside the tetrahedra; in the channels and pores (Mumpton, 1983, Gottardi, 1985; 1978).

The general formula for natural zeolite according to Gottardi can be given as:



where: $\text{Al}_{(x+2y)}\text{Si}_{n-(x+2y)}\text{O}_{2n}$ represent the framework atom

M: Na^+ , K^+ , or other monovalent cations, and

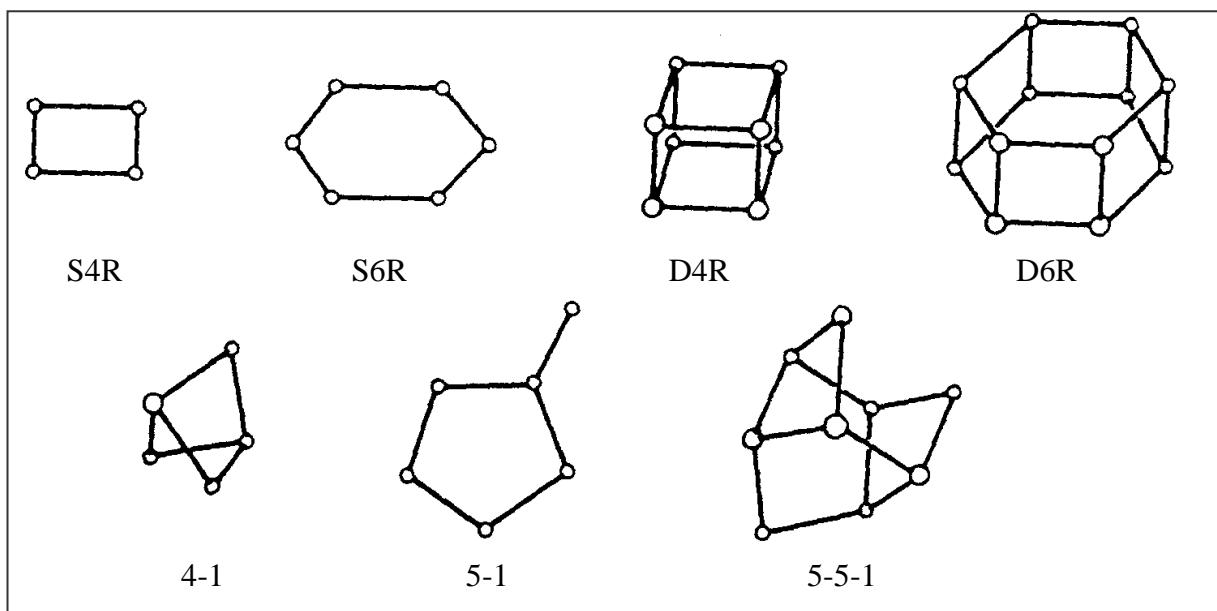
D: Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and other divalent cations, (usually $m \leq n$).

Zeolite structure also contains secondary building units (SBUs), which are formed by the linking of primary building tetrahedral (PBU). They consist of single and double rings of tetrahedra, forming the three dimensional structure of the zeolite material.

Secondary building units may be assembled in different ways to produce different types of frameworks (Figure 1.2). According to Gottardi (1978) the main secondary building units (SBUs) are:

- a.- The 4 ring silicate, single or double (S4R and D4R),
- b.- The 6 ring silicate, single or double (S6R and D6R),
- c.- The fibrous-zeolite unit (4-1),
- d.- The Mordenite-unit (5-1),
- e.- and the stilbite-unit (4-4-1).

Figure 1.2. The main secondary building units (SBUs) of zeolite. (after Gottardi, 1978)



1.3 Formation and Occurrence of zeolite minerals

The formation of sedimentary zeolites can occur by the reaction of volcanic glass (ash) or other alumino-silicate materials with pervading pore waters (ground-, lake-, or seawater). Zeolites are most readily found in alkaline environments ($\text{pH}>8$) because silica is more soluble under these conditions and thus the supply of most essential reactant is greater. Furthermore, because Ca, K, and Na are essential for zeolite structure formations; zeolites tend to form in an environment where these ions are abundant (Hawkins, 1984).

The formation of zeolites in nature is influenced by numerous factors, such as temperature, pressure, reaction time and the activities of dissolved species such as H^+ , silica, alumina, alkaline and earth- alkaline ions.

Natural zeolite deposits are abundant world wide and available in mineable amounts. Their occurrences are mostly in sedimentary rocks and can be categorised into several types of geological environments including: saline – alkaline lakes; saline, alkaline soil systems, deep sea sediments; hydro-thermal alteration systems; hydro-thermal alteration deposits; and burial diagenetic or low-grade metamorphic rocks, (Hawkins, 1984; Mumpton 1978).

1.4 Properties of natural zeolite

Zeolite mineral species have unique properties which are dependent upon its various crystal structures and thus the type of inner cavities; pores; their size and form. Many of these properties are especially desirable for environmental protection, such as cation exchange capacity, ammonium capacity, acid stability, adsorption properties and wet attrition resistance.

1.4.1 Cation-Exchange Capacity (CEC)

Total CEC is one of the most important characteristics that gives zeolite species its importance in environmental protection at an industrial level. Cation exchange capacity is a measure of the number of counter ions present per unit weight or volume of the zeolite and represents the number of cations available for exchange (Semmens, 1984), in other words, it is a function of the degree of Al substitution for Si in the zeolite framework structure; the greater the substitution, the greater the deficiency of positive charge and the greater the number of alkali or earth alkaline cations required for electrical neutrality, (Table 1.1), (Mumpton, 1984).

Chapter 1. Natural Zeolite: Introduction and Properties.

Factors which may reduce the exchange capacity;

1. The size of zeolite pores may be smaller than the ionic radius of some elements; which leads to cations being completely or partially excluded from exchange ; or when the ionic radius of the exchangeable cation is larger than the zeolites pore-volume and / or interconnecting channels and thus leads to ion sieving process (Semmens 1984).
2. Cations could be trapped in structural positions (sodalite units) and, therefore, will not be more exchangeable, (Mumpton, 1984).

Table 1.1 The relationship between Si/Al ratio and cation exchange capacity of some natural zeolites; after Colella (1996), * Data calculated from unit-cell formula; (after Mumpton (1984).

Zeolite	Structure Type cod	CEC* Meq/g	Si/Al ratio ranges
Chabazite	CHA.	3,84	1,43-4,18
Clinoptilolite	HEU.	2,16	2,92-5,04
Erionite	ERI.	3,12	3,05-3,99
Ferrierite	FER.	2,33	3,79-6,14
Heulandite	HEU.	2,91	2,85-4,31
Laumontite	LAU.	4,25	1,95-2,25
Mordenite	MOR.	2,29	4,19-5,79
Phillipsite	PHI.	3,31	1,45-2,87
Faujasite	FAU.	3,39	-

In general, the total cation exchange capacity depends on the type and volume of adsorption sites in zeolite; exchangeable cation sorts; ion radius and charge of cations in the solution, (Semmens and Seyfarth, (1978).

1.4.2 Adsorption Property

The inner structure of zeolite mineral which forms cavities and channels are generally filled with water molecules that form a hydration sphere around the exchangeable cations (such as Ca, Na, K and Mg) (Mumpton, 1984). Much of the water molecules can be removed from the cavities and channels after the zeolite minerals have been heated for several hours at different temperatures between 200 and 350°C; (zeolite dehydration or activation). This permits molecules with a fit diameter to enter the cavities and channels (e.g. water from

Chapter 1. Natural Zeolite: Introduction and Properties.

atmosphere humidity resulted in zeolite rehydration). Otherwise, a molecule with a large diameter would be excluded (Molecular sieving property). Thus, zeolite minerals have the ability to separate different gases on the basis of its size (Mumpton 1984). Also, polar gases are more preferable to be adsorbed than a non polar molecule (Flanigen 1984); for example CO₂ is more preferable than CH₄.

There are many factors which contribute to variations of zeolite adsorption properties, such as Si/Al ratio in the zeolite structure , pore volume and size, type of adsorption sites, size and shape of cages and channels in zeolite structure (Flanigen 1984). Natural zeolites (e.g. Clinoptilolite) have many commercial applications because of their adsorption and ion exchange characteristics, these include: purification of acid natural gas streams, drying and separation of air to produce oxygen and nitrogen (Flanigen 1984). Furthermore, the capability of zeolite to capture and immobilise ammonia in its structure makes it important in reducing odour intensities (Ronald Miner 1984).

1.4.3 Extensive Properties

Natural zeolite deposits are mainly soft, friable, and have a small attrition resistance; depending on its formation in the nature. For their economical uses, zeolite deposits should be rich in zeolite minerals of interest. In cases of use as cation exchange and adsorption materials, it should also have a high porosity in order to allow gases and liquids to be diffused between the grains, an acceptable packed bed density which is an important parameter by large scale applications, and the deposits should be soft enough to be crushed to their desired particle size (Mumpton, 1984). Other characteristics of zeolite deposits should also be determined, such as thermal stability and their resistance in acidic solutions.

1.5 Uses of Natural Zeolite

Based on their unique properties, including its low cost, world-wide distribution of zeolite deposits, more than 300.000 tons of zeolitic tuff is used yearly in the United States; Italy; Hungary; Bulgaria and in other countries of the world. Natural zeolites have been utilised in numerous areas of applications, such as ion exchangers in wastewater treatment (domestically-, industrial-, and agricultural origins); as lightweight aggregate in fertilisers and soil conditioners; in pozzolanic cements and concrete; as filler material in paper industry; as dietary supplements in animal husbandry; separation of nitrogen from air; as reforming petroleum catalysis; and other uses (Mumpton, 1978).

1.6 Jordanian Natural Zeolite

In Northeast Jordan in the Aritain area (120km NE Amman city- Appendix 1.1), Zeolite bearings tuff deposits were first discovered by Dwairi in 1984, who showed its presence (mainly containing Phillipsite mineral) in mineable quantities with traces of Chabazite and Faujasite, and suggested the economical utilisation of these Phillipsitic tuffs in industrial applications (Dwairi, 1987, 1991). According to his study, zeolitic tuff deposits could be subdivided into three types depending on their degree of zeolitisation as follows:

- a- Least zeolitized tuff (Violet zeolitic tuff).
- b- Moderately zeolitic tuff (Brownish zeolitic tuff), and
- c- Highly zeolitic tuff (Reddish zeolitic tuff).

Furthermore, the formation sequence of Jordanian Phillipsite, in the area of discovery, is explained as a reaction process of basaltic glass with alkaline water (Dwairi, 1987) in the following steps:

- a- The reaction between volcanic glass and pore alkaline water leads to palagonite with a thin film of inter granular phillipsite.
- b- Palagonite react with Mg-rich pore solutions leads to Mg-clay.
- c- Mg-clay by alteration guides to alumino-silicate gel.
- d- By the reaction of this gel with Na^+ - and K^+ - rich pore water, phillipsite mineral will be formed in-situ.

Chapter 2. Aqua-Environmental System Pollution with Heavy Metals and Plant Nutrients.

2.1 Heavy metals (Lead, Cadmium, Copper, Nickel and Zink)

Heavy metals occur naturally in very limited amounts of the earth's crust, such as sulphides, sulphate, carbonate or silicate, with an average concentrations of 50 mg/kg for copper (Cu^{2+}), 0,2 mg/kg for cadmium (Cd^{2+}), 15 mg/kg for lead (Pb^{2+}), 75 mg/kg for Nickel (Ni^{2+}) and 70 mg/kg for zinc (Zn^{2+}) (Moore, 1991).

In aquatic systems, heavy metals can be found in different forms, whereby influencing their toxicity for fish and other bio-organisms, including free ions, organic and inorganic complexes, precipitates, mineral particles and metals present in biota. In addition, the toxicity of individual heavy metal cations in water bodies depends on the presence of other metals or poisons as well as on water characteristics such as temperature, pH value, dissolved oxygen and salinity. Furthermore, it depends on the water living organisms like stage of life and their behavioural responses.

In general, the input of heavy metals in aquatic systems originated principally from two main sources, namely naturally or non-point sources and point sources by man's activities. Where the former includes mainly geological weathering of the earth's crust or their ore deposits. While point sources is to be considered the one which responsible for water pollution source with heavy metals. Such sources include domestic- and industrial wastewater effluents.

The widely and rapidly increasing use of heavy metals as raw materials in numerous industries, and thus the increased exploration of their raw materials and due to that the enrichment of heavy metals in wastewater, and this results in concentration ranges from a few of mg/l up to a few hundred mg/l. Their effluent concentrations depends on many factors, such as the industrial processes itself and the treatment methods of their effluents, (paterson, 1975 and Moore, 1991). The above mentioned industries include fertiliser production industries, petroleum refining, basic steel works, battery industry and many others. As a consequent, it leads to the enrichment of heavy metals in aquatic systems.

2.1.1 Environmental and health risks

The presence of heavy metals in aquatic systems is a very earnest problem, from two points of view: their accumulation in the food chain and thus in fish and other water living

Chapter 2. Aqua-Environmental Pollution with Heavy Metals and Plant Nutrients

organisms and their long resistance time. Furthermore, the food chain structure is very sensitive to this type of pollution. From the other side, the uses of such polluted water reservoirs either as drinking water (household uses) and also for industry uses will be restricted. Also this type of pollution would make the water organism more restricted as food source for humans, where it represents a very important source of protein by increasing world populations.

It is important to remember that traces of some heavy metals like Zn^{2+} , Co^{2+} , and Cu^{2+} , with very low concentrations (as traces) are essential for living organisms and have an important place in biological life as catalysts (for many enzymes functions) or to form hemoglobin. Such metals becomes toxic after excessive intakes. The intake methods are mainly from food, drinking water as well as by inhalation from the atmosphere, the latter is considered a negligible source in non polluted urban areas.

Cadmium (Cd^{2+}), a non essential element, considered the most toxic element to human life and is more toxic than Pb^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} . Cadmium has the ability to replace Zn^{2+} from Zn-containing metalloenzymes in an irreversible reaction, which results in the destruction of normal metabolism.

Copper (Cu^{2+}) is an essential element in many enzymes. It is found as a component of blood protein in snails. When lacking, it may be responsible for functional defects of some enzymatic activity of copper. An excessive intake of copper results in its accumulation in the liver. In general, its toxicity is increased by low intake concentrations of Mo^{2+} , Zn^{2+} and SO_4^- .

Lead (Pb^{2+}) is a non essential element for living organisms and is an accumulative poison. It is similar to Ca^{2+} for metabolism processes and in its mobilisation from bone as well as its deposition in bone. Under normal conditions lead is retained up to 90% in the human skeleton. Because of the large affinity of lead for thiol and phosphate-containing ligands, it inhibits the biosynthesis of heme, thus affecting the membrane permeability of kidney, liver and also brain cells.

Zinc (Zn^{2+}) and nickel are less toxic metals, the former is the most abundant trace element in human body. It functions as a cofactor, where many enzymes depends upon it as well as many body cells.

2.1.2. Treatment methods

The removal of heavy metals from waters can be achieved by several methods: chemical precipitation, adsorption on activated carbon, evaporation, reverse osmosis and ion exchange methods. (Paterson 1975 and Moore 1991).

2.1.2.1 Chemical precipitation

Chemical precipitation is the traditional method for removing heavy metal ions from wastewater as well as the polluted waters. Principally, the process involves the conversion of soluble metal salts to insoluble salts uses pH adjustment, an addition of chemical precipitant, coagulants and flocculation. Typically, heavy metal precipitate from the water solutions as hydroxides, sulphides or carbonates. These salts can be formed by the addition of limestone, lime, caustic soda, magnesium hydroxide, sodium sulphide and sodium carbonate to a volume of water.

The precipitation process can create a gelatine metal salts that remain in suspension in the solution by electrostatic surface charge, which giving rise to prevent aggregation and reduce the separation efficiency. Therefore, coagulants are often added to overcome the repulsive forces of the suspensions, the formation of complexes of the metal which may be highly charged and the entrapment of individual particles in the chemical precipitate formed. The commonly used coagulants are lime, alum, ferric- chloride or –sulphate, sodium aluminate, polyaluminum chloride and ferrous sulphate. The addition of coagulants is mainly followed by flocculation process, which is a slow mixing process in a flocculator in which the suspensions are brought into contact to promote their agglomeration through the sedimentation process.

Lime is more often preferred for this process, besides its efficiency for heavy metal removals, it is also used to remove color and turbidity, and to remove ammonia by the air stripping process. Furthermore, the characteristics of the produced sludge is easier to handle, thickening, dewatering and its suitability for filter pressing at a low cost. Additionally, lime is more available with acceptable costs and more popular base causing coagulation and sedimentation (Paterson, 1975).

The treated effluent by chemical precipitation method tends to increase in effluent alkalinity.. Also, the possibility of recovery of some heavy metal cations from the sludge for reuse might be reduced. In addition, by application of this treatment process, the heavy metal concentration limits may not be reached that is allowed by law (Appendix 2.1). Pre-treatment methods for ammonia (NH_3^+), cyanide (CN^{2+}) and chromium (Cr^{6+}) prior to the precipitation process are essential and lead to higher efficient. Where ammonia and cyanide may reduce the precipitation effectively, the chromium (Cr^{6+}) should be reduced to Cr^{3+} , which could form a poorly soluble chromiumhydroxide (Cr(OH)_3). Therefore, an additional treatment process beyond chemical precipitation methods is sometimes required for higher reductions of heavy metal concentrations, and thus, in order to achieve the land's effluent discharge limits.

Methods such as ion exchange method, electrodialysis or reverse osmosis should be used, (Herzenberg, 1983).

2.1.2.2 Ion exchange method

Ion exchange involves a reversible exchange of ions between a solution and a solid phase (ion exchanger media) that are both in direct contact. The ion exchanger could be an organic resin, synthetic zeolite, or a natural material like zeolite.

A suitable ion exchange media should have significant characteristics not only a high selectivity for an individual cation but also the capability to be regenerated, either for possible reuse for the same purpose or for the recovery process for some high economic value of metals.

Ion exchange resins are preferred for purification of wasterawters as well as polluted waters, and this is because of their high cation exchange capacity (CEC), higher reaction rates and resistance to aggressive environments. In contrast, natural zeolites are characterised by their high cation exchange selectivity, resistance to temperature and ionizing radiation (Colella, 1996)

2.1.3 Applications of natural zeolite for the removal of heavy metals from wastewater (Previous work)

Many significant factors must be taken into account, when natural zeolites is concern to be used for the removal of heavy metals from wastewater effluents as an advanced treatment. Loizidou and Townsend (1987) indicated that the selectivity property of natural zeolites for the removal of heavy metals from aqueous solutions is not the only important factor which must be taken into consideration, but also the ability of this zeolite to be regenerated. Regeneration means both the recovery capability of heavy metals from the exhausted zeolite in high concentration forms and also the possibility of reuse of this zeolite for treatment in other polluted solution bodies.

Loizidou and Townsend (1987) noted that both naturally ferrierite and mordenite have a lower exchange capacity for lead than natural clinoptilolite. Nevertheless, they have proposed their usefulness of lead removal from wastewater effluents.

Semmens and Seyfarth (1978) indicated the high selectivity of naturally Clinoptilolite (previously pretreated with a concentrated NaCl solution) for heavy metal removal from simulated and real wastewaters. In batch reactor systems this is done by adding Na-

Chapter 2. Aqua-Environmental Pollution with Heavy Metals and Plant Nutrients

Clinoptilolite directly to a solution volume, the selectivity sequence was found as follows: $Pb^{2+} \approx Ba^{2+} >> Cu^{2+}, Zn^{2+}, Cd^{2+}$.

The removal capacities for these metals was, however, influenced by the treatment methods of Na-clinoptilolite. The pre-treated Clinoptilolite sample, with 10% nitric acid and afterwards converted to Na^+ form, showed less effectiveness than the sample which was directly converted to Na form. However, the latter had shown an increasing of effluent pH value, as a result from leaching of significant concentration of sodium bicarbonate. Semmens and Seyfarth recommended the uses of Clinoptilolite in Na form for removal of heavy metals from wastewater effluents.

The treatment process for drinking water and purifying it from ammonium and/or traces of heavy metals by installation of a Clinoptilolite fixed bed was studied by Blanchard et al. (1984). They noted that Na-Clinoptilolite in bed form showed a good selectivity for water pollutants as follows: $Pb^{2+} > NH_4^+ > Cd^{2+}, Cu^{2+}, Sr^{2+} > Zn^{2+} > Co^+$. By analysis of the used zeolite in the bed, they found that the removal process of these metals was not only occurred through the exchange capacity of the zeolite bed but was also accomplished by the precipitation of some metal ions on the surface of zeolite particles. Ions like Cu^{2+} are identified on the particles as Atacamite ($CuCl_2 \cdot 2Cu(OH)_2$). Also they investigated the better regeneration conditions of the exhausted zeolite bed. By percolating a 40 bed volume (BV) of 20 g l^{-1} NaCl solution at pH 4 with flow rate of 10 BV/hour as a result is a high effectively recovery of the presorbed pollutants.

Two other interesting natural zeolite minerals that contribute to the removal of heavy metals from wastewater are Chabazite and Phillipsite. Colella and Pansini (1988); Pansini and Colella (1989 and 1990) suggested using natural Chabazite in Na-form for lead removal from wastewaters. They indicated that Campanian tuff (Chabazite), with a cation exchange capacity of about 1.7 meq/g, is very selective for the removal of this cation from solutions, either in the absence or presence of any counter cations like Na^+ , but it should not exceed 1g/l of content. Otherwise, increasing the Na-concentration in the solution may lead to less selectivity and overall efficiency of Chabazitic tuffs for lead. However, Chabazitic tuff is best for lead removal from wastewater when the lead ion concentration is not too high (few tenths mg/l Pb^{2+}) as well as the flow rate not exceeding about 10BV/min, (Pansini and Colella 1990). Also, as a result of their research on the regeneration process, they indicated that the exhausted Chabazite bed could be effectively regenerated with only 20BV of 1M $NaNO_3$ solution, achieving about 80% of the original cation exchange capacity (CEC), while by percolating 200 BV, the cation exchange capacity did not reach more than 85%. Therefore

they strongly recommended the application of campanian tuff in the battery storage manufacturing industry as a suitable alternative to the chemically precipitation method.

The recovery of lead from wastewater can also be performed by adding powdered zeolite bearings rock directly to wastewater, in this case containing 20 mg/l lead (Pb^{2+}) with interfering cations (simulated as ceramic manufacture effluent) (Pansini 1996), which contain a considerable amount of Phillipsite or Chabazite. He found that by adding 1g/l (zeolite to solution) the lead concentration is brought from 20mg/l to as low as 0.2 mg/l in slightly more than 2 hours of contact time, but that by adding more zeolite (4g/l) no more than 10 minutes is needed. The produced zeolite sludge is suggested to be reused in cement matrix manufacture (Albino et al. 1995).

An evaluation of natural Phillipsite, Chabazite, Clinoptilolite, Mordenite and Ferrierite for Cr^{3+} removal from wastewaters in batch system (direct addition of zeolite to solutions) was obtained by Pansini (1996). He found the adsorption reaction was irreversible. However, adding zeolite to a solution brings the Cr^{3+} concentration from 10-30 mg/l to below 2mg/l, which is attained in 1-10 minutes. Because of the irreversibility reaction of Cr^{3+} in the regeneration solution, he suggested the reuse of exhausted zeolite powder in cement matrix, and also because of the lower release of Chromium during the leaching process and the good compressive strength of their cement mortars, which are higher in quality for commercial blended cements, (Cioffi et al. 1991).

Na-Phillipsite, Na-Chabazite and K-Phillipsite, were compared in their applications for massive lead removal from large amounts of wastewater (in presence or absence of interfering cations) in a fixed bed system. The results were obtained by Pansini et al. (1996) and showed that the Na-Phillipsite has a higher adsorption capacity for lead than the latter two. The exhausted Phillipsite bed required about 70 BV of regenerant solution (1M of $NaNO_3$) to elute 70% of lead contained in the bed.

Concerning cadmium (Cd^{2+}) removal from wastewaters using Na-Phillipsite or Na-Chabazite, Colella et al. (1995) found that the later zeolite showed a higher selectivity for Cd^{2+} as well as faster exchange kinetics than Na-Phillipsite. From the fixed bed experiments, they noted that Na-Chabazite affinity was decreased by increasing the counter ion concentration (Na^+) in the wastewater. However, their results showed the application possibilities of Na-Chabazite as a Cd^{2+} exchanger from a solution containing about 100 mg/l Cd^{2+} and the counter ions content (Na^+) not exceeding 100-150 mg/l. The recommendation of Chabazite in Na-form for Cd^{2+} removal is based on both it is exchange capacity for Cd^{2+} and it is regeneration capability. By percolating only 20 BV of 1 M $NaNO_3$ solution, more than 70% of Cd^{2+} could be recovered from the exhausted Chabazite bed in the regenerant effluent.

Recovery of metal ions from acid mine water using natural zeolites was studied by Zamzow and Schultze (1995). They indicated the selectivity series of metal ions on Phillipsite and Clinoptilolite by direct addition of these zeolite bearing rocks to volume of water. The selectivity appears as follows: $\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Al}^{3+} > \text{Ni}^{2+}$. However, 370 g from Hector Clinoptilolite or 403 g Phillipsite was required to completely remove these metals from 1 litre water in ion exchange column with a flow rate of 5 BV/h. By considering the regeneration experiment on the exhausted Phillipsite bed, they found the effective regeneration results was by percolating 3% NaCl solution at flow rate of 4 BV/hrs., followed by CaCl₂ and KCl. Whereby the former (NaCl) 70% of pollutants were recovered. Less regeneration effectivity resulted after applying MgCl₂ solution, and it is reached only about 5%.

2.1 Plant nutrients (Ammonium and Phosphor)

2.2.1 Resources

Ammonium and phosphorus compounds are essential elements for plant growth as macro nutrients, and they should be found in natural water resources in detectable but limited amounts. The rapid increase of the concentration of such plant nutrients in water bodies may lead to the pollution of water systems. Phosphorus can be found in surface waters in soluble and insoluble, inorganic or organic forms (ortho- and poly- phosphate and organic bound phosphates). Where two naturally forms of nitrogen bearing compounds can be found, which are organic and inorganic forms. Organic nitrogen includes amino- and amide-nitrogen and some heterocyclic compounds such as pyrimidines and purines. Inorganic forms are ammonia (NH_3^+), nitrate (NO_3^-), nitrite (NO_2^-) and molecular nitrogen (N_2). Phosphorus as well as nitrogen compounds in surface water bodies originate from natural and from man-made sources (Kayser, 1987).

The main natural source of nitrogen compounds in surface water originates from the fixation process of molecular nitrogen (N_2) by water plants. In addition, the excrement and wastes of wild life flora and fauna, excrement of water plants and other aquatic organisms, and leaching of soils are another natural sources of nitrogen as well as phosphorus sources in surface water. Another main natural source of phosphorus is produced during runoff, erosion and leaching of phosphate-bearing rock in the catchment or recharge area of the water stream system.

The main pollutant sources of interest which originate from, or during man's activity in the environment include:

A. Domestic and industrial wastewater effluents.

A main source of pollution affects surface water by further increasing the concentrations of plant nutrients. This depends on the origin of the wastewater, namely if it is result of household or industrial uses as well as the type of industry.

B. Fertilisation and agricultural waste effluents.

The global increasing uses of nitrogen compounds in fertiliser industries, production of highly soluble fertiliser mixes, urea and other nitrogen based fertilisers, is a very great source of nitrogen pollutants in surface and in ground waters. Due to the fact that food industries produce high concentrations of wastewater containing ammonium, nitrate and nitrite, and a widely and intensive application of highly soluble fertilisers (nitrogen based fertilisers) in agriculture, a huge amount of these compounds are leached with water runoff and come into contact with surface- and/or ground- water.

Furthermore, the intensive uses of phosphorus and nitrogen rich animal manure as a natural fertiliser is also a source of these nutrients in water bodies during leaching and erosion of soils from agricultural areas.

2.2.2 Environmental pollution and health risks

Very low concentrations of ammonium (about 5mg/l) in surface water are very toxic for some species of fish. However, nitrite is even more toxic to aquatic invertebrates at lower concentrations (0.05 mg/l) after long times (96 hrs.) of exposure. Nitrite affects fish and other aquatic invertebrates by favourising the formation of methemoglobin in their bodies, leading to nitrite toxicity. In addition, nitrite may damage the gill membrane, whereby reducing the amount of oxygen passing through it. Under both circumstances, this leads to a reduction in aquatic organisms by making living conditions difficult.

Nitrate in combination with phosphorus compounds in surface water is the main motive for eutrophication of surface water. This phenomena can be defined as an excessive growth of aquatic plants and algae resulted from an extreme excess of nitrate and phosphorus in aquatic systems. It is relatively dominant in stagnant surface water, where the phosphorus is naturally available and also where regular feeding of nitrate and phosphorus from outside sources exists. Because of the meaning of naturally phosphorus sources in water bodies, in comparison to nitrogen, it is very limited. For example, algae needs 10 times more nitrogen than phosphorus. For this reason, phosphorus is responsible for eutrophication phenomena.

Eutrophication has a very harmful ecological effect on surface water. The common relationship between consumers and food producer becomes abnormal. Therefore, more

aquatic plants remain uneaten, and more organic materials and plant excrement are thus added to the eutrophic water system to be decomposed. Increased decomposition, in turn, results in the decrease of oxygen levels (the decomposition environment is usually an anaerobic environment). In addition, methane, hydrogen sulphide and ammonia gases are released, producing undesirable odours. In this new environment. Some fish species which are sensible to oxygen depletion levels tend to be eliminated. Furthermore, new plant species grow, which cannot be eaten or utilised from the system primary consumers, and are therefore eliminated from the system. As well, some organisms are living at the bottom of the water system which prefer the silty-or sandy media tend to die, because of the absence of such media and the accumulation of organic materials.

The eutrophic surface water systems are restricted for human uses, for example, if the water is to be used as (human) drinking water, a costly and difficult treatment process is necessary. Even in this situation, however, the water may remain undesirable, (because of taste, odours, and colour-ration and increased bacteria accumulations).

High concentrations of nitrate (NO_3^-) in drinking water (over 45 mg/l) may cause numerous cases of infant methemoglobinemia, particularly in babies up to six months in age, by reducing the capacity of the blood to carry oxygen. Furthermore, high levels of nitrate can cause changes in animal behaviour and their heart vessels (Shuval and Gruener, 1977 and Mirvish 1991). In addition, the formation of N-nitroso- compounds in the body of animals and perhaps in humans could be as a carcinogenic materials, (Forman 1991, Preussmann, 1982 and 1989, Shuval and Gruener 1977 and Mirvish 1977). N-nitroso compounds result from the reaction of oxidised nitrate to nitrite with amides and amines in animals and perhaps in humans as well.

2.2.3 Removal processes of Ammonium and Phosphor

2.2.3.1 Ammonium

Nitrogen removal from wastewater and polluted water can be achieved by both biological and physical-chemical methods. Such methods are nitrification-denitrification; breakpoint chlorination; air stripping; and selective ion exchange processes.

2.2.3.1.1 Nitrification-de-nitrification

The combination of a nitrification followed by a denitrification process can achieve removal of nitrogen from wastewater. In the nitrification process, the ammonium ions are

oxidised to nitrite (NO_2^-) with help from nitrosomonas bacteria species and the activity of other bacteria species (Nitrobacteria), nitrite is converted to nitrate. This, followed by facultative heterotrophs under anaerobic conditions, that utilise nitrate as a source of oxygen for degradation of organic matter, convert nitrate to the few soluble molecular nitrogen gas (N_2). This whole process is directly influenced by pH and temperature parameters, were the optimum conditions are 6-8 and 10°C-20°C respectively.

2.2.3.1.2 Breakpoint chlorination

Breakpoint chlorination is a process which depends on suitable dosages of chlorine (Cl_2) to treated wastewater to oxidise ammonia into molecular nitrogen (N_2). Higher dosages of chlorine tend to increase the nitrate concentration in the effluent and undesirable side effects can also arise, like the odour gas nitrogen trichloride (NCl_3). The pH is a significant factor affecting the treatment process, so that a continuous adjustment of the solution to pH 6-7 is always necessary. Associated difficulties with this process are over dosages of chlorine and the mineralisation of treated effluents, and as a result, an activated carbon column should be installed as a polishing step for these treatment methods.

2.2.3.1.3 Air stripping

Air stripping method for ammonium removal consists of increasing the solution pH above 11, whereby the ammonium ions are converted to soluble ammonia (NH_3) and then by stripping the ammonia with air. Removal efficiency using this method depends on pH, temperature and on how much air is in contact with the water surface (efficiency of mass transfer). The removal efficiency is dramatically decreased by decreasing temperature.

2.2.3.1.4 Ion exchange

Selective ion exchange is an alternative process for the removal of ammonium from wastewater when proper ion exchangers are found (Kugelmann, 1976). Naturally occurring zeolite minerals (Clinoptilolite) have been found in recent studies which have higher selective adsorption capacities for ammonium than other cations in wastewater (Kugelmann, 1976, Koon and Kaufman, 1975, Klieve and Semmens 1980, Amicarelli et al., 1987)).

2.2.3.1.4.1 Natural zeolite (Previous work)

Jorgensen et al. (1976) indicated that there are many factors which affect the adsorption of ammonium cations from either synthetic or real municipal wastewater. They included the concentration of ammonium in the solution, concentration of counter ions such as Ca^{2+} or Na^+ or other cations. Therefore, the adsorption capacity of Clinoptilolite for ammonium from synthetic wastewater is larger than from real wastewater. In batch reactor systems, the ammonium adsorption capacity is greatly dependant upon the amount of zeolite added, and/or from the contact time between the solution and the zeolite.

A very high wastewater effluent quality can be achieved by applying a combination of chemical precipitation, activated carbon column, anion exchange media and Clinoptilolite (Jorgensen et al. 1976). The removal efficiency of such pollutants like ammonium, phosphorus, suspended solids and organic matter were 90%, 90-99%, 99% and 94% respectively. The regeneration solution which is used after the exhaustion of the zeolite bed can be treated again by the air stripping method. The exhausted zeolite (clinoptilolite) with ammonium is then biologically regenerated with the help of nitrifying bacteria (Semmens et al. 1977). They reported that the regeneration efficiency using slurry can be achieved, but this process remains slow in comparison with the nitrifying process of free ammonium ions in a solution. The biological regeneration rate of the exhausted clinoptilolite may be increased by increasing the slurry concentration or by adding NaCl to the regeneration system. By adding this salt, the regeneration efficiency was increased up to 99%. Other methods of regeneration for exhausted zeolites with ammonia are discussed by Murphy et al. (1976), who indicated the efficiency of regeneration rate during chemical processes, bio-regeneration and thermal regeneration at 300-600°C. The results indicate that the bio-regeneration type required long aeration time, and just 80% of the original zeolite capacity was achieved, while thermal regeneration at 500°C has rate 100% of the original clinoptilolite effective exchange capacity. The better chemical regenerations were achieved by using a NaOH solution, although this almost more than 90% from the total effective exchange capacity.

In some countries, Phillipsite rich tuff has been studied as an alternative to Clinoptilolite. Klieve and Semmens (1980) indicated the ammonium adsorption capacity of Na^+ -regenerated phillipsite from synthetic wastewater is 26% more than that of clinoptilolite, even after its pre treated. In a comparison with different treatment methods of clinoptilolite, Klieve and Semmens found that a better adsorption capacity of ammonium was achieved after its pre-treatment by heating.

Ciambelli et al. (1985) compared Clinoptilolite and Italian phillipsitic tuff in the RIMNUT process as tertiary treatment for ammonium removal from wastewater. Phillipsite adsorption capacity for ammonium with presence of divalent cation in wastewater is comparable to the clinoptilolite, therefor phillipsite is an alternative for ammonium recovery from municipal wastewater. A combination of natural zeolite as ion exchanger for ammonium recovery and/or anionic resin for the removal of phosphors from wastewater in the RIMNUT process were discussed by Liberti et al. (1979, 1995, Lobe and Liberti 1991 and Amicarelli and Liberti (1991). After the regeneration of the exhausted zeolite and resin with Na-solution an acid solution was occurred, respectively, and by adding $MgCl_2 \cdot 6H_2O$, H_3PO_4 , Na_2CO_3 and $NaOH$ to the regeneration eluate, premium, high quality slow release fertilisers ($MgNH_4PO_4 \cdot 6H_2O$) are produced, while the supernatant $NaCl$ solution, after pH correction, can be reused (closed –loop technique). The ammonium removal efficiency achieved higher than 80%, the effluent concentration concentration of ammonium being lower than 15 mg/l..

An investigation by Amicarelli et al. (1987) was carried out on Clinoptilolite, Phillipsite,, Chabazite and a mixture of the later two types (previously converted to Na-form), for ammonium adsorption from wastewater,. They found that both Chabazite and Phillipsite were alternatives for clinoptilolite. Chabazite is a better regenerable zeolitic tuff for which about 90% NH_4^+ removal was achieved with only 10 bed volume (BV) of 0.6M $NaCl$ regenerant solution, due to that Chabazite is the chief zeolite mineral.

Hlavay et al (1983) researched the removal efficiency of ammonia and iron from drinking water by applying a naturally Na-form clinoptilolite. The total ammonium exchange capacity was detected to about 3mg NH_3-N/g zeolite, whereas these ore materials contain only 46% clinoptilolite. The removal efficiency was greatly dependant on the concentration of Ca_2^+ in the solution.

