# USE OF CLINOPTILOLITE FOR COPPER AND NICKEL REMOVAL FROM AQUEOUS SOLUTIONS

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Approval of the Graduate School of Natural and Applied Sciences

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# ABSTRACT

## USE OF CLINOPTILOLITE FOR COPPER AND NICKEL REMOVAL FROM AQUEOUS SOLUTIONS

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Heavy metals are well known toxic priority pollutants. Hence, wastewaters containing these species must be treated prior to discharge into receiving bodies. In this study, the potential of Bigadiç clinoptilolite for $Cu^{2+}$ and $Ni^{2+}$ removal from wastewaters was investigated in batch and continuous reactors.

Results of the preliminary experiments revealed the optimum operating conditions, namely, initial solution pH of 5 and 4 for $Cu^{2+}$ and $Ni^{2+}$, respectively and contact time of 48 hours. Additionally, conditioning of clinoptilolite with 2*M* NaCl solution for 24 hours was found to considerably improve the capacity utilized at breakthrough.

Maximum removal capacities and prevailing mechanisms in the system were investigated via equilibrium studies under preliminary determined optimum operating conditions. Langmuir and Freundlich models were fitted to the experimental data and Langmuir model was found to be better in describing the system behavior. Maximum removal capacities obtained from non-linear regression of Langmuir model are almost the same for $Cu^{2+}$ and $Ni^{2+}$ removal using as received

clinoptilolite samples (0.31 and 0.32 meq/g respectively). However, conditioned clinoptilolite samples exhibit higher capacity for $Cu^{2+}$ over $Ni^{2+}$ (0.5 and 0.43 meq/g, respectively). Analyses of exchangeable cations in the aqueous phase were carried out to examine the prevailing mechanisms in the system. As a result, adsorption, dissolution of clinoptilolite and surface precipitation (particularly in the case of $Cu^{2+}$ removal) are considered to accompany ion exchange.

Finally, fixed-bed column studies were conducted with conditioned clinoptilolite samples for $Cu^{2+}$ removal. An improvement in $Cu^{2+}$ uptake was observed with decreasing volumetric flow rate (from 8 BV/h to 2-4 BV/h) and decreasing particle size (from 1.180-1.400 mm to 0.833-1.180 mm). Analyses of exchangeable cations as well as $Si^{4+}$, Fe(total) and $Al^{3+}$ were also carried out to examine the prevailing mechanisms. Ion exchange was discussed as the predominant mechanism in the system with minor contributions from adsorption and dissolution of clinoptilolite to the total amount of $Cu^{2+}$ uptake and to the total amount of exchangeable cations release, respectively.

Keywords: Clinoptilolite, Copper, Nickel, Conditioning, Removal Mechanisms.

# ÖZ

## SULU ÇÖZELTİLERDEN BAKIR VE NİKEL GİDERİMİNDE KLİNOPTİLOLİT KULLANIMI

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Ağır metaller iyi bilinen öncelikli zehirli kirleticilerdendir. Bu sebepten dolayı, ağır metal ihtiva eden atıksuların alıcı ortamlara deşarj edilmeden önce arıtılmaları gerekmektedir. Bu çalışmada, Bigadiç klinoptilolitinin atıksulardan $Cu^{+2}$ ve $Ni^{+2}$ giderimindeki potansiyeli kesikli ve sürekli reaktörlerde araştırılmıştır.

Gerçekleştirilen ön çalışmalar neticesinde optimum işletim koşulları; başlangıç çözelti pH'sı için $Cu^{2+}$ ve $Ni^{2+}$ gideriminde sırasıyla 5 ve 4, tepkime süresi için 48 saat olarak belirlenmiştir. Ayrıca, 2*M* NaCl çözeltisi ile 24 saatlik etkileşim süresinde gerçekleştirilen şartlandırma işleminin prosesin etkinliğini önemli ölçüde arttırdığı tespit edilmiştir.

Her iki metal için azami kapasitelerin ve sistemdeki hakim mekanizmaların belirlenebilmesi amacıyla ön çalışmalar sonucu elde edilen optimum işletim şartlarında denge çalışmaları gerçekleştirilmiştir. Elde edilen deneysel verilerin Langmuir ve Freundlich modellerinin doğrusal olmayan denklemlerine uygunluğu araştırılmış ve Langmuir modelinin sistem davranışını açıklamada daha uygun olacağı belirlenmiştir. Azami giderim kapasiteleri Langmuir modelinden elde edilen sonuçlar ile hesaplanmıştır. Buna göre, herhangi bir ön işleme tabi tutulmamış

klinoptilolit örnekleriyle elde edilen $Cu^{+2}$ ve $Ni^{+2}$ kapasitelerinin neredeyse aynı olduğu (sırasıyla 0.31 ve 0.32 meq/g), bununla birlikte, şartlandırılmış klinoptilolit numunelerinin $Cu^{+2}$ iyonuna $Ni^{+2}$ iyonuna oranla daha yüksek kapasiteye sahip olduğu belirlenmiştir (sırasıyla 0.55 ve 0.43 meq/g). Sistemdeki hakim mekanizmaların belirlenebilmesi amacıyla değişebilir iyonlar ölçülmüştür. Sonuç olarak, adsorpsiyon, klinoptilolit yapısının bozunması ve yüzey çökelmesi (özellikle $Cu^{+2}$ gideriminde) gibi mekanizmaların iyon değişimi ile birlikte yer aldığı düşünülmüştür.

Son olarak, şartlandırılmış klinoptilolit numuneleri ile sabit yataklı kolonlarda $Cu^{+2}$ giderimi çalışılmıştır. Akış debisinin 8 yatak hacmi/saatten 2–4 yatak hacmi/saate ve parçacık boyutunun 1.180–1.400 mm'den 0.833–1.180 mm'ye düşürülmesi ile $Cu^{+2}$ gideriminde artış olduğu gözlenmiştir. Hakim mekanizmaların araştırılması amacıyla değişebilir iyonlara ek olarak $Si^{+4}$, toplam Fe ve $Al^{+3}$ iyonları ölçülmüştür. İyon değişiminin sistemdeki hakim mekanizma olduğu tartışılmakla birlikte adsorpsiyon ve klinoptilolit yapısının bozunmasının da sırasıyla tutulan toplam $Cu^{+2}$ ve toplam salınan değişebilir iyon miktarlarına küçük de olsa katkıda bulunduğu düşünülmektedir.

Anahtar Kelimeler: Klinoptilolit, Bakır, Nikel, Şartlandırma, Giderim Mekanizmaları

To My Parents

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1/n: Freundlich intensity parameter

A: As received samples

ACF: Activated Carbon Fibrous

AEi: amount of exchangeable cation i release from clinoptilolite

BV: volume of liquid equal to the volume of the bed

C: Conditioned samples

$C_c$: Concentration of the conditioning agent

$C_i$: Initial heavy metal concentration in the aqueous phase

$C_e$: Equilibrium heavy metals concentration in the aqueous phase

CSA: Classical silicate analysis

$D_c$: Column inner diameter

$d_p$: Particle size

GAC: Granulated Activated Carbon

K: Equilibrium Langmuir constant

$K_F$: Freundlich capacity factor

$L_c$: Bed height

m: Mass of clinoptilolite

M: Method

Q: Volumetric flow rate

$q_{max}$: maximum achievable capacity

$q_e$: equilibrium heavy metal concentration in the clinoptilolite phase

PCi: % contribution of exchangeable cation i to the total amount of exchangeable cations on $C_1$ and $Na_1C_1$

$RE_i$: $\frac{AE_i}{PC_i}$: Ratio of exchangeable cation i release from clinoptilolite to the % contribution of exchangeable cation i to the total content of exchangeable cations in the chemical compositions of $C_1$ and $Na_1C_1$.

S/L: Solid to liquid ratio

T: Temperature

$t_c$: Contact time

$t_s$: Sampling time

TCEC: Theoretical cation exchange capacity

V: Volume of heavy metal solution in batch mode applications

$V_b$: Volume of NaCl solution in batch mode applications

$V_c$: Total volume of solution pumped in continuous mode applications

# CHAPTER 1

# INTRODUCTION

Heavy metals are well known toxic priority pollutants and therefore wastewaters containing heavy metals are required to be treated prior to discharge into receiving waters (Diaz et al., 2005). Their amount in the environment not only increases every year but also they are not biodegradable and tend to accumulate in living organisms (Petrus and Warchol, 2003). In addition to mining and metal related industry, industrial effluents originating from the use of organic compounds containing metal additives in petroleum and chemical industries also result in heavy metal discharges (Inglezakis and Grigoropoulou, 2004). Removal of heavy metal cations from aqueous solutions can be achieved by several processes such as chemical precipitation, oxidation, ultrafiltration, reverse osmosis, electrodialysis or ion exchange (Peric et al., 2004). Among these techniques chemical precipitation is the mostly widely applied method. However, production of significant amounts of sludge, which is difficult to dewater and require careful, frequently expensive, disposal techniques, appears as the major disadvantage of this process (Kapoor and Viraraghavan, 1998). Therefore, ion exchange arises as an attractive one because of the relative simplicity and safety of application as well as recovery potential of both the adsorbent and heavy metals (Du et al., 2005, Ouki et al., 1994). Ion exchange can also be cost effective especially when a low cost ion exchanger is used (Inglezakis et al., 1999).

Zeolites have been recognized for more than 200 years, and are used in various technological areas, but they have found extensive attention in the field of wastewater treatment in recent years (Blanchard et al., 1984). There are more than 30 distinct species of zeolite that occur in nature. However, only seven of them,

mordenite, clinoptilolite, ferrierite, chabazite, erionite, philipsite and analcime occur in sufficient quantities to be considered as viable mineral resources (Ersoy and Çelik, 2002). Among these species, clinoptilolite is one of the most important natural zeolite, since it is found in extensive deposits worldwide; it has a stable structure and shows high selectivity for various cations (Malliou et al., 1994). Clinoptilolite belongs to Heulandite group, with a three dimensional framework of $Si^{4+}$ and $Al^{3+}$ tetrahedral (Tsitsishvili et al., 1992). $Al^{3+}$ and $Si^{4+}$ are linked to each other by sharing all of the oxygen to form interconnected cages and channels containing mobile water molecules and alkali ($Na^{+}$, $K^{+}$, $Li^{+}$, and $Cs^{2+}$) and / or alkaline earth ($Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ and $Mg^{2+}$) cations (Tschernich, 1992, Ouki et al., 1993). In general, clinoptilolite possesses a negatively charged surface. This negative charge results from substitutions within the lattice of $Al^{3+}$ for $Si^{4+}$, the broken bonds at the Si-O-Si (siloxene group) of clinoptilolite particularly generated at the particle surface during grinding as well as the lattice imperfections (Godelitsas and Armbruster, 2003), and presence of surface functional groups (mainly $OH^{-}$ and $H_2O$) (Mozgawa and Bajda, 2005).

Having relatively innocuous exchangeable ions in its structure and exhibiting high selectivity for certain cations make clinoptilolite gain a significant interest in recent years as a low cost ion-exchanger in studies examining removal of heavy metal cations from wastewaters. In this study, investigation of the potential of Bigadiç clinoptilolite in removing heavy metal cations ($Cu^{2+}$ and $Ni^{2+}$) from aqueous solutions both in batch and continuous mode applications was the major objective and this objective was examined in the following steps:

i. To investigate the optimum operational parameters for removal of $Cu^{2+}$and $Ni^{2+}$ in batch mode experiments,
ii. To investigate the maximum removal capacities of both as-received and conditioned forms of clinoptilolite for $Cu^{2+}$ and $Ni^{2+}$ by means of equilibrium studies,

iii. To assess the ability of conditioned clinoptilolite for the treatment of solutions containing $Cu^{2+}$ under different experimental conditions, namely volumetric flow rate and particle size in an upflow packed bed column arrangement,

iv. To develop an understanding for the dominant mechanisms involved in metal solution-clinoptilolite interaction for batch and packed bed column studies via examining exchangeable cations released from the clinoptilolite structure.

# CHAPTER 2

# THEORETICAL BACKGROUND

## 2.1. HEAVY METALS

Wastewaters contaminated with heavy metals are produced from many industrial activities, such as tanneries, metal plating facilities, petroleum refining and mining operations. Heavy metals are toxic priority pollutants because they are not biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders (Inglezakis et al., 2003). Therefore, wastewaters containing heavy metals are required to be treated prior to discharge into receiving environments.

Removal of heavy metals from aqueous wastes is a challenging task for the correct management of waste disposal. Among various treatment processes available, ion exchange has several advantages over other processes such as simplicity and safety of operation and recovery potential of both the sorbent and precious heavy metals. Activated carbon is considered to be a particularly competitive and effective sorbent for the removal of heavy metals, however; the use of activated carbon may not be suitable due to high costs associated with production and regeneration of spent carbon (Panday et al., 1985). Therefore, investigation of low cost sorbents such as; peat, clay, lignin, chitosan, fly ash and zeolites in removal heavy metals has arisen as a popular issue in recent years (Bailey et al., 1999). In Table 2.1, maximum achievable capacities obtained for $Cu^{2+}$ and $Ni^{2+}$ removal with various sorbents are presented.

It is clear from the table that, most researchers focused on $Cu^{2+}$ removal rather than $Ni^{2+}$ removal. The reason for the wider investigation of $Cu^{2+}$ removal rather than $Ni^{2+}$

in ion exchange studies may be attributed to the lower selectivity of sorbents over $Ni^{2+}$ ions. Therefore, ion exchange may not be listed among the attractive methods for $Ni^{2+}$ removal particularly when a wastewater containing a high $Ni^{2+}$ content along with other heavy metal ions and when implementation of more stringent standards for discharges of heavy metals into receiving environments are taken into consideration.

**Table 2.1.** Some examples for maximum capacities of $Cu^{2+}$ and $Ni^{2+}$ obtained with different sorbents

| **Material** | **$Cu^{2+}$ (meq/g)** | **$Ni^{2+}$ (meq/g)** | **Study** |
|---|---|---|---|
| Chitosan | 0.53 | 0.08 | Huang et al. (1996) |
| Chitosan | 0.15 | - | Ngah and Isa. (1998) |
| Chitosan | 0.41 | - | Annachhatre et al. (1996) |
| Fly ash-wollastonite | 0.04 | - | Panday et al. (1985) |
| Eutrophic peat moss | 0.38 | 0.38 | Gosset et al. (1986) |
| Oligotrophic peat moss | 0.38 | 0.40 | Gosset et al. (1986) |
| Eutrophic peat moss | 0.62 | - | Chen et al. (1990) |
| Oligotrophic peat moss | 0.20 | - | Chen et al. (1990) |
| Waste Slurry | 0.66 | - | Lee and Davis (2001) |
| Sawdust | 0.43 | - | Ajmal et al. (1998) |
| GAC | 1.20 | - | Monser and Adhoum (2002) |
| As received ACF | 0.28 | 0.07 | Shim et al. (2001) |

GAC: Granulated activated carbon
ACF: Activated carbon fibrous

When maximum capacities for both $Cu^{2+}$ and $Ni^{2+}$ removal are examined, similar values are reported for all studied sorbents except for granulated activeted carbon which has a higher removal capacity in $Cu^{2+}$ removal. Among the given low cost sorbents, natural zeolites have been proposed as one of the most promising alternative to the activated carbon (Watanabe et al., 2003) due to their abundance in nature and high selectivity for certain heavy metal cations.

## 2.2. ZEOLITES

In practice, both synthetic and natural zeolites are utilized for pollution control. In this study natural zeolites are investigated and they are called as "zeolites" throughout the following text. With the discovery of their exciting surface and structural properties, zeolites have been exploited in industrial, agricultural, and biological technology for more than 40 years. However, recently they have been utilizing in environmental technologies. Some applications of zeolites in environmental technology can be classified as; removal of ammonium from drinking and municipal wastewater, extraction of $Cs^{2+}$ and $Sr^{2+}$ from nuclear wastes and the mitigation of radioactive fallout, removal of odor and removal of heavy metals from wastewaters (Mumpton, 1999).

Zeolites are crystalline, naturally occurring hydrated aluminosilicate minerals of alkali and alkaline earth cations in particular $Na^{+}$, $K^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$. Structurally, zeolites consist of a framework of aluminosilicates which is based on an infinite three dimensional structure of $SiO_4$ and $AlO_4$ tetrahedral molecules linked to each other by shared oxygen. They belong to the class of minerals known as "tectosilicates". Most common zeolites are formed by alteration of glass-rich volcanic rocks with fresh water in playa lakes or by seawater (Almaraz et al., 2003, Ouki et al., 1994). Natural zeolites are further able to lose and gain water reversibly and to exchange extraframework cations, both without change of crystal structure (Mumpton, 1999).

There are more than 30 distinct species of zeolite that occur in nature. However, only seven of them, namely mordenite, clinoptilolite, ferrierite, chabazite, erionite, philipsite and analcime occur in sufficient quantity to be considered as viable mineral resources. Among these species, clinoptilolite is the most abundant zeolite that occurs in relatively large mineable sedimentary deposits in sufficiently high purity in many parts of the world (Ouki et al., 1994, Sarıoğlu, 2005). Additionally

clinoptilolite has received extensive attention due to its attractive capacity for certain heavy metal cations such as $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ (Inglezakis et al., 2003).

In nature, clinoptilolite is found along with other minerals of silicate class: feldspars, quartz and other zeolites (members of the tectosilicates subclass), clays (members of the phylosilicates subclass), and volcanic glass (Armbuster, 2001). From the zeolite group clinoptilolite can be found along with heulandite and mordenite, which are materials of high cation capacity (Inglezakis, 2005). Feldspars are anhydrous aluminosilicates of $K^+$, $Na^+$ and $Ca^{2+}$. The $Si^{4+}$ and $Al^{3+}$ occupy the centers of interlinked tetrahedral of $SiO_4$ and $AlO_4$. These tetrahedral connect at each corner to other tetrahedral, forming an intricate, three-dimensional, negatively charged framework. The $K^+$, $Na^+$ and $Ca^{2+}$ sit within the voids in this structure. Thus feldspars can exchange these ions with heavy metal cations (Inglezakis, 2005). From the quartz group, clinoptilolite is found along with quartz and cristobalite (Li et al., 2002). Quartz is neutrally charged inert material which has a three dimensional rigid framework but does not have the capacity for cation exchange, as there are no $Al^{3+}$ atoms present (Inglezakis, 2005). Sandy soils, which contain large amounts of quartz, have cation exchange capacities lower than 2-3.5 meq/100 g (Inglezakis, 2005). Several inorganic compounds may also be present in clinoptilolite, such as the $Ca^{2+}$ and $Mg^{2+}$ carbonates, calcite, dolomite and magnesite (Inglezakis, 2005). Some examples for the impurities found along with various clinoptilolite samples in the literature are presented in Table 2.2.

Table 2.2 reveals that quartz is found to be associated with all given clinoptilolite samples. Feldspar and calcite are also common impurities accompanying quartz. In addition to quartz, feldspar and calcite, illite, muscovite, biotite, chlorite, montmorillonite, opal, smectite, ematite, mica, albite, halite and mica are the other types of minerals found along with clinoptilolite.

**Table 2.2.** Examples for some impurities in clinoptilolite samples given in the literature

| Sample origin | Impurities | Study |
|---|---|---|
| Sardinian, Italy | Illite, Quartz | Cincotti et al. (2001) |
| Mexico | Mordenite, Muscovite, Quartz | Mier et al. (2001) |
| Bigadiç, Türkiye | K-feldspar, Quartz | Kurama et al. (2003) |
| Sokyrnytsya, Ukraine | Biotite, Calcite, Chlorite, Montmorillonite, Muscovite, Quartz | Sprynskyy et al. (2005) |
| Donje Jesenje, Croatia | Calcite, Feldspar, Halite, Illite, Quartz | Trgo and Peric (2003) |
| USA | Feldspar, Mica, Quartz | Sheta et al. (2003) |
| Mexico | Mordenite, Quartz | Ali and El-Bisthawi (1997) |
| Japan | Feldspar, Quartz | Yuan et al. (1999) |
| Greece | Feldspar, Quartz | Inglezakis et al. (1999) |
| Sardinian, Italy | Ematite, Feldspar, Mica, Opal, Quartz, Smectite | Castaldi et al. (2005) |
| Tasajeras, Cuba | Calcite, Feldspar, Quartz | Cabrera et al. (2005) |
| Chile | Albite, Mordenite, Quartz | Englert and Rubio (2005) |

In Tables 2.3 and 2.4 some examples for chemical compositions of clinoptilolite samples mined in different countries and in Türkiye are presented. In addition to being found along with other minerals of silicate class, it is evident from Table 2.3 that clinoptilolite samples of different countries differ in chemical composition.

The differences in chemical compositions also result in Si/Al ratios and in theoretical cation exchange capacities (TCEC) varying in a considerably wide range of values which are considered as to be the most significant chemical properties of clinoptilolites. Oxides of $Si^{4+}$, $Al^{3+}$, $Na^{+}$, $K^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$ and $Fe^{3+}$ are common compounds in clinoptilolite and it also contains $Ba^{2+}$, $Ti^{2+}$, $Mn^{2+}$, $S^{6+}$, $P^{5+}$ and $Sr^{2+}$ oxides, generally in trace amounts. Since these oxides are found in trace amounts, their identification strongly depends on the method employed for the determination of chemical composition. In the literature, various methods are reported for this purpose; however, XRF, SEM/EDS and classical silicate analysis arise as the ones that are most widely used.

**Table 2.3.** Some examples for the chemical composition of various clinoptilolite samples from different countries given in the literature.

| Oxide | Clinoptilolite Origin | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Bulgaria[1]** | **U.S.[2]** | **Cuba[3]** | **Italy[4]** | **Poland[5]** | **Chile[6]** | **China[7]** |
| **$SiO_2$** | 69.85 | 68.0 | 63.20 | 63.36 | 77.66 | 67.00 | 65.52 |
| **$Al_2O_3$** | 10.68 | 11.1 | 12.45 | 12.90 | 13.77 | 13.00 | 9.89 |
| **$Na_2O$** | 1.50 | 3.85 | 1.20 | 1.39 | 0.17 | 2.60 | 2.31 |
| **$K_2O$** | 4.11 | 4.24 | 2.31 | 2.16 | 1.67 | 0.45 | 0.88 |
| **CaO** | 2.74 | 0.81 | 2.36 | 3.10 | 3.2 | 3.20 | 3.17 |
| **MgO** | 0.68 | 0.26 | 0.69 | 1.29 | 0.88 | 0.69 | 0.61 |
| **$Fe_2O_3$** | 2.32 | - | 0.81 | - | 0.37 | 2.00 | 1.04 |
| **FeO** | - | 0.70 | - | - | - | - | - |
| **BaO** | - | - | - | 0.09 | 0.91 | - | - |
| **$TiO_2$** | 0.11 | - | - | - | - | 0.20 | 0.21 |
| **MnO** | 0.04 | - | - | - | - | 0.04 | 0.06 |
| **$SO_3$** | 0.22 | - | - | - | - | - | - |
| **$P_2O_5$** | 0.15 | - | - | - | - | 0.05 | - |
| **SrO** | - | - | - | - | 1.34 | - | - |
| **$H_2O$** | 7.65 | 5.40 | 15.50 | 15.71 | - | - | 7.25 |
| **M** | CSA | CSA | NI | NI | NI | SEM | NI |
| **Si/Al** | 5.55 | 5.20 | 4.31 | 4.17 | 4.79 | 4.37 | 5.62 |
| **TCEC meq/g** | 2.67 | 2.56 | 2.06 | 2.26 | 1.49 | 2.21 | 2.03 |

M: Method
TCEC: Theoretical cation exchange capacity
CSA: Classical Silicate analysis
SEM: Scanning Electron Microscopy
NI: Not Included
1) Panayotova and Velikov (2003), 2) Semmens and Martin (1988), 3) Milan et al. (1997), 4) Castaldi et al. (2005), 5) Mozgawa and Bajda (2005), 6) Englert and Rubio (2005), 7) Du et al. (2005)

**Table 2.4.** Some examples for the chemical composition of various clinoptilolite samples from Türkiye given in the literature.

| Source | Clinoptilolite origin | | | | | |
|---|---|---|---|---|---|---|
| | Bigadiç[1] | Bigadiç[2] | Bigadiç[3] | Bigadiç[4] | Gördes[5] | Doğantepe[6] |
| $SiO_2$ | 65.17 | 67.96 | 64.99 | 67.6 | 70.0 | 70.27 |
| $Al_2O_3$ | 12.40 | 10.74 | 9.99 | 11.3 | 14.0 | 12.90 |
| $Na_2O$ | 0.75 | 0.81 | 0.18 | - | 0.20 | 3.21 |
| $K_2O$ | 3.41 | 3.01 | 1.95 | 2.17 | 2.30 | 1.49 |
| CaO | 2.58 | 0.74 | 3.51 | 3.26 | 2.50 | 2.05 |
| MgO | 0.78 | 1.49 | 1.01 | 1.18 | 1.15 | 1.71 |
| $Fe_2O_3$ | 1.00 | - | 3.99 | 0.77 | 0.75 | 1.38 |
| FeO | - | - | - | - | - | - |
| BaO | - | - | - | - | - | - |
| $TiO_2$ | 0.19 | - | - | 0.07 | 0.05 | 0.19 |
| MnO | 0.02 | - | - | 0.02 | - | 0.02 |
| $SO_3$ | - | - | - | - | - | |
| $P_2O_5$ | - | - | - | - | - | 0.04 |
| $NaO_2$ | - | - | - | 0.30 | - | - |
| $H_2O$ | 12.34 | - | 14.47 | 13.4 | 9.02 | 6.57 |
| M | CSA | NI | NI | NI | NI | NI |
| Si/Al | 4.46 | 5.37 | 5.52 | 5.08 | 4.24 | 4.62 |
| TCEC, meq/g | 2.27 | 1.69 | 1.66 | 1.81 | 1.9-2.2 | 2.29 |

1) Çulfaz and Yağız (2004), 2) Çelenli et al. (1994), 3) Sirkecioğlu and Şenatalar (1995), 4) Yücel and Çulfaz (1985), 5) Turan et al. (2005), 6) Sarıoğlu (2005)

Abusafa and Yücel (2002) stated that the composition, purity and mineralogical characteristics of clinoptilolite may vary widely from one deposit to another and

even within the same deposit. This is evident when chemical composition of different Bigadiç clinoptilolite samples are examined (Table 2.4). It is clear from the table that Western Anatolia clinoptilolites are poor in $Na^+$ but rich in $Ca^{2+}$ and $K^+$. However, different from Western Anatolia clinoptilolites, Doğantepe-Amasya clinoptilolite is reported being rich in $Na^+$ content.

