

**INVESTIGATION OF ZINC AND LEAD REMOVAL FROM AQUEOUS  
SOLUTIONS USING CLINOPTILOLITE**

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Approval of the Graduate School of Natural and Applied Sciences

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## **ABSTRACT**

# **INVESTIGATION OF ZINC AND LEAD REMOVAL FROM AQUEOUS SOLUTIONS USING CLINOPTILOLITE**

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Natural zeolites, especially clinoptilolite, have the ability of removing certain cations from wastewater by utilizing ion exchange and adsorption. In this study, clinoptilolite originated from Bigadiç, Balıkesir deposit was investigated in its natural and conditioned form for its effectiveness in removing  $Zn^{2+}$  and  $Pb^{2+}$  ions from aqueous solutions. In addition, relevant mechanisms involved in heavy metal removal by clinoptilolite were examined in this study.

Throughout this work, equilibrium and kinetic studies were performed with as-received and conditioned clinoptilolite, having particle size of 0.15 – 0.80 mm. Conditioning aimed to replace exchangeable cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) on clinoptilolite with a cation that is more willing to undergo ion exchange. The results of equilibrium studies revealed that clinoptilolite had different capacities for  $Zn^{2+}$  and  $Pb^{2+}$  ions. Clinoptilolite had high capacity for  $Pb^{2+}$  ions, whereas lower capacities were attained for  $Zn^{2+}$ . Conditioning with concentrated NaCl solution

increased the removal capacity for both metals. Maximum capacities attained were 0.14 meq/g (as-received) and 0.39 meq/g (conditioned) for  $Zn^{2+}$ , and 0.51 meq/g (as-received) and 1.10 meq/g (conditioned) for  $Pb^{2+}$ . Furthermore, kinetic studies performed under pH-uncontrolled and pH-controlled conditions revealed that heavy metal removal can not only be explained by ion exchange. These studies also indicated that  $Zn^{2+}$  ions were weakly bound to clinoptilolite structure, whereas there was a strong bonding between  $Pb^{2+}$  ions and clinoptilolite structure.

To examine possible removal mechanisms, relationship between exchangeable ions released from clinoptilolite structure and  $Zn^{2+}$  and  $Pb^{2+}$  ions removed from aqueous solutions were investigated during equilibrium and kinetic studies. For equilibrium studies, it was observed that the higher the heavy metal equilibrium concentration, the higher is the amount of exchangeable ions released. However, the results indicated that the release of exchangeable ions were not only due to ion exchange. Examination of  $Si^{4+}$ , the main central metal ion of clinoptilolite, during kinetic studies showed that destruction of clinoptilolite framework was partly responsible for the release of exchangeable ions. Release of  $Si^{4+}$  was more pronounced in  $Pb^{2+}$  removal studies, indicating dependency of framework destruction on the type of heavy metal species.

Keywords: Clinoptilolite; removal; zinc; lead; ion exchange; adsorption

## ÖZ

# KLİNOPTİLOLİT KULLANARAK SULU ÇÖZELTİLERDEN ÇİNKO VE KURŞUN GİDERİMİNİN İNCELENMESİ

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Doğal zeolitler, özellikle klinoptilolit, iyon değişimi ve adsorpsiyon mekanizmalarını kullanarak bazı katyonları atıksulardan giderebilme kapasitesine sahiptir. Bu çalışmada, Bigadiç, Balıkesir rezervinden elde edilen klinoptilolit örneğinin doğal ve şartlandırılmış halde sulu çözeltilerden  $Zn^{2+}$  ve  $Pb^{2+}$  giderim etkinliği araştırılmış ve klinoptilolit ile ağır metal giderimindeki ilgili mekanizmalar incelenmiştir.

Bu çalışma boyunca, denge ve kinetik çalışmaları 0.15 – 0.80 mm parçacık boyutuna sahip doğal ve şartlandırılmış klinoptilolit ile gerçekleştirilmiştir. Şartlandırma işlemi klinoptilolitteki değişebilir iyonları ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) iyon değişimine daha istekli bir katyon ile yer değiştirmeyi amaçlamıştır. Denge çalışmalarının sonucu klinoptilolitin  $Zn^{2+}$  ve  $Pb^{2+}$  iyonları için farklı kapasitelere sahip olduğunu ortaya çıkarmıştır. Klinoptilolit  $Pb^{2+}$  iyonları için yüksek kapasiteye sahipken,  $Zn^{2+}$  için düşük kapasiteler elde edilmiştir. Konsantre NaCl çözeltisi ile yapılan şartlandırma işleminin zeolitin metal giderim kapasitesinin her iki metal için de artırdığı görülmüştür. Elde edilen maksimum kapasiteler  $Zn^{2+}$  için 0.14 meq/g (doğal) ve 0.39

meq/g (şartlandırılmış),  $Pb^{2+}$  için 0.51 meq/g (doğal) ve 1.10 meq/g (şartlandırılmış) olarak bulunmuştur. Ayrıca, pH'ın kontrol edildiği ve edilmediği ortamlarda yapılan kinetik çalışmalar ile ağır metal gideriminin sadece iyon değişimi ile açıklanamadığı görülmüştür. Çalışma sonuçları  $Zn^{2+}$  iyonlarının klinoptilolit yapısına daha zayıf bağlarla bağlı olduğunu, buna karşın  $Pb^{2+}$  iyonları ile klinoptilolit yapısı arasında güçlü bir bağ olduğunu göstermiştir.

Ağır metal giderimindeki muhtemel mekanizmaları incelemek amacıyla, klinoptilolit yapısından sulu çözeltilere salınan değişebilir iyonlar ile sulu çözeltilerden giderilen  $Zn^{2+}$  ve  $Pb^{2+}$  iyonları arasındaki ilişki incelenmiştir. Denge çalışmalarında, artan ağır metal denge konsantrasyonu ile değişebilir iyon miktarlarının arttığı görülmüştür. Bununla birlikte, sonuçlar, ortama salınan değişebilir iyonların sadece iyon değişiminin bir ürünü olmadığını göstermektedir. Klinoptilolit merkezi atomlarından olan  $Si^{4+}$ 'ün ve değişebilir iyonların kinetik çalışmalar sırasında ölçülmesi, klinoptilolit yapısının bozunmaya uğramasının da değişebilir iyonların klinoptilolit yapısından ortama salınmasından sorumlu olduğu görülmüştür.  $Si^{4+}$ 'ün salınması,  $Pb^{2+}$  giderim çalışmalarında daha belirgindir ve klinoptilolit yapısının bozunmasının ağır metal türüne bağlı olduğunu göstermektedir.

Anahtar kelimeler: Klinoptilolit; giderim; çinko; kurşun; iyon değişimi; adsorpsiyon

To My Family



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## ABBREVIATIONS

AAS: Atomic Absorption Spectrometry

FP: Flame Photometer

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence

SEM-EDS: Scanning Electron Microscopy – Energy Dispersive Spectroscopy

TCEC: Theoretical Cation Exchange Capacity

$q$  : amount of adsorbate per unit weight of adsorbent (meq/g)

$C_i$  : initial concentration of adsorbate (mg/L)

$C_e$  : equilibrium concentration of adsorbate (mg/L)

$V$ : volume of solution (L)

$m$ : amount of clinoptilolite added to solution (g)

Eq. Wt.: equivalent weight based on ion charge (g/eq)

MW: Molecular Weight (g/mol)

$z$ : ion charge (eq/mol)

$K_f, n$ : Freundlich equilibrium constants

$a, b$ : Langmuir empirical constants

meq/g: milliequivalent per gram

$r^2$ : goodness of fit



# CHAPTER 1

## INTRODUCTION

### 1.1. General Information

Heavy metal containing wastewaters originate mainly from electroplating, metal finishing, metallurgical, chemical manufacturing, mining and battery manufacturing processes in considerable amounts. Heavy metals are well-known toxic elements and their discharge into receiving waters causes detrimental effects on human health and the environment. Since they are not biodegradable, they tend to accumulate in living organisms. Therefore they cause numerous diseases and disorders. Also, due to their toxicity, presence of metals in excessive quantities interferes with beneficial use of water (Tchobanoglous and Burton, 1991). Therefore, there is a need to treat heavy metal containing wastewaters before being discharged into the environment.

Several processes exist for removing dissolved heavy metals, including, but not limited to, ion exchange, precipitation, ultrafiltration, reverse osmosis, electrodialysis and adsorption (Tchobanoglous and Burton, 1991; Eckenfelder, 1989). Many of these approaches demand high energy (hence, cost) or advanced operational requirements, result in large amounts of sludge requiring treatment or difficult to treat and be disposed off in an environmentally sound manner, or do not enable recovery of metals or material. Recently, natural zeolites are gaining attention in wastewater treatment as appropriate materials for removing heavy metal ions due to their unique physical and chemical properties, their abundance in many deposits and especially their local availability, combined with a recovery potential for both metals and the mineral.

Natural zeolites are crystalline aluminosilicates of alkaline and alkaline-earth metals. They have a net negative charge due to isomorphous replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  and this negative charge is balanced by the extra-framework cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). Two main mechanisms are attributed to heavy metal removal by natural zeolites: (i) ion exchange and (ii) adsorption (Doula and Ioannou, 2003; Trgo and Perić, 2003; Mozgawa and Bajda, 2005). Ion exchange properties of zeolites are due to the weakly bonded extra-framework cations which are mobile and easily exchanged with solution cations (Mumpton, 1999; Tsistsishvili, 1992). Adsorption of positively charged cations and complex formation are enabled because of the different shape of surface crystal faces, surface imperfections, broken bonds and edge sites, as well as the amphoteric nature of hydroxyl groups [ $\equiv(\text{Al/Si})\text{-OH}$ ] (Trgo and Perić, 2003; Altın *et al.*, 1998). Besides ion exchange and adsorption, the other mechanisms indirectly involved during heavy metal removal from aqueous solutions via zeolites are surface precipitation (Trgo and Perić, 2003; Inglezakis *et al.*, 2003b; Semmens and Seyfarth, 1978) and destruction of clinoptilolite structure, i.e. dissolution of the clinoptilolite framework cations (Trgo and Perić, 2003; Doula and Ioannou, 2003; Doula *et al.*, 2002). Efficiency of heavy metal removal via clinoptilolite is affected by several factors related to the material and the metal ion or the solution, such as pH of solution, temperature at which reaction takes place, hydrated radii of heavy metal ions, pretreatment applied to the material, which aims to improve ion exchange ability of material.

Natural zeolites, especially clinoptilolite, are abundant in the world. Furthermore, Turkey has very high reserves for clinoptilolite, and therefore investigation of the potential of this natural material in wastewater treatment may lead to its establishment as a viable alternative to conventional heavy metal treatment technologies by utilizing local resources.

## 1.2. Objectives of the Study

In this study, clinoptilolite originated from Bigadiç, Balıkesir deposit is investigated for its use in removal of  $Zn^{2+}$  and  $Pb^{2+}$  ions from aqueous solutions. More specifically, the objectives of this study were:

- To examine the  $Zn^{2+}$  and  $Pb^{2+}$  removal capacity of clinoptilolite in both as-received and conditioned form
- To examine relevant mechanisms for  $Zn^{2+}$  and  $Pb^{2+}$  removal using clinoptilolite via
  - Equilibrium studies: comparison of exchangeable cations released from the clinoptilolite structure and metal uptake from solution under equilibrium conditions
  - Kinetic studies: investigation of exchangeable cations released from the clinoptilolite structure and metal uptake from solution with time under pH-uncontrolled and pH-controlled conditions
  - Investigation of the behavior of clinoptilolite in metal - free solutions

## CHAPTER 2

### THEORETICAL BACKGROUND

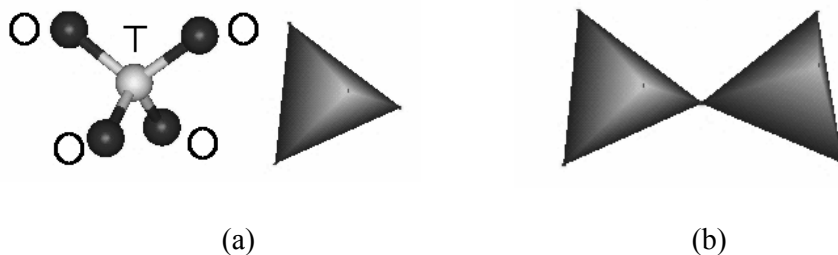
#### 2.1. Natural Zeolites

##### 2.1.1. Description of Natural Zeolites

Zeolites are well-known for more than 200 years and since 1950s, they have attracted attention of scientists and their industrial and commercial potential have been recognized (Mumpton, 1978; Ouki *et al.*, 1994). However, most of the research has been concentrated on synthetic zeolites (man-made production of zeolites) since it was thought that sufficient amounts of natural zeolites were not available (Mumpton, 1999). With the discovery of natural zeolites in large minable deposits and due to their low costs, natural zeolites gained a significant interest (Ouki *et al.*, 1994; Mumpton, 1999). Henceforth, the term “zeolite” will be used instead of “natural zeolite” throughout this thesis.

A zeolite is a crystalline hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure. It is able to lose and gain water reversibly and exchange extra-framework cations, both without change of crystal structure (Mumpton, 1999). The primary building block of the zeolite framework is the tetrahedron, the centre of which is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices (Figure 2.1a). Each oxygen atom is shared between two tetrahedrons and the tetrahedrons form a continuous framework (Figure 2.1b). Substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  defines the negative charge of the framework, which is compensated by monovalent or divalent cations located together with water

molecules in structural channels. Cations in the channels are substituted easily and therefore they are termed as exchange or extra-framework cations, whereas  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  are not exchanged under ordinary conditions and are termed as tetrahedral or framework cations (Tsitsishvili *et al.*, 1992).



**Figure 2.1.** Representation of (a) primary building block of zeolite (b) two tetrahedral sharing oxygen atoms

Compositionally, zeolites may be expressed by the general formula:



$\text{M}^+$  is usually  $\text{Na}^+$  or  $\text{K}^+$  and  $\text{M}^{2+}$  is  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  or  $\text{Fe}^{2+}$ ; more rarely  $\text{Li}^+$ ,  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$  may substitute for  $\text{M}^+$  or  $\text{M}^{2+}$ .  $\text{Fe}^{3+}$  is commonly assumed to substitute into the tetrahedral framework position (Vaughan, 1978).

Zeolite structure is mainly composed of three components (Tsitsishvili *et al.*, 1992):

1. alumino-silicate framework
2. exchangeable cations
3. zeolite water

The aluminosilicate framework is the most conserved and stable component of zeolite. The topology of the framework, the numbers and distribution of charges ( $\text{Al}^{3+}$  sites) are basically formed at the crystal growth stage and define a series of

technologically important properties of zeolites (Tsitsishvili *et al.*, 1992). Both Si/Al ratio and cation contents determine the properties of most zeolites (Vaughan, 1978). The Si/Al ratio in natural zeolites lies within the limits of 1 to 6 (reaching 5 to 6 for clinoptilolite, mordenite, ferrierite, dachiardite) (Tsitsishvili *et al.*, 1992).

The most significant feature of zeolite structure is the presence of voids and channels which defines the specific properties of these minerals (Tsitsishvili *et al.*, 1992). These structural cavities and channels are occupied by alkaline and alkaline-earth cations and water molecules (Tsitsishvili *et al.*, 1992; Gottardi, 1978) and they constitute 20%-50% of total volume (Chamber of Mining Engineers of Turkey, 2003). The cation-water complexes determine to a large extent the various physicochemical properties displayed by the zeolite, many of which are of potential industrial interest (Doula *et al.*, 2002).

Due to the fact that extra-framework cations are weakly bonded to zeolite structure and that they are mobile, they can be removed from zeolite structure or exchanged readily by solution cations. The theoretical cation exchange capacity (TCEC) of zeolite is basically a function of the amount of  $\text{Al}^{3+}$  that substitutes for  $\text{Si}^{4+}$  in the framework tetrahedral, i.e. amount of extra-framework cations to compensate the negative charge due to this substitution; the greater the  $\text{Al}^{3+}$  content, the more extra-framework cations needed to balance the charge. Generally, zeolites have theoretical cation exchange capacities in a range of 2 - 4 milliequivalents/g (meq/g) (Mumpton, 1999).

The water content varies within certain limits depending upon the character of the exchange cations and conditions of crystallization. Under ordinary conditions, the water molecules completely fill the free volume of channels and voids in the zeolite structure (Tsitsishvili *et al.*, 1992). The channels in natural zeolites contain water that makes up 10-25% of their weight (Ouki *et al.*, 1994). Upon removal of water by heating to 350-400°C, small molecules can pass through entry channels, but larger molecules are excluded, which defines the “molecular sieve” properties of crystalline zeolites (Mumpton, 1999).

### **2.1.2. Abundance in the World and in Turkey**

Zeolites are known to be distributed rather unevenly in nature. Although there are approximately 40 known zeolites (Chamber of Mining Engineers of Turkey, 2003), only clinoptilolite, mordenite, phillipsite, chabazite, eronite, ferrierite, analcime occur in sufficient quantity and purity to be considered as exploitable natural resources (Ouki *et al.*, 1994), whereas some type of zeolites are very rare and sometimes limited to single occurrences (Tsitsishvili *et al.*, 1992). Extensive deposits of these zeolites occur in North and Central America, Europe, Russia, Japan, Korea and New Zealand (Chamber of Mining Engineers of Turkey, 2003). Clinoptilolite is the most widely distributed zeolite in nature and therefore huge occurrences of clinoptilolite are mined in many countries. Although, zeolites are widely distributed around the world, their use is often limited to the countries that have their own deposits (Biškup and Subotić, 2004).

Turkey has high reserves of zeolite deposits and large reserves of clinoptilolite can be found in Bigadiç, Balıkesir and Gördes, Manisa deposits (Chamber of Mining Engineers of Turkey, 2003). However, the only comprehensive survey has been performed for Gördes, Manisa deposit and it has been estimated that approximately 20 million tons of clinoptilolite are available (URL 1). In Bigadiç, Balıkesir deposit, approximately 500 million tons of clinoptilolite reserves have been detected. No comprehensive studies have been conducted for the other regions, however it has been estimated that about 50 billion ton zeolite reserves (analcim, chabazite, eronite and clinoptilolite being the most abundant one) are available in Turkey (URL 1).

### **2.1.3. Applications of Zeolites in Pollution Control**

Zeolites have been utilized for many applications in several fields such as pollution control, energy conservation, agriculture, etc. and recently zeolites have found increasing application in the field of pollution control owing to their low cost and

unique characteristics. The potential environmental applications of zeolites can be given as:

- Radioactive waste treatment (Abusafa and Yücel, 2002; Dyer and Zubair, 1998; Faghihian *et al.*, 1999; Gennaro *et al.*, 2003; Shahwan *et al.*, 2005; Um and Papelis, 2004),
- $\text{NH}_4^+$  removal from municipal wastewaters (Langella *et al.*, 2000; Cincotti *et al.*, 2001, Watanabe *et al.*, 2003; Sarioğlu, 2005; Du *et al.*, 2005; Ramos *et al.*, 2004),
- Heavy metal removal from industrial effluents (Ouki and Kavannagh, 1999; Mier *et al.*, 2001; Langella *et al.*, 2000; Cincotti *et al.*, 2001; Ćurković *et al.*, 1997; Blanchard *et al.*, 1984; Perić *et al.*, 2004; Semmens and Seyfarth, 1978),
- Air pollution control (Khulbe *et al.*, 1994; Axente *et al.*, 1983; Ackley *et al.*, 2003).

## 2.2. Use of Zeolites for Heavy Metal Removal

Structural properties of zeolites, together with their availability in large deposits, make them attractive in heavy metal removal. The usefulness of zeolites depends primarily on their ion exchange and adsorption properties, which are mainly attributed to their:

- relatively innocuous exchangeable ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) giving zeolites ion exchange abilities (Ćurković *et al.*, 1997; Mumpton, 1999)
- porous structure and availability of large volumes of internal space (Tsitsishvili *et al.*, 1992)
- specific chemical composition (Si/Al ratio, cation exchange capacity, etc.)
- various negatively charged surfaces (Trgo and Perić, 2003; Ersoy and Çelik, 2002)



Since, clinoptilolite is the most abundant natural zeolite that occurs in relatively large mineable deposits in sufficiently high purity in many parts of the world (Mumpton, 1978) and known to have high selectivity for certain cations (Semmens and Seyfarth, 1978; Zamzow *et al.*, 1990; Ouki and Kavannagh, 1999), it has been investigated by many researchers for removal of various heavy metal ions from wastewaters. The selectivity series obtained through various investigations for different heavy metal ions are summarized in Table 2.1. Depending on the metal ions tested and the origin of clinoptilolite, the selectivity series tend to show variations. A common finding, however, is the high selectivity of clinoptilolite for  $Pb^{2+}$ .

**Table 2.1.** Selectivity series for various heavy metal ions

Selectivity Series	Reference
$Pb^{2+} > Cd^{2+} > Cs^+ > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$	Zamzow <i>et al.</i> (1990)
$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$	Ouki and Kavannagh (1999)
$Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$	Panayotova and Velikov (2002)
$Pb^{2+} > Cr^{2+} > Fe^{2+} \geq Cu^{2+}$	Inglezakis and Grigoropoulou (2004)
$Pb^{2+} > NH_4^+ > Cu^{2+}, Cd^{2+}, Sr^{2+} > Zn^{2+} > Co^{2+}$	Blanchard <i>et al.</i> (1984)

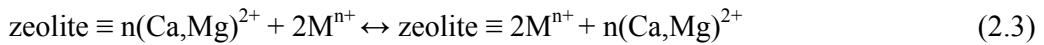
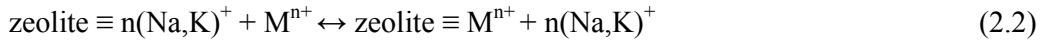
### 2.2.1. Removal Mechanisms

Several processes are involved in uptake of heavy metal ions from aqueous solutions by zeolite. These processes are mainly:

- ion exchange
- adsorption
- surface precipitation
- dissolution of clinoptilolite

where the last two mechanisms are indirectly involved in heavy metal uptake mechanism.

