

Removal of Heavy Metals From Wastewaters by Use of Natural Zeolites

By

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ABSTRACT

In the present study, clinoptilolite rich local natural zeolite was proposed as an ion-exchanger for the removal of heavy metals (Pb^{2+} , Cu^{2+} , Zn^{2+}) from wastewaters. Natural zeolite samples were exposed to a simple pretreatment process which included washing and drying to remove impurities and dust.

Thermal and adsorption related properties of washed and original zeolite samples were determined by TGA and N_2 adsorption analyses. In TGA analyses, average water content for washed and original samples were found as 9.44 and 10.13 % respectively. In N_2 adsorption studies, both washed and original samples showed the characteristic Type IIb isotherm. BET surface areas of the samples were calculated as 39.73 and 47.72 m^2/g for washed and original samples respectively. Pretreatment process was found to improve the adsorption capacity of clinoptilolite due to the removal of impurities and dust.

In ion-exchange studies, efficiency of natural zeolite in removal of heavy metals from the solutions was investigated based on some physical and chemical variables. For this purpose, particle size and the amount of zeolite in the solution, contact time of the metal containing solution with zeolite were selected as physical variables and pH, metal concentration of the solution, and the presence of other ions were selected as chemical variables. The chemical analyses of all exchange solutions were performed by using ICP-AES. Removal % of the metal ions from the solutions were obtained. Based on the experimental results, zeolite exhibited a significant affinity to Pb^{2+} , followed by Cu^{2+} and Zn^{2+} even in the presence of competing cations.

To test the applicability of natural zeolite for the treatment of Acid Mine Drainage (AMD), zeolite samples were allowed to contact with simulated AMD solutions.

Consequently, natural zeolite was found to be an efficient ion exchanger for removing lead, copper and zinc ions from aqueous solutions.

ÖZ

Bu çalışmada, klinoptilolitçe zengin yerel doğal zeolit, atıksulardan ağır metallerin (Pb^{2+} , Cu^{2+} , Zn^{2+}) uzaklaştırılmasında iyon değiştirici olarak öngörülmüştür. Doğal zeolit örnekleri, safsızlıkların ve tozun giderilmesi için yıkama ve kurutma işlemlerini içeren basit bir ön işleme tabi tutulmuştur.

Yıkanmış ve orijinal zeolit örneklerinin termal ve adsorpsiyonla ilgili özellikleri TGA ve N_2 adsorpsiyonu analizleriyle belirlenmiştir. TGA analizlerinde, yıkanmış ve orijinal zeolit örneklerindeki su içerikleri sırasıyla % 9.44 ve 10.13 olarak bulunmuştur. N_2 adsorpsiyonu çalışmalarında yıkanmış ve orijinal örnekler karakteristik IIb izotermi göstermişlerdir. Yıkanmış ve orijinal örneklerin BET yüzey alanları 39.73 ve 47.72 $m^2/gram$ olarak hesaplanmıştır. Uygulanan ön işlemin, safsızlıkları ve tozu gidermesi nedeniyle klinoptilolitin adsorpsiyon kapasitesini geliştirdiği bulunmuştur.

İyon değişimi çalışmalarında, doğal zeolitin ağır metal giderimindeki verimliliği bazı kimyasal ve fiziksel değişkenlere dayanarak incelenmiştir. Bu amaçla, parçacık boyutu ve solüsyondaki zeolit miktarı, metal içeren solüsyonun zeolitle temas süresi fiziksel değişkenler olarak, pH, metal konsantrasyonu ve diğer iyonların varlığı kimyasal değişkenler olarak seçilmiştir. Bütün solüsyonların analizleri ICP-AES kullanılarak gerçekleştirilmiştir. Metal iyonlarının solüsyondan giderim yüzdeleri elde edilmiştir. Deneysel sonuçlarda, zeolit diğer iyonların varlığında bile Pb iyonuna belirgin bir eğilim göstermiştir, bunu sırasıyla Cu ve Zn iyonları izlemiştir.

Doğal zeolitin Asit Maden Drenajının (AMD) arıtılmasında uygulanabilirliğini test etmek amacıyla, zeolit simüle edilmiş AMD solüsyonuyla temas ettirilmiştir.

Sonuç olarak, doğal zeolitin sulu ortamda kurşun, bakır ve çinko gideriminde verimli bir iyon değiştirici olduğu bulunmuştur.

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Chapter 1

INTRODUCTION

1.1. Definition of The Problem

Industrial wastewaters often contain considerable amounts of heavy metals that would endanger public health and the environment if discharged without adequate treatment. Heavy metals are elements such as Pb (Lead), Hg (Mercury), Ni (Nickel), Cd (Cadmium), Cu (Copper) and Zn (Zinc) which have high atomic densities and are usually associated with toxicity [Al-Haj Ali et al. 1997].

Discharge of heavy metals such as lead, copper, and zinc has increased exponentially with industrial development. Between 1850 and 1990, production of these three metals increased nearly 10-fold, with emissions rising in tandem. Heavy metals have been used in a variety of ways for at least 2 millennia. For example, lead has been used in plumbing, and lead arsenate has been used to control insects in apple orchards. The Romans added lead to wine to improve its taste, and mercury was used as a salve to alleviate teething pain in infants.

Once emitted, metals can reside in the environment for hundreds of years or more. Evidence of human exploitation of heavy metals has been found in the ice cores in Greenland and sea water in the Antarctic. The lead contents of ice layers deposited annually in Greenland show a steady rise that parallels the mining renaissance in Europe, reaching values 100 times the natural background level in the mid-1990s.

Mining itself, not only of heavy metals but also of coal and other minerals, is another major route of exposure. Despite some noted improvements in worker safety and cleaner production, mining remains one of the most hazardous and environmentally damaging industries. In Bolivia, toxic sludge from a zinc mine in the Andes had killed aquatic life along a 300-kilometer stretch of river systems as of 1996. It also threatened the livelihood and health of 50,000 of the region's subsistence farmers. Uncontrolled smelters have produced some of the world's only environmental "dead zones," where little or no vegetation survives. For instance, toxic emissions from the Sudbury, Ontario, nickel smelter have devastated 10,400 hectares of forests downwind of the smelter.

The control of heavy metal pollution is made difficult by the great variety of contamination sources (metal extraction, metal fabrication, surface finishing, paint and

pigment production), inasmuch as heavy metals and their derivatives are widely used in many industrial and manufacturing processes.

In Turkey, the situation is not so different from highly industrialized countries. In recent years, heavy metal concentrations, besides other pollutants, are observed to increase and have reached dangerous levels for living environment in many regions of Turkey, creating a serious environmental problem. Industrial wastewater discharges such as those from the metal plating industries, are the main sources of metal pollution and therefore the level of pollution is much higher in industrialized regions such as the Izmit Bay and Izmir Bay.

According to the second survey of Waste Inventory of Manufacturing Industry in Turkey, carried on by The State Institute of Statistics, in 1992, among 1870 establishments, 1391 of them did not have a wastewater treatment plant. Among 479 establishments treating their wastewater, 39 establishments had a domestic wastewater treatment plant, 353 had industrial wastewater treatment plant and 87 had both treatment plants [The State Institute of Statistics Of Turkey 1992].

The results of the survey showed that establishments discharged wastewaters containing heavy metals such as copper, lead, cadmium, mercury, zinc and chromium to the receiving environment. Pollution loads from industrial effluents by parameters are listed in Table 1.

Table 1. Pollution Loads From Industrial Effluents*

Pollutant	Amount (kg/year)	
	From the Outlet of ww Treatment Plant	Having No ww Treatment Plant
Zinc (Zn)	97000	3500
Lead (Pb)	149	374
Cadmium (Cd)	2050	600

*The State Institute of Statistics Of Turkey, 1992

Environmental protection agencies fix their maximum allowed concentration of heavy metals in wastes at very low values, ranging from a few milligrams per liter to a few micrograms per liter, depending on the toxicity of the individual cation. Table 2 lists the Drinking Water Standards for certain metals and heavy metals of EPA.

Table 2. EPA Drinking Water Standards*

Metal Ion	Drinking Water Concentration, ppm
Cd	0.01
Cr	0.05
Cu	1
Fe	0.3
Mn	0.05
Ni	0.015
Pb	0.05
Zn	5

*Zamzow and Eichbaum, 1990

1.2 Health Effects of Heavy Metals

Both copper and zinc are essential elements for both animals and human. For instance copper have roles in erythrocyte formation, release of tissue iron, and the development of bone, the central nervous system and the connective tissue. Similarly, zinc is also necessary for the functioning of various enzyme systems. More than 70 zinc metallo-enzymes are known. The recommended dietary intake of zinc, depending upon age and sex, is between 4 and 15 mg/day.

However, intake of excessively large doses of such elements by human, leads to severe damages in health. Symptoms of zinc toxicity in humans include vomiting, dehydration, electrolyte imbalance, abdominal pain, dizziness and lack of muscular coordination. On the other hand large doses of copper causes mucosal irritation and corrosion, widespread capillary damage and central nervous system irritation followed by depression. Moreover, severe gastrointestinal irritation and possible necrotic changes in liver and kidneys could occur. Copper in water has also an unpleasant, astringent taste. The taste threshold is above 5.0 mg/l. Lead in high doses has been recognized for centuries as a cumulative general metabolic poison. Some of the symptoms of acute poisoning are tiredness, lassitude, slight abdominal discomfort, irritability, anemia and behavioral changes in children. In addition, lead has a tendency to bind mitochondria, leading to interference in the regulation of oxygen transport and energy generation [World Health Organization, 1984].

The toxicity of these metals has also been documented throughout history: Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology

became a science. Today, much more is known about the health effects of heavy metals. Exposure to high levels of mercury, gold, and lead has been associated with the development of autoimmunity, in which the immune system starts to attack its own cells, mistaking them for foreign invaders. Autoimmunity can lead to the development of diseases of the joints and kidneys, such as rheumatoid arthritis, or diseases of the circulatory or central nervous systems. Table 3 summarizes the common health effects and sources of the heavy metals.

Despite abundant evidence of these health effects, exposure to heavy metals continues and may increase in the absence of concerted policy actions. Mercury is still extensively used in gold mining in many parts of the world. Arsenic, along with copper and chromium compounds, is a common ingredient in wood preservatives. Lead is still widely used as an additive in gasoline. Increased use of coal in the future will increase metal exposures because coal ash contains many toxic metals and can be breathed deeply into the lungs. Health implications are ominous especially in developing countries, which continue to rely on high-ash coal as a primary energy source.

1.3. The Methods Used In Removal of Heavy Metals

The removal of heavy metals from wastewater can be achieved by electrodialysis, chemical precipitation, solvent extraction, reverse osmosis, ultrafiltration, adsorption or ion-exchange. Precipitating hydrous oxides of the metals with lime (CaO) or soda (NaOH) is the most commonly used primary treatment method in removal of heavy metals. The cost of most of the coagulants, chemical and polyelectrolytes used for precipitation of the metals, in the conventional methods, makes the processes economically unattractive.

Precipitation, generates large amount of sludge, which is costly to dispose of and often hazardous besides requiring long settling times despite the use of coagulants [Colella et al. 1993]. The problem of the disposal of sludge that is produced has not been satisfactorily solved, mainly because of accumulated heavy metals, which are easily released from it into the soil. On the other hand, after removal of the sludge by filtration and sedimentation, the resulting effluent, sometimes may still need further reduction in metals content to meet the regulatory requirements for discharge, which may be accomplished by the use of ion-exchange resins, electrodialysis and reverse osmosis [Guray et al. 1991].

Table 3. Health Effects and Sources of Some Metals.

Inorganic Chemicals	MCLG* (mg/L)	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Copper	1.3	Short term exposure: Gastrointestinal distress. Long Term Exposure: Liver or kidney damage. People with Wilson's Disease should consult a doctor if their water systems exceed the copper action level.	Corrosion of household plumbing systems; erosion of natural deposits.
Lead	Zero	Infants and children: Delays in physical or mental development. Lead substitution for calcium in bony tissue. Adults: Kidney problems high blood pressure.	Corrosion of household plumbing systems; erosion of natural deposits. Exhaust fumes.
Zinc	5	Vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea, lethargy, dizziness, lack of muscular coordination.	Corrosion of household plumbing systems and zinc containing fittings.

*MCLG: Maximum Contaminant Level Goal

(Level of a contaminant in drinking water below which there is no known or expected risk to health.)