## 2.3. HEAVY METAL REMOVAL STUDIES USING CLINOPTILOLITE

There are several factors affecting heavy metal removal both in batch and continuous mode applications. Presence of surface dust, particle size, contact time, pH, agitation speed, conditioning, presence of anions, initial metal concentration, flow rate, flow mode and column dimensions can be given as some examples for the most significant factors affecting removal of heavy metals using clinoptilolite.

### 2.3.1. Effect of Surface Dust and Particle Size

Metal uptake by clinoptilolite takes place at sites on the exterior surface of the particle as well as sites within the particle. However, only a fraction of the internal sites is accessible to metal ions. The reason for this partial accessibility of internal sites may be attributed to the presence of fine particles (surface dust) and pore diffusion resistance (Sarıoğlu, 2005). Thus, increasing the external surface area by decreasing particle size and removing the surface dust by pre-washing of the clinoptilolite samples result in an increase in the number of available sites for metal uptake (Inglezakis et al., 1999).

The effect of surface dust and particle size on the process effectiveness of heavy metal removal using clinoptilolite samples is reported by several researchers. For example, Inglezakis et al. (1999) studied $Pb^{2+}$ removal with both as received and dust free Northern Greek clinoptilolite samples and concluded that pore clogging leads to slower ion exchange rates and smaller ion exchange capacity that accounts for about 15%.

Despite it is a common fact that decreasing the particle size results in higher heavy metal removal efficiencies (Tchobanoglus et al., 2003), a concurrent increase in contact time results in a decrease in the degree of particle size effect (Malliou et al., 1994). Therefore, the impact of particle size is expected to be more profound in continuous mode applications since such applications utilize relatively lower contact times compared to batch mode ones. Ineffectiveness of decreasing particle size in batch mode applications was also verified by Panayotova (2001), who reported that 0.09-0.325 mm and 0.325-0.400 mm size fractions of Bulgarian clinoptilolite exhibit 82.64% and 78.33% removal efficiencies respectively in $Cu^{2+}$ removal. Employment of very fine particles may also cause some operational problems such as difficulty in solid-liquid separation in batch mode, and partial exploitation of the sorbent in accordance with a considerable pressure drop in continuous mode (Inglezakis et al., 2001). Ali and El-Bisthawi (1997), studied $Pb^{2+}$ and $Ni^{2+}$ removal with different size fractions of Iranian zeolites in batch mode and the authors encountered some problems in the handling of the material for particles smaller than 0.090 mm. Similarly, Bektaş and Kara (2004) concluded that sorption of $Pb^{2+}$ on Bigadiç clinoptilolite slightly increased with decreasing particle size and 0.315-0.500 mm size fraction was selected for further studies to prevent handling problems with smaller particles.

In the case of continuous mode applications, despite, it is reported in the literature that use of a clinoptilolite fraction finer than 0.35 mm is ineffective for ammonium removal under dynamic conditions because of high flow resistance (Sprynskyy et al., 2005), Inglezakis et al. (2001) concluded that using clinoptilolite particles with a size fraction even smaller than 0.80 mm results in operational problems.

### 2.3.2. Equilibration Time

Contact time is one of the most significant operational parameters in heavy metals removal using clinoptilolite. The need for the investigation of the effect of contact time on the process effectiveness has arisen from the fact that heavy metal-

clinoptilolite interaction is a dynamic process and amount of metal uptake is a function of time.

In the literature most research on the effect of contact time was conducted to determine the equilibration period for the interaction, and by this way researchers found the required contact time for their further equilibrium studies. Several researchers reported different contact times for their system to reach equilibrium and these contact times range from a several minutes to even weeks, i.e. a recent study on Turkish (Doğantepe) clinoptilolite revealed that 20 minute contact time is sufficient for the system equilibrium (Sarioğlu, 2005). Similarly, Bektaş and Kara (2004), found 120 minutes of contact time as the equilibration period for $Pb^{2+}$ removal using Bigadiç clinoptilolite. However, in another study, three days of reaction time was found to be required for the system equilibrium when Italian (Sardinian) clinoptilolite was used as the sorbent material (Langella et al., 2000).

### 2.3.3. Effect of pH

pH has an obvious impact on metal removal by clinoptilolite since it can influence both the character of the exchanging ions and the character of the clinoptilolite itself. As solution pH decreases, heavy metal removal efficiency also decreases because $H^+$ ions compete with heavy metal cations for the same exchange sites (Inglezakis et al., 2001, Haggerty and Bowman, 1994, Wingenfelder et al., 2005) and electrostatic repulsion between the heavy metal cations and the protonated clinoptilolite surface increases (Cabrera et al., 2005). Moreover, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium carbonate, unaltered glass, etc., are perhaps removed by $H^+$ ions at lower pH (Haggerty and Bowman, 1994).

Several researchers investigated the effect of solution pH on heavy metal removal using clinoptilolite samples. Ouki and Kavannagh (1999) studied various initial mixed heavy metal solution pHs ranging between 3 and 6 and pH between 4 and 5

were determined to be optimum for all studied heavy metal cations. In the same way, Panayotova (2001) found pH of 5 as the optimum value for $Cu^{2+}$ removal using Bulgarian clinoptilolite.

### 2.3.4. Effect of Agitation Speed

Effect of agitation speed is a typical parameter in batch mode applications of a heavy metal-clinoptilolite interaction. Agitation of suspension during experiments has led to abrasion of clinoptilolite grains, producing freshly broken and highly reactive locations on the surface. So this mechanical effect increases the number of possible adsorption locations and accordingly process effectiveness improves (Trgo and Peric, 2003). However, with the increase in the production of fine particles due to abrasion, operation may be exposed to some problems such as an increasing difficulty in solid liquid separation. Another effect of production of fine particles via abrasion may be experiencing a difficulty in differentiating between effectiveness of various particle sizes in heavy metal removal (Inglezakis et al., 1999).

### 2.3.5. Effect of Conditioning

Conditioning aims to remove certain cations from the structure of the zeolite and locates more easily removable ones, prior to any ion exchange application. The final homoionic or near-homoionic state of the zeolites was found to improve their effective exchange capacity. (Ouki et al., 1994, Semmens and Martin, 1988, Bremmer and Schultze, 1995, Gradev et al., 1998, Panayotova and Velikov, 2003).

Several conditioning methods with various agents (Table 2.5) are employed for the modification of clinoptilolites. In Table 2.5 some initial experimental conditions used for batch mode conditioning are presented.

**Table 2.5.** Various batch mode pretreatment conditions given in the literature.

| Study | Conditioning agent | | | T ($^0$C) | $t_c$ (hrs) | S/L (g/mL) |
|---|---|---|---|---|---|---|
| | Name | $V_b$ (mL) | $C_c$ (M) | | | |
| Mier et al. (2001) | NaCl | 200 | 1 | 120 | 2 | 0.15 |
| Milan et al. (1997) | NaCl | 1600 | 1 | 90 | 2 | 0.06 |
| Milan et al. (1997) | KCl | 1600 | 1 | 90 | 2 | 0.06 |
| Milan et al. (1997) | $CaCl_2$ | 1600 | 1 | 90 | 2 | 0.06 |
| Milan et al. (1997) | $MgCl_2$ | 1600 | 1 | 90 | 2 | 0.06 |
| Sprynskyy et al. (2005) | HCl | 250 | 2 | - | 24 | 0.06 |
| Trgo and Peric (2003) | NaCl | - | 2 | 37±1 | 72 | 0.05 |
| Panayotova (2001) | NaCl | 1000 | 2 | 100 | 24 | 0.10 |
| Panayotova (2001) | NaOH | 1000 | 2 | 100 | 24 | 0.10 |
| Panayotova (2001) | HCl | 1000 | 2 | 100 | 24 | 0.10 |
| Top and Ülkü (2004) | NaCl | 1250 | 1 | 60 | 168 | 0.10 |
| Papadopoulous et al. (2004) | NaCl | 100 | 2 | 20 | 24 | 0.10 |

Vb: Volume of NaCl solution in batch mode applications
$C_c$: Concentration of the conditioning agent
T: Temperature
$t_c$: contact time
S/L: Solid/Liquid ratio

It is evident from Table 2.5 that $Na^+$ is preferred against other alkali and alkaline earth cations, as its homoionic forms are produced much more easily. Also, $Na^+$ is the most weakly bound ion in clinoptilolite and thus it is easily exchanged with cations from the solution (Rozic et al., 2002, Zamzow et al., 1990). Milan et al. (1997) investigated the effect of treatment of clinoptilolite samples on $NH_4^+$ removal performance and for this purpose Cuban clinoptilolite was transformed into its $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ forms (Table 2.5). Following conditioning, each form of clinoptilolite samples were exhausted in a packed bed column via pumping the feed solution containing 600 mg/L $NH_4^+$ in up-flow mode at a volumetric flow rate of 2 BV/hr for 30 hours. The results revealed $NH_4^+$ exchange capacity in the order of; $Na^+$-Zeo > $Ca^{2+}$-Zeo > $K^+$-Zeo > $Mg^{2+}$-Zeo and it is obvious that the column packed with homoionic sodium clinoptilolite exhibited the best behavior compared to the others. Similarly, Inglezakis et al. (1999) studied the effect of batch mode NaCl treatment on $Pb^{2+}$ removal with Greek clinoptilolite and found that effective capacity was increased by 100%. Effect of $Na^+$ conversion with different chemicals was also

examined by several researchers. Panayotova (2001) studied the ability of $Na^+$ form Bulgarian clinoptilolites prepared with NaOH and NaCl in $Cu^{2+}$ removal (Table 2.5) and reported that NaCl treatment results in a greater improvement in $Cu^{2+}$ uptake when compared to NaOH treatment. The author attributed the reason for this difference to the limited ability of NaOH in displacing $K^+$, $Ca^{2+}$ and $Mg^{2+}$. Among reported conditioning agents, HCl has a destroying effect on the clinoptilolite structure (Sprynskyy et al., 2005, Rozic et al., 2005). Kurama et al. (2003) treated Bigadiç clinoptilolite with 1 N HCl solution and found that HCl results in nearly 40% loss in crystalline phase particularly in $Al^{3+}$ content, amount of which in clinoptilolite structure is directly related to the ability of the material to remove cationic species from aqueous solutions. As a result, it can be concluded that despite acid treatment may offer some advantages for the adsorption/separation of non-polar molecules from water or gas-flows, it is not a convenient method in the case of cation removal (Kurama et al., 2003).

In addition to batch mode conditioning, another common procedure is the use of ion exchange packed beds. Different from batch mode applications, packing material is washed with a conditioning agent under specific operating conditions such as; flow rate, solution volume and temperature. As observed in the case of batch mode, NaCl is the most frequently used conditioning agent (Inglezakis et al., 2001). A variety of flow rates are used in the literature for conditioning of clinoptilolite samples in packed beds, ranging from down-flow 1 BV/h (Semmens and Martin, 1988), to up-flow 21.3 BV/h (Klieve and Semmens, 1980). Semmens and Martin (1988) reported that $Na^+$ content of the conditioned samples is increased with volumetric flow rate decreasing from 5 to less than 1 BV/h.

The effect of concentration is another factor in conditioning of clinoptilolite samples. Carland and Aplan (1988) reported that use of concentrations greater than 0.5 M had no effect on Cu removal effectiveness of clinoptilolite. Similarly, Inglezakis et al. (2001) studied several NaCl concentrations (0.1-3.3 M) for pretreatment of Greek clinoptilolite and concluded that rising NaCl concentration above 0.4 M has practically no effect on $Pb^{2+}$ removal capacity.

Consequently, it is clear from above that, conditioning results in a considerable improvement in metal uptake capacity of clinoptilolite samples however, prior to implementation of clinoptilolite based technologies in practice, the treatment and modification of the zeolite as an ion exchange material must undergo an economical and environmental analysis for the actual benefits (Englert et al., 2005).

### 2.3.6. Effect of Presence of Anions

In general, heavy metals often exist in the bulk aqueous phase as complexes with inorganic or organic ligands. Such ligands are present in all natural aquatic systems and may have a dramatic effect on metal ion behavior and on the surface properties of potential sorbents (Doula and Ioannou, 2003).

Interactions between metal ions and complexing ligands in the presence of a sorbent surface may be divided into three groups based on the origin and the strength of the interaction: (i) Metal-ligand complexes may form in solution (ion-pairing) and adsorb only weakly or not at all. In this case formation of soluble complexes may be considered to compete with reactions forming "surface complexes", and ion exchange is decreased compared to the ligand-free system. (ii) The species may interact indirectly at the surface, by altering the surface electrical properties. For instance, it may adsorb on clinoptilolite and make the surface more favorable for a metal ion, (iii) The metal-ligand complex may adsorb strongly, thereby enhancing removal of metal or ligand, or both from solution compared to the case where either one is present alone (Doula and Ioannou, 2003).

Several researchers examined the effects of anion presence on the removal of heavy metals using clinoptilolite. For example, Inglezakis et al., 2003, looked into the effects of $SO_4^{2-}$, $HPO_4^{2-}$ and $NO_3^-$ on ion exchange of $Cu^{2+}$, $Fe^{3+}$ and $Cr^{3+}$ on natural Greek clinoptilolite. The authors observed that among the studied heavy metal cations, mainly $Cu^{2+}$ uptake is lowered in the presence of $HPO_4^{2-}$ and $SO_4^{2-}$ and the reason for this situation was attributed to the formation of metal-anion complexes and adsorption of these complexes weakly.

### 2.3.7. Investigation of Sorption Capacity of Clinoptilolite

Equilibrium behavior is usually described in terms of equilibrium isotherms which depend on the system temperature, the total initial concentration of the solution in contact with the exchanger and on the characteristics of the ion exchange system, such as solution composition, mineral type and pH (Inglezakis et al., 2002). They are the most widely used method for evaluating the capability of a clinoptilolite for the uptake of heavy metals. Many researchers carried out equilibrium studies with various clinoptilolite samples under different initial experimental conditions to determine the capability and capacity of their sorbent materials towards heavy metal cations (Trgo and Peric, 2003, Doula and Ioannou, 2003, Bektaş and Kara, 2004). In Table 2.6 maximum removal capacities obtained in various studies are presented respectively.

**Table 2.6.** Some examples for maximum capacities obtained with different clinoptilolite samples in batch mode applications for $Cu^{2+}$ and $Ni^{2+}$ in the literature.

| $Cu^{2+}$ (meq/g) | | $Ni^{2+}$ (meq/g) | | Study |
|---|---|---|---|---|
| **A** | **C** | **A** | **C** | |
| 0.150 | 0.380 | - | - | Cincotti et al. (2001) |
| 0.093 | - | - | - | Cincotti et al. (2001) |
| 0.160 | - | - | - | Tillman et al. (2004) |
| - | 0.700 | - | - | Kurama and Kaya (1995) |
| 0.370 | - | - | - | Inglezakis et al. (2004) |
| 0.280 | - | - | - | Erdem et al. (2004) |
| - | 0.590 | - | - | Petrus and Warchol (2003) |
| 0.280 | - | 0.130 | - | Panayotova and Velikov (2002) |
| 0.820 | - | - | - | Peric et al. (2004) |

A: As received samples
C: Conditioned samples

It is clear from Table 2.6 that maximum capacities obtained for $Cu^{2+}$ differ significantly and conditioned samples exhibit greater capacities. However, very few

researchers studied $Ni^{2+}$ removal and it is clear from maximum capacities (Table 2.6) that clinoptilolite exhibited a higher capacity over $Cu^{2+}$ when compared to $Ni^{2+}$.

***Application of Freundlich and Langmuir Models to the Equilibrium Data***

Evaluation of the equilibrium data obtained from equilibrium studies with a suitable mathematical description is of great importance not only in the design of ion exchange processes but also in the investigation of the mechanisms involved in heavy metal-clinoptilolite interactions. Langmuir and Freundlich are the most widely used mathematical models since they are simple and they have an ability to describe equilibrium data in wide range of concentrations (Altın et al., 1998, Peric et al., 2004). Although most researchers use linearized forms of these models, linearization does not satisfy on fitting the experimental data (Peric et al., 2004).

Kumar and Sivanesan (2005) studied the adsorption of Bismarck brown onto rice husk particles and applied both linear and non-linear forms of Freundlich and Langmuir models to the equilibrium data. For this purpose, four different linearized forms of Langmuir and one linearized form of Freundlich models were studied and the authors observed that especially Langmuir equation shows the mathematical complexities associated with using linear method in estimating the rate parameters. The reason for obtaining different $R^2$ values in each linearized form of Langmuir equation was attributed to the variation in distribution of error structure for different linear equations. The variation in error distribution was ascribed to the different axial settings; as a result, the dependent variables are transformed to different axial positions. Thus, according to the authors it not is an appropriate method to get isotherm parameters by fitting the experimental data by linear method; instead it is better to go for non-linear method which has a uniform error distribution for the whole range of experimental data.

### 2.3.8. Selectivity of Clinoptilolite for Different Metal Cations

Table 2.7 reveals that almost each clinoptilolite sample has its unique selectivity series. The reason for this difference may be attributed not only to the different experimental conditions but also to the chemical composition of the clinoptilolite (Inglezakis et al., 2003).

**Table 2.7.** Some examples for selectivity series obtained in different studies

| Study | Selectivity Series |
|---|---|
| 1 | $Cu^{2+}>Cr^{3+}>Cd^{2+}> Zn^{2+}>Ni^{2+}$ |
| 2 | $Pb^{2+}>NH_4^+$, $Ba^{2+}> Cu^{2+}$, $Zn^{2+}>Cd^{2+}>Co^{2+}$ |
| 3 | $Pb^{2+}>K^+>Ba^{2+}>NH_4^+>Ca^{2+}>Cd^{2+}> Cu^{2+}>Na^+$ |
| 4 | $NH_4^+ > Pb^{2+} > Cd^{2+} > Cu^{2+} \approx Zn^{2+}$ |
| 5 | $Pb^{2+} > Cd^{2+} > Cs^{2+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ |
| 6 | $Pb^{2+} > Cr^{3+} > Fe^{3+} > Cu^{2+}$ |
| 7 | $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ |
| 8 | $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$ |
| 9 | $Pb^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Cs^{2+} > Ni^{2+}$ |
| 10 | $Cu^{2+} > Zn^{2+} > Ni^{2+}$ |

1) Tillman et al. (2004), 2) Blanchard et al. (1988), 3) Semmens and Martin (1988), 4) Cincotti et al. (2001), 5) Zamzow et al. (1990), 6) Inglezakis et al. (2002), 7) Ali and El-Bisthawi (1997), 8) Ouki and Kavannagh (1999), 9) Faghihian et al. (1999), 10) Cabrera et al. (2005)

Despite the observation of different selectivity series in every single research (Table 2.7) it is common for almost all studies that clinoptilolite has the highest affinity towards $Pb^{2+}$ among studied heavy metal cations. As mentioned earlier, the reason for this situation was attributed to the fact that, heavy metal cations with low hydration energies are sorbed preferably compared to cations with high hydration energies (Langella et al., 2000**,** Wingenfelder et al., 2005]. Some example for Gibbs free energies of hydration are -1425 kj/mol for $Pb^{2+}$, -1755 kj/mol for $Cd^{2+}$, 2105 kj/mol for $Ni^{2+}$ and -2100 kJ/mol for $Cu^{2+}$ (Wingenfelder et al., 2005, Panayotova and Velikov, 2002). In addition to hydration energy, physicochemical and stereochemical factors such as the hydrated radii, space requirements in the micropores of clinoptilolite and the type, number and location of exchangeable

cations (Abusafa and Yücel, 2002) also affect both selectivity order and dependence of total uptake (Inglezakis et al., 2003).

### 2.3.9. Possible Mechanisms Involved in Heavy Metal Solutions-Clinoptilolite Interaction

Different physicochemical reactions such as dissolution, ion exchange, sorption and possibly surface precipitation are known to prevail in a heavy metal solution-clinoptilolite interaction. Investigation of this interaction is important for their application in environmental chemistry, especially in development of tertiary wastewater treatment processes with extreme pH values and saline environments (Trgo and Peric, 2003).

Adsorption is one of the most important processes in a heavy metal solution-clinoptilolite interaction. The forces involved in adsorption can range from weak, physical, Van der Waals forces and electrostatic outer-sphere complexes (e.g. ion exchange) to chemical interactions. Chemical interactions can include inner-sphere complexation that involves a ligand exchange mechanism, covalent bonding, hydrogen bridges, and steric or orientation effects (Doula and Ioannou, 2003). When the process of adsorption begins, outer-sphere complexes are formed on external surface sites. The outer-sphere complexation involves the ion-exchange reactions between metal ions and surface counterbalance cations. As metal concentration increases, metal ions are forced into internal surface sites and also form inner-sphere complexes. This kind of complexation leads to more stable surface groups due to the formation of covalent bonds. Scheidegger and Sparks (1996) states that the type of surface complex, i.e. outer-sphere versus inner-sphere, affects the rate and reversibility of sorption reactions. Outer-sphere complexation is usually rapid and reversible, whereas inner-sphere complexation is slower and may appear to be "irreversible". $H^+$ ions are released as products of these complex formations and the process causes a total decrease in solution pH (Doula and Ioannou, 2003).

As the amount of a metal cation or anion sorbed on a surface increases to a higher surface coverage, surface precipitation can form. There is a continuum between surface complexation (adsorption) and surface precipitation. According to Scheidegger and Sparks (1996) at low surface coverage, complexation tends to dominate. As surface coverage increases, nucleation occurs and results in the formation of distinct entities or aggregates on the surface. As surface loading increases further, surface precipitation becomes the dominant mechanism (Doula and Ioannou, 2003).

In addition to ion exchange, sorption and surface precipitation, dissolution also takes place in a heavy metal solution-clinoptilolite interaction. Metal ions and ligands can impact on surface sites and provoke dissolution of $Al^{3+}$ and/or $Si^{4+}$. Generally, the reactivity of a surface, i.e., its tendency to dissolve, depends on the type of surface species present, e.g., an inner-sphere complex with a ligand such as $Cl^-$ facilitates the detachment of a central metal ion and enhances dissolution. The explanation of the above behavior is based on an electron density shift from ligands toward the central metal ion at the surface. This excess of electron density brings the negative charge into the coordination sphere of the Lewis acid center and simultaneously enhances the surface protonation and can labilize the critical S-O (S: central metal, $Si^{4+}$, $Al^{3+}$) lattice bonds, thus enabling the detachment of the central metal ion solution (Doula and Ioannou, 2003). Similarly, surface protonation tends to increase the dissolution, because it leads to highly polarized interatomic bonds in the immediate proximity of the surface central ions and thus facilitates the detachment of a cationic surface group into the solution. The dissolution of most aluminosilicates increases both with increasing protonation and with decreasing surface protonation, equivalent to the binding of $OH^-$ ligands (Rivera et al., 2000); thus under alkaline conditions dissolution increases with increasing pH (Doula and Ioannou, 2003).