One of the significant mechanisms involved in heavy metal uptake is known as ion exchange (Mozgawa and Bajda, 2005; Trgo and Perić, 2003), which is defined as stoichiometric replacement of one equivalent of an ion in solid phase by equivalent of another ion in liquid phase (Petrus and Warchoń, 2003; Inglezakis *et al.*, 2004). Ion exchange reaction takes place between exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) located in zeolite structure and cations ( $\text{M}^{n+}$ ) in solution and can be given by (Benhammou *et al.*, 2005):



Ion exchange reaction is also referred as outer sphere complexation (Duff, 2002; Mozgawa and Bajda, 2005; Doula and Ioannou, 2003) and it does not involve formation of bonds between metal ions and zeolite surface, hence it is usually rapid and reversible and results in formation of unstable complexes (Doula and Ioannou, 2003). During ion exchange process, metal ions have to move through the pores and channels of zeolite and they have to replace exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) (Ćurković *et al.*, 1997). The diffusion of metal ions from surface to intraparticle sites are considered as the rate-controlling step in ion exchange (Helfferich, 1966; Trgo *et al.*, 2005). Diffusion is slower due to unavailability of some sites, which are occupied by framework cations, long diffusion paths and retardation due to interaction of metal ions with surface functional groups (i.e. electrostatic attraction, bond formation) (Helfferich, 1966).

Another mechanism involved in heavy metal uptake process is adsorption. As opposed to the situation in ion exchange, it involves formation of bonds, which are mainly covalent and also some combinations of covalent and ionic bonding (Doula and Ioannou, 2003; Duff, 2002). This mechanism is often referred to as chemisorption or inner sphere complexation (Doula and Ioannou, 2003; Mozgawa

and Bajda, 2005; Um and Papelis, 2004). Owing to formation of bonds, adsorption is slower and it is an irreversible process and therefore results in stable complex formation (Doula and Ioannou, 2003; Mozgawa and Bajda, 2005). Adsorption on zeolite particles can be simply defined as reaction of heavy metal species with surface functional groups forming a chemical bond. However, it is a complex process due to their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds and other imperfections on the surface (Perić *et al.*, 2004).

Outer sphere (i.e. ion exchange) and inner sphere (i.e. adsorption) complexation is interrelated such that as metal concentration increases on zeolite surface, metal ions bound to zeolite structure via outer sphere complexation are forced into internal sites and form inner sphere complexes (Doula and Ioannou, 2003). Fractions of amounts of heavy metal adsorbed to zeolite surface and exchanged with zeolite cations depend mainly on the type of heavy metal cation (Mozgawa and Bajda, 2005). Mozgawa and Bajda (2005) stated that for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , chemisorption predominates, whereas in the case of  $\text{Ni}^{2+}$  ion exchange prevails. Also, Panayotova and Velikov (2002) carried out desorption experiment to check how strongly heavy metal ions were immobilized by zeolite and observed that  $\text{Pb}^{2+}$  ions are strongly bound to zeolite and immobilization of the other heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ) is relatively weaker.

Increase in the amount of heavy metal cation retained in zeolite structure results in supersaturation of metal containing phases on zeolite surface (Duff, 2002). When the metal is concentrated on the zeolite, precipitation may occur at the zeolite surface or within the zeolite itself (Semmens and Seyfarth, 1798). As a result of surface precipitation, new solid phases occur on zeolite surface and distinct entities or aggregates are formed. Formation of precipitates in zeolite pores or surface leads to pore clogging, which results in reduced metal uptake by zeolite (Inglezakis *et al.*, 2003b; Inglezakis *et al.*, 2005).

Together with ion exchange, adsorption and surface precipitation, dissolution of zeolites is also a process involved in heavy metal uptake by zeolites. It can be defined as destruction of zeolite framework by detachment of central metal ions ( $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ ). Several factors exist that can influence dissolution of zeolite by facilitating detachment of the central metal ion (Doula *et al.*, 2002):

- presence of surface species, such as  $\text{Cl}^-$ ,
- increasing and decreasing surface protonation,
- presence of cations capable of forming inner sphere complexes.

At acidic pH range,  $\text{Al}^{3+}$  dissolution is higher, whereas  $\text{Si}^{4+}$  dissolution can occur under both acidic and basic conditions. Wingenfelder *et al.* (2005) observed that at pH values below 2,  $\text{Al}^{3+}$  concentration in solution was markedly increased, indicating dissolution of clinoptilolite. Also, Doula and Ioannou (2003) observed that at higher  $\text{Cu}^{2+}$  concentrations, higher  $\text{Si}^{4+}$  dissolution was realized owing to capability of  $\text{Cu}^{2+}$  forming inner sphere complexes. Furthermore, according to Trgo and Perić (2003), dissolution of zeolites leads to increase in number of potential sorption sites.

### **2.2.2. Factors affecting heavy metal removal**

Uptake of heavy metal cations from aqueous solutions by zeolite is affected by several factors, mainly:

- pH, temperature, presence of other contaminants in solution, characteristics of heavy metal cations as “solution specific factors”
- pretreatment applied to zeolite, pore clogging, particle size, mineral properties as “solid specific factors”

### ***Effect of pH***

pH has a significant impact on heavy metal removal by zeolites since it can influence metal speciation, integrity of zeolite and also H<sup>+</sup> ions are considered as competitive in ion exchange.

The speciation of any metal in solution, i.e. whether it is a free ion or bound to a ligand in a complex, has a significant impact on removal by zeolites. Selectivity of zeolite for heavy metal ions is influenced by type of metal complex that predominates at a particular solution pH (Ouki and Kavannagh, 1999). Furthermore, the kinetics of the removal may be adversely affected if a large complex is formed and this may reduce the effective exchange capacity of zeolite (Semmens and Seyfarth, 1978). Mier *et al.* (2001) emphasized the pronounced effect of pH on metal removal and stated that removal by ion exchange with natural zeolite is more effective when the metal species are cationic and they found out that Pb<sup>2+</sup> was completely removed from solution at near-neutral or acidic pH, but its removal efficiency decreased in basic pH range and Cd<sup>2+</sup> also exhibited similar behavior (Mier *et al.*, 2001).

pH of solution can also affect removal efficiency by affecting the integrity of zeolite. Clinoptilolite is known to partially degrade and lose its ion exchange capacity in alkaline media (Mier *et al.*, 2001). Also, clinoptilolite structure breaks down in highly acidic solutions (Tsitsishvili, 1992). On the other hand, as the solution pH increases, the number of negatively charged sites increases (Benhammou *et al.*, 2005), which can be given by the following reaction:



This favors the adsorption of metal cations and their hydroxides, forming surface metal complexes as described by the following reactions (Benhammou *et al.*, 2005; Doula *et al.*, 2002):



On the contrary, at low pH values protonation of neutral and negative surface hydroxyl groups takes place (Doula and Ioannou, 2003):



Therefore, at near-neutral or neutral pH values, the surface has a low net negative charge due to increase in positively charged surfaces (Doula and Ioannou, 2003; Mozgawa and Bajda, 2005). This results in decrease in ability of surface groups to form complexes with metal ions (Benhammou *et al.*, 2005; Mozgawa and Bajda, 2005). Although, net negative charge of surface is decreased, it was reported that clinoptilolite surface can maintain its negativity at neutral and even very acidic conditions (Ersoy and Çelik, 2002; Englert and Rubio, 2005). Similarly, Athanasiadis and Helmreich (2005) observed that clinoptilolite surface has a negative charge at pH 3, 5, 6 and 7.

In addition, at low pH values, since  $\text{H}^+$  ions are considered as competitive in ion exchange, heavy metal uptake is reduced correspondingly (Ouki and Kavannagh, 1999; Inglezakis *et al.*, 2003a). Generally, no significant changes were observed in  $\text{Pb}^{2+}$  uptake at pH range of 3-11 (Payne and Abdel-Fattah, 2004; Ponizovsky and Tsadilas, 2003; Ouki and Kavannagh, 1999; Um and Papelis, 2004). However, while Ali and El-Bishtawi (1997) observed a decrease in  $\text{Pb}^{2+}$  uptake with decreasing pH in the range of 2.5-4.5, almost stable  $\text{Pb}^{2+}$  uptake was observed by Inglezakis *et al.* (2003a) in the range of 2-4.

Zeolites are not only influenced by pH but also they are capable of affecting the solution pH. It was found out that clinoptilolite tends to neutralize the solution by acting as  $\text{H}^+$  acceptor or  $\text{H}^+$  donor (Rivera *et al.*, 2000; Ersoy and Çelik, 2002) as described by equations 2.4, 2.7 and 2.8. Ersoy and Çelik (2002) revealed that

clinoptilolite-deionized water suspensions at neutral, acidic and basic pH values exhibited a buffer pH around  $9 \pm 1$ . This case was also observed by Trgo and Perić (2003) and at all initial pH's examined (2-11) in deionized water-clinoptilolite suspensions pH became stable between 8 and 9.

### ***Effect of Temperature***

Ali and El-Bishtawi (1997) found out that removal of  $Pb^{2+}$  was independent of temperature in  $20^{\circ}C-35^{\circ}C$  range, whereas increasing temperature affected  $Ni^{2+}$  removal positively. On the other hand, Payne and Abdel-Fattah (2004) revealed that  $Pb^{2+}$  removal increases with temperature in  $23-45^{\circ}C$  range and also Bektaş and Kara (2004) obtained higher  $Pb^{2+}$  removal capacities in  $20-50^{\circ}C$  range. In addition, Malliou *et al.* (1994) found out that  $Pb^{2+}$  and  $Cd^{2+}$  uptake is favored at higher temperatures.

In general, heavy metal uptake is enhanced by increasing temperature due to activation of metal ions by enhancing adsorption at the coordination sites of zeolites (Babel and Kurniawan, 2003). Also, at higher temperatures ions become smaller due to their reduced hydration and their movement becomes faster (Inglezakis *et al.*, 2004), resulting in higher removal efficiencies.

### ***Presence of other contaminants***

Removal of heavy metal ions can be influenced by presence of:

- inorganics (anions and/or cations), and
- organics.

Anions can affect adsorption of heavy metal ions by direct or indirect ways (Doula and Ioannou, 2003). Presence of anions together with heavy metal ions leads to formation of metal-anion complexes, which may adsorb weakly or not at all to

zeolite surface, thus, resulting in reduced heavy metal uptake (Doula and Ioannou, 2003). As the concentration of anion increases, participation of cation in complexes gets higher. Heavy metal – anion complexes may possess negative charge, which, in turn, results in reduced heavy metal removal (Inglezakis *et al.*, 2003b; 2005). In addition, if very large complexes are formed, they are excluded by sieve action (Inglezakis *et al.*, 2003b).

Also, anionic species may interact with surface sites of zeolites leading to increase in surface negative charge (Doula and Ioannou, 2003). This, in turn, would probably enhance heavy metal removal by zeolites. In addition, complex formation with heavy metal ions following adsorption of anion to surface sites (Doula and Ioannou, 2003) is also one of the mechanisms involved in removal process.

Mier *et al.* (2001) observed that when anions are present, efficiency of  $Pb^{2+}$  and  $Cd^{2+}$  removal was significantly diminished. They revealed that presence of  $Cr^{6+}$  decreased  $Pb^{2+}$  removal efficiency due to formation of insoluble complexes, leading to precipitation and blockage of channels in zeolite structure (Mier *et al.*, 2001). Also, Inglezakis *et al.* (2003b) examined the effect of  $SO_4^-$  and  $HPO_4^{2-}$  on ion exchange of  $Cu^{2+}$ ,  $Fe^{3+}$  and  $Cr^{3+}$  on clinoptilolite and observed lower uptakes, especially for  $Cu^{2+}$ . On the other hand, Doula and Ioannou (2003) stated  $Cu^{2+}$  uptake was enhanced in the presence of  $Cl^-$  and  $NO_3^-$  due to possible increase in surface negative charge, which further results in a surface complexation mechanism.

Other than anions, cations present in solutions together with heavy metal ions can affect heavy metal removal due to competition between cations for the sites in clinoptilolite structure. Panayotova and Velikov (2002) investigated the influence of water hardness ( $Ca^{2+}$  and  $Mg^{2+}$  ions) on uptake of heavy metal ions and stated that  $Pb^{2+}$  uptake was not influenced by the presence of  $Ca^{2+}$  and  $Mg^{2+}$ , whereas lower uptakes were attained for  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  in the presence of  $Ca^{2+}$ . On the other hand, Petruzzelli *et al.* (1999) investigated that  $Pb^{2+}$  uptake in tap water and deionized water resulted different capacities, lower capacity was obtained for tap water in which other cations and also anions are present.



Among organic contaminants, phenol has been reported to hinder heavy metal removal by Mier *et al.* (2001). This was attributed to the formation of organometallic complexes that are generally too large to penetrate the ion exchange channels in zeolite (Mier *et al.*, 2001). Also, Turan *et al.* (2005) investigated that the removal of  $\text{Pb}^{2+}$  exhibits higher performance in the absence of acetic acid.

### ***Hydrated radii of heavy metals***

Hydration of cations is an important factor, which affects their selectivity, thus removal, by clinoptilolite. In Table 2.2, ionic and hydrated radii of certain cations are demonstrated. According to values presented in Table 2.2, high selectivity of clinoptilolite for  $\text{Pb}^{2+}$  can be attributed to its relatively small hydrated radius (Semmens and Seyfarth, 1978; Inglezakis *et al.*, 2004; Inglezakis *et al.*, 2003a; Petrus and Warchoł, 2003).

**Table 2.2.** Ionic and hydrated radii of certain cations (Semmens and Seyfarth, 1978)

Cation	Ionic radius (Å)	Hydrated ionic radius(Å)	Free energy of hydration (kcal/g-ion)
$\text{Cd}^{2+}$	1.03	4.26	-430.5
$\text{Cu}^{2+}$	0.82	4.19	-498.7
$\text{Pb}^{2+}$	1.32	4.01	-357.8
$\text{Zn}^{2+}$	0.83	4.30	-484.6
$\text{Na}^+$	0.98	3.58	-98.2

Hydrated ions occupy large spaces; therefore dimensions of channels in clinoptilolite structure should be large enough to allow passage of hydrated metal ions (Castaldi *et al.*, 2005; Semmens and Seyfarth, 1978). The ions with hydrated radii smaller than the channel size are able to move easily within the channel. Although, hydrated radii of ions are related to their preference by clinoptilolite, not only hydration energies can explain selectivity of clinoptilolite. Inglezakis *et al.* (2004) stated that formation

of precipitates, adsorption or fixation of metal complexes on surface sites could reduce uptake of heavy metal cations, lowering their selectivity even if their hydration energies are low.

### ***Effect of Pretreatment***

Pretreatment applied to natural material aims to improve its ion exchange ability. For this purpose, certain cations from the structure of the material are removed and more easily removable ones are located (Inglezakis *et al.*, 2001). As a result, material is converted to near-homoionic form with the increase of content in a single cation (Semmens and Martin, 1988). Natural clinoptilolite contains  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as exchangeable ions in its structure. Among these ions, selectivity of clinoptilolite for  $\text{Na}^+$  is the lowest (Stefanović *et al.*, 1996; Semmens and Martin, 1988). Therefore, increasing  $\text{Na}^+$  content of clinoptilolite by pretreatment improves its ion exchange ability.

To replace  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which are strongly held by clinoptilolite (Ćurković *et al.*, 1997), with  $\text{Na}^+$  ions, extensive exposure of material to high  $\text{Na}^+$  concentration is required (Semmens and Martin, 1988; Ćurković *et al.*, 1997). However, it is not possible to displace all other exchangeable ions from the structure with  $\text{Na}^+$  (Inglezakis *et al.*, 2005; Semmens and Seyfarth, 1978; Faghihian *et al.*, 1999; Langella *et al.*, 2000; Çulfaz and Yağız, 2004).

Pretreatment agents used for conversion of clinoptilolite to homoionic or near-homoionic form are mainly HCl (Kurama *et al.*, 2002; Spryskyy *et al.*, 2005), NaOH (Kang and Egashira, 1997; Ouki *et al.*, 1993; Panayatova, 2001) and NaCl being the most usually used one (Çulfaz and Yağız, 2004; Bektaş and Kara, 2004; Semmens and Seyfarth, 1988; Ouki *et al.*, 1993; Athanasiadis and Helmreich, 2005; Inglezakis *et al.*, 2001). Different concentration of NaCl solution used for pretreatment of natural material has been reported in literature. Inglezakis *et al.* (2001) investigated the effect of NaCl concentration on the effective capacity of the conditioned

clinoptilolite in fixed-bed reactors and found out that rising the concentration above 0.4 mol/L has practically no effect on the effective capacity. Most widely used concentration ranges, however, are 0.5-2 M NaCl (Çulfaz and Yağız, 2004; Ouki *et al.*, 1993; Athanasiadis and Helmreich, 2005; Ćurković *et al.*, 1997; Cincotti *et al.*, 2001; Top and Ülkü, 2004; Langella *et al.*, 2000; Trgo *et al.*, 2005).

Washing after pretreatment process is critical in order to remove excess NaCl entrapped within the zeolite structure (Ouki and Kavannagh, 1997). Inglezakis *et al.* (2001) emphasized that if no washing is applied, excess NaCl might diffuse out in the solution, leading to unexpected results during capacity determination. They also investigated the effect of washing water quality after conditioning process and concluded that use of tap water and deionized water give the same product quality. Some investigators studied the effect of the conditioning of natural zeolite on the crystal structure of zeolite and found out that NaCl conditioning has no effect on the crystal structure of the zeolites (Ouki *et al.*, 1993; Çulfaz and Yağız, 2004).

### ***Effect of Pore Clogging***

Pore clogging gives rise to decrease in heavy metal uptake by preventing heavy metal ions from entering into zeolite structure. Fine particles on zeolite surface and precipitation as a result of heavy metal accumulation on the surface are possible causes of pore clogging.

Inglezakis *et al.* (1999) stated that pore clogging, as a result of dust particles produced during grinding makes clinoptilolite surface and pore openings partially covered, caused slower ion exchange rates. Athanasiadis and Helmreich (2005) found out that dust particles produced during the grinding process makes up 8% (w/w) of clinoptilolite and suggested removal of fine fraction prior to any application of clinoptilolite. Also, surface precipitation most probably reduces the ion-exchange ability of the zeolites due to blockage of the pores (Inglezakis *et al.*, 2003b; 2005).

### ***Effect of Particle Size***

The study by Ouki *et al.*(1993) revealed that particle size had no significant effect on the zeolites exchange capability and they stated that uptake is not surface controlled and it is mainly ion exchange. Also, Malliou *et al.* (1994) investigated that removal of  $Pb^{2+}$  is increased by decreasing the particle size, but at equilibrium the difference is minimized. On the other hand, Ali and El-Bishtawi (1997) showed that the finer the zeolite particles used, the higher the metal ion removal.

### ***Properties of Mineral***

Specific chemical composition of zeolites (amount of exchangeable ions, Si/Al ratio), purity of natural material, channel dimensions are among the factors that affect heavy metal removal. According to Godelitsas and Armbruster (2003), the rather low Si/Al ratio and the consequently increased TCEC are advantageous for removing dissolved cations from aqueous solutions. In this sense, Ouki and Kavannagh (1999) demonstrated that chabazite is more efficient than clinoptilolite for metals removal owing to its larger window size that controls access to the pore system and higher  $Al^{3+}$  substitution of  $Si^{4+}$  providing a negative framework favorable to superior ion exchange capability (Ouki and Kavannagh, 1999).

In addition, the cation exchange capacity of clinoptilolite is markedly dependent on its original chemical composition and sample purity. For instance, Cincotti *et al.* (2001) studied clinoptilolite samples originated from the same source but having different purities (20% and 50%) and observed lower capacities with sample having low clinoptilolite content. Also, Gedik and İmamoğlu (2005) studied two different clinoptilolite sources having different purities and chemical compositions and compared them for their  $Cd^{2+}$  removal from aqueous solutions. They observed that higher capacity was attained for the sample having high clinoptilolite and  $Na^+$  ion content, even though its TCEC was lower.

### 2.3. Adsorption Isotherms

Adsorption isotherms define degree of equilibrium or distribution of dissolved substances between solution and solid phases at constant temperature. Equations that are often used to describe the experimental isotherm data are given as Langmuir, Freundlich and Brunauer, Emmet and Teller (BET) isotherms (Tchobanoglous and Burton, 1991). Among these, Langmuir and Freundlich models are widely used for heavy metal solutions and clinoptilolite systems (Altın *et al.*, 1998; Erdem *et al.*, 2004; Payne and Abdel-Fattah, 2004; Petrus and Warchoł, 2003; Trgo and Perić, 2004; Sheta *et al.*, 2003) since they are simple and capable of describing experimental results in wide ranges of concentrations (Altın *et al.*, 1998).