Adding Clinoptilolite bearing rocks to the municipal wastewater before the biological treatment unit could improve the treatment efficiency (Kallo 1995). Kallo found that the addition of 40-80 mg of clinoptilolite tuff to 1 litre of sewage resulted in an increase of the settling rate of suspended solids as well as an increase in the biological activity of living sludge and that with the composting and de-watering of the produced sludge is made easier when compared with normal sludge. In addition, an elimination of phosphor was observed. The regeneration solution (alkaline KCl and $NaCl$) was treated by the air stripping method producing ammonia. The ammonia was then adsorbed in phosphoric acid producing a solution of ammonium-hydrophosphat fertiliser.

Garcia Hernandez et al. (1992) found that the tertiary treatment of wastewater using phillipsite rich tuff is very useful not just for removing ammonium but also for the removal of

phosphor, calcium, magnesium, inorganic contaminants, bacteria (total coliforms, faecal coliforms and fecal streptococci) and for soluble organic matter. Depending on the amount of ammonium, phosphor and other plant nutrients, they suggested that the exhausted zeolite could be used as a slow-releasing fertiliser.

Kithome et al. (1998) worked on the adsorption-desorption properties of ammonium on natural clinoptilolite. They indicated the ability of clinoptilolite to absorb and desorb ammonia from simulated ammonia solutions where the pH value and the ammonia concentration have significant effects. They found that the sorbed amounts of ammonium was increased by increasing pH value and the influent concentration of the solution contains ammonia. By increasing the initial NH_4^+ concentration, the NH_4^+ exchange rate was decreased. An increase in pH also results in faster sorption and in a greater amount of NH_4^+ being sorbed. They indicated the potential use of clinoptilolite as an adsorbent for NH_4^+ which could be used as a slow release fertiliser.

Park and Komarneni (1998) made a comparison between different zeolite type (clinoptilolite, phillipsite erionite and chabazite) for nitrogen absorption from a NH_4Cl saturated solution or by applying the molten treatment method with NH_4NO_3 . They found that more nitrogen was occluded by Phillipsite mineral (76g N/Kg). In contrast, when Phillipsite was treated with the saturated ammonium solution, it was only able to adsorb a capacity of 46g N/kg. With the help of simulated soil solution as an extract solution, they found that phillipsite is the slowest released nitrogen fertiliser material. It is therefore evident that salt occluded zeolites, and especially Phillipsite are potential candidates as slow release fertilisers.

Zeolite materials can also be applied (as ion exchange columns) to remove ammonium from fish hatchery systems, (see Piper and Smith (1983) and Colella et al. (1984) and Ciambelli et al (1984)).

Since the discovery of phillipsite bearing rocks in NE Jordan, many investigations of this material, including the physical characteristics and the possibility for industrial applications, have been carried out (Dwairi, 1991, 1993, 1998). Jordanian phillipsitic tuffs are characterised by their high cation exchange capacity (phillipsite content 35-60%), low thermal stability, where the phillipsite structure collapsed at a temperature range between 250-350°C, and after heating it gained 10% water after 24 hrs. at room temperature.

Jordanian Phillipsite is fairly unstable. It loses about 7% of its crystal structure after 24 hrs. at pH 5. The efficiency of phillipsitic tuff in removing ammonium from solutions (containing 5 and 30 mg/l) was determined by Dwairi (1993). He found that Phillipsitic tuff (60% Phillipsite) is more effective for ammonium adsorption than the Hungarian Clinoptilolite bearings rock (55% Clinoptilolite).

2.2.3.2 Phosphorus Removal

The main method for phosphorus removal from water and wastewater depends principally on the formation of an insoluble form. This can be achieved by adding chemicals to the solutions to form the insoluble precipitation as salts. Many varieties of chemicals can be used for these purposes but, economically, the use of iron, aluminium salts, or lime is recommended (Kugelman 1976, Wuhrmann 1968).

2.2.4 Alternative environmental friendly fertiliser materials

The uses of fertilisers in agriculture play a big role for successful and economical agriculture yields. Chemical fertilisers such as nitrogen bearing fertilisers or mixed fertilisers are highly soluble in soil solutions and directly available from the plant roots to absorbed, therefore they function as a short term nutrient source for plants. The rapid leaching of such nutrients, especially nitrogen compounds (as NO_3^-), from agricultural soils to ground or surface water should be considered an important source of pollution with nitrate.

Due to the difficulties in determining the accurate amount of nitrogen to be utilised from plants, which results from other naturally occurring nitrogen sources not being taken into consideration, such as the native soil nitrogen, nitrate concentration in irrigation water, nitrogen income by precipitation, and biological fixation of nitrogen. Other factors should be also take into consideration, namely, the type and texture of soil, the availability of other plant nutrients in the soil system including macro and micro nutrient, which are P, K, Ca, and Mg , Cu, Mo, Mn, and Zn respectively.

The application method of chemically-based fertiliser either by injection (spreading on the soil) or dissolution with the irrigation water (in case of soluble fertiliser) must also be taken into consideration. In order to achieve more benefits from chemically based fertilisers as well as to minimise the leachability of nitrate from agriculture production fields, and therefore to prevent water pollution from these source, some application methods were discussed by Pereira and dos Santos (1991). The addition of urea's inhibitors to organic nitrogen fertiliser may increase the residence time of nitrogen in soil and achieve a function as slow release fertiliser, but the best inhibitors for this function must be take into account and is until now has not been sufficient researched. Another method of concern is the use of coated fertiliser, which are less soluble nutrients material, from such fertiliser the availability ratio is in combined to its uptake from the plants.

In contrast, uses of organic fertilisers in both natural types as animal or agricultural waste and synthetic as urea could provide more plant utilisations for the nutrients and soil fertility. Organic fertilisers are characterised by containing huge amounts of plant nutrients (N, P, K, Na, and others), their longer time of residence in soil (available for the plants over time), and relatively solubility in soil solutions. As a result, these worked as long term nutrient sources, and also the leachability of nitrate from such organic fertilisers with irrigation water is very limited. Therefore, the naturally organic fertilisers could be the better alternative for chemically based fertilisers (Pereira and dos Santos, 1991).

Factors that make the uses of animal waste inappropriate as a fertiliser include odour releasing, storage and handling problems, difficulties in transport including costs, and the difficulty of assessing their fertilisation value (Organisation for economic co-operation and development-OECD (1986). On the other hand, the intensive applications and misuses of organic fertiliser may lead to a serious environmental pollution with nitrate, phosphate, as well as with heavy metals, (OECD, 1986, Pereira and Santos, 1991 and Kithome et al. (1998).

The high affinity of natural zeolites for ammonium adsorption and the possibility of releasing it over a long time is of special interest in its application as long term fertiliser (see above section 2.2.3.1.4.1). However, the uses of zeolite as soil conditioner may not only enhance the availability of plant nutrients but also the physical and chemical characteristics of the soil, such as pH, cation exchange capacity, minimum loss of nutrients by leaching and the soil structure, (Allen and Ming 1995).

The characteristics (its high cation exchange capacity, its high affinity for ammonium adsorption, its capacities for ammonia immobilisation and capturing, and due to its content of soluble calcium and iron, which may reduce the concentration of phosphor by precipitation) could influence its uses in the treatment of animal waste, as well as the fixation of ammonium from the liquid or solid waste by using natural zeolites. These properties could prevent the nitrification process and thus the leaching to ground and surface water (Barbarick and Pierela, 1984; Lewis, et al. 1984).

Natural zeolite bearings rock (Clinoptilolite) have the ability to fix immobilised ammonia from the air, thus in effect to reduce odours or to immobilise ammonia nitrogen in manure by adding Phillipsitic tuff (Dwairi, 1998 and Ronald Miner, 1984), which is a great problem for live stocks producers and the neighbouring residents. By adding zeolitic tuff (Phillipsitic tuff) to the manure the ammonia conservation is prolonged (Dwairi, 1998). Dwairi also found that phillipsite bearing tuff has a higher efficiency for this purpose than by adding gypsum, super phosphate and phosphoric acid.

Chapter 2. Aqua-Environmental Pollution with Heavy Metals and Plant Nutrients

Many recent researches have continued the application of NH_4^+ -saturated zeolite-phosphate rock system as a slow release fertiliser for the NH_4^+ , PO_4^{3-} , and Ca^{2+} (Lai and Eberl, 1986 and Dwairi, 1998) and also for soil conditioners. The process by which Ca^{2+} is exchanged on the NH_4^+ leads to more dissolution of Apatite. Other investigations was done by Eberl et al. (1995) and Ming et al. (1995) on Zeolite-soil phosphate rock in greenhouse experiments. Eberl et al. (1995) found that as a result of adding NH_4^+ -clinoptilolite to phosphate rock in the soil in a ration of 0-7-5 and 100-400mg P/kg respectively, a top growth of Sudan grass was obtained and the yields were increased by as much as 65% over the control experiments. By making an analysis on the plant tissue and soil matrix, they indicated a significant increase of nutrient concentration in both plant matter and soil, which resulted by increasing the amount of clinoptilolite added to the system. However, Ming et al. (1995) indicated that by using a mixture of synthetic apatite with NH_4^+ - and K^+ - saturated clinoptilolite to form Zeoponic substrata for growing wheat in greenhouse, a higher dry matter of growing wheat is produced in comparison to the control samples , where other substrata were used. Also, they found a higher capacity of supplying micro and macro nutrients (such as N, P, K, Ca, Mg, and others) to plants.

Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser

This research reviews the experimental work in which zeolitic tuffs have been used for the removal of plant nutrients from soluble animal waste (manure), and evaluates the exhausted zeolite tuffs with ammonium and phosphate for use as slow release fertilisers for these two nutrients.

4.1 Material

Non pre-treated Jordanian zeolitic tuffs (1-0.315 mm grain size fractions) were used in the experiments. Their characteristics have been previously studied in detail (Chapter 2). Cow manure for this research was obtained from an animal husbandry in north-west Germany (city of Oldenburg) (table 4.1).

Table 4.1 Concentration of plant nutrients in the manure.

Nutrients	TKN-N*	PO ₄ ³⁻ -P	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	pH	λ μScm ⁻¹
concentration (mg/l)	1922	123	436	61	307	3195	7,98	16180

* TKN. represents total kjeldahl nitrogen

4.2 Methods

The zeolitic tuff materials were applied in Batch reactor systems and Ion exchange columns for the exhaustion process, and the extraction process, the batch system was only applied, as follows:

4.2.1 Exhaustion process

The exhausted zeolite bearings rocks were achieved by percolating an ammonium standard solution (1M NH₄Cl) or during their contact with the animal manure in a batch reactor system.

4.2.1.1 Standard solution.

1M of NH₄Cl solution was percolated throughout a 20 g. zeolite bed (in up-down flow) with an effluent ratio of about 200ml/h, which was controlled by a peristaltic pump (B-Braun type 870-202). After a 6.1 litre (equal to about 310 BV) of ammonium standard solution was passed through the zeolitic beds, the concentrations of Ca²⁺, Mg²⁺, Na⁺ and K⁺ in the ammonium effluent solution were approximately 0.5mg/l. Theoretically, this means that the zeolite beds are totally exhausted with ammonium cations and the ion exchange process can no longer occur.

4.2.1.2 Animal manure

Zeolitic tuffs weighing 1-5 g. of 1-0.315 mm grain size fractions were brought in contact with a filtered amount of manure (25 ml) in polyethylene bottles. The contact time ranged between 1 and 5 days. Other samples of zeolitic tuffs were shacked with manure for two weeks. After that, the contents were filtered and the filtrate was analysed for ammonium, phosphor, sodium, potassium, calcium and magnesium. Additionally, for each experimental group, a sample containing filtered manure without any addition of zeolite materials was taken as a control sample. After 2 weeks contact time, the solution was filtered, and the zeolites was washed several times with de-ionised water, in order to remove the access plant nutrients from the surface of the zeolitic materials, and the zeolite samples were dried at 105 °C for 4 hrs. and cooled in desiccator for the extraction process of plant nutrients.

4.2.2 Released process

The released process (extraction process) of plant nutrients, such as ammonium (NH₄⁺-N) from the previously treated zeolitic tuffs with ammonium standard solution, and NH₄⁺-N, PO₄³⁻-P, K⁺, Na⁺, Ca²⁺ and Mg²⁺ from the pre-treated zeolitic tuffs with manure, was evaluated by monitoring their released concentrations in the extraction solutions in distilled- or tap-water (table 4.2).

Table 4.2: Chemical analysis of tap water used for the extraction of NH₄⁺-N.

Cation Concentration (mg/l)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Tap water (Used for NH ₄ ⁺ -N extraction)	15-45.5 (28.6*)	3.1-7.2 (4.5*)	8.8-17 (12.7*)	N.D.**

* average of 23 analysis ** N.D (concentrations are less than 1 mg/l)

Different weights of the previously treated zeolitic tuffs (0.5, 1, 1.5, 2 and 2.5 grams) were placed in a polyethylene bottles containing distilled- or tap-water (200 ml and 250ml for the extraction process from NH_4^+ - and manure- treated zeolitic tuffs, respectively). The bottles were shaken for 24 hours by using a rotating shaker at room temperature (40 rpm.). The contents were filtered, and the filtrates were analysed for their nutrient concentrations. NH_4^+ -N and PO_4^{3-} -P using photometric methods (Schimadzu-Spectrophotometer UV –120-02); K^+ and Na^+ using a flame photometer (Eppendorf-Beckmann-Photometer 34); and Ca^{2+} and Mg^{2+} were analysed using Polarized Zeeman Atomic absorption Spectrophotometer (Type 180-70). In addition, the total amount of adsorbed plant nutrients in the zeolitic tuffs were determined using acid extractions; the Total Kjeldahl Nitrogen-N (Gerhardt, Vapodest 3-automatic); the total phosphate using the potassium-permanganate extraction method (in an acid solution); and other nutrients using H_2O_2 - HNO_3 extraction method.

4.3 Results and Discussion

4.3.1 Standard solution

4.3.1.1 Nitrogen Exchange Capacities of Zeolite

According to the Total Kjeldahl Nitrogen (TKN), it is found that the 1-0.315 mm grain size fraction of reddish zeolitic tuffs absorbed about 46 g.-N/kg-Zeolite, while the same grain size from the brownish zeolitic tuffs adsorbed only about the half amount (20 g N/kg zeolite). The total adsorption capacities of NH_4^+ -N on zeolitic tuffs show a close correlation with the total cation exchange capacity (CEC) results. In both, the CEC was evaluated from the zeolitic minerals contents or according to the eluted (de-sorbed) cations from zeolitic tuffs during the regeneration process with ammonium standard solution. Similar results of the ammonium exchange capacity (46 g/kg) were previously obtained by Park and Komarneni (1998) for Phillipsitic tuffs with impurities of Clinoptilolite after pretreatment with ammonium standard solution.

4.3.1.2 Release Properties

The release properties of NH_4^+ ions from the NH_4^+ - zeolitic tuffs were tested using tap water as the extraction solution. Each day the zeolite was analysed using a new volume of tap water and the amount of released ammonium in the filtrate after 24 hrs. was determined during 23 days time periods (figure 4.1). The filtrate was analysed for ammonium (NH_4^+ -N) as well as Ca^{2+} , Mg^{2+} , Na^+ and K^+ (figures 4.2a-d).

Figure 4.1 The kinetic of NH_4^+ -N released from the previously treated zeolitic tuffs with An ammonium standard solution.

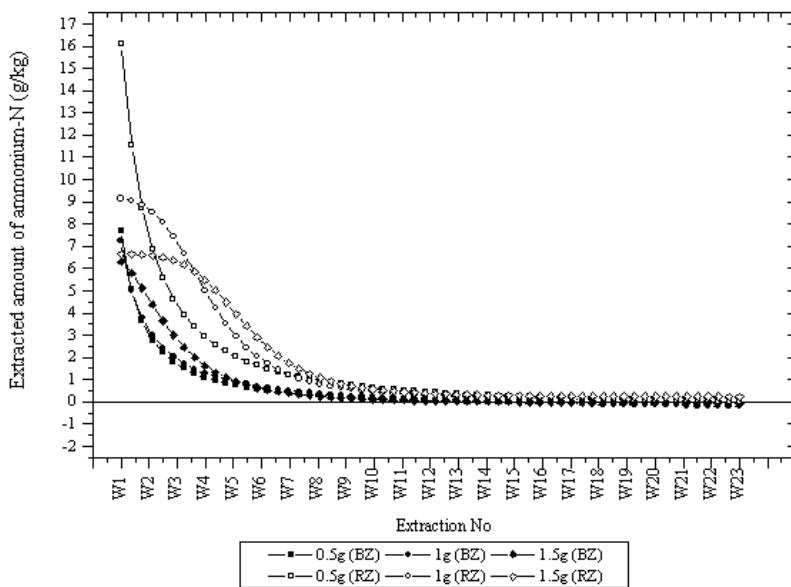


Figure 4.1 shows the release properties of NH_4^+ -N from reddish as well as brownish zeolitic tuffs corresponding to the extraction number. It is clear that the reddish zeolitic material releases ammonium slower than the brownish zeolitic material, and these results were obtained for all weights of zeolitic tuffs (up to the twelfth extraction number). After the 12th extraction number, the release properties of both materials are similar. In the other hand, a more slowly releasing properties are seen better when more reddish zeolitic tuffs was added to the solution (in this case 1.5 g. reddish zeolitic tuffs).

A comparison is made between the released amount of NH_4^+ -N and the total amount of adsorbed total nitrogen (Kjeldahl values) from their exhausted grains fraction 1-0.315mm sample (Table 4.3). The released percent of ammonium ion could approach the total adsorbed amount of nitrogen, if the extraction procedure is repeated more than 23 times. Furthermore, to get a better view of the ammonium extraction kinetics, the filtrates were also analysed for the cations Ca^{2+} , Mg^{2+} and Na^+ , which are represent in figures 4.2a-c.

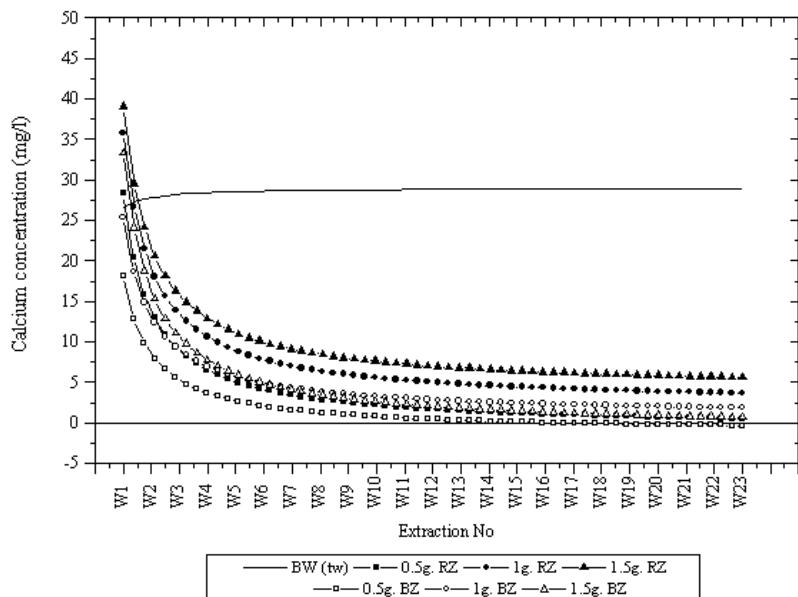
Table 4.3 Comparison between the released amount of NH_4^+ -N and the total nitrogen

Zeolitic tuff	TKN-N	NH_4^+ -N released	Released %
RZT	46 g/kg	40 g/kg	87 %
BZT	21 g/kg	16 g/kg	76 %

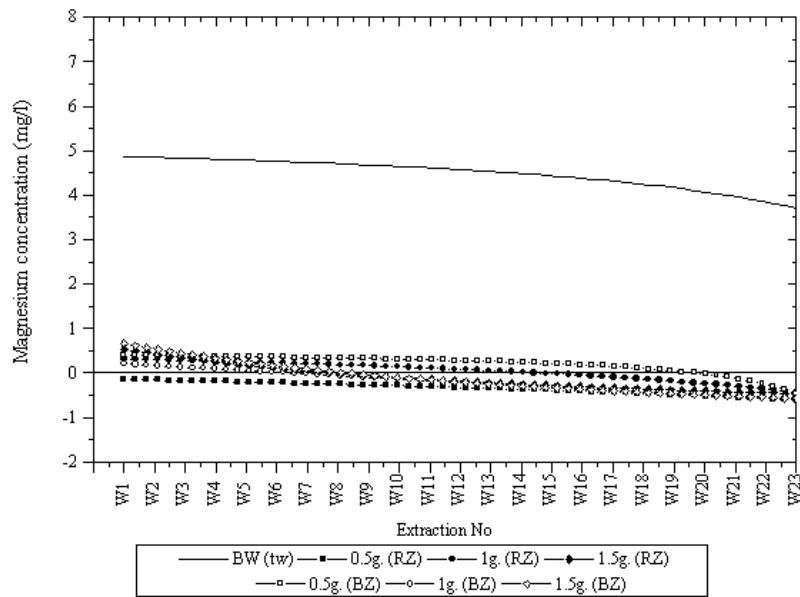
Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

Figure 4.2a, b and c Cations adsorbed from the tap water used in relation to ammonium ions extraction from the zeolitic tuffs (Appendices 4.1-4.3).

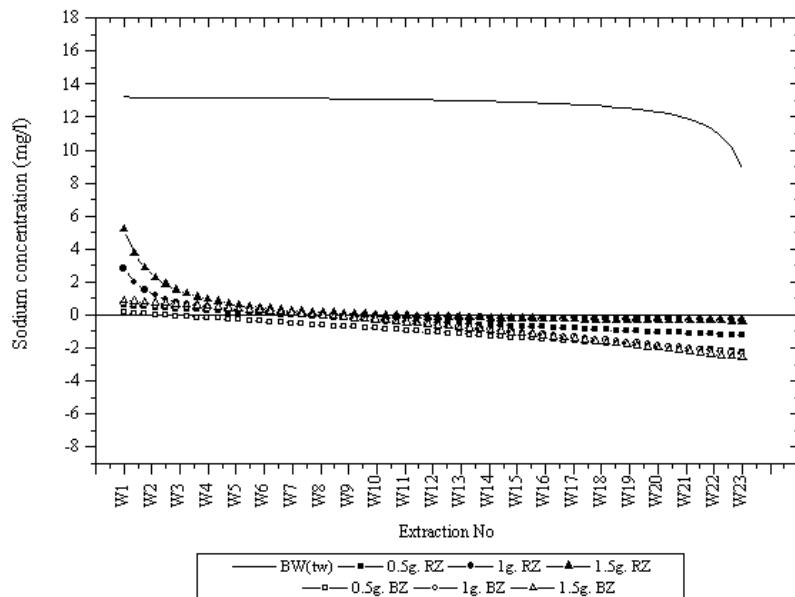
a. Calcium



b. Magnesium



c. Sodium



The kinetics of cation adsorption are shown in table 4.4, which are fitting curves calculated from the data of the cation adsorption from the extracted solution. It is apparent that, the reddish zeolitic tuffs have a higher selectivity for Ca^{2+} and thus a higher ammonium desorption from their exhausted zeolitic tuffs.

Table 4.4 Cations adsorption / desorption (negative values) from / on the NH_4^+ - form zeolitic tuffs, (all values are in mg/l).

Zeolite sample	Desorbed NH_4^+ -N	Adsorbed Ca^{2+}	Adsorbed Mg^{2+}	Adsorbed Na^+
0.5g. NH_4^+ -BZT	31	45	5	16
1g. NH_4^+ -BZT	62	110	-5	16
1.5g. NH_4^+ -BZT	96	108	-3	18
0.5g. NH_4^+ -RZT	81	91	-8	40
1g. NH_4^+ -RZT	163	91	1	41
1.5g. NH_4^+ -RZT	238	224	-3	40

4.3.2 Animal Manure

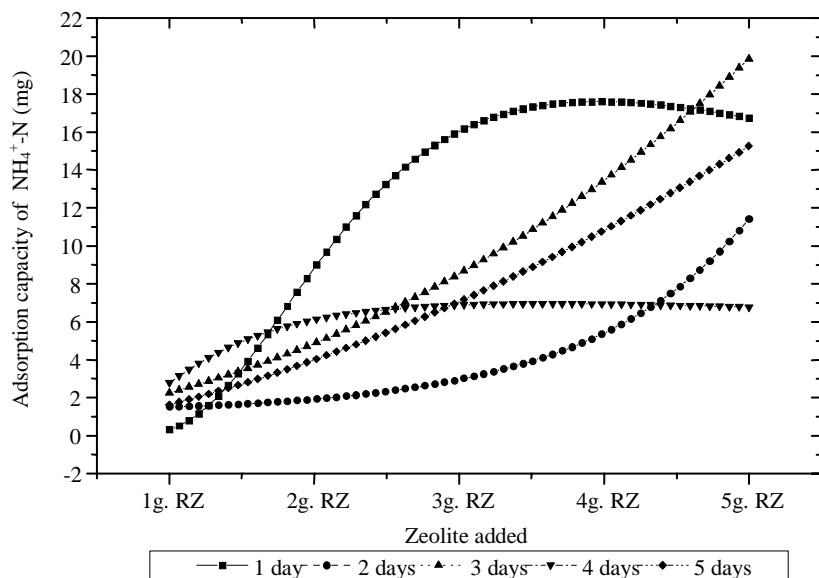
4.3.2.1 Plant nutrient loading capacities of zeolitic tuffs

The uptake rate of the total kjeldahl nitrogen-N from the manure by adding both reddish or brownish zeolitic tuffs are plotted against the contact time (time of shaking) and are shown

in figures 4.3a and b. The total nitrogen uptake by addition both zeolitic tuffs are seen to be homogeneous, and that depends on the amount of zeolitic tuffs added in the same group of experiment (Jorgensen et al., 1976). In contrast, a longer contact time does not necessarily lead to a reduction in the amount of ammonium from the manure. This could be explained by the adsorption properties of zeolitic tuffs for ammonium ions, which could take place fast, that shaking for one day is enough to achieve a higher adsorption capacity for ammonium ions. In general, a longer contact time between the manure and the used zeolitic tuffs (in a period of 2-5 days contact time) had not achieved a same result, but somehow show the effect of the contact time, whereby a longer contact time as well as increasing the addition amount of zeolitic tuffs, a higher adsorption capacity of ammonium ion were achieved. This results indicate the highly effect of counter cations in the manure (figure 4.4 a and b).

Figure 4.3a and b Adsorbed amount of ammonium in relation to the addition amount of zeolitic tuffs and the contact time (Appendices 4.4) .

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuff

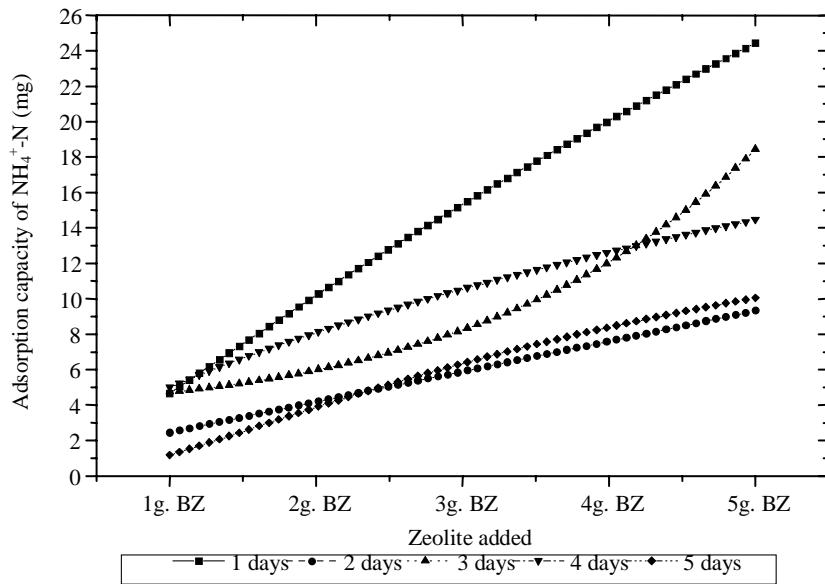
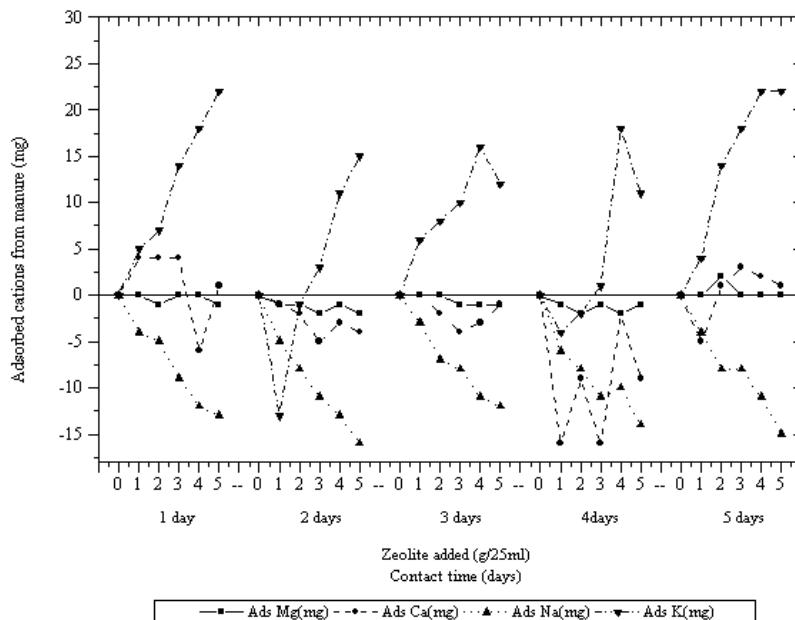


Figure 4.4a and b Adsorption-desorption amount (in mg) of counter cations (Appendix 4.5)

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuff

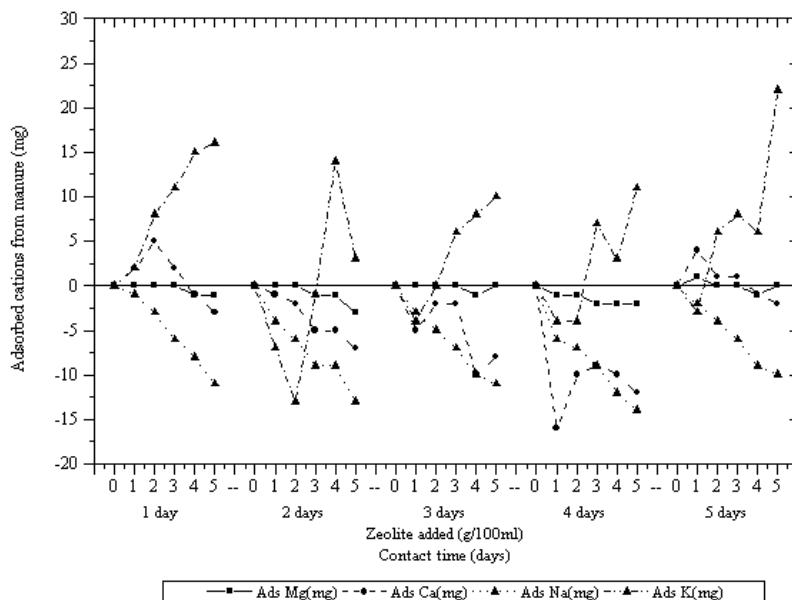


Figure 4.4 a and b represent the kinetic adsorption or desorption of cations from the manure on/or from the zeolitic tuffs. In both figures, the zeolite minerals mainly tend to adsorb potassium ions, while calcium and sodium are more likely to be desorbed from the zeolite material. This indicates that, the cation exchange capacity of zeolitic tuffs for ammonium adsorption is highly affected by the counter cation (mainly K^+ , which was found in very high concentrations in the manure (3195 mg/l)). It is necessary to remember that the data in these figures are not to be take as definite values, but only the apparent adsorption, because of the high concentration of these cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) which are found in the manure in relation to the desorbed cations from the added zeolite bearing rocks (zeolitic tuff) to the manure.

The amount of nitrogen eliminated, through ammonium (NH_4^+-N) from the manure, after two weeks of contact time was very low (2200 mg/kg reddish zeolitic tuffs and 862 mg/kg brownish zeolitic tuffs) when compared with the adsorption capacity from the ammonium standard solution, which are. The observed cation exchange capacities are less than the results obtained by using clinoptilolite bearings material (Hlavay et al. 1983). Hlavay found that the clinoptilolite bearing tuff (46% clinoptilolite) shows a capacity for ammonium adsorption of about 3 mg/g in a process for drinking water treatment, but the concentration of counter cations in the manure is much higher than in any type of drinking water. These low adsorption values are mainly a result from the effect of the high concentrations of counter cations like Ca^{2+} , Mg^{2+} , Na^+ and K^+ (Jorgensen et al., 1976, Hlavay et al., 1983, Kithome et

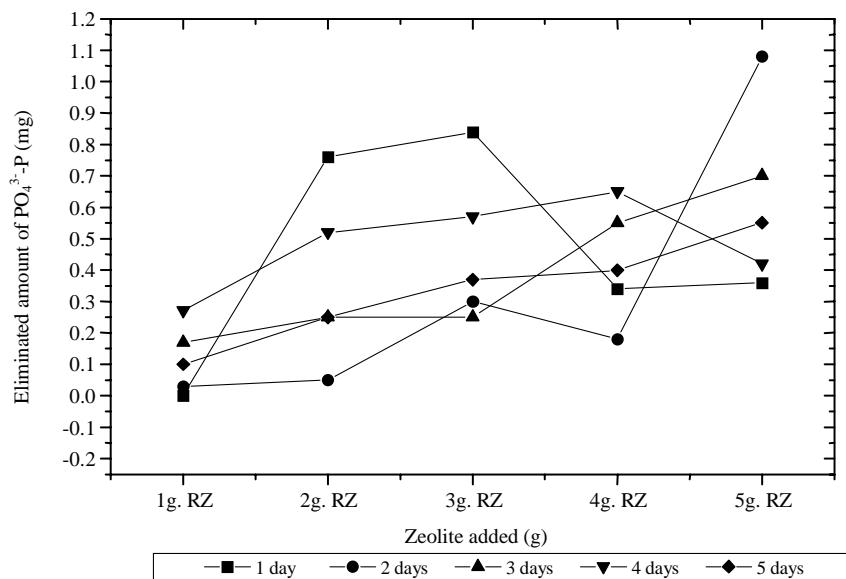
Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

al., 1998) (see table 4.1), and a high concentration of nitrogen compounds found in different forms of its occurrence (organic forms of nitrogen)

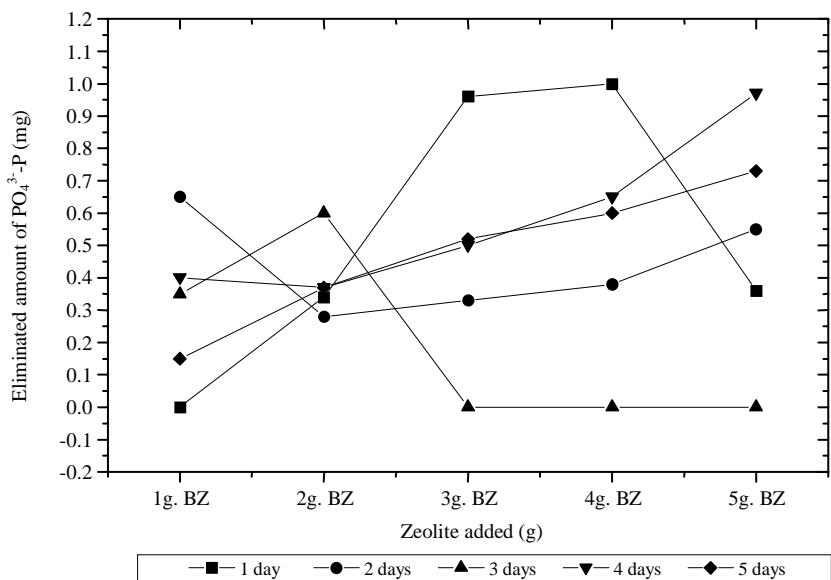
In addition, the total amount of eliminated phosphor is 592 mg/kg and 723 mg/kg for reddish and brownish zeolitic tuffs, respectively. The percent of removal after two weeks of shaking is mainly due to a precipitation process of phosphorus with calcium carbonate containing zeolitic tuffs. Whereby the brownish zeolitic tuff contains a higher percentage of calcium oxide (9.2) than that of the reddish material (8.8), (table 3.2 and 3.3) The elimination properties of zeolitic tuffs for phosphor from the manure are highly dependent on the amount of zeolitic tuffs added (that means adding a higher amount of calcium carbonate) but its independence on the contact time, for periods longer than a day, (figures 4.5 a and b).

Figure 4.5a and b The amount of phosphor eliminated from the manure

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuff



4.3.2.2 Extraction Process

The desorption properties of both zeolitic tuffs (Reddish and Brownish zeolitic tuffs) were carried out using distilled, and tap water as an extraction solution. The extraction process was continuously repeated 10 times until the eluted concentrations of NH_4^+ -N and PO_4^{3-} -P were seen to be constant in concentration.