### 2.3.10. Effect of Flow Rate, Flow Mode and Column Dimensions on Heavy Metal Removal in a Fixed-Bed Reactor Configuration

Most ion exchange operations, whether lab-scale of full-scale are carried out in columns. A solution is passed through a fixed bed of ion exchange material, and its composition is changed either by ion exchange, sorption or other mechanisms (Inglezakis et al., 2002). During the process, as the feed solution containing the cations passes through the packed material, the ion exchange zone moves in the direction of the flow and, eventually, reaches the exit (Inglezakis and Grigoropoulou, 2003). The time when the ion exchange zone reaches the exit is termed as breakthrough point. In practice, breakthrough point is defined as the time when the effluent concentration is reaching a target percentage of the influent concentration (Inglezakis et al., 2002). The curve representing the cation exit concentration versus time (or effluent volume) is called the breakthrough curve and is used to characterize the process (Inglezakis and Grigoropoulou, 2003). Generally; breakthrough curve is illustrated as "S" shape for most adsorption processes. Certain parameters, such as initial pollutant concentration, pH, flow rate, particle size, conditioning, and column dimensions affect the real shape of a breakthrough curve (Sarıoğlu, 2005, Inglezakis et al., 2002).

In actual column operations, any volume element of the solution is in contact with a given layer of the bed for only a limited period of time, usually insufficient for attainment of equilibrium. Thus the failure of attaining local equilibrium results in a lower uptake of cations from the feed solution (Inglezakis and Grigoropoulou, 2003). Since relatively slow loading kinetics of zeolites requires relatively long residence times, lower flow rates are favored in column studies (Milan et al., 1997). A wide range of flow rates for the treatment of heavy metal solutions using zeolites is presented in the literature. For example, flow rates between 0.75 and 25 Bed Volumes per hour (BV/h) are used for the treatment of solutions containing $Pb^{2+}$, $Cu^{2+}$ and $Fe^{2+}$ with natural clinoptilolite and flow rates lower than 12 BV/h are favored (Blanchard et al., 1984). Inglezakis and Grigoropoulou (2004) studied the ability of natural and modified Northern Greece clinoptilolite for the treatment of

solutions containing $Pb^{2+}$, $Cu^{2+}$, $Cr^{3+}$ and $Fe^{3+}$ in continuous mode at flow rates of 5-15 BV/h and concluded that 5 BV/h revealed the best performance among the studied flow velocities.

Although lower flow rates are reported to result in better utilization of capacity in column applications, they have some side effects such as high flow resistance. High flow resistance is a serious problem particularly in up flow mode operations in bench scale applications (Inglezakis and Grigoropoulou, 2004). In addition to high flow resistance, the flow in beds may suffer from non-idealities like flow channeling or insufficient wetting of the material. Such problems may reduce the process efficiency and lead to erroneous results in capacity determinations (Inglezakis et al., 2001). Depending on the flow rate, flow channeling and accordingly insufficient wetting of the material may result from the mode of operation that is whether feed solution is pumped in down-flow or up-flow. In up-flow mode, perfect wetting of the material is assured for a wide range flow rates. However, in down-flow mode, relatively higher flow rates may result in channeling. In addition to flow modes, channeling may also be observed in large columns compared to smaller ones. For this reason, the column should be long enough (typically longer than 20-30 cm) and operated under up-flow conditions. In the literature, various column dimensions are used (Table 2.8).

**Table 2.8.** Some examples of column dimensions employed in the literature

| $D_c$ (cm) | $L_c$ (cm) | $V_c$ ($cm^3$) | $L_c/D_c$ (cm/cm) | Study |
|---|---|---|---|---|
| 2.10 | 70 | 242 | 33.3 | Inglezakis and Grigoropoulou (2004) |
| 3.00 | 100 | 707 | 33.3 | Turan et al. (2005) |
| 1,60 | 23 | 46 | 14.4 | Cincotti et al. (2001) |
| 7.62 | 76.2 | 3475 | 10.0 | Tillman et al. (2004) |
| 1.00 | 12 | 9 | 12.0 | Mier et al. (2001) |
| 1.50 | 30 | 53 | 20.0 | Semmens and Martin (1988) |
| 1.43 | 38-48 | 61-77 | 26.6-33.6 | Pansini et al. (1991) |
| 4.50 | 25 | 400 | 5.6 | Ibrahim et al. (2002) |
| 2.20 | 70 | 266 | 31.8 | Inglezakis et al. (2002) |
| 3.26 | 15 | 125 | 4.6 | Milan et al. (1997) |
| 1 | 30 | 24 | 30 | Petruzzelli et al. (1999) |

$D_c$: column inner diameter
$L_c$: bed height

BV: volume of liquid equal to the volume of the bed
$L_c/D_c$: height to inner diameter ratio

It is clear from Table 2.8 that, columns are generally narrow in inner diameter and long in bed height. Accordingly, length to diameter ratio generally ranges in between 10 to 35 cm/cm.

## 2.4. DISPOSAL OF METAL SATURATED ZEOLITES

Disposal of zeolites loaded with heavy metal cations is a significant issue in zeolite science. Utilization of zeolites in removal of heavy metals is nothing but transforming the phase of contamination from aqueous phase to solid phase. Therefore, management of heavy metal loaded zeolites must also be taken into account for the further fate of heavy metals at the site they are disposed of. In addition to disposal, metal loaded zeolites can also be made use of in various technological areas.

Many researchers studied regeneration of metal saturated zeolites and concluded that regeneration of metal saturated zeolites works well and effective capacity does not decrease significantly even after several exhaustion-regeneration cycles (Zamzow et al., 1990, Kim and Keane, 2002, Petruzzelli et al., 1999). Apart from reuse in removal of heavy metals via regeneration, it has been known that heavy metals possess antibacterial properties and the exchange with these metals imparts antibacterial activity to the zeolites (Rivera et al., 2000, Mumpton, 1999, Top and Ülkü, 2004). Top and Ülkü (2004), studied the antibacterial activities of $Ag^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ exchanged Gördes clinoptilolite with different exchange levels and the authors reported that a considerable suppression in the growth of *P.aeruginosa* and *E.coli* was achieved. Heavy metal saturated zeolites can also be converted to glass which has an extremely low leach-rate (Ouki et al., 1994). Additionally, sorption and desorption characteristics of micronutrients ($Fe^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and $Cu^{2+}$) by zeolites

make addition of them attractive in soils either directly or as a component of other fertilizers (Sheta et al., 2003).

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1. CHEMICALS

All chemicals used during the experimental progress are analytical grade reagents. $Cu^{2+}$, $Ni^{2+}$ and NaCl solutions were prepared by dissolving $CuCl_2 \cdot 2H_2O$ (Merck Grade), $Ni(NO_3)_2 \cdot 6H_2O$ (Carlo Erba Grade) and NaCl (Merck Grade) salts, respectively, in high-purity deionized water. Atomic Absorption Spectrometry and Flame Photometry were calibrated prior to each measurement with standards that were prepared regularly from commercially provided 1000 mg/L stock solutions (Merck Grade) of related metals. Sample calibration curves for Atomic Absorption Spectrometry and Flame Photometry are presented in Appendix A in Figures A.1, A.2 and A.3. Additionally, pH meter was calibrated before each set of experiment with buffer solutions of pH 4, 7 and 10 (Merck Grade).

## 3.2. ANALYTICAL TECHNIQUES

Measurement of various parameters during experimental procedure was carried out by the following methods/instruments;

i. Atomic Absorption Spectrometry (ATI Unicam 929): $Cu^{2+}$, $Ni^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$ and Fe(total)
ii. Flame Photometry (Jenway PFP7): $Na^{+}$ and $K^{+}$
iii. Spectrophotometry (Hach DR 2400): $Si^{4+}$ (as $SiO_2$)
iv. Argentometric Method: $Cl^{-}$ (Standard Methods, 1998)
v. pH meter (CyberScan 500): pH and temperature

### 3.3. SORBENT

The material used in this study was collected from two different locations of a sedimentary deposit in Bigadiç basin, located in Western Anatolia. In spite of the fact that both samples were collected from the same deposit, mineral characterization studies yielded quite different results for the samples. First sample was obtained from Civil Engineering Department of METU. They received it in bulk in October 2002 from the Bigadiç reserve. However, second sample was directly obtained from Bigadiç, ETİBANK A.Ş. in April 2005. For that reason, these two samples and their conditioned forms have been code-named as follows;

$C_1$: "As received" form of the first sample. It was ground and sieved to different fractions, of which 0.150-0.833 mm was used in this study. Samples were dried at 105 $^0$C for 24 hours and kept in a desiccator for further use.

$Na_1C_1$: Conditioned form of the first sample, $C_1$. Conditioning was carried out in batch mode under specified conditions given in Table 3.1. After conditioning, the material was washed with deionized water repeatedly until no $Cl^-$ was detected in the suspension after filtration. Following washing, samples were dried at 105 $^0$C for 24 hours and put in a desiccator. Prior to use, conditioned samples were sieved once more to a size fraction of 0.150-0.833 mm in order to eliminate the smaller particles that might be resulted from the attrition during conditioning procedure.

**Table 3.1.** Experimental conditions for the preparation of $Na_1C_1$ samples

| Conditioning agent | | | T | $t_c$ | m | S/L | Agitation speed |
|---|---|---|---|---|---|---|---|
| **Name** | **$C_c$ (M)** | **$V_b$ (mL)** | **($^0$C)** | **(hrs)** | **(g)** | **(g/mL)** | **(rpm)** |
| NaCl | 2 | 250 | 30 | 24 | 10 | 0.04 | 150 |

$C_c$: Concentration of the conditioning agent
$V_b$: Volume of NaCl solution in batch mode applications
T: Temperature
$t_c$: Contact time
m: Mass of clinoptilolite

$Na_2C_1$: Conditioned form of the first sample, $C_1$. Conditioning was carried out in batch mode under the same conditions for $Na_1C_1$ except for the contact time, which was 168 hours (7 days).

$C_2$: "As received" form of the second sample. It was ground and sieved to different fractions, of which 0.833-1.18 and 1.18-1.40 mm were used in this study. Samples were dried at 105 $^0$C for 24 hours and kept in a desiccator for further use.

$Na_1C_2$: Conditioned form of the second sample, $C_2$. Conditioning was carried out in two steps. In the first step, samples were rinsed in a 2 L glass beaker with deionized water for several times until achieving almost a clear supernatant and rinsed samples were let to dry for 24 hours at 105 $^0$C in an oven and then put in a desiccator. The aim of rinsing step was to remove fine particles from clinoptilolite grains in order to prevent clogging in the columns during operation (Abadzic and Ryan, 2001). In the second step, samples were conditioned in a 2.5 cm inner diameter and 26.5 cm long column packed with $C_2$ under specified conditions given in Table 3.2. NaCl solution was introduced at a constant volumetric flow rate, using a peristaltic pump in up-flow mode in order to warrant complete wetting of samples (Inglezakis and Grigoropoulou, 2004).

**Table 3.2**. Experimental conditions for the preparation of $Na_1C_2$ samples

| **Conditioning agent** | | | **Conditioning step** | | | **Washing step** | |
|---|---|---|---|---|---|---|---|
| **Name** | **$C_c$ (M)** | **$V_c$ (BV)** | **T ($^0$C)** | **$t_c$ (hrs)** | **Q (BV/hr)** | **$t_c$ (hrs)** | **Q (BV/hr)** |
| NaCl | 1 | 40 | 29±2 | 20 | 2 | 1 | 10 |

$V_c$: Total volume of solution pumped in continuous mode applications
Q: Volumetric flow rate
BV: volume of liquid equal to the volume of the bed.

Following introduction of NaCl solution into the packed-bed column, clinoptilolite samples were washed with deionized water in order to remove the associated $Cl^-$ from the conditioned samples and let to dry within the column for 24 hours.

*$Na_2C_2$*: Conditioned form of the second sample (*$C_2$*). Conditioning was carried out in a packed bed column under the same conditions for *$Na_1C_2$* except for the flow rate and accordingly contact time, which are 10 BV/hr and 4 hours respectively.

Conditioning of the samples aimed an enhancement in the ion exchange capacity of the material and NaCl was selected as the conditioning agent due to the fact that $Na^+$ ions are the weakest bound ions in clinoptilolite and thus are most easily exchanged with cations from solutions (Inglezakis, 2005).

### 3.4. MINERAL CHARACTERIZATION

**X**-**R**ay **F**luorescence (XRF) and **S**canning **E**lectron **M**icroscopy-**E**nergy **D**ispersive **S**pectroscopy (SEM/EDS) (JEOL JSM-6400 Scanning Microscope NORAN Instrument) techniques were used for the determination of the chemical composition of clinoptilolite samples. XRF analyses were performed for only as-received forms of the samples (*$C_1$* and *$C_2$*) in MTA. On the other hand, SEM/EDS analyses were carried out for all samples in Metallurgical and Materials Engineering of METU. The difference between these two methods of chemical analysis is that SEM/EDS measurements are unable to reveal the $H_2O$ content within the structure of the material. From the scope of this fact, SEM/EDS measurements were carried out particularly to observe the difference in the chemical compositions of as-received and conditioned forms of the samples. In addition to chemical analysis, SEM analysis also provided us with the micrographs of the samples. These micrographs gave visual information not only on the crystal structure of the samples' surfaces but also on the distribution of the fine particles on the surface of the grains and the effect of conditioning on the removal of these fine particles.

**X**-**R**ay **D**iffractometry (XRD) (Rigaku X-Ray Diffractometer Ultima Model:D/MAX 2200/PC) analyses were performed in Metallurgical and Materials Engineering of METU for mineralogical composition measurements of as-received forms of the samples. In other words, purity of the original samples and the existing impurities were determined.

Physical properties, namely specific surface area, pore size distribution and density of the clinoptilolite samples were measured in Central Laboratory of METU using following methods and instruments.

i. *Specific surface area*: BET method using $N_2$ as adsorbate by Quantochrome Autosorb Automated Gas Sorption System.
ii. *Pore size distribution*: Quantochrome Autosorb Automated Gas Sorption System.
iii. *Density*: Helium pycnometer.

### 3.5. BATCH SORPTION TESTS

Batch mode experiments were conducted by contacting 1 gram of clinoptilolite samples with 100 mL metal solutions in 250 mL Erlenmeyer flasks. Flasks were sealed and shaken using an orbital shaker (Edmund Buhler KS-15) at 125 rpm. Before each set of experiments, solution pHs were adjusted with 0.1*N* $HNO_3$ or 0.1*N* NaOH solutions. Samples were taken from the suspensions at selected time intervals and at the end of equilibration period. Immediately after withdrawal, these samples were centrifuged at 3800 rpm for 5 minutes to achieve solid liquid separation. Following centrifugation, samples were acidified with concentrated $HNO_3$ to keep all ions in their free forms and then stored at 4 $^0$C until the time of analysis which was no more than seven days. All tests were run in duplicates.

#### 3.5.1. Preliminary Experiments

In practical applications, gathering information on the effects of each operational parameter on the operation performance is important. For that reason, investigation of the use of clinoptilolite samples commenced with preliminary experiments. The objective of the preliminary studies was to examine the degree of influence of initial pH, contact time and conditioning method on metal removal performance of Bigadiç clinoptilolite.

*Effect of pH*

Determination of the optimum initial pH value was the first step of the preliminary experiments. In Table 3.3, initial experimental conditions for optimum pH experiments that were carried out at ambient temperature are presented.

**Table 3.3.** Initial experimental conditions for the determination of optimum pH.

| Metal | pH | $C_i$ (mg/L) | $t_c$ (hrs) | Sample | $d_p$ (mm) | S/L (g/mL) |
|---|---|---|---|---|---|---|
| $Cu^{2+}$ | 2,4,5,6,7,9 | 30 | 48 | $C_1$ | 0.150-0.833 | 1/100 |
| $Ni^{2+}$ | 3,4,5,6,7 | 25 | 48 | $C_1$ | 0.150-0.833 | 1/100 |

$C_i$: Initial heavy metal concentration in the aqueous phase
$d_p$: particle size

*Determination of Equilibration Period*

Following selection of the optimum initial pH values, the objective of the next step was to determine the equilibration period for the heavy metal solution-clinoptilolite interaction. For this purpose, $Cu^{2+}$ removal was studied at an initial pH of 5 under initial experimental conditions that are given in Table 3.4. Investigation of equilibration period on $Ni^{2+}$ removal was not studied and it was accepted as the same with the one determined for $Cu^{2+}$ removal.

**Table 3.4.** Initial experimental conditions for the determination of equilibration period.

| Metal | T ($^0$C) | $C_i$ (mg/L) | $t_s$ (hrs) | Sample | $d_p$ (mm) | S/L (g/mL) |
|---|---|---|---|---|---|---|
| $Cu^{2+}$ | Ambient temperature | 30 | 0, 3, 48, 72 | $C_1$ | 0.150-0.833 | 1/100 |

$t_s$: Sampling Time

*Effect of Conditioning*

In addition to as received forms, conditioned forms of Bigadiç clinoptilolite were also used in this study. Conditioning of the samples aimed an enhancement in the ion exchange capacity of the material by replacing exchangeable cations on clinoptilolite structure with a single cation (e.g. $Na^+$)and NaCl was selected as the conditioning agent since $Na^+$ ions are the most weakly bound ions on clinoptilolite and thus once the clinoptilolite is converted to near homoionic form, they can easily exchange with heavy metal cations (Inglezakis, 2005). For this purpose, $C_1$ was conditioned and two different conditioned samples were prepared, namely $Na_1C_1$ and $Na_2C_1$. Following preparation of the conditioned samples, $Cu^{2+}$ removal was carried out with $C_1$, $Na_1C_1$ and $Na_2C_1$ to determine the effect of conditioning and duration of conditioning on process efficiency under specific conditions given in Table 3.5.

**Table 3.5.** Initial experimental conditions for the determination of the effect of conditioning on process efficiency.

| Metal | pH | T ($^0$C) | $C_i$ (mg/L) | $t_c$ (hrs) | Sample | $d_p$ (mm) | S/L (g/mL) |
|---|---|---|---|---|---|---|---|
| $Cu^{2+}$ | 5 | 25±2 | 200 | 48 | $C_1$<br>$Na_1C_1$<br>$Na_2C_1$ | 0.150-0.833 | 1/100 |

### 3.5.2. Equilibrium Studies

The main objective of the equilibrium studies was to determine the maximum capacity of both as-received and conditioned samples of Bigadiç clinoptilolite towards $Cu^{2+}$ and $Ni^{2+}$ removal under studied conditions and accordingly to make a selectivity comparison for these cations and to investigate the reasons of the differences in removal of the two metal ions. Investigation of the existing mechanisms in the heavy metal solution-clinoptilolite system was another objective of equilibrium studies. For this purpose, amount of exchangeable cations released from the clinoptilolite was measured. Experimental data was also fit to conventional

sorption models, namely Freundlich and Langmuir. Equations 3.1 and 3.2 give the non-linear forms of Langmuir and Freundlich models, respectively;

$$q_e = \frac{q_{\max} K C_e}{1 + K C_e} \qquad \text{Equation (3.1)}$$

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \text{Equation (3.2)}$$

*Where*;

$q_e$: equilibrium heavy metal concentration in the clinoptilolite phase (meq/g)

$q_{max}$: maximum achievable capacity (meq/g)

K: equilibrium Langmuir constant (L/mg)

$C_e$: equilibrium heavy metal concentration in the aqueous phase (mg/L)

1/n: Freundlich intensity parameter, unitless

$K_F$: Freundlich capacity factor (L/mg)

In Table 3.6 the initial experimental conditions applied in equilibrium studies are presented.

**Table 3.6.** Initial experimental conditions for equilibrium studies

| Metal | Sample | $C_i^*$ (mg/L) | T ($^0$C) | $t_c$ (hrs) | pH | $d_p$ (mm) | S/L (g/mL) |
|---|---|---|---|---|---|---|---|
| $Cu^{2+}$ | $C_1$ | 5-1500 | 25 ± 2 | 48 | 5 | 0.150-0.833 | 1/100 |
| | $Na_1C_1$ | 10-1500 | | | | | |
| $Ni^{2+}$ | $C_1$ | 5-10000 | 25 ± 2 | 48 | 4 | 0.150-0.833 | 1/100 |
| | $Na_1C_1$ | 10-10000 | | | | | |

* These are intended initial concentrations. Actual measured initial concentrations are; 6-1689 mg/L for $Cu^{2+}$-$C_1$, 10-1454 mg/L for $Cu^{2+}$-$Na_1C_1$, 8-10206 mg/L for $Ni^{2+}$-$C_1$, 10-10392 mg/L for $Ni^{2+}$-$Na_1C_1$.

Equilibrium $Cu^{2+}$, $Ni^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ concentrations were determined in the aqueous phase for all reactors. Concentration of $Cu^{2+}$ and $Ni^{2+}$ in the solid phase was calculated as follows;

$$q_e = \frac{(C_i - C_e) \times V}{m}$$ Equation (3.3)

*Where*;

$C_e$: equilibrium heavy metal concentration in the aqueous phase (mg/L)

$C_i$: Initial heavy metal concentration in the aqueous phase

m: Mass of clinoptilolite

$q_e$: equilibrium heavy metal concentration in the clinoptilolite phase

V: Volume of heavy metal solution in batch mode applications

### 3.5.3. Deionized Water-Clinoptilolite Interaction

In order to investigate the effect of solution pH on dissolution of clinoptilolite, the chemical behavior of both $C_1$ and $Na_1C_1$ samples in an aqueous medium free from metal ions was examined in batch mode under the initial experimental conditions presented in Table 3.7.

**Table 3.7.** Initial experimental conditions employed in deionized water-clinoptilolite interaction study

| pH | T ($^0$C) | $t_c$ (hrs) | Sample | $d_p$ (mm) | S/L (g/mL) |
|---|---|---|---|---|---|
| 4<br>5 | 25±2 | 48 | $C_1$<br>$Na_1C_1$ | 0.150-0.833 | 1/100 |

At equilibrium, samples taken from the suspensions were centrifuged and the concentrations of $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Si^{4+}$ and $Al^{3+}$ were determined in the aqueous phase. Initial pH values in the reactors were adjusted to 4 and 5 (Table 3.7) which were preliminary determined to be optimum for $Ni^{2+}$ and $Cu^{2+}$ removal, respectively.

### 3.6. PACKED-BED COLUMN STUDIES

Packed bed column studies were conducted in 26.5 cm long glass columns of 2.5 cm internal diameter. Feed solutions were introduced at a constant volumetric flow rate, using a peristaltic pump in upflow mode, in order to assure complete wetting of the particles. Only $Cu^{2+}$ removal was tested in column studies since better removal efficiencies were obtained for $Cu^{2+}$ removal in batch studies. For all runs, $Cu^{2+}$ concentration, pH, temperature of the feed solution and packed density of the columns were kept initially at 200 ± 10 mg/L, 5 ± 0.1, 29 ± 2 $^0$C and 0.98 ± 0.01 g/cm$^3$ (packed volume = 130 cm$^3$ and amount of clinoptilolite packed = 127 ± 2 g) , respectively. In Table 3.8, the experimental conditions for each run are presented.

**Table 3.8.** Experimental conditions for removal of $Cu^{2+}$ using clinoptilolite in packed bed column studies.

| Run | Q (BV/hr) | $d_p$ (mm) | Sample |
|---|---|---|---|
| 1 | 2 | 0.833-1.180 | $Na_1C_2$ |
| 2 | 4 | 0.833-1.180 | $Na_1C_2$ |
| 3 | 8 | 0.833-1.180 | $Na_1C_2$ |
| 4 | 4 | 1.180-1.400 | $Na_1C_2$ |

During operation, samples were collected from the exit of the column at designated time intervals and recorded for pH and temperature. Then samples were acidified with $HNO_3$ and kept at 4 $^0$C prior to analyses. $Cu^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ measurements were conducted for all withdrawn samples at each run and $Si^{4+}$, $Al^{3+}$ and Fe (total) measurements were carried out only for the selected samples of the second run. By plotting the exit metal concentration versus percolated metal solution volume, the breakthrough curves were obtained. In addition to breakthrough curves, trends of the exchangeable cations, pH and $Si^{4+}$ (only for Run 2) versus percolated metal solution volume were also plotted.

# CHAPTER 4

# RESULTS AND DISCUSSIONS

## 4.1. MINERAL CHARACTERIZATION

In Figures 4.1 and 4.2, results of the XRD analyses of clinoptilolite samples ($C_1$ and $C_2$ respectively) are presented.