Langmuir adsorption isotherm can be defined as:

$$q = \frac{x}{m} = \frac{abC_e}{1 + bC_e} \quad (2.9)$$

where

$q = x/m$  = amount of adsorbate per unit weight of adsorbent (mass/mass)

$a, b$  = empirical constants

$C_e$  = equilibrium concentration of adsorbate in solution after adsorption (mass/volume)

Freundlich isotherm can be defined as follows:

$$q = \frac{x}{m} = K_f C_e^{1/n} \quad (2.10)$$

where

$q = x/m$  = amount of adsorbate per unit weight of adsorbent (mass/mass)

$K_f, n$  = empirical constants

$C_e$  = equilibrium concentration of adsorbate in solution after adsorption (mass/volume)

Langmuir model assumes identical adsorption sites, fixed capacity of adsorption, monolayer adsorption and uniform energies of adsorption at the surface. As opposed to Langmuir model, Freundlich isotherm assumes heterogeneous surface energies (Tchobanoglous and Burton, 1991). Other than Langmuir and Freundlich adsorption isotherms, there are several models in literature to define equilibrium data between heavy metals and clay minerals (Altın *et al.*, 1998; Trgo and Perić, 2004). New isotherms have been introduced to handle nonhomogeneous surfaces of clay minerals (Altın *et al.*, 1998). These are namely Langmuir-Freundlich, Redlich Peterson, Toth, Dubinin-Radushkevich and its modified form, Lineweaver-Burk, and Competitive Langmuir model (Altın *et al.*, 1998; Trgo and Perić, 2004; Benhammou *et al.*, 2005; Petrus and Warchoł, 2005). Among these models, Dubinin-Radushkevich and its modified form were found out to give better fits because they assume heterogeneous sorption (Trgo and Perić, 2004; Erdem *et al.*, 2004).

## **CHAPTER 3**

### **MATERIALS AND METHODS**

#### **3.1. Mineral Preparation and Characterization**

##### **3.1.1. Clinoptilolite Source**

The clinoptilolite sample used throughout the studies is originated from Bigadiç deposit located near Balıkesir in Western Anatolia. A few kg of sample was obtained from a bulk of the mineral from the Civil Engineering Department at METU, which received the sample in October, 2002. Throughout the studies, two types of clinoptilolite were used: (1) as-received clinoptilolite for which no pretreatment was applied (2) conditioned clinoptilolite.

##### **3.1.2 Sample Preparation**

###### ***Grinding and Sieving***

Samples were ground in the Mineral Processing Laboratory in the Department of Mining Engineering of METU. Then, these samples were sieved to different size fractions in Unit Operations Laboratory in the Department of Environmental Engineering at METU. Throughout the study, clinoptilolite samples with particle size of 0.15 – 0.80 mm were used.

### ***Pretreatment of Clinoptilolite***

After grinding and sieving, clinoptilolite samples were dried at 105°C for 24 hours to remove moisture and then stored in a desiccator. The clinoptilolite processed in this manner was named as “as-received clinoptilolite”.

To improve ion exchange ability of the mineral, Na<sup>+</sup> content of clinoptilolite is increased since selectivity of clinoptilolite for Na<sup>+</sup> is the lowest. The conditioned clinoptilolite was obtained by exposing as-received clinoptilolite samples to concentrated NaCl solution. For this purpose, 10 g clinoptilolite/250 mL of 2M NaCl solution was shaken at a constant temperature of 30°C and at 150 rpm speed for 1 day and 1 week period at a temperature controlled shaker. At the end of the conditioning period, samples were washed with deionized water until no Cl<sup>-</sup> was detected in washing water. Subsequently, the conditioned samples were dried at 105°C for 24 hours and sieved again to remove fine particles and stored in desiccator until further use. To determine the conditioning method used throughout the study, the efficiencies of 1-day and 1-week conditioned clinoptilolite samples was compared for removal of 100 mg/L Zn<sup>2+</sup>.

#### **3.1.3. Mineral Identity**

X-ray diffraction (XRD) analysis was performed on as-received clinoptilolite samples to verify the mineral identity. The analysis was carried out with Rigaku X-Ray Diffractometer (Ultima Model) in the Department of Metallurgical and Materials Engineering at METU.

#### **3.1.4. Mineralogical Composition**

Identification of the mineralogical contents of clinoptilolite sample was performed via microscopic examination by Prof. Dr.Cemal Göncüoğlu in the Department of



Geological Engineering at METU. The aim was to identify the purity of the sample and to identify other existing phases, i.e. impurities. The analysis was performed on as-received clinoptilolite sample only.

### **3.1.5. Chemical Composition**

Chemical composition was determined via two analyses: (1) Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) analysis on as-received and conditioned clinoptilolite samples and (2) X-ray Fluorescence (XRF) analysis on as-received clinoptilolite samples. SEM-EDS analysis was performed via JEOL JSM-6400 Scanning Microscope (NORAN) instrument in the Department of Metallurgical and Materials Engineering at METU, whereas XRF analysis was performed at MTA laboratories.

Elemental percentages of mainly  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by means of these analyses. As a result of XRF analysis, chemical composition of clinoptilolite was determined and based on this composition; theoretical cation exchange capacity and Si/Al ratio of clinoptilolite were estimated. Since water content of clinoptilolite could not be determined by means of SEM-EDS analysis, the results obtained in this manner were only used to interpret the changes occurred as a result of the conditioning process. By SEM-EDS analysis, 2000 times magnified picture of each sample was taken to be able to analyze the surfaces of different types of clinoptilolite and to designate the differences between as-received and conditioned clinoptilolite.

### **3.1.6. Physical Properties of Clinoptilolite**

The BET specific surface area and pore size distribution analysis of clinoptilolite in its as-received and conditioned form was determined via an automated gas sorption system (Quantachrome Autosorb Automated Gas Sorption System) using  $\text{N}_2$  gas as

adsorbate and density of as-received clinoptilolite sample was measured with helium pycnometer (Ultracycrometer 1000) in the Central Laboratory at METU.

### **3.2. Heavy Metal Removal Studies**

Heavy metal removal studies were composed of preliminary, equilibrium and kinetic studies. All heavy metal removal studies were performed in batch reactors with a solid to liquid ratio of 1g/100mL in sealed flasks placed in an orbital shaker at a speed of 125 rpm and at  $25^{\circ}\text{C}\pm 2^{\circ}\text{C}$  for equilibrium and kinetic studies, whereas at ambient temperature for preliminary studies. However, only for equilibrium studies for  $\text{Pb}^{2+}$  with conditioned clinoptilolite, the solid to liquid ratio was 0.5g/100mL. All reactors, except those used in kinetic studies, were run in parallel and control reactors without added clinoptilolite were prepared each time.

Solutions containing  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  were prepared by dissolving appropriate amounts of  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  salts in deionized water. The pH of solutions was adjusted by 0.1 N  $\text{HNO}_3$  and 0.1 N  $\text{NaOH}$ . pH and temperature were recorded at each sampling time during the studies in order to follow the pH change during the removal processes and to check the temperature of the solution.

Samples taken from test reactors for analysis were centrifuged (in preliminary and equilibrium studies) or filtered (in kinetic studies) for liquid-solid separation within a few minutes of sample withdrawal and then, they were acidified with concentrated  $\text{HNO}_3$  to bring  $\text{pH}<2$  and stored in a refrigerator at about  $4^{\circ}\text{C}$  until further analysis.

The samples containing heavy metals were diluted with acidified deionized water to the concentration ranges appropriate for measurements by atomic absorption spectrometry (AAS). The dilutions and subsequent measurements were repeated several times to ensure the accuracy of the results.

### 3.2.1. Preliminary Studies

In the preliminary studies, as-received clinoptilolite samples were used in order to investigate the effect of initial solution pH on the heavy metal removal. Additionally, these studies were performed to determine the equilibration period for clinoptilolite-heavy metal solution interactions. The equilibrium and kinetic studies were performed under the conditions specified by these preliminary studies.

For  $Zn^{2+}$ , pH of solutions containing 30 mg/L metal was adjusted to 4, 5 and 6. At different contact times (0-72 hours), the process was interrupted and samples were taken for analysis of remaining  $Zn^{2+}$  in the liquid phase. For  $Pb^{2+}$ , pH of solutions containing 250 mg/L metal was adjusted to 3, 4, 4.5, 5 and 5.5 for 48 hours and as in the case for  $Zn^{2+}$ , samples were taken for analysis at different contact times. The volume of samples taken for analysis was no more than 10% of the total volume.

### 3.2.2 Equilibrium Studies

Equilibrium studies were carried out with both as-received and conditioned clinoptilolite in order to find the maximum removal capacity of the sample for  $Zn^{2+}$  and  $Pb^{2+}$ . The initial pH of solutions was adjusted to 4 and equilibrium studies were performed for 48 hours for both metal ions. The selection of initial pH and equilibration period is discussed in Section 4.3.1. Initial concentration ranges tested for  $Zn^{2+}$  and  $Pb^{2+}$  throughout the equilibrium studies are summarized in Table 3.1.

**Table 3.1.** Targeted initial concentration ranges for equilibrium studies

	as-received clinoptilolite	conditioned clinoptilolite
$Zn^{2+}$ (mg/L)	5-400	10-2000
$Pb^{2+}$ (mg/L)	100-5000	100-10000

At the end of the equilibration period (48 hours), aside from  $Zn^{2+}$  and  $Pb^{2+}$ , exchangeable cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) expected to be released from clinoptilolite structure were also analyzed in the liquid phase.

### 3.2.3. Kinetic Studies

The lowest concentration at which maximum metal removal capacity observed is used in kinetic studies. The concentrations tested are given in Table 3.2.

**Table 3.2.** Targeted initial concentrations for kinetic studies

	as-received clinoptilolite	conditioned clinoptilolite
$Zn^{2+}$ (mg/L)	150	400
$Pb^{2+}$ (mg/L)	1000	-

Kinetic studies were carried out with 10 g clinoptilolite/1000 mL solution and the sampling times were 2, 5, 10, 20, 30, 60 minutes and 3, 6, 10, 24 and 48 hours. At each sampling, 10 mL of sample was drawn from the system and analyzed for  $Zn^{2+}$  or  $Pb^{2+}$  and  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  in the liquid phase. The initial pH of solutions was adjusted to 4 as determined by preliminary studies, the results of which are described in Section 4.3.1.

Kinetic studies were carried out under two conditions: pH-uncontrolled and pH-controlled. In pH-uncontrolled conditions, after an initial pH adjustment (to pH=4) the pH of clinoptilolite-heavy metal solution system was not controlled. Due to the nature of clinoptilolite – heavy metal aqueous system, the pH increases as metal removal takes place. In pH-controlled kinetic studies, pH-control was accomplished by the use of Cole Parmer pH/ORP Controller (Model 5656-00) in order to keep the solution pH at around 4 and nevertheless, pH of solution was controlled with a pH-meter, which was calibrated before measurements. 0.1 N  $HNO_3$  used for pH

adjustment was placed in a 100-mL graduated cylinder so that the amount of acid used at each time interval could be recorded (Table D.1 in Appendix D).

Total sampling volume throughout the kinetic studies was no more than 10% of the total volume and change in solution volume with each sampling was taken into account during calculations. Also, the amount of HNO<sub>3</sub> added during pH-controlled kinetic studies was included in the calculations.

### **3.3. Deionized Water-Clinoptilolite Interactions**

Equilibrium and kinetic studies were also carried out with deionized water and clinoptilolite with an initial pH adjustment to investigate the behavior of clinoptilolite in a medium free from heavy metal ions and also to be able to explain dissolution of clinoptilolite. For this purpose, Si<sup>4+</sup>, Al<sup>3+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in liquid phase were analyzed after 48 hours contact time and pH and temperature were recorded.

### **3.4. Analytical Techniques**

Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> ions were analyzed by using flame atomic absorption spectrometry (ATI Unicam 929) and Na<sup>+</sup> and K<sup>+</sup> ions were determined on a flame photometer (Jenway Model PFP7). In all these measurements, standard solutions used for calibration of these devices were prepared by 1000 mg/L reference solutions of corresponding ions and during the measurements, analytical methods described in Standard Methods (APHA, 1989) were followed (sample calibration curves are given in Figures A.1-A.6 in Appendix A). Cl<sup>-</sup> was detected by Argentometric method as described by Standard Methods (APHA, 1989). SiO<sub>2</sub> concentrations were measured spectrophotometrically by HACH DR/2400.

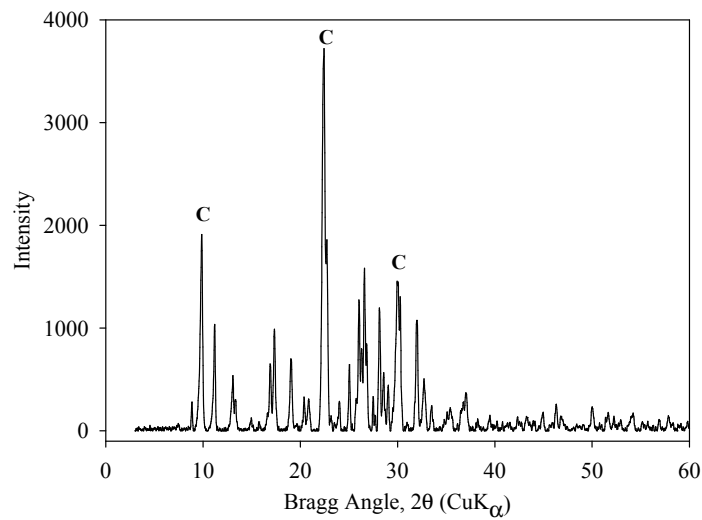
## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1. Mineral Characterization

##### 4.1.1. Mineral Identity and Mineralogical Composition

X-ray diffraction (XRD) pattern of the sample used throughout the studies is demonstrated in Figure 4.1. Characteristic clinoptilolite peaks in the XRD pattern are indicated on the figure. Microscopic examination of the samples yielded a clinoptilolite content of 80%, with 13% quartz and 5-6% biotite as the other phases.



**Figure 4.1.** X-ray diffraction (XRD) pattern of Bigadiç clinoptilolite

#### 4.1.2. Chemical Composition

Chemical composition analysis were performed via (1) X-ray fluorescence (XRF) as well as (2) Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The difference between these two methods is that water content of samples could not be determined by means of the SEM-EDS analysis, whereas a detailed analysis could be performed via XRF. Therefore, the chemical composition results obtained via SEM-EDS analysis were only used in order to interpret the changes occurred as a result of conditioning.

In Table 4.1, the chemical composition of the sample obtained via XRF analysis is presented. Si/Al ratio of the sample has been calculated as 5.22, which is within typical limits (5-6) for clinoptilolite (Tsitsishvili, 1992).

**Table 4.1.** Chemical composition of as-received Bigadiç clinoptilolite

Oxides	%(w/w)
SiO <sub>2</sub>	71.83
Al <sub>2</sub> O <sub>3</sub>	11.68
Fe <sub>2</sub> O <sub>3</sub>	1.15
CaO	3.39
MgO	1.25
Na <sub>2</sub> O	0.43
K <sub>2</sub> O	3.70
MnO	0.03
TiO <sub>2</sub>	0.07
H <sub>2</sub> O	2.60
Total	96.01

According to Table 4.1, theoretical cation exchange capacity (TCEC) of the material is 2.75 meq/g, which is calculated as the sum of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> cation content of clinoptilolite. The contribution of each exchangeable ion to the theoretical exchange capacity are 0.14 meq/g Na<sup>+</sup> (5%), 0.79 meq/g K<sup>+</sup> (29%), 1.21 meq/g Ca<sup>2+</sup> (44%) and 0.62 meq/g Mg<sup>2+</sup> (23%). Also, TCEC can be calculated from Al<sup>3+</sup> content of clinoptilolite and it is calculated as 2.4 meq/g, which is lower than the TCEC

calculated as sum of exchangeable ions. This indicates that impurities contain Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>. The sample is poor in Na<sup>+</sup> content and this case has been observed for other Bigadiç clinoptilolite samples in the literature (Çulfaz and Yağız, 2004; Bektaş and Kara, 2004; Abusafa and Yücel, 2002; Toprak and Girgin, 1999).

SEM-EDS was used to analyze the structure and the chemical composition of clinoptilolite samples. The results of chemical compositions of as-received and conditioned clinoptilolite samples obtained via SEM-EDS analysis are summarized in Table 4.2. The chemical composition obtained for as-received sample with SEM-EDS analysis is mostly in agreement with that obtained from XRF. The differences between two chemical composition results (Table 4.1 and 4.2) are mainly due to the incapability of determining water content by means of SEM-EDS analysis and possibly due to the mineral heterogeneity.

**Table 4.2.** Chemical composition of as-received and conditioned Bigadiç clinoptilolite samples obtained via SEM-EDS analysis

	as-received	1-day conditioned	1-week conditioned
Oxides	%(w/w)	%(w/w)	%(w/w)
SiO <sub>2</sub>	75.06	77.56	77.88
Al <sub>2</sub> O <sub>3</sub>	11.43	14.47	12.44
Fe <sub>2</sub> O <sub>3</sub>	4.56	1.49	1.51
CaO	2.91	1.46	0.93
MgO	1.04	0.94	0.68
Na <sub>2</sub> O	0.59	3.42	4.15
K <sub>2</sub> O	4.43	2.23	0.93
Total	100.02	101.57	98.52

According to the chemical composition results presented in Table 4.2, the contribution of each exchangeable ion to the TCEC of as-received and conditioned samples is calculated and the results are given in Table 4.3.



**Table 4.3.** Contribution of each exchangeable ion to the theoretical cation exchange capacity

	Exchangeable ions (eq/eq %)				TCEC (meq/g)
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	
as-received	7	35	39	19	2.69
1 day conditioned	43	18	20	18	2.56
1 week conditioned	61	9	15	15	2.21

The TCEC of as-received clinoptilolite according to SEM-EDS analysis is 2.69 meq/g and it is close to the value calculated from XRF results (2.75 meq/g). The cation exchange capacities calculated for 1-day and 1-week conditioned samples are 2.56 meq/g and 2.21 meq/g, respectively. Theoretically, the TCEC of clinoptilolite should not change as a result of conditioning, since it is independent of any pretreatment applied (Inglezakis *et al.*, 2001). However, a decrease is observed in the capacity of 1-week conditioned clinoptilolite, which can be due to destruction of the framework during conditioning that could lead to destruction of sites where exchangeable cations are located and also dissolution of soluble impurities containing exchangeable cations. When considering the effect of Cl<sup>-</sup> ions on dissolution as stated by Doula *et al.* (2002), it is an expected outcome.

From the results in Table 4.3, it is clear that Na<sup>+</sup> content of clinoptilolite has been increased significantly by displacing the other exchangeable cations from clinoptilolite structure. The results indicate that it was very difficult to displace Mg<sup>2+</sup> ions from the clinoptilolite structure. As a result of conditioning, Ca<sup>2+</sup> and K<sup>+</sup> content of as-received clinoptilolite is decreased. At the end of 1 week conditioning period, a further decrease in Ca<sup>2+</sup> and K<sup>+</sup> is observed. However, Na<sup>+</sup> ions, still, were incapable of displacing Mg<sup>2+</sup> from structure since Mg<sup>2+</sup> ions are strongly bonded to clinoptilolite structure.

The pictures of as-received and conditioned clinoptilolite samples obtained via SEM-EDS analysis are presented in Figure 4.2. Visual examination of clinoptilolite structure before and after conditioning process reveals that surface and pore openings of as-received clinoptilolite samples were covered with dust particles which are

produced during grinding. Clogging of pores by dust particles would result in a lower ion exchange capacity and slower kinetics (Inglezakis *et al.*, 1999; 2003b; 2005; Athanasiadis and Helmreich, 2005) preventing ions from entering into clinoptilolite structure or making diffusion through pores difficult. Comparison of surface structure of as-received and conditioned clinoptilolite samples demonstrates that as a result of conditioning dust particles were removed and clinoptilolite surface was cleaned up, and the clinoptilolite crystal structure and openings of pores became apparent. Besides the increase of Na<sup>+</sup> content via conditioning, it is shown that the removal of dust particles also enhances performance of clinoptilolite in heavy metal removal (Inglezakis *et al.*, 1999).

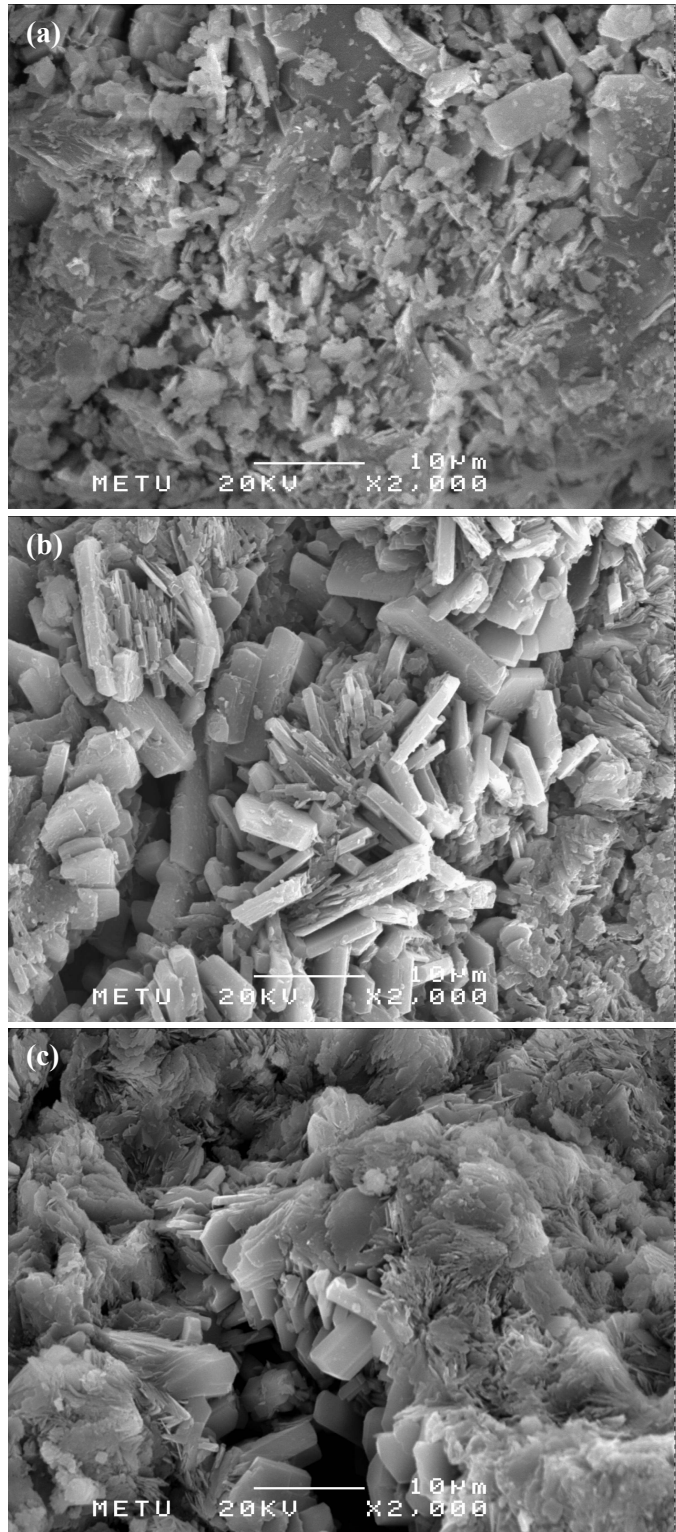
#### 4.1.3. Physical Properties of Clinoptilolite

The physical properties of the clinoptilolite samples are given in Table 4.4.