1.4. The Scope of The Study

In this study, clinoptilolite rich local natural zeolite, obtained from Western Anatolia, was investigated for its potential to be used as an ion-exchanger for the removal of heavy metals, namely lead, copper and zinc, from wastewaters. Besides its abundance in Turkey, clinoptilolite rich natural zeolite is also one of the most important zeolite type and its ion-exchange characteristics have been studied in detail compared with other natural zeolites, due to its extensive deposits worldwide, stable structure and high selectivity for various cations which have led to its use in several plants for wastewater treatment.

The effect of physical and chemical variables on the efficiency of the removal of heavy metals by natural zeolite was evaluated. In the study, particle size and the amount of zeolite in the solution, contact time of the metal containing solution with zeolite were selected as physical variables and pH, metal concentration of the solution, and the presence of other ions were selected as chemical variables.

Chapter 2

ION-EXCHANGE THEORY IN REMOVAL OF HEAVY METALS BY ZEOLITES

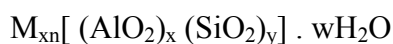
2.1. Zeolite Structure

The first commercially used ion-exchange materials were naturally occurring porous sands, that were commonly called “zeolites”. Zeolites are aluminosilicate minerals that contain alkali and earth metals, such as sodium, calcium and potassium, as well as water, in their structural framework.

The physical structure is porous, enclosing interconnected cavities in which the metal cations and water molecules are contained. They have reversible hydration properties in addition to their ion-exchange properties [Zamzow and Murphy 1992]. The low cost of obtaining natural zeolites, coupled with the fact that their exchangeable ions (sodium, calcium and potassium) are innocuous, make them especially attractive alternatives for removing undesirable heavy metal ions from industrial effluent waters.

Zeolites consist of a framework of aluminosilicates, which is based on an infinite three-dimensional structure of SiO_4 and AlO_4 tetrahedra molecules linked to each other by shared oxygen. Because aluminum has one less positive charge than silicon, the framework has a net negative charge of one at the site of each aluminum atom and is balanced by the exchangeable cation [Barros et al. 1997]. This structure of zeolites makes them suitable for many ion-exchange applications. The aluminosilicate framework of zeolites are remarkably open and contain channels and interconnected voids partially filled with exchangeable cations and water molecules. The cations (e.g. , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ti^{2+}) are quite mobile and can usually be exchanged, to varying degrees, by other cations [Demirci 1996].

The structural formula of zeolite is best expressed for the crystallographic unit cell as:



where M is the cation valance n, w is the number of water molecules and the ratio y/x (Si/Al), usually has values of 1-5 depending upon the structure. The sum $(x+y)$ is the

total number of tetrahedra in the unit cell. The portion with [] represents the framework composition [Breck 1974].

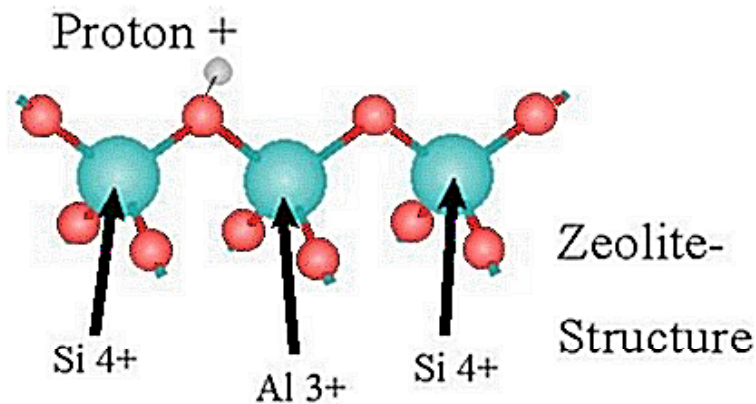


Figure1. Molecular Structure of Zeolite

Aluminum and silicon atoms having +3 and +4 charges respectively, neutralizes only -4 charge of oxygen atoms. This brings the necessity of combination with another silicon atom. Secondary Building Units (SBU) are formed by the linkage of Al and Si tetrahedras with each other through the corners of tetrahedra structures. Zeolite framework structure is seen in Figure 2.

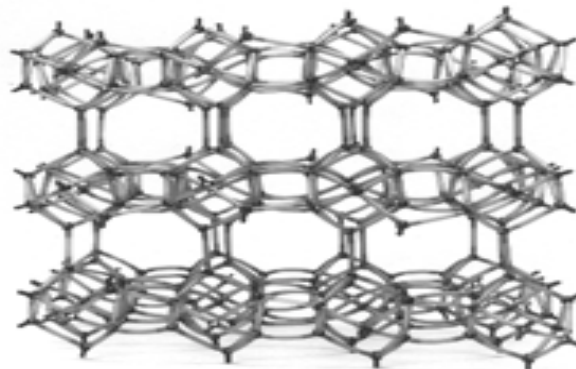


Figure 2. Zeolite Framework Structure

Channels and interconnected voids are formed during the connection of a secondary building unit with another. Pore or window diameters differ from each other depending on the temperature, the structural properties and the existing cation type in the structure. Pore openings are proportional with the number of atoms in the rings. Zeolites, which are used in industrial applications usually have 8, 10, 12 rings in their framework structures. Their pore openings are 5, 6, 7 Å respectively. Whereas, zeolites

having 4-6 rings in their structure have pore openings of 2.5 Å, which allow passage of only very small molecules such as water. As can be seen, molecular sieving ability of zeolites strongly depends on these pore openings [Kurama 1994].

Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature. This kind of zeolite was considered a new mineral by Schaller in 1923. In 1934, Hey and Bannister showed that clinoptilolite could be considered to be a rich silicon heulandite [Barros et al. 1997]. Clinoptilolite has a high thermal resistance. Heating up to 750 °C does not modify its original structure. It has a Si/Al ratio between 4.25 and 5.25 [Breck 1974].

Clinoptilolite rich zeolite contains three channels, limited by a system of tetrahedral rings: two channels of eight and ten tetrahedra, a third channel formed by eight rings and connected to other two channels. These channels are occupied by water molecules and compensating cations, which neutralize the anionic charge of the framework [Rivera et al. 2000]. Four types of channels form the channel system of clinoptilolite. Two of them are parallel to the c-axis and consist of 8 and 10-membered rings of tetrahedra. A third channel system is directed parallel to the a-axis and consists of 8-membered rings. A fourth type of channel also consists of 8-membered rings and forms an angle of 50° with the axis. The c-axis projection of the clinoptilolite structure is given in Figure 3.

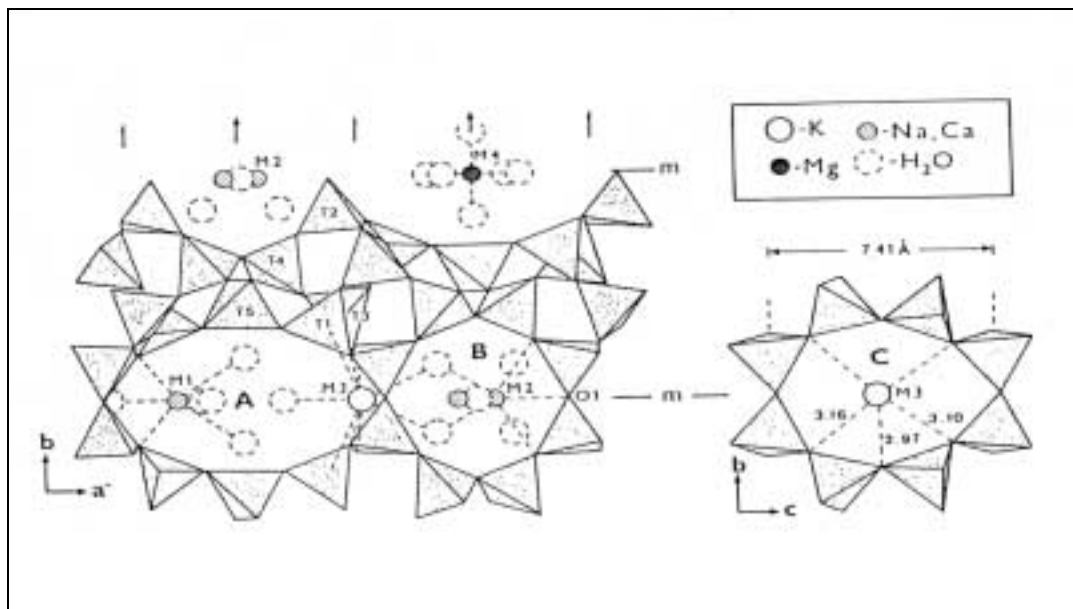


Figure 3. Main components in the clinoptilolite Structure

2.2. Ion-Exchange Theory

The ion-exchange process can be defined as a chemical reaction between ions in a liquid phase and ions in solid phase. The ion-exchanger solid preferentially sorbs certain ions in the solution and, since electroneutrality must be maintained, the exchanger solid releases replacement ions back into the solution. Ion-exchange is one of the methods used for the removal of several toxic substances including heavy metals, from industrial and municipal wastewater.

Ion exchangers are materials that can exchange one ion for another, hold it temporarily, and release it to a regenerant solution. Ion-exchange is used extensively in both water and wastewater treatment. The most common applications are water softening, demineralization, desalting, ammonia removal, treatment of heavy metals containing wastewaters, and treatment of some radioactive wastes [Reynolds 1982].

2.2.1. Zeolites and Ion-Exchange

The cation exchange property of zeolite minerals was first observed 130 years ago. The ease of cation exchange in zeolites and other minerals led to an early interest in ion exchange materials for use as water softening agents. Synthetic, nanocrystalline aluminosilicate materials were primarily used.

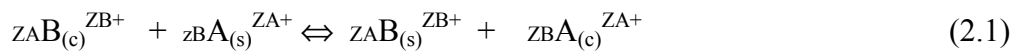
Because of their three-dimensional framework structure, most zeolites and feldspathoids do not undergo any appreciable dimensional change with ion-exchange; clay minerals, because of their two-dimensional structure, may undergo swelling or shrinking with cation exchange [Breck 1974]. The main features of zeolites that make them advantageous are as follows:

1. Their well defined framework structure leads to a uniformity of molecular sized channels and cavities through which cations diffuse in order to undergo exchange in sites within the crystals. The nature of these intracrystalline penetrations is important in ion sieving and diffusion control, and depends mainly upon the framework topology.
2. Because of their three dimensional framework structure most zeolites do not undergo any appreciable dimensional change with ion-exchange.

3. The aluminum content, that is the number of tetrahedrally oriented aluminum atoms per unit cell of framework, defines the maximum number of negative charges available to cations. The ion-exchange capacity is directly related to the quantity of aluminum present in the zeolite framework. In such a case, a low Si/Al ratio, in other words, high aluminum concentration favors this process. In zeolites; this feature can be altered by dealumination.
4. The sieving and partial sieving effects of zeolites toward various cations is one of the most important features of them and have potential applicability in many areas.

2.2.2. Kinetics Of Ion-Exchange In Zeolites

Ion-exchange reaction may be written as:



where cations A and B have Z_A and Z_B charges, respectively. The letters “c” and “s” are related to the crystalline phase and to the solution [Barros et al.1997]. Ion-exchange can be characterized by the ion-exchange isotherm which is showing ionic composition of the ion exchanger and the solution characteristics, relative amounts of counterions. Equivalent ionic fraction, A_z in the ion exchanger is plotted as a function of the equivalent ionic fraction A_s in the solution.