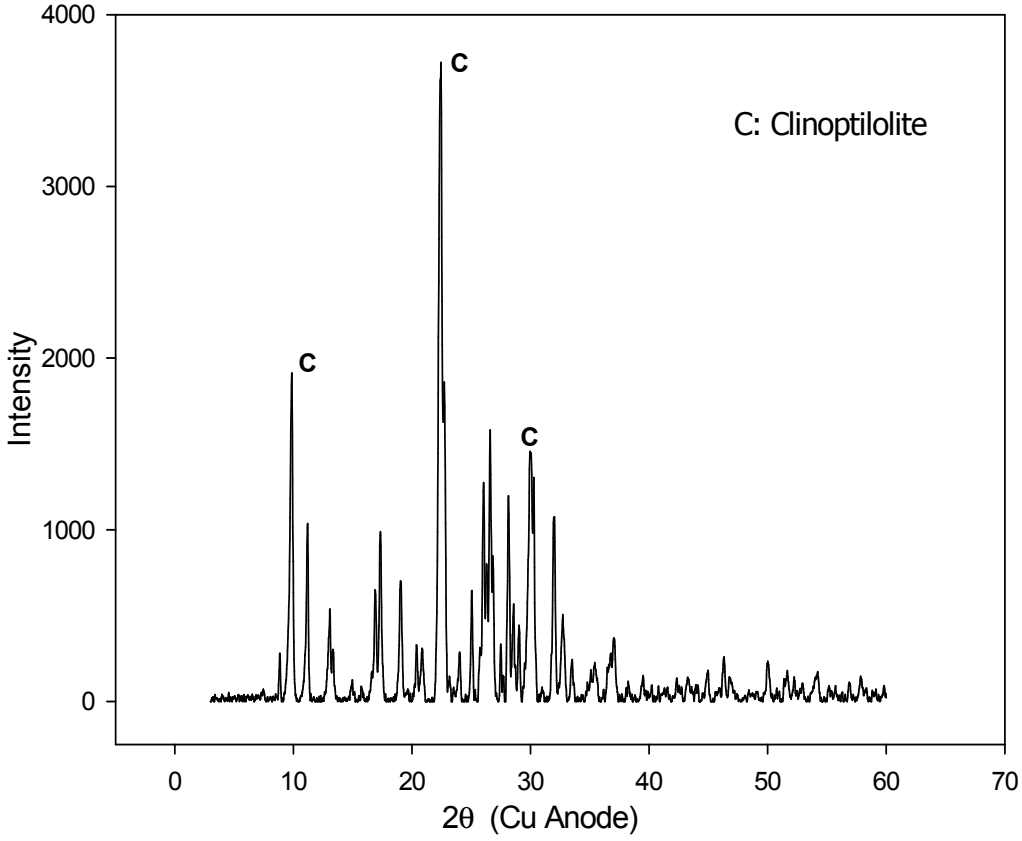


**Figure 4.1.** XRD analysis of $C_1$

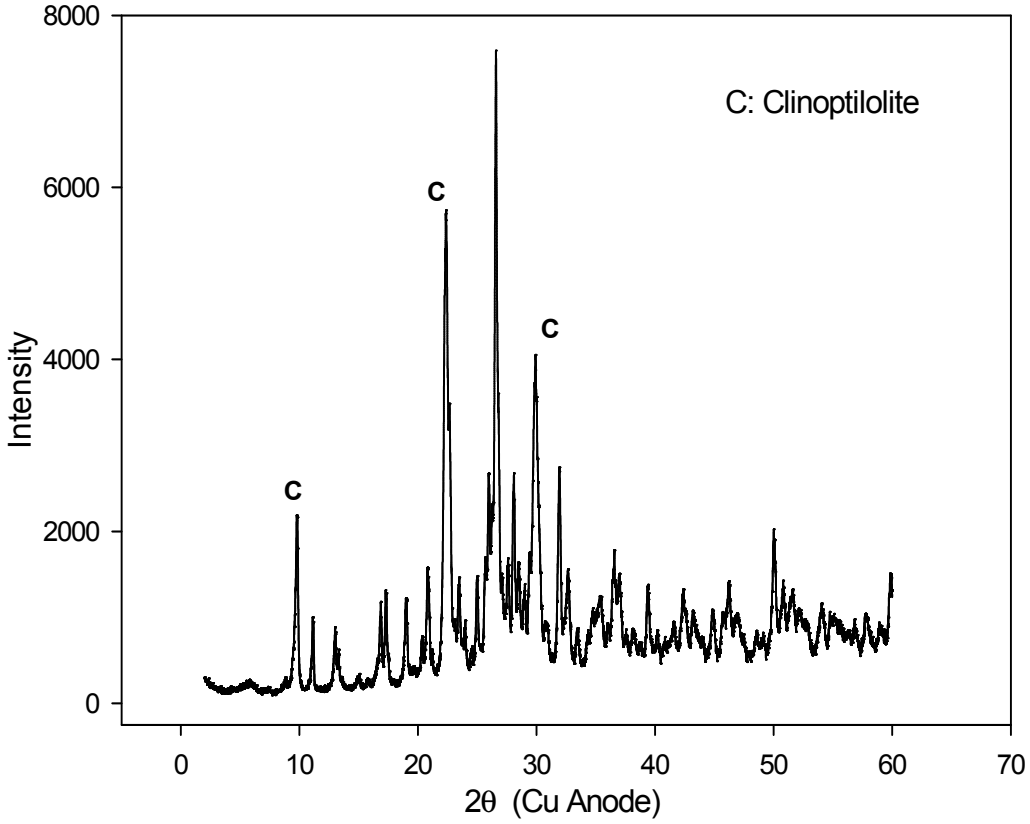


**Figure 4.2.** XRD analysis of $C_2$

Purity of the as received form of the first sample ($C_1$) was determined to be ≈80% with main impurities identified as quartz and biotite. However, even though the second sample ($C_2$) was from the same reserve, its purity was determined to be ≈50% with main impurities identified as quartz, illite and biotite.

The results of the chemical analyses of each clinoptilolite sample performed both by XRF and SEM/EDS are presented in Tables 4.1 and Table 4.2, respectively.

**Table 4.1.** Chemical analysis of as-received clinoptilolite samples performed with XRF (% wt/wt)

| Oxide | $C_1$ | $C_2$ |
|---|---|---|
| $SiO_2$ | 71.83 ± 0.13 | 72.76 ± 0.02 |
| $Al_2O_3$ | 11.68 ± 0.03 | 11.93 ± 0.09 |
| $Fe_2O_3$ | 1.15 ± 0.12 | 1.26 ± 0.00 |
| MgO | 1.25 ± 0.01 | 1.26 ± 0.04 |
| CaO | 3.39 ± 0.01 | 4.16 ± 0.01 |
| $Na_2O$ | 0.43 ± 0.01 | 0.10 ± 0.01 |
| $K_2O$ | 3.70 ± 0.03 | 3.13 ± 0.05 |
| MnO | 0.03 ± 0.00 | 0.03 ± 0.01 |
| $TiO_2$ | 0.07 ± 0.01 | 0.09 ± 0.01 |
| $H_2O$ | 2.50 ± 0.00 | 1.40 ± 0.00 |

**Table 4.2.** Chemical analysis of clinoptilolite samples performed with SEM/EDS (% wt/wt)

| Oxide | $C_1$ | $Na_1C_1$ | $Na_2C_1$ | $C_2$ | $Na_1C_2$ | $Na_2C_2$ |
|---|---|---|---|---|---|---|
| $SiO_2$ | 75.06 | 77.56 | 77.88 | 78.31 | 76.37 | 76.75 |
| $Al_2O_3$ | 11.43 | 14.47 | 12.44 | 11.44 | 12.68 | 12.15 |
| $Na_2O$ | 0.59 | 3.42 | 4.15 | 0.26 | 3.09 | 1.73 |
| $K_2O$ | 4.43 | 2.23 | 2.42 | 3.37 | 2.90 | 2.70 |
| MgO | 1.04 | 0.94 | 0.68 | 0.48 | 1.13 | 0.92 |
| CaO | 2.91 | 1.46 | 0.93 | 4.23 | 2.20 | 3.13 |
| $Fe_2O_3$ | 4.56 | 1.49 | 1.51 | 1.93 | 1.64 | 2.63 |

According to the XRF analysis, theoretical cation exchange capacity (TCEC) and Si/Al ratio were calculated and these values are presented in Table 4.3.

**Table 4.3.** Some significant chemical properties of clinoptilolite samples.

| Sample | TCEC (meq/g) | Si/Al (mol/mol) |
|---|---|---|
| $C_1$ | 2.75 | 5.22 |
| $C_2$ | 2.81 | 5.18 |

The original materials, $C_1$ and $C_2$ contain $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ as exchangeable cations; and $Mn^{2+}$ and $Ti^{2+}$ in trace amounts. Like other zeolite occurrences of

Western Anatolia, both Bigadiç clinoptilolite samples are poor in $Na^+$ (Çulfaz and Yağız, 2004).

Si/Al ratio typically ranges from 4 to 5.5, (Tsitsishvili et al., 1992, Çulfaz and Yağız, 2004), and Si/Al ratio of both *C1* and *C2* lie within this typical limit. Çulfaz and Yağız (2004) claimed that low-silica member clinoptilolites are enriched with $Ca^{2+}$, whereas high-silica clinoptilolites are enriched with $K^+$, $Na^+$ and $Mg^{2+}$. However, XRF analyses reveal that, samples from the Bigadiç reserve used in this study are high-silica member clinoptilolites and they are enriched not only with $K^+$ but also with $Ca^{2+}$. This finding is consistent with the information given in a recent study in which Bigadiç clinoptilolite is classified as a $Ca^{2+}$ rich clinoptilolite (Kurama et al., 2003).

SEM/EDS results indicate that conditioning results in a considerable improvement in the $Na^+$ content of each clinoptilolite sample and presumably in the cation exchange capacity of both materials. Correspondingly, the change in the distribution of exchangeable cation in chemical compositions with conditioning can be seen in Table 4.4.

**Table 4.4.** Distribution of the exchangeable cations in as-received and conditioned forms of clinoptilolite samples. (as % eq/eq)

| Exchangeable Cation | *C1* | *Na1C1* | *Na2C1* | *C2* | *Na1C2* | *Na2C2* |
|---|---|---|---|---|---|---|
| **$Na^+$** | 12.5 | 52.8 | 66.0 | 6.7 | 44.0 | 30.3 |
| **$K^+$** | 35.9 | 13.2 | 8.6 | 64.1 | 18.3 | 32.0 |
| **$Ca^{2+}$** | 21.6 | 14.2 | 10.6 | 12.2 | 15.8 | 15.8 |
| **$Mg^{2+}$** | 30.0 | 19.8 | 14.8 | 17.0 | 21.9 | 22.0 |

In batch mode conditioning, apart from $Na^+$, percent by weight contribution of all of the cations that are accepted as exchangeable decrease (Table 4.2). $Mg^{2+}$ content of the material decreases following conditioning and this decrease is more prominent with increasing contact time (from one day to seven days) because as duration of

conditioning increases, more $Na^+$ ions may overcome pore diffusion resistance, reaches the positions where $Mg^{2+}$ ions are located and exchange with $Mg^{2+}$ ions. $K^+$ content also decreases to the half of its initial value in batch mode conditioning and any considerable change is not observed with increasing contact time as seen in continuous mode conditioning (Table 4.2). When $Ca^{2+}$ content is examined, it decreases further with increasing contact time as it is observed in the continuous mode conditioning.

In column conditioning, $Mg^{2+}$ content of the samples increases and this increase is considered to be a result of replacement of $Na^+$ ions with $K^+$ and $Ca^{2+}$ rather than $Mg^{2+}$ ions and presence of a negligible amount of $Mg^{2+}$ ions in readily soluble impurities associated with clinoptilolite (Table 4.2). The reason for the higher selectivity of clinoptilolite for $Mg^{2+}$ rather than $Na^+$ may be attributed to the pore diffusion resistance, to the location of $Mg^{2+}$ ions in the pores of the clinoptilolite and hydration energy of $Mg^{2+}$ (Panayotova and Velikov, 2002). In continuous mode conditioning, $Na^+$ ions are considered unable to overcome pore diffusion resistance because of the limited contact time and as a result can not replace $Mg^{2+}$ ions (Semmens and Martin, 1988). Despite $Mg^{2+}$ amount within the clinoptilolite structure is assumed to have remained constant nonetheless the increase in its percent by weight contribution to the chemical composition may be mainly attributed to $Ca^{2+}$ and $K^+$ release along with dissolution of $Al^{3+}$ and $Si^{4+}$ during conditioning. It is also derived from SEM/EDS analyses that as the contact time between NaCl solution and clinoptilolite samples increases (or in other words, volumetric flow rate decreases), $Na^+$ and $Mg^{2+}$ content of the samples also increases. However, $Ca^{2+}$ content decreases.

The increase in $Na^+$ content is expected since as contact time increases, $Na^+$ ions have a greater chance to occupy the exchanging sites of the material. It can also be concluded from the results that degree of $Na^+$ replacement with $K^+$ ions is not significantly related to contact time (or volumetric flow rate) when all other operational parameters are kept constant. However, degree of $Na^+$ replacement with $Ca^{2+}$ strongly depends on volumetric flow rate (contact time). As volumetric flow

rate decreases, $Ca^{2+}$ content within the clinoptilolite structure also decreases during conditioning since $Ca^{2+}$ ions are considered to locate at most favorable sites for exchange and have the lowest hydration energy among the exchangeable cations except for $Na^{+}$.

It can be derived from the results of both modes of conditioning (batch or continuous) that an increase in contact time is ineffective in displacement of $K^{+}$ from the clinoptilolite structure. The reason for this outcome may be attributed to the assumption that release of $K^{+}$ ions, which are associated with impurities and exchange with heavy metal cations and exist within the readily soluble impurities, occurs immediately when the material comes in contact with NaCl solution. Achieving a complete exchange of cations, especially $K^{+}$, with $Na^{+}$ may not be possible in most cases. This is also reported in literature by several researchers working with clinoptilolites of different origins (Faghihian et al., 1999, Langella et al., 2000, Tarasevich et al., 2002). This behavior is explained with the location occupied by $K^{+}$. It is proposed that $K^{+}$ is located at a specific site which is situated in an eigth-membered ring and has the highest coordination among all the cation sites in the unit cell (Jama and Yücel, 1990). This poor ion-exchange ability of $K^{+}$ might be attributed to the strong bonding at this site (Çulfaz and Yağız, 2004).

Micrographs of all clinoptilolite samples obtained from SEM/EDS analyses are given in Figure 4.3. It can bed derived from the figure that that conditioning removed a substantial fraction of the fine particles originally present in $C_1$ and $Na_1C_1$. Additionally, in micrographs of conditioned samples (Figure 4.3-B, C, E and F) well defined crystals that could be related to clinoptilolite structure and could not be seen in micrographs of as received forms (Figure 4.3-A and D) are also observed.

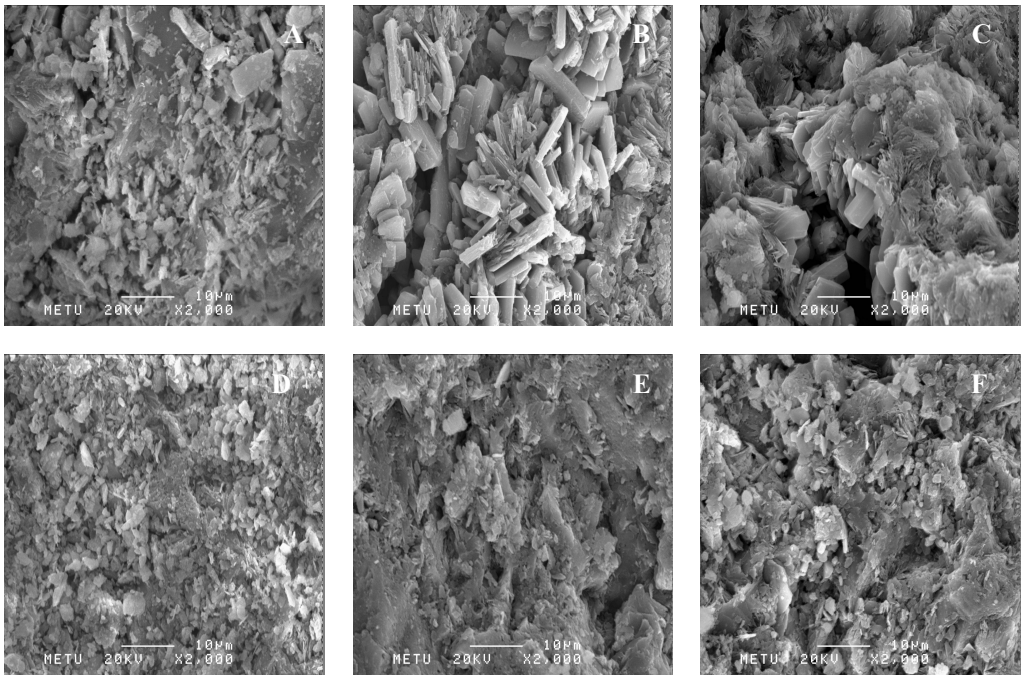


**Figure 4.3.** Micrographs of the clinoptilolite samples. A) $C_1$, B) $Na_1C_1$, C) $Na_2C_1$, D) $C_2$, E) $Na_1C_2$, F) $Na_2C_2$

The physical properties of $C_1$ and $C_2$ along with the data given in the literature are shown in Table 4.5.

**Table 4.5.** Physical properties of $C_1$, $Na_1C_1$ and clinoptilolite samples of different origins

| Clinoptilolite origin | Physical Property | | |
|---|---|---|---|
| | Specific surface area ($m^2/g$) | Average pore diameter Å | Density (g/L) |
| $C_1$ | 13.4 | 17.0 | 2.242 |
| $Na_1C_1$ | 11.8 | 17.2 | - |
| $C_2$ | 11.7 | 17.0 | 2.244 |
| $Na_1C_2$ | 11.9 | 17.0 | - |
| U.S.A. (1) | 6.4 | - | - |
| Ukraine (2) | 13.1 | 131.8 | - |
| Croatia (3) | 12.0 | 11.8 | 1.812 |
| Cuba (4) | 27.0 | 10.1 | - |
| Greece (5) | 14.5 | 195.0 | 2.330 |

(1) Tillman et al. (2004), (2) Sprynskyy et al. (2005), (3) Trgo and Peric (2003), (4) Cabrera et al. (2005), (5) Athanasiadis and Helmreich (2005)

It is apparent from Table 4.5 that specific surface area, average pore diameter and density of $C_1$, $C_2$ and their conditioned forms are comparable with the given data in the literature. Specific surface area of $C_1$ is higher than that of $Na_1C_1$ due to the removal of fine particles during conditioning. However, effect of conditioning on specific surface area of $C_1$ seems to be negligible.

## 4.2. BATCH STUDIES

### 4.2.1. Preliminary Studies

#### *Effect of Initial pH*

pH has an obvious impact on metal removal by clinoptilolite since it can influence both the character of the exchanging ions and the chemical behaviour of the clinoptilolite itself (Ouki and Kavannagh, 1999). At lower pH, the metal ions have to compete with hydrogen ions for the same exchange sites (Godelitsas and Armbruster, 2003, Cabrera et al., 2005). Moreover, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium carbonate, unaltered glass, etc., are perhaps removed by $H^+$ ions at lower pH (Haggerty and Bowman, 1994). Wingenfelder et al. (2005) carried out XRD analysis of Slovakian clinoptilolite after acid treatment and XRD spectra exhibited that, feldspar and illite peaks determined to be the main impurities within the material, were considerably reduced.

Optimum pH experiments were carried out as the first step of the study in order to determine an initial solution pH that is low enough to avoid the hydrolysis of heavy metals and high enough to minimize proton exchange and hydrolysis of clinoptilolite as a result of protonation. Results of the optimum pH experiments for $Cu^{2+}$ and $Ni^{2+}$ are presented in Figure 4.4.

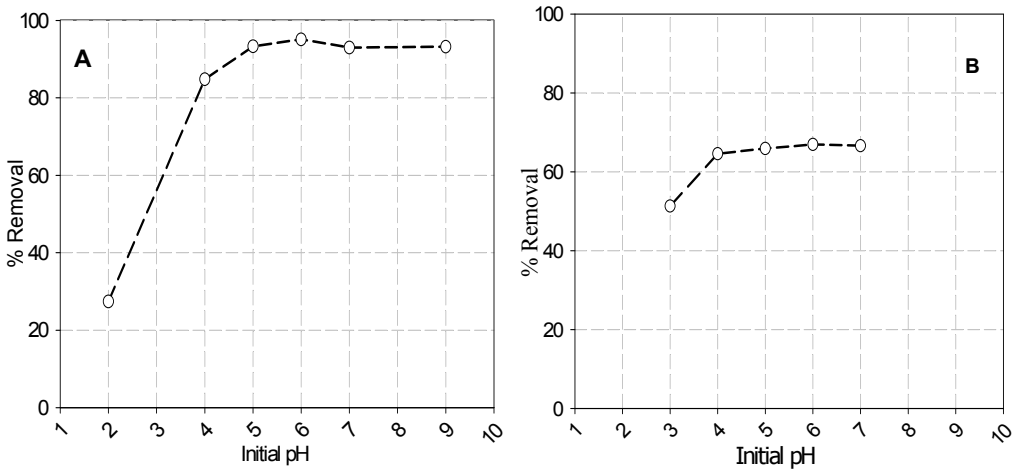


**Figure 4.4.** Effect of initial solution pH on A) $Cu^{2+}$ removal B) $Ni^{2+}$ removal efficiency of $C_1$ samples at 48 hours.

The reason for obtaining the lowest removal efficiency in the reactors with initial solution pH of 2 (Figure 4.4-A) may be attributed not only to the competition of the $H^+$ with $Cu^{2+}$ ions for the active sites of Bigadiç clinoptilolite (Inglezakis et al., 2001), but also to the increase in electrostatic repulsion between the metal ions and the surface (Cabrera et al., 2005). Consequently, low solution pH is found to inhibit the sorption of $Cu^{2+}$ ions on Bigadiç clinoptilolite. Similarly, Carland and Aplan (1988) found that $Cu^{2+}$ uptake by a clinoptilolite containing tuff significantly decreased at pH values below 4 and in the literature optimum pH for $Cu^{2+}$ removal is given as 5 by several researchers (Ouki et al., 1994, Panayotova, 2001).

Despite reactors with initial solution pHs of 5, 6, 7 and 9 have almost same $Cu^{2+}$ removal efficiencies, initial solution pH of 5 is selected as the optimum initial pH for $Cu^{2+}$-clinoptilolite system due to the fact that $Cu^{2+}$ has quite a low solubility product constant ($2.20\times10^{-20}$) (Sun et al., 2005). Also, high removal efficiencies obtained for initial solution pHs of 6, 7 and 9 may be attributed to the possible formation of copper-hydroxyl species and accordingly precipitation. The meso- and macro-pores as well as the irregular surface of the material could be considered as an appropriate environment for surface precipitation. In the literature it is stated that formation of

copper-hydroxyl species result in surface precipitation on the clinoptilolite particles and this situation may be considered to have a negative impact on $Cu^{2+}$ removal efficiency of clinoptilolite (Inglezakis et al., 2003, Ouki and Kavannagh, 1999). This can be explained by the reduction in the available active sites of the grains for relatively higher initial heavy metal concentrations. In optimum pH experiments for $Cu^{2+}$, initial concentration was kept at 30 mg/L and this concentration level is considered to make the decreasing effect of surface precipitation of copper-hydroxyl complexes on removal efficiency negligible.

A similar trend is observed in optimum initial pH determination experiments for $Ni^{2+}$ when compared to those of $Cu^{2+}$. The lowest removal efficiency is observed at initial pH of 3 which can be explained by the $Ni^{2+}$-$H^{+}$ competition, as discussed above. Hence, pH 4 is selected as the optimum pH for $Ni^{2+}$ removal with clinoptilolite, which is also parallel with other researchers' findings (Ouki and Kavannagh, 1999, Ali and El-Bisthawi, 1997).

***Determination of Equilibration Time***

During optimum pH experiments, it was observed that a considerable removal efficiency difference exists between 24 and 48 hours of contact times. Consequently, it is concluded from the results of the optimum pH experiments that 48 hours may not be enough for the equilibration of the interaction between heavy metal cations and clinoptilolite samples (Figure B.1 in Appendix B). As a result, an additional study aiming the determination of the equilibration period for the system of concern was required to be carried out for an extended contact time that is, 72 hours.