**Table 4.4.** Physical properties of as-received and conditioned Bigadiç clinoptilolite

	as-received	conditioned
BET specific surface area (m <sup>2</sup> /g)	13.4	11.9
Average diameter of pores (Å)	17.0	17.2

The specific surface area of as-received clinoptilolite (13.4 m<sup>2</sup>/g) is slightly higher than that of conditioned clinoptilolite (11.9 m<sup>2</sup>/g). Presence of dust particles in as-received samples can be responsible for the slightly higher surface area. Also, the average pore diameter of as-received samples stays almost unchanged as a result of conditioning. In addition, the density of as-received clinoptilolite is found as 2.242 g/cm<sup>3</sup>. The results given in Table 4.4 and the density of clinoptilolite are comparable with the ones reported in literature for Bigadiç clinoptilolite (Bektaş and Kara, 2004; Abusafa and Yücel, 2002; Çulfaz *et al.*, 1995).



**Figure 4.2.** SEM-EDS pictures of (a) as-received (b) 1-day and (c) 1-week conditioned clinoptilolite samples

## 4.2. Determination of the Method for Conditioning

To determine the method to be used throughout the study, the removal efficiencies of  $Zn^{2+}$  from a solution containing 100 mg/L  $Zn^{2+}$  was investigated for as-received, 1-day and 1-week conditioned clinoptilolite samples. The removal efficiencies and amount of exchangeable ions released from clinoptilolite structure are given in Table 4.5. It is obvious that conditioning process enhances the removal of  $Zn^{2+}$  from solution with an increase in removal efficiency from 44% to 82% and 83% for 1-day and 1-week conditioned clinoptilolite, respectively. As a result of  $Zn^{2+}$  uptake by as-received clinoptilolite,  $Na^+$  ions released from the structure only constitutes 14.8% of exchangeable ions, whereas in the case with conditioned clinoptilolite  $Na^+$  released to solution is increased to 92.0% and 96.7% for 1-day and 1-week conditioned samples, respectively.

**Table 4.5.** Exchangeable ions in solution for 100 mg/L  $Zn^{2+}$  removal with as-received, 1-day and 1-week conditioned clinoptilolite

Zn <sup>2+</sup> removal		Exchangeable ion amounts in solution (eq/eq %)				Σ(Na <sup>+</sup> +K <sup>+</sup> +Ca <sup>2+</sup> +Mg <sup>2+</sup> ) (meq/g)
Removal efficiency (%)	meq/g	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	
44	0.140	14.8	3.5	66.3	15.4	0.181
82	0.276	92.0	0.6	1.3	6.1	0.310
83	0.284	96.7	0.6	1.2	1.5	0.330

Results given in Table 4.5 show that while the amount of  $Na^+$  is increased in the solution, there is a pronounced decrease in the amount of  $Ca^{2+}$  released. This decrease is due to displacement of  $Ca^{2+}$  ions by  $Na^+$  during conditioning and removal of impurities, which previously might have resulted in high  $Ca^{2+}$  concentration in solution. The chemical composition results in Table 4.3 indicate no significant decrease in  $Mg^{2+}$  content of clinoptilolite by 1-day conditioning. Therefore, detection of high amounts of  $Mg^{2+}$  in solution can be attributed to presence of impurities in as-

received samples and also it can be concluded that  $Zn^{2+}$  ions can replace  $Mg^{2+}$  ions from clinoptilolite structure, whereas  $Na^+$  ions can not. Also, for 1-week conditioned clinoptilolite a further decrease in  $Mg^{2+}$  released from the structure is observed.

Although  $Na^+$  content of 1-week conditioned clinoptilolite is higher (Table 4.3 and 4.5), there is almost no difference between the  $Zn^{2+}$  removal efficiencies with 1-day and 1-week conditioned clinoptilolite. Therefore, 1-day conditioned clinoptilolite was selected to be used in the subsequent experiments.

### **4.3. Heavy Metal Removal Studies**

#### **4.3.1. Preliminary Studies**

Preliminary experiments for  $Zn^{2+}$  were performed with 30 mg/L initial concentration at initial pH's of 4, 5 and 6. These values have been selected because pH values lower than 4 would induce protonation of clinoptilolite binding sites (Doula and Ioannou, 2003) and high pH values would lead to precipitation of metal ions (Schnoor, 1996). The change of  $Zn^{2+}$  concentration with time under different initial pH values are given in Figure 4.3a. Since no significant change in metal concentration was observed between 48<sup>th</sup> and 72<sup>nd</sup> hours (Figure 4.3a) and also depending on the results of earlier studies where equilibrium was not reached between 24<sup>th</sup> and 48<sup>th</sup> hours, the equilibration period for  $Zn^{2+}$  removal is determined to be 48 hours.

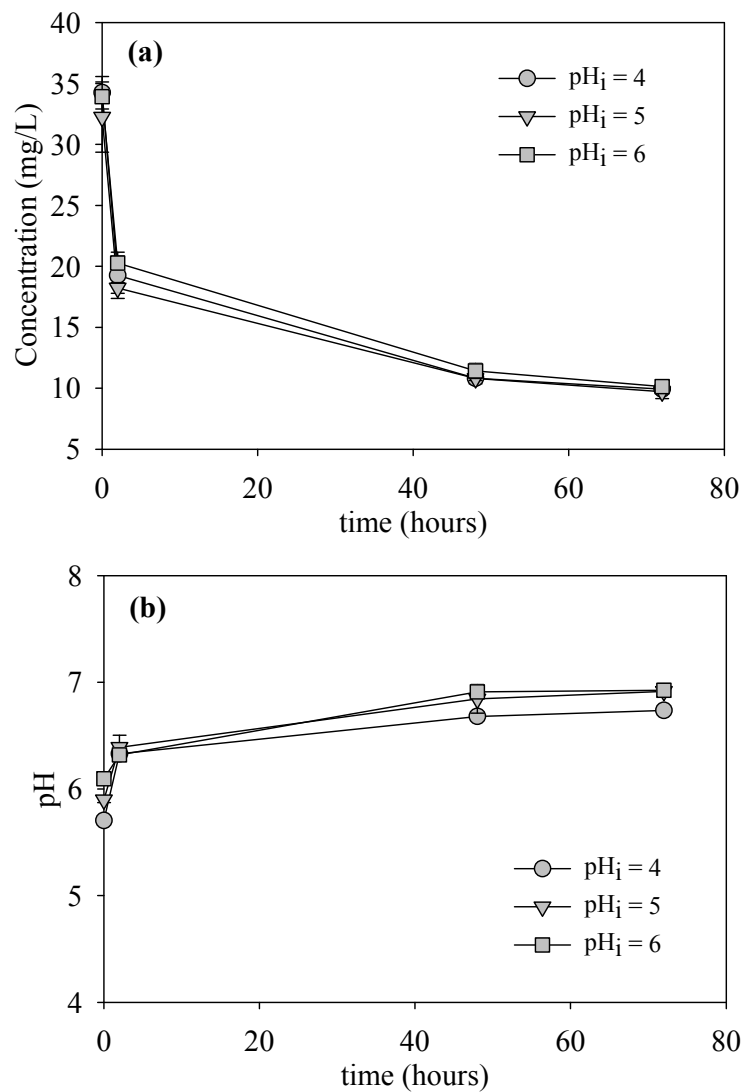
The results of preliminary studies performed with 250 mg/L  $Pb^{2+}$  initial concentration with different initial pH values (3, 4, 4.5, 5 and 5.5) are given in Figure 4.4a. At the end of 24 hours almost complete removal ( $\approx 100\%$ ) is achieved for all initial pH values. However, equilibration period is selected as 48 hours to ensure equilibrium at higher  $Pb^{2+}$  concentrations.

For both metals tested, results indicate that metal removal is independent of solution pH at pH ranges tested. For  $Zn^{2+}$ , the removal efficiencies are 75, 76 and 74 % for initial pH of 4, 5 and 6, respectively; whereas for  $Pb^{2+}$  greater than 99% removal is observed for all initial pH's examined. Therefore, three important factors were taken into account during initial pH determination, which are:

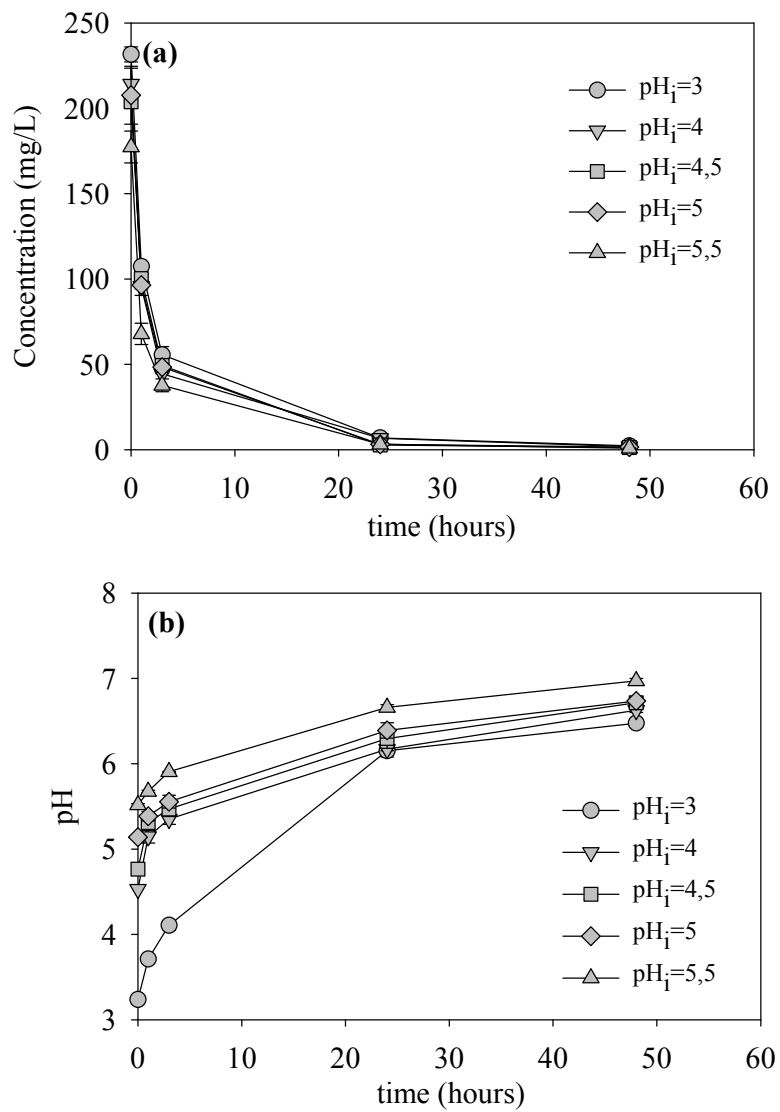
- pH of the solution should be high enough to prevent competition of  $H^+$  ions with metal ions for the same exchange sites,
- pH should be low enough to avoid precipitation of metal-hydroxides,
- pH should be acidic, considering the real-life application of this technology, since metal bearing wastewaters are usually acidic.

Therefore, for both  $Pb^{2+}$  and  $Zn^{2+}$ , the initial pH value was chosen as 4. In literature, for heavy metal-clinoptilolite interactions, low initial pH values were recorded and mainly pH value around 4 was studied (Inglezakis *et al.*, 2004; Inglezakis and Grigoropoulou, 2003; Ouki *et al.*, 1993; Ponizovsky and Tsadilas, 2003; Ćurković *et al.*, 1997).

The change of pH with time under different initial pH values for  $Zn^{2+}$  and  $Pb^{2+}$  are given in Figures 4.3b and 4.4b, respectively. pH values during removal studies increased continuously and the equilibrium values were between 6,7 – 7 and 6,5 – 7 for  $Zn^{2+}$  and  $Pb^{2+}$ , respectively. This increase in pH can be attributed to  $H^+$  ion uptake by clinoptilolite or clinoptilolite surface protonation. For  $Zn^{2+}$ , pH values reached higher values when compared to those of  $Pb^{2+}$ . This is due to different initial heavy metal concentrations used in the studies and high affinity of clinoptilolite towards  $Pb^{2+}$  ions. Therefore, initially  $Pb^{2+}$  ions are preferred over  $H^+$  ions and when  $Pb^{2+}$  ions were depleted,  $H^+$  ions are taken into the clinoptilolite structure (i.e. competition between  $Pb^{2+}$  and  $H^+$  ions).



**Figure 4.3.** Preliminary studies for Zn<sup>2+</sup> under different initial pH values (a) change of concentration with time, (b) change of pH with time



**Figure 4.4.** Preliminary studies for  $Pb^{2+}$  under different initial pH values (a) change of concentration with time, (b) change of pH with time



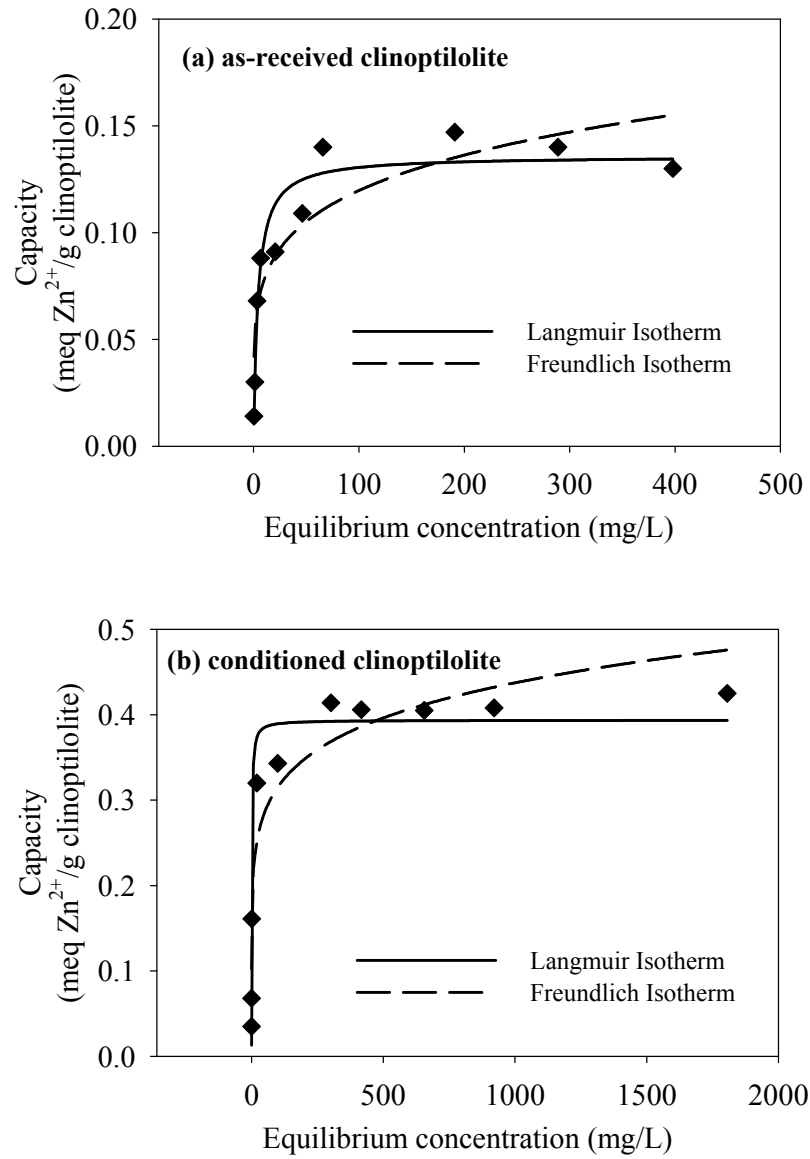
### 4.3.2. Equilibrium Studies

#### *Maximum Effective Capacities*

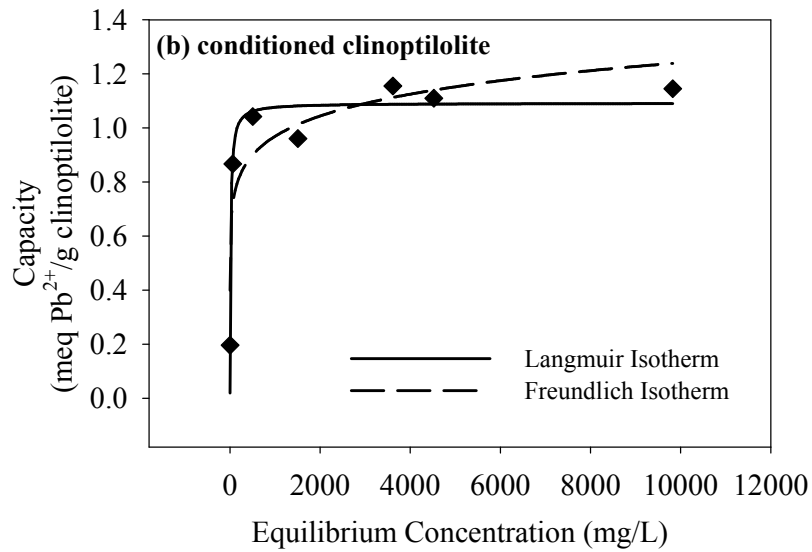
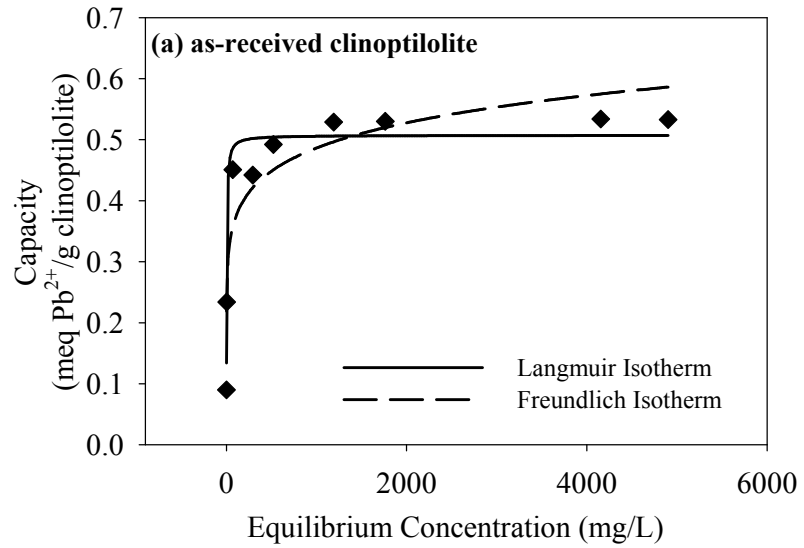
To determine maximum effective capacities, equilibrium studies were performed with as-received and conditioned clinoptilolite. Different initial concentrations of  $Zn^{2+}$  and  $Pb^{2+}$  were tested at initial pH of 4 and for 48 hours equilibration period. The metal ions retained in clinoptilolite structure were determined by calculating the difference between initial and equilibrium concentration of metal ions in aqueous phase (a sample calculation is given in Appendix C). The experimental equilibrium results of  $Zn^{2+}$  and  $Pb^{2+}$  uptake are given in Figures 4.5 and 4.6, respectively (corresponding data is given for each isotherm in Tables B.1-B.4 in Appendix B). Also, the results have been non-linearly fitted to Langmuir and Freundlich adsorption isotherm models and the fitting of these models to experimental data points are demonstrated in figures. Goodness of fit of experimental results to Langmuir and Freundlich isotherm models are given in Table 4.6.

**Table 4.6.** Goodness of fit of experimental results to Langmuir and Freundlich isotherm models and isotherm parameters

Parameters and goodness of fit	$Zn^{2+}$		$Pb^{2+}$	
	as-received	conditioned	as-received	conditioned
	Langmuir			
a	0.14	0.39	0.51	1.10
b	0.24	0.93	0.33	0.07
$r^2$	0.94	0.96	0.94	0.92
	Freundlich			
$K_f$	0.05	0.16	0.22	0.46
n	5.34	7.02	8.52	9.30
$r^2$	0.84	0.91	0.83	0.86



**Figure 4.5.** Fitting of Langmuir and Freundlich isotherm models to experimental data points for Zn<sup>2+</sup> removal with (a) as-received (b) conditioned clinoptilolite



**Figure 4.6.** Fitting of Langmuir and Freundlich isotherm models to experimental data points for Pb<sup>2+</sup> removal with (a) as-received (b) conditioned clinoptilolite

Experimental data points best fit to Langmuir isotherm model yielding the following maximum capacities:

- For  $Zn^{2+}$ : 0.14 meq/g (as-received) and 0.39 meq/g (conditioned)
- For  $Pb^{2+}$ : 0.51 meq/g (as-received) and 1.10 meq/g (conditioned)

The maximum effective capacities attained for  $Zn^{2+}$  and  $Pb^{2+}$  demonstrate that clinoptilolite shows very different capacities towards the two metal ions. It is apparent that capacity of clinoptilolite for  $Pb^{2+}$  is higher. Conditioning significantly increases the capacity of clinoptilolite for  $Zn^{2+}$  and  $Pb^{2+}$ . With the conditioning, the effective capacity of clinoptilolite is increased by more than two fold for  $Zn^{2+}$  (179%) and  $Pb^{2+}$  (116%). Even though  $Zn^{2+}$  removal capacity is almost three times increased, it is still low when compared to  $Pb^{2+}$  removal capacity.