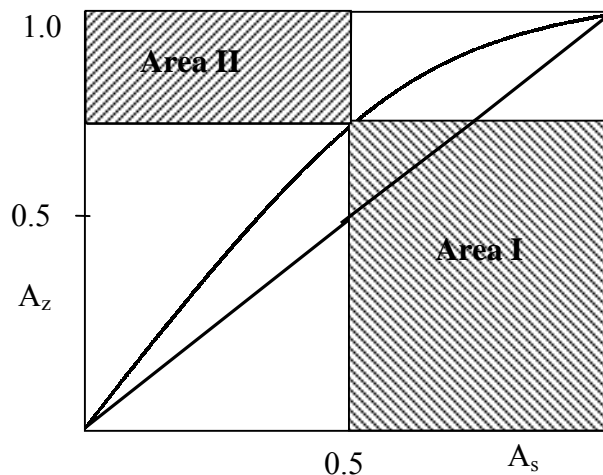


Figure 4. Derivation of the separation factor through exchange isotherm

According to Eqn.2.1, the equivalent fractions of the exchanging cation in the solution and zeolite are defined by:

$$A_s = \frac{zA.m_s^A}{zA.m_s^A + zB.m_s^A} \quad (2.2)$$

where m_s^A and m_s^B are the molalities of the ions A and B, respectively.

$$A_z + B_z = 1 \text{ and } A_s + B_s = 1$$

$$A_z = \frac{\text{Number of equivalents of exchanging cation A}}{\text{Total equivalents of cations in the zeolite}} \quad (2.3)$$

Separation factor (α) is defined to express the preference of the ion exchanger for one of the two counter ions. Figure 4 expresses the derivation of separation factor through the exchange isotherm.

$$\alpha_B^A = \frac{A_z \cdot B_s}{B_z \cdot A_s} = \frac{\text{Area I}}{\text{Area II}} \quad (2.4)$$

If A is preferred α_B^A is larger than unity, and if B is preferred, the factor is smaller than unity. Ratio of the areas lying below and above an exchange isotherm gives an idea about which ion is preferred by ion exchanger. The kinetics of ion-exchange using zeolite may be divided into five steps [Cooney et al. 1999]:

1. Diffusion of the counter ions through the film solution to the surface of the zeolite (film diffusion)
2. Diffusion of the counter ions within the zeolite (particle diffusion)
3. Chemical reaction between the counter ions and the ion-exchange sites.
4. Diffusion of the displaced ions out of the zeolite.
5. Diffusion of the displaced ions from zeolite surface into the bulk solution.

As can be seen, steps 4 and 5 are reverse of steps 1 and 2. The slowest step of the ion exchange process for a given system controls the speed of ion-exchange and is said to be the rate-limiting step.

Two mechanisms generally control the rate of adsorption within porous solids: these are either film diffusion (Step 1) or particle diffusion (Step 2). Both mechanisms are present in practice, although normally one mechanism (the slower) dominates.

For particle diffusion control:

$$\text{Rate} \propto \frac{1}{r_p^2}$$

and for film diffusion control:

$$\text{Rate} \propto \frac{1}{r_p}$$

where r_p is the radius of the particle. By using these relationships it is possible to identify the rate-controlling mechanism. In zeolites particle diffusion controls the overall rate [Breck 1974].

2.2.3. Factors Affecting Ion-Exchange Behaviour

Similar to other ion-exchangers, besides various transport mechanisms, ion-exchange depends also upon the cation exchange behaviour of the zeolite itself. These properties are:

1. The nature of the cation species, the cation valance and both the anhydrous and hydrated size of cation.
2. The temperature
3. The cation concentration of cation species in the solution
4. The anion species associated with the cation in the solution
5. The solvent
6. The structural characteristics of the particular zeolite [Sing 1981].

Ion exchangeability, in other words, the affinity of an ion towards a given exchanger depends mainly on the charge of the ion, the ionic radius and the degree of hydration.

Because of their size, certain cations may not be able to exchange with the cations within the crystal structure of the zeolite. Table 4 presents ionic radii, hydrated ionic radii and free energies of hydration for certain ions. If the ionic radii is compared with the free dimensions of the clinoptilolite channels (4.0x5.5 – 4.4x7.2 Å), it is apparent that all of the unhydrated ions can pass readily through the channels, but since the hydrated ions are approximately the same size as the channel dimensions, they may exchange only with difficulty [Barros 1997, Semmens 1974].

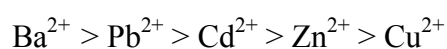
Table 4. Properties of Certain Cations*

Cation	Ionic Radius (Å)	Hydrated Ionic Radius (Å)	Free Energy of Hydration (kcal/g-ion)
Ba ²⁺	1.43	4.04	-315.1
Cd ²⁺	1.03	4.26	-430.5
Cu ²⁺	0.82	4.19	-498.7
Pb ²⁺	1.32	4.01	-357.8
Zn ²⁺	0.83	4.30	-484.6
Na ⁺	0.98	3.58	-98.2

*Semmens 1974

Eisenman indicated that selectivity of exchange cations is accounted for only in terms of their hydration free energies and of their energies of electrostatic interaction with the zeolite-fixed anions. He assumes that cations and the anionic sites form ion pairs with no water interposed between the cations and sites. Thus, if a cation exchanger is placed in an aqueous solution of the salts ACl and BCl, the preference of the exchanger for ion A⁺ or B⁺ depends on whether the difference in their hydration free energies or their coulombic energies of interaction with the fixed anionic exchange sites predominates [Marinsky 1966]

According to Eisenman's Theory, the free energies of hydration listed in Table 4 indicates the following selectivity sequence.



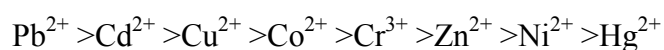
Therefore, copper with the largest hydration energy, prefers the solution phase where it may satisfy its hydration requirements, and barium and lead with the lowest hydration energy, prefers the zeolite phase [Semmens 1974].

In their study with Na-Y synthetic zeolites, Ahmed, Chughtai and Keane (1998) expressed that the exchange selectivity within the rigid zeolite channel system is governed by the extent of metal coordination with framework oxygens and with water molecules. While the bare metal ions can readily enter the sodalite units, the more bulky hydrated metal ions will have limited access to sodium ions located in the more “hidden” positions. In the hydrated zeolite, the ions with the lower charge density, which are present in a less hydrated state, interact more strongly with the aluminosilicate framework. Ahmed, Chughtai and Keane explains higher selectivity by comparing enthalpy of hydration of both metals, which is -1807 kJ/mole for Cd^{2+} and, -1481 kJ/mole for Pb^{2+} . As a result, since hydration free energy of lead is lower than it is for cadmium, efficiency of lead removal from aqueous phase is the highest.

Many authors state that the natural zeolite, containing several exchangeable cations, needs a pretreatment, which tends to replace them by only one kind of cation. Practically, the result of any pretreatment operation is the increase of the content in a single cation, what is called “homoionic form”. Therefore, pretreatment aims to remove certain ions from the structure of the material and locates more easily removable ones, prior to any ion-exchange application of it. The most of the research on metal sorption with natural zeolites have focused primarily not only on identifying the selectivity series for various zeolites but also effect of pretreatment of zeolites on the ion-exchange efficiency.

Washing the zeolite sample is the simplest and effective way of increasing exchange capacity of the zeolite. Inglezakis et al. (2001) have investigated the effect of washing surface dust of the zeolite sample on the exchange capacity (q). According to their experimental results, they concluded that surface dust is clogging part of the pore openings in zeolite structure leading in slower ion exchange kinetics.

Zamzow and Eichbaum (1990) have studied the removal of heavy metals and other cations from wastewaters using two types of clinoptilolites in shake, column and series column experiments. It has been found that pretreatment with sodium enhances the capacity of the zeolite. Their results indicated that the heavy metal ion-exchange loading values could range from 1.6 meq/g for lead to zero meq/g for mercury. The selectivity series of the studied metal cations is:



Semmens and Seyfarth (1988), Semmens and Martin (1974) have also reported that clinoptilolite, one of the most abundant type of zeolite, is highly selective for

barium and lead but showed considerably less selectivity toward copper, cadmium and zinc.

Loizidou and Haralambus (1992) showed that trivalent chromium cations can also be removed from aqueous solutions in a short period of time by using Na^+ and NH_4^+ forms of naturally occurring zeolites. According to their study, actual exchange capacities of all zeolite samples were under 50% of their theoretical exchange capacities. Although 24 hours are needed for maximum exchange capacity, they have reported that a substantial percentage of the equilibrium value was retained within one hour.

Semmens and Martin (1988) studied on the cation selectivity, cation composition, and effect of conditioning clinoptilolite collected from California, USA. Samples have been exposed to the different concentrations of NaCl solutions, then observed the efficiency of one untreated and three treated clinoptilolite samples in removal of certain heavy metal cations (Cu^{2+} and Cd^{2+}). Exchange isotherms and breakthrough curves of Cu^{2+} and Cd^{2+} ions were obtained by both batch and column studies. It has been concluded that increasing levels of conditioning make significant increase in effective capacity of the zeolite samples for both cadmium and copper. Nevertheless, cadmium has been found more selectively removed than copper for all the untreated and treated zeolite samples.

Semmens and Martin (1980) have studied on the removal of lead, silver and cadmium by clinoptilolite in the presence of competing ions, such as calcium, magnesium and sodium. According to their studies, the removal efficiency of clinoptilolite strongly depends on the concentration of competing ions. The obtained selectivity sequence is $\text{Pb}^{2+} > \text{Ag}^{2+} > \text{Cd}^{2+}$. Besides the effect of the concentration of competing ions, effects of pretreatment methods in the removal efficiency of clinoptilolite have been also examined with acid and base treatment. The acid pretreatment has been found to be less effective in improving either selectivity or the kinetics of heavy metal removal. On the other hand, base treatment was found more effective in changing the zeolite surface which improves the exchange of heavy metals more successively.

Mier et al. (2001) have studied about the interactions of Pb^{2+} , Cd^{2+} and Cr^{6+} competing for ion-exchange sites in natural clinoptilolite. In batch reactors and in acidic pH, dissolved Pb^{2+} and Cd^{2+} were effectively (>95%) removed in 18 hours. However the presence of Cr^{6+} ion has significantly diminished the Pb^{2+} and Cd^{2+}

removal efficiencies since the interaction between the Cr^{6+} , Pb^{2+} and Cd^{2+} to form anionic complexes. On the other hand, a decrease in Pb^{2+} removal efficiency has been observed at $\text{pH} > 10$. This was attributed to the formation of anionic hydroxo-complexes with cationic ion exchange sites. Therefore, process efficiency can be increased by the prevention of ligands that form complexes with reduced accessibility and/or affinity for ion-exchange. Results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Yuan and Seyama (1999) have investigated the ion-exchange capacities and the removal efficiencies of mordenite and clinoptilolite for four highly toxic heavy metals (Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+}) at a low-to-medium concentration range. Ion-exchange experiments were conducted using batch method. The amount of metal adsorbed was calculated from the difference between the amount initially added and that remaining in the supernatants. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) was used to determine the change in concentrations. According to the study, both mordenite and clinoptilolite removed more Pb^{2+} than Cu^{2+} , Cd^{2+} and Zn^{2+} from the solution. Moreover, X-Ray Photoelectron Spectroscopy (XPS) analysis showed that, adsorbed Pb^{2+} was more or less evenly distributed within the zeolite particles, whereas adsorbed Cd accumulated on particle surfaces.

Brigatti and Franchini (1999) investigated the ability of natural microporous materials such as zeolite-rich tuff (chabazite-phillipsite) and sepiolite to compare their efficiency in removal of heavy-metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+}) from simulated inorganic polluted industrial wastewater. Elemental content of samples was determined by using AAS and ICP. Structural, thermal and thermogravimetric analyses were performed by XRD and DTA/TGA respectively. Breakthrough and elution curves were obtained for zeolite-rich tuff, sepiolite and activated carbon. On the basis of their findings, zeolite-rich tuff shows high selectivity for heavy metals (Pb^{2+} more than Cd^{2+}). Although adsorption capacity of sepiolite was limited, it was found that sepiolite has also a significant selectivity for Cu^{2+} and Zn^{2+} . On the other hand, uptake efficiency of activated carbon towards Pb^{2+} ions is less than zeolite-rich tuff, whereas it is more than sepiolite towards Cu^{2+} . Their study confirms that natural materials, such as zeolite-rich tuff and sepiolite can effectively treat effluent contaminated with mixed heavy metals.

Due to the strong dependency of ion-exchange process on characteristics of both exchanger solid, liquid and experimental conditions, there are many studies related to the examination of the effect of certain parameters such as, particle size, conditioning

and the amount of the exchanger, initial ion concentration, presence of competing ions, pH and temperature of the solution, and contact time on the efficiency of ion-exchange process.

In the study of Kesraoui-Ouki and Kavannagh (1997), clinoptilolite and chabazite have been investigated in their selectivity and removal performance in treatment of wastewaters containing mixed heavy metals (Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Cr, Ni^{2+} and Co^{2+}).

Effects of competing cation presence, pH and metal concentration were considered in ion-exchange capacity of natural zeolites by using batch method. Maximum cation removal was achieved at 10 ppm initial metal concentration which was ranging from 1 ppm to 30 ppm. Impact of pH was also found so significant in the removal process in terms of the characters of both metal ions and the zeolite itself. Optimum removal has been reached when the pH was between 4 and 5. According to the experimental results, calcium as a competing cation for ion exchange could affect the removal performance of zeolite, especially at higher concentrations exceeding 1000 mg/l. It was also indicated that chabazite has higher exchange capacity than clinoptilolite due to its higher Al content which provides a negative framework for better ion-exchange capability.