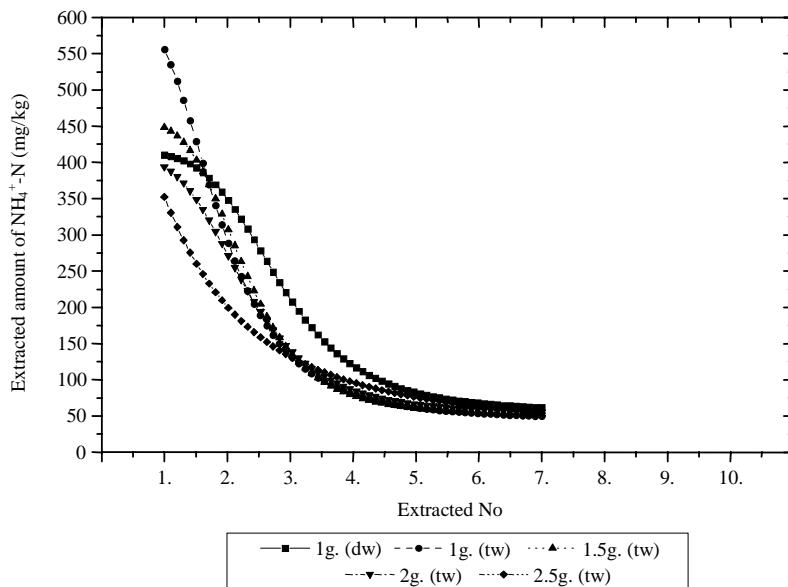
4.3.2.2.1 Ammonium

The extraction amount of ammonium ions from the previously treated zeolitic tuffs with manure are represented in figures 4.6a and b.

Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

Figure 4.6a and b Amount of NH_4^+ -N desorbed from the pretreated zeolitic tuffs with the manure.

a. Reddish zeolitic tuff



b. Brownish zeolitic tuff

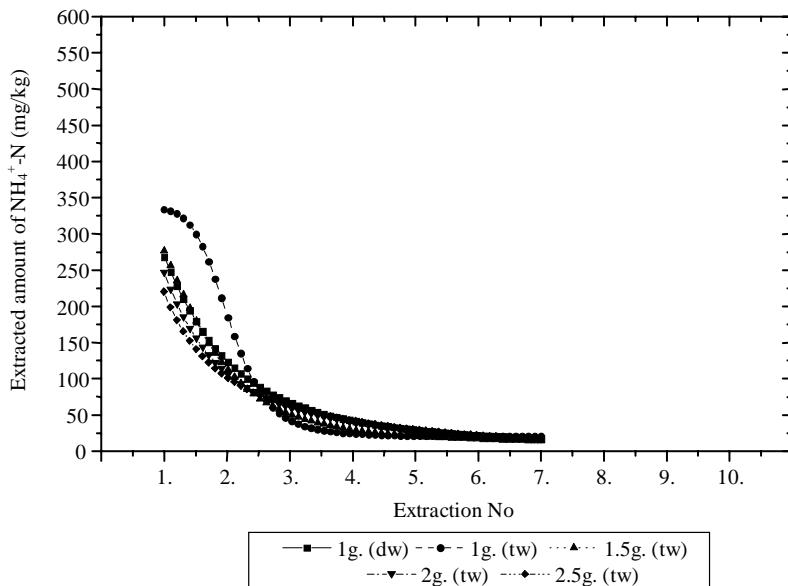


Figure 4.6a and b show that, either by using distilled, or tap water, an extracted amount of NH_4^+ -N was achieved. In the case of distilled water, an exchange reaction occurred between the ammonium ion in the zeolite minerals and the eluted amount of cations (either

Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

during the attrition between the zeolite grains themselves (table 4.5), or some cations which are adsorbed from the manure on the surface of zeolite particles). In addition, when tap water was used as an extraction solution, a cation exchange balance could not be evaluated, and this is because the exchange reaction not only occurred between the cations in the solution and the adsorbed ammonium ion in the zeolite, but also with the another previously adsorbed cation from the manure (e.g. K⁺). Furthermore, the desorption process also depends on the amount of desorbed cations from the exhausted zeolitic tuffs and the amount of cations presents in the tap water.

Table 4.5. Extracted amount of cations (mg/kg) from zeolitic tuffs after shaking in distilled water.

Zeolitic tuffs	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Sum
Reddish zeolitic tuff	26	172	388	26	612
Brownish zeolitic tuff	9	101	825	26	961

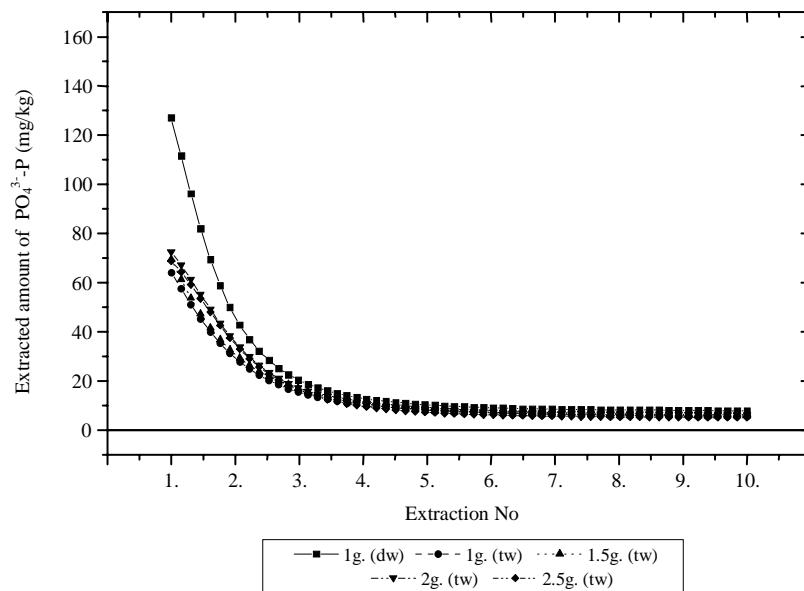
4.3.2.2.2 Phosphor

The concentration of extracted phosphor in the solutions from zeolitic tuffs can be influenced by the desorption capacity of ammonium ions from the zeolitic tuffs during the cation exchange process, as well as by the extracted cations from the zeolitic tuffs, and thus may influence the pH value of the extracted solutions. Consequently, a dissolution process of the precipitated phosphate occurred (Lai and Eberl, 1986 and Dwairi 1998). The pH values of the extraction solutions in tap water at the end of the process were not very different from the initial pH values. Figures 4.7a and b show that the amount of extracted phosphor is higher when using distilled water than using tap water. These results could again demonstrate the effect of pH-value of the extraction solutions, while the distilled water used has a pH value of 5.5-5.9, and the pH-value of the tap water ranges 7.6-7.8. The dissolution property of phosphor from zeolitic tuffs under this extraction conditions seems homogeneous and the pretreated zeolitic tuffs are able to dissolve phosphor continuously with the extraction time. The amount of zeolitic tuff used did not effect the released behaviour of phosphor in this case.

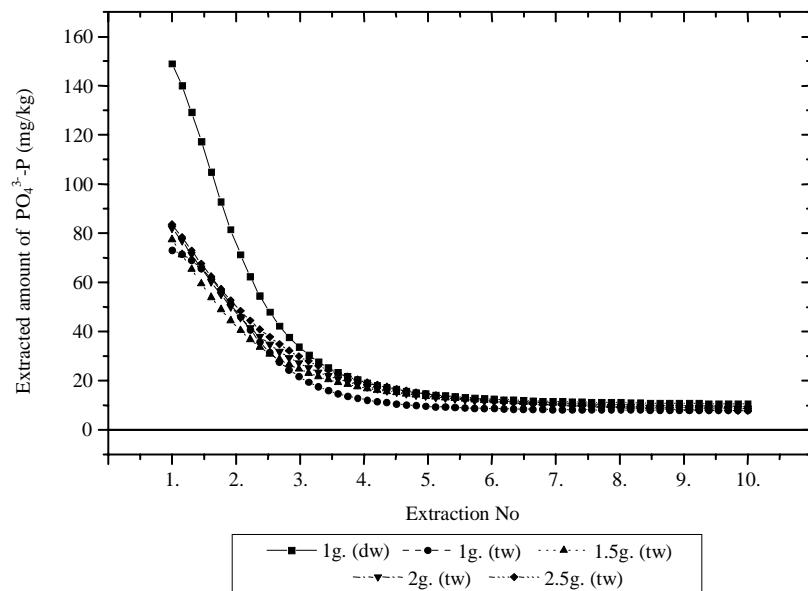
Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

Figure 4.7a and b The dissolution properties of phosphor from pre-treated zeolitic tuffs

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuff



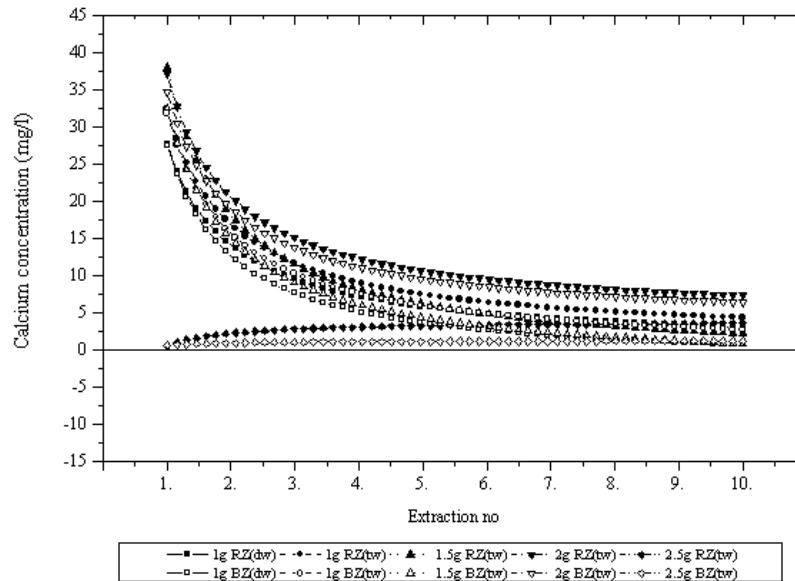
4.3.2.2.3 Other plant nutrients

Figure 4.8 a, b, c and d. represent the desorption / adsorption properties of pretreated zeolitic tuffs with manure for Ca^{2+} , Mg^{2+} , Na^+ and K^+ .

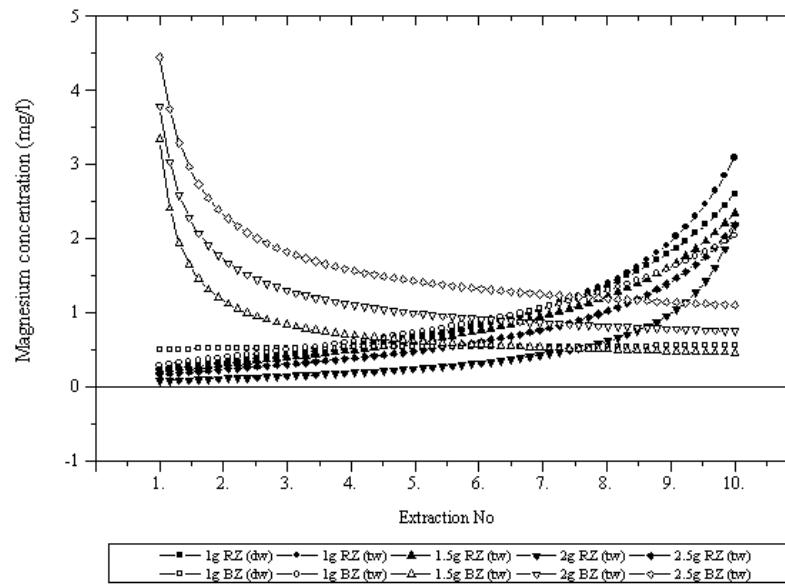
Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

Figures 4.8a-d Adsorbed/desorbed cations (mg) from the pretreated tuffs (Appendix 4.6).

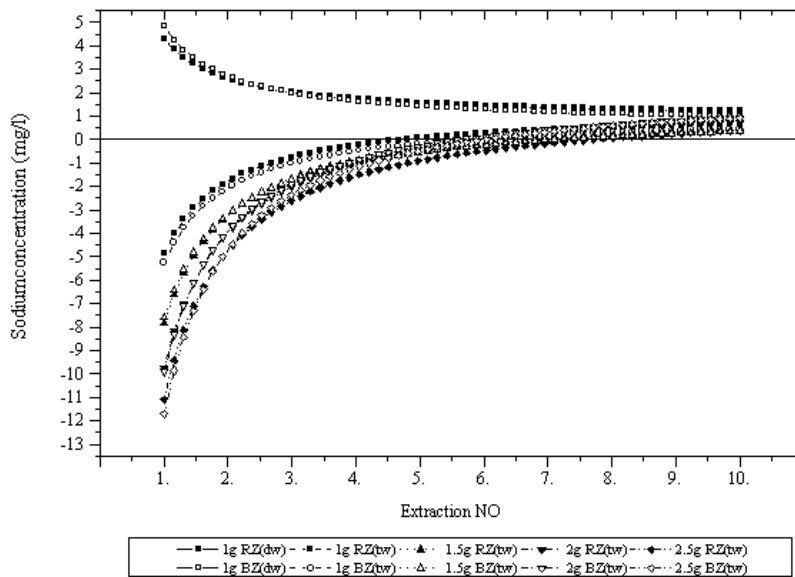
a. Calcium



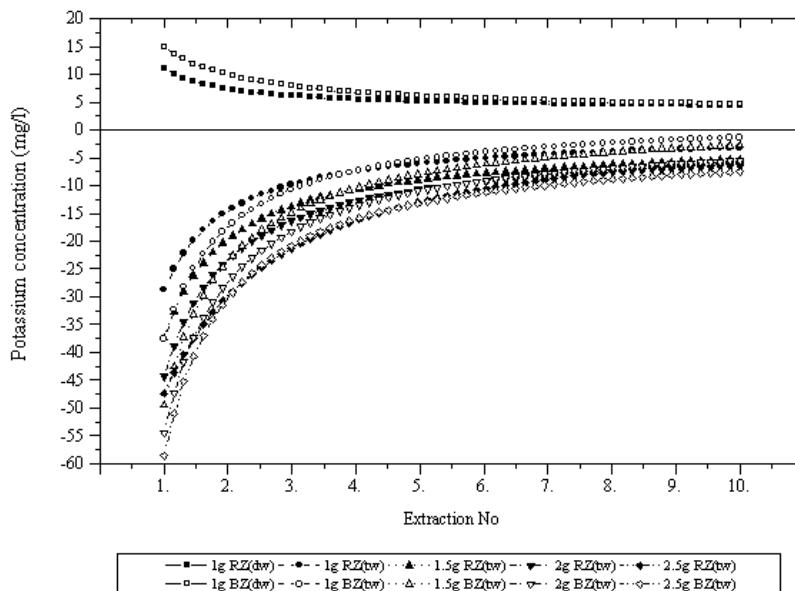
b. Magnesium



c. Sodium



d. Potassium



As shown in the figures above, the main adsorbed cation on the zeolitic tuffs from the extraction solution (tap water) is the calcium ion. The adsorption of Ca^{2+} shows a good relation to the amount of ammonium ions released from the zeolitic tuffs. In addition, it may improve the amount of phosphorus released from the zeolitic tuffs. Lai and Eberl, (1986) and

Chapter 4. Evaluation of Zeolitic tuffs as Slow release Fertiliser materials

Dwairi (1998) found that the dissolution properties of zeolitic tuffs for phosphor (in a mixed system of NH_4^+ - form zeolitic tuffs-Apatite rock) depend on an exchange reaction between Ca^{2+} (dissolved from Apatite) and NH_4^+ from the zeolite, which leads to more dissolution of Apatite rock and thus phosphor from such a system. In contrast, other cations (Mg^{2+} , Na^+ and K^+) tend to be desorbed in the solution, and this is also in a connection with the number of repeated extraction.

An adsorption-desorption balance for this system could not be evaluated, because the tap water contains a concentration of these cations, and the reaction time (24 hrs.) might be too long. In this system, an adsorption-desorption balance might have been achieved, but the amount of cations adsorbed (e.g. Ca^{2+}) in relation to the extracted amount of ammonium as well as the other cations (Mg^{2+} , Na^+ and K^+) could not be calculated.

Chapter 5. Removal of heavy metals from industrial wastewater using natural zeolite

5.1 Introduction

The use of natural zeolites as an ion exchanger for the removal of heavy metal ions from water and wastewater could be applied in tow main mechanisms, namely batch system and ion exchange columns (as packed bed or fluidised bed).

5.1.1 Batch reactor system

These systems include an addition of certain amount of zeolite materials in proportion to a certain volume of water or wastewater. This mixture will be shaken in a tank for a period of time (Contact time) until a condition of equilibrium reaction between the cations in the solution and the zeolite materials has been reached. By using this system, it should be known that the utilisation of the exchanger media capacity is fractionally and not completely useable (Dorfner, 1990). Additionally, the exhausted zeolite materials could be separated from the solution by means of sedimentation or filtration, then they could be regenerated for a second cycle of reuse or it may be wasted into sludge (Hernandez, et al., 1992). In batch operation systems powdered or granular ion exchange media could be used. While the granular material had a quite long contact time, the powdered media allows shorter contact time to reduce the pollutants into a desirable level. In the contrary, granular media are much easier to be separated from the treated solution than the fine media.

In general the removal of pollutants from liquids depends greatly on the amount of the added ion exchanger media and the period of contact time. The removal efficiency tends to increase by expanding the amount of the used media or by extending the shaking time.

5.1.2 Ion Exchange Process

The column operation technique is the most widely practised in wastewater treatment systems using ion exchange media, (Hindin, 1979 and Abrams, 1979). It might consist of single or multiple columns, containing one or more types of ion exchanger materials (Abrams, 1979 and Salem, 1979). The mechanism of ion exchange process could be subdivided into two main systems depending on the solution flow direction, the fixed (or packed) bed column

and the fluidised bed column, whereby the first is as the down- direction and the second as the up-flow direction.

Three processes are included in a cycle of an ion exchange column process, and they are as follows: exhaustion, back washing and regeneration process (Dorfner, 1990).

a. Exhaustion process

A solution to be processed is passed through an ion exchange bed column in down or up flow direction. The removal process of the concerned pollutants takes place by exchanging them with other equivalent ions in the exchanger media.

b. Back washing

This step is considered to be necessary before and/or after the exhaustion process. This process removes the air bubbles as well as the fine materials from the ion exchange bed, which may be found in the media and also which might be produced from the attrition between the media particles themselves. Furthermore, this step is necessary after the regeneration process to rearrange the materials within the ion exchange bed and also to remove the excess regenerate. Back washing could be achieved by passing a de-ionised water stream in up-flow direction, whereby the flow rate should be controlled so that no loss of the ion exchange media could be occurring.

c. Regeneration step

Regeneration process could be processed by percolating a suitable Homo-ionic solution (e.g. NaNO₃, KNO₃, CaCl₂, etc.) through the exchanger media. As a result, the pre absorbed ions might be totally or partially back-desorbed from the ion exchange bed, and thus the it has been prepared for a new cycle of service step.

5.2 Materials

Two natural zeolitic tuffs were used as ion exchanger for the removal of heavy metals from aqueous solutions, firstly a homogeneously zeolitic tuff sample or brownish zeolitic tuff (BZT) obtained from the Jordan factory for soil conditioners (Irbid-Jordan), and secondly, reddish zeolitic tuff sample (RZT) collected from Aritain area in Northeast of Jordan (120 km NE of Amman capital city). The characteristics of both zeolitic tuffs have been studied in detail (Chapter 3). For a comparison, the synthetic zeolite mineral NaA was used as a exchanger media. Synthetic solutions of heavy metal ions (Pb²⁺, Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺) were prepared from their salts mainly nitrates.

5.2.1 Samples preparation

The grain size fractions (1-0.315 mm) of both Jordanian zeolitic tuff materials have been used for this study as follows: in their natural form (non treated-original as obtained) and in Ca-, K- and Na- form. The regeneration process was performed by percolating a concentrated solution of CaCl_2 , KNO_3 or NaNO_3 with a very low flow rate velocity throughout the zeolitic tuff beds Semmens (1984), Colella (1996), Hagiwara and Uchida (1978), Murphy et al.,(1978) and Klieve and Semmens(1980).

5.3 Methods

5.3.1 Batch system

5.3.1.1 Adsorption capacity of metal ions

The total adsorption capacity of Jordanian zeolitic tuffs for heavy metal ions was evaluated by mixing a weight of non treated zeolitic tuff with a solution (at pH 5.5) in polyethylene bottles for 7 days, where the solid to solution ratio was taken 1:450 (Sammens and Martin, 1988; Colella et.al. 1995, Cioffi, et a. 1996 and Semmens and Seyfarth 1978). The solution contains a one type of heavy metal ions as follows: Pb^{2+} (445 mg/l), Cd^{2+} (104 mg/l), Cu^{2+} (40 mg/l), Ni^{2+} (69 mg/l) or Zn^{2+} (200 mg/l). After the agitation of the mixtures, the solutions have been filtered using filter paper, acidified and analysed for their metal ions as well as Ca^{2+} , Mg^{2+} , K^+ and Na^+ .

Furthermore, the worked exchange capacity of zeolitic tuff for heavy metals was determined by adding a 100 ml solution (pH ranges between 6.5 and 6.8 using NaOH) to 1g of non treated zeolitic tuff samples (Albino, et. al. 1995). The samples were agitated for a time range between 20 and 120 min. The used solutions contain different ions Pb^{2+} (6 mg/l), Cd^{2+} (4.5 mg/l), Cu^{2+} (3.2 mg/l), Ni^{2+} (4.6 mg/l) and Zn^{2+} (20 mg/l) as well as Na^+ (60-140 mg/l) as counter ion. After each period of contact time, the solutions were filtered, acidified and analised for their cations, and a similarly fresh solution was added to the same 1 g. zeolitic tuff sample. This procedure was repeated 15 times until the adsorption capacity of zeolitic tuff samples for the heavy metal ions was less than 0.1 mg/ g. tuff sample. With exception to lead ion, whose adsorption capacity was also nearly complete after the 15th time of adding the fresh heavy metal solutions.

5.3.1.2 Effect of regeneration form

The effect of the treatment type of zeolitic tuffs on their adsorption capacity for heavy metal ions were conducted after Semmens and Martin (1988) and Pansini et. al. (1996)

Three samples (0.5g.) of zeolitic tuffs (reddish and brownish zeolitic tuffs) previously converted to Ca-, K- or Na-form were mixed with a 100ml heavy metal solution in polyethylene bottles for 7 days (using a rotating shaker controlled to 40rpm.). The solutions contain Pb^{2+} (191mg/l), Cd^{2+} (62 mg/l), Cu^{2+} (25 mg/l), Ni^{2+} (53 mg/l) or Zn^{2+} (123mg/l), at pH ranges between 5.5-5.7,. After 7 days of agitation, the contents were filtered, acidified and analysed for the remaining heavy metal ion and the desorbed cations from the zeolitic tuffs.

5.3.1.3 Effect of counter cation types

In case that natural zeolite minerals are applied as a tertiary treatment method for an industrial wastewater effluents, which mostly have a pH value ranges between 2-2.5. It should be concerned that zeolite minerals are characterised by their low resistance to acidic environments (chapter 3, section 3.2.5). Thus, the effluents to be treated should be neutralised prior to the application of zeolites as ion exchanger. Therefore, this part of research concerns the influence of Ca^{2+} and Na^+ (resourced from CaO or NaOH as neutralised materials) on the adsorption capacity of Jordanian zeolitic tuffs in their Ca-, K,- and Na-form.

Three (1g.) samples of 1-0.315 mm grain size fractions of both zeolitic tuffs were placed in polyethylene bottles containing 200 ml of heavy metal solutions with the presence or the absence of counter Ca^{2+} or Na^+ ions (table 5.1). The contents were mixed for 7 days, filtered, acidified and analysed for their ions.

Table 5.1 Heavy metal solutions with different types of counter ions.

Zeolitic tuff added	Cation concentration (mg/l)						
	Pb^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Ca^{2+}	Na^+
Ca-form	75	12	9.0	11	38	-	-
K-form	83	10	10	12	40	84	-
Na-form	85	10	9.0	11	36	-	118

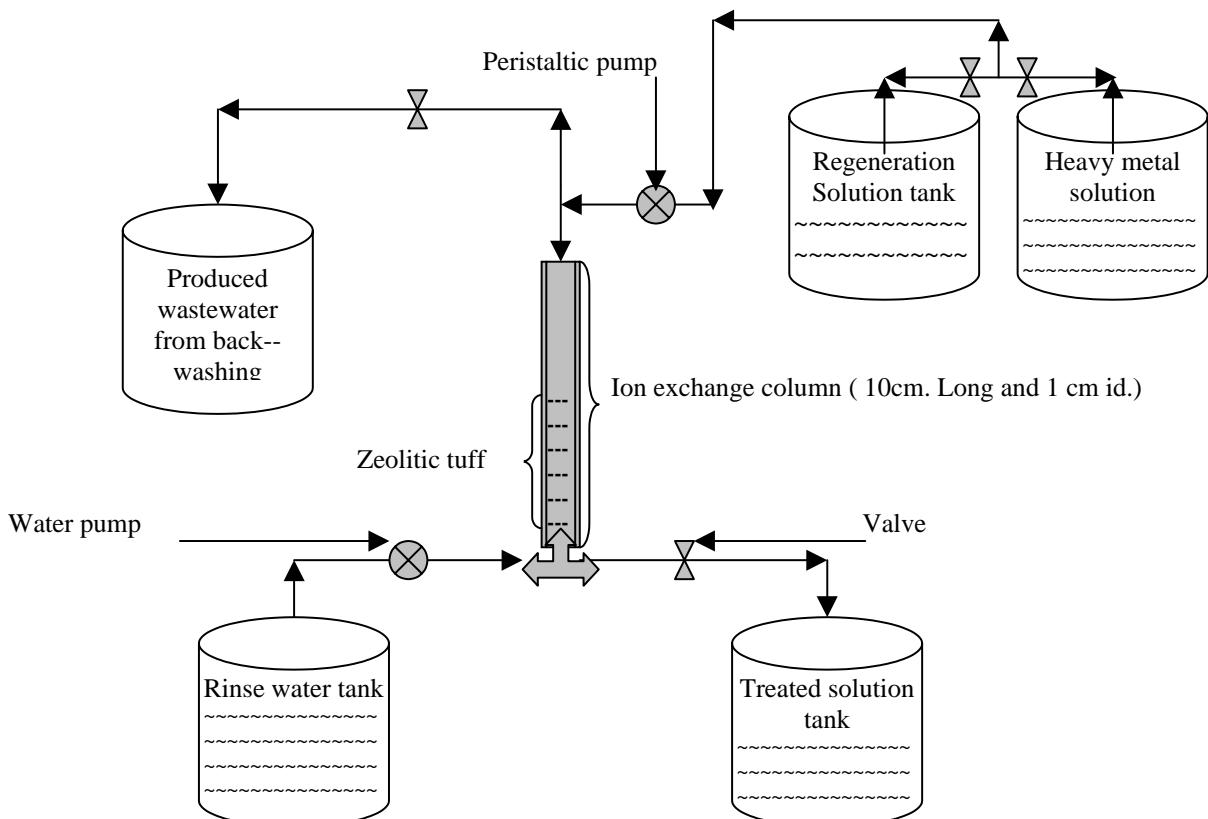
5.3.2 Ion exchange column

5.3.2.1 Adsorption capacity

The fixed bed test was used to carry out the breakthrough curves of Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} using Jordanian zeolitic tuffs; the total exchange capacity of these ions and the equilibrium of the ion exchange reaction. A solution containing one of these metal ions was neutralised with NaOH to obtain a pH value of 6.8-7 and then percolated throughout a zeolitic tuff bed in their natural form (non treated form).

The effluent velocity (600ml/hrs. equal to ca. 120 BV) was controlled using peristaltic pump and valves (figure 5.1). Different samples were manually collected from the effluents, whereby every 100 ml (20BV) were taken as a sample. The samples were acidified, with nitric acid (0.8 ml/100ml sample), and then analysed for their cations.

Figure 5.1 Laboratory scale ion exchange column apparatus.



The column operation conditions for all process or heavy metal ions for this test are as follow:

Column internal diameter: 0.9-1.1 cm.

Bed depth: ca. 4.5 cm.

Weight of the used zeolitic tuffs: 5 g.

Feed flow rate: 580- 600 ml/hrs. (120 BV/hrs.)

Solution composition:

Lead solution: Pb^{2+} 42 -57 mg/l and Na^+ 3-135 mg/l, (pH 6.8-7).

Cadmium: Cd^{2+} 4-9 mg/l and Na^+ 4 mg/l, (pH 6.8-7).

Copper: Cu^{2+} 7.2 mg/l and Na^+ 4 mg/l, (pH 6.8-7).

Nickel: Ni^{2+} 5.8 mg/l and Na^+ 7 mg/l, (pH 6.8-7).

Zinc: Zn^{2+} 20-22 mg/l and Na^+ 2 mg/l, (pH 6.8-7).

5.3.2.2 Effluent velocity effect on the adsorption capacity

The effect of a flow rate velocity on the worked adsorption capacity of heavy metal ions on zeolitic tuffs (reddish and brownish zeolitic tuffs) was determined under conditions of equilibrium. For these tests, solutions containing different concentrations of heavy metal ions (Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} (table 5.2) were percolated (after they are neutralised with NaOH to pH value 6.5-7) throughout a separated, non treated, 5 g. zeolitic tuff bed with two different flow rate velocities for each bed (400ml/hrs or 600 ml/hrs). Each 100 ml from the treated solutions were obtained as a sample to be analysed for the metal ions, and also for the outgoing Ca^{2+} , Mg^{2+} , Na^+ and K^+ from the zeolitic tuff beds themselves.

Table 5.2 Concentration of ions containing solutions percolated with different flow rate velocities.

Zeolitic tuff / flow rate	Cation concentrations (mg/l)					
	Pb^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Na^+
Reddish zeolitic tuff (400ml/hr.)	13	5.4	2.0	4.5	28	4.0
Brownish zeolitic tuff (400ml/hr.)	10	5.0	1.0	4.4	26	7.0
Reddish zeolitic tuff (600ml/hr.)	17	5.0	3.7	4.6	24	2.0
Brownish zeolitic tuff (600ml/hr.)	17	4.8	4.0	4.6	23	2.0

5.3.2.3 Effect of regeneration type

To explain the effect of regenerating the zeolite materials, it has to be evaluated as an ion exchange media in wastewater treatment. The influence of the occupied ion within the zeolite minerals themselves has to be tested for effecting the reddish and brownish zeolitic tuffs. Therefore a three different forms of zeolitic tuffs (Ca-, K- and Na forms) have been used for this application method as fixed bed.

Different 2.5 g. ion exchange columns from both types of zeolitic tuff (in their natural form, Ca-, K-, or Na form) were packed in a 10 cm glass column (1 cm id). The zeolitic tuff beds have been treated with solutions containing heavy metal ions (table 5.3) with flow rate of 600 ml/hrs. The effluent solutions were collected manually for different samples (each 100ml equal to ca. 40 BV as a sample), and the remaining concentrations of metal ions and the eluted-cations from the zeolite bearing's materials were monitored.

Table 5.3 Ion concentrations of the different percolation cycles of solutions

Zeolitic tuff bed and cycle No.	Cation concentrations (mg/l)					
	Pb ²⁺	Cd ²⁺	Cu ²⁺	Ni ²⁺	Zn ²⁺	Na ⁺
Reddish zeolitic tuff (1 st and 3 ^d cycles)	5-5.5	3-3.5	2	2-2.5	8-11	2
Reddish zeolitic tuff (2 nd cycle)	10	2.7	2.2	2.4	10	2
Brownish zeolitic tuff (1 st , 2 nd and 3 ^d cycles)	7.5-10	3-3.5	2	3	8-11	2

After the exhaustion process was proceeded, the zeolitic beds were washed with deionised water, and then reactivated again with the same salt solutions (300 ml of 1M CaCl₂, KNO₃ or NaNO₃ solutions for the previously Ca-, K- or Na-form beds; with an effluent velocity of 80-100 ml/hrs respectively. The regeneration effluents were collected periodically (each 25 ml as a sample). The samples were acidified and analysed for their contents of heavy metal ions. This procedure has been repeated three times for each form of zeolitic tuff beds. Thus, the regeneration efficiency of both zeolitic tuff materials in their different regeneration types has been evaluated.

5.4 Results and Discussion

5.4.1 Batch reactor system

5.4.1.1 Adsorption capacity of heavy metals

The total adsorption capacity of reddish and brownish zeolitic tuffs for Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} from their solutions without any interfering cations are represented in table 5.4.

Table 5.4 Total adsorption capacities of zeolitic tuffs for heavy metal ions (mg/g).

Used zeolitic tuff	Absorbed cations				
	Pb^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
Reddish zeolitic tuff	145	12.2	2.3	5	9
Brownish zeolitic tuff	150	30.6	9	14	54

It is clear, from table 5.4, that brownish zeolitic tuff has a significantly higher adsorption capacity for all tested heavy metal ions than the reddish zeolitic tuff, with one exception to Pb^{2+} ions, which shows to be similar selective on both tuff materials. By comparing these capacities with the total exchange capacity obtained from the mineralogical analysis of the grain size fraction 1-0.315 mm (Chapter 3, section 3.2.3) or with the total amounts of desorbed cations (table 5.5), it was found that the brownish zeolitic tuff has a higher capacity for Pb^{2+} ; Cd^{2+} and Zn^{2+} ions than the total cation exchange capacity. It might be indicated that either an amount of these metal ions were absorbed on the surface of zeolite particle or also that the non identifiable minerals in both tuffs could have a considerable role on the adsorption process (as ion exchange media !). Although, the adsorption process of Pb^{2+} ions on the reddish zeolitic tuff could be explained in the same method. In contrast, the amounts of adsorbed Cd^{2+} ; Cu^{2+} ; Ni^{2+} and Zn^{2+} on the reddish tuff and Cu^{2+} and Ni^{2+} on the brownish zeolitic tuff are lower than the total cation exchange capacity of both tuffs. It might be that not the whole zeolitic tuff capacity was available to adsorb these cations, depending on the type of ions exchanged from the exchangeable sites in the zeolite minerals or the properties of other non identified minerals in the tuffs.

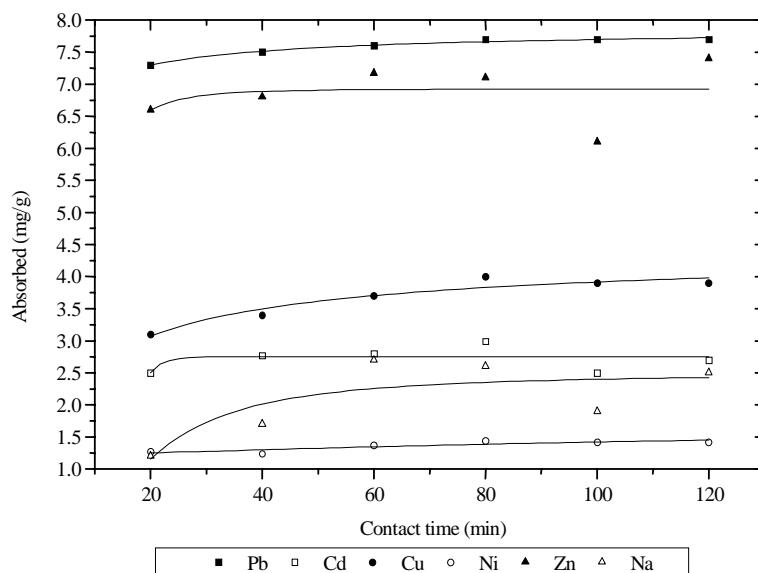
Table 5.5 Desorbed amounts of cations in the equilibrium reaction (mg/g)

Type of reaction	Desorbed cations			
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
Pb ²⁺ +RZT	5.5	0.6	5.9	8.6
Cd ²⁺ +RZT	12	1.0	5.4	14
Cu ²⁺ +RZT	1.0	0.3	0.9	4.0
Ni ²⁺ +RZT	3.6	0.5	0.3	5.0
Zn ²⁺ +RZT	6.4	0.5	0.8	3.6
Pb ²⁺ +BZT	7.4	1.0	0.2	6.4
Cd ²⁺ +BZT	5.0	0.4	0.4	2.3
Cu ²⁺ +BZT	7.8	1.0	0.1	3.8
Ni ²⁺ +BZT	5.5	0.5	0.6	3.2
Zn ²⁺ +BZT	10.6	0.8	0.2	4.7

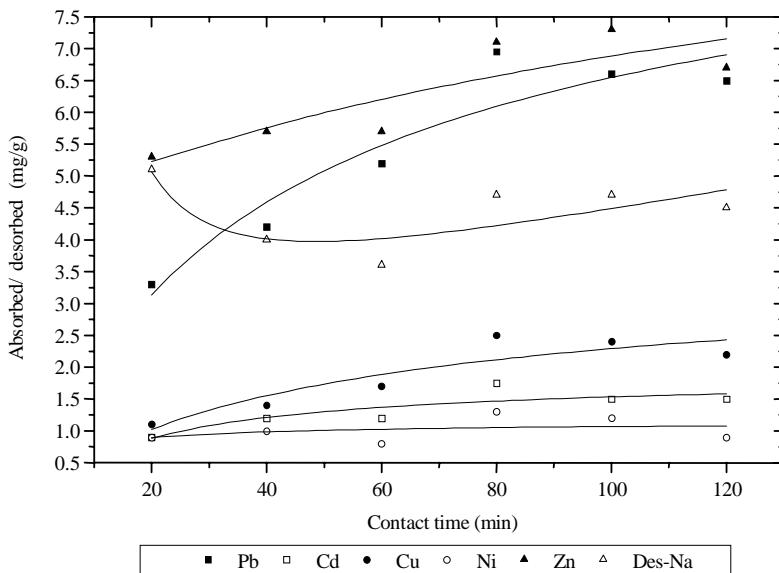
The worked cation exchange capacity of both zeolithic tuffs in the non-treated-form for heavy metals were evaluated according to the shaking time range between 20 – 120 min with a solid to liquid ratio of 1:100. A new solution of heavy metal ions (100 ml) was periodically added to the filtered zeolithic tuff samples (figure 5.2 a and b).