In literature, there are many studies reporting the effective capacity of clinoptilolite in its as-received and conditioned form for  $Zn^{2+}$  and  $Pb^{2+}$ , though most are focused on  $Pb^{2+}$  removal. A summary of these studies and the results obtained from this study are presented in Table 4.7 for comparison purposes. The capacities reported in literature are generally different from each other, even though they belong to clinoptilolite originated from the same source due to heterogeneity of mineral, different chemical composition and purity of clinoptilolite, as well as experimental conditions at which removal was performed.

The effective capacities obtained from this study are comparable with the ones in literature. The capacity of as-received clinoptilolite for  $Zn^{2+}$  obtained in this study (0.14 meq/g) is similar to some of the studies given in Table 4.7, whereas for conditioned clinoptilolite, the capacity obtained from this study (0.39 meq/g) is generally superior. For  $Pb^{2+}$ , the capacity obtained in this study is generally comparable to those listed in the table.

In literature, studies exist in which clinoptilolite originated from Balıkesir – Bigadiç was used for metal removal. Çulfaz and Yağız (2004) and Bektaş and Kara (2004) have studied  $Pb^{2+}$  removal with conditioned clinoptilolite. The chemical composition and clinoptilolite content of samples are similar to those used in this study. Bektaş and Kara (2004) found the capacity of clinoptilolite as 1.07-1.6 meq/g at 20°C-50°C temperature range, which is comparable with the result obtained in this study (1.1 meq/g) if the results obtained at similar temperatures are compared. The capacity obtained in Çulfaz and Yağız's (2004) study is 1.74 meq/g, which is superior to the capacity obtained in this study. This can be attributed to conditioning procedure they applied, where they treated clinoptilolite for 2 weeks with renewal of NaCl solution.

**Table 4.7.** Summary of literature on capacity of as-received and conditioned clinoptilolite for Zn<sup>2+</sup> and Pb<sup>2+</sup>

Researchers	Clinoptilolite Source	Zn <sup>2+</sup> (meq/g)		Pb <sup>2+</sup> (meq/g)	
		As-received	Conditioned	As-received	Conditioned
Cincotti <i>et al.</i> (2001)	Sardinia, Italy	0.14	0.25	0.16,0.31	0.62
Athanasiadis and Helmreich (2005)	Greece	0.098, 0.135	0.21,0.24	-	-
Erdem <i>et al.</i> (2004)	Gördes, Manisa	0.27	-	-	-
Top and Ülkü (2004)	Gördes, Manisa	-	0.87	-	-
Perić <i>et al.</i> (2004)	Donje Jesenje, Croatia	0.4	-	0.86	
Trgo and Perić (2003)	Donje Jesenje, Croatia	-	0.33	-	-
Ćurković <i>et al.</i> (1997)	Donje Jesenje, Croatia	-	-	0.76	0.82,0.88
Kesraoui-Ouki <i>et al.</i> (1993)	American Colloid Co.	-	-	1.57	1.69, 1.93
Inglezakis <i>et al.</i> (1999)	Northern Greece	-	-	0.94	1.95
Mozgawa and Bajda (2005)	Poland	-	-	0.218	-
Ponizovsky and Tsadilas (2003)	Bulgaria	-	-	0.72	-
Malliou <i>et al.</i> (1994)	Greece	-	-	-	1.270-1.312
Ali and El-Bishtawi (1997)	Jordan	-	-	-	1.31,1.09
Petruzzelli <i>et al.</i> (1999)	California	-	-	-	0.8-1.1
Langella <i>et al.</i> (2000)	Sardinia, Italy	-	-	-	1.69
Çulfaz and Yağız (2004)	Bigadiç, Balıkesir	-	-	-	1.74
Bektaş and Kara (2004)	Bigadiç, Balıkesir	-	-	-	1.07-1.6
<i>This study</i>	<i>Bigadiç, Balıkesir</i>	<i>0.14</i>	<i>0.39</i>	<i>0.51</i>	<i>1.1</i>

### *Equilibrium pH values*

Throughout the equilibrium experiments, pH of the solutions continuously increased and it was observed as a general trend that as equilibrium heavy metal concentration increased, equilibrium pH of solution decreased. Figures 4.7 and 4.8 represent the change of pH with equilibrium concentrations for  $Zn^{2+}$  and  $Pb^{2+}$ , respectively. The results show that as the clinoptilolite reaches its maximum capacity for  $Zn^{2+}$  or  $Pb^{2+}$ , no major changes occur in equilibrium pH, whereas at lower equilibrium metal concentrations, where the metal removal is lower than the maximum capacity, higher equilibrium pH values are observed when compared to the initial.

The increase in pH values throughout the equilibrium experiments was attributed to  $H^+$  exchange with clinoptilolite exchangeable ions as well as surface protonation. They can shortly be described as follows:

➤  $H^+$  exchange:



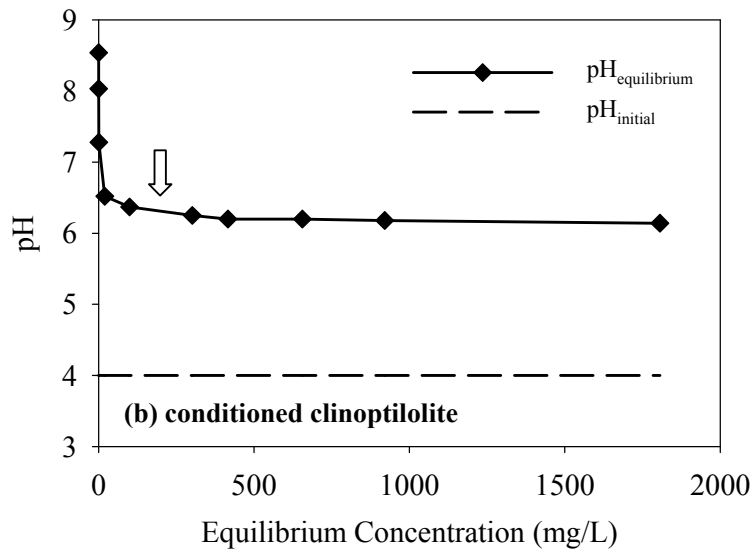
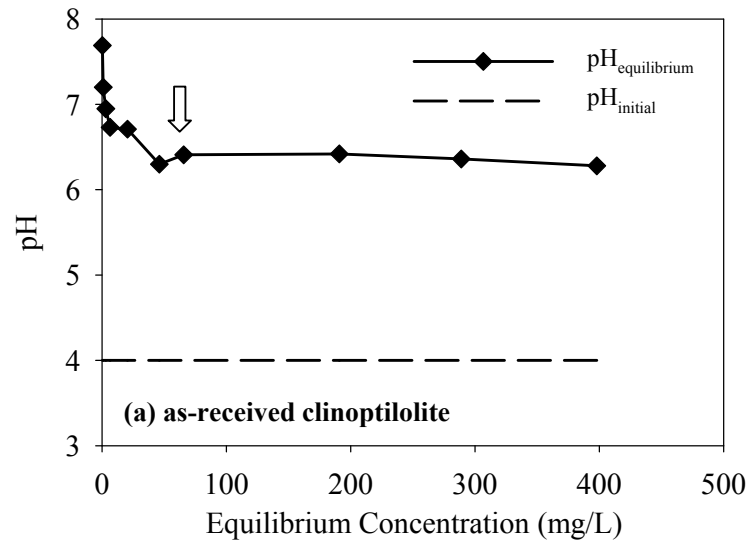
➤ Surface protonation (Doula and Ioannou, 2003):



The reason for relatively low equilibrium pH values for high initial heavy metal ion concentrations can be explained by hydrolysis of heavy metal ions.

➤ Hydrolysis (Schnoor, 1996):

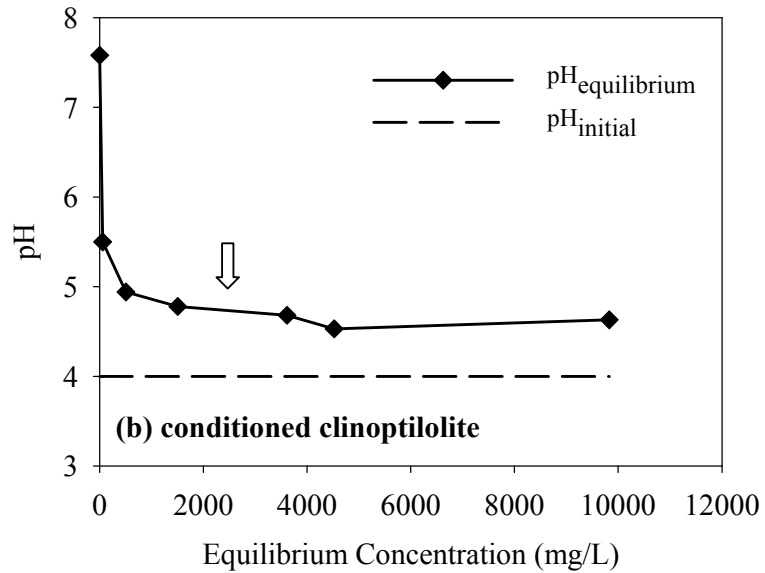
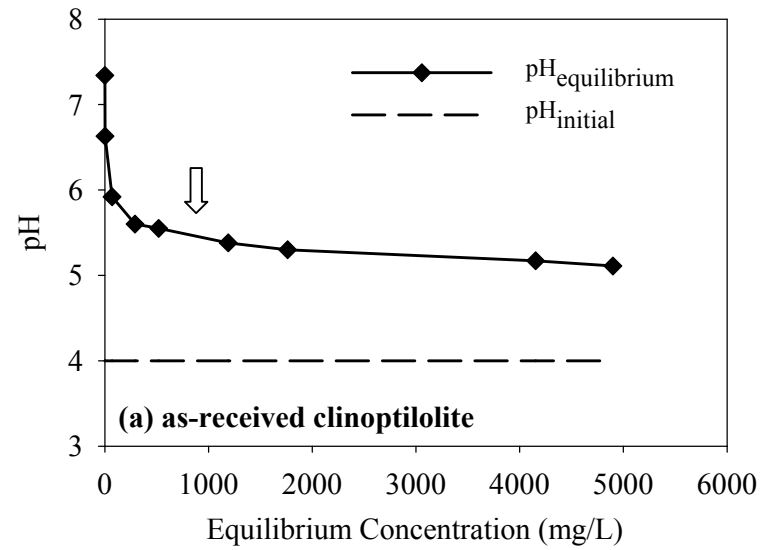




**Figure 4.7.** Change of pH with equilibrium concentration for Zn<sup>2+</sup> removal with (a) as-received (b) conditioned clinoptilolite

( ↓ represents equilibrium concentration at which maximum metal removal capacity is approximately reached.)





**Figure 4.8.** Change of pH with equilibrium concentration for Pb<sup>2+</sup> removal with (a) as-received (b) conditioned clinoptilolite

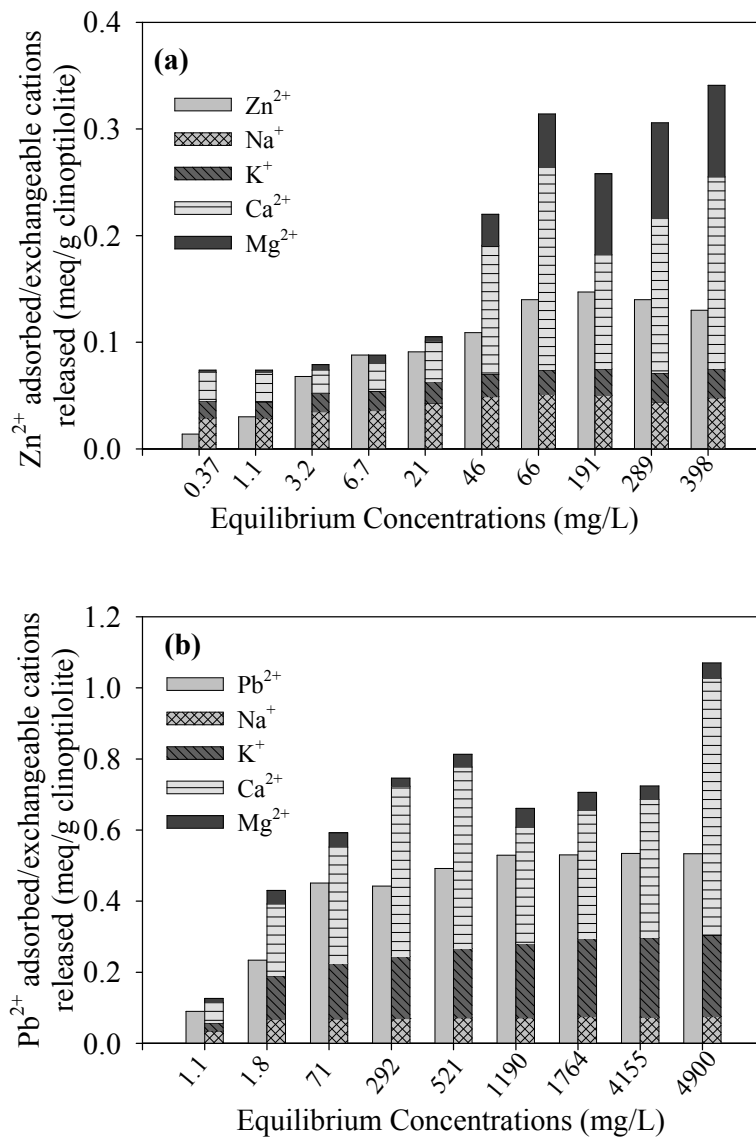
( ↓ represents equilibrium concentration at which maximum metal removal capacity is approximately reached.)

The hydrolysis reaction indicates that at high (low) equilibrium heavy metal concentrations,  $H^+$  ion concentration gets higher (lower), which explains the behavior of pH in the equilibrium experiments throughout this study. In addition, if metal ions and  $H^+$  compete for the same ion exchange sites on clinoptilolite, then with increasing affinity for the metal ion, one would expect less change in the pH of the system. That is, metal ions are removed from solution when  $H^+$  ions remain in solution-which could provide another explanation for the pH variation in equilibrium studies.

### ***Exchangeable Ions***

The relationship between the cations released from clinoptilolite structure (outgoing ions) and heavy metal ions removed from aqueous solution (incoming ion) using as-received and conditioned clinoptilolite for both metals tested are presented in Figures 4.9 and 4.10, respectively. Investigation of outgoing ions demonstrates that they are released from the structure at different quantities depending on the identity and concentration of the heavy metal ion. If ion exchange is the only mechanism involved in heavy metal uptake by clinoptilolite, there should be a balance between the ions released from and taken into the clinoptilolite structure. However, this is not the case for the situations encountered in all equilibrium studies.

The results obtained from  $Zn^{2+}$  and  $Pb^{2+}$  uptake by as-received clinoptilolite indicates that, generally, the total amount of exchangeable ions are higher than the amount of  $Zn^{2+}$  or  $Pb^{2+}$  ions taken into clinoptilolite structure. The relationship between  $Zn^{2+}$  ions removed from solution and the ions released from as-received clinoptilolite samples are given in Figure 4.9a.



**Figure 4.9.** Relationship between incoming ions and outgoing ions of as-received clinoptilolite with respect to equilibrium concentrations of (a) Zn<sup>2+</sup> and (b) Pb<sup>2+</sup>

The results indicate that at lower equilibrium  $Zn^{2+}$  concentrations the exchangeable ions detected in the solution are mostly  $Na^+$  followed by  $Ca^{2+}$  and  $K^+$  ions and a small amount of  $Mg^{2+}$  ions. However, as the equilibrium metal concentration increases, while amounts of  $Na^+$  and  $K^+$  ions released stay constant, a significant increase in  $Ca^{2+}$  and  $Mg^{2+}$  ions are observed.

Figure 4.9b demonstrates the relationship between incoming and outgoing ions in  $Pb^{2+}$ /as-received clinoptilolite system. At the lowest equilibrium metal concentration, amounts of  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  ions are almost equal to each other, while  $Mg^{2+}$  ion is detected in a very small amount. However, as the amount of  $Pb^{2+}$  retained in clinoptilolite structure increases, the ions released from clinoptilolite structure also increases and this increase is noticeable especially for  $K^+$  and  $Ca^{2+}$  ions. As the initial  $Pb^{2+}$  concentration increases, the amount of  $Na^+$ ,  $K^+$  and  $Mg^{2+}$  released from clinoptilolite does not show much change whereas the amount of  $Ca^{2+}$  released increases significantly and show variations.

For  $Zn^{2+}$  and  $Pb^{2+}$  removal by as-received clinoptilolite, high amounts of  $Ca^{2+}$  are detected in the solution. This  $Ca^{2+}$  is not only a product of ion exchange, but it could also be due to dissolution of clinoptilolite which is considered to be dominant at relatively low pH values (Doula *et al.*, 2002). From theoretical cation exchange capacity calculations, it is known that  $Ca^{2+}$  content of clinoptilolite is very high, therefore it is not surprising to detect high amounts of  $Ca^{2+}$  in solution. Especially if the clinoptilolite framework is somehow destroyed, then  $Ca^{2+}$  would be expected in considerable concentrations in aqueous phase.

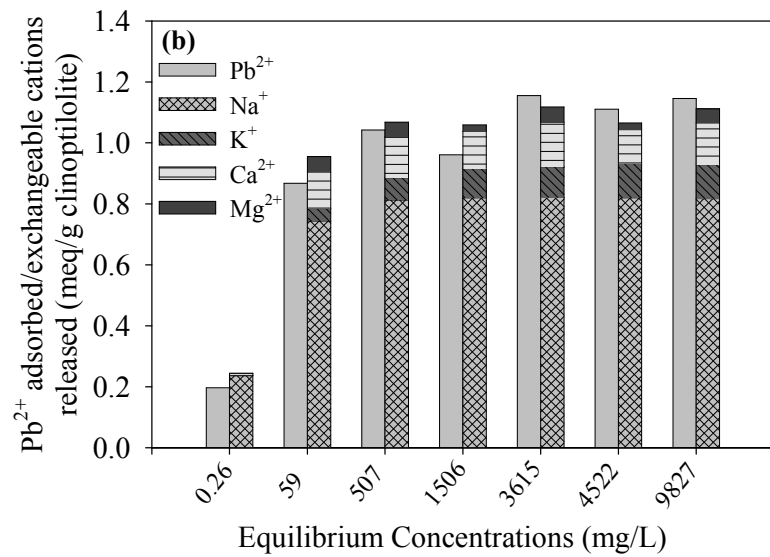
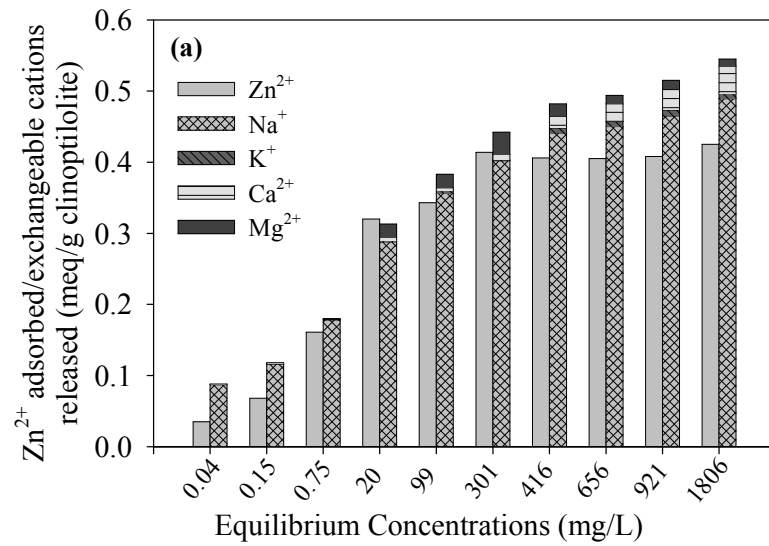
Another interesting point is the detection of  $K^+$  at high concentrations in  $Pb^{2+}$ /as-received clinoptilolite system. It is known that  $K^+$  ions are strongly bound to clinoptilolite structure (Malliou *et al.*, 1994; Çulfaz and Yağız, 2004), therefore it is difficult to replace these ions. However, the results indicate that  $Pb^{2+}$  can displace  $K^+$  in the clinoptilolite structure, which was also emphasized by Malliou *et al.* (1994). This can be attributed to the high selectivity of clinoptilolite to  $Pb^{2+}$  ions.

In  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$ /conditioned clinoptilolite system (Figures 4.10), it is apparent that  $\text{Na}^+$  is the dominant exchangeable ion released into the solution from clinoptilolite structure. This result is expected because conditioning with NaCl enriches the  $\text{Na}^+$  content of the clinoptilolite. When the relationship between outgoing and incoming ions in  $\text{Zn}^{2+}$ /conditioned clinoptilolite system is overviewed (Figure 4.10a), other than  $\text{Na}^+$ , only small amounts of other exchangeable ions, especially at higher equilibrium concentrations, can be seen. However, for the  $\text{Pb}^{2+}$ /conditioned clinoptilolite system, while  $\text{Na}^+$  is still the predominant ion released, amount of  $\text{Ca}^{2+}$  and  $\text{K}^+$  ions can not be disregarded.

In accordance with the results in Table 4.3, it can be stated that although conditioning method was able to increase  $\text{Na}^+$  content of clinoptilolite, it was insufficient to remove all other exchangeable ions from the clinoptilolite structure. Since clinoptilolite is highly selective for  $\text{Pb}^{2+}$  ions, it can replace  $\text{Ca}^{2+}$  and  $\text{K}^+$  ions present in the structure.