Blanchard, Maunaye and Martin (1984) have examined the usage of clinoptilolite as an ion-exchanger for the removal of ammonium and heavy metal cations from drinking water. Selectivity sequence of Na^+ -exchanged clinoptilolite has been obtained by plotting the exchange isotherms for various cations using batch method. Selectivity sequence of clinoptilolite was found as $\text{Pb}^{2+} > \text{NH}_4^+ > \text{Cd}^{2+}$, Cu^{2+} , $\text{Sr}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$. After static experiments, heavy metal removal efficiency of clinoptilolite has been studied dynamically by flow through a bed of Na-clinoptilolite. They investigated the effect of flow rate through the column and the regeneration of the bed in a laboratory pilot plant. Optimum exchange has been obtained at flow rate of 12 BV/h. Regeneration experiments have been conducted by passing concentrated (20-25 g/l) NaCl through the column with a flowrate of 10 BV/h. Best results have been met with a 40 BV of NaCl solution at pH between 4.0-4.5 at which, precipitation of metalhydroxides could be avoided. It has also been found that heavy metal ions are released if the inlet metal concentration shows a sudden increase. Blanchard et al. have proved that an important part of heavy metal as well as ammonia can be removed effectively by using clinoptilolite.

Al-Haj Ali and El-Bishtawi (1997) have also studied about the change in lead and nickel removal capacity of zeolite tuff (phillipsite rich) with change particle size, initial solution pH, initial metal ion concentration, zeolite amount and the solution temperature. Experiments have been conducted with Na-phillipsite, having size fraction in the range of 45-710 μm , metal nitrate concentration in the range of 50-400 mg/l, initial pH between 2.5-4.5, zeolite amount between 1.5-8.0 g/l and the temperature in the range of 20-35 $^{\circ}\text{C}$. Langmuir and Freundlich models were applied to the experimental data to obtain adsorption isotherms for lead and nickel. Both models gave good fit for the data for both metal ions.

Al-Haj Ali and El-Bishtawi showed that Jordanian phillipsite is an efficient ion exchanger in removal of lead and nickel ions from aqueous solutions. Lead removal efficiency has been found higher than nickel removal efficiency of zeolite, regardless of the operating conditions. It has also been observed that, as the particle size of the zeolite got finer, exchange rates for both metals increased. Moreover, they indicated that higher metal removal could be achieved at an initial solution pH of 4.0-4.5 with the carefully selection of other operating conditions.

Loizidou and Malliou (1994) examined the ion-exchange kinetics of lead and cadmium at two different temperatures (25 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$) with Na-Clinoptilolite having four different particle size fractions (160-600 μm , 0-600 μm , 600-1000 μm , 1000-2000 μm). They observed that the exchange rates for both lead and cadmium are higher for the smaller particle diameters and at elevated temperatures. Calculated diffusion coefficients also showed a decrease when particle size was decreased.

Acid Mine Drainage (AMD) is one of the most serious environmental problems in all over the world. It results from the weathering of sulfide minerals such as pyrite (FeS_2). AMD is very low in pH (as low as 2) and is enriched with iron (Fe^{2+} , Fe^{3+}), aluminum (Al^{3+}) and sulfate (SO_4^{2-}). It also contains large concentrations of dissolved metals such as calcium (Ca), magnesium (Mg), mangan (Mn), copper (Cu), arsenic (As), lead (Pb), mercury (Hg), cadmium (Cd), and in some cases thorium (Th) and uranium (U). Discharge of AMD on land and into the rivers and lakes possess an instant threat to biota and ecological balance. State water quality standards in Turkey require that mine-water discharges have a pH between 6 and 9, and iron concentration of less than 3.0 mg/L for the protection of the living environment [Güler 2001].

When acid mine waters mix with the surface waters, there is potential for gross pollution. An orange ferric oxide precipitate can blanket the receiving water source and

kill aquatic flora and fauna which can devastate the food chain. Neutralization and precipitation by the addition of alkaline chemicals such as limestone, lime, sodium hydroxide and sodium carbonate are the conventional mine drainage treatment methods. However, this technology produces sludge, which must be disposed of. In other words, it changes an aqueous pollution problem to a solid waste disposal problem and the contained metal ions are never recovered [Mohan and Chander 2001].

Zamzow and Shultze (1993) have investigated the efficiency of five types of zeolite-rich tuffs originated from different regions of United States (4 clinoptilolite, 1 phillipsite) on the treatment of AMD waste streams (Acid Mine Drainage), which refers to wastewater that originates from metal ore bodies. Typically, these streams contain high concentrations of Al^{3+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+} and other metals. Both column and shake tests have been conducted. According to the results of shake tests, almost all ion-exchange took place within the first 4 hours of 48 hours. In shake tests, all types of zeolite-rich tuffs showed a high effective Cation Exchange Capacity (CEC) for Pb^{2+} , which was followed by Ca^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , Al^{3+} , and Ni^{2+} . In column tests, Cu^{2+} , Fe^{2+} , Mn^{2+} and Zn^{2+} concentrations were reduced to less than the EPA drinking water standards. However, it was concluded that, for appreciable exchange to take place in a column, a long contact time is required. With sufficient contact time, the zeolites would reduce the concentrations of cations in AMD to or less than drinking water standards and simultaneously increase the pH to near neutral.

In order to test the applicability of a local clinoptilolite (Bigadic/Turkey) to the heavily polluted waters, Şenatalar et al. (1991) have studied with water samples taken from Golden Horn, one of the most industrialized and polluted regions of Turkey. No pretreatment was applied to the water samples prior to the ion-exchange experiments with zeolite, except for the simple filtration to remove mud and turbidity. Similarly, clinoptilolite sample was also used without any pretreatment except for washing with distilled water. Ion-exchange experiments have been carried out with 2-4 w/volume %, at room temperature for a period of 4 days with gentle stirring. The results showed that the highest removal efficiency was for manganese, followed by nickel, iron, chromium, copper, zinc and cadmium.

The presence of ammonia and ammonium ions in effluents which pass into the freshwater environment is a toxic hazard to fish and some other forms of aquatic life. Eutrophic conditions in lakes and rivers are directly related with ammonia and ammonium concentration especially phosphate exists. As a consequence of these

problems, removal of ammonium ion to concentrations below 1 ppm, is required; clinoptilolite is one example of zeolite which is used for this purpose. In their study, three natural material, clinoptilolite, mordenite and ferrierite have been tested in their selectivity towards ammonium and sodium. Clinoptilolite, mordenite and ferrierite all maximally exchanged with sodium besides exhibiting partial exchange with ammonium. Despite the observed partial exchange levels, both clinoptilolite and mordenite show a very high preference for ammonium over sodium (ΔG° -4.033 and -4.590 kJ/mol respectively) [Townsend 1983].

Ülkü (1984) has also studied the effect of natural zeolites on the pollution control of Porsuk River to which, wastewater of Kutahya Fertilizer Plant is discharged. In the study, natural zeolites provided from Balıkesir region of Turkey has been used. At the end of the study, 91% of ammonium removal efficiency has been obtained. It has been concluded that natural zeolites could be a good material that can be used in pollution control, especially ammonium removal, applications.

Kallo (1993) has investigated the application of clinoptilolite rich tuff in two stages of municipal treatment plant. First stage was the biological treatment stage, in which an increase in biological activity was obtained based on the adherence of bacteria-flocs to small clinoptilolite rock grains, resulting in an increase in settling rate. Secondly, in the removal of residual ammonium from the biologically treated and settled sewage as a result of cation-exchange in a column filled with clinoptilolite-rich tuff. It was reported that sedimentation rate of suspended solids has been increased by 100% due to the attachment of flocs onto relatively heavier clinoptilolite particles. Moreover, the zeolite-containing sludge was more easily dewatered than normal sludge. This phenomenon was attributed to the promotion of composting of sludge by clinoptilolite.

Depending on the studies mentioned above, it can be concluded that, ion-exchange behavior of an exchanger, in this case natural zeolite, mainly depends upon the characteristics of both the solution and the exchanger. Solution characteristics can be listed as cation-anion species and their concentrations in the solution, pH and temperature. On the other hand, whether the exchanger is pretreated or not, its size and amount that is in contact with the solution, presence of competing cations and the contact time are the other important criteria in ion-exchange phenomenon.

2.3. Comparison of Ion-Exchange Method and Other Methods Used In Heavy Metal Removal.

Different technologies are described in the literature for the removal of heavy metals such as chemical precipitation, solvent extraction, electroflotation, reverse osmosis, adsorption on activated carbon and ion-exchange. Among these methods, reverse osmosis is an expensive membrane process. Solvent extraction and electroflotation are also expensive and hard in application.

The removal of heavy metals from wastewaters is usually accomplished by chemically precipitating hydrous oxides of the metals with lime or soda. However, other than being strongly dependent to pH, similar to the neutralization process, it has many disadvantages:

- ◆ It generates large amount of sludge, which is costly to dispose of and often hazardous.
- ◆ It results in unacceptably high levels of residual metals in wastewaters and also results an increase in the pH of wastewaters and also receiving surface water.
- ◆ It requires long settling times despite the use of coagulants which are the main reasons of the increase in the cost of the process.

On the other hand, ion-exchange offers a series of advantages [Colella et al. 1993].

- ◆ It is simple and economical especially in case of using a natural exchanger.
- ◆ Reaction is usually rapid, specific and characterized by a rigorous stoichiometry.
- ◆ pH, depending on the original heavy metal concentration, remains practically unaffected or moves towards neutrality, provided the heavy metal cation is replaced in solution by an alkali or alkaline earth cation
- ◆ The process allows selectively cation exchange when appropriate exchanger is used.
- ◆ Also allows recovery of metals from the solution and from the solid phase.

Due to the advantages listed above, among all other methods, ion-exchange seems to be an attractive method especially when low cost materials, such as natural zeolites, can be used as exchangers. It is attractive for being not only economical but also being simple especially for the countries having their own deposits.

Chapter 3

EXPERIMENTAL

3.1. Materials

Clinoptilolite rich natural zeolite mineral used in this study, was obtained from Gördes, Western Anatolia.

During the experimental studies, all solutions and dilutions were made using deionized water (Barnstead Ultrapure-UV). pH values were measured with a WTW(Wissenschaftlich-Technische Werkstätten) pH330. All metal analysis were performed using Inductively Coupled Atomic Emission Spectrometry (ICP-AES 96, Varian). The standards employed during these analysis were prepared from stock solutions (Merck). Nitric Acid solution (5% v/v) was used for washing glassware and polypropylene sample bottles.

In ion-exchange studies nitrate salts of metals were used. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) (Sigma, ACS Reagent, assay 101.8%), Copper(II)nitratehemipentahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) (Aldrich, ACS Reagent, 98% pure) and Zinc(II)nitratehexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fluka, >99% pure) were used in metal solutions. The pH of the samples was adjusted by using diluted (0.1 M) solutions of Nitric acid (Merck, 65%) and Sodium hydroxide (NaOH) (Carlo Erba, 99.5-100.5% pure). In experiments performed to see the effect of competing cations, Sodiumchloride (NaCl) (Carlo Erba, 99.5% pure), Sodiamsulfate (Na_2SO_4) (Carlo Erba, 99% pure) and Calciumchloridedihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (Sigma, 99% pure)

Simulated Acid Mine Drainage (AMD) solutions containing lead, zinc, copper, iron and aluminum were prepared by using Iron(II)sulfateheptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Carlo Erba, 99% pure) and Aluminumchloride (AlCl_3) (Merck, 99.5% pure) were used in addition to the nitrate salts of lead, copper and zinc.

3.2. Method

Experiments were performed in two main parts, which are characterization studies and ion-exchange studies. In characterization studies, clinoptilolite rich natural zeolite samples were characterized in terms of their size distributions, thermal and

adsorption related properties with the help of different instrumental techniques. Experimental procedure is given in Figure 5.