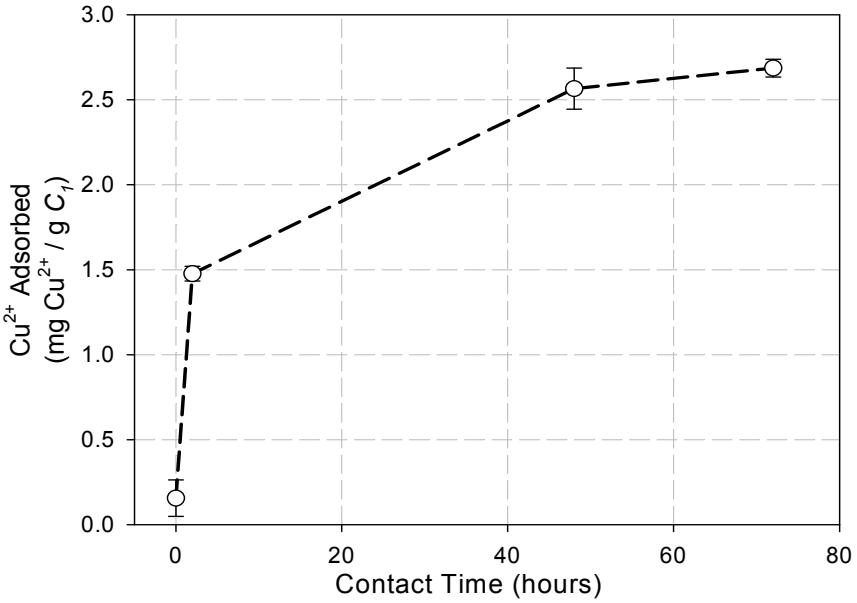


**Figure 4.5.** $Cu^{2+}$ uptake by $C_1$ with time at initial pH of 5.

$Cu^{2+}$ uptake versus contact time is presented in Figure 4.5. It is evident from the figure that only a minor increase exists between the $Cu^{2+}$ uptake at 48 and 72 hours of contact time. As a result, 48 hours of contact time is selected as the equilibration period for heavy metal solution-clinoptilolite interaction not only due to the equilibration period experiment but also according to the results of the optimum pH experiments which indicate that 48 hours of contact time may not be adequate for equilibration of the system (Figure B.1). Çulfaz and Yağız (2004) also found 48 hours to be sufficient for reaching equilibrium in heavy metal solution-Bigadiç clinoptilolite interaction.

***Effect of Conditioning***

Conditioning of zeolite samples was found to improve their effective exchange capacity and performance in ion exchange applications (Ouki et al., 1994, Semmens and Martin, 1988, Bremmer and Schultze, 1995, Gradev et al., 1998). Therefore, conditioning of Bigadiç clinoptilolite aiming to remove certain cations ($K^{+}$, $Ca^{2+}$ and

$Mg^{2+}$) from the structure of the clinoptilolite and to locate more easily removable $Na^+$ ions were carried out and effect of conditioning and its duration on the performance of clinoptilolite samples in $Cu^{2+}$ removal was investigated. Table 4.6 summarizes the effect of conditioning on $Cu^{2+}$ removal and percent contribution of each exchangeable cation to the total release amount.

**Table 4.6.** Effect of conditioning on $Cu^{2+}$ removal and percent contribution of each exchangeable cation to total release amount (% eq/eq)

| Sample | $Cu^{2+}$ Removal, % | Exchangeable cation | | | |
|---|---|---|---|---|---|
| | | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
| $C_1$ | 36 | 21.3 | 15.5 | 31.0 | 32.2 |
| $Na_1C_1$ | 70 | 96.4 | 0.7 | 0.7 | 2.2 |
| $Na_2C_1$ | 74 | 97.7 | 0.6 | 0.5 | 1.2 |

It is clear from the table that $C_1$ can remove only 36 % of 200 mg/L $Cu^{2+}$ and only 21.3% of the total amount of the exchangeable cations released from the clinoptilolite structure is $Na^+$. However, conditioning is found to improve $Cu^{2+}$ removal efficiency for $Na_1C_1$ and $Na_2C_1$ by more than two fold. The improvement in the removal efficiency via conditioning is attributed to the increase in the easy removable $Na^+$ ions content of the clinoptilolite samples (Table 4.6).

The significant increase in the $Na^+$ content in the total amount of the exchangeable cations released from $Na_1C_1$ and $Na_2C_1$ indicate effectiveness of the conditioning. This is also evident from the decrease in $K^+$, $Mg^{2+}$ and $Ca^{2+}$ content of $Na_1C_1$ and $Na_2C_1$ when compared to $C_1$. The reason for this enormous decrease may be attributed to the replacement of $Na^+$ with these cations during conditioning. It is supposed that this phenomenon takes place for exchangeable cations that are located at the accessible sites of $C_1$ samples as discussed earlier.

When the results of the SEM/EDS analyses are examined (Table 4.2), conditioning process is found to be ineffective in displacement of all exchangeable cations and the reason for this situation may be attributed to the location of these cations that are

supposed to be inaccessible for ion exchange. Semmens and Martin (1988) stated that extended exposure of clinoptilolite samples to concentrated $Na^+$ solutions has been found to be ineffective in displacing all the $Ca^{2+}$ and $K^+$ ions from the structure. In addition to the location of these cations, low mobility and strong bonding forces of these cations within the structure of the material are other inhibiting factors affecting their displacement by conditioning procedures (Inglezakis et al., 2001, Klieve and Semmens, 1980).

Finally, since there is a negligible difference in the removal efficiencies and in the $Na^+$ content within the total amount of the released exchangeable cations for $Na_1C_1$ and $Na_2C_1$, extension of duration of conditioning procedure from 1 day to 7 days is determined to be unnecessary from the feasibility point of view.

### 4.2.2. Equilibrium Studies

Following preliminary experiments, equilibrium studies were carried out with the optimum experimental conditions for $Cu^{2+}$ and $Ni^{2+}$ for both $C_1$ and $Na_1C_1$. Figure 4.6 gives the metal uptake as a function of equilibrium concentration for $Cu^{2+}$-$C_1$, $Cu^{2+}$-$Na_1C_1$, $Ni^{2+}$-$C_1$ and $Ni^{2+}$-$Na_1C_1$ systems respectively. It is clear from Figure 4.6 that as the equilibrium concentration of heavy metal cations increases, amount of metal sorbed per gram of clinoptilolite increases due to the fact that higher the metal concentration in solution is, higher the solute concentration gradient; and this provides the necessary driving force for metal ions to replace cations on the surface of the internal micropores of clinoptilolite within the given contact time (Du et al., 2005, Abadzic and Ryan, 2001). However, this increasing trend is valid up to a point at which maximum capacity of the clinoptilolite samples for the heavy metal cation of concern is achieved.

When the change in the amount of $Cu^{2+}$ sorbed per gram of both $C_1$ and $Na_1C_1$ is examined (Figures 4.6-A, 4.6-B and Table C.1 in Appendix C), a considerable decrease is evident in the amount of $Cu^{2+}$ sorbed per gram of clinoptilolite for the

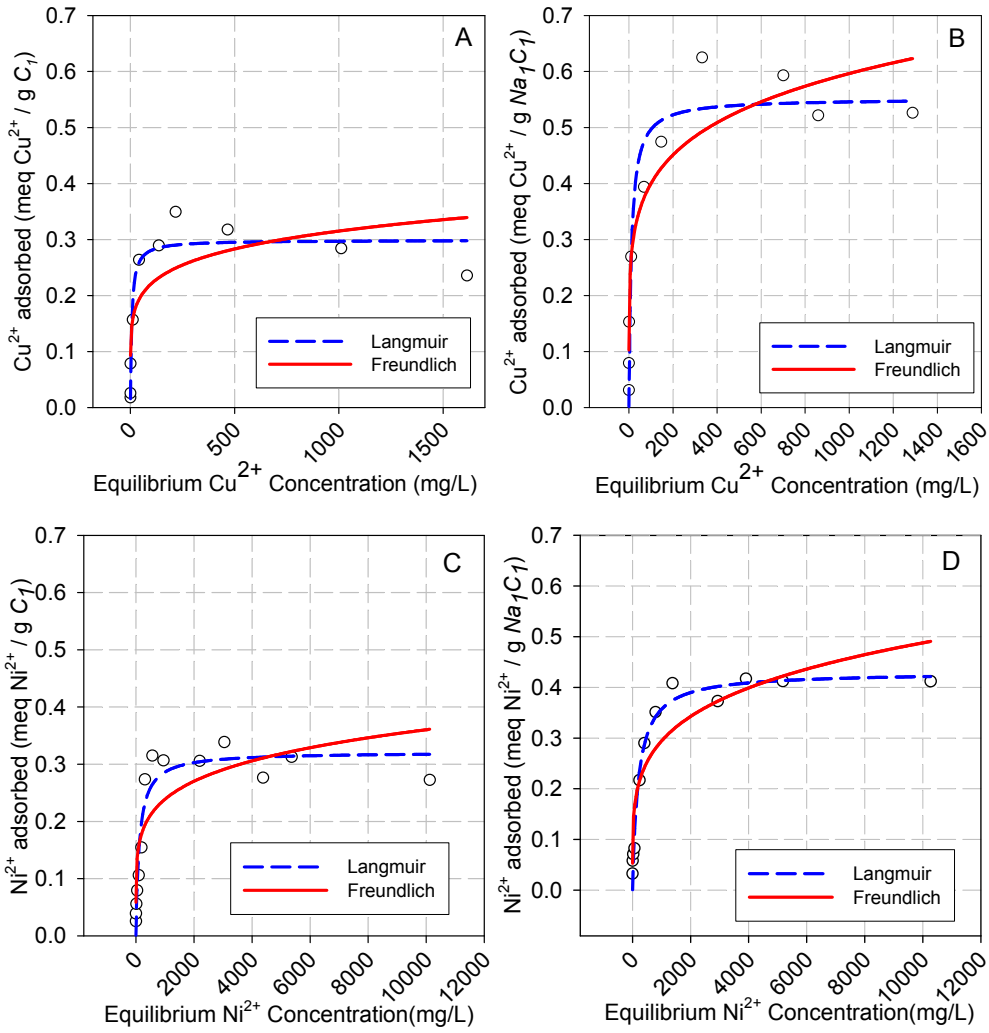


**Figure 4.6.** Metal uptake with respect to various equilibrium metal concentrations. A. Amount of $Cu^{2+}$ sorbed per gram $C_1$, B. Amount of $Cu^{2+}$ sorbed per gram $Na_1C_1$, C. Amount of $Ni^{2+}$ sorbed per gram $C_1$, D. Amount of $Ni^{2+}$ sorbed per gram $Na_1C_1$.

highest studied initial $Cu^{2+}$ concentrations. This situation is attributed to the formation of a considerable amount of inner-sphere copper-hydroxyl complexes as well as precipitation of soluble and insoluble neutral complexes on the active sites of clinoptilolite surface (Sparks, 1999, Barthomeuf, 1996, Baeyens and Bradbury, 1997, Manceau et al., 1999, Stipp et al., 1992, Smith, 1998, Trgo and Peric, 2003). These complexes are suspected to have a negative impact on the further uptake of $Cu^{2+}$ ions

by preventing free $Cu^{2+}$ and copper-hydroxyl species from interaction (either adsorption or ion exchange) both with internal and external surface sites of clinoptilolite.

Experimental data obtained from the equilibrium experiments are fitted to conventional isotherm models, namely Freundlich and Langmuir (Figure 4.6). Langmuir and Freundlich models are widely used because they are convenient to describe experimental results in a wide range of concentrations (Altın et al., 1998). In practice, in describing equilibrium experimental results, both linear and non-linear forms of Langmuir and Freundlich equations can be used. However, it was found that linearizion of particularly Langmuir does not provide satisfactory fit to experimental data (Peric et al., 2004, Kumar and Sivanesan, 2005). For that reason, in this study, the suitability of these models to the experimental data was investigated using non-linear method via SigmaPlot 8.0 software (Equations 3.1 and 3.2). In Table 4.7 results of the non-linear method of both Langmuir and Freundlich models are presented.

**Table 4.7.** Results of non-linear regression of Langmuir and Freundlich models for each equilibrium study.

| Metal | Sample | $R^2$ | | $q_{max}$ (meq/g) | K | $K_F$ | n |
|---|---|---|---|---|---|---|---|
| | | Langmuir | Freundlich | | | | |
| $Cu^{2+}$ | $C_1$ | 0.98 | 0.80 | 0.31 | 0.15 | 0.11 | 6.49 |
| | $Na_1C_1$ | 0.91 | 0.90 | 0.55 | 0.09 | 0.18 | 5.76 |
| $Ni^{2+}$ | $C_1$ | 0.92 | 0.76 | 0.32 | 0.01 | 0.07 | 5.59 |
| | $Na_1C_1$ | 0.98 | 0.83 | 0.43 | 0.01 | 0.06 | 4.55 |

It is obvious from the correlation factors that Langmuir fits better to the experimental data than Freundlich does for all equilibrium studies except for $Cu^{2+}$-$Na_1C_1$ system and this seems to agree with Minura et al's. (1992) argument that Langmuir model is valid not only in the cases when cations in liquid and clinoptilolite phase are singly charged, but also when they have equal charges and compete with each other. The main reason for still inadequate consistence of the Langmuir model with

experimental data is that Langmuir theory assumes homogeneity of adsorption sites, whereas like most of natural adsorbents, clinoptilolite exhibits heterogeneity of adsorption sites (Polzer et al., 1992, Abusafa and Yücel, 2002). Different shape of surface crystal faces and their imperfections, such as corners, broken bond and edge sites, as well as amphoteric nature of hydroxyl surface groups [= (Al/Si)-OH], leads to formation of heterogeneous adsorption sites with different sorption affinities on the surface of clinoptilolite grains and accordingly, results in nonhomogeneous distribution of different heavy metal species being adsorbed and/or exchanged (Baeyens and Bradbury, 1997, Charistos et al., 2001, Trgo and Peric, 2003).

Maximum achievable capacities for both metals are calculated from the equilibrium amount of $Cu^{2+}$ and $Ni^{2+}$ bound per gram of $C_1$ and $Na_1C_1$ according to the Langmuir isotherm (Trgo and Peric, 2003). When the maximum achievable capacities are examined, it can be concluded that, conditioning has a profound effect on both $Cu^{2+}$ and $Ni^{2+}$ removal. However, when the maximum capacities are compared to the TCEC, that is 2.75 meq/g, it is clear that at most 20% of the TCEC can be used up under the studied conditions (for $Cu^{2+}$- $Na_1C_1$ system). TCEC is defined as the number of exchangeable cations, in equivalents, present in a specified amount of the material, and is a constant used for characterizing ion exchangers. However, not all of these exchangeable cations are always available for ion exchange. In most cases, some of the incoming ions are excluded by clinoptilolite, because they are too large to fit into the channels of the aluminosilicate framework (Ouki and Kavannagh, 1999). Furthermore, some of the exchangeable cations are components of impurities such as feldspar, biotite, illite, quartz and salts or they are either located at inaccessible sites of the material structure or strictly bound to the clinoptilolite structure (Inglezakis et al., 2002).

A recent study carried out with the same clinoptilolite samples used in this study confirms the above statement regarding metal ions being too large for the channels of clinoptilolite. Moralı et al. (2005) determined the maximum capacity for $Pb^{2+}$ as 1.00 meq/g with $Na_1C_1$. The reason for this superior capacity may be attributed to the large ionic radius (means low charge density and accordingly small hydrated radii) of

$Pb^2$ (1.21 Å), which is higher than that of both $Cu^{2+}$ and $Ni^{2+}$ (0.80 Å and 0.69 Å, respectively) (Panayotova and Velikov, 2002). In other words, $Cu^{2+}$ and $Ni^{2+}$ ions and their hydroxyl complexes may be assumed unable to penetrate into the micropores of clinoptilolite samples that have smaller channel diameters than their hydrated radii. According to XRD analysis, $C_1$ are determined to contain quartz and biotite as main impurities which are known to have considerable amount of exchangeable cations content in their structure and are proven to have relatively very low cation exchange capacities, i.e. 0.02-0.035 meq/g for quartz (Inglezakis, 2005). Additionally, SEM/EDS analysis revealed that even after conditioning, clinoptilolite contains a considerable amount of $Ca^{2+}$, $K^{+}$ and $Mg^{2+}$ which could be located at inaccessible sites of the material.

It is apparent from Table 4.7 that maximum capacities obtained with $C_1$ for both $Cu^{2+}$ and $Ni^{2+}$ are almost equal to each other and the reason for this situation can be attributed to the almost same hydration energy of $Cu^{2+}$ and $Ni^{2+}$, that are -2100 kj/mole and -2105 kj/mole, respectively (Panayotova and Velikov, 2002). It is stated in the literature that ion-exchange, that is considered to be one of the predominant mechanisms within the heavy metal-clinoptilolite interaction, depends particularly on the hydration energy of the dissolved ions and the optimum conditions for successful metal-loading should be related to exchange of cations of low valance and low hydration energy (Godelitsas and Armbruster, 2003).

Presence of surface dust on the as received samples is considered to clog part of the pore openings, in other words surface dust is considered to be primarily responsible particularly for the partial accessibility of active surface sites in the internal surface (pores) sites of clinoptilolite (Inglezakis et al., 1999; 2001, Athanasiadis and Helmreich, 2005). Micrographs of clinoptilolite samples revealed that (Figure 4.3) removal of a substantial portion of these fine particles was achieved during conditioning with NaCl and further washing with deionized water. With the removal of surface dust, active sites on clinoptilolite surface are expected to become more accessible both for free $Cu^{2+}$ and $Ni^{2+}$ ions and for their hydroxyl species.

In spite of the fact that $C_1$ has approximately equal affinity for both $Cu^{2+}$ and $Ni^{2+}$, conditioning results in a greater enhancement in $Cu^{2+}$ uptake than in $Ni^{2+}$ uptake (Figure 4.6). The difference between the $Cu^{2+}$ and $Ni^{2+}$ uptake using $Na_1C_1$ is considered as a reasonable outcome due to the fact that adsorption and/or ion exchange of charged hydroxyl species of metal ions is another significant mechanism prevailing within the system particularly on the sites in the pores (Peric et al., 2004). The formation of hydroxyl-complexes of metal ions is a function of solution pH and initial metal ion concentration. It can affect the mechanism of metal ions binding by changing it from ion exchange to adsorption of monovalent hydroxyspecies (Barthomeuf, 1996, Smith, 1998, Godelitsas and Armburster, 2003). As initial metal concentration increases, more free and charged hydroxyl complexes are forced to interact with the surface of the internal micropores. Doula and Ioannou (2003) states that metal-hydroxyl species may adsorb on clinoptilolite surface i) only weakly or not at all and compete with reactions forming surface complexes (involving ion exchange) and adsorption is decreased compared to complex free system or ii) strongly, thereby enhancing removal of heavy metals.

As described earlier, surface dust present in $C_1$ is substantially removed during conditioning (Figure 4.3) and subsequently, an increase in the number of available sites is expected with an enhancement in accessibility of metal ions to the pores. Additionally, for the pH levels and the initial heavy metals concentrations studied in equilibrium experiments, $Cu^{2+}$ is known to be more prone to form hydroxyl complexes than $Ni^{2+}$ ions. Consequently, the reason for the higher capacity of $Na_1C_1$ for $Cu^{2+}$ ions when compared to $Ni^{2+}$ ions may be attributed to the formation of copper-hydroxyl complexes and strong adsorption of these species on the increasing number of available active sites particularly on the internal micropores.

Possible mechanisms causing pH change during equilibrium studies

In a heavy metal solution-clinoptilolite interaction there are several mechanisms governing the pH change. These mechanisms can be classified as follows;

i) $H^+$ in the solution exchanges with $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ on outer surface or inner surface of clinoptilolite samples in acid to neutral pH range (Doula et al., 2002, Ersoy and Çelik, 2002, Rozic et al., 2002, Trgo and Peric, 2003).

→ *Effect on solution pH*: Solution pH increases

→ *Effect on metal removal*: $H^+$ competes with heavy metal cations and decreases metal uptake

ii) $H^+$ in surface hydroxyl groups of Si-OH and Al-OH behaves as an exchangeable cation present like in the case of clay minerals at acidic and neutral pH range (Doula et al., 2002, Ersoy and Çelik, 2002, Trgo and Peric, 2003).

→ *Effect on solution pH*: Solution pH decreases

iii) Protonation of neutral and negative surface hydroxyl groups by $H^+$ at acidic and neutral pH range (Doula et al, 2002, Ersoy and Çelik, 2002).

$$\equiv Al\text{-}OH + H^+ \leftrightarrow \equiv Al\text{-}OH^+_2 \qquad \text{Equation (4.1)}$$

$$\equiv Si\text{-}O^- + H^+ \leftrightarrow \equiv Si\text{-}OH \qquad \text{Equation (4.2)}$$

→ *Effect on solution pH*: Solution pH increases

iv) At relatively high pH values $OH^-$ ions may react with clinoptilolite surface;

$$\equiv Si\text{-}OH + OH^- \leftrightarrow S\text{-}O^- + H_2O \qquad \text{Equation (4.3)}$$

→ *Effect on solution pH*: Solution pH decreases

→ *Effect on metal removal*: Increases negative charge on the clinoptilolite framework, which results in an enhancement in electrostatic sorption of heavy metal cations. (Doula et al., 2002, Ersoy and Çelik, 2002).

v) Formation of metal-hydroxyl complexes (hydrolysis of metal ions).

$$\equiv Cu^{2+} + H_2O \leftrightarrow CuOH^{+} + H^{+} \qquad \text{Equation (4.4)}$$

$$\equiv CuOH^{+} + H_2O \leftrightarrow Cu(OH)_2 + H^{+} \qquad \text{Equation (4.5)}$$

→ *Effect on solution pH*: Solution pH decreases

→ *Effect on metal removal*: Increases metal uptake up to a level due to the formation of charged metal hydroxyl species and adsorption/ion exchange of these species on the active sites of clinoptilolite surface (Equation 4.4). However with the formation of neutral metal-hydroxyl species metal uptake decreases due not only to the clogging of clinoptilolite pores via surface precipitation but also to the loss of electrostatic attraction (Equation 4.5).

Figure 4.7 presents the variation in the equilibrium pH values with respect to initial metal concentration in each equilibrium study. In $Cu^{2+}$ equilibrium studies equilibrium pH values are greater than the initially adjusted pH values and this increase exhibits a descending trend with increasing initial $Cu^{2+}$ concentration due to the limited competition between $H^{+}$ and $Cu^{2+}$ with increasing concentration (Figure 4.7-A and B). However, equilibrium pH values observed in reactors with an initial $Cu^{2+}$ concentration greater than 600 mg/L are smaller than the initial pH value and the reason for that may be attributed to the formation of soluble and insoluble $Cu^{2+}$ complexes because of low solubility of $Cu^{2+}$ and precipitation of these complexes on the clinoptilolite surface. Release of $H^{+}$ ions from clinoptilolite structure with increasing heavy metal concentration as products of inner-sphere complexation may also be given as another reason for decreasing equilibrium solution pH (Doula et al., 2002). As initial $Cu^{2+}$ concentration increases, formation of charged $Cu^{2+}$ hydroxyl

species, in other words hydrolysis of $Cu^{2+}$ becomes predominant in the system and this may be considered to suppress the mechanisms causing the increase in the solution pH ($H^+$ exchange and protonation) in these concentration ranges. Furthermore, as discussed earlier, for the highest studied initial $Cu^{2+}$ concentrations, formation of copper-hydroxyl species is considered as the predominant mechanism which resulted in a decrease not only in the solution pH via production of $H^+$ ions but also in the uptake capacity.

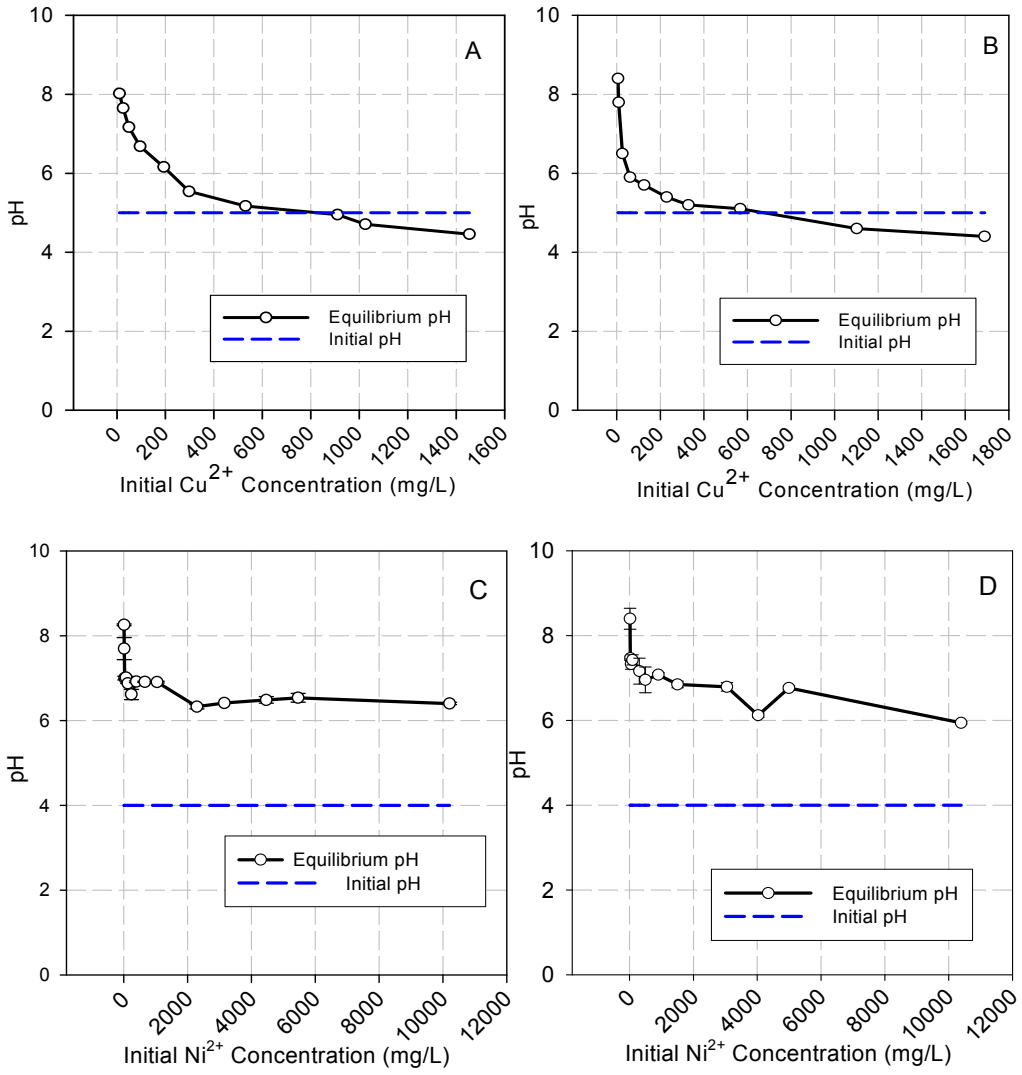


**Figure 4.7.** Equilibrium pH change with respect to various initial metal concentrations. A) $Cu^{2+}$-$C_1$, B) $Cu^{2+}$-$Na_1C_1$, C) $Ni^{2+}$-$C_1$, D) $Ni^{2+}$-$Na_1C_1$.