In  $\text{Zn}^{2+}$ /as-received clinoptilolite system (Figure 4.9a), the difference in total concentration of ions released from clinoptilolite structure is noticeable when compared to the concentrations of metal ions taken into clinoptilolite structure. This difference is noticeable in  $\text{Zn}^{2+}$ /conditioned clinoptilolite and  $\text{Pb}^{2+}$ /as-received clinoptilolite systems as well, whereas no excessive discrepancy between the incoming and outgoing ions is observed for  $\text{Pb}^{2+}$ /conditioned clinoptilolite system. Overall, these results indicate that all of the released ions from clinoptilolite structure are not product of only ion exchange process.

A probable explanation for the presence of extra exchangeable ions in the aqueous phase is the dissolution of clinoptilolite. As the sorbent is a natural material, destruction of its framework leading to the release of these ions is possible and investigated by many (Trgo and Perić, 2003; Rožić *et al.*, 2005; Doula and Ioannou, 2003; Doula *et al.*, 2002).

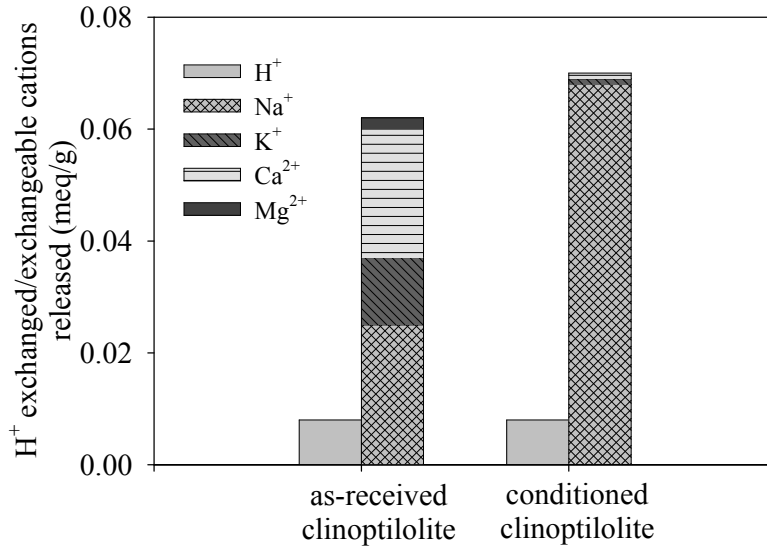


**Figure 4.10.** Relationship between incoming ions and outgoing ions of conditioned clinoptilolite with respect to equilibrium concentrations of (a) Zn<sup>2+</sup> and (b) Pb<sup>2+</sup>

In order to understand the behavior of clinoptilolite under the experimental conditions of this study and evaluate its tendency to undergo dissolution, tests were carried out by subjecting clinoptilolite to deionized water under the same conditions of the metal removal experiments (that is, same initial pH, temperature, rpm, solid to liquid ratio, duration of experiment, etc.). Deionized water-clinoptilolite experiments are not expected to simulate the same chemical conditions of metal-clinoptilolite experiments, yet they are expected to provide some insight into the discrepancy observed between exchangeable ions and metal removed.

Figure 4.11 demonstrates the relationship between ions released from and taken into the clinoptilolite structure.  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  are also measured in the aqueous phase in order to detect framework destruction. High amounts of  $\text{Si}^{4+}$  (0.53 meq/g for as-received, 0.41 meq/g for conditioned clinoptilolite) are detected, yet  $\text{Al}^{3+}$  analysis was not sensitive enough therefore it can only be said that  $\text{Al}^{3+}$  is lower than 10 mg/L (0.11 meq/g) in solution. These results point to another source for exchangeable cations, however a comparison of the relative amounts of total cations for the deionized water and metal removal experiments is made, a ten fold difference is evident showing potentially a much greater role of ion exchange when compared to dissolution of clinoptilolite. However, it should be pointed out that in heavy metal/clinoptilolite systems, metal ions can also induce clinoptilolite framework destruction (Doula and Ioannou, 2003). This effect is discussed in the next section.

In deionized water-clinoptilolite interaction, the pH of the suspension at the end of 48 hours was increased from 4 to 9.24 and to 9.51 for as-received and conditioned clinoptilolite system, respectively. Without the counteracting effect of hydrolysis of metal ions and subsequent ease of movement of  $\text{H}^+$  ions, the pH of the solutions increased significantly.



**Figure 4.11.** Behavior of as-received and conditioned clinoptilolite in metal-free medium and release of exchangeable cations

This increase of suspension pH is attributed to the exchange of H<sup>+</sup> ions and surface protonation. Moreover, as the suspension pH increases and reaches basic pH values, OH<sup>-</sup> ions become predominant in the system and they also interact with clinoptilolite surface and deprotonation reaction takes place:

➤ Surface protonation (Doula and Ioannou, 2003):



➤ Surface deprotonation (Benhammou *et al.*, 2005):

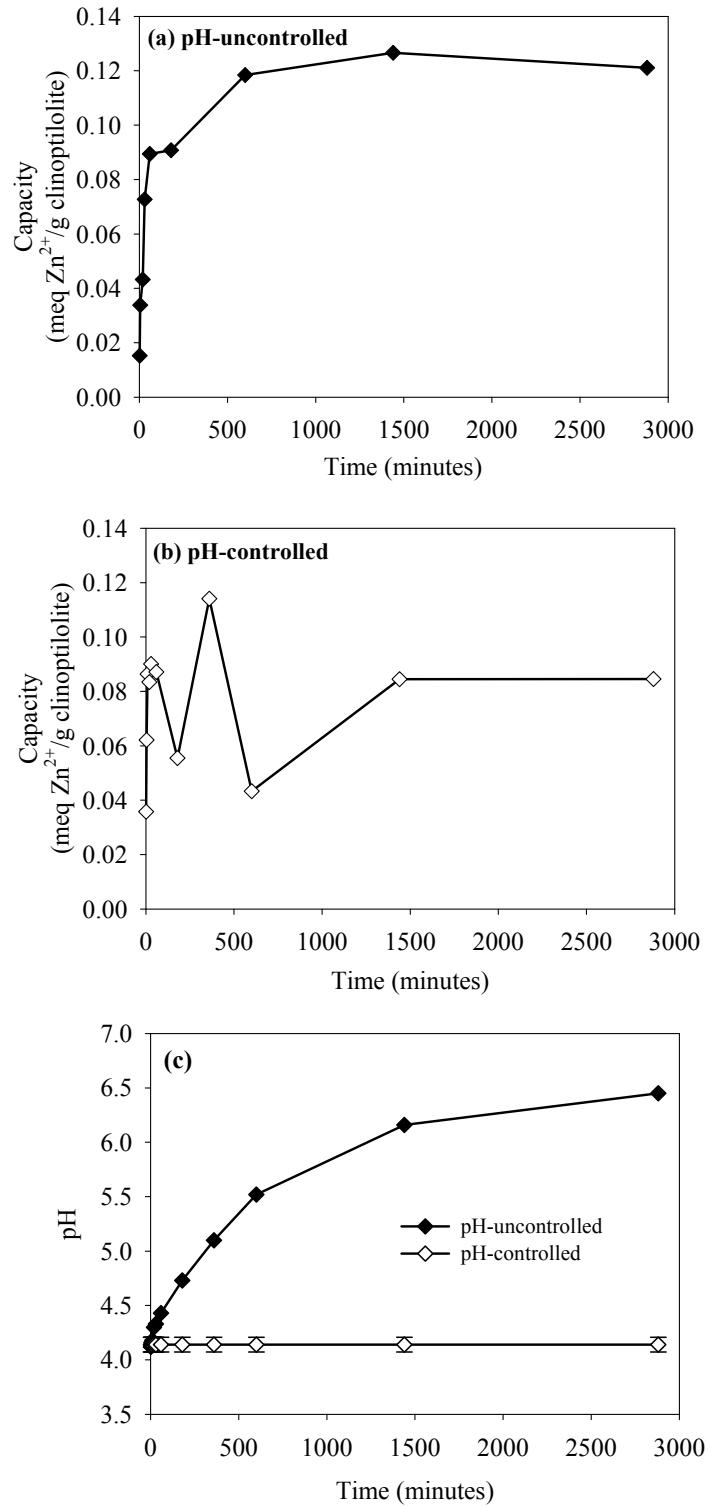




### 4.2.3. Kinetic Studies

Kinetic studies were performed in order to investigate the behavior of heavy metal/clinoptilolite system and understand the possible removal mechanisms involved in the system. These studies were performed under pH-uncontrolled and pH-controlled conditions. Throughout the equilibrium experiments, it was observed that pH of the system increased from its initial value of 4. Therefore to keep pH of the system constant,  $H^+$  ions were added to the system externally in a continuous fashion. The results of pH-controlled studies were compared to that of the system under pH-uncontrolled conditions. In addition, release of exchangeable ions was investigated with respect to time.

The time dependent  $Zn^{2+}$  removal with as-received clinoptilolite under pH-uncontrolled and pH-controlled conditions is presented in Figure 4.12. As can be seen from the figure, the effective capacity of clinoptilolite is achieved within 10 hours under pH-uncontrolled conditions (Figure 4.12a). However, under pH-controlled conditions (Figure 4.12b) a distinct fluctuation in the  $Zn^{2+}$  uptake is observed. It is clear that the added  $H^+$  ions affected the  $Zn^{2+}$  uptake negatively and resulted in about 75% of the metal removal capacity of the pH-uncontrolled system.

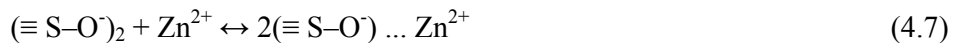


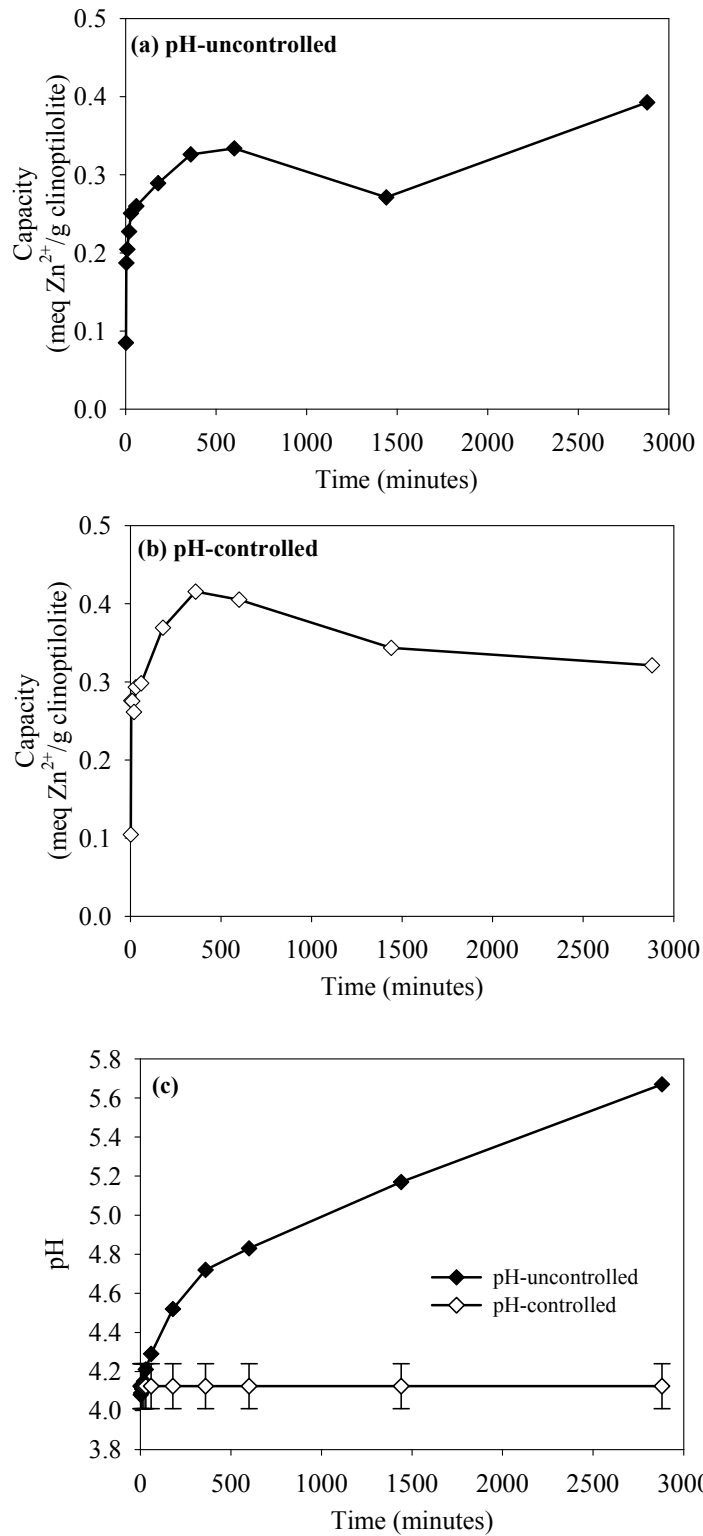
**Figure 4.12.** Kinetics of Zn<sup>2+</sup> uptake with as-received clinoptilolite under (a) pH-uncontrolled (b) pH-controlled conditions (c) pH change with time (C<sub>i</sub> = 150 mg/L)

Figure 4.13 demonstrates  $Zn^{2+}$  removal kinetics with conditioned clinoptilolite under pH-uncontrolled and pH-controlled conditions. Although, the removal within 6 hours is slightly enhanced by external  $H^+$  addition, beyond this point, retained  $Zn^{2+}$  in clinoptilolite structure is released with further addition of  $H^+$  ions and at the end of 48 hours, slightly lower capacity is attained under pH-controlled conditions.

The lower capacities attained for  $Zn^{2+}$ /clinoptilolite systems is due to the release of  $Zn^{2+}$  ions back to the solution and this could be attributed mainly to weak bonding of  $Zn^{2+}$  ions to clinoptilolite structure. The added  $H^+$  ions upset the order of  $Zn^{2+}$  ions bound to clinoptilolite structure and as more  $H^+$  ions are introduced to the system, their possibility of being included in the clinoptilolite structure increased. Therefore the added  $H^+$  ions take the place of  $Zn^{2+}$  ions in the structure by decreasing the sites available for them, thus leading to decreased capacity under pH-controlled conditions. Also, as more  $H^+$  is added to the system, more surface sites are protonated and continuous increase in  $H^+$  addition results in higher  $H^+$  adsorption and finally become the predominant mechanism (Doula and Ioannou, 2003). The protonation of surface sites continuously by  $H^+$  ions could also affect the uptake of  $Zn^{2+}$  by lowering the availability of negatively charged surface sites, which is probably involved in the process of charge neutralization by electrostatic attraction between negative surface charge and  $Zn^{2+}$  ions and thus, inhibiting  $Zn^{2+}$  ions being included in the clinoptilolite structure.

➤ Electrostatic attraction (Doula and Ioannou, 2003):

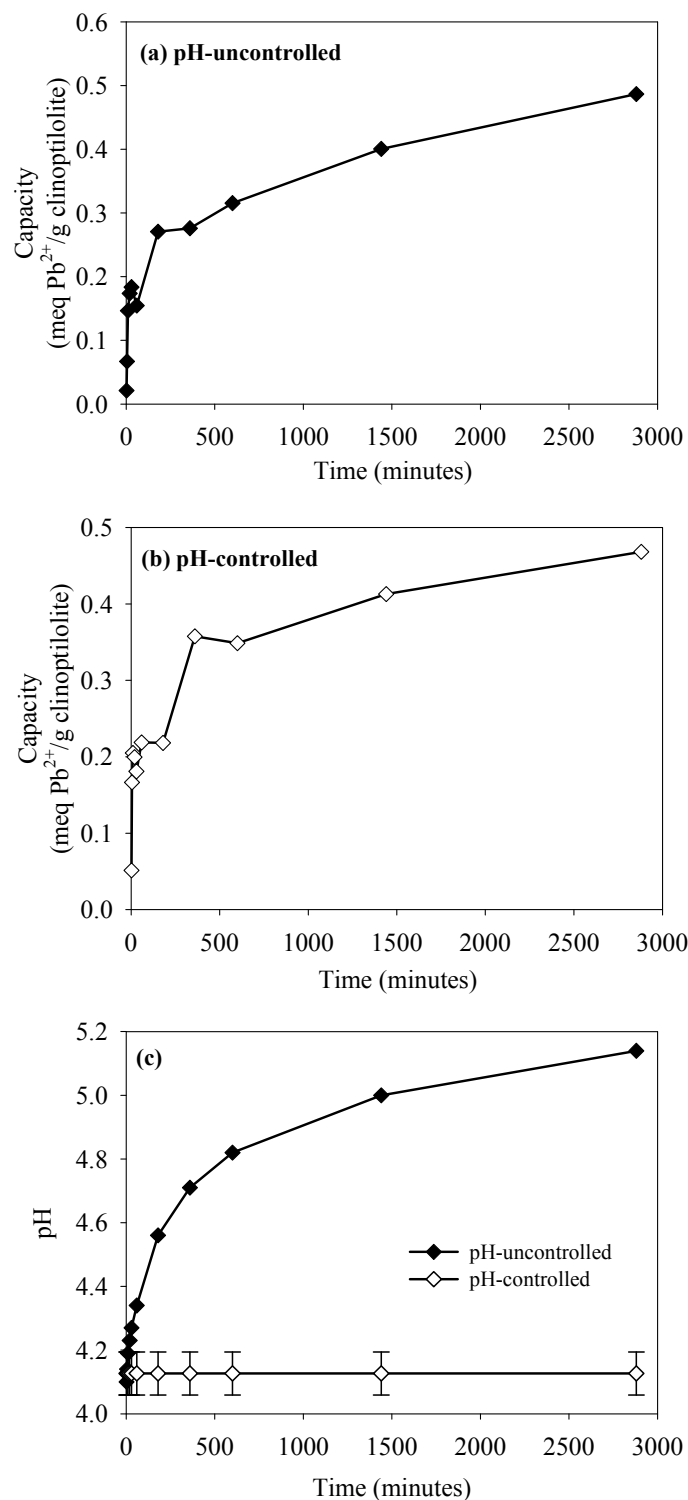




**Figure 4.13.** Kinetics of Zn<sup>2+</sup> uptake with conditioned clinoptilolite under (a) pH-uncontrolled (b) pH-controlled conditions (c) pH change with time ( $C_i = 400$  mg/L)

Figure 4.14 presents  $\text{Pb}^{2+}$  uptake by as-received clinoptilolite under pH-uncontrolled and pH-controlled conditions. The results indicate that external  $\text{H}^+$  addition has no influence on effective capacity of clinoptilolite, just at the initial minutes of interaction pH-controlled system shows slightly higher uptake capacities, but eventually almost same capacities are attained under both pH-uncontrolled and pH-controlled conditions.

In  $\text{Pb}^{2+}$ /as-received clinoptilolite system, the added  $\text{H}^+$  ions to the system are incapable of influencing the  $\text{Pb}^{2+}$ -clinoptilolite interaction. Contrary to the situations in  $\text{Zn}^{2+}$ /clinoptilolite systems,  $\text{Pb}^{2+}$  ions seem to be insensitive to added  $\text{H}^+$  ions, indicating their strong bonding to clinoptilolite structure. Although in the system, surface protonation is supposed to occur and  $\text{H}^+$  ions occupy clinoptilolite surface sites, owing to high selectivity of clinoptilolite for  $\text{Pb}^{2+}$  and possible formation of stable complexes with clinoptilolite surface functional groups,  $\text{H}^+$  ions could not disturb the system as in the case for  $\text{Zn}^{2+}$ . The formation of stable complexes can be explained by prolonged uptake of  $\text{Pb}^{2+}$  ions from solution, since complex formation is a slow process and takes longer time when compared to ion exchange. The strong bonding of  $\text{Pb}^{2+}$  ions to clinoptilolite structure and formation of stable complexes were confirmed by many (Um and Papelis, 2004; Wingenfelder *et al.*, 2005; Ponizovsky and Tsadilas, 2003; Mozgawa and Bajda, 2005). Particularly, Mozgawa and Bajda (2005) observed that in  $\text{Pb}^{2+}$  uptake by clinoptilolite chemisorption is a dominant mechanism.