3.2.1. Material Preparation and Characterization

Three groups of clinoptilolite rich minerals, having different particle size distribution ranges (0-0.7 mm, 0.7-1.8 mm and 1.8-3.5 mm), were mixed to obtain representative samples. After mixing of zeolites, they were grouped into small portions. For exchange experiments, clinoptilolite samples were washed with deionized water at 100 °C for three times to remove soluble impurities. Then, samples were dried at 100 °C, for 1 hour, in an oven. Samples were dried at 160 °C under vacuum for 30 minutes to desorb water in the zeolite structure,

Washed and dried clinoptilolite rich mineral samples were ground in the ball-mill (Retsch S1000) at 90 amplitude for three different time periods (10, 30, and 60 minutes) to obtain different particle size distributions. Similarly, unwashed natural zeolite samples were also ground during same periods with washed samples in order to investigate the change in the characteristics of zeolite with washing. After grinding the samples, they were sieved by using stainless steel sieves. Three different groups of zeolite samples, having mean diameters of 122, 87 and 68 µm were obtained for 10, 30, and 60 minutes grinding in ball mill, respectively.

After preparation of washed and unwashed clinoptilolite rich mineral samples, thermal and adsorption-related properties of the samples were determined. Prior to thermal analyses, saturated NH₄Cl was placed in a desiccator. Then, washed and unwashed clinoptilolite samples were kept in it for 10 days to provide constant relative humidity. Saturated NH₄Cl provides 75% humid air at 25 °C. Thermogravimetric Analyser (TGA-51/51H, Shimadzu) was used for thermal analyses of natural zeolite samples. A volumetric adsorption system (Micromeritics, ASAP 2010) was used in determining adsorption-related properties of clinoptilolite. Adsorption and desorption curves were determined by using N₂ as adsorptive.

3.2.2. Ion-Exchange Experiments

In the second part, ion-exchange experiments were performed in order to see the effects of different parameters on the heavy metal uptake efficiency of clinoptilolite rich

natural zeolites and to investigate the applicability of these minerals in the area of wastewater treatment.

Ion-exchange experiments were carried out to measure the selectivity trends and capacities of clinoptilolite rich minerals towards Pb^{2+} , Zn^{2+} and Cu^{2+} , and to determine the time required for the system to reach the equilibrium. In this part of study, metal ion concentration, combinations of metal species and existence of competing cations in the solution, pH of the solution, particle size and the percentage of the zeolite in the solution were considered as parameters.

3.2.2.1. Kinetic Studies

Kinetic ion-exchange studies for Pb^{2+} , Zn^{2+} and Cu^{2+} were conducted at room temperature for two different initial concentrations (10^{-2} N and 10^{-3} N) of each metal. Solutions were prepared with nitrate salts of lead, copper and zinc. The beakers, 100-ml metal solution and a certain percentage of zeolite in them (0.5%, 1%, 1.5%) (weight zeolite/volume of solution), were shaken at a speed of 450 rpm, at room temperature (25 ± 2 °C). Since samples were taken with time, to eliminate any change in the metal concentration/zeolite ratio, separate beakers were used for each time period (0.5, 1, 2, 4, 8, 16, 32, 64, 128, 256 minutes, 8 hrs, 24 hrs, 48 hrs, 72 hrs and 120 hrs).

3.2.2.2. Effect of pH and Particle Size

In order to compare the efficiency of zeolite at different pH values, 10^{-2} and 10^{-3} N $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions were shaken at 450 rpm shaking speed with 1.5 g. natural zeolite, for 256 minutes. Initial pH values were adjusted to four different values (i.e., pH 2.5, 4.5, 6, 10) by adding 0.1 N NaOH or 0.1 N HNO_3 . In these experiments, three different size of natural zeolite (122, 87 and 68 μm) were used to compare not only the change in efficiency with pH but also with the size of the zeolite. Similar to equilibrium studies, to separate solid and liquid phases filtered syringes were used. At the end of each the time period, final pH values of the solutions were recorded.

3.2.2.3. Removal of Heavy Metals in Single Component and Multi-component Systems in the Absence and Presence of Electrolytes

After pH effect experiments, presence of competing cations in the metal solutions were examined in terms of their effect on the metal removal efficiency of zeolites when the solutions contain single, binary and ternary metal species with the addition of 0.1% and 0.01% (weight/volume of solution) of NaCl, Na₂SO₄ or CaCl₂.

In the single, binary and ternary systems, initial metal concentrations were kept constant at 30 mg/L. In other words, concentration of each metal was 30 mg/L for single metal solutions, 15 mg/L for binary solutions, and 10 mg/L for ternary metal solutions.

To perform the ion-exchange, 1.5% (weight(g)/ volume of the solution(ml)) of natural zeolite was also added to each solution. The beakers, in which there are 100 ml. of solutions, were shaken at 450 rpm for 128 minutes. Prior to shaking, the pH of these solutions containing competing cations were adjusted to the pH value which had given the best result in the previously performed “pH effect on metal removal” experiments by adding 0.1 N NaOH or 0.1 N HNO₃. At the end of the time period, final pH values of the solutions were recorded again.

The metals chosen for the investigation in single component studies were Pb, Cu and Zn and the same solutions with the addition of 0.1% or/and 0.01% NaCl, Na₂SO₄ or CaCl₂. In multi-component(binary and ternary) systems investigations, three binary systems and one ternary systems were chosen. Binary systems were Pb-Cu, Pb-Zn, Cu-Zn, ternary system was Pb-Cu-Zn. Similar to the single component system, these systems were also investigated in terms of the effect of competing cation addition on the metal removal efficiency of natural zeolites. In the study, same competing cation with different anion species (NaCl, Na₂SO₄) were chosen to compare the effect of different anions on the efficiency of the process.

3.2.2.4. Ion-Exchange Studies With Simulated Acid Mine Drainage(AMD) Solutions

Simulated Acid Mine Drainage(AMD) solutions containing lead, copper, zinc, iron and aluminum were prepared. Information about content of the wastewater has been obtained from the study of M.J. Zamzow and L.E Shultze (1993), which is about

the treatment of AMD using natural zeolites. The content of the AMD that they had used in their study had a pH of 2.2 and contained, in mg/L, 152 Al, 502 Ca, 101 Cu, 595 Fe, 24 K, 382 Mg, 80 Mn, 95 Na, and 61 Zn.

In our study, simulated wastewater was prepared to contain 13 mg/L Pb, 112 mg/L Cu, 84 mg/L Zn, 665 mg/L Fe and 150 mg/L Al at pH 2.5. In these experiments six different time periods (10 min., 30 min., 1 hr, 2 hrs, 4 hrs and 8 hrs) were used to see the change in metal concentrations and also in the pH. Zeolite content of the solutions were 1.5 g. Shaking speed was chosen as 450 rpm.

At the end of the each time period, final pH values of each solution were recorded to test whether zeolite would result any increment in pH of these highly acidic solutions.

3.2.3. Analysis of the solutions

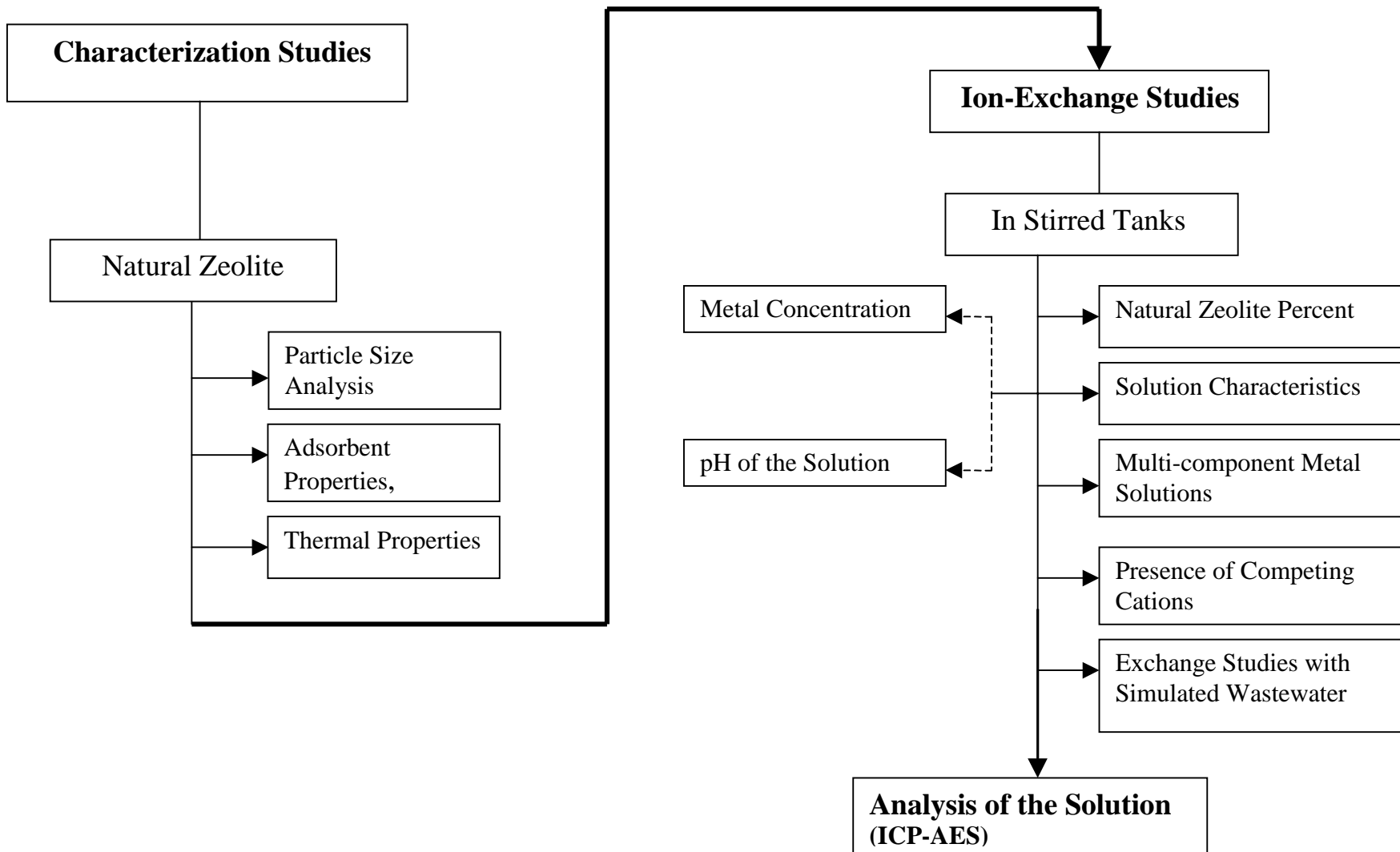
During whole experimental work, filtered syringe having pore opening of 0.25 μm , was used in sampling to separate solid (zeolite) and liquid (metal solution) phases. Clear metal solutions (20 ml) were taken into small polypropylene sample bottles before elemental analyses with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES 96, Varian). Before the analysis, 5% nitric acid (Merck, 65% purity) was added to each sample to minimize chemical associations and attendant problems.

In elemental analyses with ICP-AES, argon was used as plasma gas. During analysis, tubing material of the instrument was rinsed with blank solution containing 5% HNO_3 to remove residue of previous samples. Table 5 expresses the method conditions used during analyses.

Table 5. ICP-AES Analysis Method Conditions

Pump Rate	15 rpm
Plasma Gas	Argon
Plasma Gas Flowrate	15.0 L/min
Auxiliary Gas Flowrate	1.5 L/min
PMT Voltage	650 V
Rinse Time	10 sec
Sample Uptake	30 sec

EXPERIMENTAL PROCEDURE



Chapter 4

RESULTS AND DISCUSSION

4.1. Characterization of Natural Zeolites

In this part, adsorption and thermal related properties of clinoptilolite rich natural zeolite were investigated.

4.1.1. Particle Size Distribution Analysis

Size distribution of the zeolite samples used in this study were determined by sieving after grinding the samples for different time duration to measure the effect of grinding time on the mean particle size and particle size distribution of the zeolite samples. The results are presented in Figure 6. The mean particle sizes of the zeolite samples changed from 122 μm -68 μm with increasing grinding time from 10 minutes to 60 minutes for both washed and unwashed samples. In this study, 30 minutes grinding was applied to the zeolite samples. In some experiments, the effect of particle size of the zeolite on its metal removal efficiency was also investigated.