Figure 5.2a and b Worked exchange capacity of Jordanian zeolithic tuff for heavy metal ions

a. Brownish zeolithic tuff (BZT)



b. Reddish zeolitic tuff (RZT)



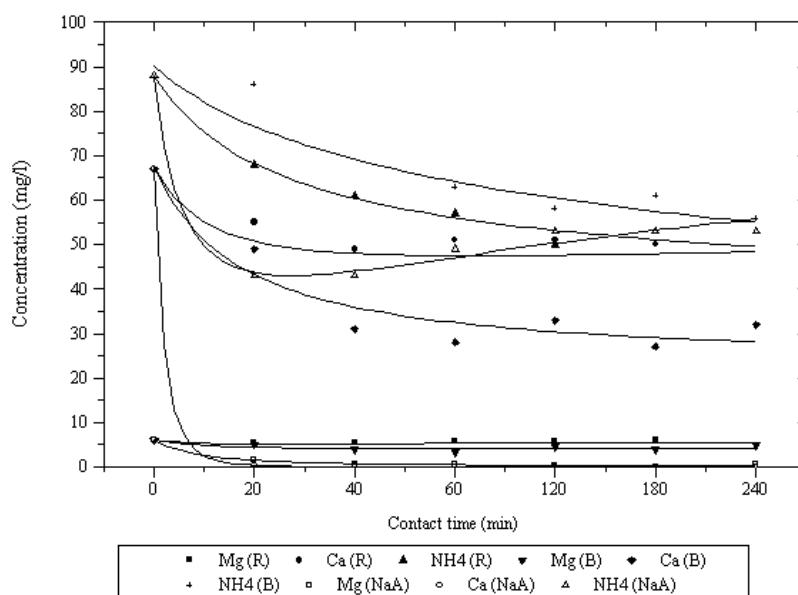
The amount of cations adsorbed on the brownish zeolitic tuffs did not appear to be highly influenced by the increase of the agitation time. Figures 5.2 a shows that the worked exchange capacities of heavy metal ions range between 7.3-7.7 mg/g for Pb^{2+} ; 2.5-2.7 mg/g for Cd^{2+} ; 1.27-1.4 mg/g for Ni^{2+} . In contrast, a slightly increase by extending the agitation time was observed on the adsorption capacities of Cu^{2+} (3.1-3.9 mg/g), Zn^{2+} (6.6-7.4 mg/g) and Na^+ (1.2-1.2.5 mg/g). Similarly, the worked exchange capacity of Pb^{2+} (3.3-6.5 mg/g); Cd^{2+} (0.9-1.5 mg/g); Cu^{2+} (1.1-2.2 mg/g); and Zn^{2+} (5.3-6.7 mg/g) using reddish zeolitic tuff was affected by the contact time ranges between 20 and 120 min (figure 5.2 b). With one exception to the adsorption capacity of Ni^{2+} which was not affected (0.9-1.2 mg/g).

The uptake kinetics of Pb^{2+} and Cd^{2+} from their solutions using the brownish zeolitic tuff (figure 5.2 a) indicates a very fast process of adsorption . It might indicate the high selectivity of this tuff type for these ions (Albino, et. Al. 1995 and Cioffi, et. al. 1996)).

In comparison, the synthetic zeolite (NaA) shows a much more selectivity for removing of Pb^{2+} ; Cd^{2+} ; Cu^{2+} ; Ni^{2+} ; Zn^{2+} ; NH_4^+ ; Ca^{2+} and Mg^{2+} by adding only 0.5g to a 200 ml solution containing these ions. The first five metal ions as well as Ca^{2+} and Mg^{2+} have been totally absorbed (100% removal was achieved) in not more than 20 min of agitation, while it seems to have a similar capacity for NH_4^+ adsorption as the reddish zeolitic tuff (figure 5.2 c). It might indicated that the synthetic zeolite (NaA) is more effective for removing of pollutants from wastewater (Herzenberg, 1983), who found that NaA shows to be effective for removing of heavy metals (Pb^{2+} ; Cd^{2+} ; Cu^{2+} ; Ni^{2+} and Zn^{2+}) from concentrations of 1-2 mg/l down to

<0.3 mg/l. This result has achieved only in less than 5 min of agitation by dosing a 0.25 g to a 1 l solution. However, the NaA zeolite is relative soluble in water solution; low resistance in acidic solutions and it should be strengthened with a binder to be used for water treatment as an ion exchanger in column method. From an economic point of view, furthermore, it is much more expensive comparing with the natural zeolitic tuffs.

Figure 5.2c Ions uptake from solutions using NaA zeolite and the Jordanian zeolitic tuffs in Na-form.



Therefore, it is highly recommended for the uses of Jordanian zeolitic tuffs for removing heavy metal ions by directly adding the zeolitic tuffs to a tank containing wastewater, where it could be practically applied .

5.4.1.2 Effect of regeneration form

The effect of regeneration type on the metal ions adsorption capacity was evaluated using three different forms of reddish and brownish zeolitic tuff (Ca-; K- and Na-forms) in a batch system. The results are represented in figure 5.3 a.

Figure 5.3a Effect of regeneration type on the total adsorption capacity of zeolitic tuffs.

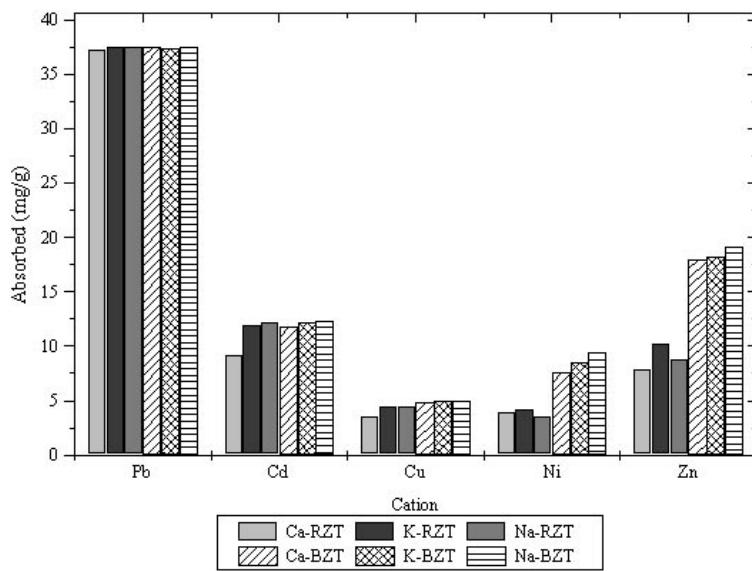


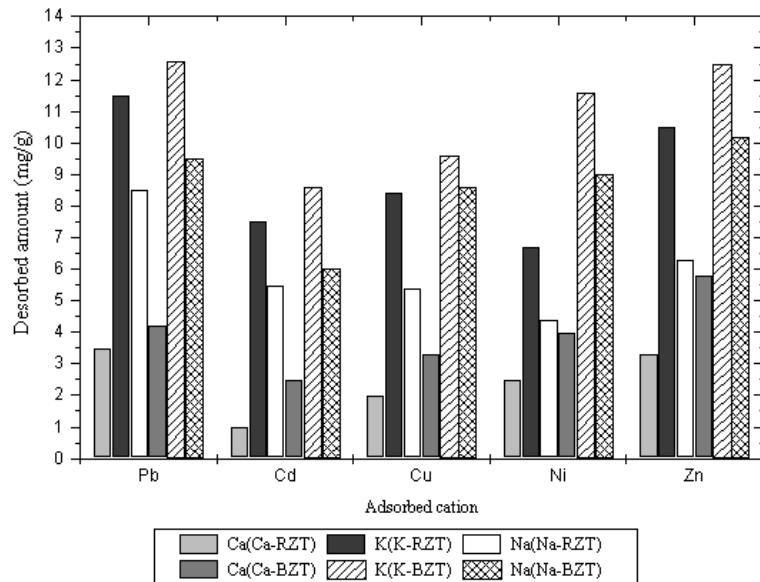
Figure 5.3a shows that the adsorption capacities for Pb^{2+} (37 mg/g); Cd^{2+} (12.4 mg/g) and Cu^{2+} (4.5 mg/g) were not influenced by the type of regeneration using both types of zeolitic tuff. In contrast, the adsorption capacity of Cd^{2+} (9 mg/g) and Cu^{2+} (3.5 mg/g) on reddish zeolitic tuff in Ca-form show a small difference. It might due to the high selectivity of the zeolite minerals as well as the other identifiable minerals in this tuff to Ca^{2+} ions. It was observed that the remaining concentrations of copper, in the treated solutions with brownish zeolitic tuffs in K- and Na-form, were less than 0.5 mg/l, indicated that the K- and Na- form brownish zeolitic tuffs are able to absorb a higher amount of copper than was obtained. Similar results for the amount of Cd^{2+} (10 mg/g) absorbed was achieved by using Na-form of Clinoptilolite (ca. 95%), while a higher amount of Cu^{2+} (12 mg/g) absorbed was found (Semmens and Martin, 1988).

The adsorption capacities for Ni^{2+} and Zn^{2+} obtained, were not highly dependent on the type of regeneration but more on the type of zeolitic tuff used. They range between 3.6 –4.2 mg/g for Ni^{2+} and 8-10.2 mg/g for Zn^{2+} as the reddish material was used, and 7.6-9.4 mg/g for Ni^{2+} and 18-19.2 mg/g for Zn^{2+} by using brownish zeolitic tuff. It could concluded that the brownish zeolitic tuff have a higher efficiency for removing Ni^{2+} and Zn^{2+} than the reddish tuff.

By comparing the exchange capacities obtained using the different forms of zeolitic tuff and the in the non-treated form (section 5.4.1.1). Its found that the untreated form of brownish zeolitic tuff seems to have 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 the unidentifiable minerals in

the brownish zeolitic tuff. However, the treated metal solutions were analysed for their cations (Ca^{2+} ; K^+ and Na^+) eluted from the zeolitic tuffs during the equilibrium reaction (figure 5.3 b)

Figure 5.3 b Desorbed cations (mg/g) from the different forms of zeolitic tuffs as the effect of regeneration type.



The amounts of cations desorbed from the zeolitic tuff during the exhaustion process (figure 5.3b) were compared with the total amount of heavy metals absorbed (figure 5.3a). Therefore, the adsorption equilibrium has been obtained according to the following reaction and are summarised in table 5.6:



Where X represents Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} or Zn^{2+} , and Y represents Ca^{2+} , K^+ or Na^+ .

s and z denote solution and zeolite respectively

Table 5.6 Adsorption-desorption equilibrium on the zeolitic tuffs.

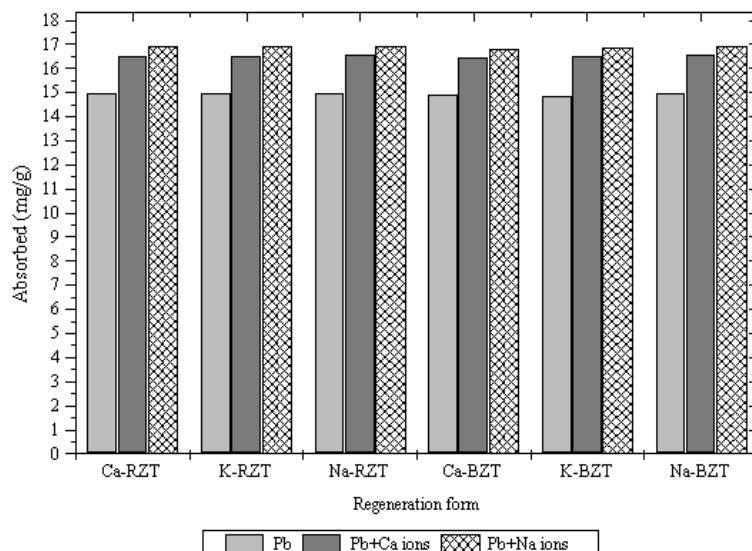
Desorbed cation/ Adsorbed cation Ys/Xz	Ca^{2+} Ca-RZT	K^+ K-RZT	Na^+ Na-RZT	Ca^{2+} Ca-BZT	K^+ K-BZT	Na^+ Na-BZT
Pb^{2+}	11	3	5	9	3	4
Cd^{2+}	9	2	2	5	1	2
Cu^{2+}	2	1	1	2	1	1
Ni^{2+}	2	1	1	2	1	1
Zn^{2+}	2	1	1	3	1	2

5.4.1.3 Effect of counter cations

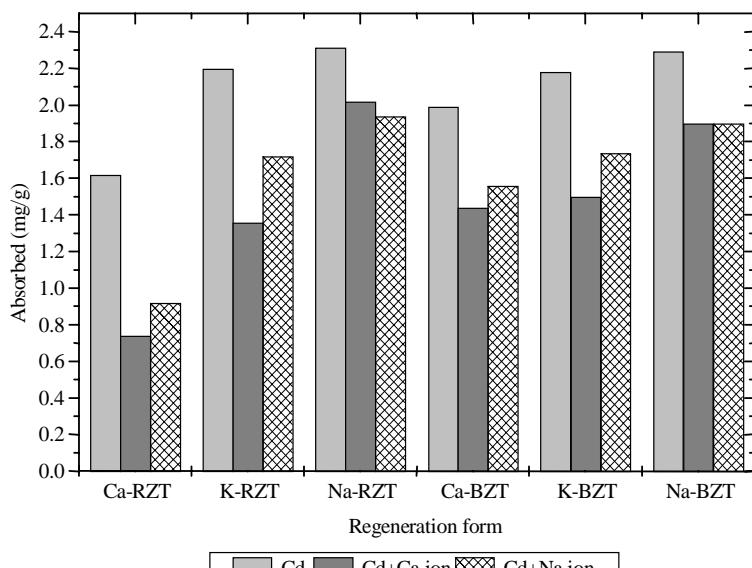
The effect of the counter ions (Ca^{2+} or Na^+) on the worked adsorption capacity of zeolitic tuffs in their treated forms was conducted in a batch system as represent in figures 5.4 a-e (influent concentrations are represented in table 5.1).

Figures 5.4 a-e Worked exchange capacities for heavy metals as an effect of the neutralisation type.

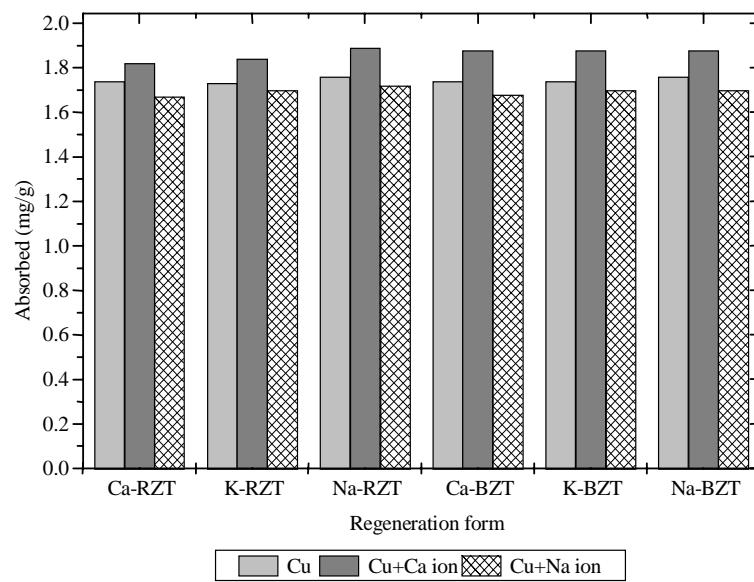
a. Lead.



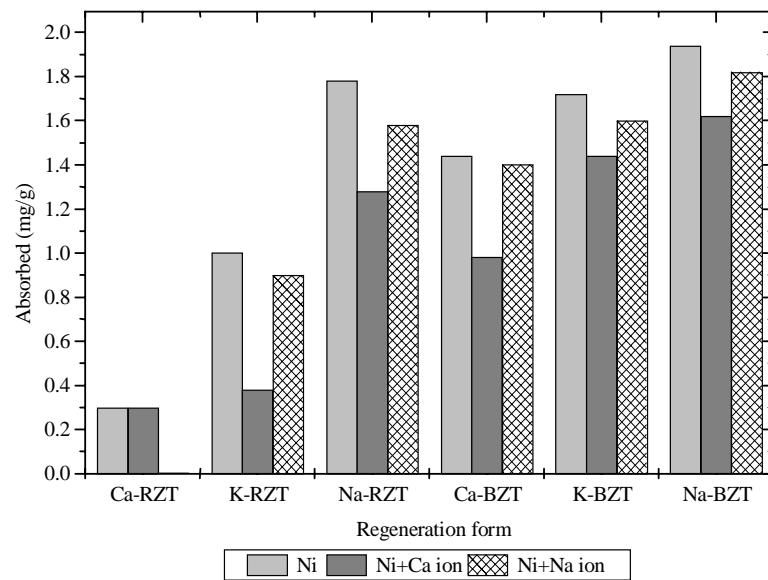
b. Cadmium



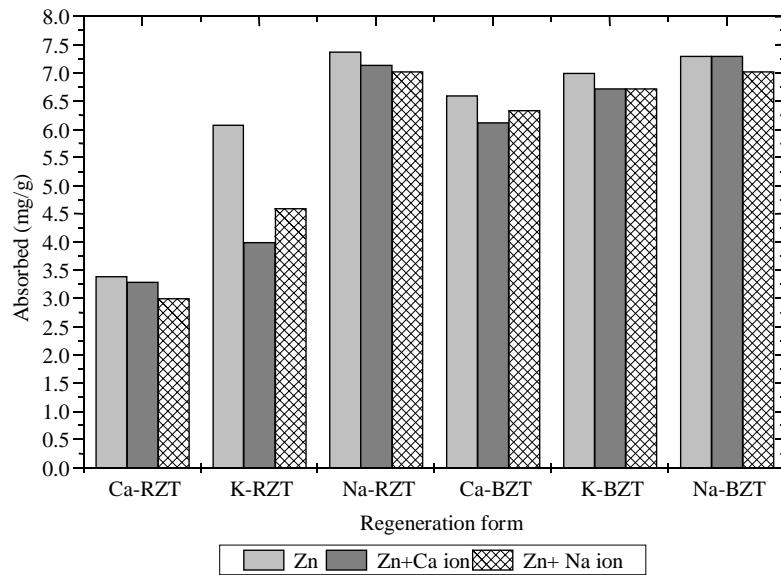
c. Copper



d. Nickel



e. Zinc



The Jordanian zeolitic tuffs (reddish and brownish) show very high selectivity for Pb^{2+} (15-17 mg/g) and Cu^{2+} (1.7-1.9 mg/g) ions from the solutions (figure 5.4 a). The results obtained were independent on the type of regeneration used as well as the presence of counter Ca^{2+} or Na^+ ions. The amounts of Pb^{2+} and Cu^{2+} absorbed did not represent the total adsorption capacity, where the concentration of both ions in the elute was less than 0.2 mg/l, meaning that a 100 % of removal percent was achieved. The slightly difference (ca. 2mg/g) on the amount of Pb^{2+} absorbed is mainly resulted from original Pb^{2+} concentrations added.

The amount of Zn^{2+} absorbed seem to be highly dependent on the regeneration form of zeolitic tuff and less than on the type of cations (Ca^{2+} or Na^+) present as shown in figure 5.4e. The highest amount of Zn^{2+} absorbed (7-7.4 mg/g) was obtained on both zeolitic tuffs in Na-form with an independence of counter cation types. Furthermore the brownish tuff in Ca- and K- form shows to be higher selective for Zn^{2+} than same forms of reddish zeolitic tuff.

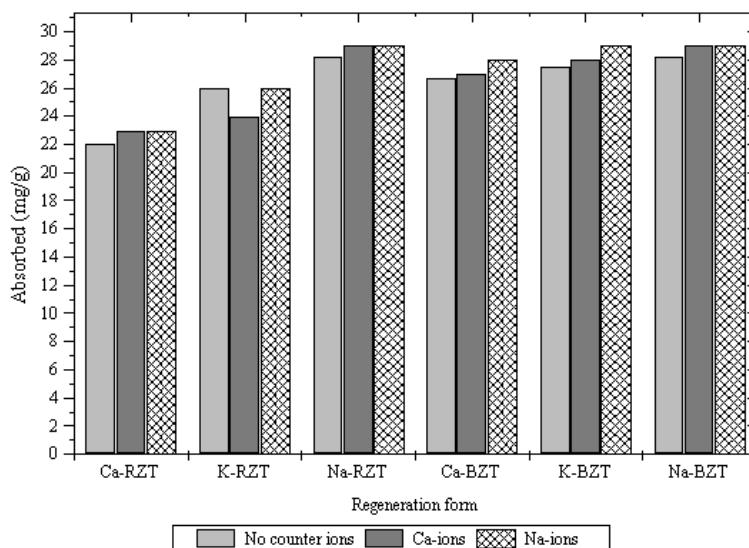
Different adsorption properties of zeolitic tuffs for Cd^{2+} were observed. Figure 5.4 b shows that a higher adsorption capacity of Cd^{2+} ions from the complex solutions was achieved on both zeolitic tuffs by utilising the metal solutions containing neither Ca^{2+} or Na^+ ions in the following series: Na-, K- and Ca-form On the other hand, there is no significant difference was reported in the adsorption capacity of Cd^{2+} related to the presence of counter ion types. The effect of counter Ca^{2+} ions on the adsorption properties of Cd^{2+} on the Clinoptilolite was observed by Semmens and Martin (1988). They reported that the exchange capacity of

Clinoptilolite for Cd^{2+} with the presence of counter Ca^{2+} and Na^+ ions was less than its capacity obtained only by the presence of Na^+ as counter ions

Its clear from figure 5.4 d, that the brownish zeolitic tuff in its different forms have a higher efficiency for removing Ni^{2+} ions from a solution containing neither Ca^{2+} or Na^+ ions than the reddish zeolitic tuff. In general, the effect of counter cation type are only recognised for Ca-form brownish zeolitic tuff as well as the K-form reddish zeolitic tuff.

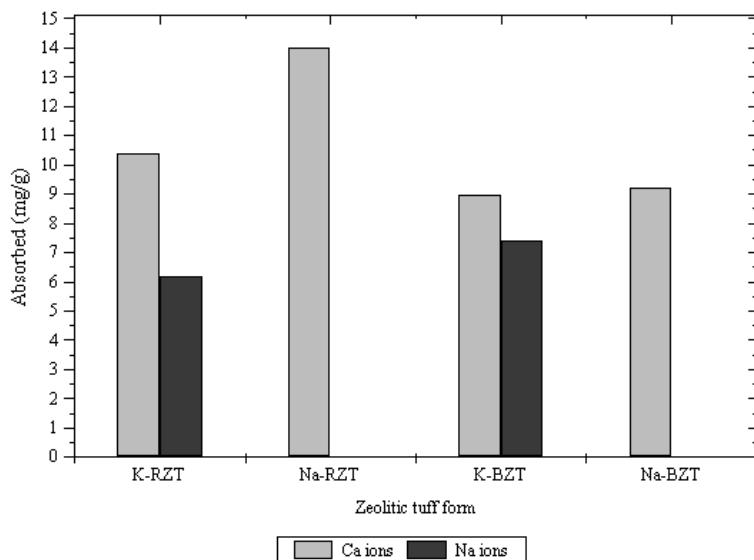
A clear effect of the counter cation type (Ca^{2+} or Na^+) on the total adsorption capacity of Pb^{2+} ; Cd^{2+} ; Cu^{2+} ; Ni^{2+} and Zn^{2+} is represented in figure 5.5. Its shown that the absorption efficiency of brownish zeolitic tuff in K- and Ca-form is higher than of the reddish materials in the same forms of regeneration, where both materials in Na-form have the same effect for the removal of these metal ions.

Figure 5.5 Counter ions effect on the adsorption capacity



In the equilibrium reaction, its found that the reddish tuff in Na-form tends to absorb a higher amount of Ca^{2+} (14 mg/g) than its K-form as well as the Na- and K- forms of brownish tuffs (figure 5.6). On the contrary, the Na^+ has been absorbed from the solution only on the Ca-form of both zeolitic tuffs with an amount of 6.2 and 7.4 mg/g for the reddish and brownish tuffs respectively. It may indicate that the reddish zeolitic tuff have more selectivity for Ca^{2+} ions in Na-form than the K-form of the same tuff and also the K- and Na- forms of the brownish tuffs.

Figure 5.6 Amount of Ca^{2+} or Na^+ absorbed on the zeolitic tuffs.

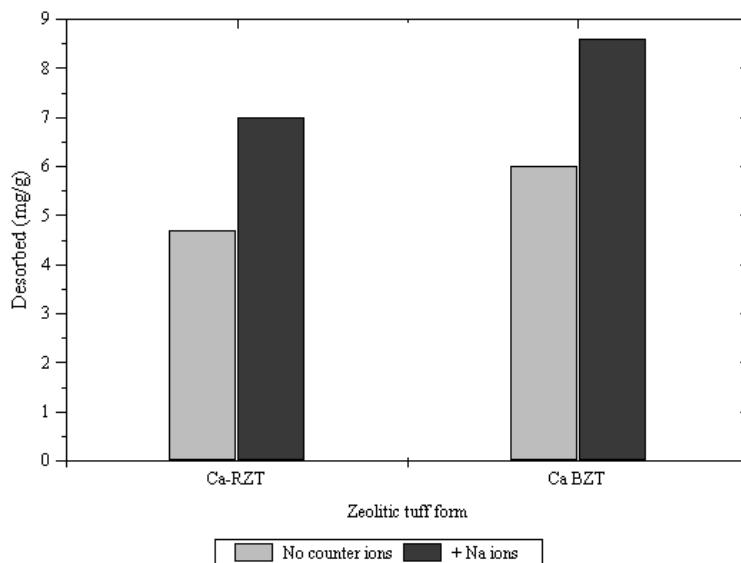


The higher amount of Ca^{2+} exchanged from the brownish zeolitic tuffs (figure 5.7a) resulted after treating the solution containing Na^+ as counter ions. While a less amount was obtained by treating the solution without any interfering Na^+ cations. This might indicate that 1. The ion exchange process between the adsorption of Na^+ ions from the solution and the desorption of Ca^{2+} from the zeolitic tuffs was occurred and 2. The reddish zeolitic tuff have a higher selectivity for Ca^{2+} than the brownish tuff (figure 5.7 c). Furthermore, the reddish zeolitic tuff shows a high selectivity for K^+ than the brownish zeolitic tuff. Therefore, the amounts of K^+ ions desorbed from the reddish zeolitic tuff were less than from the brownish zeolitic tuff (figure 5.7b)

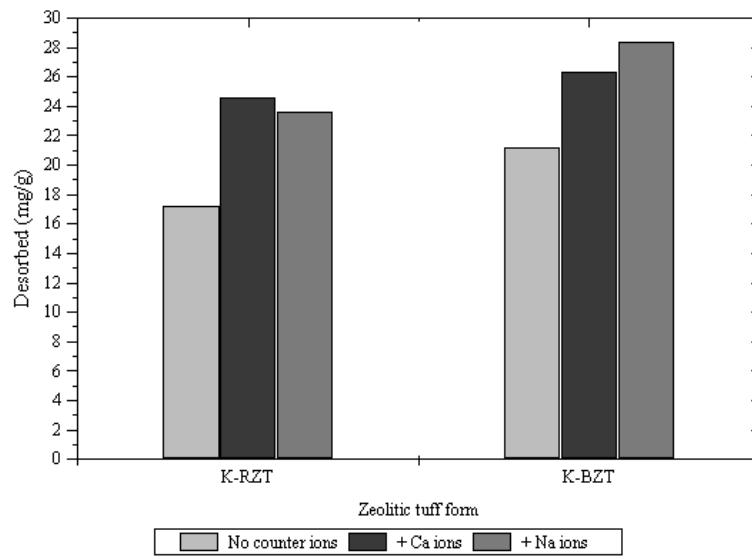
It could be concluded that the ion exchange reaction was not only happened between the metal ions and the zeolitic tuffs but also the Na^+ or Ca^{2+} (as counter ions) and the zeolitic tuffs, they also indicated that the regeneration type have a significant effect on the adsorption capacities of the tuffs, from a point of view that the different forms of both zeolitic tuffs used show a different selectivity's not only for the metal ions but also for the counter ions (Na^+ or Ca^{2+}).

Figure 5.7 a-c Desorbed amounts of cations (mg/g) in the equilibrium reaction.

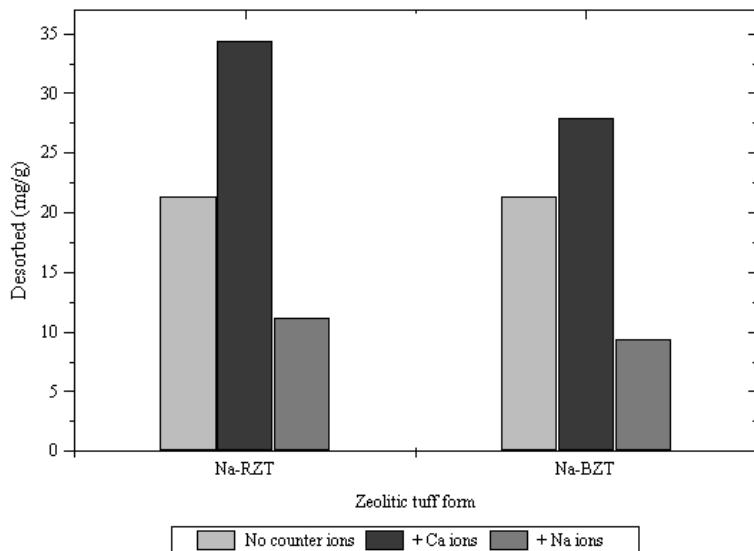
a. Calcium ions



b. Potassium ions



c. Sodium ions



5.4.2 Ion exchange column

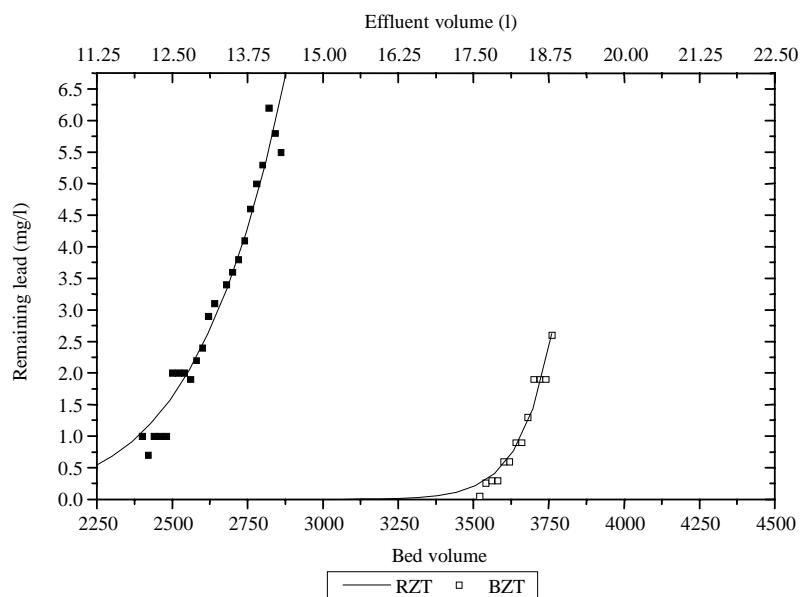
5.4.2.1 Adsorption capacity of heavy metals

5.4.2.1.1 Lead

The breakthrough curves of Pb^{2+} for reddish and brownish zeolitic tuffs in the natural form (figure 5.8 a) show a steep rise with little deviation. The curves are influenced by the affinity for exchanged and types of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) found in the exchange sites of zeolite minerals (Pansini and Colella, 1990).

It is clear that the brownish zeolitic tuff shows a significant higher exchange capacity for lead ions compared with the reddish tuff, where its effluent concentration was first observed after percolating a volume of about 11l through the reddish zeolitic tuff bed. In contrast, the effluent concentration through the brownish tuff bed appeared after percolating 16l from a solution containing Pb^{2+} . These results are not only depend upon the different zeolite minerals in both tuffs, perhaps also being dependant upon the exchangeable cation types from the minerals themselves.

Figure 5.8 a. Lead breakthrough curves on Jordanian zeolitic tuffs.



The exchanged cations from the zeolitic tuffs beds were monitored in the lead effluent solution, whereby the sequence of eluted cations was obtained (figures 5.8b and c). The deviation of the eluted cations from the curve is mainly due to back--washing of the beds as well as some problems by controlling the effluent velocity.

Figures 5.8a and b show that Na^+ appear to be easily exchanged from both types of tuff (reddish and brownish tuff) as well as K^+ from the reddish zeolitic tuff, where Ca^{2+} from both tuffs do not appear to be easily exchanged as well as K^+ exchanged from the brownish zeolitic tuff. The eluted sequence of Mg^{2+} ions in both beds effluents is less than 1 mg/l, therefore it was not taken into consideration.

Figure 5.8 b. Elution curves of Ca^{2+} and Mg^{2+} from the zeolitic tuffs

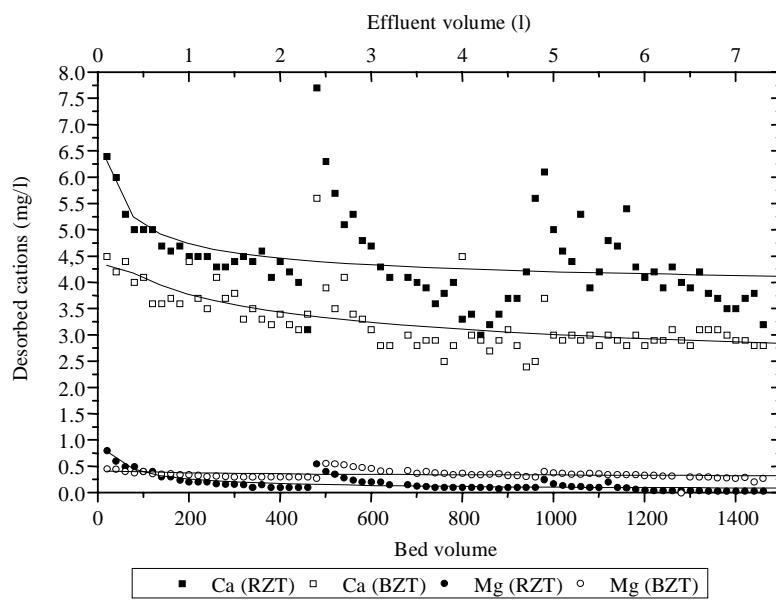
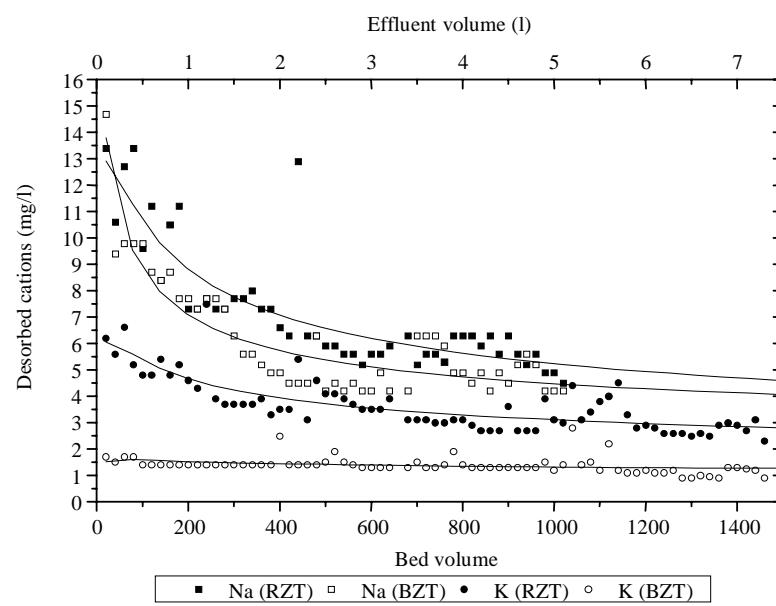


Figure 5.8 c. Elution curves of Na^+ and K^+ from the zeolitic tuffs



To obtain the total exchange capacity of Jordanian zeolitic tuffs for Pb^{2+} , the partially exhausted zeolitic tuffs beds were washed with deionised water, and then extracted with hydrofluoric-hydrochloric acid. It was found that the partial adsorption capacity of reddish zeolitic tuff (91 mg/g) is less than that which was obtained for the brownish zeolitic tuff (108 mg/g). By comparing the remaining amounts of K^+ and Na^+ in these zeolitic tuff beds to the original zeolitic tuff samples (all samples were extracted in the same conditions with

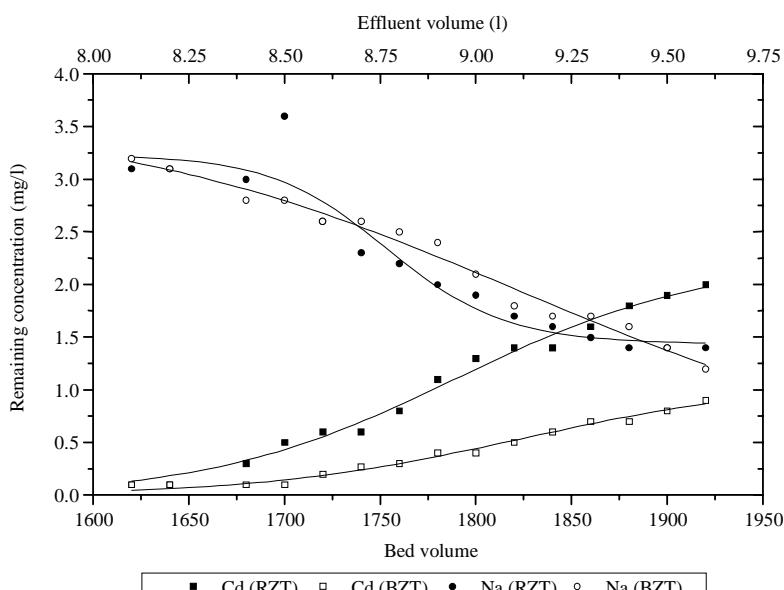
hydrofluoric-hydrochloric acid) it was found that Na^+ are nearly totally exchangeable (85-90% from both zeolitic tuffs, while a less amount of K^+ was exchanged from the zeolitic tuffs to the solution (30% and 70% exchanged from the reddish and brownish tuffs respectively). These results might explain not only the effect of zeolite minerals content in the tuff but also the exchangeability of the occupied cations in the exchange sites of zeolite minerals. It is to be remember that the mineral content analysis of zeolitic tuffs is semi-quantitative and not complete because of a few non-identifiable x-ray patterns.