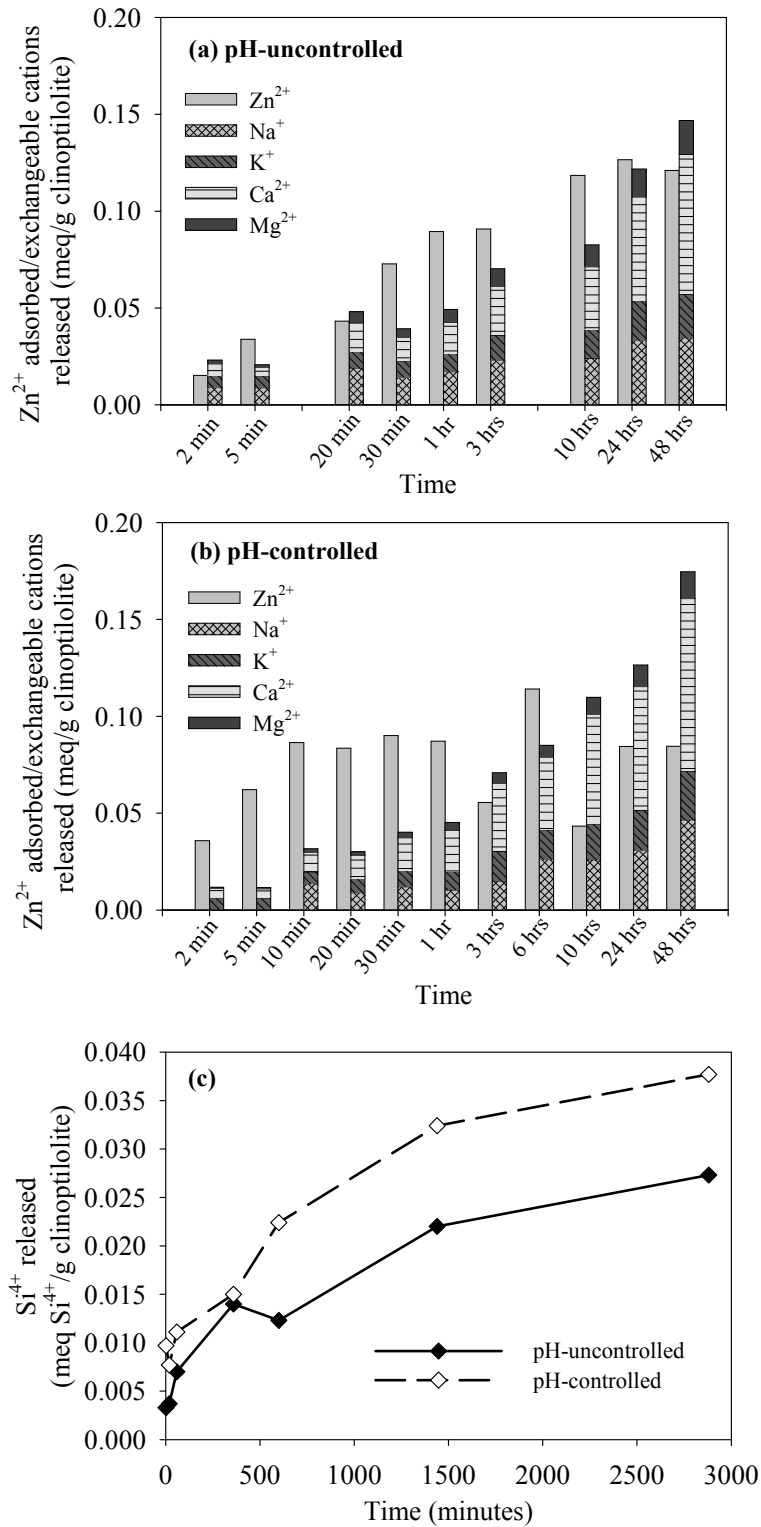


**Figure 4.14.** Kinetics of Pb<sup>2+</sup> uptake with as-received clinoptilolite under (a) pH-uncontrolled (b) pH-controlled conditions (c) pH change with time (C<sub>i</sub> = 1000 mg/L)

### ***Exchangeable Ions***

The time dependent release of exchangeable ions from as-received clinoptilolite in relation to  $Zn^{2+}$  uptake under pH-uncontrolled and pH-controlled conditions are presented in Figures 4.15a and b. The results demonstrate that amount of  $Zn^{2+}$  removed from solution is generally greater than the ions released from the clinoptilolite structure although equilibrium is reached, the total exchangeable ion concentration is greater than the total  $Zn^{2+}$  removal. These findings indicate that the removal mechanism can not be explained only by ion exchange. As well as ion exchange, attraction of positively charged  $Zn^{2+}$  ions or relevant  $Zn^{2+}$  species [i.e.  $Zn(OH)^+$ ] to negatively charged surfaces is involved. Probably, after  $Zn^{2+}$  ions are attracted to clinoptilolite negatively charged surfaces, then they start to move within the pores and channels of clinoptilolite exchanging with its extra framework cations, which is indicated by slow increase of exchangeable ions as a function of time.

The amounts of exchangeable ions in solution continuously increase with time as a result of exchange between solution cations (mainly  $Zn^{2+}$  and  $H^+$ ) and slow dissolution of clinoptilolite with time, as indicated by the aqueous  $Si^{4+}$  concentrations (Figure 4.15c). However, especially, at initial times of uptake ( $t \leq 3$  hours) dissolution is not significant, indicated by low  $Si^{4+}$  concentration in solution phase, therefore it can be stated that initially the ions released from the structure are products of ion exchange. Even though the effective capacity of clinoptilolite is achieved within 10 hours (that is, no further  $Zn^{2+}$  uptake under pH-uncontrolled conditions is realized) a further increase in the exchangeable ions is observed owing to dissolution of clinoptilolite over time. To be able to explain this, change in concentration of  $Si^{4+}$  in solution is measured at the same sampling times. The result of  $Si^{4+}$  release with time under pH-uncontrolled and pH-controlled conditions is demonstrated in Figure 4.15c. The  $Si^{4+}$  amount in solution continuously increases under both conditions with slightly higher amounts detected for pH-controlled studies.



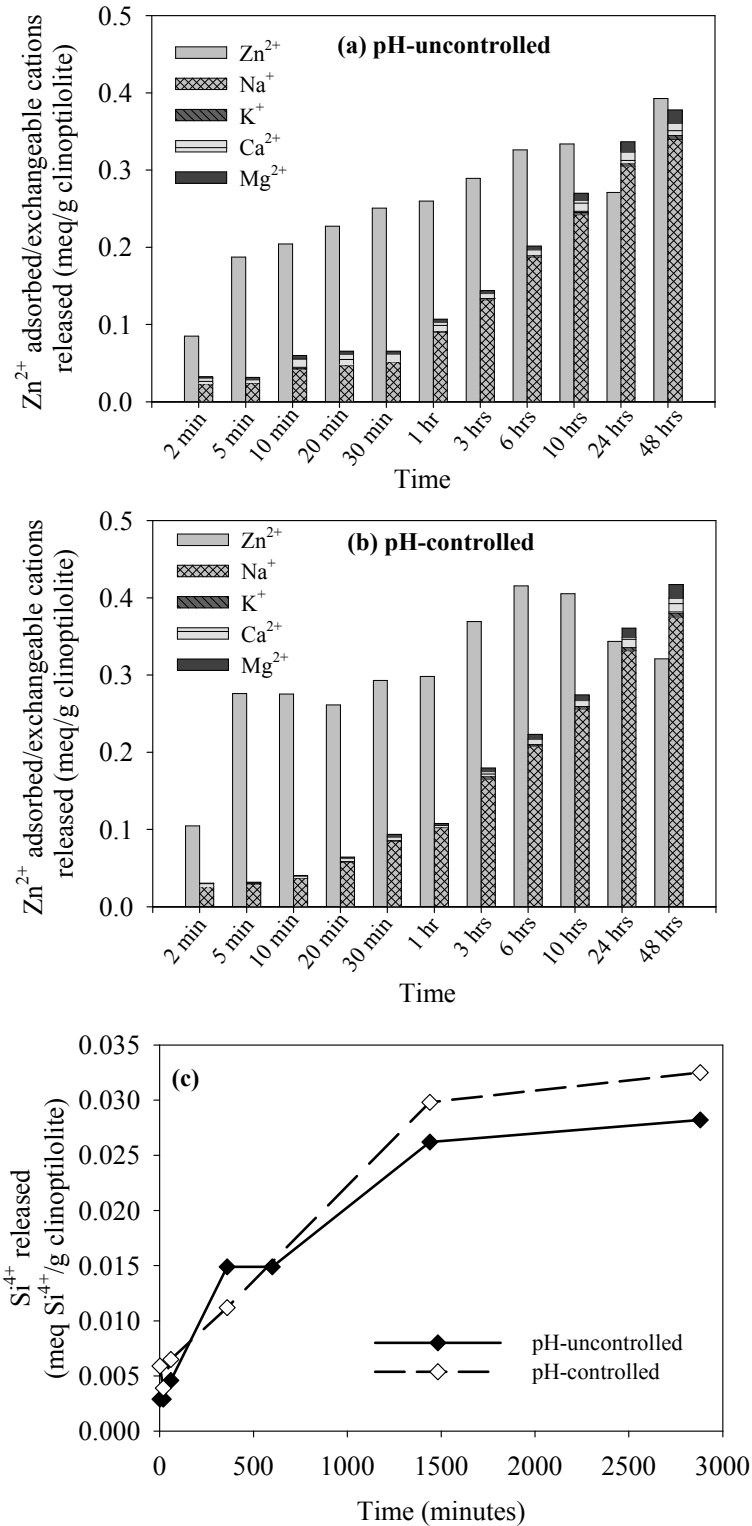
**Figure 4.15.** Relationship between incoming and outgoing ions with time in Zn<sup>2+</sup>/as-received clinoptilolite system under (a) pH-uncontrolled (b) pH-controlled conditions (c) release of Si<sup>4+</sup> with time



At the end of 48 hours the ions released from clinoptilolite structure are higher than the amount of  $Zn^{2+}$  retained in clinoptilolite structure, concurrent analysis of  $Si^{4+}$  reveal that they are partly the product of dissolution of clinoptilolite with time (Figure 4.15c). The difference between exchangeable ions released to the solution and  $Zn^{2+}$  ions taken into clinoptilolite structure in pH-controlled system is more pronounced owing to greater dissolution of clinoptilolite (Figure 4.15b) and possible exchange of  $H^+$  ions added to system with exchangeable ions in clinoptilolite structure.

Figures 4.16a and b present the relationship between the ions released from and taken into clinoptilolite structure in  $Zn^{2+}$ /conditioned clinoptilolite system under pH-uncontrolled and pH-controlled conditions. The results reveal that at initial time of uptake, the extent of ion exchange process involved in  $Zn^{2+}$  uptake is low, which means initially positively charged species are attracted to the surface to neutralize the negative charge, which is known as a rapid process (Doula and Ioannou, 2003; Trgo and Perić, 2003). The effect of electrostatic attraction is more pronounced in initial times of uptake when compared to  $Zn^{2+}$ /as-received clinoptilolite system. This may be due to removal of dust particles with conditioning, leading to easy access of  $Zn^{2+}$  ions to the binding sites on clinoptilolite. Also, slow increase in exchangeable ions is observed and this increase is mainly attributed to ion exchange process, considering insignificant dissolution of clinoptilolite within 10 hours, as in the case for  $Zn^{2+}$ /as-received clinoptilolite system.

The concentration of ions released from clinoptilolite structure is slightly higher under pH-controlled conditions due to exchange of added  $H^+$  ions and slightly higher dissolution of clinoptilolite. Figure 4.16c demonstrates release of  $Si^{4+}$  with time under pH-uncontrolled and pH-controlled conditions. The amount of  $Si^{4+}$  detected in solution phase is close to that detected in  $Zn^{2+}$ /as-received clinoptilolite system.

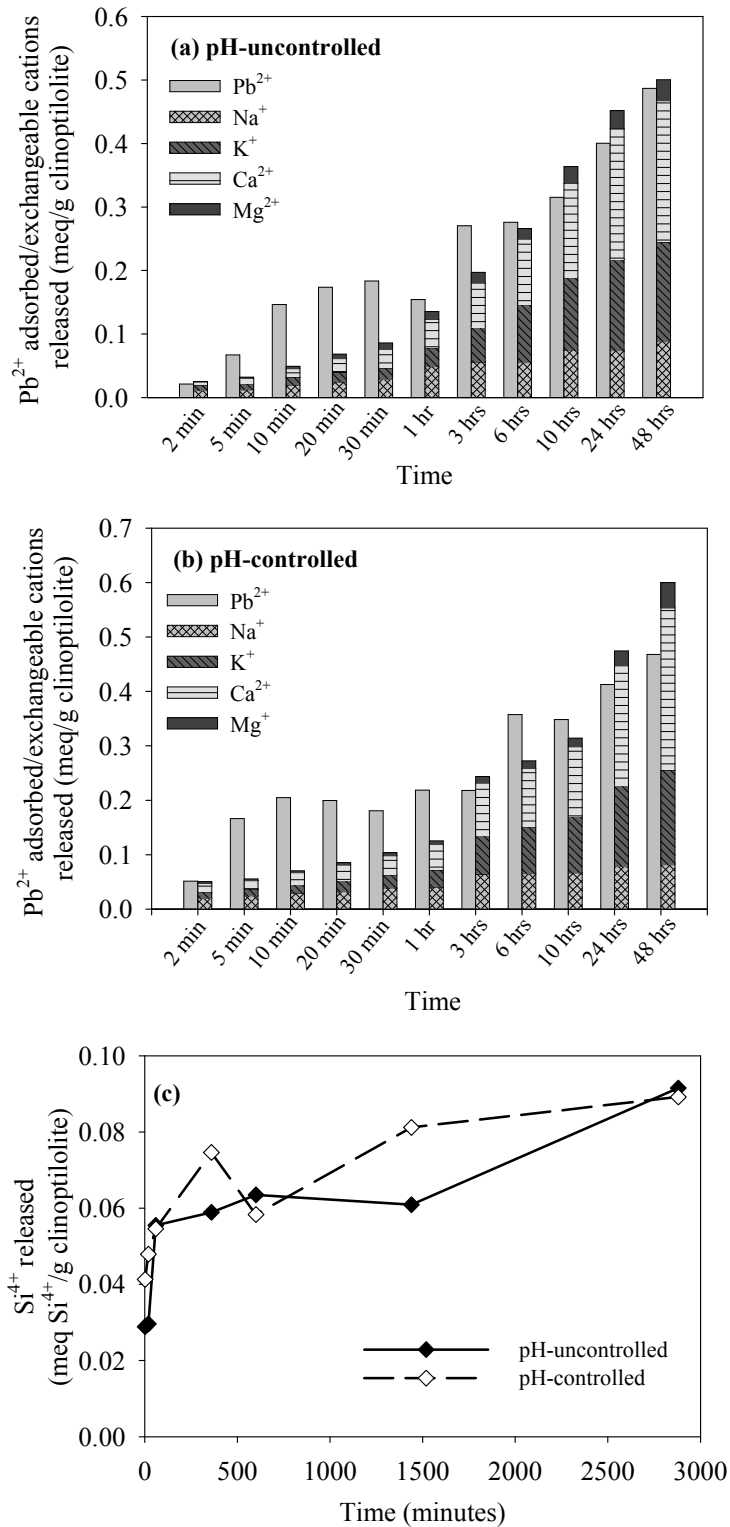


**Figure 4.16.** Relationship between incoming and outgoing ions with time in Zn<sup>2+</sup>/conditioned clinoptilolite system under (a) pH-uncontrolled (b) pH-controlled conditions (c) release of Si<sup>4+</sup> with time

Results show that the amount of exchangeable ions increases with time and so does the dissolution of clinoptilolite, which may be considered to be responsible for a part of the exchangeable ions in solution. Although, the amount of  $Zn^{2+}$  ions retained in clinoptilolite structure is high when compared to exchangeable ions within 10 hours, beyond this point the situation is reversed. This can be attributed to ion exchange process, which could be retarded as a result of diffusion through porous structure of clinoptilolite and also probably the increase in dissolution of clinoptilolite, indicated by presence of higher amounts of  $Si^{4+}$  in solution.

Figures 4.17 a and b show the relationship between incoming and outgoing ions in  $Pb^{2+}$ /as-received clinoptilolite system under pH-uncontrolled and pH-controlled conditions, respectively. The uptake of  $Pb^{2+}$  increases with time for both systems, and so does the amount of exchangeable ions released into the solution. However, this release could not solely be due to the ion exchange process, since considerable concentrations of  $Si^{4+}$  are detected (about three times as much when compared to  $Zn^{2+}$ /clinoptilolite system), indicating dissolution of clinoptilolite. Due to the nature of the system, it is very difficult to differentiate between exchangeable cations released as a result of ion exchange with heavy metal ions and those released due to dissolution of clinoptilolite. In order to observe the rate of change of clinoptilolite dissolution and the resulting concentration of exchangeable ions in metal-free solutions, behavior of as-received clinoptilolite in metal-free solution was investigated and the results are presented subsequently.

According to Doula and Ioannou (2003),  $Si^{4+}$  dissolution is facilitated by the presence of cations capable of forming inner-sphere complexes and they observed that as more  $Cu^{2+}$  was added, higher  $Si^{4+}$  dissolution was realized. In this study, higher dissolution in  $Pb^{2+}$ /as-received clinoptilolite system as compared to  $Zn^{2+}$ /clinoptilolite system can be explained by this manner owing to evidence of ability of  $Pb^{2+}$  forming more stable complexes. Also, relatively slower uptake of  $Pb^{2+}$  ions can be due to formation of complexes with surface functional groups, which results in slower uptake and strong bonding of  $Pb^{2+}$  ions.



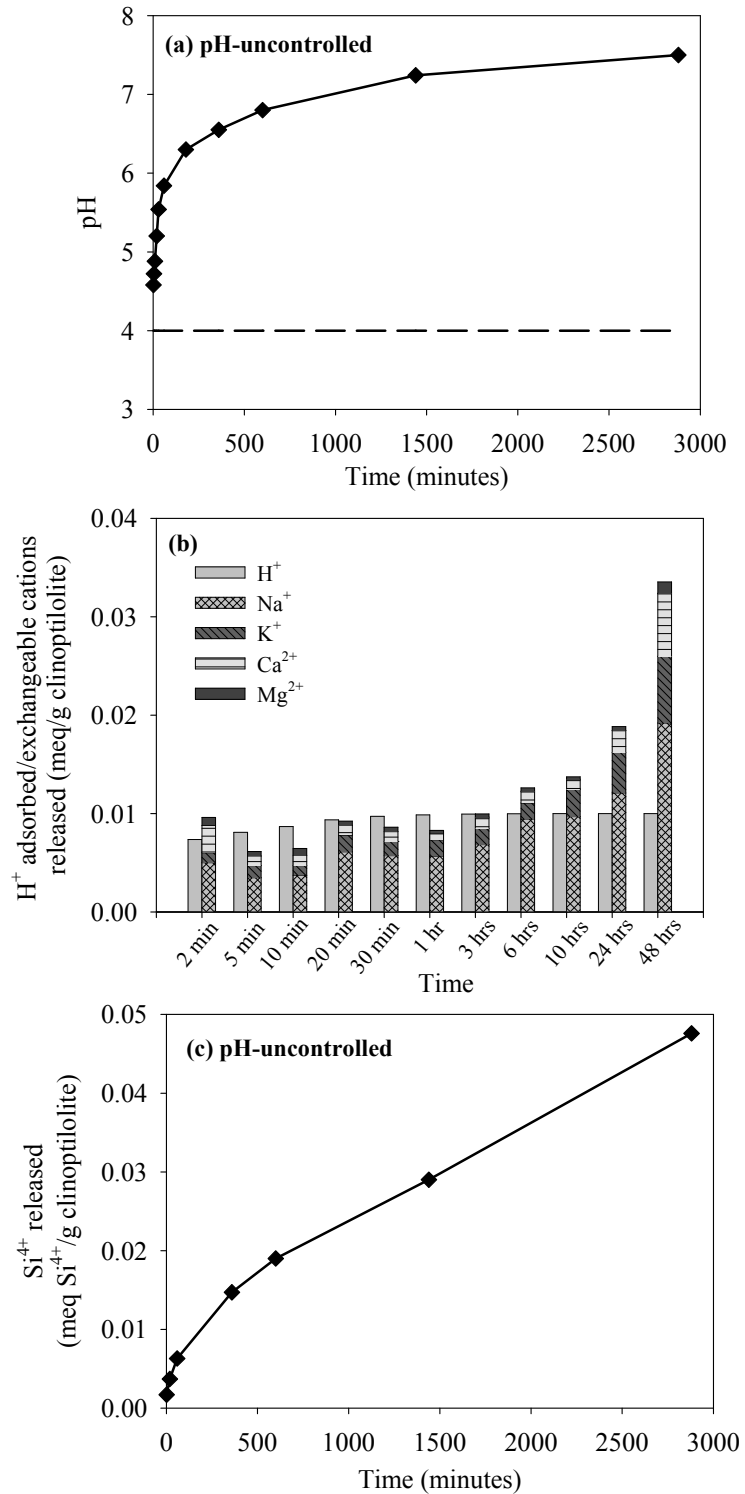
**Figure 4.17.** Relationship between incoming and outgoing ions with time in Pb<sup>2+</sup>/as-received clinoptilolite system under (a) pH-uncontrolled (b) pH-controlled conditions (c) release of Si<sup>4+</sup> with time

Also, as in  $\text{Zn}^{2+}$ /clinoptilolite systems, higher amounts of exchangeable ions released under pH-controlled conditions could be ascribed to introduction of  $\text{H}^+$  ions to the system continuously. It seems that  $\text{H}^+$  facilitates detachment of framework cations from structure as a result of protonation of surface sites.

Behavior of as-received clinoptilolite in heavy metal-free solution (deionized water) is demonstrated in Figure 4.18. Figure 4.18a presents change of pH with time and it is observed that pH of suspension continuously increased and at the end of 48 hours pH of system was approximately 7.5. When the results of deionized water/clinoptilolite system are compared with that of heavy metal/clinoptilolite systems, it is found out that higher pH values are attained in heavy metal-free medium. This is mainly due to higher chance of  $\text{H}^+$  ions to interact with clinoptilolite and absence of heavy metal ions which tends to decrease pH via hydrolysis.

Figure 4.18b shows the relationship between ions taken into ( $\text{H}^+$ ) and released from clinoptilolite structure. Up to the 24<sup>th</sup> hour, discrepancy between the ions is insignificant and also amount of ions released stayed almost constant until the 3<sup>rd</sup> hour and it starts to increase after this point. Together with the results of  $\text{Si}^{4+}$  release with time, which is demonstrated in Figure 4.18c, it is clear that the increase in exchangeable ions is due to dissolution of clinoptilolite. As the amount of  $\text{Si}^{4+}$  released to solution increases from 24<sup>th</sup> hour to 48<sup>th</sup> hour, there is a remarkable increase in exchangeable ion amount even though no further increase in pH is realized. With an increase in pH, extent of dissolution is also increased. This might be due to increase in  $\text{OH}^-$  ions in solution, which causes deprotonation of surface sites, facilitating detachment of  $\text{Si}^{4+}$  (Doula *et al.*, 2002).