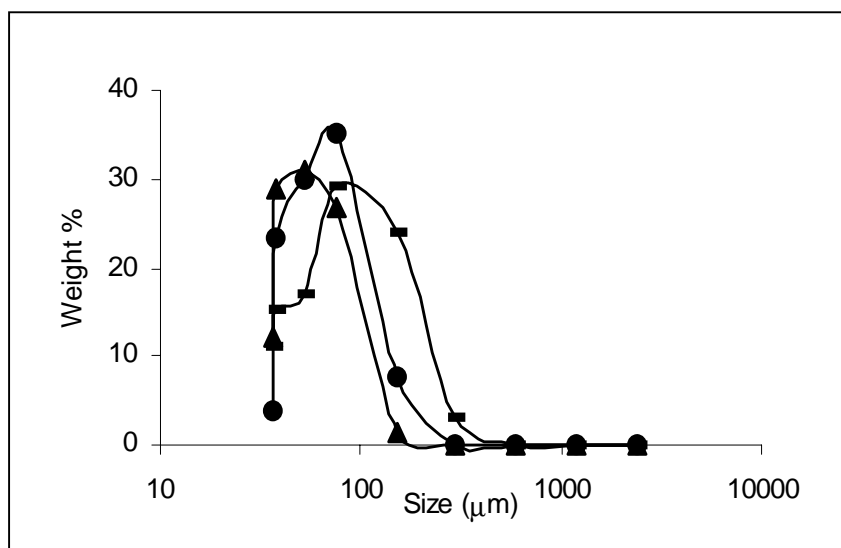


Figure 6. Particle Size Distributions of washed clinoptilolite samples (log-scale)

◆— 68 μm , ●— 87 μm , —+— 122 μm

4.1.2. Adsorption Analysis

Adsorption related properties of washed and unwashed zeolite samples were determined. Adsorption isotherms for washed and unwashed clinoptilolite for N_2 at 77 K are shown in Figure 7.

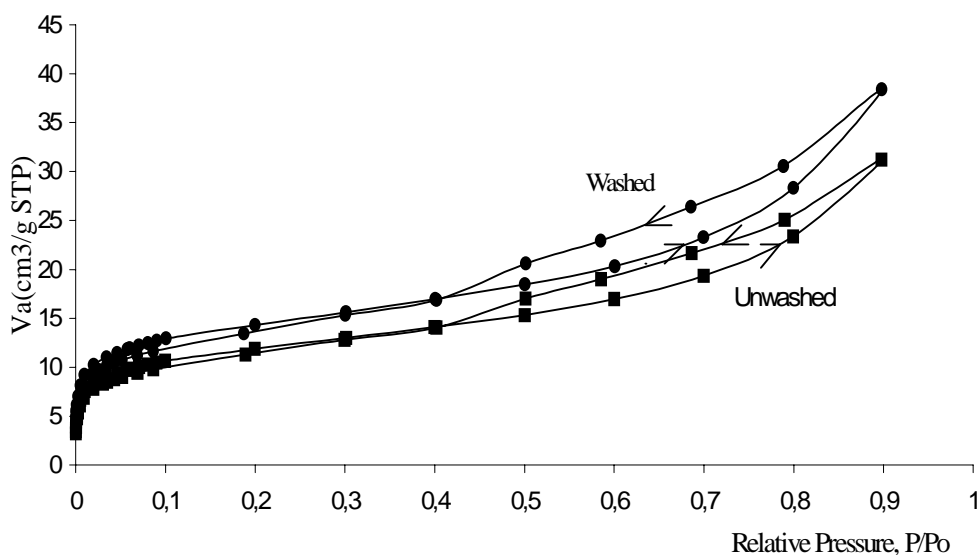


Figure 7. N_2 Adsorption-Desorption curves for washed and unwashed clinoptilolite samples (Degassed at 350 °C)

According to the IUPAC Classification, results for both washed and unwashed samples are showing the characteristic Type IIb isotherm by possessing a hysteresis loop. The lower branch of the isotherm represents measurements obtained by progressive addition of gas (N_2) to the system, and the upper branch by progressive withdrawal [Sing et al. 1999]. This type of isotherm indicates that, there occurs both monolayer and multilayer adsorption. Initial rise in the isotherm is due to the monolayer adsorption on the pore walls, whereas deviation of the isotherm shows that the beginning of the multilayer adsorption. This multilayer adsorption continues until the interception of the hysteresis loop where the capillary condensation begins in mesopores.

Based on these studies, Table 6 summarises the surface areas, found from N_2 adsorption in washed and unwashed clinoptilolite samples, calculated by using different models. Results show that surface area of washed sample is larger than that of

unwashed sample. This increase indicates that the removal of impurities with washing and drying, improves the adsorption capability of clinoptilolite.

Table 6. Summary of the Calculated Surface Areas

Method	Unwashed	Washed
Single Point Surface Area	39.49 m ² /g (at P/P ₀ = 0.30115340)	47.50 m ² /g (at P/P ₀ =0.30131214)
BET Surface Area	39.73 m ² /g	47.72 m ² /g
Langmuir Surface Area	48.79 m ² /g	59.14 m ² /g
BJH Adsorption Cumulative Surface Area of Pores (17-3000Å)	23.95 m ² /g	28.72 m ² /g
BJH Desorption Cumulative Surface Area of Pores (17-3000Å)	31.92 m ² /g	39.44 m ² /g
Dubinin-Astakhov Micropore Surface Area	25.22 m ² /g	64.58 m ² /g

4.1.3. Thermal Analysis

In thermogravimetric analysis, while the N₂ gas was used as inert gas with a flowrate of 40 ml/min, 1000 °C was reached with 10 °C/min increments. Before the analysis, all of the zeolite samples were kept in constant relative humid desiccator over saturated NH₄Cl. During analysis, the instrument recorded the weight losses of samples. Table 7 summarizes the percent weight losses of washed and unwashed samples. Graphics of thermogravimetric analyses of washed and unwashed samples, having different particle sizes, are shown in Appendix A.

Weight losses in clinoptilolite are resulted from the elimination of three groups of water: external, loosely bound and tightly bound water. External water is eliminated when the mineral is heated to 75±10°C, loosely bound water is evaporated at 171±2 °C, and tightly bound water is removed at 271±4 °C. Thus, the dehydration occurs in

stepwise manner at three steps due to the different binding energies among water molecules and cations in the clinoptilolite structure.

Table 7. % Weight losses of Clinoptilolite Samples

Sample	External Water <85 °C	Loosely Bound Water 85-275 °C	Tightly Bound Water >275 °C	Total Weight Loss
Unwashed 122 µm	3.33	4.16	2.35	9.84
Unwashed 87 µm	4.06	4.06	2.20	10.32
Unwashed 68 µm	3.44	4.11	2.69	10.24
Washed 122 µm	2.64	3.99	2.80	9.43
Washed 87 µm	3.23	3.93	2.13	9.29
Washed 68 µm	3.08	4.1	2.42	9.6

When percent weight losses of washed and unwashed samples are compared, higher weight loss percentages in unwashed samples are realized. These difference could be resulted from the removal of impurities in washed samples previously and the amount and the type of cations in the clinoptilolite structure. On the other hand, external water content of unwashed samples were found greater than that of in washed samples which could be resulted from the opening of pores in washed samples by previously washing and drying both in oven and vacuum oven. By washing and drying the zeolite samples, pores were opened and passage of water molecules into the inner pores become easier. According to results, there is average 2.41% tightly bound water loss in unwashed samples, whereas it is average 2.45 % in washed samples. When the percent weight losses and mean particle sizes were compared, no linear relationship was found between the values. However, increase in total weight percent loss had been expected as the mean particle size got smaller.

Average percent weight losses for washed and unwashed samples were calculated as 9.44% and 10.13% respectively. However, these values were found less than that was reported by Akdeniz [1999] as 13.90% for the clinoptilolite taken from the same region of Turkey. Results of these two studies may differ from each other due to the difference in the cation composition, the change in the structural characteristics of

the samples from place to place even in the same region, and the operational conditions during the analysis.

Results obtained from adsorption studies and thermal analysis are in accordance with each other by proving that washing the zeolite samples improves their both thermal and adsorption related properties.

4.2. Removal of Heavy Metals: Ion-Exchange Experiments

Ion exchange experiments were carried out to investigate the removal of heavy metals by zeolites according to the method given in Chapter 3. The results are presented and discussed in the following paragraphs.

4.2.1. Kinetics of Heavy Metal Removal

Kinetics of the removal of heavy metals, such as Pb, Cu and Zn, were studied as a function of solid percentage, pH and particle size.

4.2.1.1. Effect of Solid Percentages

These studies were conducted at different solid (zeolite) percent (1.5, 1, and 0.5%) and two different initial metal concentrations (10^{-3} and 10^{-2} N). The results for lead, copper and zinc are given in Figures 8-25 as change in final metal concentration, removal % and gram metal/gram zeolite as a function of time.

As seen from the Figures 8-13, lead removal is highly favorable with natural zeolites even in a short contact time. According to the figures, removal of cation per gram of zeolite increases with increasing metal concentration in the solution at the same time interval. However, in case of higher metal ion concentration, longer contact time is needed for the system to reach the equilibrium. At higher concentration, maximum amount of lead removed per gram of natural zeolite is twice that of at lower concentration for the same time periods (256 minutes). According to the results, almost 100% lead removal has been obtained with 1% zeolite even in 64 min when the metal concentration is low. In addition, maximum 0.01 g of Pb^{2+} has been removed per gram of zeolite when 1% of zeolite was used for the 10^{-3} N concentration of metal ion. However, as the initial Pb^{2+} concentration increased, exchanged Pb^{2+}

amount per gram of zeolite increased to 0.043 g at the end of 3 days shaking period. Decrease in removal percentage, increase in final Pb^{2+} concentration and increase in gram Pb^{2+} removed per gram zeolite at the end of 5 days, indicate that reverse exchange took place for longer contact times. Ouki and Kavannagh (1997), have stated that especially in low initial metal concentrations (1-30 ppm), Pb^{2+} removal efficiency was unaffected by the initial metals concentration and 100% removal was achieved in most case. Semmens and Seyfarth had also obtained a 100% maximal Pb^{2+} exchange level with a sharp selectivity, in their study with clinoptilolite. Results obtained from current study have also coincided with the literature by expressing the strong affinity of clinoptilolite towards lead, especially at low initial metal concentrations.

Figures 14 and 15 are indicating the change in copper concentration with time for initial Cu^{2+} concentrations of 10^{-3}N (29 ppm) and 10^{-2}N (346 ppm). For both concentrations, zeolite content of the solution was changed (1.5-1-0.5%). Longer shaking time(24 hours) was used to see the system has reached to the equilibrium for higher initial Cu^{2+} concentration. At the end of shaking period, Cu^{2+} concentration in the solution having highest zeolite content (1.5%) decreased from 346 ppm to 265 ppm. However, it was measured as 268 ppm at the end of 256 minutes shaking period. Therefore, it can be said that even for high metal concentrations, 256 minutes shaking period is enough for the system to reach to the equilibrium.

According to the results, for the same initial metal concentration and as the zeolite content of solution was increased, higher copper removal has been obtained. For instance, after 256 minutes shaking at 450 rpm, 10^{-3}N (29 ppm) initial Cu^{2+} concentration decreased to 15 ppm with 1.5% zeolite content, 19 ppm with 1% zeolite content and 23 ppm with 0.5% zeolite content. Although minimum removal efficiency was obtained in the solution having 0.5% zeolite content, highest amount of Cu^{2+} removal per gram of zeolite (gr/gr) was found in that solution having 0.5% zeolite content. Although minimum removal efficiency was obtained in the solution having 0.5% zeolite content, highest amount of Cu^{2+} removal per gram of zeolite (gr/gr) was found in that solution having 0.5% zeolite content. This is due to existence of lower amount of zeolite for the same initial metal concentration.