For $Ni^{2+}$ equilibrium studies, equilibrium solution pH values (Figure 4.7-C and D) in the reactors are higher than the initial solution pH (pH 4) as observed in $Cu^{2+}$ equilibrium studies and the increase in the solution pH decreases with increasing concentration. Equilibrium solution pH becomes steady at around 6.5 for the reactors with initial $Ni^{2+}$ concentration greater than 2000 mg/L. However, different from $Cu^{2+}$ equilibrium studies, equilibrium solution pH never decreases below the initially adjusted solution pH. The prevailing mechanisms governing the pH change in $Ni^{2+}$ equilibrium studies are supposed to be similar with $Cu^{2+}$ except for the unlikely formation of neutral $Ni^{2+}$-hydroxyl species, presence of which is responsible for clogging of the pores within the clinoptilolite structure via precipitation and accordingly responsible for the decrease in the metal uptake as observed in the $Cu^{2+}$ equilibrium studies.

Possible mechanisms involved in metal solution-Bigadiç clinoptilolite interaction

Use of clinoptilolite particles for heavy metal removal is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface (Altın et al., 1998). Ion-exchange, adsorption, surface precipitation and detachment of framework cations of clinoptilolite (dissolution) can be listed as the main mechanisms prevailing in a heavy metal solution-clinoptilolite interaction (Trgo and Peric, 2003).

Investigation of the prevailing mechanisms in a heavy metal solution-clinoptilolite interaction was one of the main objectives of this study. For this purpose, exchangeable cations released from the clinoptilolite structure were analyzed in samples taken from the reactors at the beginning of the equilibrium studies as well as at the end of 48 hours.

Concentrations of exchangeable cations in aqueous phase in $Cu^{2+}$-$C_1$, $Cu^{2+}$-$Na_1C_1$, $Ni^{2+}$-$C_1$ and $Ni^{2+}$-$Na_1C_1$ systems are presented in Figure 4.8. For ease of discussion on the prevailing mechanisms in the overall process each figure in Figure 4.8 is

divided into three sections with respect to initial heavy metal concentrations and these sections are code-named as given in Table 4.8. In sections coded with capital A, C, D and capital F, it is typical that total amount of exchangeable cations release is greater than amount of metal uptake. However, in sections coded with capital B and E the situation is completely different, in other words, amount of metal uptake is greater than the total amount of exchangeable cations release.

**Table 4.8**. Abbreviations of the sections

| Figure No | Section Code | Initial Concentration Range, mg/L | Equilibrium Study |
|---|---|---|---|
| Figure 4.8-A | $A_{Cu}$ | $0 \leq C_i < 26$ | $Cu^{2+}$-$C_1$ |
| | $B_{Cu}$ | $26 \leq C_i < 1102$ | $Cu^{2+}$-$C_1$ |
| | $C_{Cu}$ | $1102 \leq C_i \leq 1689$ | $Cu^{2+}$-$C_1$ |
| Figure 4.8-B | $D_{Cu}$ | $0 \leq C_i < 193$ | $Cu^{2+}$-$Na_1C_1$ |
| | $E_{Cu}$ | $193 \leq C_i < 911$ | $Cu^{2+}$-$Na_1C_1$ |
| | $F_{Cu}$ | $911 \leq C_i \leq 1454$ | $Cu^{2+}$-$Na_1C_1$ |
| Figure 4.8-C | $A_{Ni}$ | $0 \leq C_i < 126$ | $Ni^{2+}$-$C_1$ |
| | $B_{Ni}$ | $126 \leq C_i < 4461$ | $Ni^{2+}$-$C_1$ |
| | $C_{Ni}$ | $4461 \leq C_i \leq 10206$ | $Ni^{2+}$-$C_1$ |
| Figure 4.8-D | $D_{Ni}$ | $0 \leq C_i < 494$ | $Ni^{2+}$-$Na_1C_1$ |
| | $E_{Ni}$ | $494 \leq C_i < 4991$ | $Ni^{2+}$-$Na_1C_1$ |
| | $F_{Ni}$ | $4991 \leq C_i \leq 10392$ | $Ni^{2+}$-$Na_1C_1$ |

In $Cu^{2+}$-$Na_1C_1$ and $Ni^{2+}$-$Na_1C_1$ interactions (Figure 4.8-B and D) predominance of $Na^+$ among exchangeable cations is apparent as a result of conditioning. In addition to $Na^+$ release or exchange, trace amounts of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ are also observed in the aqueous phase at equilibrium particularly for relatively high initial concentrations, which may be attributed to the ineffectiveness of conditioning on displacing all of the exchangeable cations located even at accessible sites. This is also consistent with the results given in the literature that no significant amount of $Ca^{2+}$ and $Mg^{2+}$ was observed in the liquid phase after $Pb^{2+}$ and $Cd^{2+}$ exchange, although the $Na^+$ form of clinoptilolite still contains some $Ca^{2+}$ and $Mg^{2+}$ (Çulfaz and Yağız, 2004).

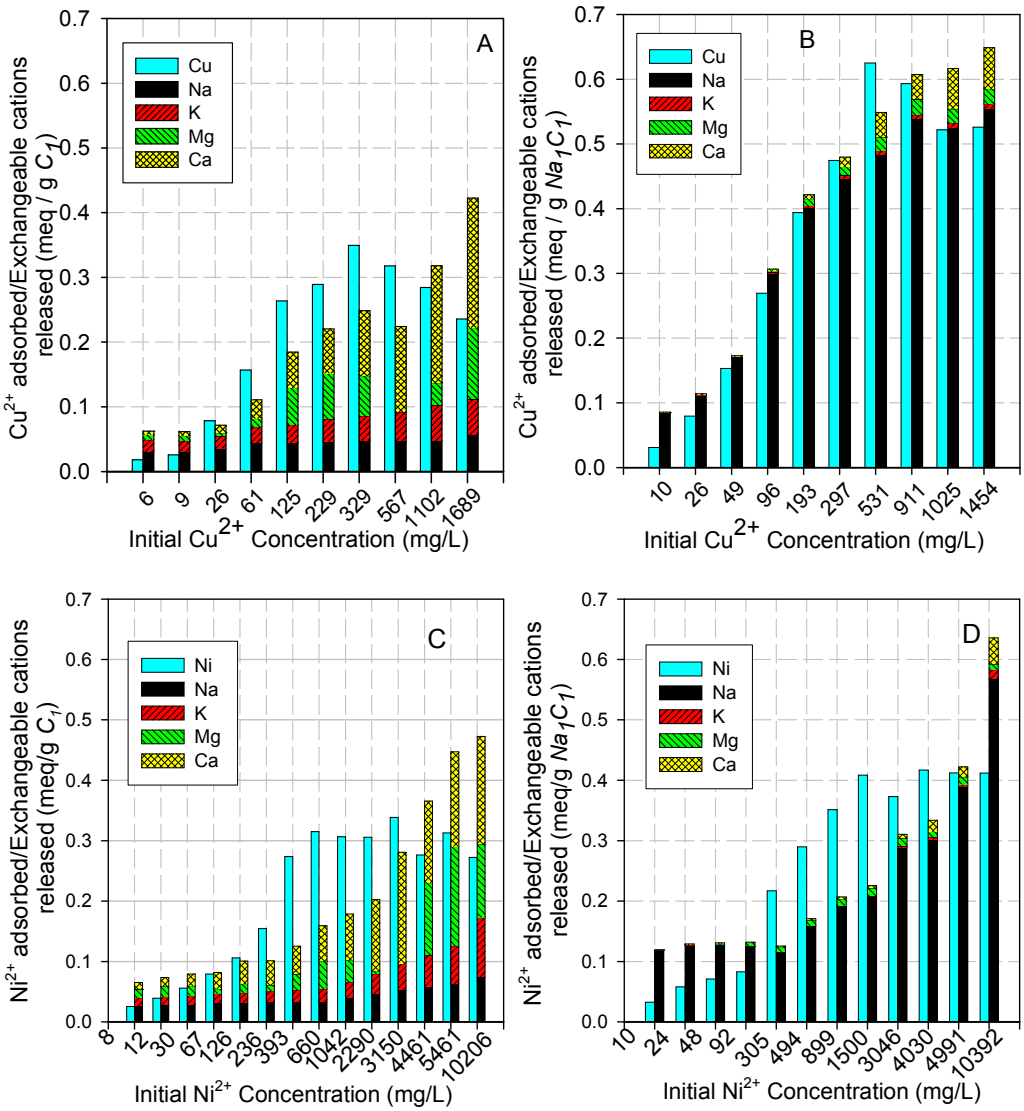


**Figure 4.8.** Comparison of equilibrium metal and exchangeable cation concentrations in clinoptilolite phase and in aqueous phase respectively. A) $Cu^{2+}$-$C_1$, B) $Cu^{2+}$-$Na_1C_1$, C) $Ni^{2+}$-$C_1$, D) $Ni^{2+}$-$Na_1C_1$.

As discussed earlier, characterization studies revealed that $C_1$ possesses considerable amounts of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ in its structure (Table 4.1). Therefore, these ions are also expected to accompany $Na^+$ ions in exchanging with heavy metal cations. It is clear from Figure 4.8-A and C that heavy metal cations are primarily exchanged with the readily available $Na^+$ ions. However, with the consumption of $Na^+$ ions due to the

increasing metal uptake with increasing initial heavy metal concentration, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ ions begin to take place in ion exchange. Consequently, selectivity series for $Cu^{2+}$ and $Ni^{2+}$ over exchangeable cations are determined and given in Table 4.9. In Table 4.9 selectivity series for each exchangeable cation is investigated with respect to its real and relative amounts. Real amount is the amount of each exchangeable cation released from clinoptilolite at equilibrium. However, relative amount is the amount of each exchangeable cation released from clinoptilolite at equilibrium with respect to its % contribution to the total amount of exchangeable cations on the clinoptilolite structure.

**Table 4.9.** Selectivity series for $Cu^{2+}$ and $Ni^{2+}$ over exchangeable cations in each section of all equilibrium studies.

| Section | Selectivity Series with respect to $AE_i$ | Selectivity Series with respect to $RE_i$ |
|---|---|---|
| $A_{Cu}$ | $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ | $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ |
| $B_{Cu}$ | $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| $C_{Cu}$ | $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ | $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ |
| $D_{Cu}$ | $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ | $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ |
| $E_{Cu}$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| $F_{Cu}$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| $A_{Ni}$ | $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| $B_{Ni}$ | $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ | $Na^+ \approx Ca^{2+} > Mg^{2+} > K^+$ |
| $C_{Ni}$ | $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ | $Ca^{2+} > Na^+ \approx Mg^{2+} > K^+$ |
| $D_{Ni}$ | $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ | $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ |
| $E_{Ni}$ | $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ | $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ |
| $F_{Ni}$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |

$AE_i$: amount of exchangeable cation i release from clinoptilolite

$PC_i$: % contribution of exchangeable cation i to the total amount of exchangeable cations on $C_1$ and $Na_1C_1$. (Table 4.4)

$RE_i$: $\frac{AE_i}{PC_i}$: Ratio of exchangeable cation i release from clinoptilolite to the % contribution of exchangeable cation i to the total amount of exchangeable cations on $C_1$ and $Na_1C_1$.

It is clear from Table 4.9 that according to $RE_i$ basis both $Cu^{2+}$ and $Ni^{2+}$ have the highest preference over $Na^+$ in $Na_1C_1$ for all studied initial heavy metal concentrations as expected. In case of $C_1$, heavy metal cations have again the highest preference over $Na^+$ for most of the studied initial metal concentrations. However, in

sections $C_{Cu}$ and $C_{Ni}$ heavy metal cations have the highest selectivity over $Ca^{2+}$. The reason for the increasing preference over $Ca^{2+}$ rather than $Na^{+}$ and $K^{+}$ with increasing initial heavy metal concentration may be attributed to the valances of exchanging cations. Theoretically, in cases where the exchanging ions are not of equal valance, the equilibrium is shifted to favor pickup of lower charged cations (i.e. charged metal-hydroxyl species) and consequently to exclude higher charged cations (i.e. $Ca^{2+}$ and $Mg^{2+}$) from the clinoptilolite phase (Inglezakis and Grigoropoulou, 2004). On the other hand, higher preference of heavy metal cations over $Ca^{2+}$ rather than $Mg^{2+}$ emerges from another reason that is the higher selectivity of clinoptilolite for $Mg^{2+}$ ions when compared to $Ca^{2+}$ (Top and Ülkü, 2004).

In a heavy metal solution-clinoptilolite system, the decrease in heavy metals concentration in the liquid phase is partly due to exchange with ions from the structure and partly to other possible uptake mechanisms (adsorption). The increase in the $Na^{+}$, $K^{+}$, $Ca^{2+}$ and $Mg^{2+}$ ion concentration is partly due to the exchange with heavy metal cations from the solution and partly to dissolution of clinoptilolite (Trgo and Peric, 2003).

Clinoptilolite surface maintains its negative character even in very acidic conditions and this negative charge results in an electrostatic attraction of heavy metal cations (Ersoy and Çelik, 2002, Abadzic and Ryan, 2001, Athanasiadis and Helmreich, 2005). The increase in the suspension pH as a result of the mechanisms discussed earlier is also considered to contribute to the net negative charge of the clinoptilolite surface. Consequently, it is clear from Figure 4.7 that, solution pHs of heavy metal solutions initially adjusted and equilibrium pH values observed in each equilibrium study are within a pH range of 4.0 and 8.5. Therefore, clinoptilolite samples are considered to maintain their negative character in all studied concentrations both for $Cu^{2+}$ and $Ni^{2+}$ and as a result, electrostatic sorption of both free metal ions and their charged hydroxyl species on $C_1$ and $Na_1C_1$ seems to be theoretically possible.

When electrostatic sorption begins, free metal ions and charged metal-hydroxyl species attracted by the negatively charged surface form outer-sphere complexes

(physisorption) with surface functional groups of clinoptilolite (mainly $O^-$ and $OH^-$) on external sites (Trgo and Peric, 2003). The outer-sphere complexation also involves the ion exchange reactions between metal ions and/or charged metal-hydroxyl species and exchangeable cations. During ion exchange process, cations that are bound to the surface functional groups from the clinoptilolite structure enter the solution and heavy metal ions from the solution bind to outer-sphere sites (Colella, 1996). As metal concentration in the aqueous solution increases, more heavy metal ions are attracted by clinoptilolite surface and are forced into internal surface sites. Moreover, more heavy metal ions interact with the internal surface sites and as a result more inner-sphere complexes are formed. This kind of complexation is called "chemisorption" and leads to the formation of more stable inner-sphere surface groups due to the involvement of covalent bonding. With the formation of covalent bonds, hydrogen ions are released as products and the process causes a decrease in solution pH (Doula and Ioannou, 2003, Abadzic and Ryan, 2001, Godelitsas, 1999, Blanchard et al., 1984).

When amount of metal uptake is compared to total amount of exchangeable cations release, it is apparent that there exits a non-stoichiometry for almost all studied initial metal concentrations in each equilibrium study (Figure 4.8). As mentioned earlier, in sections coded with capital A, C, D and capital F, it is obvious that total amount of exchangeable cations release is greater than amount of metal uptake. This may be mainly attributed to the dissolution of clinoptilolite. It is typical for clinoptilolite that presence of surface imperfections and mineralogical heterogeneity promote the solubility of the amorphous aluminosilicate surface layers and detachment of framework ions, namely $Si^{4+}$ and $Al^{3+}$. (Barthomeuf, 1996, Trgo and Peric, 2003, Doula et al., 2002, Manceau et al., 1999).

Type of dissolution (either $Si^{4+}$ or $Al^{3+}$) depends on the pH and the ionic strength of the solutions. $Si^{4+}$ release increases with a decrease in ionic strength and an increase in solution pH. However, $Al^{3+}$ dissolution increases with an increase in ionic strength and a decrease in solution pH. Furthermore, $Cl^-$ binding to the aluminosilicate

framework can be given as another reason for dissolution phenomenon (Doula et al., 2002).

Mechanisms involved in dissolution of clinoptilolite are presented in the following equations; (Inglezakis et al., 2003, Doula et al., 2002, Rozic et al., 2005)

$$\equiv Al\text{-}OH + H^+ \leftrightarrow \equiv Al\text{-}OH^+_2 \leftrightarrow Al^{3+} + H_2O \qquad \text{Equation (4.6)}$$

$$\equiv Al\text{-}OH + Cl^- + H^+ \leftrightarrow Al\text{-}Cl + H_2O \qquad \text{Equation (4.7)}$$

$$\equiv Si\text{-}OH + Cl^- + H^+ \leftrightarrow Si\text{-}Cl + H_2O \qquad \text{Equation (4.8)}$$

In sections $A_{Cu}$, $D_{Cu}$, $A_{Ni}$ and $D_{Ni}$, nonstoichiometry in the amount of exchanging cations is in favor of the exchangeable cations ($Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$). Ion-exchange is considered as the predominant uptake mechanism because of relatively negligible formation of metal hydroxyl species at studied initial solution pHs. On the other hand, release of exchangeable cations may be attributed to both ion-exchange and dissolution. In these sections, $H^+$ ions considerably compete with metal ions because of relatively low initial heavy metal concentrations (Godelitsas and Armbruster, 2003, Cabrera et al., 2005) and $H^+$ uptake drives protonation of clinoptilolite samples. Protonation of clinoptilolite results in not only an increase in solution pH but also in $Al^{3+}$ dissolution presumably at the earlier phase of metal solution-clinoptilolite interaction. Nevertheless, with increasing pH, $OH^-$ concentration increases and this results in an improvement in the degree of binding of this species to the clinoptilolite surface. ≡Si-O bonds are polarized and weakened by the presence of the charged surface species ≡Si-$O^-$. This ultimately leads to the detachment of $Si^{4+}$. As a result, $Si^{4+}$ dissolution becomes predominant particularly in the later phase of metal solution-clinoptilolite interactions (Trgo and Peric, 2003, Doula and Ioannou, 2003, Doula et al, 2002).

Different from sections coded with capital A, C, D and capital F, in sections $B_{Cu}$, $E_{Cu}$, $B_{Ni}$ and $E_{Ni}$ nonstoichiometry in the amount of exchanging ions shifts in favor of amount of metal uptake. The reason for this situation may be attributed to the formation of a considerable amount of charged metal-hydroxyl species and sorption

of these species both on the external and internal surface sites (pore surface) of clinoptilolite. Therefore, in these sections of equilibrium studies, adsorption processes (physisorption and chemisorption) are assumed to accompany ion-exchange in the overall metal uptake mechanism. On the other hand, release of exchangeable cations from clinoptilolite structure may be attributed mainly to ion-exchange, because dissolution is not expected to contribute considerably to the total amount of exchangeable cations release due to the limited variation in solution pH and possibly limited contribution of chemisorption to the overall uptake process.

As mentioned earlier, in sections $C_{Cu}$, $F_{Cu}$, $C_{Ni}$ and $F_{Ni}$, nonstoichiometry in the amount of exchanging ions is in favor of total amount of exchangeable cations release. The reason for this may be mainly attributed to the increasing ionic strength of the aqueous solutions. As discussed earlier, with increasing heavy metal concentration, more heavy metal ions either in free or charged hydroxyl complex forms are forced into the inner-sphere surface sites of clinoptilolite and formation of covalent bonds between metal ions and inner-sphere surface sites of clinoptilolite are assumed to dominate the overall sorption process. However, increasing contribution of chemisorption in overall sorption process results in blocking the diffusion of metal ions to the exchangeable sites particularly located in the channels of the porous structure and hence decreases the ion exchange capacity (Peric et al., 2004). Therefore, adsorption process, particularly chemisorption is considered as the dominating mechanism in overall metal uptake.

It is clear from Figure 4.8 that there seems a considerable decrease in total $Cu^{2+}$ uptake in sections $C_{Cu}$ and $F_{Cu}$ when compared to other sections of the same equilibrium studies. The reason for this may be attributed to the formation of both soluble and insoluble neutral copper-hydroxyl species due to the low solubility of $Cu^{2+}$ at studied pH values. Formation of these complexes results in precipitation on clinoptilolite surface and consequently in hindering action not only on ion exchange but also on adsorption process (Inglezakis et al., 2003). On the other hand, despite ion exchange is assumed to be suppressed with the formation of inner-sphere complexes and surface precipitation, interestingly there is a considerable amount of

exchangeable cations in the aqueous phase. Increasing impact of $Al^{3+}$ and $Si^{4+}$ dissolution processes on the overall process with increasing ionic strength may be taken as the main reason for this situation. Formation of $Cl^-$ containing inner-sphere complexes is considered as another effect of increasing ionic strength on dissolution particularly in sections $C_{Cu}$ and $F_{Cu}$ because $Cu^{2+}$ solutions were prepared by dissolving $CuCl_2 \cdot 2H_2O$ in deionized water.

The reason for the facilitation of the detachment of $Si^{4+}$ and $Al^{3+}$ ions in a chlorinated inner-sphere complex may be ascribed to the electron density shift from $Cl^-$ toward the central metal ion. The excess of electron density brings the negative charge into the coordination sphere of the Lewis acid center and simultaneously enhances the surface protonation and subsequent destruction of the critical Al-O and Si-O lattice bonds (Doula and Ioannou, 2003).

### 4.2.3. Deionized Water-Clinoptilolite Interaction

The relationship between the concentrations of exchangeable cations leaving the clinoptilolite and $H^+$ ions that enter the structure during interaction in $C_1$- deionized water and $Na_1C_1$-deionized water systems are shown in Figure 4.9.

It is clear from the figure that total amount of the exchangeable cations release is considerably higher than the amount of $H^+$ uptake in all cases. Moreover, only a small portion of exchangeable cation release may be attributed to the exchange of $H^+$ ions. As discussed earlier, the reason for this substantial difference may be attributed to the dissolution process. Dissolution phenomenon may be considered to be mainly driven by the detachment of $Si^{4+}$ ion with the increase in the solution pH in time and subsequent sorption of $OH^-$ ions on the material because solution pHs (9.2-9.6) are basic in all reactors towards reaching equilibrium. In Table 4.10, $Si^{4+}$ concentrations in the reactors are presented.