The Pb^{2+} exchange capacity obtained for both zeolitic tuffs is very high when compared with the total cation exchange capacity (Chapter 3), indicating strongly that Pb^{2+} ions might not have been exchanged on the zeolite minerals alone but also on other minerals contained in the tuffs.

5.4.2.1.2 Cadmium

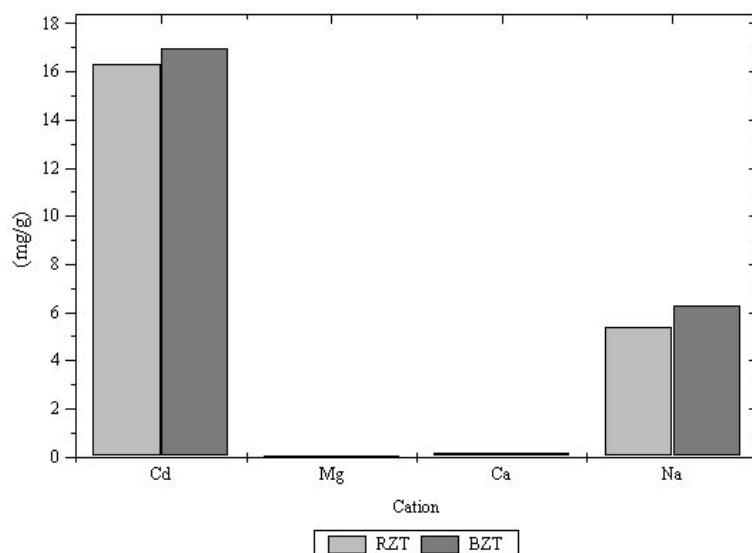
Figure 5.9 shows the breakthrough curves for Cd^{2+} and the eluted concentrations of Na^+ , obtained after percolating a Cd^{2+} containing solution through non treated 5 g zeolitic tuffs beds. They show the high affinity for Cd^{2+} removal, as seem from the slow rise of the curves. Figure 5.9 indicates that the brownish zeolitic tuffs have a higher efficiency for the removal of cadmium ions than the reddish tuff. The outgoing concentration of Na^+ from the zeolitic tuffs during the exhaustion process could indicate that this ion is easier to be exchanged (Colella and Pansini 1988), while K^+ , Mg^{2+} and Ca^{2+} show very low extractable cations in the effluent solution, which are less than 0.3 mg/l in concentration. Therefore, only a part of the cation exchange capacity of zeolitic tuffs are available for this ion (Cd^{2+}).

Figure 5.9a Cd^{2+} breakthrough curves and the outgoing of Na^+ ion.



The calculated amount of Cd^{2+} ions adsorbed from the processed solution as represented in figure (5.9 b) range between 16-17 mg/g for both reddish and brownish zeolitic tuffs. The amounts of Na^+ ions exchanged from the beds are in agreement with the adsorbed amount of Cd^{2+} . On the other hand, the total eluted amount of K^+ , Mg^{2+} and Ca^{2+} , as monitored in the effluent solution, is less than 1 mg/g.

Figure 5.9 b Absorbed amount of Cd^{2+} and desorbed amount of cations from zeolitic tuffs.

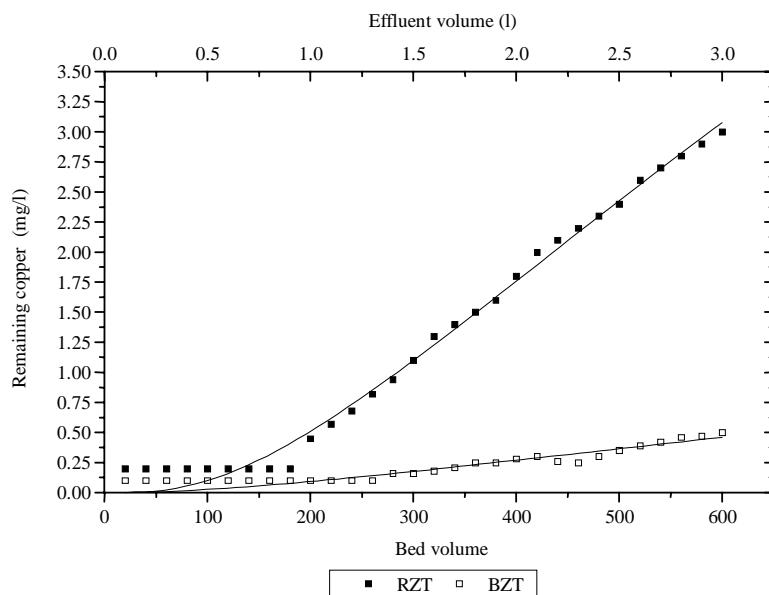


Different results (real absorbed amount of Cd^{2+}) were obtained after extracting the used zeolitic tuff samples with hydrofluoric-hydrochloric acid. They are found to range between 12.1 and 12.4 mg/g for the reddish and brownish tuffs. The exchangeable percent of Na^+ is higher for the brownish zeolitic tuffs (65%) than from the reddish tuff (55%). In contrast, the percent exchangeable of Ca^{2+} ions from both zeolitic tuffs had not exceed 5%. Thus, the brownish tuff has a higher exchange capacity and selectivity for Cd^{2+} ions. Colella et. al. (1995) reported a higher capacity for Cd^{2+} removal (1.86 meq/g), from a synthetic Cd^{2+} solution without interfering Na^+ cation in the natural Chabazite (64% Chabazite with Phillipsite traces) in Na-form. Therefore, the capacity was significantly decreased by increasing the amount of Na^+ counter ions.

5.4.2.1.3 Copper

The breakthrough curves of Cu^{2+} were obtained after pumping a solution containing copper (pH 6.5) through reddish or brownish zeolitic tuff beds with an effluent velocity of 600 ml/hr. (figure 5.10a).

Figure 5.10 a. Cu^{2+} breakthrough curve on Jordanian zeolitic tuffs.

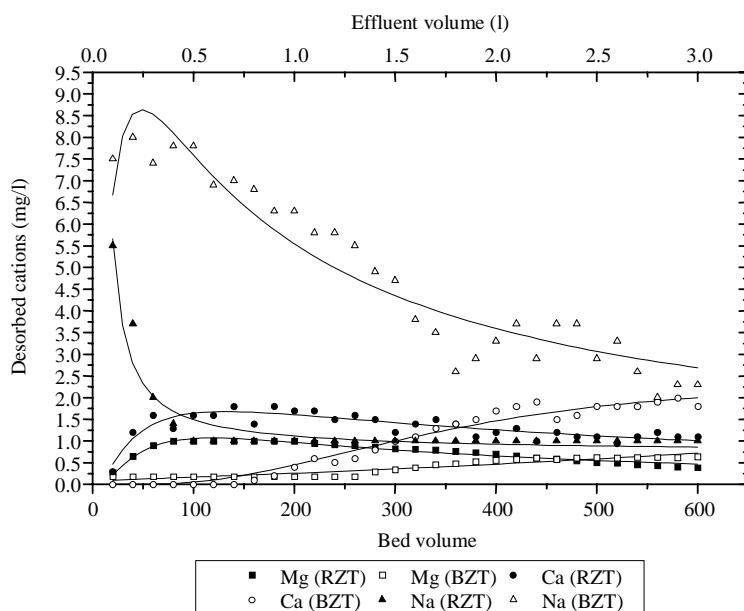


The brownish tuff shows a significantly higher adsorption capacity for Cu^{2+} than the reddish material (figure 5.10a). It was noted that the zeolite particles in the beds were coated with a white-bluish substance, which could be a precipitant of Cu^{2+} such as Atacamite ($\text{CuCl}_2 \cdot 2\text{Cu(OH)}_2$) as was observed by Blanchard et al. (1984)).

The precipitation effect could be clearly determined by comparing the Cu^{2+} exchange capacities from analysis of the effluent solutions with the obtained capacities after extracting the exhausted zeolitic tuff samples with acid solution (HF-HCL). It was found that the Cu^{2+} exchange capacities from analysis of the effluents are 3.5 and 5.2 mg/g for reddish and brownish zeolitic tuffs, While the Cu^{2+} exchange capacities obtained after the extraction process are 1 and 1.67 mg/g for reddish and brownish zeolitic tuffs grains, respectively. Therefore, the different in the evaluated capacities for the same tuff, according to both determination methods, represents that an precipitation of Cu^{2+} has been occurred.

The effluent solution of Cu^{2+} was also analysed for desorbed cations (Ca^{2+} , Mg^{2+} and Na^+), which might have been exchanged from the zeolitic tuffs with Cu^{2+} . The desorbed sequence of cations is represented in figure 5.10 b.

Figure 5.10 b Extracted cations from the treated zeolitic tuffs with Cu^{2+} containing solution.



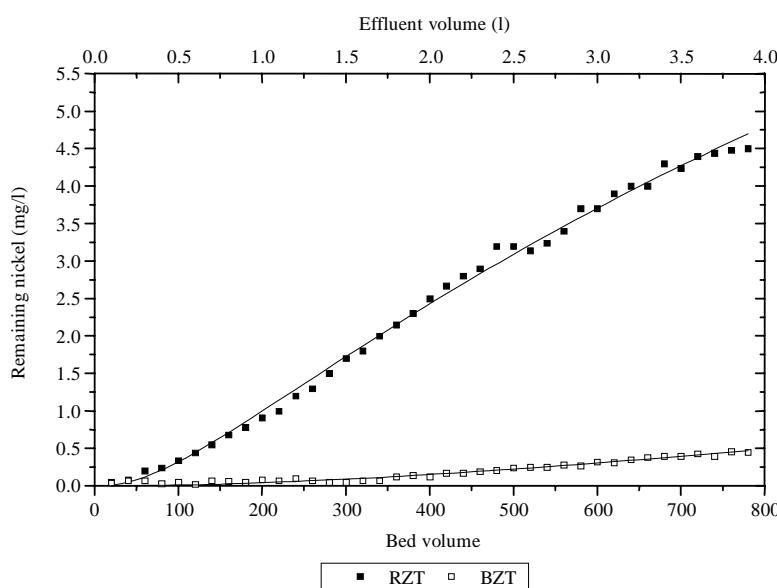
The amount of desorbed cations calculated during the exhaustion process (figure 5.10 b) are 0.8 and 2.9 mg/g (Na^+); 0.8 and 0.6 mg/g (Ca^{2+}) and a negligible amount of Mg^{2+} (0.4 and 0.2 mg/g) from the reddish and brownish zeolitic tuffs respectively. The concentration of the exchanged K^+ in the effluent solutions from both ion exchange beds could not be determined (less than 1 mg/l), and the exchanged percent of this ion (K^+) according to the extraction method with HF-HCL acids was nearly 0%. These results suggested that Na^+ ions are far easier to be exchanged from the ion exchange material than Ca^{2+} and K^+ . The percent of the Na^+ exchanged was 15% and 27% from reddish and brownish tuffs, respectively.. This might be indicate that not all of the exchangeable sites in the zeolitic tuff are available for the exchange of Cu^{2+} ions.

5.4.2.1.4 Nickel

Figure 5.11 a. shows the Ni^{2+} breakthrough curve on Jordanian zeolitic tuffs (reddish and brownish tuffs) in their natural form, processed by up-down flow direction (600 ml/hr.) of 5.8 mg/l in the presence of Na^+ counter ions (7 mg/l). The concentration of Ni^{2+} ions in the

effluents of the brownish zeolitic tuffs were less than 0.1 mg/l up to 250 BV. The same concentration appeared in the effluent of reddish tuff bed earlier (50 BV of treated solution), also, the reddish zeolitic tuff was shown to be nearly exhausted after passing a volume of 800 BV of the solution containing Ni^{2+} cations, while the same volume of the solution treated on the brownish zeolitic tuff was still far away from the exhaustion. This indicates the higher adsorption capacity of brownish zeolitic tuff (4.3 mg/g) than reddish tuff material (2.7 mg/g), which is obtained from analysis of the beds effluent solution.

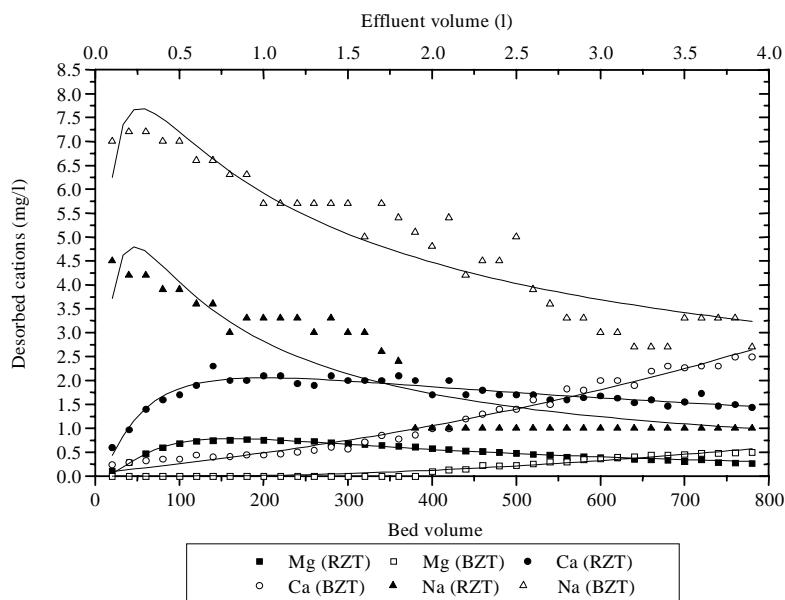
Figure 5.11 a. Breakthrough curves of Ni^{2+} on Zeolitic tuffs



The results obtained of the Ni^{2+} exchange capacities of both zeolitic tuffs agree highly with the exchange capacities obtained from the extraction of the pre-used tuff beds with HF-HCL-acids, which are 2.8 mg/g for reddish tuff and 5.3 mg/g for the brownish zeolitic tuff.

The elution process of cations from the zeolitic tuffs during the equilibrium reaction under processing conditions are represented in figure 5.11 b. It is easily seen that Ca^{2+} has difficulty being exchanged from the both zeolitic tuffs in contrast with Na^+ ; K^+ could not be identified in the effluent solutions (0% was exchanged) from the same zeolitic tuff. Where the amount of desorbed cations from both beds, as calculated from analysis of the effluents, are : Mg^{2+} 0.4 and 0.1mg/g; Ca^{2+} 1.3 and 1 mg/g and Na^+ 1.6 and 2.2 mg/g from the reddish and brownish zeolitic tuffs respectively. This might indicate that the exchange process mainly occurred by exchanging Na^+ from zeolitic tuff.

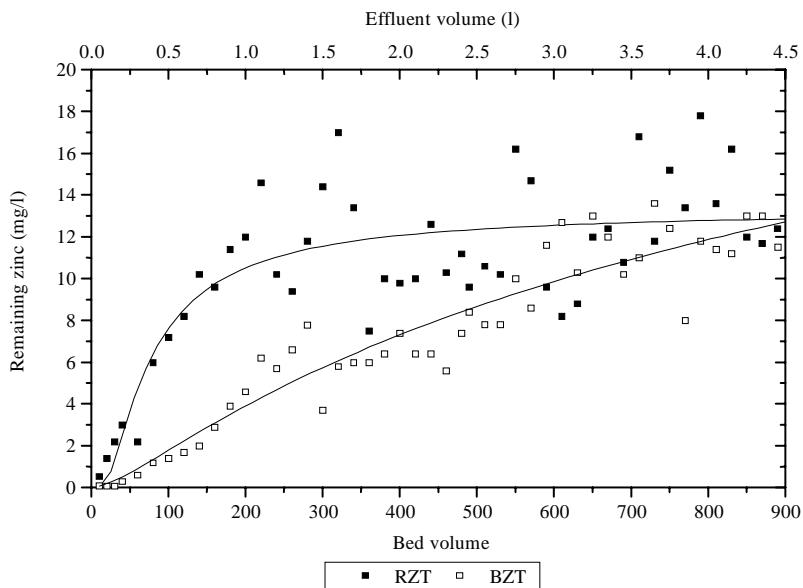
Figure 5.11b. Cations eluted from untreated Jordanian zeolitic tuffs after treated with a solution containing Ni^{2+} .



5.4.2.1.5 Zinc

The breakthrough curves for Zn^{2+} (figure 5.12 a) on the Jordanian zeolitic tuffs in their non treated form show that the plotted points are highly scattered around the fitting curves, which could be due to the diffusion mechanism between the solution and the zeolitic tuff particles in the beds (Colella and Pansini 1988), or because of the fact that the analytical method using atomic absorption spectrometer (the absorbency values of the standard solutions) was very unstable. In contrast, all fitting curves obtained for the absorption of Pb^{2+} , Cd^{2+} , Cu^{2+} and Ni^{2+} are in agreement with the experimental data, which make them useful for predicting breakthrough curves of these heavy metal ions for practical purposes (Pansini and Colella, 1989).

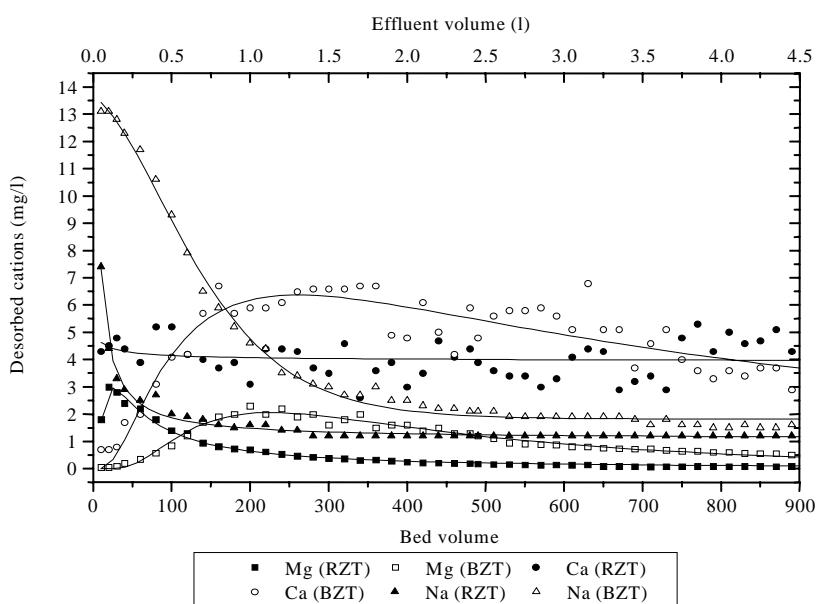
Figure 5.12a. Breakthrough curves of Zn^{2+} on the Jordanian zeolitic tuffs.



To avoid the neutralisation effect with NaOH (to control the influent solution to pH value of 6.8) on the real adsorption capacity of zeolitic tuffs beds, were calculated using two methods: 1. By analysing the effluent solutions (9.5 mg/g and 15.5 mg/g for reddish and brownish zeolitic tuffs) and 2. Extracting Zn^{2+} from the zeolitic tuff beds with HF-HCl acids (5.3 mg/g and 14.6 mg/g for reddish and brownish).

The exchanged amount of cations with Zn^{2+} on the zeolitic tuffs (figure 5.12 b) show that Na^+ is lesser exchangeable, although the amount of exchanged is very little (0.4 mg/g from reddish and 1.9 mg/g from brownish tuffs) compared with the Ca^{2+} ions extracted from both beds of tuffs (3.7-3.8 mg/g).On the other hand, Ca^{2+} ions do not appear to be easily exchanged with Zn^{2+} ions. The amounts of Mg^{2+} and K^+ ions eluted from the zeolite did not exceed 0.5-1 mg/g and about 0.2-0.3 mg/g from reddish and brownish tuffs respectively.

Figure 5.12b. Eluted sequence of cations from zeolitic tuffs pretreated with Zn^{2+} solutions.

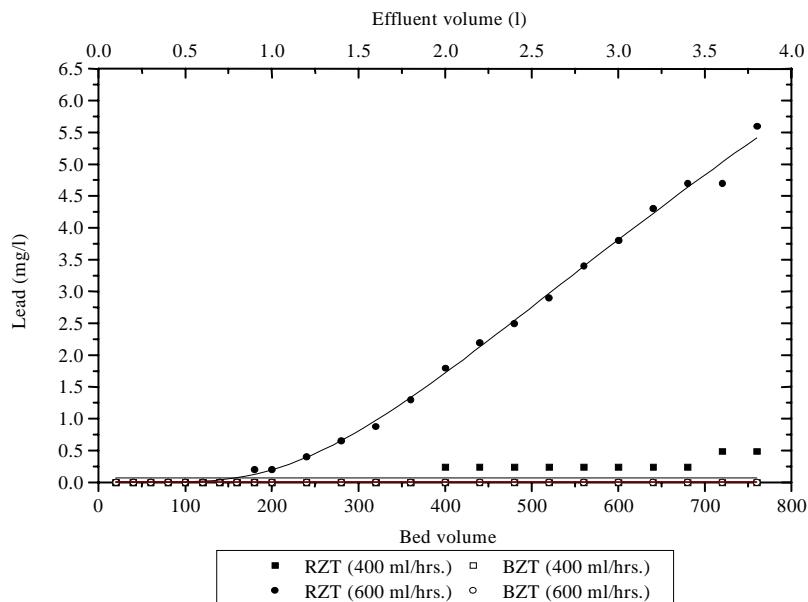


5.4.2.2 Effect of the effluent velocity on the adsorption capacity

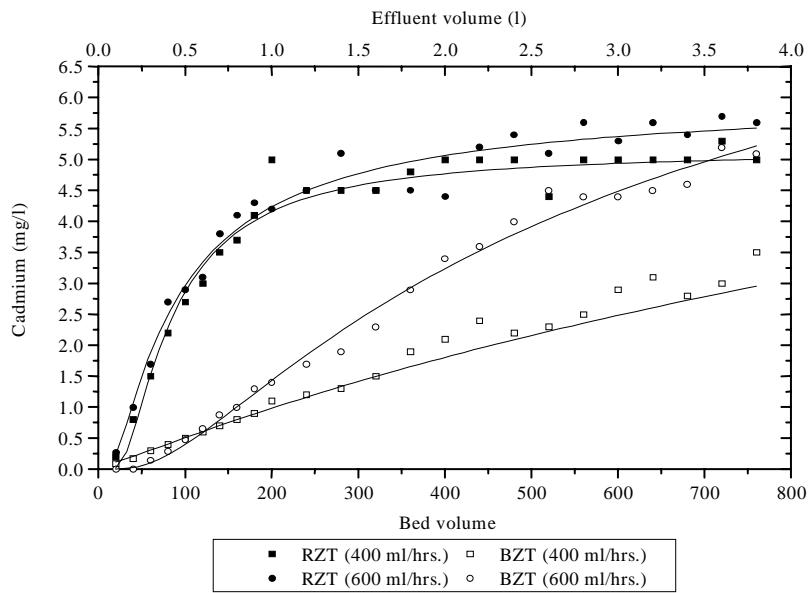
The cation exchange capacities for metals ions (Pb^{2+} ; Cd^{2+} ; Cu^{2+} ; Ni^{2+} and Zn^{2+}) from reddish and brownish zeolitic tuffs were tested in column studies, in two different conditions of flow rates, in grain sizes of 1-0.315 mm.. Feed solutions containing these heavy metal ions, previously neutralised with $NaOH$ to pH 6.8, were percolated through a 5 g non treated form of zeolitic tuffs. The breakthrough curves of the studied metal ions were taken as a function of effluent volume (treated bed volumes of solution) and are represented in Figures 5.13a-e.

Figures 5.13 a-e Breakthrough curves of heavy metal ions on natural form Jordanian zeolitic tuffs

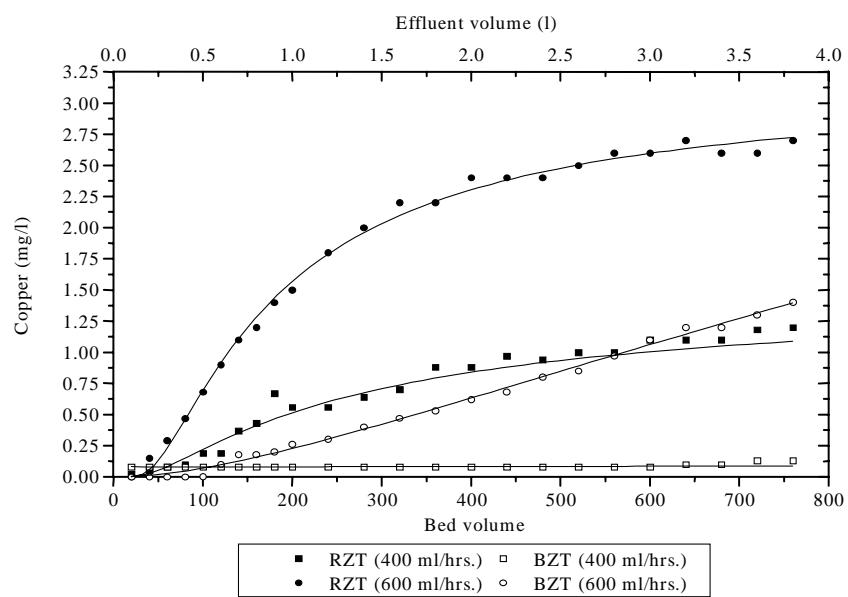
a. Lead



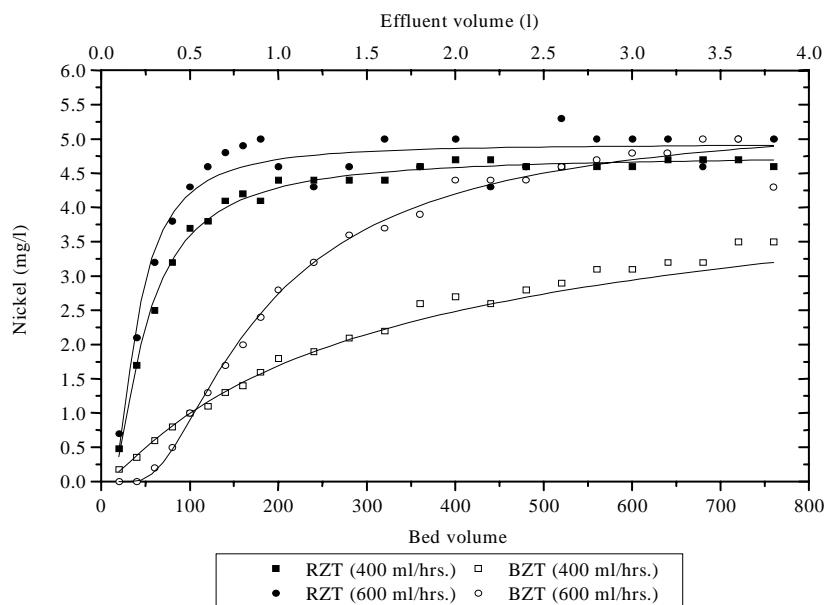
b. Cadmium



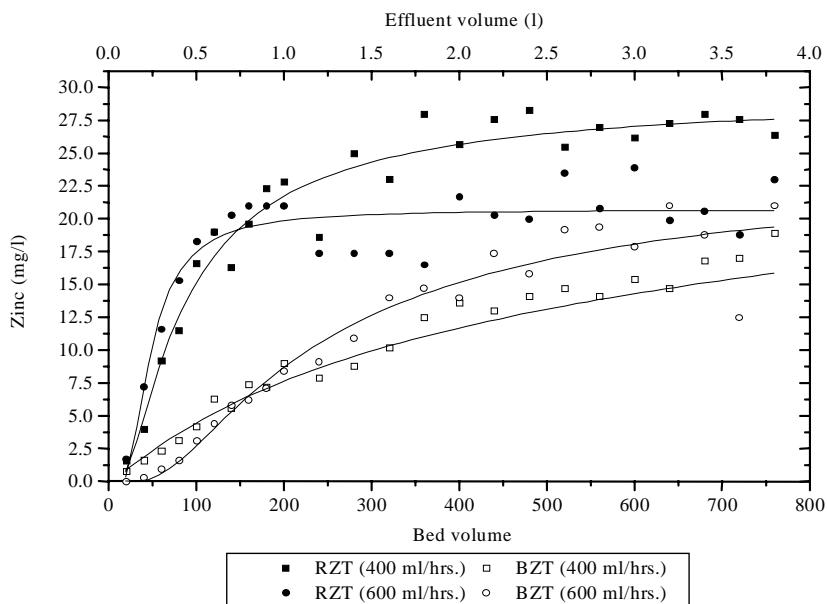
c. Copper



d. Nickel



e. Zinc

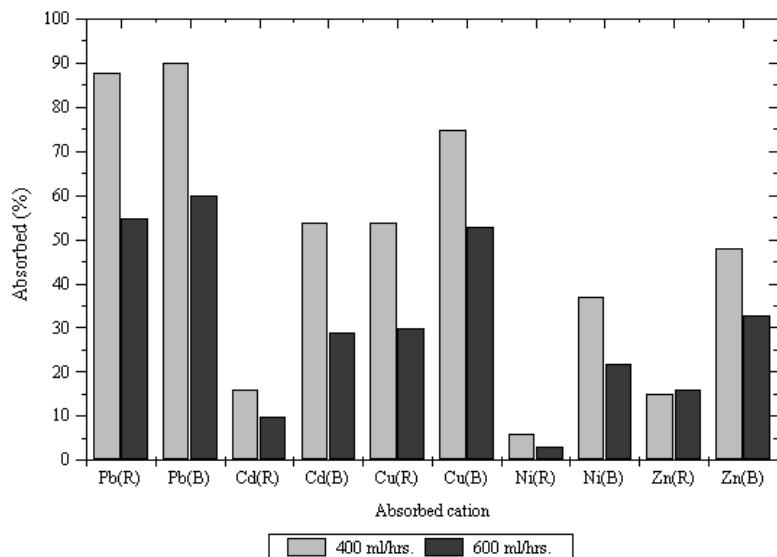


Figures 5.13a-e clearly demonstrate that the performance of both zeolitic tuffs (reddish and brownish) is strongly affected by the amount of retention time (Pansini, 1996). It tends to increase by decreasing the flow rate velocity. Therefore, the breakthrough curves are shifted further to the right on the x-axis (volume of treated effluent) as with Pb^{2+} and Cu^{2+} . In addition, the curves are made steeper (Cd^{2+} ; Ni^{2+} and Zn^{2+}) by increasing the effluent velocity, which indicates that (by the lower flow rate) both zeolitic tuffs (especially the brownish tuff) are more effective in the removal of these heavy metals from the solutions. When the reddish zeolitic tuffs were applied for the removal of cadmium and nickel ions from their solutions, the breakthrough curves were shown to be slightly dependent on flow rate velocities.

Similar results for Pb^{2+} ions were obtained by Pansini and Colella (1989 and 1990), who found that the ability of Campanian tuff (Chabazitic tuff) in Na-form to remove Pb^{2+} , with an effluent velocity of 810 ml/hr., was less than at an effluent velocity of 540ml/hr under the treatment conditions.

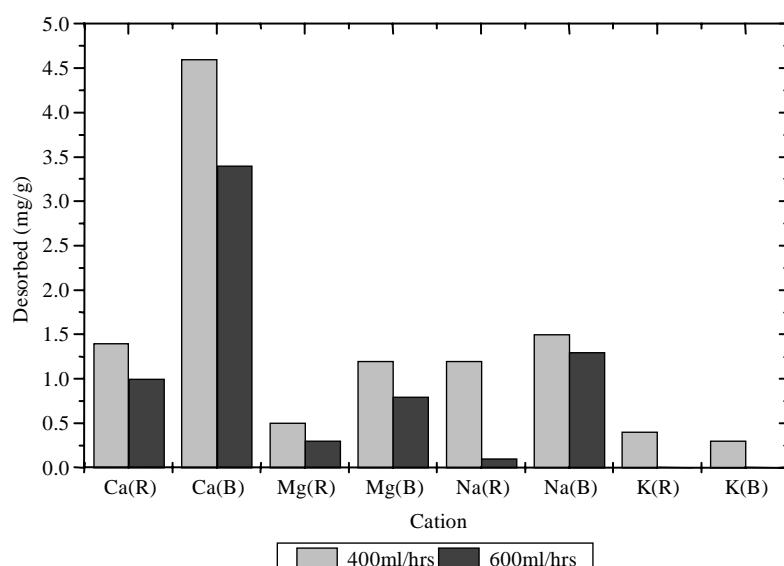
It is clear from the adsorption percent of the heavy metal ions (figure 5.14) that both zeolitic tuffs achieved higher values with a lower velocity of percolation (400 ml/hr.) than at a higher flow rate (600 ml/hr), with the sole exception of Zn^{2+} when the heavy metal solution was passed through the reddish zeolitic tuff bed. In contrast, the selectivity of both types of zeolitic tuffs for these metal ions was not influenced by the flow rate velocity, which its as follows: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+} > \text{Ni}^{2+}$. Figure (5.14) also denotes that the brownish tuff has a higher capacity of adsorption for Zn^{2+} , Ni^{2+} and Cu^{2+} .

Figures 5.14 Absorbed percent of heavy metals during the processes with different flow rates (influent concentrations in mg/l are represented in table 5.2 and appendix 5)



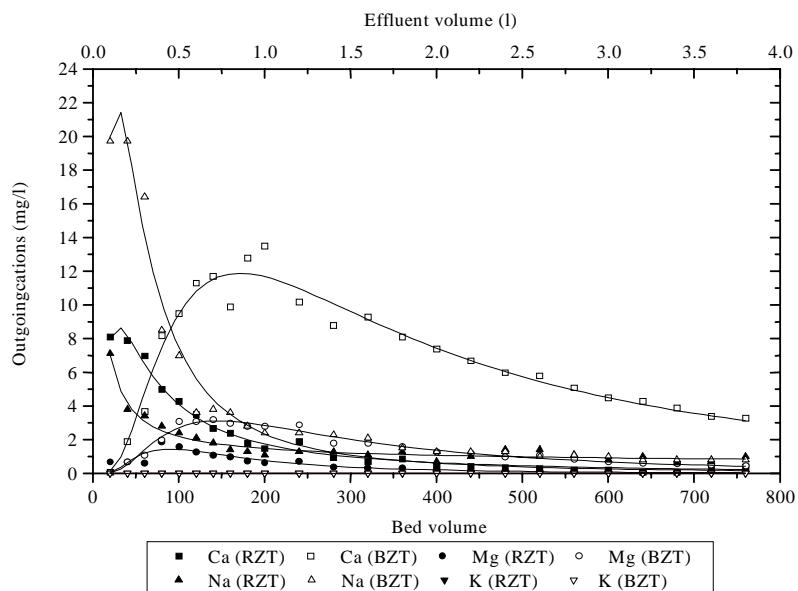
The amount of the outgoing cations as well as the removal efficiency using the untreated zeolitic tuffs beds were highly affected by the effluent flow rates. Figure 5.15 shows that the amount of cations extracted is increased by decreasing the flow rate (400ml/hr), and thus a higher amount of metal ions were removed from the solution. The sequence of the eluted cations from the beds show significant differences depending on the flow rate (figures 5.16 a and b).