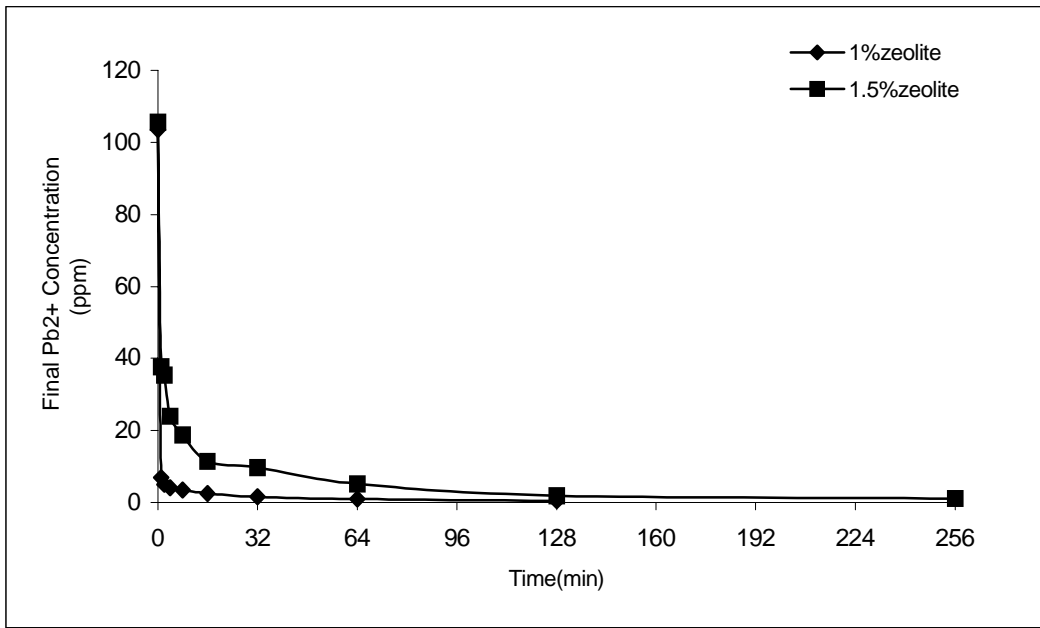


Figure 8. Change in Pb²⁺ Concentration with Time. Co=103 ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

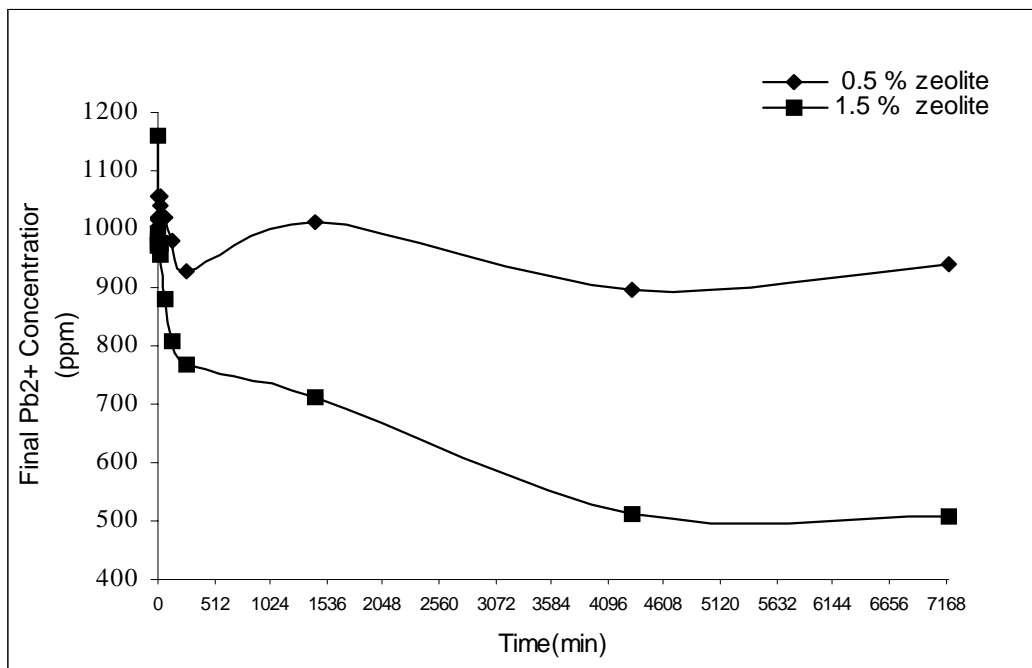


Figure 9. Change in Pb²⁺ concentration with time, Co=1161ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5, Shaking Period= 5 Days

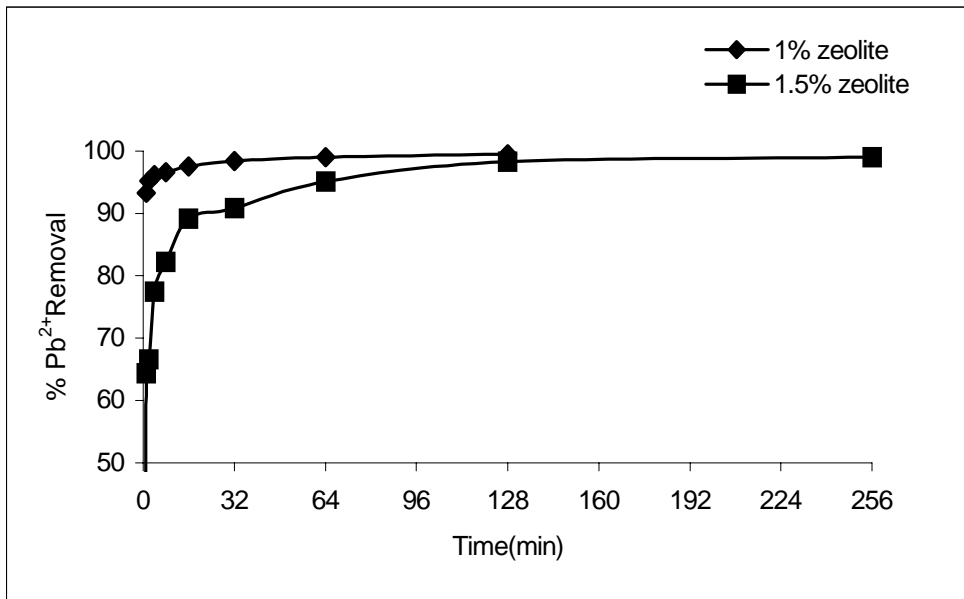


Figure 10. Change in %removal of Pb²⁺ with time. C_o=103 ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

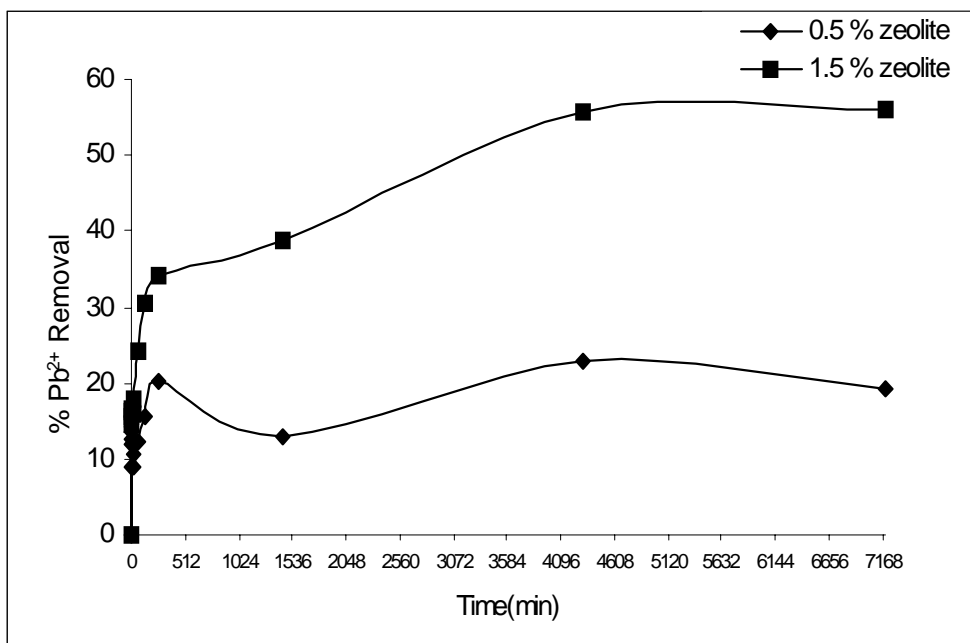


Figure 11. Change in % removal of Pb²⁺ with time. C_o =1161 ppm, D_p=87 μm Shaking Rate=450 rpm, pH=3.5, Shaking Period= 5 Days

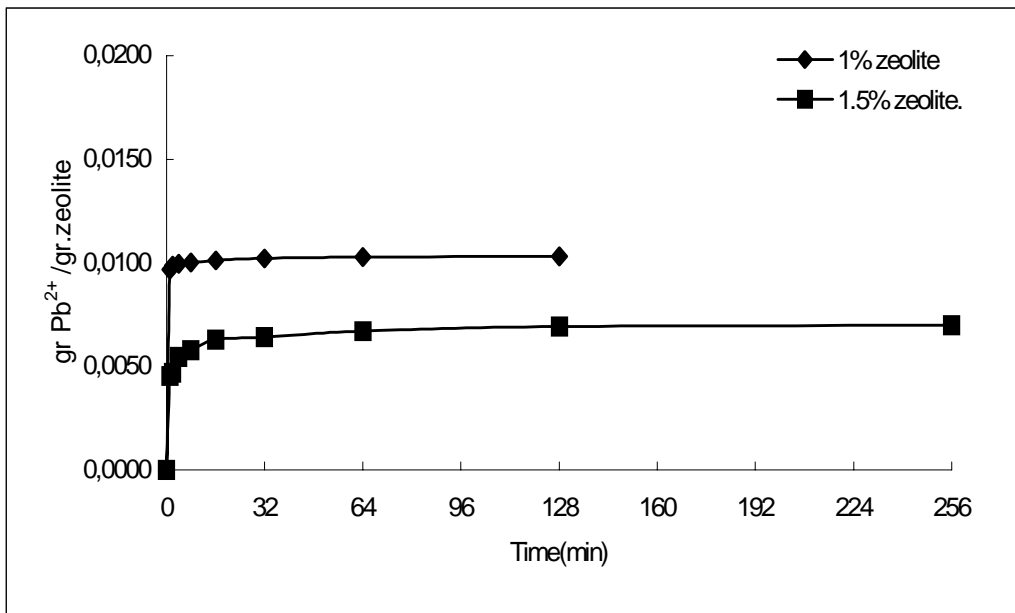


Figure 12. Pb²⁺ Removal per gram zeolite. C_o=103 ppm, D_p=87 μm,
Shaking Rate=450 rpm, pH=3.5

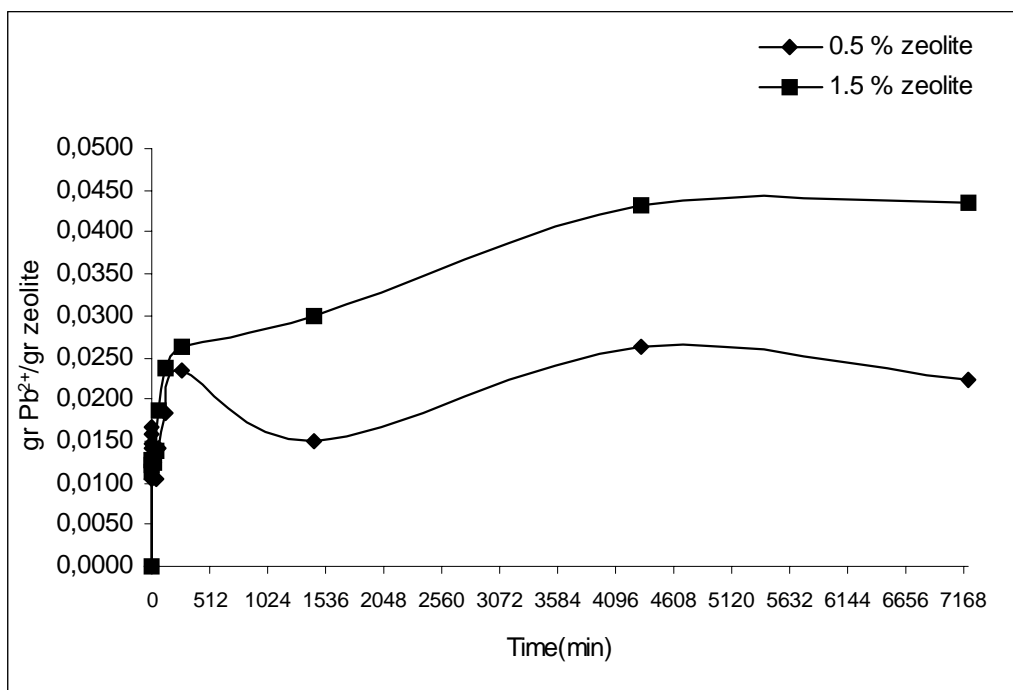


Figure 13. Pb²⁺ Removal per gram of zeolite. C_o =1161 ppm, D_p=87 μm
Shaking Rate=450 rpm, pH=3.5, Shaking Period= 5 Days

Change in Cu^{2+} removal percentage with time are given in Figures 16 and 17 respectively. In Figures 18 and 19, removed Cu^{2+} per gram of zeolite with time at the different initial metal concentrations and different zeolite contents, are presented. It can be concluded from the figures that, at the same time period (256 minutes) exchange capacities of zeolites in the solution having 346 ppm initial metal concentration, are higher than those of in the solution having 29 ppm initial metal concentration. After 256 minutes of shaking and 0.5 % of zeolite, maximum gram of Cu^{2+} removed per gram of zeolite reached to 0.0023 gr/gr (Figure 19), whereas it was only 0.0012 gr/gr (Figure 18). Apparently, increase in initial metal concentration made a positive effect in exchange efficiency of zeolite but the final solution is still need to be treated since the equilibrium is reached before the completion of the metal removal.