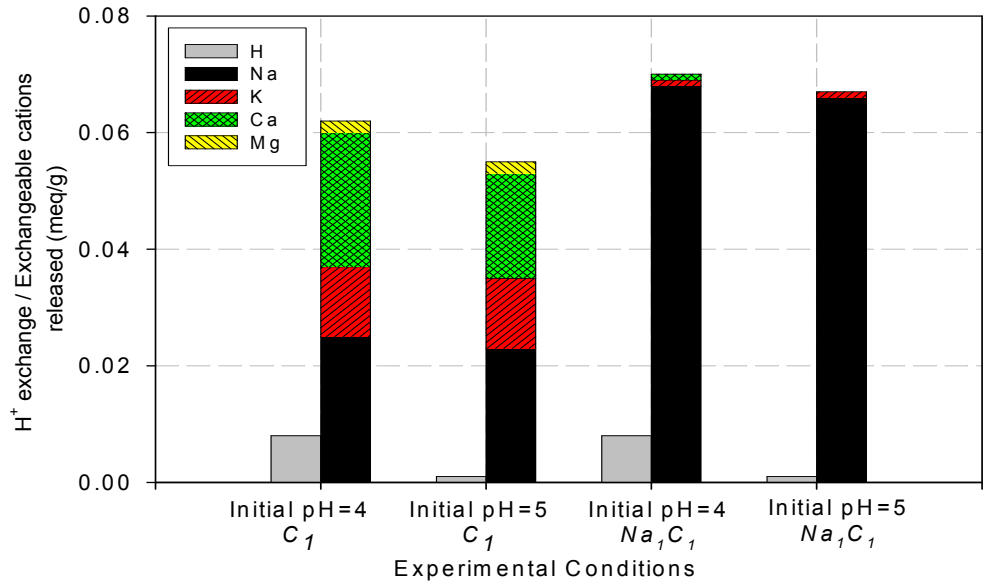


**Figure 4.9.** Equilibrium concentrations of exchangeable cations in initially metal free aqueous medium.

**Table 4.10.** $Si^{4+}$ release from $C_1$ and $Na_1C_1$ in reactors with initial pH of 4 and 5.

| Sample | $Si^{4+}$ concentration (meq/g) | |
|---|---|---|
| | Initial pH 4 | Initial pH 5 |
| $C_1$ | 0.053 | 0.053 |
| $Na_1C_1$ | 0.041 | 0.046 |

It is clear from the table that $Si^{4+}$ release is higher in reactors containing $C_1$ than in reactors containing $Na_1C_1$. The reason for this difference may be ascribed to the dissolution of readily soluble impurities associated with as received samples during conditioning. $Al^{3+}$ dissolution may also exist as a part of the dissolution process because of the protonation of the material particularly in the earlier phase of the interaction. Unfortunately, AAS used in this study was unable to perform a sound detection of $Al^{3+}$ for concentrations less than 0.11 meq/g and accordingly $Al^{3+}$ could not be detected in the samples (that is as a rough estimation, $Al^{3+}$ concentration is smaller than 0.11 meq/g for all samples).

When the participation of each ion to the total amount of exchangeable cations is investigated, it is clear that in deionized water-$C_1$ interaction $Na^+$ and $Ca^{2+}$ have the greatest contribution to the total amount of the exchangeable cations release followed by $K^+$ and to a small extent $Mg^{2+}$. However, in deionized water-$Na_1C_1$ interaction $Na^+$ is the dominant released cation as expected and only trace amounts of $K^+$ and $Ca^{2+}$ accompany $Na^+$. These results indicate that a substantial portion of these cations ($K^+$, $Mg^{2+}$ and $Ca^{2+}$) are associated with readily soluble impurities which dissolve when they come in contact with an aqueous medium. During conditioning, these readily soluble impurities are possibly removed and therefore trace amounts of $Ca^{2+}$ and $K^+$ and no $Mg^{2+}$ are detected in the suspensions (Figure 4.9). Detection of these exchangeable cations in trace amounts may also be considered as an indication of the limited effect of dissolution due to solution pH change on the release of these cations that are strictly bound to the clinoptilolite structure.

Additionally, deionized water with lower initial solution pH (pH 4) exhibits higher exchangeable cation release than does with higher initial solution pH (pH 5). It can be observed from Figure 4.9 that the difference in the total amounts of exchangeable cations release between the two initial solution pHs is approximately equal to the difference in the amounts of $H^+$ uptake. Therefore, the reason for the difference in the total amounts of exchangeable cations release between the two initial solutions pHs may be attributed to $H^+$ exchange. With a decrease in $H^+$ uptake, amount of $Ca^{2+}$ and $Na^+$ release also decreases for both initial pHs. $H^+$ exchange with $Ca^{2+}$ and $Na^+$, rather than $Mg^{2+}$ and $K^+$ may be considered as the principle cause for this situation. Accordingly, all of the $K^+$ and $Mg^{2+}$ ions released may be attributed to dissolution.

As a result, examination of the behavior of $C_1$ and $Na_1C_1$ in a metal free aqueous medium revealed the effect of pH on ion-exchange and dissolution mechanisms. This experiment is not expected to simulate heavy metal solution-clinoptilolite interactions, yet the results provide some evidence relating to the possible mechanisms prevailing in particularly low strength heavy metal solutions. In other words, the results of these experiments provide some insight into the key role of pH in protonation, $OH^-$ binding and ion exchange.

## 4.3. PACKED-BED COLUMN STUDIES

In practical applications ion exchange processes including those using zeolites are generally conducted in columns. In column studies, a solution is percolated through a fixed bed of zeolite (up-flow and down-flow) and a continuous removal of heavy metals are provided for a time period until the effluent heavy metal concentration reaches a certain percentage of the influent heavy metal concentration, that is typically termed as breakthrough point. The curve representing the effluent heavy metal concentration versus time (or effluent volume) is called the breakthrough curve and is used to characterize the process in column operations packed with clinoptilolite.

There are several factors affecting the behavior of the breakthrough curves and some examples for these factors can be given as; column dimensions, direction of flow (up-flow or down-flow), influent heavy metal concentration, volumetric flow rate, presence of surface dust and clinoptilolite particle size.

### 4.3.1. Selection of Column Dimensions and Direction of the Flow

It is a common fact that column dimensions and the direction of flow have profound effects on heavy metal removal in continuous mode applications particularly for proper operation. Channeling is one of the most significant operational problems encountered in column operations packed with porous sorbent materials such as clinoptilolite. Channeling is often encountered in larger columns rather than smaller ones ($L_c/D_c > 20$) and in down-flow operations when relatively higher volumetric flow rates are employed. Therefore, narrower columns are generally employed and introduction of feed solution to the columns is generally conducted in up-flow mode in order to warrant perfect wetting of clinoptilolite and accordingly maximize the contact between clinoptilolite and heavy metal ions in the feed solution. Consequently, the column dimensions of 26.5 cm in length and 2.5 cm in diameter and the up-flow operation mode were selected for $Cu^{2+}$ removal from aqueous

solutions in the light of the past experiences of the researchers dealing with heavy metal removal in columns packed with clinoptilolite (Table 2.8).

### 4.3.2. Elimination of Clogging and Selection of Influent $Cu^{2+}$ Concentration

As mentioned in materials and methods part of this study, rinsing was applied for clinoptilolite samples prior to use in column studies. The reason for rinsing was to eliminate the fine particles associated with clinoptilolite grains and consequently prevent packed bed column from clogging. Nevertheless, in some cases rinsing alone can not be a remedy for the clogging problem. Low ionic strength of the feed solution and/or considerably high flow velocities may results in clogging in column operations. For low ionic strength and high flow rate cases, particle release is driven by electrostatic repulsion and flow induced shear forces respectively (Abadzic and Ryan, 2001). In this study, 200 mg/L $Cu^{2+}$ solution was employed throughout column studies to eliminate clogging and no operational problems were encountered associated with flow velocity. Another reason for the selection of 200 mg/L as the influent metal concentration of the feed solution is that influent solution does not require any pH adjustment to achieve the preliminary determined optimum pH value (pH 5).

### 4.3.3. Effect of Volumetric Flow Rate

Zeolites generally exhibit relatively slow loading kinetics (Inglezakis and Grigoropoulou, 2004). Therefore, effect of the volumetric flow rate on heavy metal removal in columns packed with clinoptilolite arises as probably the most important parameter for continuous applications since volumetric flow rate determines the contact time between the heavy metal ions in the feed solution and clinoptilolite.

According to the results of exhaustion experiments, 2 and 4 BV/h runs with 0.833-1.18 mm size samples exhibited approximately identical trends and almost same capacities utilized at breakthrough and a total capacity of around 1 meq/g was

calculated for 4 BV/h run with 0.833-1.18 mm size samples (Figure 4.10). However, as the flow rate was increased to 8 BV/h, a decrease in the capacity utilized at breakthrough was observed (Figure 4.10). The increase in the capacity utilized at breakthrough however, is not proportional to the change in the flow rate. The reason for the decreasing capacity with increasing flow velocity may be attributed to the lower residence time for higher flow rates and the corresponding failure of attaining local equilibrium (Inglezakis and Grigoropoulou, 2004). It is well known that because of the relatively slow loading kinetics of zeolites, relatively long residence times are needed for attainment of equilibrium (Inglezakis and Grigoropoulou, 2004).

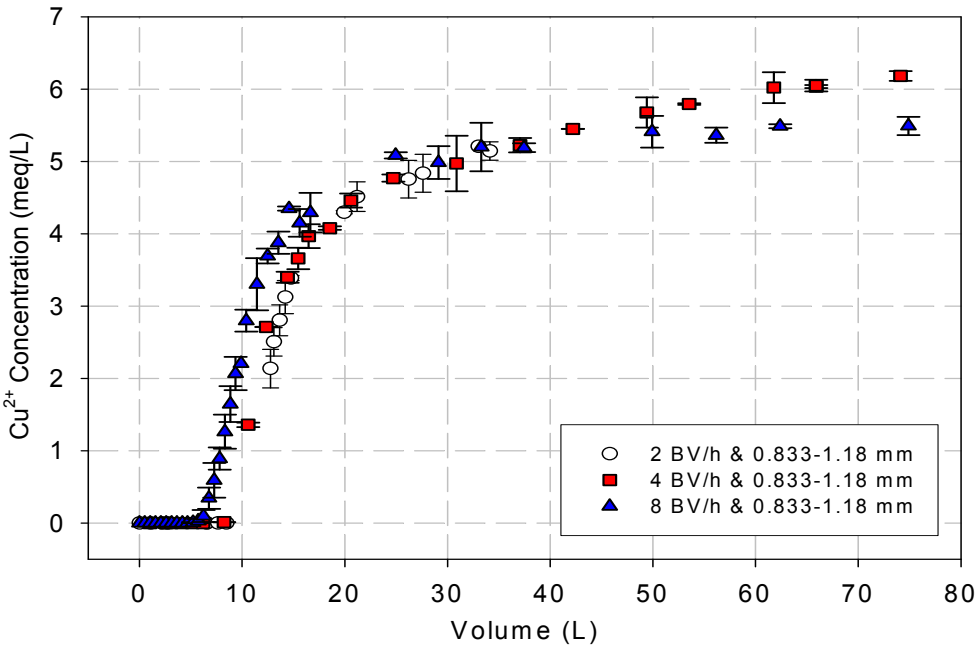


**Figure 4.10.** Effect of volumetric flow rate on breakthrough curves for the removal of $Cu^{2+}$ on $Na_1C_2$.

Results of the present study indicate that, flow rates higher than 8 BV/h should be avoided since breakthrough would occur faster and with less sharpened boundaries (Figure 4.10). Lower than 2-4 BV/h flow rates are expected to be beneficial on the

capacity utilized at breakthrough, however this decrease may result in an increase in film resistance and decreases the capacity via blocking mass transfer. Additionally, performing exhaustion studies in up flow mode might also have resulted in high flow resistance when volumetric flow rates lower than 2 BV/h were studied. Consequently, 4 BV/h is considered to be a reasonable flow rate to be used for the investigation of the effect of particle size on process performance.

### 4.3.4. Effect of Particle Size

As mentioned in the theoretical background section of this study, a change in the particle size results in more profound effects in column operations when compared to batch mode applications. The reason for this difference may be attributed to the relatively lower contact times in column studies which are theoretically considered to be inadequate for heavy metal ions overcoming the pore diffusion resistance particularly in higher size fractions of clinoptilolite. Therefore, investigation of the effect of particle size on $Cu^{2+}$ removal performance of columns packed with $Na_1C_2$ was carried out for the optimum volumetric flow rate of 4 BV/h and results are presented in Figure 4.11.

The experimental run carried out with 1.180-1.400 mm and 0.833-1.180 mm samples at 4 BV/h revealed that as particle size increases, capacity utilized at breakthrough decreases (Figure 4.11). This finding is also consistent with the literature (Inglezakis and Grigoropoulou, 2004, Hashimoto et al., 1977). The reason for this decrease is attributed to the fact that; most of the active exchange sites are located within the channels of the clinoptilolite structure and with an increase in the particle size these sites become less accessible to $Cu^{2+}$ ions because of the increase in the pore diffusion resistance (Sarıoğlu, 2005). Although smaller particle size led to a considerable improvement in capacity utilized at breakthrough, samples having particle size smaller than 0.833 mm were not employed in this study for further investigation because small particle sizes are shown to result in high flow resistance within the

column and accordingly in operational problems such as high flow resistance, particularly in up-flow mode operations (Inglezakis and Grigoropoulou, 2004).

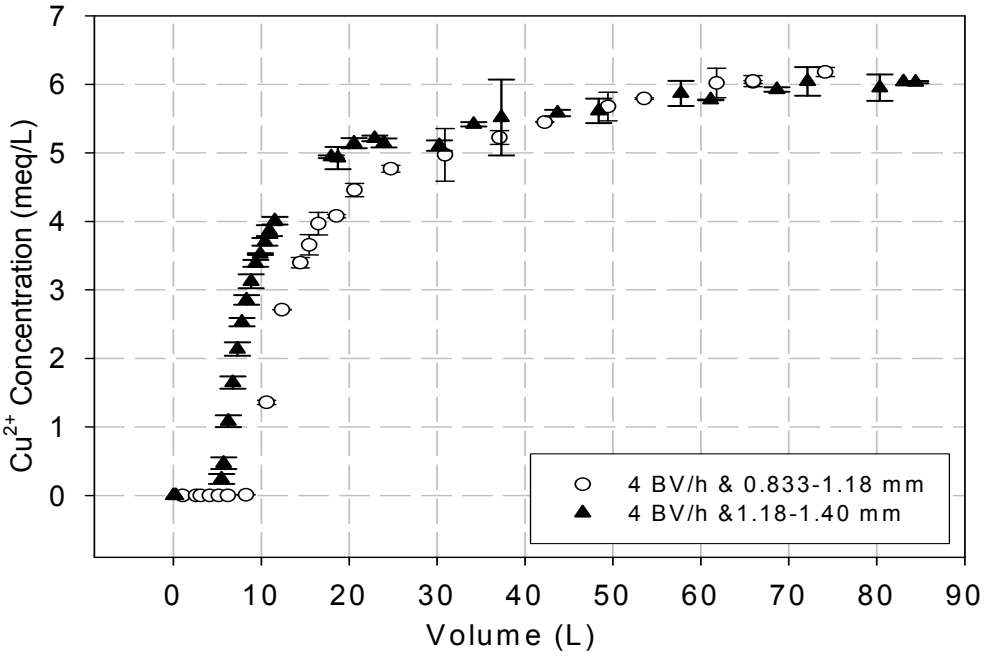


**Figure 4.11.** Effect of particle size on breakthrough curves for the removal of $Cu^{2+}$ using $Na_1C_2$.

### 4.3.5. Dominant Mechanisms Involved in $Cu^{2+}$ Removal in Packed-Bed Column

The trend of the exchangeable cations with volume for each experimental run is given in Figure 4.12. It is clear in all runs that $Na^+$ is the primarily released ion among the exchangeable cations. There seems almost no $Ca^{2+}$, $K^+$ and $Mg^{2+}$ until $Cu^{2+}$ ions are first detected in the effluent. At this level, $Na^+$ concentration in the effluent begins to descend in accordance with a decrease in capacity utilized at breakthrough. However, $Mg^{2+}$ concentration exhibits a sharp increase right after this level (breakthrough point) and a gradual decrease follows this peak. $Ca^{2+}$ concentration also begins to increase at this level however it was not as sharp as that

of $Mg^{2+}$. In addition, except for the fourth run (4 BV/h & 0.833-1.180 mm), $Ca^{2+}$ peak at this level is much smaller. Following this slight increase in the $Ca^{2+}$ concentration, a gradual decrease is also observed as in the case of $Mg^{2+}$ trend. However, different from $Mg^{2+}$, another gradual increase is observed for $Ca^{2+}$ at a level where columns begin to exhaust. This second peak of $Ca^{2+}$ is also higher than the single peak of $Mg^{2+}$.

Different from $Na^{+}$, $Ca^{2+}$ and $Mg^{2+}$, almost no $K^{+}$ is detected in the effluent despite $Na_1C_2$ samples have a considerable $K^{+}$ content (Table 4.2). $K^{+}$ concentration does not exhibit any trend with time neither when flow rate nor particle size is changed. As discussed earlier, decreasing volumetric flow rate in other words increasing contact time is found to have almost no effect on the $K^{+}$ content of the conditioned forms of $C_2$ (Table 4.2). During conditioning, almost all of the $K^{+}$ ions that are accessible to $Na^{+}$ ions and those that are associated with the readily soluble impurities are assumed to be removed. Subsequently, remaining $K^{+}$ ions are considered to be located at either partially accessible or completely inaccessible sites

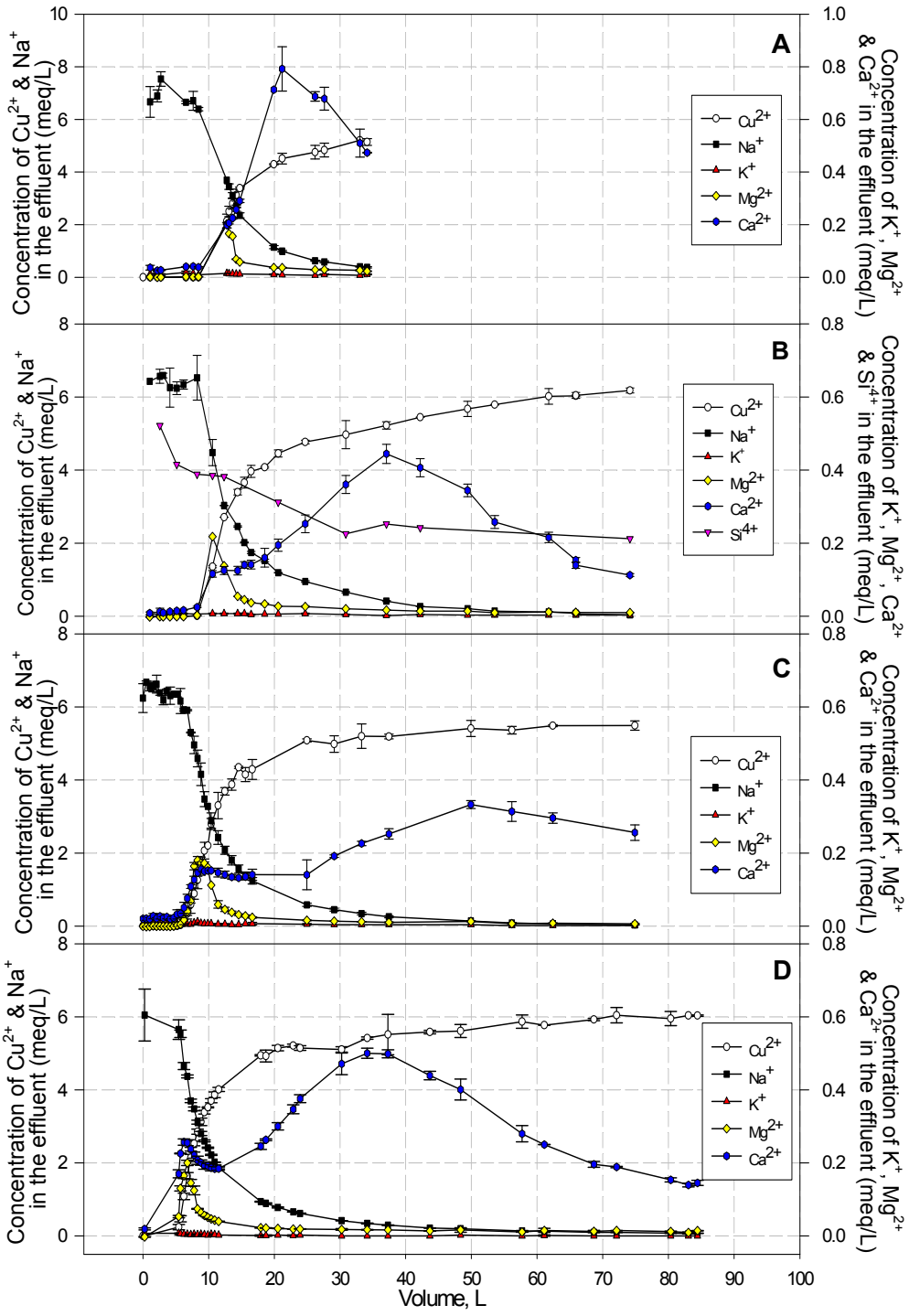


**Figure 4.12.** Relationship between breakthrough curves and exchangeable cations in each run. A) 2 BV/hr & 0.833-1.180 mm, B) 4 BV/hr & 0.833-1.180 mm, C) 8 BV/hr & 0.833-1.180 mm, D) 4 BV/hr & 1.180-1.400 mm.

Sequence of exchangeable cations released in fixed bed columns studies with respect to release priority and total amount of ion release are given in Table 4.11. The reason for the difference between the sequence of exchangeable cations released with respect to two different criteria used may be attributed to the difference in the amount of $Ca^{2+}$ and $Mg^{2+}$ contents of $Na_1C_2$ (1.13 for $Mg^{2+}$ and 2.20 for $Ca^{2+}$ on %wt/wt basis).

**Table 4.11.** Sequence of exchangeable cations released

| Run | Basis | Sequence of cations released |
|---|---|---|
| 2, 4, 8 BV/h & 0.833-1.180 mm | Release Priority | $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ |
| | Total amount of cation release | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| 4 BV/h & 1.180-1.400 mm | Release Priority | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |
| | Total amount of cation release | $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ |

It is evident from the table that $Cu^{2+}$ ions have the highest preference over $Na^+$ and this does not change with flow rate or particle size. Besides, sequence of exchangeable cations released is same in all runs with respect to the total amount of cation release basis. However, the sequence on release priority basis shifts in favor of $Ca^{2+}$ with increasing particle size. The reason for this may be attributed to the increase in pore diffusion resistance and location of $Mg^{2+}$ ions within the material structure. It is a common fact that increasing particle size results in an increase in the pore diffusion resistance in the pores between the crystals (Sarıoğlu, 2005) and the increase in pore diffusion resistance results in a decrease in the number of accessible sites at which $Cu^{2+}$ and $Mg^{2+}$ exchanges. In other worlds, less $Mg^{2+}$ becomes available for $Cu^{2+}$ interaction and as a result $Cu^{2+}$ ions are directed to the sites where $Ca^{2+}$ ions are located.

Apart from analysis of exchangeable ions, $Si^{4+}$ measurements demonstrate that (Figure 4.12) dissolution of the clinoptilolite is also present particularly in the earlier phase of the experimental runs. Doula et al. (2002) state that $Si^{4+}$ release from clinoptilolite structure is mainly due to relatively high pH values. In the earlier phase

of the experimental runs, pH at the column exit exhibits a basic character (Figure 4.13) and a higher $Si^{4+}$ content (Figure 4.12-B) when compared to further times.

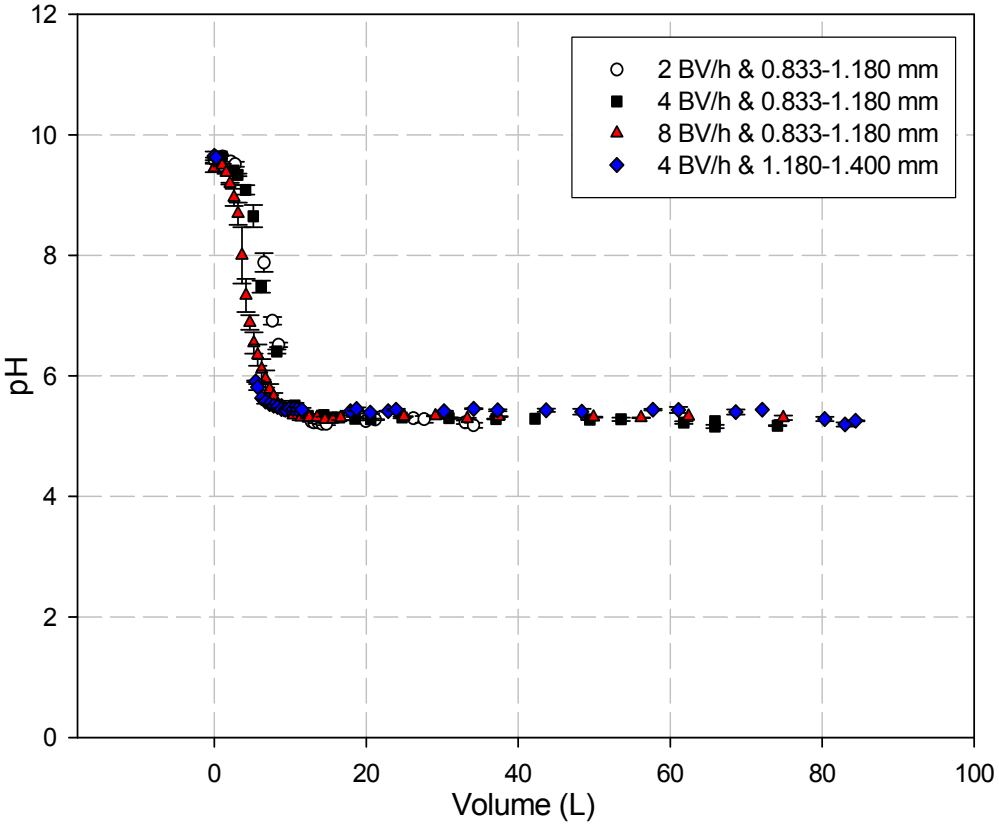


**Figure 4.13.** pH change with percolated volume in all runs

An almost perfect stoichiometry between the $Cu^{2+}$ uptake and the total amount of exchangeable cations (Figure 4.14) released from clinoptilolite point to ion exchange as the dominant mechanism. However, presence of $Si^{4+}$ along with basic pHs indicate presence of dissolution of clinoptilolite as well. Since some portion of the amount of exchangeable cations release is attributed to dissolution and there exists almost a perfect stoichiometry between exchanging ions, some portion of the amount of $Cu^{2+}$ uptake is attributed to adsorption as another prevailing mechanism in the system.