Figure 5.15 Total desorbed cations from the zeolitic tuff beds (mg/g)

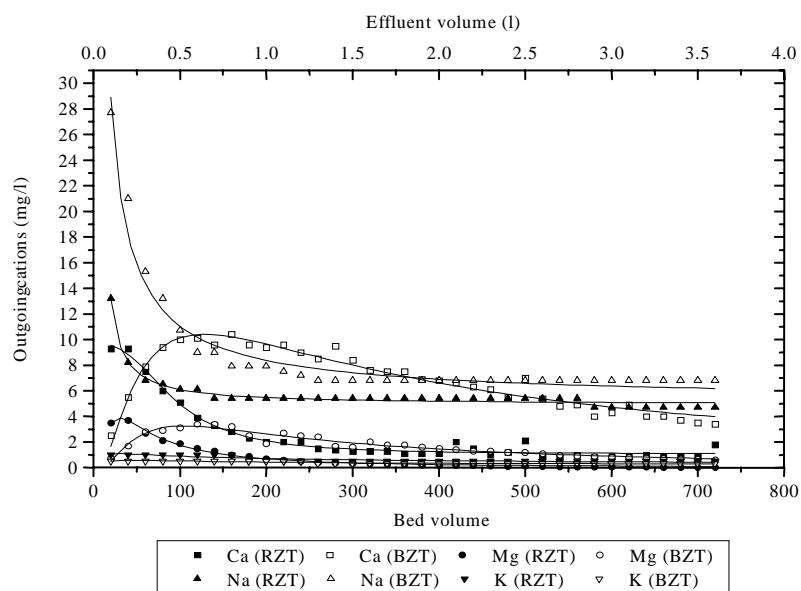


Figures 5.16a and b. Extracted cations during the equilibrium process

a. Effluent velocity of 600 ml/hrs.



b. Effluent velocity of 400 ml/hrs.



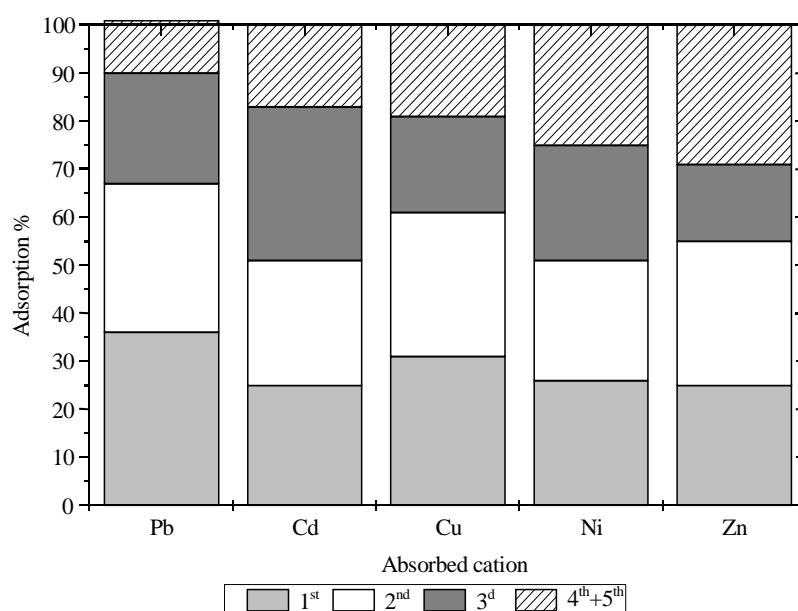
It appears from figure 5.16 a, that Ca^{2+} ions are more difficult to remove from brownish zeolitic tuffs in natural form than from the reddish tuffs and the same holes for other extractable cations from both types of zeolitic tuffs. As an exception, sodium ions were not easily extracted from both zeolitic tuffs when processed at a flow rate of 400ml/hrs (figure

5.16 b), and K^+ ions were not extractable at either flow rate. All the above results could be dependent upon the kinetic reasons; selectivity of Phillipsite for Ca^{2+} and Chabazite mineral for Na^+ and K^+ (Colella and Pansini, 1988). and the total adsorption capacity of zeolitic tuff beds did not achieve under these conditions of operation, meaning that, both beds have the ability to adsorb a higher amount of heavy metals from the solution (the equilibrium reaction of ions exchange process was not completely achieved) . It should be noted that both zeolitic tuffs contain an amount of other minerals, for example calcium carbonate, and thus these results could also highly influence the extraction by a dissolution process of these impurities. As well some of the unidentified minerals (Chapter 3) could play a role in the ion exchange process.

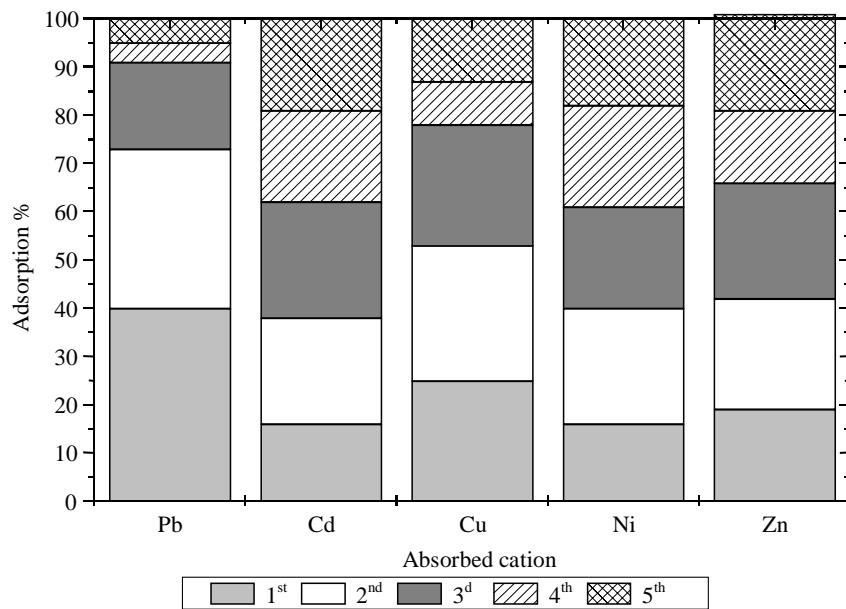
The length of the mass transfer zone (MTZ) was analysed for the exhausted zeolitic tuff beds at an effluent velocity of 600ml/hr, by extracting 1 cm at a time from the bed with HF-HCL acids. It was found that the heavy metals were absorbed throughout the whole bed depth (5 cm deep) and the MTZs were not evaluated (figures 5.17 a and b). The results obtained lead to the conclusion that the bed depth was not deep enough, and thus had a negative effect on the adsorption capacity of zeolitic tuffs as well as the leach-ability of some metal ions (breakthrough point) without any favourable treatment (figures 5.17 a and b).

Figure 5.17 a and b. Formation of mass transfer zone in the zeolitic tuff beds

a. Reddish zeolitic tuff bed



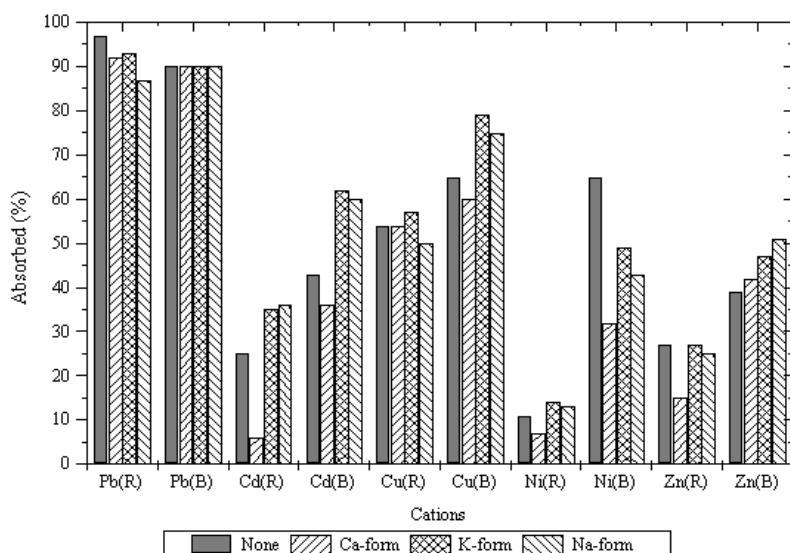
b. Brownish zeolitic tuff bed



5.4.2.3 Effect of the regeneration form

The first equilibrium sequence of the heavy metal adsorbed on the different forms of zeolitic tuffs are represented (as a percent of adsorption) in figure 5.18 (the influent concentrations of metal ions are represented in table 5.3).

Figure 5.18 Percent of heavy metals absorbed in relation to the type of regeneration



The removal efficiency of both zeolitic tuffs for Pb^{2+} ions was not affected by which pretreatment Homo ionic solution of Ca^{2+} ; K^+ or Na^+ (figure 5.18) was used, with exception of the Na-form reddish tuff, which shows a relatively less percent of adsorption. Additionally, the results of the adsorption effectively of reddish zeolitic tuffs for Cu^{2+} , Ni^{2+} and Zn^{2+} were similar when using the original zeolitic tuff sample as well as the samples in Na- and K-forms. The non-regenerated reddish or brownish zeolitic tuffs have higher adsorption capacities for Cd^{2+} than the Ca-form samples, but Na- or K-form samples have higher adsorption capacities than both. Na- and K-form brownish zeolitic tuffs obtained the highest adsorption (in percent) of Cu^{2+} and Zn^{2+} . The highest percent of adsorption of Ni^{2+} for the brownish tuff was obtained in non-treated form, followed by the K-, Na- and Ca-forms in that order. In general, the brownish zeolitic tuffs show a higher selectivity for heavy metal adsorption in all forms of regeneration than the reddish tuffs with the exception of Pb^{2+} ions, as represented in table 5.8

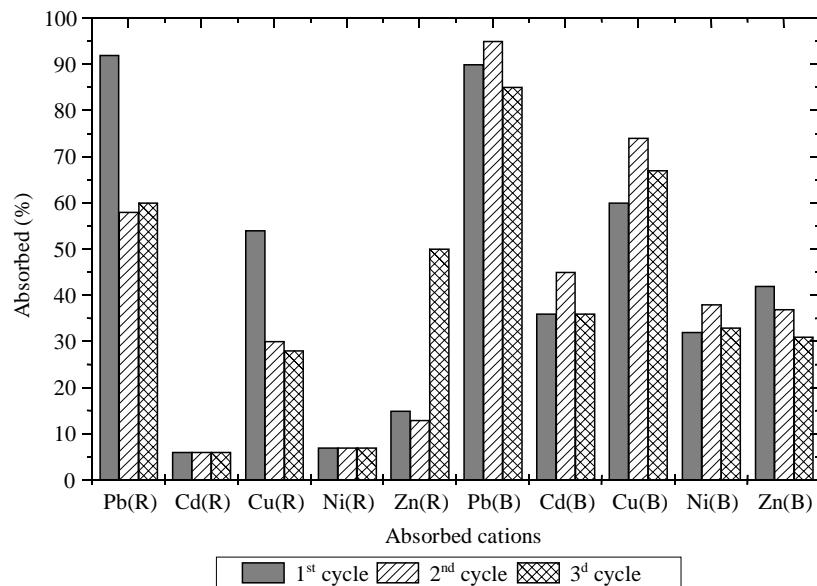
Table 5.8 Selectivity of zeolitic tuffs for heavy metal ions.

Zeolitic tuff / Forms	Reddish zeolitic tuff (RZT)	Brownish zeolitic tuff (BZT)
Non treated	$Pb^{2+} >> Cu^{2+} > Zn^{2+}, Cd^{2+} > Ni^{2+}$	$Pb^{2+} >> Cu^{2+}, Ni^{2+} > Cd^{2+} > Zn^{2+}$
Ca-form	$Pb^{2+} >> Cu^{2+} > Zn^{2+} > Ni^{2+}, Cd^{2+}$	$Pb^{2+} >> Cu^{2+} > Zn^{2+}, Cd^{2+} > Ni^{2+}$
K-form	$Pb^{2+} >> Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$	$Pb^{2+} >> Cu^{2+} > Cd^{2+} > Ni^{2+}, Zn^{2+}$
Na-form	$Pb^{2+} >> Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$	$Pb^{2+} >> Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$

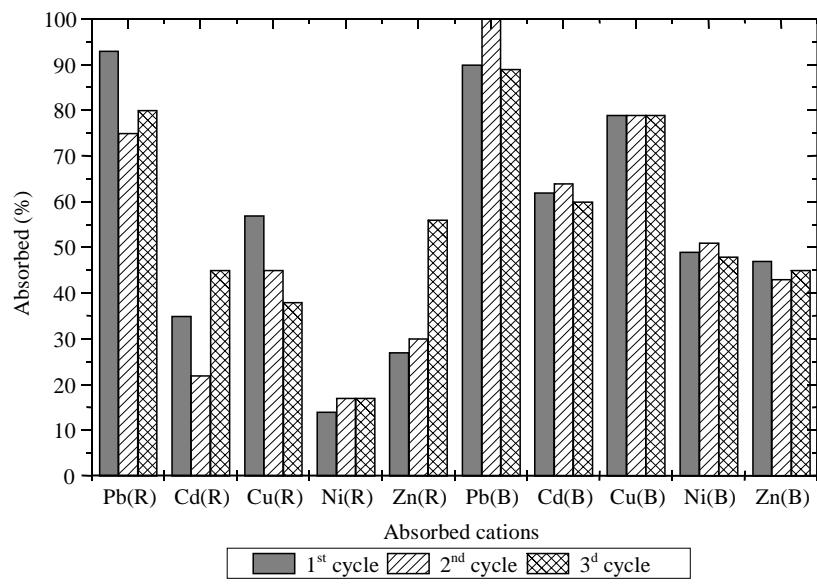
The exhaustion-regeneration-operations had an effect on the adsorption capacity and was repeated three times for zeolitic tuff beds in their Ca-, K- and Na-forms. The results are represented in figures 5.19a, b and c respectively.

Figure 5.19a-c The effect of regeneration-exhaustion processes on the adsorption capacity

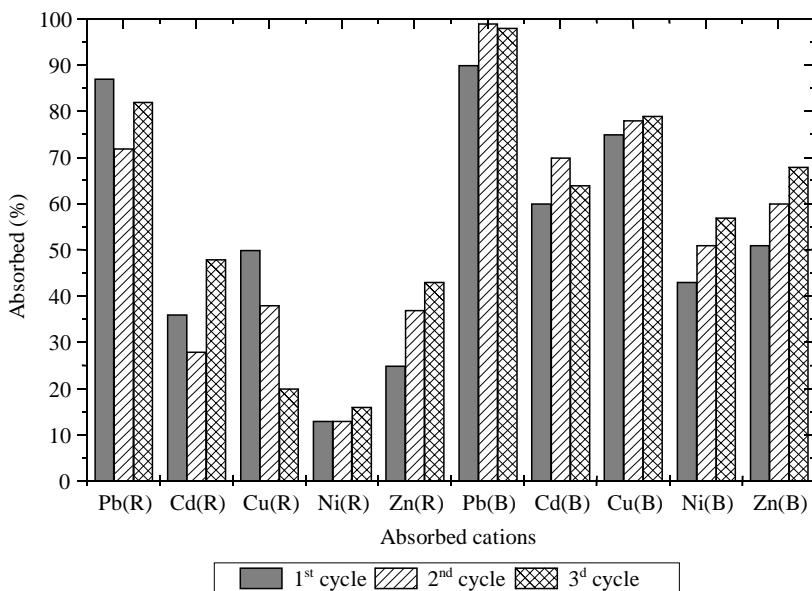
a. Ca-form



b. K-form



c. Na-form

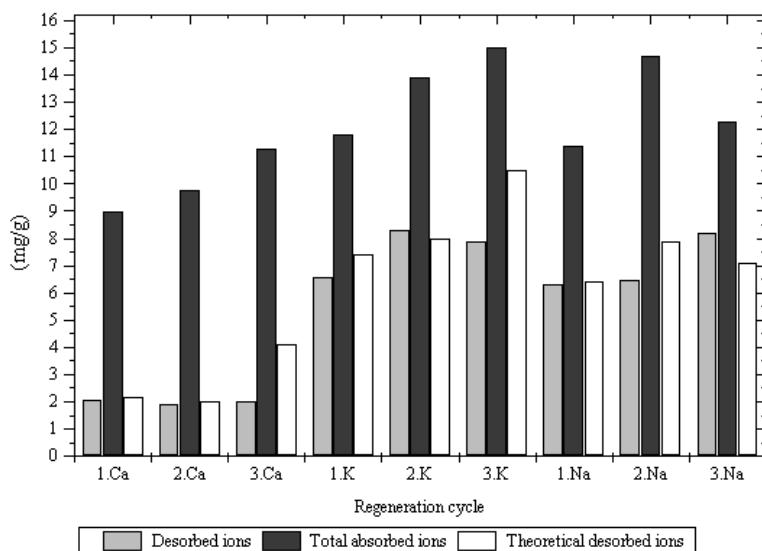


The results (figure 5.19 a, b and c) show that the brownish zeolithic tuffs in Na-form have an especially high efficiency for removing metal ions. The main differences of the adsorption capacity obtained from the repeating processes of exhaustion-regeneration sequences, might be: 1.Related to the number of exchange cycles that the zeolite is exposed to (Semmens and Seyfarth, 1978); 2. Greater amount of desorbed cations from the zeolithic tuff (such as K^+ and Ca^{2+}) 3. The regeneration efficiency which will be discussed in the next section, 5.4.2.1.4. 4. It was remarked that a drop in the flow rate occurred at times during the exhaustion processes, and 5. By back washing process with deionized water after each exhaustion step, which might lead to a rearrangement of particles in the tuff bed (effect of MTZ). It should be remembered that the absorption values of zinc using the atomic absorption apparatus (AAS) are greatly variable (not only for the water samples but also for the standard solution), and this might reflect some of the results concerning this ion.

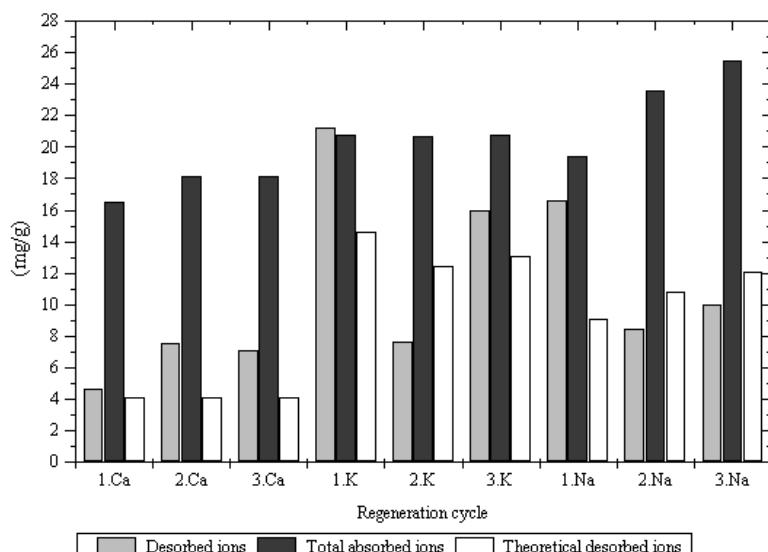
A comparison between the total amount of metal ions (Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) absorbed in different forms (and types) and the total amount of de-sorbed cations was made (figures 5.20 a and b).

Figure 5.20a and b Total absorbed/desorbed amount of heavy metal ions (mg/g).
 (The theoretical desorbed ions have been evaluated according to table 5.7 (section 5.4.1.2))

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuff



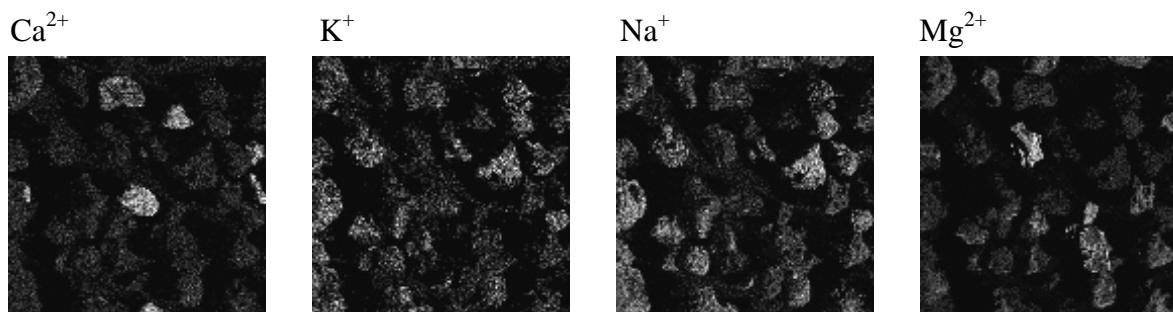
From these tests, two important results should be noted: 1. The highest adsorption efficiency for reddish zeolitic tuff beds is obtained when the bed is in K-form, 2. The highest adsorption efficiency for brownish zeolitic tuff beds is obtained when the bed is in Na-form. The amount absorbed here was the highest of both reddish and brownish zeolitic tuffs. In addition, the ion exchange capacity of Na- form of brownish zeolitic tuffs increased evermore

by repeating the exhaustion-regeneration processes. This could be due to much greater amounts of desorbed Ca^{2+} and K^+ ions resulting in a higher adsorption capacity for heavy metal ions (Semmens and Martin, 1988). Semmens and Martin found that the ion exchange capacity of Cd^{2+} and Cu^{2+} from solutions increased by repeating the exhaustion- regeneration process of Clinoptilolite in Na-form. Furthermore also after the third regeneration process of zeolite beds with a concentrated NaNO_3 solution found that, a significant amount of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were detected in the preused zeolite samples, which make it clear that also up to the third cycle of regeneration, some of these cations are existed in the zeolite sample as an exchangeable or non exchangeable cations, which are represented by the intensity of white portions in the zeolite minerals (figure 5.21a and b).

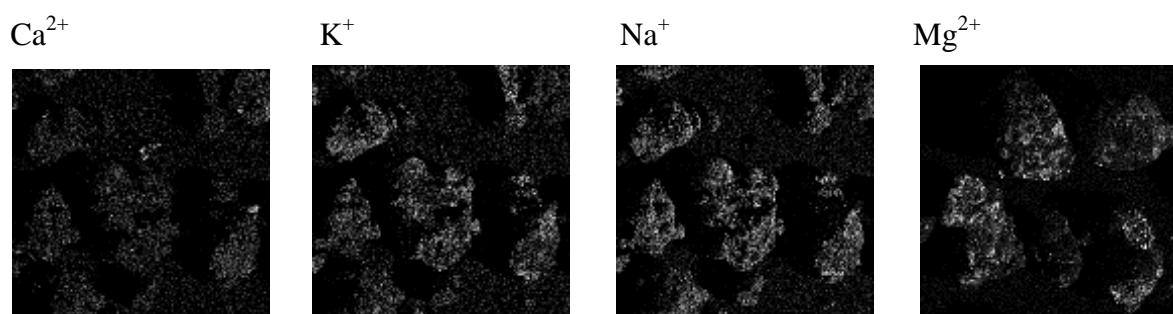
The amounts of desorbed cations, as the total desorbed ions was compared with the theoretically desorbed ions, from the mono-ionic zeolitic tuff columns (figures 5.20 a and b) show that an amount did not only exchanged from the zeolitic tuffs but also were found as excess ions on the surface of zeolitic tuff particles. The main variability in which the theoretical desorbed amount of ions (Ca^{2+} , K^+ or Na^+) are higher than the results obtained from the analytical methods, might due to the analytical method of zinc and also a personal false of the analysis of cations.

Figure 5.21a and b Microphotographs of cations distribution zeolitic tuffs after the 3^d treatment with concentrated NaCl solution.

a. Brownish zeolitic tuff



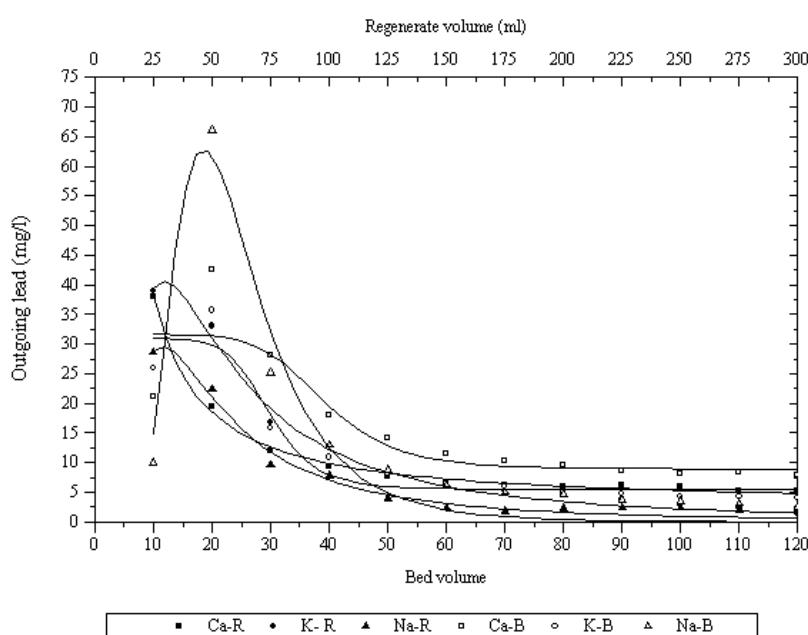
b. Reddish zeolitic tuff



5.4.2.3.1 Regeneration efficiency of zeolitic tuff

The previously used zeolitic beds in Ca-; K- and Na-forms were again reactivated with 1M, 300ml (120 BV) of CaCl_2 ; KNO_3 and NaNO_3 solutions with an effluent velocity of about 80-100 ml/hrs. Many samples of these effluent solutions were collected (each 25 ml equal to ca. 10BV) and analysed for heavy metals (figures 5.22-25).

Figures 5.22 Lead elution curves from the zeolitic tuff beds.



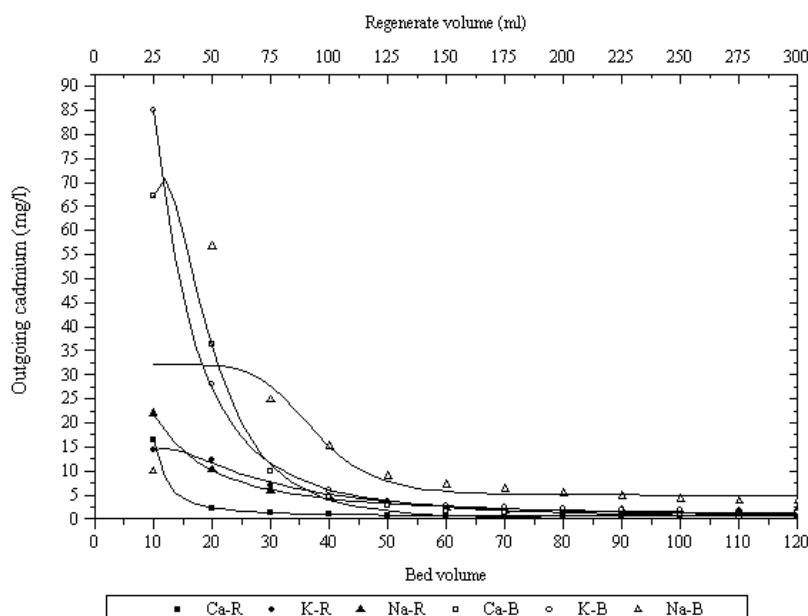
The elution of lead ions are highly depending on the type of regenerate. Figure 5.22 shows that the Pb^{2+} ions are exchanged with Ca^{2+} , K^+ or Na^+ in different percentages. The highest elution values of Pb^{2+} ions (25% from the adsorbed Pb^{2+}) was achieved by treating the previously used Ca-form brownish and reddish zeolitic tuffs with a CaCl_2 solution and the treating the exhausted K-form brownish tuffs with a KNO_3 solution. It is clear from figure (5.22) that this percentage of lead removal from the tuff beds has been achieved by a volume of regenerate equal to 120 BV, which might be due to the higher selectivity of both zeolitic tuffs for Pb^{2+} than Ca^{2+} as well as the brownish tuff for K^+ ions. The regeneration process with a NaNO_3 solution indicates a low percentage of lead elution from the Na-form zeolitic tuffs with an average values of 17% from the absorbed amount, which was achieved with only about 80 BV. This percentage of Pb^{2+} extracted might influenced by the regeneration process itself (the effect of flow rate velocity). The percentage of Pb^{2+} extracted

from the three used forms of zeolitic tuffs suggested the high selectivity of the zeolitic tuffs for Pb^{2+} ions (Pansini et al, 1996).

A higher regeneration efficiency of the exhausted Na-Chabazitic tuffs (Campanian tuff) was obtained by Colella and Pansini (1988). They found that a regeneration volume of 20 BV from $NaNO_3$ solution was enough to elute about 80% of the adsorbed Pb^{2+} on the Chabazitic tuff, while with using more regenerate volumes from $NaNO_3$ (200 BV) it reaches hardly 85%. Other results concern the regeneration process of the exhausted philipsitic tuff with Pb^{2+} ions was applied by the uses of $NaNO_3$ solution. Pansini et al (1996) and Pansini (1996) reported that the uses of 20 BV of this regenerate could remove about 60% of the absorbed Pb^{2+} on Phillipsitic tuff in Na-form, while to remove a higher percentage (70%), more regenerate from $NaNO_3$ are needed (75 BV).

The sequence of the cadmium extracted from the exhausted zeolitic tuff beds was obtained (figure 5.23)

Figure 5.23 Elution curves of cadmium from the zeolitic tuff beds.

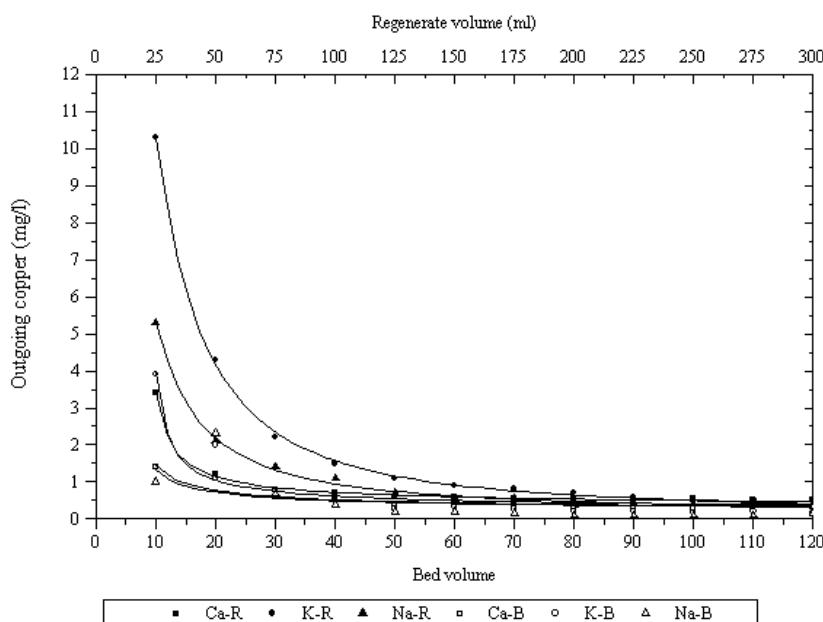


The Cd^{2+} ions, as shown in figure 5.23, tend to be highly exchanged by Ca^{2+}, Na^+ or K^+ from the reddish zeolitic tuff beds using a volume less than 80 BV of the regenerate, in percentages of 100%, 100% and 80% of the pre-absorbed amount, respectively. Similar results (100%) achieved for Cd^{2+} exchanged from the pre-used Ca-form bed of brownish zeolitic tuff using only 60 BV of a $CaCl_2$ regenerate. On the contrary, by using a 100 BV of

concentrated solution of KNO_3 exchange only 38% of the absorbed Cd^{2+} . This percentage of Cd^{2+} desorbed (38%) was also resulted by using 120 BV of a NaNO_3 solution (figure 5.23). While, Pansini (1996) reported that 70% of the present Cd^{2+} from the exhausted Chapazitic tuffs in Na-form (with a total cation exchange capacity for Cd^{2+} equal to 1.86 meq/g, with the absence of Na^+ as interfering ions) is eluted with not more than a 20 BV of NaNO_3 regenerate.

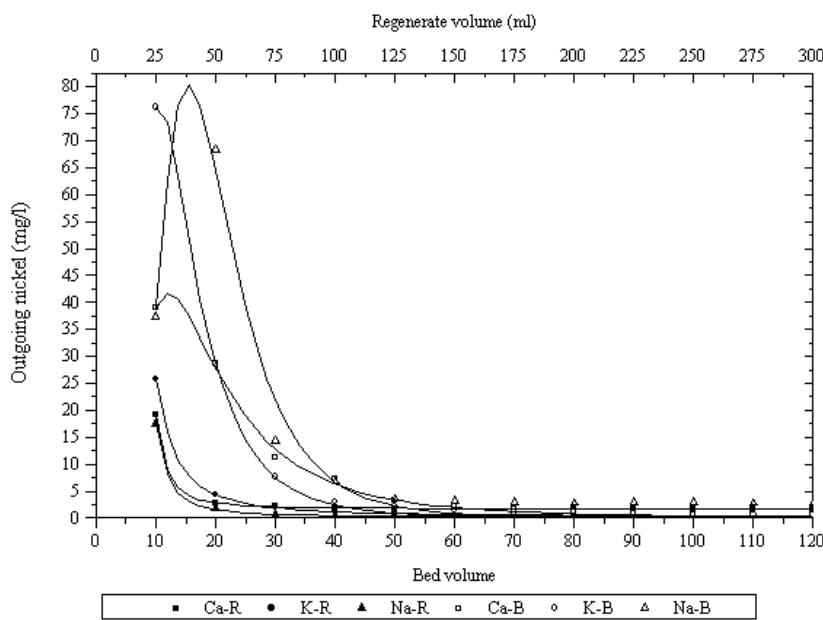
The amounts of Cu^{2+} back-exchanged from the used zeolitic tuffs are very low as the three regenerate solutions were used (figure 5.24). The maximum elution capacity of Cu^{2+} obtained from the reddish or brownish zeolitic tuffs, by using 120BVs of a CaCl_2 and a NaNO_3 regenerate, did not exceed 6-8% from the amount absorbed. The highest regeneration efficiency of Cu^{2+} obtained by percolating a KNO_3 solution throughout the exhausted brownish zeolitic tuff bed (15%).

Figure 5.24 Elution curves of copper from the zeolitic tuff beds



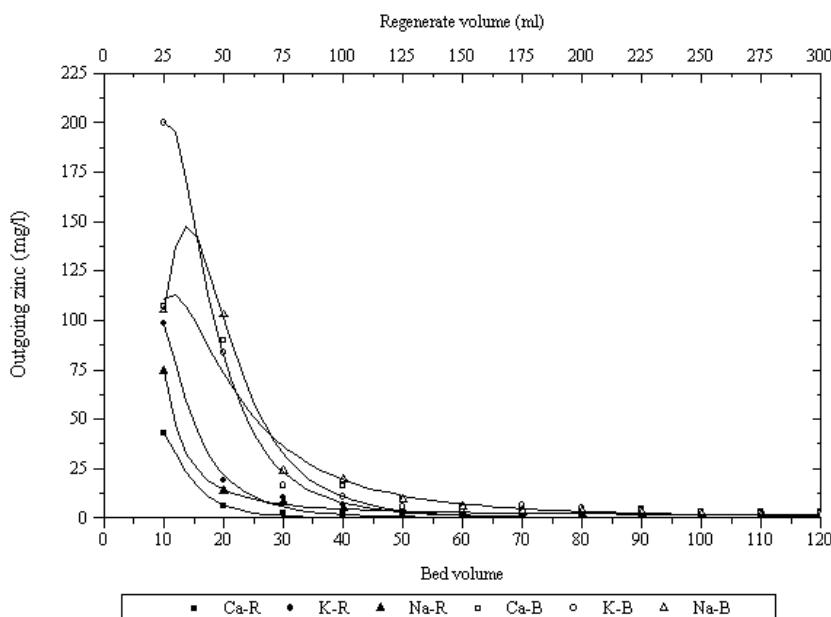
The high efficiencies (100%) for Ni^{2+} ions eluted from reddish and brownish zeolitic tuffs were obtained by using a CaCl_2 solution (figure 5.25). The same efficiency of regeneration was also obtained when the reddish zeolitic tuff was treated with NaNO_3 solution or by the treatment of brownish zeolitic tuff with KNO_3 solution. Lower efficiencies (75% and 50%) were obtained by passing a KNO_3 solution throughout the reddish zeolitic tuff and a solution of NaNO_3 on the brownish zeolitic tuff beds, respectively.

Figure 5.25 Elution curves of nickel from the zeolitic tuff beds



In concern to Zn^{2+} ions eluted from the zeolitic tuffs (figure 5.26) found that the regeneration efficiency of the reddish zeolitic tuffs ranges between 44% and 48% by using about 80 BV of either $CaCl_2$, KNO_3 or $NaNO_3$ solution, while the highest efficiency (50%) was obtained from the brownish zeolitic tuff using about 60 BV of KNO_3 solution, 40% and 33% obtained by applying also about 60BV of $NaNO_3$ or $CaCl_2$ solution respectively.