It should be pointed out that in the previous experiment with deionized water and as-received clinoptilolite (Figure 4.11), the pH of suspension has been increased from 4 to 9.24. However, for the present case, at the end of 48 hours, pH of the system is approximately 7.5.



**Figure 4.18.** Behavior of as-received clinoptilolite in deionized water (a) pH change with time (b) Relationship between incoming and outgoing ions with time (c) Release of Si<sup>4+</sup> with time

There is a remarkable difference between these two systems in terms of their pH values, even though the experimental conditions are identical (i.e. temperature, rpm, solid to liquid ratio). This difference between pH values is probably arisen as a result of different size of reactors (i.e. for equilibrium studies 250 mL erlenmeyer flask and for kinetic studies 2 L beaker). In addition, throughout the kinetic studies with deionized water it was observed that 10 g clinoptilolite added to the 2-L beaker was not homogeneously distributed at the bottom and it was heaped up in the middle, inhibiting the complete interaction of clinoptilolite particles.

#### 4.2.4. Overview of Mechanisms Involved in Heavy Metal Removal

Equilibrium and kinetic studies reveal that in heavy metal-clinoptilolite interaction, several processes are included in the removal, such as ion exchange between metal ions and exchangeable ions, destruction of clinoptilolite structure and possibly complex formation with surface functional groups. However, the extent of these processes depends on the type of metal ion. The overall mechanisms involved in metal removal via clinoptilolite can be summarized as follows:

- ***Ion Exchange:*** It is considered as one of the significant mechanisms involved in heavy metal uptake via clinoptilolite. Investigation of cations released from clinoptilolite structure in both equilibrium and kinetic studies leads to understanding of the ion exchange process.
  - Contrary to the conventional ion exchange resins, more than one cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) is involved in exchange process.
  - The results of equilibrium studies indicate that affinities of clinoptilolite exchangeable ions to  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions are different.
  - $\text{Pb}^{2+}$  can displace strongly bounded exchangeable cations from clinoptilolite structure such as  $\text{K}^+$ , owing to high selectivity of clinoptilolite for  $\text{Pb}^{2+}$ .

- The results of kinetic studies reveal that although ion exchange reaction is known to be instantaneous, diffusion of metal ions through the pores and their access to the sites available for ion exchange seem to cause retardation of ion exchange process.
- **Dissolution of Clinoptilolite:** Observation of non-stoichiometry between metal uptake and total exchangeable ion released as well as the results of deionized water studies show that cations can be released from the clinoptilolite structure as a result of dissolution of clinoptilolite.
- In heavy-metal free medium,  $H^+$  and  $OH^-$  ions are responsible for destruction of framework and release of exchangeable cations from the clinoptilolite structure.
  - In metal ion containing medium, the extent of dissolution depends on the type of metal ion.
  - For  $Zn^{2+}$ , the extent of dissolution is relatively less, therefore, it can be concluded that the released cations are mostly due to ion exchange process and together with the results of pH-uncontrolled and pH-controlled studies it can be concluded that ion exchange is the predominant mechanism involved in the system.
  - On the other hand,  $Pb^{2+}$  ions can induce clinoptilolite dissolution and therefore it can be stated that the contribution of dissolution process is higher in the cations released from the structure. In accordance with the results of pH-uncontrolled and pH-controlled studies it can be stated that as well as ion exchange, surface complexation is involved in removal mechanism owing to strong bonding of  $Pb^{2+}$  to clinoptilolite structure.
- **Complex Formation:** Metal ions can form complexes with surface functional groups of clinoptilolite. Although interpretation of ion exchange is possible by investigation of exchangeable ions, it is very difficult to distinguish adsorption. However, kinetic studies under pH-uncontrolled and pH-



controlled conditions provide some insight together with investigation of exchangeable ions and examination of  $\text{Si}^{4+}$  release as a function of time from clinoptilolite structure.

- $\text{Zn}^{2+}$  ions are bound to clinoptilolite structure with weak bonding mechanisms (i.e. ion exchange, electrostatic attraction) therefore added  $\text{H}^+$  ions can disturb  $\text{Zn}^{2+}$ /clinoptilolite system and result in release of retained  $\text{Zn}^{2+}$  ions back to the solution. Therefore, the extent of complex formation in  $\text{Zn}^{2+}$ /clinoptilolite system is supposed to be limited when compared to that of  $\text{Pb}^{2+}$ .
- On the contrary to  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  ions can form more stable complexes with clinoptilolite structure since added  $\text{H}^+$  ions have no influence on  $\text{Pb}^{2+}$ /clinoptilolite system. Also, investigation of exchangeable ions together with  $\text{Si}^{4+}$  release from clinoptilolite structure with time and prolonged uptake of  $\text{Pb}^{2+}$  ions are indicative of adsorption mechanism.

## CHAPTER 5

### CONCLUSIONS

In this study, clinoptilolite originated from Balıkesir-Bigadiç deposit was found to be effective for  $\text{Pb}^{2+}$  removal from aqueous solutions in its as-received and conditioned form. Although lower capacities were attained for  $\text{Zn}^{2+}$ , it was found that conditioning improved relatively lower capacity of clinoptilolite for  $\text{Zn}^{2+}$ . The Langmuir isotherm model best fits to experimental results with the maximum capacities of 0.14 meq/g (as-received) and 0.39 meq/g (conditioned) for  $\text{Zn}^{2+}$ , and 0.51 meq/g (as-received) and 1.10 meq/g (conditioned) for  $\text{Pb}^{2+}$ .

The increase in pH throughout the experimental studies was attributed to  $\text{H}^+$  exchange and surface protonation. Also in all equilibrium studies, it was observed that the equilibrium pH's decreased with increased equilibrium heavy metal concentration, which could be attributed to hydrolysis of heavy metal ions and competition between  $\text{H}^+$  and heavy metal ions for exchange sites.

Investigation of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) released from clinoptilolite structure indicated that depending on type of heavy metal ( $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$ ) and its concentration, they were released from clinoptilolite structure in various amounts. Although an irregular trend was observed, mostly the amount of exchangeable ions released to solution was increased with increase in equilibrium heavy metal concentration.

Heavy metal removal mechanisms by clinoptilolite are investigated via kinetic studies. Results indicate the presence of mechanisms other than ion exchange. During kinetic studies, amounts of exchangeable ions released from clinoptilolite structure were shown to increase with time. However, it was found out that this

increase could not only be attributed to ion exchange. Additionally, ions were released as a result of dissolution of framework cations from clinoptilolite structure, which was indicated by increase in  $\text{Si}^{4+}$  concentration in solution with time. For  $\text{Zn}^{2+}$ , at initial time of uptake by clinoptilolite, electrostatic attraction between positively charged cations, i.e.  $\text{Zn}^{2+}$  ions or Zn species [i.e.  $\text{Zn}(\text{OH})^+$ ] and negatively charged surfaces presumably occur and this was followed by ion exchange as the metal ions move through the pores and channels of the clinoptilolite. For  $\text{Pb}^{2+}$ , complex formation with surface functional groups as well as ion exchange presumably occurs.

Kinetic studies performed under pH-uncontrolled and pH-controlled conditions indicated that external  $\text{H}^+$  ion addition to heavy metal/c clinoptilolite system could influence the system depending on how strongly metal ions bind to clinoptilolite structure. In  $\text{Zn}^{2+}$ /clinoptilolite systems,  $\text{H}^+$  ions had a pronounced negative effect on uptake due to weak bonding of  $\text{Zn}^{2+}$  ions to clinoptilolite structure, whereas no influence was observed for the  $\text{Pb}^{2+}$ /clinoptilolite system, which could be ascribed to strong bonding of  $\text{Pb}^{2+}$  ions.

Therefore, it could be suggested that in  $\text{Zn}^{2+}$  uptake by clinoptilolite, weak electrostatic bonding mechanism was included in removal. On the other hand,  $\text{Pb}^{2+}$  ions were strongly bonded to clinoptilolite structure and they presumably form complexes with surface functional groups, leading to formation of stable complexes, which could explain strong bonding of  $\text{Pb}^{2+}$  ions.

The dissolution of clinoptilolite was found to take place in all systems with clinoptilolite. In metal-free solutions and  $\text{Pb}^{2+}$ /clinoptilolite systems, the extent of dissolution was higher, whereas in  $\text{Zn}^{2+}$ /clinoptilolite system, extent of dissolution was relatively less. pH of solution and type of heavy metal species are observed as the factors influencing the extent of dissolution.

## CHAPTER 6

### RECOMMENDATIONS

In this study, clinoptilolite originated from Balıkesir-Bigadiç deposit has been investigated for its effectiveness in removing  $Zn^{2+}$  and  $Pb^{2+}$  from their single ion solutions. However in actual systems, together with these ions some inorganics and organics could be present. Therefore, effect of presence of inorganics and organics on removal of these heavy metal ions should be investigated.

Kinetic and equilibrium studies were performed throughout this study and as a further study, column studies could be realized, especially for  $Pb^{2+}$ , to simulate full-scale applications. Also, investigation of recovery of heavy metals from clinoptilolite and examination of regeneration potential of clinoptilolite could be a guide to real applications.

Heterogeneity of clinoptilolite samples, even when they have the same origin, could be a problem when wastewater treatment systems utilizing clinoptilolite are planned to be developed. Therefore, it is very important to characterize the reserves in order to make them attractive in developing treatment technologies.

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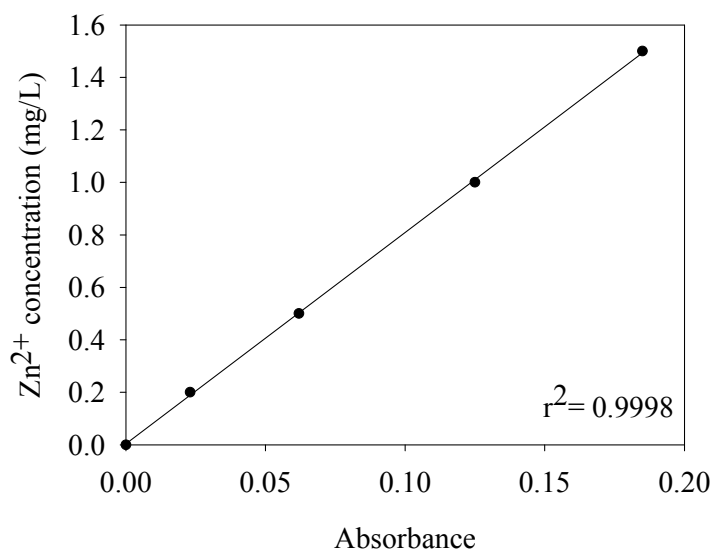
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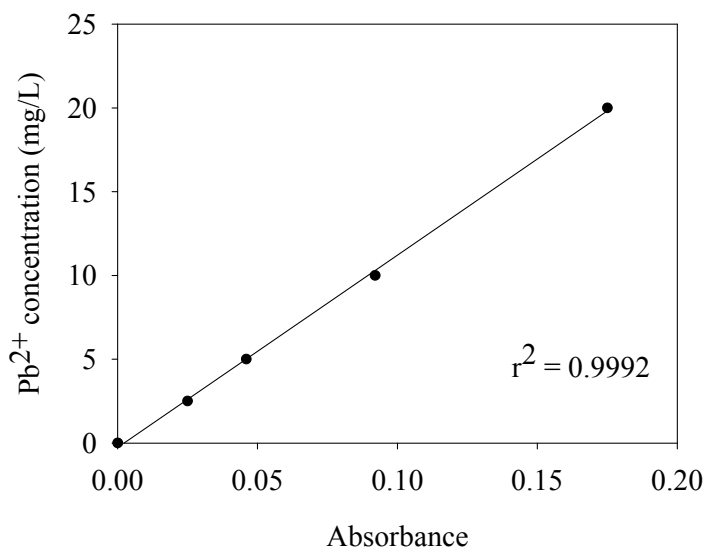
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## APPENDIX A

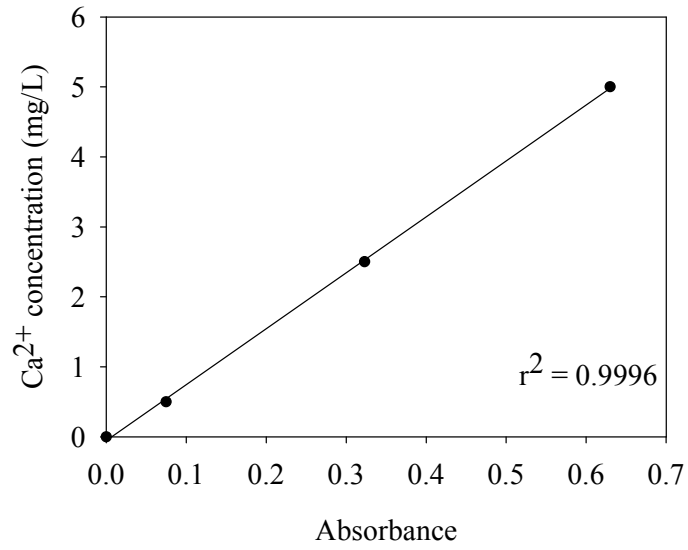
### CALIBRATION CURVES



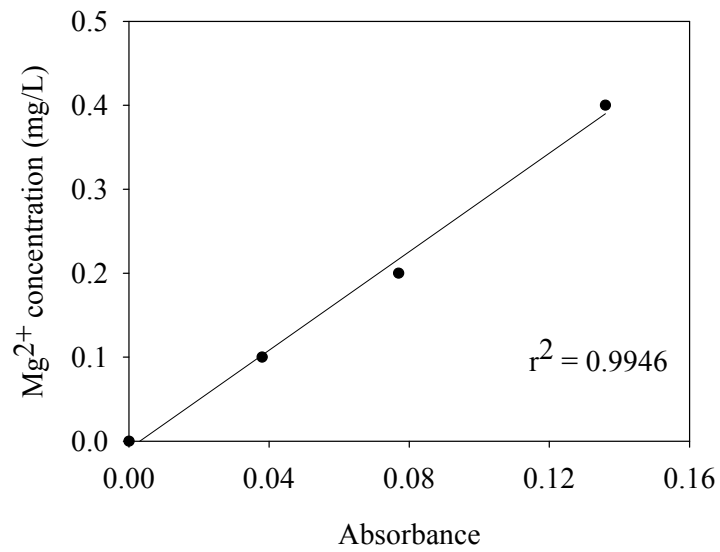
**Figure A.1.** Calibration curve for Zn<sup>2+</sup> measured by AAS



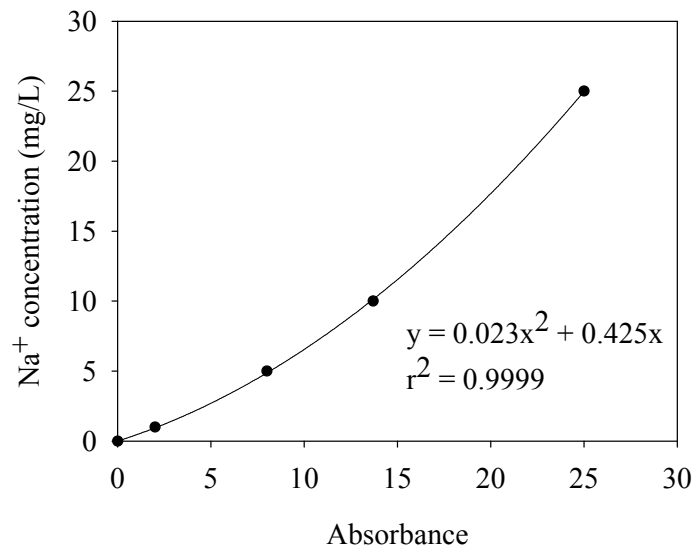
**Figure A.2.** Calibration curve for Pb<sup>2+</sup> measured by AAS



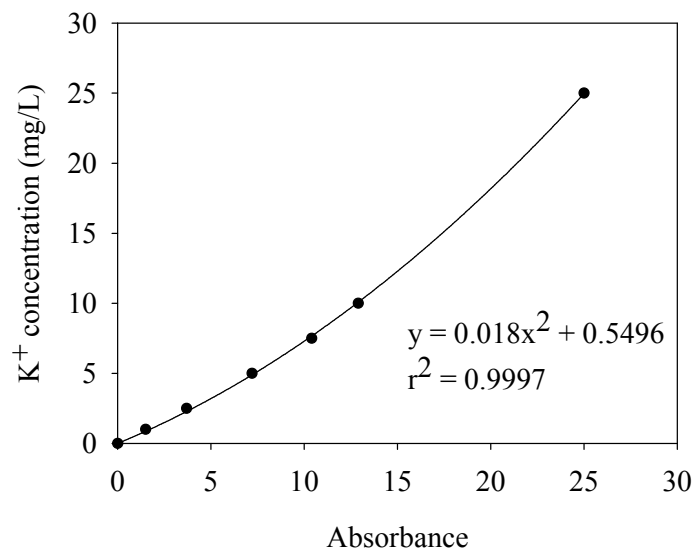
**Figure A.3.** Calibration curve for Ca<sup>2+</sup> measured by AAS



**Figure A.4.** Calibration curve for Mg<sup>2+</sup> measured by AAS



**Figure A.5.** Calibration curve for Na<sup>+</sup> measured by FP



**Figure A.6.** Calibration curve for K<sup>+</sup> measured by FP



## APPENDIX B

### EXPERIMENTAL EQUILIBRIUM DATA FOR ISOTHERMS

**Table B.1.** Equilibrium Data for Zn<sup>2+</sup>/as-received clinoptilolite system at 25°C ±2°C

Zn <sup>2+</sup> /as-received clinoptilolite	
Equilibrium Concentration C <sub>e</sub> (mg/L)	Capacity q (meq/g)
0.37	0.014
1.14	0.030
3.19	0.068
6.66	0.088
20.5	0.091
46.2	0.109
65.8	0.140
191	0.147
289	0.140
398	0.130

**Table B.2.** Equilibrium Data for Pb<sup>2+</sup>/as-received clinoptilolite system at 25°C ±2°C

Pb <sup>2+</sup> /as-received clinoptilolite	
Equilibrium Concentration C <sub>e</sub> (mg/L)	Capacity q (meq/g)
1.11	0.090
1.83	0.234
71.3	0.451
292	0.442
521	0.492
1190	0.529
1764	0.530
4155	0.534
4901	0.533

**Table B.3.** Equilibrium Data for Zn<sup>2+</sup>/conditioned clinoptilolite system at 25°C ±2°C

Zn <sup>2+</sup> /conditioned clinoptilolite	
Equilibrium Concentration	Capacity
C <sub>e</sub> (mg/L)	q (meq/g)
0.04	0.035
0.15	0.068
0.75	0.161
20.1	0.320
99.4	0.343
301	0.414
416	0.406
656	0.405
921	0.408
1806	0.425

**Table B.4.** Equilibrium Data for Pb<sup>2+</sup>/conditioned clinoptilolite system at 25°C ±2°C

Pb <sup>2+</sup> /conditioned clinoptilolite	
Equilibrium Concentration	Capacity
C <sub>e</sub> (mg/L)	q (meq/g)
0.26	0.197
59.1	0.867
507	1.043
1506	0.961
3615	1.156
4522	1.110
9827	1.146

## APPENDIX C

### CALCULATION OF EQUILIBRIUM CAPACITY OF CLINOPTILOLITE

The amounts of ions taken into clinoptilolite structure at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  are calculated as follows:

$$q = \frac{(C_i - C_e) \times V}{m} \times \frac{1}{\text{Eq.Wt.}} \quad (\text{C.1})$$

where,

q: amount of adsorbed  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  per unit weight of clinoptilolite (meq/g)

$C_i$ : initial  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  concentration in solution (mg/L)

$C_e$ : equilibrium  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  concentration in solution (mg/L)

V: volume of solution (L)

m: amount of clinoptilolite added to solution (g)

Eq.Wt. : equivalent weight based on ion charge (g/eq)

Equivalent weight based on ion charge is calculated as follows:

$$\text{Eq.Wt.} = \frac{\text{MW}}{z} \quad (\text{C.2})$$

where,

MW: molecular weight of  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  (g/mol)

z: ion charge of  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  (eq/mol)

A sample calculation is illustrated as follows:

$$C_i = 4.98 \text{ mg/L Zn}^{2+}$$

$$C_e = 0.37 \text{ mg/L Zn}^{2+}$$

$V = 0.1 \text{ L}$  solution containing  $\text{Zn}^{2+}$  ions

$m = 1 \text{ g}$  clinoptilolite

$$\text{Eq. Wt.} = \frac{65.39 \text{ g/mol}}{2 \text{ eq/mol}} = 32.695 \text{ g/eq}$$

$$q = \frac{[(4.98 - 0.37) \text{ mg/L}] \times 0.1 \text{ L}}{1 \text{ g}} \times \frac{1}{32.695 \text{ g/eq}} \cong 0.014 \text{ meq/g}$$

## APPENDIX D

### AMOUNTS OF 0.1 M HNO<sub>3</sub> ADDED TO SYSTEM DURING KINETIC STUDIES

The amounts of 0.1 M HNO<sub>3</sub> added to heavy metal/clinoptilolite system intermittently during the kinetic studies are given in Table D.1 as the total volume added to the system up to each sampling time.

**Table D.1.** Volume of 0.1 M HNO<sub>3</sub> added to the system up to each sampling time

time (minutes)	Cumulative volume of 0.1 M HNO <sub>3</sub> added up to each sampling time (mL)		
	Zn <sup>2+</sup> /as-received	Zn <sup>2+</sup> /conditioned	Pb <sup>2+</sup> /as-received
2	1	1	0.5
5	1	1	0.5
10	1	1	0.5
20	1	1	0.5
30	2	1	0.5
60	2	1	1
180	3.5	2	2
360	4	3.5	3
600	5	5.5	3.5
1440	7	7.5	5
2880	10	9.5	7.5