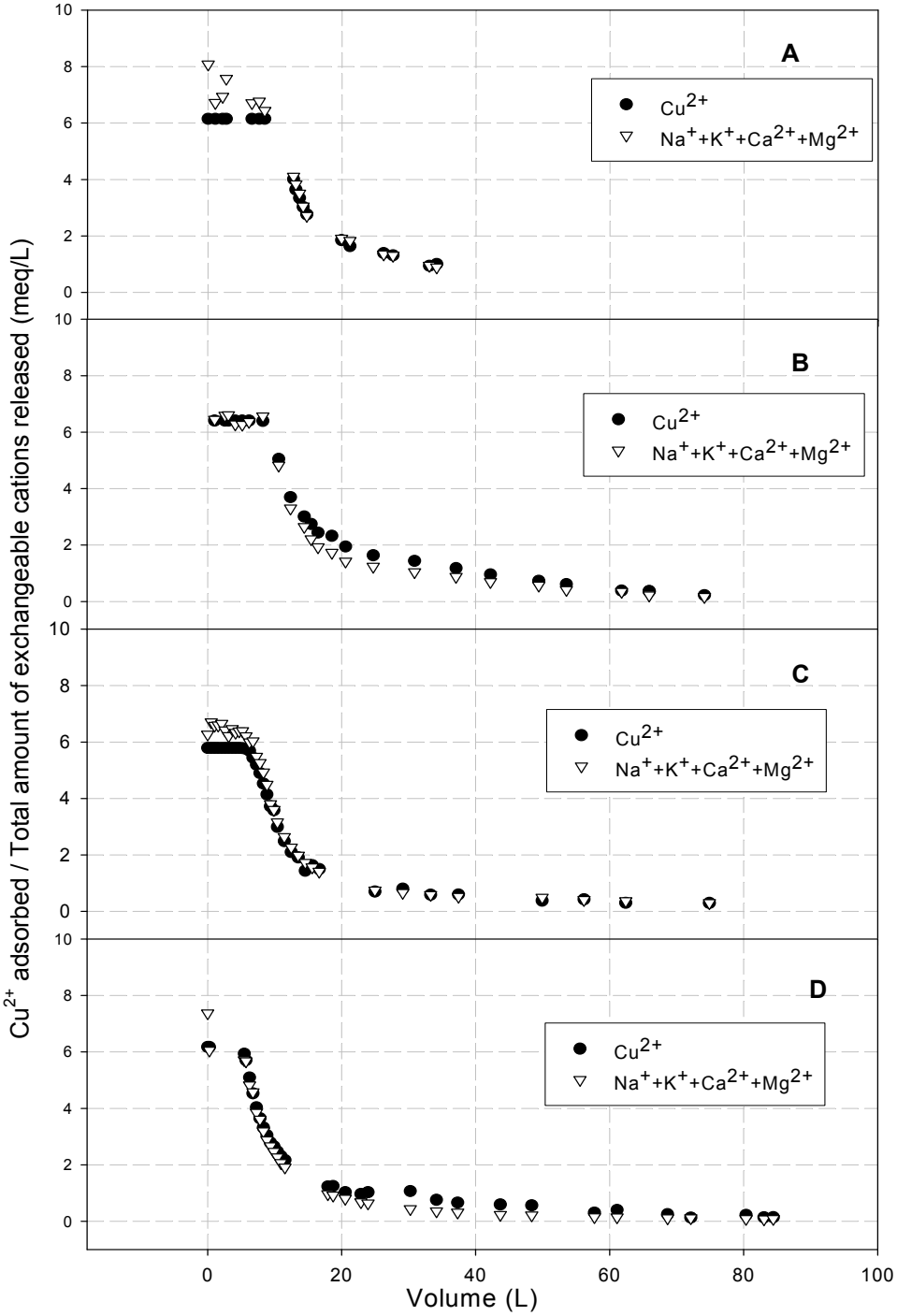


**Figure 4.14.** Stoichiometry between $Cu^{2+}$ uptake and total amount of exchangeable cations. A) 2 BV/h & 0.833-1.180 mm, B) 4 BV/h & 0.833-1.180 mm, D) 8 BV/h & 0.833-1.180 mm, D) 4 BV/h & 1.180-1.400 mm.

# CHAPTER 5

# CONCLUSIONS

Preliminary experiments revealed that initial solution pH of 5 and 4 are the optimum values for $Cu^{2+}$ and $Ni^{2+}$ removal, respectively and 48 hours of contact time is determined as the equilibration period for the heavy metal-clinoptilolite interaction. Additionally, conversion of Bigadiç clinoptilolite into its $Na^{+}$ form is found to result in a considerable improvement in $Cu^{2+}$ removal capacity (approximately 100%). However, an increase in duration of conditioning is found to have a negligible impact on the metal removal capacity of clinoptilolite.

Equilibrium studies revealed that despite $C_1$ has similar capacity for $Cu^{2+}$ (0.31 meq/g) and $Ni^{2+}$ (0.32 meq/g), $Na_1C_1$ has a higher capacity for $Cu^{2+}$ (0.55 meq/g) than for $Ni^{2+}$ (0.43 meq/g). Maximum removal capacities were calculated by fitting non-linear form of Langmuir model to the experimental data which exhibited a better correlation with the experimental data than Freundlich model does.

Examination of the exchangeable cations in the aqueous phase at equilibrium indicated a non-stoichiometry between the amount of heavy metal uptake and total amount of exchangeable cations release. This non-stoichiometry between the incoming and outgoing ions is mainly attributed to the prevalence of adsorption and dissolution phenomena which may be considered to accompany ion exchange. Among these mechanisms, ion exchange may be considered to prevail in all isotherm studies and for all studied initial heavy metal concentrations. On the other hand, dissolution of clinoptilolite structure is supposed to be a dominant mechanism in the system particularly for the lowest and highest studied initial heavy metal concentrations. The reason for the increasing impact of dissolution on the system

may be attributed to protonation and high ionic strength at the lowest and the highest initial heavy metal concentrations, respectively. Different from dissolution, impact of adsorption on the overall process may be considered to increase with increasing initial heavy metal concentrations. However, this is suppressed by the action of dissolution due to increasing contribution of chemisorption in adsorption process. With increasing contribution of chemisorption (formation of inner-sphere complexes via covalent bonding) dissolution of the central framework ions also increases and detachment of even these inner-sphere complexes occurs.

It can be concluded from the results of the investigation of the exchangeable cations released that both metal ions have the highest preference over $Na^+$ for all studied initial heavy metal concentrations using $Na_1C_1$. However, for equilibrium studies using $C_1$ as the sorbent, $Cu^{2+}$ and $Ni^{2+}$ have the highest selectivity over $Na^+$ but this preference shifts in favor of $Ca^{2+}$ ions as initial heavy metal concentrations increase. Neither $Cu^{2+}$ nor $Ni^{2+}$ can replace $K^+$ in any equilibrium experiment for all studied concentrations.

According to fixed-bed column studies, volumetric flow rates of 2 and 4 BV/h were determined to result in almost the same capacities whereas 8 BV/h resulted in a considerable decrease in the capacity utilized at breakthrough. Additionally, increasing the particle size from 0.833-1.18 mm to 1.18 to 1.40 mm was found to decrease the capacity.

Examination of the exchangeable cations released in effluent revealed almost a perfect stoichiometry between the amount of $Cu^{2+}$ uptake and the total amount of exchangeable cations release throughout the operation. However, analysis of $Al^{3+}$, Fe(total) and $Si^{4+}$ reveal a considerable amount of $Si^{4+}$ pointing to the presence of dissolution in the system. Since some portion of the total amount of exchangeable cations in the aqueous phase is attributed to dissolution, some portion of $Cu^{2+}$ uptake is considered to emerge from presence of adsorption in the system.

# CHAPTER 6

# RECOMMENDATIONS

Some recommendations for further studies may be listed as follows;

- A comprehensive mineralogical, chemical and physicochemical characterization and classification of each deposit in Türkiye.
- Investigation of the effect of both cationic and anionic competition on metal removal capacity and on prevailing mechanisms.
- Investigation of different conditioning and regeneration methods under different experimental conditions and from an economical and feasibility point of view.
- Investigation of the process performance on industry originated wastewaters.
- Investigation of the principle disposal methods and possible recovery and recycling alternatives for the metal saturated zeolites.

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# APPENDIX A

## CALIBRATION CURVES

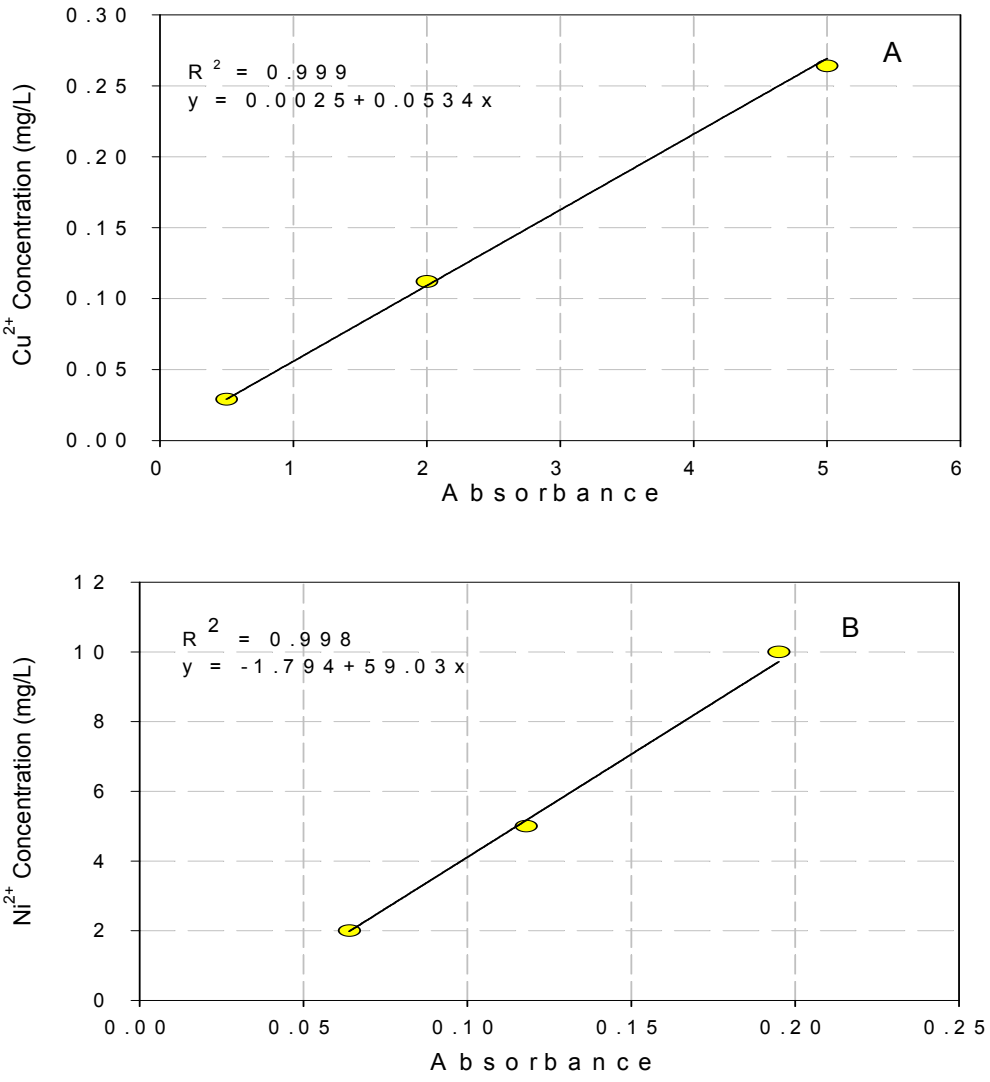


**Figure A.1**. Sample calibrations curves used for calculation of actual concentrations, A) $Cu^{2+}$ calibration, B) $Ni^{2+}$ calibration.

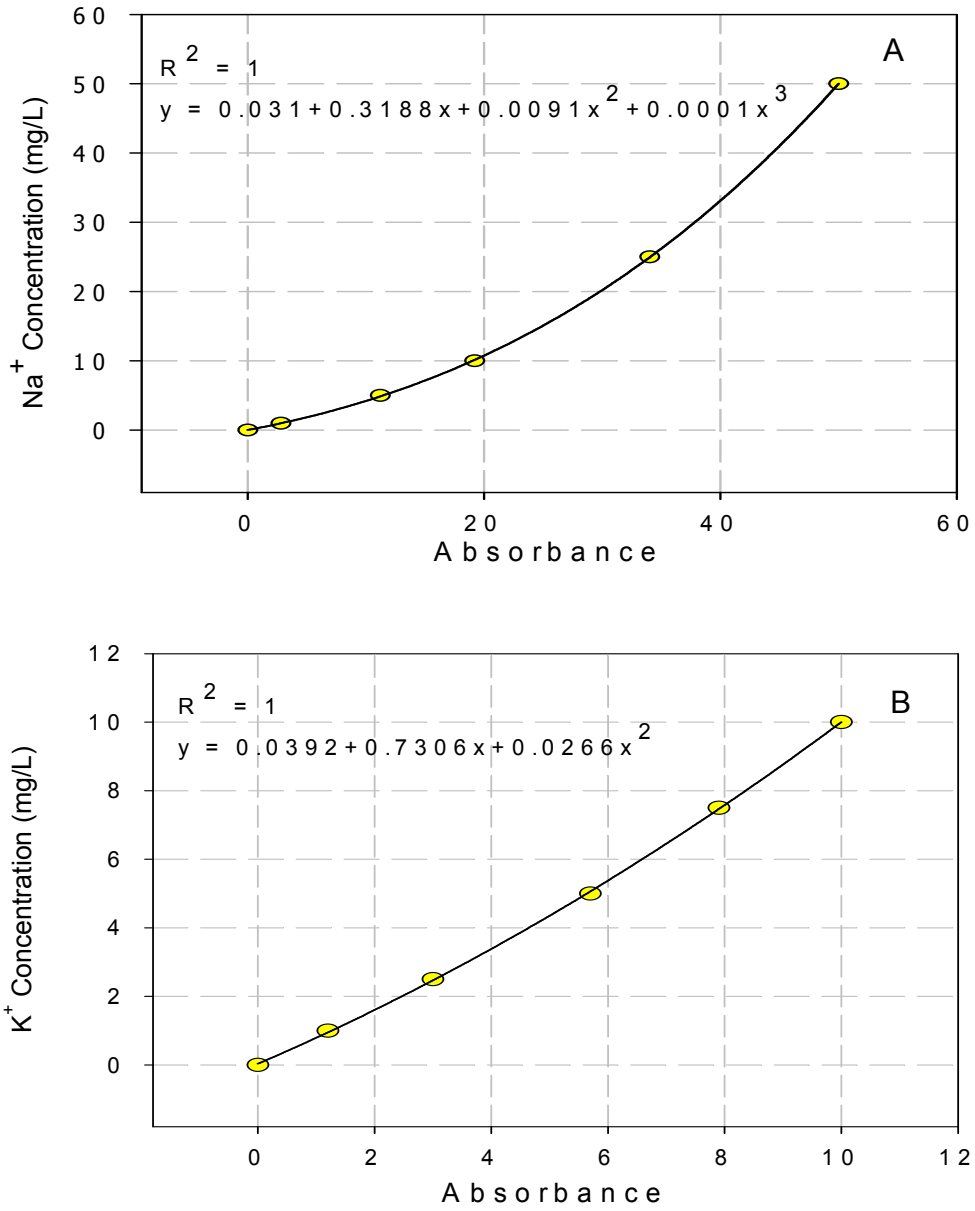


**Figure A.2**. Sample calibrations curves used for calculation of actual concentrations, A) $Na^+$ calibration, B) $K^+$ calibration.

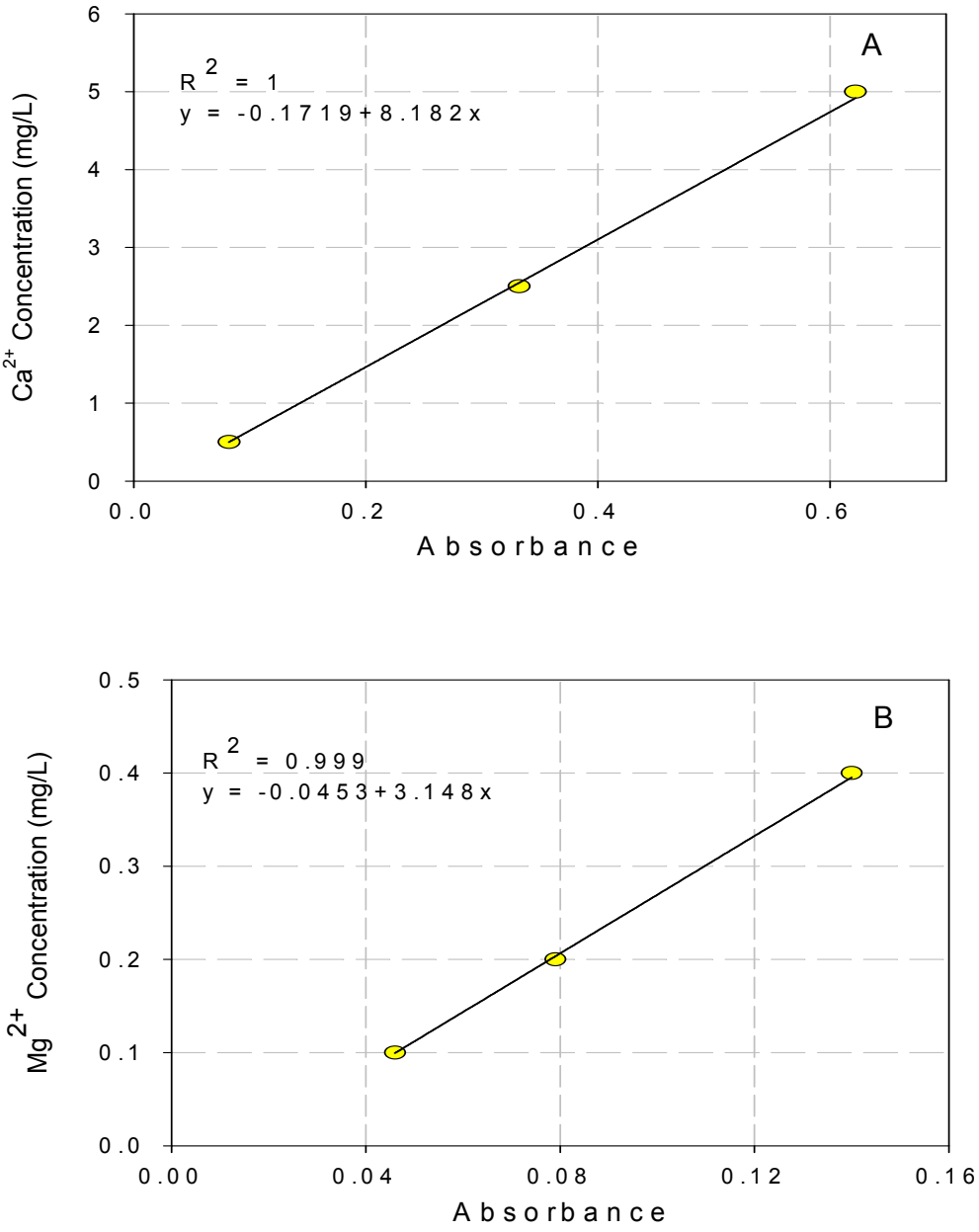


**Figure A.3.** Sample calibrations curves used for calculation of actual concentrations, A) $Ca^{2+}$ calibration, B) $Mg^{2+}$ calibration.

# APPENDIX B

## CONCENTRATION CHANGE IN OPTIMUM pH EXPERIMENTS

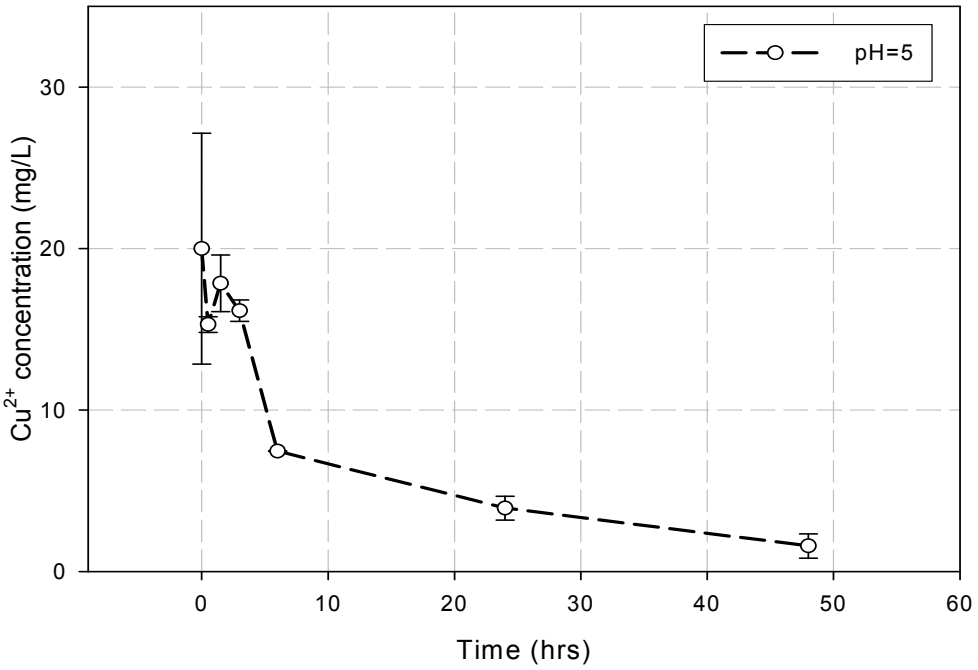


**Figure B.1.** Concentration change in optimum pH experiments for initial pH of 5

# APPENDIX C

## EQUILIBRIUM DATA

**Table C.1.** Equilibrium data for each isotherm

| $Cu^{2+}$-$C_1$ | | $Cu^{2+}$-$Na_1C_1$ | | $Ni^{2+}$-$C_1$ | | $Ni^{2+}$-$Na_1C_1$ | |
|---|---|---|---|---|---|---|---|
| $q_e$ | $C_e$ | $q_e$ | $C_e$ | $q_e$ | $C_e$ | $q_e$ | $C_e$ |
| 0.01 | 0.4 | 0.03 | 0.0 | 0.03 | 0.4 | 0.03 | 0.4 |
| 0.03 | 0.5 | 0.08 | 0.2 | 0.04 | 0.8 | 0.06 | 6.4 |
| 0.08 | 1.1 | 0.15 | 0.6 | 0.06 | 13.6 | 0.07 | 27.0 |
| 0.16 | 11.1 | 0.27 | 10.2 | 0.08 | 43.8 | 0.08 | 67.4 |
| 0.26 | 41.4 | 0.39 | 68.1 | 0.11 | 100 | 0.22 | 241 |
| 0.29 | 137 | 0.48 | 146 | 0.15 | 191 | 0.29 | 409 |
| 0.35 | 218 | 0.63 | 332 | 0.27 | 312 | 0.35 | 796 |
| 0.32 | 466 | 0.59 | 701 | 0.32 | 568 | 0.41 | 1380 |
| 0.28 | 1012 | 0.52 | 859 | 0.31 | 952 | 0.37 | 2937 |
| 0.24 | 1614 | 0.53 | 1287 | 0.31 | 2200 | 0.42 | 3908 |
| | | | | 0.34 | 3050 | 0.41 | 5180 |
| | | | | 0.28 | 4380 | 0.41 | 10271 |
| | | | | 0.31 | 5369 | | |
| | | | | 0.27 | 10126 | | |