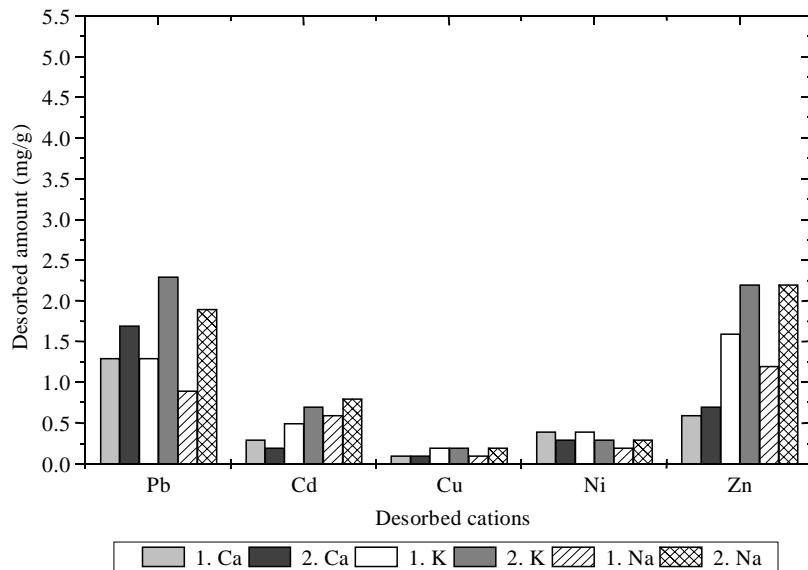
Figure 5.26 Elution curves of zinc from the zeolitic tuff beds



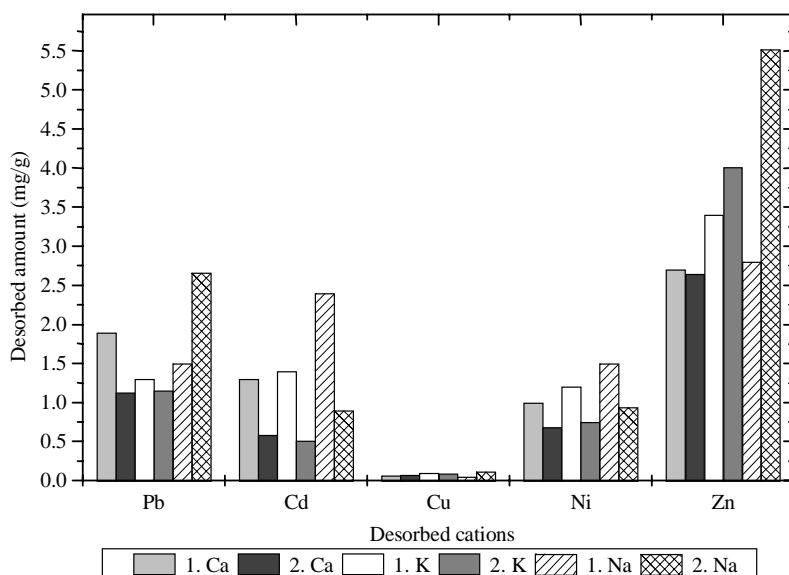
The regeneration efficiency of the exhausted zeolitic tuffs with heavy metals by their retreated with a concentrated solutions of CaCl_2 , KNO_3 or NaNO_3 during the first and second cycle of regeneration (exhaustion-regeneration-exhaustion-regeneration) are represented in figures 5.27 a and b.

Figures 5.27a and b Regeneration efficiencies of exhausted zeolitic tuffs.

a. Reddish zeolitic tuffs



b. Brownish zeolitic tuffs



Figures 5.27 a and b show that the amount of heavy metals extracted from their exhausted zeolitic tuffs are variable with a relation to the number of regeneration cycle. They make it clear that by the second regeneration cycle a greater amount of Pb^{2+} and Zn^{2+} tend to be desorbed, and thus, a higher efficiency of regeneration was obtained. The amount of Ni^{2+} and Cd^{2+} extracted from the brownish bearing's tuff seem to be less than the amount extracted from the first cycle, this might depend on the conditions of regeneration process during the second cycle (flow rate velocity). On the other hand, Cu^{2+} shows to be non extractable from both tuffs also by applying any of the regeneration solutions ($CaCl_2$; KNO_3 or $NaNO_3$), where their extracted amount are not exceeded, in all cases, 0.3 mg/g. The very low eluted values of Cu^{2+} ions from zeolitic tuffs are not clear when its compared with the fact that, Cu^{2+} with a very high free energy of hydration (-498.7 Kcal/g-ion) prefers the solution phase (as remarked by Semmens and Seyfarth (1978)). This may indicate that the main process of Cu^{2+} elimination from solutions has been achieved by a precipitation methods (within the minerals structure or might be on the zeolitic tuffs particles) more than the ion exchange process itself (Semmens and Seyfarth, 1978). The result concerns the elution of Cu^{2+} should be studied in detail.

It can be concluded that the regeneration efficiency of zeolitic tuffs for reuse purposes might be improved by repeating the regeneration-exhaustion processes.

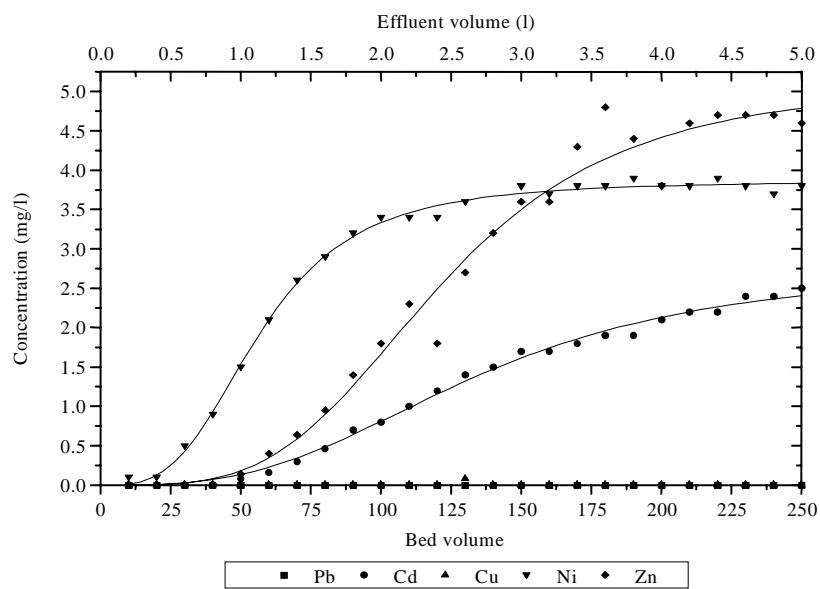
5.4.2.4 Synthetic wastewater

Two ion exchange columns (20 cm long and 2cm id.) were filled with 20g (approximately 10cm in length) of either brownish or reddish zeolitic tuffs in Na-form. The beds were treated by percolating a complex solution in a down flow direction with a flow rate of 600 ml/hr. The synthetic solution used contained Pb^{2+} (4.1 mg/l), Cd^{2+} (3.7-4.1 mg/l), Cu^{2+} (2.6 mg/l), Ni^{2+} (3.8 mg/l), Zn^{2+} (6.8 mg/l), NH_4^+-N (92 mg/l) and a matrix of tap water, containing Mg^{2+} 4.7-5.1 mg/l and Ca^{2+} ranging from 95 to 105 mg/l. These Ca^{2+} ions were added separately to the solution through the addition of CaO. This gave the water solution a pH of 6.5.

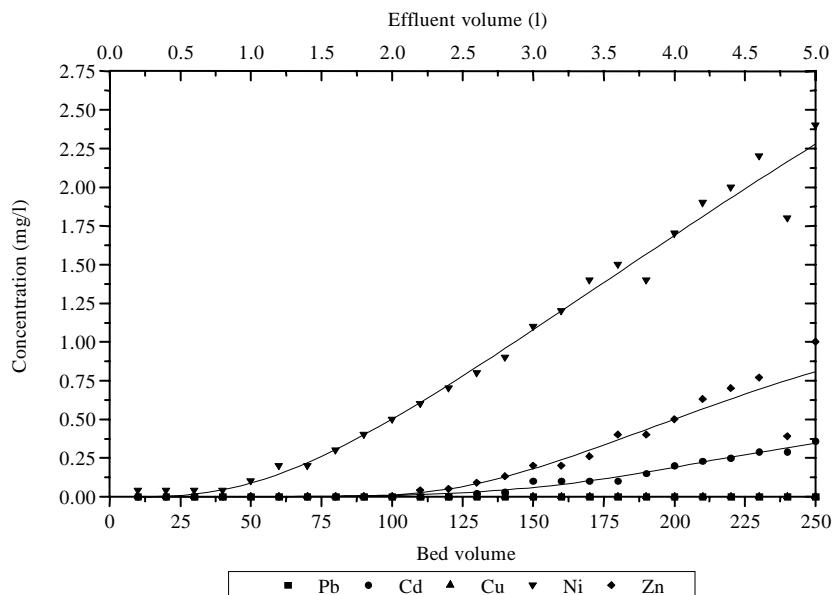
The effluents of the tuff beds were collected manually in relation to the volume of solution, then they were acidified and analysed for their cation content. The results are shown in figures 5.28a and b, and figure 5.29.

Figure 5.28a and b. Breakthrough curves of metal ions for both beds of zeolitic tuffs in Na-form.

a. Reddish zeolitic tuff



b. Brownish zeolitic tuff

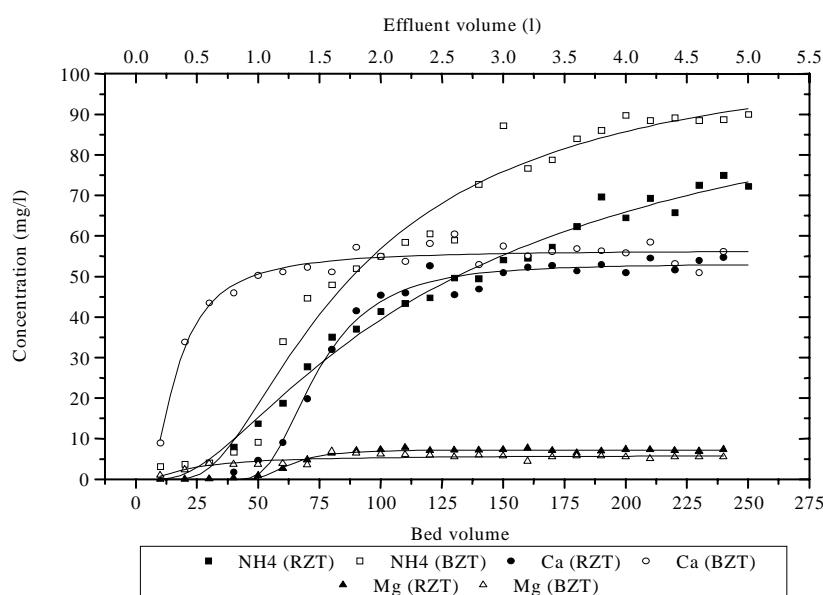


It is obvious from figures 5.28a and b that brownish zeolitic tuff (under these condition of operation) is much more effective at removing metal ions from solutions when highly concentration of counter Ca^{2+} and NH_4^+ ions are present.

The maximum values of heavy metal concentrations which are allowed in Jordan (Appendix 2) were used as the breakthrough points in figures 5.28a and b. It was found that both tuffs were a very suitable alternative for treatment of wastewater containing either Pb^{2+} or Cu^{2+} ions up to 250BVs. The brownish zeolitic tuff appeared to have a higher efficiency for removing Cd^{2+} , Ni^{2+} and Zn^{2+} at 120 BVs, 70 BVs and 250BVs. On the other hand, the use of reddish zeolitic tuff in wastewater treatment resulted in a higher removal percentage of NH_4^+ , Ca^{2+} and Mg^{2+} (figure 5.29).

It can be concluded that the uses of brownish zeolitic tuff in column operation systems for the removal of heavy metal ions in wastewater treatment is an alternative for the chemical precipitation method.

Figure 5.29 .Breakthrough curves of counter ions on zeolitic tuffs in Na-form.



It was noted that the pH values of the treated solutions were not highly affected by the treatment process because the final pH values did not exceed 1-0.5 units. The increasing of the pH value of the effluents resulted from the leaching of sodium bicarbonate from the tuffs.

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 measuring 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

Chapter 6. Conclusion and Recommendation

- 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 $\text{NH}_4^+ \text{-N}$ (46g/kg) in comparison with the brownish zeolitic tuff (20g/kg). Its capacity to absorb $\text{NH}_4^+ \text{-N}$ 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 $\text{NH}_4^+ \text{-N}$ 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 $\text{NH}_4^+ \text{-N}$ ions.
 10. The percentage of $\text{PO}_4^{3-} \text{-P}$ 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 $\text{PO}_4^{3-} \text{-P}$ 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 $\text{NH}_4^+ \text{-N}$ 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 $\text{NH}_4^+ \text{-N}$ 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 $\text{PO}_4^{3-} \text{-P}$ 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

Chapter 6. Conclusion and Recommendation

- amount of cation adsorption was obtained using the reddish zeolitic tuff: Cd²⁺ (12.2 mg/g); Cu²⁺ (2.3 mg/g); Ni²⁺ (5 mg/g) and Zn²⁺ (9 mg/g). With the one exception of Pb²⁺ ions, whose that were shown to be similarly absorbed on both zeolitic tuffs (145-150 mg/g).
16. The removal process of Pb²⁺ on both tuffs as well as Cd²⁺ and Zn²⁺ 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 Cd²⁺; Cu²⁺; Ni²⁺ and Zn²⁺ on reddish zeolitic tuff as well as Cu²⁺ and Ni²⁺ 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 Pb²⁺ (37 mg/g); Cd²⁺ (12.4 mg/g) and Cu²⁺ (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 Zn²⁺, Ni²⁺, Cu²⁺ or Cd²⁺, 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 Ca²⁺ 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. Pb²⁺ and Cu²⁺ 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 Zn²⁺ absorbed was highly dependent on the regeneration form used and was not affected by the presence of Ca²⁺ or Na⁺ ions.
 - c. Similar effects of the Ca²⁺ or Na⁺ were observed on the adsorption capacity of Cd²⁺ and Ni²⁺ ions.
 - d. The Na form of reddish zeolitic tuff showed a higher efficiency for Ca²⁺ 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

Chapter 6. Conclusion and Recommendation

number of regeneration-exhaustion repetitions. One exception was recognised for Cu²⁺ ions, which had the lowest extraction percentage from both zeolitic tuffs using a CaCl₂, KNO₃ or NaNO₃ regenerate. This might indicate that Cu²⁺ 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 NaNO₃ 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 NH₄⁺ and Ca²⁺ ions.

6.2 Recommendations

The results obtained through these experiments are:

1. The use of the exhausted reddish zeolitic tuff with NH₄⁺ as a slow release fertiliser.
2. When NH₄⁺ or Ca²⁺ 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 (Pb²⁺, Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺) 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 NH₃ 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.

References

1. Ahmad, Z. B. and Dyer, A. (1984): Ion-exchange in Ferrierte, a natural zeolite. In Naden, D. and Streat, M. :Ion Exchange Technology. Society of Chemical Industry. England. pp.519-532.
2. Albino, V., Cioffi, R. and Colella, C. (1995): Disposal of lead-containing zeolite sludge in cement matrix, Environmental technology, Vol. 16., pp. 147-156.
3. Allen, E. R. and Ming, D. W. (1995): Recent progress in the use of natural zeolites in agronomy and horticulture: In Natural Zeolites '93, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 477-490.
4. Amicarelli, V., Baldassarre, G., Boghetich, G., Liberti, L. and Limoni, N. (1988): Use of Italian zeolites for deammoniation of municipal wastewater. 2nd International Conference on Environment Protection, S. Angelo, Ischia (Na) Italy (personal contact with L. Liberti), pp. 2.A-75-81.
5. Amicarelli, V. and Liberti, L. (1991): Zeolite ammonia removal at Manfredonia municipal plant: In Atti I° Convegno Nazionale di Scienza e Tecnologie delle Zeoliti, C.Colella edt., L'Aquila, (personal contact with L. Liberti)
6. Axente, D., Abrudean, M. and Baldea, A. (1983): Adsorption on Romanian natural Clinoptilolite. Zeolite, Vol. 3, pp. 259-260.
7. Bannyan, H. (1990): The inadequacy of stabilization ponds treatment as manifested by the effects of khirbet es-Samra effluent on the ground water quality of the surrounding area: In Water Pollution in Jordan, E. Salameh, edt., Friedrich Ebert Stiftung. Jordan
8. Barbarick, K. A. and Pirela, H. J. (1984): Agronomic and horticultural uses of zeolites: A Review: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 93-105.
9. Barrer, R. M. and Munday, B. M. (1971): Cation exchange reactions of a sedimentary Phillipsite. J. Chem. Soc., pp. 2904-2909.
10. Bayerischen Landesanstalt für Wasserforschung (1989):Aktuelle Probleme des Gewässerschutzes: Nährstoffbelastung und-elimination, Oldenbourg Verlag, Münschen.
11. Bish, D. L. (1984): Effects of exchangeable cation composition on the thermal expansion / contraction of Clinoptilolite. Clays and Clay Minerals, Vol. 32, No. 6, pp. 444-452.
12. Black, J. A. (1977 Water pollution technology, Reston publishing Company, Reston, Virginia.
13. Blanchard, G., Maunaye, M., and Martin, G. (1984): Removal of heavy metals from waters by means of natural zeolites. Water Research, Vol. 18, No. 12., pp. 1501-1507.

References

14. Breck, D. W. (1974): Zeolite molecular sieves.. John Wiley and Sons.
15. Brown, J. and Ray, N. J. (1984): Ion Exchange in Water Purification, Where do we Stand?. In Naden, D. and Streat, M. : Ion Exchange Technology. Society of Chemical Industry. England. pp. 14-24.
16. Burriesci, N., Valente, S., Zipelli, C. and Bart, J. C. J. (1984): Studies on zeolites in agriculture. Effect on crop growth of *Prunus persica* and *Vitis vinifera*. *Zeolites*, Vol. 4, pp. 373-376.
17. Calligaris, M. and Nardin, G. (1982): Cation site location in hydrated Chabazites. crystal structure of barium- and cadmium- exchanged Chabazites. *Zeolites*, Vol. 2, pp. 200- 204.
18. Ciambelli, P., Corbo, P., Porcelli, C., and Rimoli, A. (1985): Ammonia removal from wastewater by natural zeolites. I. Ammonium Ion Exchange Properties of an Italian Phillipsite Tuff. *Zeolites*, Vol. 5, May, pp. 185-212.
19. Ciambelli, P., Corbo, P., Liberti, L., Lopez, A., and Porcelli, C. (1985): Ammonia removal from municipal water by Phillipsite. In Drzaj, B., Hocevar, S. and Pejovnik, S., : *Zeolites: Synthesis, Structure, Technology and Application*. Elsievier Science.
20. Ciambelli, P., Corbo, P., Lumare, F. and Porcelli, C. (1984): Ammonium ion exchange with Phillipsite tuff in relation to aquacultural systems: Use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 245-253.
21. Cioffi, R., Colella, C., Marroccooli, M., Pansini, M. and Valenti G. L. (1991): Stabilisation of Cr³⁺-loaded zeolite tuffs in cement matrix. Reprinted from: Proc. Int. Conf. On Heavy Metals in the Environment, J. G. Farmer Edt., Vol. 2, Edinburgh 1991, (Personal Communication with Colella).
22. Cioffi, R., Pansini, M., Caputo, D. and Colella, C. (1996): Evaluation of mechanical and leaching properties of cement-based solidified materials encapsulating Cd-exchanged natural zeolites. *Environmental Technology*, Vol. 17., pp. 1215-1224.
23. Colella, C. (1995): Use of Italian Chabazite and Phillipsite for the removal of heavy metals from wastewater: a review: In *Natural Zeolites '93*, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 363-376.
24. Colella, C. (1996): Ion exchange equilibria in natural zeolites. *Mineralium Deposita*, Vol. 31, pp. 554-562.
25. Colella, C. and Pansini, M. (1988): Lead Removal from Wastewaters using Chabazite Tuff. ACS Symposium Series 368, Flank, W. H. and Whyte, Jr. T edition. Perspectives in Molecular Sieve Science, chapter 32, Washington, DC. pp. 500-510.

References

26. Colella, C., Aiello, R. and Nastro, A. (1984): Evaluation of Phillipsite tuff for the removal of ammonia from aquacultural wastewaters: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 239-245.
27. Colella, C., DE'Gennaro, M., Langella, A. and Pansini, M. (1995): Cadmium removal from wastewaters using Chabazite and Phillipsite: In Natural Zeolites '93, , D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 377-384.
28. De`Gennaro, M. and Colella, C. (1989): Use of Thermal Analysis for the Evaluation of Zeolite Content in Mixtures of Hydrated Phases. *Thermochimica Acta*, Vol. 154, pp. 345-353.
29. Deutsche Gesellschaft for Technische Zusammenarbeit -GTZ- (1984): *Abwassertechnologie*. Springer-Verlag, Berlin.
30. Dorfner, K.(1990): Ion exchangers. Walter de Gruyter, Berlin
31. Dwairi, I. M. (1991): Evaluation of Jordanian Phillipsite tuff in removal of ammonia from wastewater: Experimental study, Al-Balqa Journal, vol. 1, pp. 53-66.
32. Dwairi, I. M. (1992): Jordanian zeolites: Evaluation for possible industrial application of natural Aritain Phillipsite tuffs, *Dirasat*, Vol. 18 B, No. 1, pp. 23-44.
33. Dwairi, I. M. (1993): Removal of ammonium from water using Phillipsite tuff from North-eastern Jordan: An evaluation study, Mu'tah Journal for Research and Studies, Vol. 8, no. 4., pp. 7-22.
34. Dwairi, I. M. (1998): Evaluation of Jordanian zeolite tuff as a controlled slow-release fertiliser for NH_4^+ , *Environmental Geology*, Vol. 34, no. 1, pp. 1-4.
35. Dwairi, I. M. (1998): Renewable, controlled and environmentally safe phosphorus release in soils from mixtures of NH_4^+ -phillipsite tuff and phosphate rocks, *Environmental Geology*, Vol. 34, No. 4, pp. 293-296.
36. Dwairi, I. M: (1998): Conserving toxic ammoniacal nitrogen in manure using natural zeolite: A comparative study, *Bull. Environ. Contam. Toxicol.* Vol. 60, pp. 126-133.
37. Dyer, A. and Zubair, M. (1998): Ion Exchange in Chabazite. *Microporous and Mesoporous Materials*, Vol. 22, pp. 135-150.
38. Dyer, A. and Faghihian, H. (1998): Diffusion in Heterionic Zeolites: Part 1. Diffusion of Water in Heterionic Natrolites. *Microporous and Mesoporous Materials*, Vol. 21, pp. 27-38.
39. Dyer, A. and Faghihian, H. (1998): Diffusion in Heterionic Zeolites: Part 2. Diffusion of Water in Heterionic Stilbites. *Microporous and Mesoporous Materials*, Vol. 21, pp. 39-44.

References

40. Eberl, D. D., Barbarick, K. A. and Lai, T. M: (1995): Influence of NH₄-exchanged clinoptilolite on nutrient concentrations in Sorgham-Sudangrass: : In Natural Zeolites '93, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 491-504.
41. Eraifej, N. and Abu-Jaber, N. (1999): Geochemistry and pollution of shallow aquifers in the Mafraq area, North Jordan. Environmental Geology, Vol. 37, No. 1-2, pp.162-170.
42. Eyde, T. H. (1993): Using zeolites in recovery of heavy metals from mining effluents. EPD Congress, The minerals, metals and materials society, (Personal communication with the GSA Resources, Inc, USA).
43. Fangmeier, A., Hadwiger-Fangmeier, A., Van der Eerden, L. and Jäger, H. (1994): Effects of atmospheric ammonia on vegetation-A review. Environmental Pollution, Vol. 86, pp. 43-82.
44. Flanigen, E. M. (1984): Adsorption properties of molecular sieve zeolites: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 55-69.
45. Flank, W. H. (1977): Properties of synthesised, ion-exchanged, and stabilised zeolite Rho. ACS Symposium Series 40. Katzer, James. edi. Molecular Sieve II. pp. 43-52.
46. Fletcher, P. and Townsend, R. (1982): Exchange of Ammonium and Sodium Ions in Synthetic Faujasites. J. Chem. Soc., Farady Trans. I, Vol. 78, pp. 1741-1753.
47. Forman, D. (1991): Nitrate exposure and human cancer: In Nitrate Contamination: Exposure, Consequence and Control, I. Bogardi, R. Kuzelka and W. Ennenga, eds., Springer-Verlag, Berlin, pp. 281-288.
48. Förstner, U. and Wittmann, G. (1981): Metal pollution in the aquatic environment. Springer- Verlg Heidelberg, Germany.
49. Gal, I. J. and Radovanov, P. (1975): Ion exchange of synthetic 13X zeolite with Ni²⁺, Co²⁺, Zn²⁺ and Cd²⁺ Ions. J. of Chem. Society., Farady Trans. I 71, pp. 1671-1677.
50. Gharaibeh, S. and Rawajfih, Z. (1989): Abwasserbehandlung und Energieverbrauch in Jordanien, Fallstudie für Entwicklungsländer. Wasserwirtschaft, Vol. 79, No. 9, pp. 458-463.
51. Gottardi, G. (1978): Mineralogy and crystal chemistry of zeolites: in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, pp. 31-44.
52. Gottardi, G. and Galli, E. (1985): Natural zeolites, Springer-Verlag, Berlin Heidelberg.

References

53. Hawkins, D. B. (1984): Occurrence and availability of natural zeolites: Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 69-79.
54. Hayhurst, D. T. (1978): The potential use of natural zeolites for ammonia removal during coal-gasification: In Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, pp. 503-508.
55. Hernandez, J. E. G., Martin, M. M. G., Pino, J. S. N. and Rodriguez, C. D. A. (1992): Treatment of wastewater effluents with Phillipsite rich tuffs. Environmental Pollution, Vol. 76, pp. 219-223.
56. Hertzenberg, E. P. (1983): Use of zeolite NaA for removal of trace heavy metals from metal plating wastewater. In: Olson, D. and Bisio, A.(1983) : Proceedings of the Sixth International Zeolite Conference.
57. Hiller, F. (1987): Die Batterie und die Umwelt, Expert Verlag, Germany.
58. Himsley, A. and Bennett, J. A. (1984): A New Continuous Packed-Bed Ion Exchange System Applied to Treatment of Mine Water: In Naden, D. and Streat, M. :Ion Exchange Technology. Society of Chemical Industry. England. pp.144-152.
59. Hlavay, J., Vigh, G., Olasz, V. and Inczedy, J. (1982): Investigations on natural Hungarian zeolite for ammonia removal, Water Res., Vol. 16, pp. 417-420.
60. Hlavay, J., Vigh, G., Olasz, V. and Inczedy, J. (1983): Ammonia and iron removal from drinking water with Clinoptilolite tuff. zeolites, Vol. 3, pp. 17-19.
61. Howden, M. and Pilot, J. (1984): The choice of ion exchanger for British nuclear fuels Ltd's Site ion exchange effluent plant: In Naden, D. and Streat, M. : Ion Exchange Technology. Society of Chemical Industry. England. pp.66-73.
62. Hulbert, M. H. (1987): Sodium, calcium, and ammonium exchange on Clinoptilolite from the Fort Laclede deposit. Sweetwater county, Wyoming. Clays and Clay Minerals, Vol. 35, No. 6, pp. 458-462.
63. James, R. and Sampath, K. (1999): Effect of zeolite on the reduction of cadmium toxicity in water and a freshwater fish, Oreochromis mossambicus. Bull. Environ. Contam. Toxicol. Vol. 62, pp. 222-229.
64. Jing, J. and Logan, T. (1992): Heavy metals in the environment. J. Environ. Qual. Vol. 21. Pp. 73-81.
65. Jorgensen, S. E. and Barkacs, K. (1976): Ammonia removal by use of Clinoptilolite. Water Research, Vol. 10, pp. 213-224.

References

66. Kallo, D. (1995): Wastewater purification in Hungary using natural zeolites: : In Natural Zeolites '93, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 341-350.
67. Kayabali, K. and Kezer, H. (1998): Testing the ability of Bentonite-amended natural zeolite (Clinoptilolite) to remove heavy metals from liquid waste. Environmental Geology, Vol. 34, No. 2/3, pp. 95-102.
68. Kayser, R. (1987): Biologische Stickstoff- und Phosphor-elimination in Abwasserreinigungsanlagen Veröffentlichungen des Institutes für Städtebauwesen (Heft 42), Technische Universität Braunschweig.
69. Kithome, M., Paul, J. W., Lavkulich, L. M. and Bomke, A. A. (1998): Kinetics of ammonium adsorption and desorption by the natural zeolite Clinoptilolite. Soil Sci. Am. J., vol. 62, pp. 622-629.
70. Klieve, J.R. and Semmens, M.J. (1980): An evaluation of pretreated natural zeolites for ammonium removal. Water Research, Vol. 14, pp. 161-168.
71. Knowlton, G. D. and White, T. R. (1981): Thermal study of types of water associated with Clinoptilolite. Clays and Clay Minerals, Vol. 29, No. 5, pp. 403-411.
72. Komarneni, S. (1985): Phillipsite in Cs decontamination and immobilization, Calys and clay minerals, Vol. 33, No. 2, pp. 145-151.
73. Koon, J. H. and Kaufman, W. J. (1975): Ammonia removal from municipal wastewater by ion exchange. WPCF., Vol. 47, No. 3., pp. 449-465.
74. Kugelman, I. J. (1976): Status of advanced waste treatment: in Handbook of Water Resources and Pollution Control. H. W. Gehm and J. I. Bregman, eds., Litton Educational Publishing. Pp. 593-633.
75. Lai, T. and Eberl, D. (1986): Controlled and renewable release of phosphorous in soils from mixtures of phosphate rock and NH₄-exchanged clinoptilolite. zeolites, Vol. 6, pp. 129-132.
76. Leithe, W. (1974): Die Analyse der Luft und ihrer Verunreinigungen in der freien Atmosphäre und am Arbeitsplatz, Wissenschaftliche Verlagsgesellschaft, Stuttgart, Germany.
77. Lewis, M. D., Moore, F. D. and Goldsberry, K. L. (1984): Ammonium-exchanged Clinoptilolite and granulated Clinoptilolite with urea as nitrogen fertilisers: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 105-112.

References

78. Liberti,L., Boari G., and Passino R. (1979): Phosphates and ammonia recovery from secondary effluents by selective ion exchange with production of a slow- release fertiliser. Water Research, Vol. 13, pp 65-73.
79. Liberti, L., Boari, G., Petruzzelli, D., and Passino, R., (1981): Nutrient removal and recovery from wastewater by ion exchange. Water Research, Vol. 15, pp. 337-342.
80. Liberti, L., Limoni, N., Longobardi, C., Lopez, A., Passino, R., Kang, S. J. and Horvatin, P. J. (1988): Field demonstrations of the Rim-Nut process for nutrients recovery from municipal wastewater. Nuclear and Chemical waste Management. Vol. 8. Pp. 83-86.
81. Liberti, L., Lopez, A., Amicarelli, V. and Boghetich, G. (1995): Pollution-abatement technologies by natural zeolites: The Rim-Nut process: : In Natural Zeolites '93, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 351-362.
82. Loizidou, M., and Townsend, R., P. (1987): Ion exchange properties of natural Clinoptilolite, Ferrierte and Mordenite: Part 2. Lead-Sodium and Lead-Ammonium Equilibria. Zeolites, Vol. 7, March, pp. 153-159.
83. Loizidou, M., and Townsend, R., P. (1987): Exchange of cadmium into the sodium and ammonium forms of the natural zeolites Clinoptilolite, Mordenite, and Ferrierite. J. Chem. Soc., Dalton Trans., pp. 1911-1916.
84. Loizidou, M. and Townsend, R. P. (1987): Ion-exchange properties of natural Clinoptilolite, Ferrierite and Mordenite: Part 2. Lead-sodium and lead-ammonium equilibria. Zeolites, vol. 7, March, pp. 153-159.
85. Lopez, A. and Liberti, L. (1991): Zeolites “closed-loop” regeneration. Proc.I Convegno Naz. Di Scienza e Technologia delle Zeoliti, C. Colella eds., Napoli, pp. 139-146 (Personal communication with L. Liberti).
86. Martinola, F. and Siegers, G. (1984): Experience Data with lift-bed and rinse-bed processes. In Naden, D. and Streat, M. :Ion Exchange Technology. Society of Chemical Industry. England. pp.127-137.
87. Meier, W. M., Olson, D. H. and Baerlocher, Ch. (1996): Atlas of zeolite structure types. The Structure Commission of the International Zeolite Association.
88. Mercer, B. W. and Ames, L. L. (1978): Zeolite ion exchange in radioactive and municipal wastewater treatment: : In Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, pp. 451-462.
89. Minato, H. (1985): Chemical treatment of natural zeolites, and properties and utilisation of the reacted materials. In Drzaj, B., Hocevar, S. and Pejovnik, S., : Zeolites: Synthesis,Structure, Technology and Application. Elsevier Science. pp. 513-522.

References

90. Ming, D. W. and Dixon, J. (1987): Quantitative determination of Clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Minerals*, Vol. 35, No. 6, pp. 463-468.
91. Ming, D. W., Barta, D. J., Golden, D. C., Galindo, C. and Henninger, D. L. (1995): Zeoponic plant-growth substrates for space applications: : in *Natural Zeolites '93*, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 505-514.
92. Mirvish, S. S. (1991): The significance for human health of nitrate, nitrite and N-nitroso compounds: In *Nitrate Contamination: Exposure, Consequence and Control*, I. Bogardi, R. Kuzelka and W. Ennenga, eds., Springer-Verlag, Berlin, pp. 253-266..
93. Mirvish, S. S. (1977): N-nitroso compounds, nitrite and nitrate: Possible implications for the causation of human cancer. *Prog. Wat. Tech.* Vol. 8, pp. 195-207.
94. Möbius, Ch. H. (1980): Adsorption and ion exchange processes for treatment of white water and wastewater of Paper-Mills. *Prog. Wat. Tech.*, Vol. 12, pp. 681-695.
95. Moore, J. W. (1991): Inorganic contaminants of surface water: Research and monitoring priorities, Springer Verlag, New York.
96. Mumpton, F. A. (1978): Natural zeolites: a new industrial mineral commodity: in *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, pp. 3-29.
97. Mumpton, F. A. and Clayton Ormsby, W. (1978): Morphology of zeolites in sedimentary rocks by scanning electron microscopy: in *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, eds.,Pergamon Press, Elmsford, New York, pp. 113-133.
98. Mumpton, F. A. (1984): Natural zeolites: In *Zeo-Agriculture: Use of natural zeolites in agriculture and aquaculture*, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 33-45.
99. Murphy, C. O., Hrycyke, O. and Gleason, W. T. (1978): Natural zeolites: Novel uses and regeneration in wastewater treatment: : In *Natural Zeolites: Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, eds.,Pergamon Press, Elmsford, New York, pp. 471-478.
100. Nicholas Hewitt, C., Metcalfe, P. J., and Street, R. A. (1991): A Method for the sampling and removal of ionic alkyllead compounds from aqueous solution using ion exchange media. *Water Research*, Vol. 25, No. 1, pp. 91-94.
101. O'Connor, J., F. and Townsend, R., B. (1984): Exchange of lead (II) ions in synthetic Faujasitic zeolites: The Effect of Framework Charge. *Zeolites*, Vol. 5, May, pp. 159-164.
102. Organisation for economic co-operation and development (1986): Water pollution by fertilisers and pesticides, OECD, France.

References

103. Ottewill, R. H., Rochester, C. H. and Smith, A. L. (1983): Adsorption from solution. Academic Press. London.
104. Pansinni, M and Colella, C (1989): Lead pollution control by zeolite, Materials engineering, Vol. 1, no. 2, pp. 623-630.
105. Pansinni, M and Colella, C (1990): Dynamic data on lead uptake from water by Chabazite. Desalination, Vol. 78, pp. 287-295.
106. Pansini, M. (1996): Natural zeolites as cation exchangers for environment protection. Mineralium deposita, vol. 31, pp. 563-575.
107. Pansini, M., Colella, C., Caputo, D., De'Gennaro, M. and Langella, A. (1996): Evaluation of Phillipsite as cation exchanger in lead removal from water. Microporous Materials, vol. 5, pp. 357-364.
108. Park, M and Komarneni, S. (1998): Ammonium nitrate occlusion vs. Nitrate ion exchange in natural zeolites, Soil Sci. Soc. Am. J. Vol. 62, pp. 1455-1459.
109. Patterson, J. W. (1975): Wastewater treatment technology, Ann Arbor Science Publishers, Michigan.
110. Pereira, L. S. and Quelhas dos Santos, J. (1991): Fertiliser and water application, and control of nitrate pollution: management issue: In Nitrate Contamination: Exposure, Consequence and Control, I. Bogardi, R. Kuzelka and W. Ennenga, eds., Springer-Verlag, Berlin, pp. 141-159.
111. Peterson, D. (1981): Influence of presorbed water on the sorption of nitrogen by zeolites at ambient temperatures, Zeolites, Vol. 1, pp.105-112.
112. Piper, R. G. and Smith, C. E. (1984): Use of Clinoptilolite for ammonia removal in fish culture systems: Use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 223-229.
113. Preußmann, R. (1982): Nitrosaminbedingte Cancerogenese: In Nitrat-Nitrit-Nitrosamine in Gewässern, DFG, Verlagsgesellschaft, Weinheim, Germany.
114. Roberts, P., Hegi, H. R., Weber, A. and Krähenbühl, H. R. (1977): Metals in municipal wastewater and their elimination in sewage treatment. Prog. Wat. Tech. Vol. 8, No. 6, pp. 301-306.
115. Rodriguez, G. R., Sanchez, C. L., Romero, J. C. and Malherbe, R. R. (1985): Cuban natural zeolites: Morphological studies by electron microscopy. In Drzaj, B., Hocevar, S. and Pejovnik, S., : Zeolites: Synthesis, Structure, Technology and Application. Elsievier Science. pp. 375-384..

References

116. Ronald Miner, J. (1984): Use of natural zeolites in the treatment of animal wastes: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 257-263.
117. Rüffer, H. and Rosenwinkel, K. (1991): Taschenbuch der Industrieabwasserreinigung. Oldenburger Verlag Münschen.
118. Rykl, D. and Pechar, F. (1991): Thermal decomposition of natural Phillipsite, Zeolites, Vol. 11, pp. 680-683.
119. Salameh, E. (1987): The potential of surface water utilisation for domestic purposes in Jordan, International Journal of Environmental Studies, Vol. 28, pp. 291-300.
120. Semmens, M. J. (1984): Cation-exchange properties of natural zeolites: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 45-55.
121. Semmens, M. J. and Goodrich, R. R. (1977): Biological regeneration of ammonium-saturated Clinoptilolite. I. Initial observations. Environmental Science and Technology, Vol. 11, No. 3, pp. 255-259.
122. Semmens, M. J., Wang, J. T. and Booth, A. C. (1977): Biological regeneration of ammonium-saturated Clinoptilolite. II. Mechanism of regeneration and influence of salt concentration. Environmental Science and Technology, Vol. 11, No. 3, pp. 260-265..
123. Semmens, M.J. and Martin, W. P. (1988): The influence of pretreatment on the capacity and selectivity of Clinoptilolite for metal ions. Water Research, Vol. 22, No. 5, pp. 537-542.
124. Semmens, M. J. and Seyfarth, M. (1978): The selectivity of Clinoptilolite for certain heavy metals: : In Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, Elmsford, New York, pp. 517-526.
125. Sheppard, R. A. (1984): Characterisation of zeolitic materials in agricultural research: In Zeo-Agriculture, use of natural zeolites in agriculture and aquaculture, W. G. Pond and F. A. Mumpton, eds., Westview Press, Boulder, Colorado, pp. 79-89.
126. Shibue, y. (1981): Cation-exchange reactions of siliceous and aluminous Phillipsites. Clays and Clay Minerals, Vol. 29, pp. 397-402.
127. Shuval, H. I. and Gruener, N. (1977): Infant methemoglobinemia and other health effects of nitrates in drinking water. Prog. Wat. Tech. Vol. 8, pp. 183-193.
128. Sierp, F. (1967): Die gewerblichen und industriellen Abwässer, Springer verlag, Heidelberg, Germany.

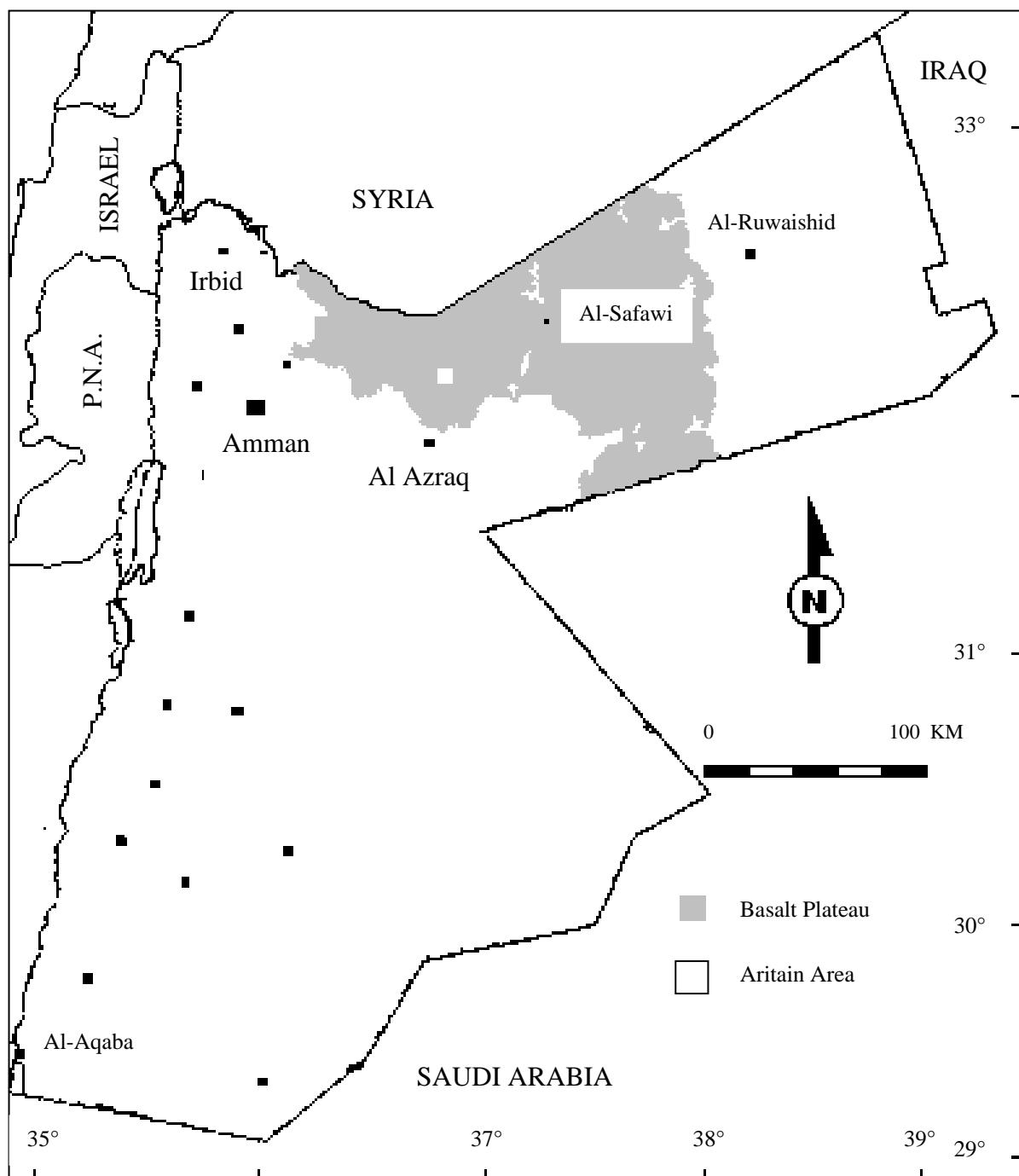
References

129. Treacy, M. M., Higgins, J. B. and von Ballmoos, R. (1996): Collection of simulated XRD powder patterns for zeolites. The structure Commission of the International Zeolite Association.
130. Townsend, R., P., and Loizidou, M. (1984): Ion exchange properties of natural Clinoptilolite, Ferrierte and Mordenite: I. Sodium-Ammonium Equilibria. *Zeolites*, Vol. 4, April, pp. 191-195.
131. Van Bekkum, H., Flanigen, E. M. and Jansen, J. C. (1991): Introduction to zeolite science and practice .Elsevier Science Publishers.The Netherlands
132. World health organisation (1971): Waste stabilisation ponds, Earnest F. Gloyne eds., Monograph series no. 60, Geneva.
133. Yamanaka, S., Malla, P. B. and Komarneni, S. (1989): Water sorption and desorption isotherms of some naturally occurring zeolites, *Zeolites*, Vol. 9, pp. 18-22.
134. Zamzow, M. J. and Schultze, L. E. (1995): Treatment of acid mine drainage using natural zeolites: : In *Natural Zeolites '93*, D.W. Ming and F.A. Mumpton, eds., Int. Comm. Natural Zeolites, Brockport, New York, pp. 405-414.

Appendices

Appendix 1

1.1 Location map of Aritain area



Appendices

Appendix 2

2.1 The maximum values of some pollutants concentrations (mg/l) which are allowed in the discharged industrial wastewater effluent (after the Jordanian standards number 202/1990, personal contact with ministry of water and irrigation).

		Reuse purpose of the treated wastewater	
Type of pollutants	Agricultural reuse	Ground water recharge	Discharge to the surface water reservoirs
BOD5	-	50	50
COD	-	150	150
NO ₃ ⁻ -N	30	12*	12*
NH ₃	5	5	5
TKN-N	50		
PO ₄ ³⁻ -P	-	-	15
Na ⁺	-	400	-
Mg ²⁺	-	-	-
Ca ²⁺	-	-	-
Pb ²⁺	1	0.1	0.1
Cd ²⁺	0.01	0.02	0.01
Total Cu ²⁺	0.2	2	2
Ni ²⁺	0.2	0.1	0.2
Zn ²⁺	2	15	15

*Depends on their concentration in the received water reservoir.

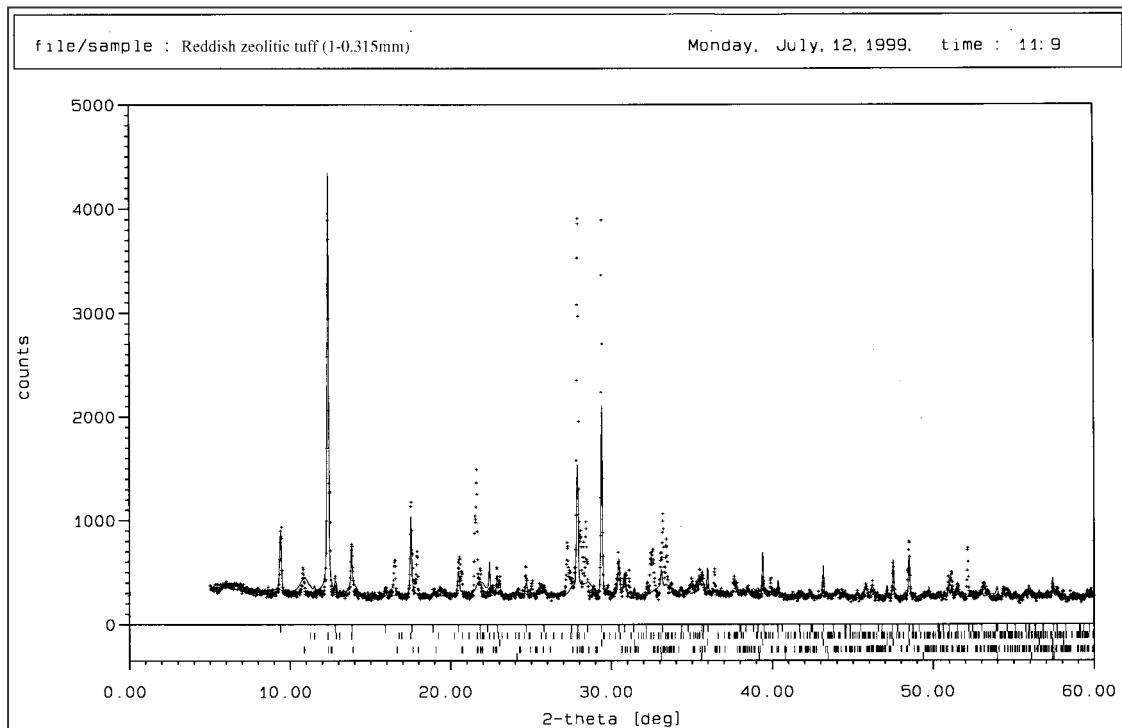
Appendices

Appendix 3

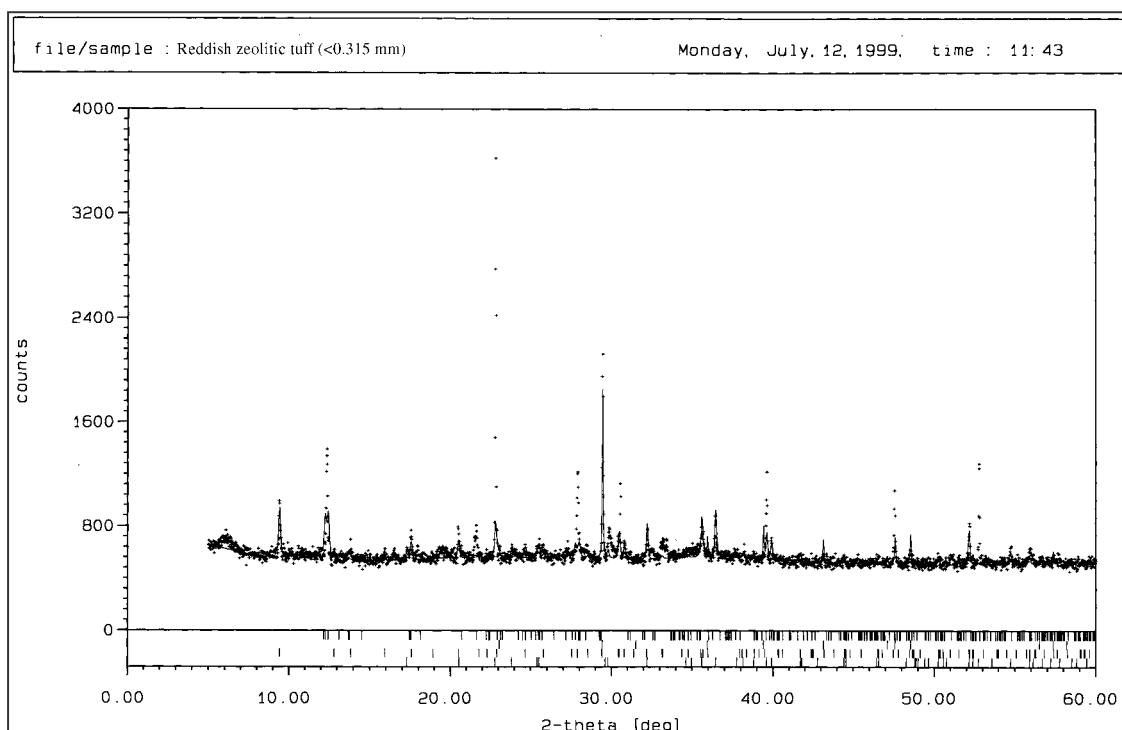
3.1 X-ray diffraction diagrams of Jordanian zeolitic tuffs

(Diffractometer: Phillips X'Pert Alph-1, CuK α , Sample porter 26 mm, radiation width 15 mm)

- a. Resddish zeolitic tuff (1-0.315 mm)

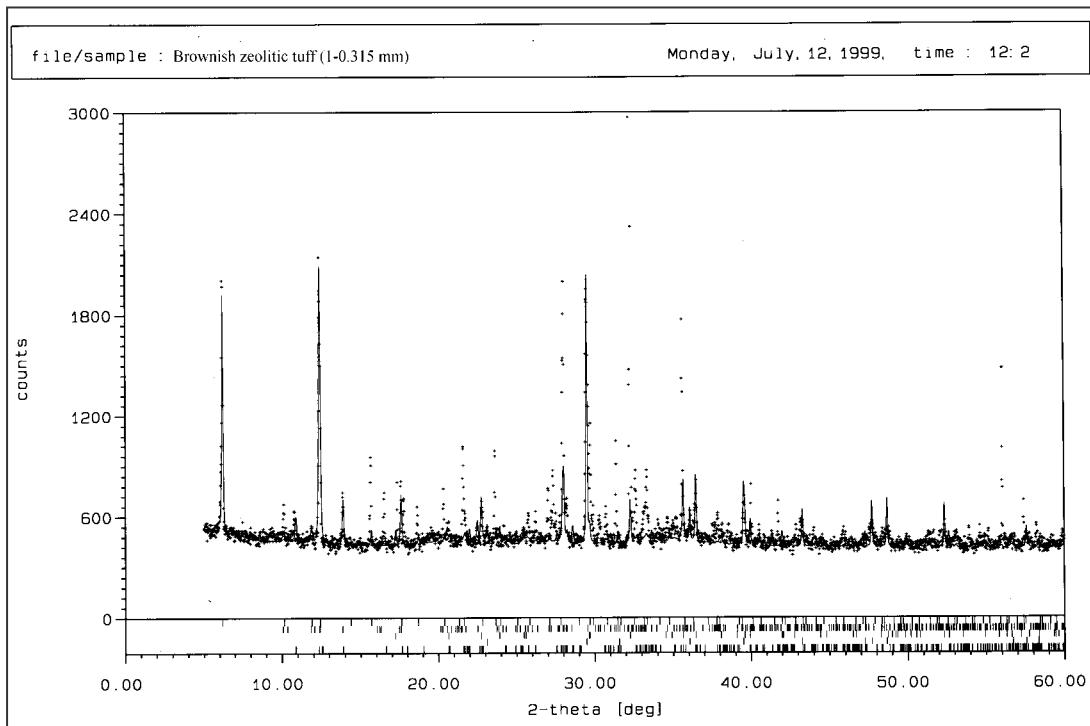


- b. Reddish zeolitic tuff (<0.315 mm)

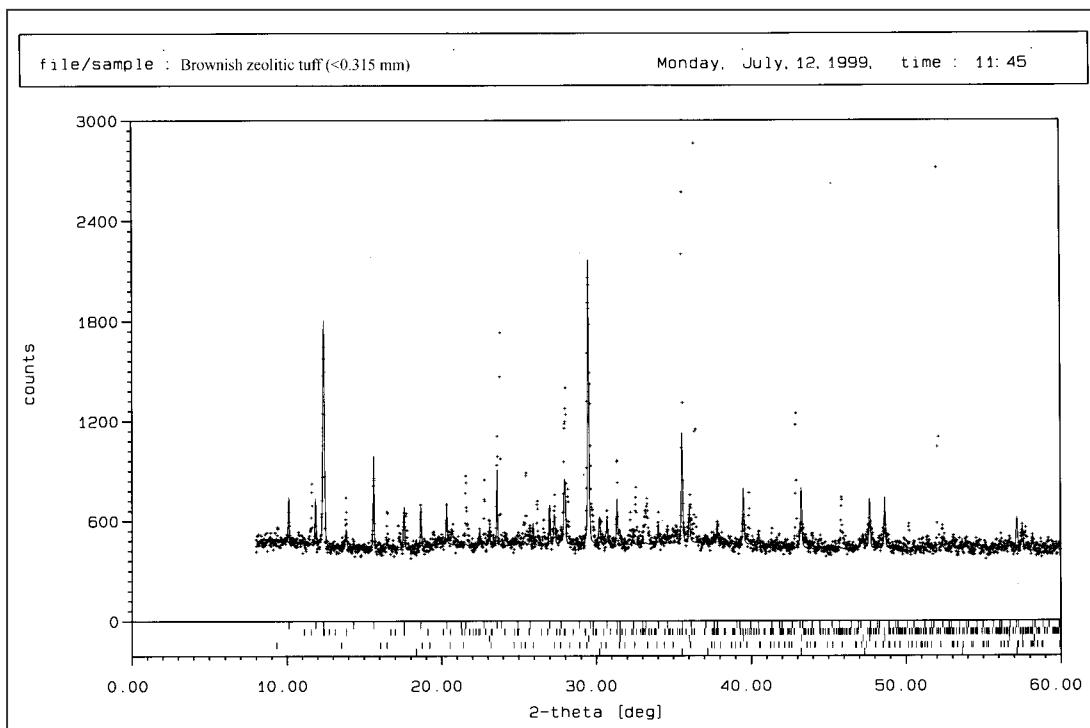


Appendices

c. Brownish zeolitic tuff (1-0.315 mm)



d. Brownish zeolitic tuff (<0.315 mm)



Appendices

3.2 Weight lost (%) of zeolitic tuffs after the treatment by heating for 4 hrs.

	Reddish zeolitic tuff		Brownish zeolitic tuff	
Temperature °C	1-0.315mm	-0.315mm	1-0.315mm	-0.315mm
150	8.40	6.60	4.70	2.10
200	9.30	6.20	6.00	3.90
250	8.80	5.20	5.00	1.90
300	10.8	7.50	6.30	5.90
350	8.70	7.10	7.30	6.50
400	11.0	7.30	7.60	5.30
500	10.4	9.30	8.20	5.60
600	13.0	8.80	11.5	6.40
700	13.3	11.9	14.6	15.0
800	17.1	12.3	14.7	11.6
900	17.5	13.0	14.7	16.2

3.3 Water gain (%) after cooling the, previously heated, zeolitic tuffs at room temperature for 24 hrs.

	Reddish zeolitic tuff		Brownish zeolitic tuff	
Temperature °C	1-0.315mm	-0.315mm	1-0.315mm	-0.315mm
150	9.70	8.50	9.50	8.60
200	10.0	8.10	10.5	8.90
250	8.00	7.40	9.00	8.30
300	4.70	5.20	8.00	7.10
350	9.60	8.00	8.50	9.20
400	4.40	4.70	8.10	5.60
500	4.20	4.90	7.60	5.60
600	3.80	4.60	6.60	5.00
700	3.10	3.20	6.60	3.80
800	3.20	1.50	5.50	3.90
900	0.80	1.80	0.90	1.10

Appendices

3.4 The effect of heat regeneration on the adsorption amount of NH₃ and H₂O on the 1-0.315 mm grain size zeolitic tuffs from a gas stream.

Temperature °C	Reddish zeolitic tuff		Brownish zeolitic tuff	
	NH ₃ (mg/100g)	H ₂ O (%)	NH ₃ (mg/100g)	H ₂ O (%)
105	21.0	5.77	20.0	8.72
150	20.0	5.50	52.0	8.47
200	39.0	7.37	61.0	7.88
250	40.0	6.92	74.0	10.3
300	20.0	1.97	63.0	6.20
400	12.0	2.25	53.0	5.80
500	11.0	2.10	11.0	7.13
600	8.0	1.35	10.0	4.55
700	9.0	1.31	3.0	4.40
800	1.00	0.00	3.0	2.65

Appendices

Appendix 4

4.1 Adsorbed /desorbed Ca²⁺ ions from the NH₄⁺-zeolitic tuffs after their treatment by using tap water.

Wash number	The weight of zeolitic tuff used (g)					
	0.5 RZT	1 RZT	1.5 RZT	0.5 BZT	1 BZT	1.5 BZT
W1	18	20	20	10	14	18
W2	40	45	45	29	38	42
W3	7	24	28	3	9	18
W4	7	17	23	-4	3	13
W5	10	16	27	6	16	10
W6	6	8	17	3	0	5
W7	-8	-4	8	0	1	2
W8	-2	0	7	2	2	1
W9	10	10	13	8	13	9
W10	-11	-2	-3	-7	-4	-4
W11	-2	3	4	7	-1	6
W12	-1	0	-6	-3	-7	-4
W13	0	6.4	6	-3	2	2
W14	5	1	-1	0	-1	2
W15	-3	-11	-3	-12	-4	-5
W16	-17	2	5	4	8	1
W17	3	4	3	6	7	-5
W18	12	17	12	0	8	12
W19	10	10	11	3	14	4
W20	7	7	7	4	0	-4
W21	-3	-1	-2	-11	-6	-12
W22	2	2	3	0	-2	-2
W23	2	2	2	0	0	-1

Appendices

4.2 Adsorbed /desorbed Mg²⁺ ions from the NH₄⁺-zeolitic tuffs after their treatment by using tap water.

Wash number	The weight of zeolitic tuff used (g)					
	0.5 RZT	1 RZT	1.5 RZT	0.5 BZT	1 BZT	1.5 BZT
W1	-2	-1	0	-1	-2	0
W2	2	3	3	3	3	4
W3	0	-2	0	-1	-1	-2
W4	-2	-1	-1	-1	-1	1
W5	1	1	0	1	2	0
W6	0	0	1	1	0	-1
W7	0	0	1	1	0	0
W8	0	0	-1	0	-1	0
W9	-2	1	-1	1	0	0
W10	0	1	0	0	-1	0
W11	0	1	-1	1	1	1
W12	1	1	1	1	1	1
W13	-1	2	1	1	1	1
W14	-2	0	1	1	-1	0
W15	0	-2	-1	-2	-1	-2
W16	-2	0	-1	1	0	0
W17	-1	-2	-2	-2	-3	-3
W18	0	-1	-1	1	-1	-1
W19	0	1	-1	1	1	0
W20	-1	0	0	-1	0	-1
W21	0	0	0	-1	-1	-1
W22	-1	0	1	1	0	0
W23	-1	-1	-1	-1	-1	0

Appendices

4.3 Adsorbed /desorbed Na⁺ ions from the NH₄⁺-zeolitic tuffs after their treatment by using tap water.

Wash number	The weight of zeolitic tuff used (g)					
	0.5 RZT	1 RZT	1.5 RZT	0.5 BZT	1 BZT	1.5 BZT
W1	-2	2	4	-4	-4	-1
W2	6	7	9	6	6	6
W3	0	-1	1	0	1	1
W4	-6	-7	-7	-5	-6	-6
W5	3	2	0	2	5	2
W6	0	0	-1	0	1	0
W7	0	0	0	1	1	1
W8	0	-1	0	0	0	0
W9	4	4	4	2	2	3
W10	-1	0	0	-1	-1	0
W11	2	2	1	2	0	3
W12	-2	-2	-1	-3	-3	-3
W13	1	1	0	0	0	0
W14	-2	-1	-3	-3	-3	-3
W15	-7	-1	-1	-7	-1	-2
W16	0	0	0	-1	-1	-1
W17	-2	1	2	-2	-2	-2
W18	1	2	2	-1	0	0
W19	1	2	2	1	1	1
W20	-4	-4	-4	-6	-6	-6
W21	1	2	2	-1	-3	-3
W22	-1	-2	-1	-1	-1	-1
W23	-1	-1	-1	-1	-1	-2

- RZT and BZT represent reddish and brownish zeolitic tuff respectively.

Appendices

4.4 Adsorbed amount of ammonium (mg) in relation to the amount of zeolitic tuffs added and the contact time

Amount and type of zeolitic tuff added	Agitation time (days)				
	1	2	3	4	5
1g Reddish zeolitic tuff	1	1	2	3	2
2g Reddish zeolitic tuff	8	3	5	6	5
3g Reddish zeolitic tuff	18	3	9	6	6
4g Reddish zeolitic tuff	15	5	13	9	12
5g Reddish zeolitic tuff	18	12	20	6	15
1g Brownish zeolitic tuff	4	2	4	5	1
2g Brownish zeolitic tuff	12	5	8	8	4
3g Brownish zeolitic tuff	16	6	9	11	6
4g Brownish zeolitic tuff	17	8	11	12	8
5g Brownish zeolitic tuff	25	9	19	15	10

Appendices

4.5 Adsorption-desorption amount (in mg) of counter cations.

Amount of zeolitic tuff added	Adsorbed-desorbed cations (mg)									
	Reddish Zeolitic tuff					Brownish zeolitic tuff				
Agitated for 1 day	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Tot.	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Tot.
1g	0	2	-1	2	3	0	4	-4	5	5
2g	0	5	-3	8	10	-1	4	-5	7	5
3g	0	2	-6	11	7	0	4	-9	14	9
4g	-1	-1	-8	15	5	0	-6	-12	18	0
5g	-1	-3	-11	16	1	-1	1	-13	22	9
Agitated for 2 days										
1g	0	-1	-4	-7	-12	-1	-1	-5	-13	-20
2g	0	-2	-6	-13	-21	-1	-2	-8	-1	-12
3g	-1	-5	-9	-1	-16	-2	-5	-11	3	-15
4g	-1	-5	-9	14	-1	-1	-3	-13	11	-6
5g	-3	-7	-13	3	-20	-2	-4	-16	15	-7
Agitated for 3 days										
1g	0	-5	-3	-4	-12	0	0	-3	6	3
2g	0	-2	-5	0	-7	0	-2	-7	8	-1
3g	0	-2	-7	6	-3	-1	-4	-8	10	-3
4g	-1	-10	-10	8	-13	-1	-3	-11	16	1
5g	0	-8	-11	10	-9	-1	-1	-12	12	-2
Agitated for 4 days										
1g	-1	-16	-6	-4	-27	-1	-16	-6	-4	-27
2g	-1	-10	-7	-4	-22	-2	-9	-8	-2	-21
3g	-2	-9	-9	7	-13	-1	-16	-11	1	-27
4g	-2	-10	-12	3	-21	-2	-2	-10	18	4
5g	-2	-12	-14	11	-17	-1	-9	-14	11	-13
Agitated for 5 days										
1g	1	4	-2	-3	0	0	-5	-4	4	-5
2g	0	1	-4	6	3	2	1	-8	14	9
3g	0	1	-6	8	3	0	3	-8	18	13
4g	-1	-1	-9	6	-5	0	2	-11	22	13
5g	0	-2	-10	22	10	0	1	-15	22	8

Appendices

4.6 Concentrations of cations eluted from previously agitated zeolitic tuff with the manure by adding of distilled (*) or tap water (mg/l).

a. Ca²⁺ ions

Wash number	Reddish Zeolitic tuff					Brownish zeolitic tuff				
	1g*	1g	1.5g	2g	2.5g	1g*	1g	1.5g	2g	2.5g
W1	0	27	31	35	34	1	26	30	31	33
W2	1	25	24	29	31	2	20	24	23	27
W3	2	-6	5	3	6	2	1	-1	-4	4
W4	2	1	3	9	8	3	3	6	2	8
W5	3	10	9	7	9	3	7	9	9	8
W6	2	14	28	19	30	2	12	22	26	28
W7	0	-3	2	-4	6	8	-6	1	4	-2
W8	0	3	1	-1	7	2	2	-3	-2	5
W9	1	7	3	0	3	3	-6	1	-7	5
W10	0	5	-2	2	2	2	6	0	-6	8

b. Mg²⁺ ions

Wash number	Reddish Zeolitic tuff					Brownish zeolitic tuff				
	1g*	1g	1.5g	2g	2.5g	1g*	1g	1.5g	2g	2.5g
W1	1	2	2	2	2	0	2	3	4	5
W2	1	1	0	0	1	1	0	1	1	3
W3	1	-1	-1	0	0	1	0	0	1	2
W4	1	0	0	0	-1	1	0	-1	0	0
W5	1	1	3	1	1	1	1	2	2	1
W6	0	0	0	1	0	1	1	0	1	0
W7	1	-1	0	-2	2	1	1	1	1	1
W8	1	3	1	3	1	0	1	1	1	3
W9	2	3	2	1	1	1	1	1	1	2
W10	3	3	2	2	2	1	2	2	3	2

Appendices

c. Na⁺ ions

Wash number	Reddish Zeolitic tuff					Brownish zeolitic tuff				
	1g*	1g	1.5g	2g	2.5g	1g*	1g	1.5g	2g	2.5g
W1	4	-5	-7	-9	-11	5	-5	-8	-10	-12
W2	3	-2	-5	-6	-6	3	-3	-4	-5	-5
W3	2	0	-1	-1	-2	2	0	-1	-1	-1
W4	2	1	0	0	-1	1	0	0	0	0
W5	21	1	1	0	1	1	1	0	1	1
W6	1	0	1	0	0	1	0	1	1	1
W7	1	-1	-1	-2	-1	1	0	-1	0	-1
W8	1	-1	-1	0	0	0	0	0	0	0
W9	1	2	3	4	1	1	1	1	1	2
W10	2	1	-2	-2	-2	3	-2	-1	1	-2

d. K⁺ ions

Wash number	Reddish Zeolitic tuff					Brownish zeolitic tuff				
	1g*	1g	1.5g	2g	2.5g	1g*	1g	1.5g	2g	2.5g
W1	10	-28	-35	-41	-47	15	-38	-49	-52	-55
W2	9	-17	-27	-31	-33	12	-19	-27	-34	-38
W3	7	-9	-12	-15	-18	7	-7	-12	-17	-21
W4	6	-6	-9	-11	-14	6	-7	-10	-15	-18
W5	6	-6	-8	-10	-12	5	-4	-6	-11	-15
W6	5	-5	-7	-9	-11	5	-4	-6	-8	-10
W7	6	-5	-7	-11	-11	10	-3	-5	-7	-9
W8	4	-5	-6	-8	-10	3	-3	-5	-7	-8
W9	4	-3	-4	-10	-8	3	-2	-4	-5	-5
W10	3	-3	-7	1	-2	6	-4	-5	-4	-5

Appendices

Appendix 5

5.1 Absorbed amounts /percents of metal ions during the treatment processes in ion exchange columns using zeolitic tuffs

a. Reddish zeolitic tuff (RZT)

Cation	Effluent velocity					
	400ml/hr			600ml/hr		
	Total (mg/g)	Adsorbed (mg/g)	Absorbed (%)	Total (mg/g)	Adsorbed (mg/g)	Absorbed (%)
Pb ²⁺	10.4	9.2	88	13.6	7.5	55
Cd ²⁺	4.3	0.7	16	4.1	0.4	10
Cu ²⁺	1.7	0.9	54	2.9	0.9	30
Ni ²⁺	3.6	0.2	6	3.7	0.1	3
Zn ²⁺	22.4	3.4	15	19	3	16

b. Brownish zeolitic tuff (BZT)

Cation	Effluent velocity					
	400ml/hr			600ml/hr		
	Total (mg/g)	Adsorbed (mg/g)	Absorbed (%)	Total (mg/g)	Adsorbed (mg/g)	Absorbed (%)
Pb ²⁺	8	7.2	90	13.6	8.2	60
Cd ²⁺	4.1	2.2	54	3.84	1.1	29
Cu ²⁺	0.8	0.6	75	3.2	1.7	53
Ni ²⁺	3.5	1.3	37	3.7	0.8	22
Zn ²⁺	20.8	9.9	48	18.4	6	33

Curriculum Vita

Zaid Ali Fadel Al-Rashdan

Personal Details:

Name:	Al-Rashdan	Zaid	Ali Fadel
	Surname	first name	middle names
Date of birth:	October 4, 1969		
Place of birth:	Deir Abu Said, Jordan		
Martial Status:	Single		
Sex:	Male		
Nationality:	Jordanian		
Address:	Germany, D-26127 Oldenburg, Johan-Justus-Weg 136/2/61		
	Tel: + 49 (0) 441-6834304		
	E-mail: zaidrashdan@hotmail.com		

Education:

1987-1991	Department of earth and environmental sciences	Yarmouk University Irbid, Jordan
	• B.Sc. degree in geology and environmental sciences	
1991-1994	Department of earth and environmental sciences	Yarmouk University Irbid, Jordan
	• M.Sc. degree in Geology and Environmental sciences (Thesis Title: Treatment of Domestic Wastewater Effluent From Stabilisation Ponds Using Jordanian Zeolitic Tuffs).	
1995- 2000	Chemistry department, Oldenburg University, D- 26111 Oldenburg, Germany	
	• Ph.D. degree in Natural Science (Dissertation Title: Investigation of Natural Zeolitic Tuffs on their Ability for Sewage Cleaning Purposes)	

Languages:

Arabic (Mother language)
German and English

Experiences:

1991-1994:	Yarmouk University, Irbid, Jordan Teacher and research assistant for the following labs.: • Practical geology (1 and 2) • Hydrology • Environmental Pollution
1992-1994:	Ministry of water and irrigation,-Amman, Jordan • Laboratory assistant at the Irbid wastewater treatment plant.
1994-1995:	Department of earth and environmental sciences, Yarmouk University, Irbid, Jordan (Research assistant with Prof. Dr. Sameh Gharaibeh)
1995-2000	Ökochemie+Umweltanalytik, Oldenburg, Germany • Water, wastewater and soil analysis

References:

- Prof. Dr. Dieter Schuller
Office: Ökochemie+Umweltanalytic AG.
Fachbereich Chemie
Postfach 2503
Universität Oldenburg
D-26111 Oldenburg
Germany
Tel: +49 (0) 441 798 3797
Fax: +49 (0) 441 798 3800
*Home: Charlottenburger Weg 8
D-26655 Westerstede
Germany
Tel: +49 (0) 4488 2985
Fax: +49 (0) 4488 1201

*** Contact address after August 31, 1999**

- Prof. Dr. Sameh Gharaibeh
Office: Department of earth and environmental sciences
Yarmouk University
Irbid-Jordan
Tel.: +962 (0) 2 727 1100 Ext. 2954
Fax: +962 (0) 2 727 4682
E-mail: Samehgh@hotmail.com
- Prof. Dr. Frank Rößner
Office: Technische Chemie 2
Fachbereich Chemie
Postfach 2503
Universität Oldenburg
D-26111 Oldenburg
Germany
Tel: +49 (0)441 798 3355
Fax: +49 (0)441 798 3360
E-mail: frank.roessner@uni-oldenburg.de

Membership:

1998- until now: German association of zeolite, a part from German Association for engineering, chemistry and Biotechnology (DECHEMA)
DECHEMA e.V., Postfach 150104, D-60061 Frankfurt am Main,
Germany.

Versicherung:

Hiermit versichere ich, daß ich diese Arbeit selbstständig angefertigt und keine anderen als die angegebenen Hilfsmittel verwendet habe.

Oldenburg, den 09.03.2000

Zaid Al Rashdan