Figures 20 and 21 shows the, change in Zn^{2+} concentration with time and different zeolite contents (1.5%, 1%, 0.5%) for both the initial Zn^{2+} concentrations of 10^{-3} N (30 ppm) and 10^{-2} N (355 ppm). Similar to the previous experiments performed for copper and lead, metal removal increased with increasing zeolite content. After 256 minutes shaking period, 38%, 22% and 15% Zn^{2+} removal have been obtained by using 1.5%, 1% and 0.5% zeolite contents respectively for 10^{-3} N Zn^{2+} . Longer contact time (5 days) was used for the metal solutions having higher Zn^{2+} concentrations (10^{-2} N, 355 ppm).

Zn^{2+} removals were illustrated in Figures 22 and 23. If we compare the removal percentages for both concentrations at the end of 256 minutes and for 1.5% zeolite contents; removal percentage is 8% for 355 ppm initial Zn^{2+} concentration, whereas it is 38% for 30 ppm initial Zn^{2+} concentration.

Amount of Zn^{2+} removed per gram of zeolite for 10^{-3} N and 10^{-2} N initial metal concentrations are given in Figure 24 and Figure 25 respectively. According to the results, at the lower Zn^{2+} concentration, maximum 0.00093 gram Zn^{2+} has been removed per gram of zeolite in 256 minutes. However, this value has reached to 0.0061 in case of using higher Zn^{2+} concentration for 3 days of shaking. In addition, as Figure 25 indicates, 0.0058 gram of Zn^{2+} has been exchanged per gram of zeolite at the end of 5 days of contact time. It can be concluded that to prevent reverse exchange, 3 days of contact time is suitable for the system to reach to the equilibrium especially at higher initial metal concentrations.

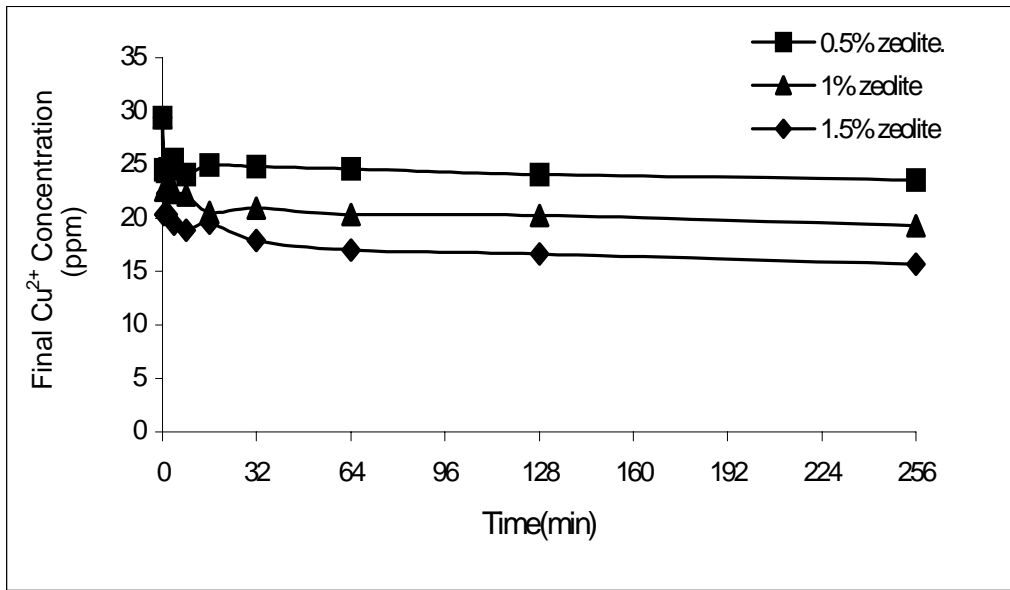


Figure 14. Change in Cu²⁺ concentration with time. Co=29ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

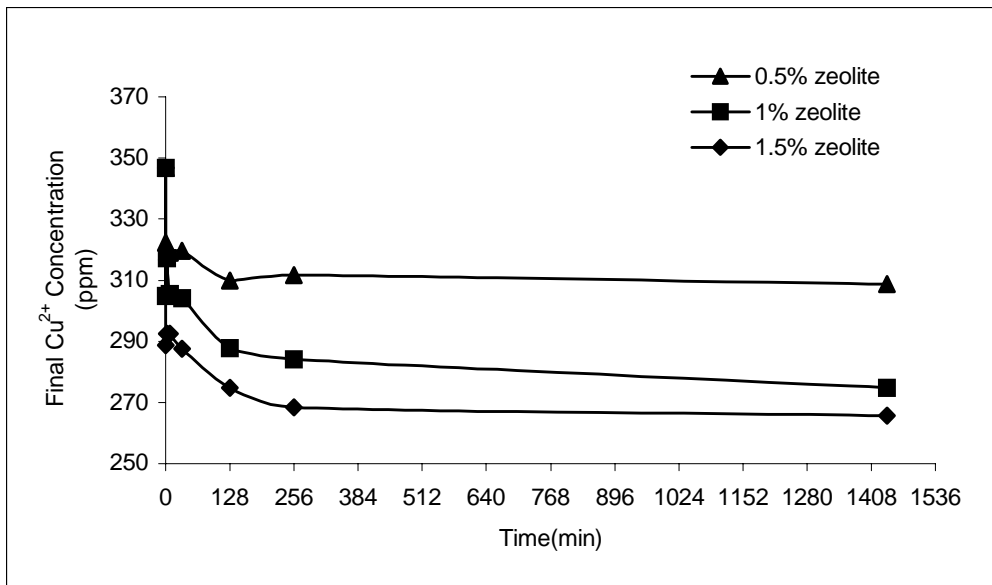


Figure 15. Change in Cu²⁺ concentration with time. Co=346 ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

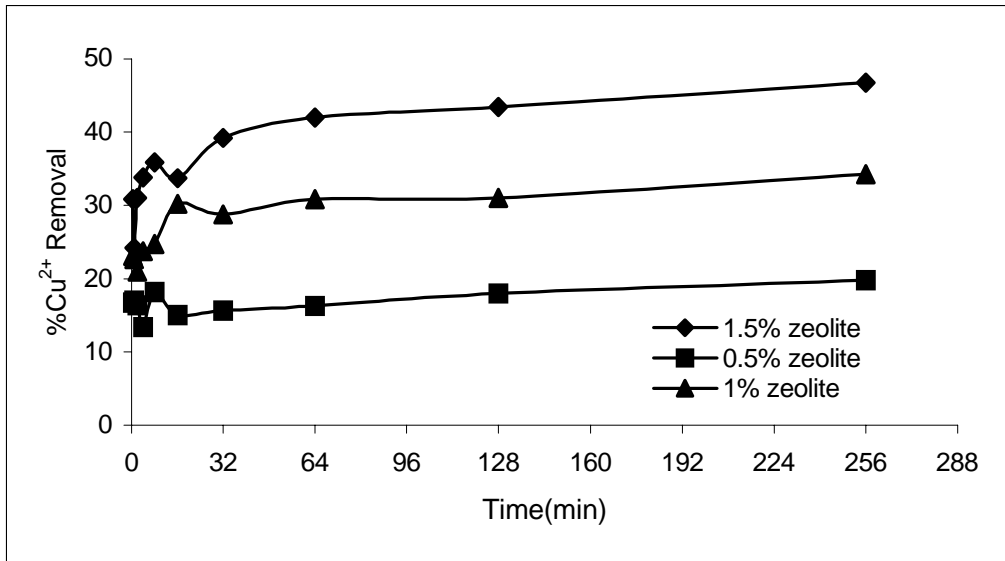


Figure 16. Change in % removal of Cu^{2+} with time. $\text{Co}=29\text{ppm}$, $D_p=87\ \mu\text{m}$,
Shaking Rate=450 rpm, $\text{pH}=3.5$

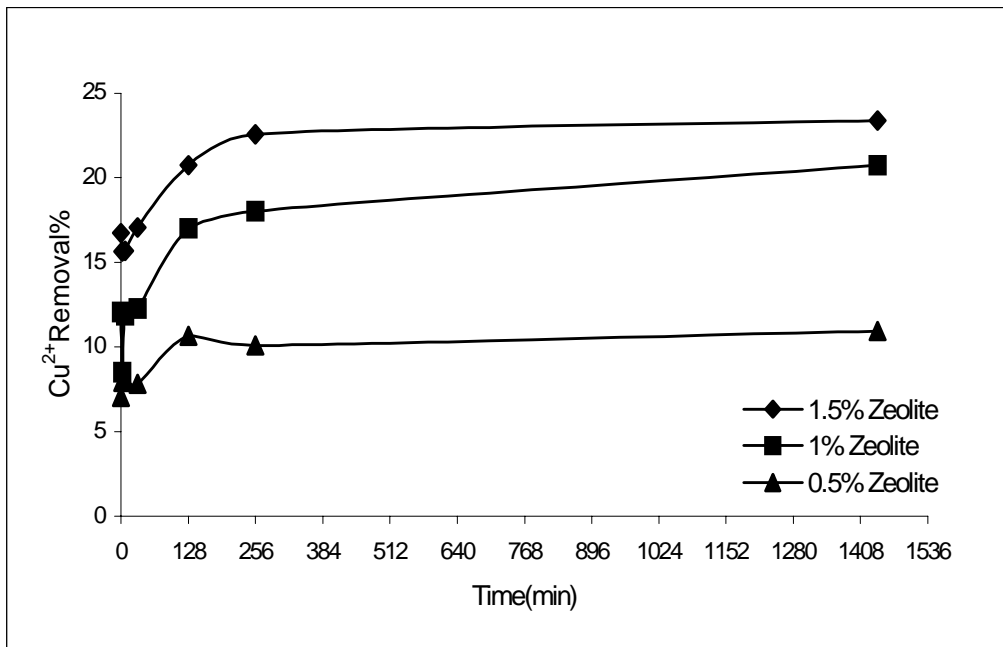


Figure 17. Change in % removal of Cu^{2+} with time. $\text{Co}=346\ \text{ppm}$, $D_p=87\ \mu\text{m}$,
Shaking Rate=450 rpm, $\text{pH}=3.5$

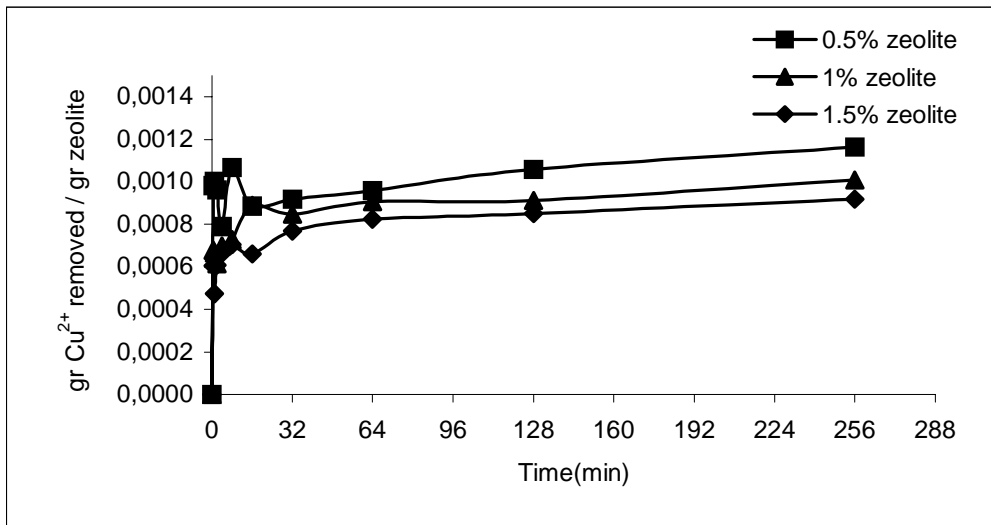


Figure 18. Cu²⁺ Removal per gram of zeolite. Co=29ppm, D_p=87 μm,
Shaking Rate=450 rpm, pH=3.5

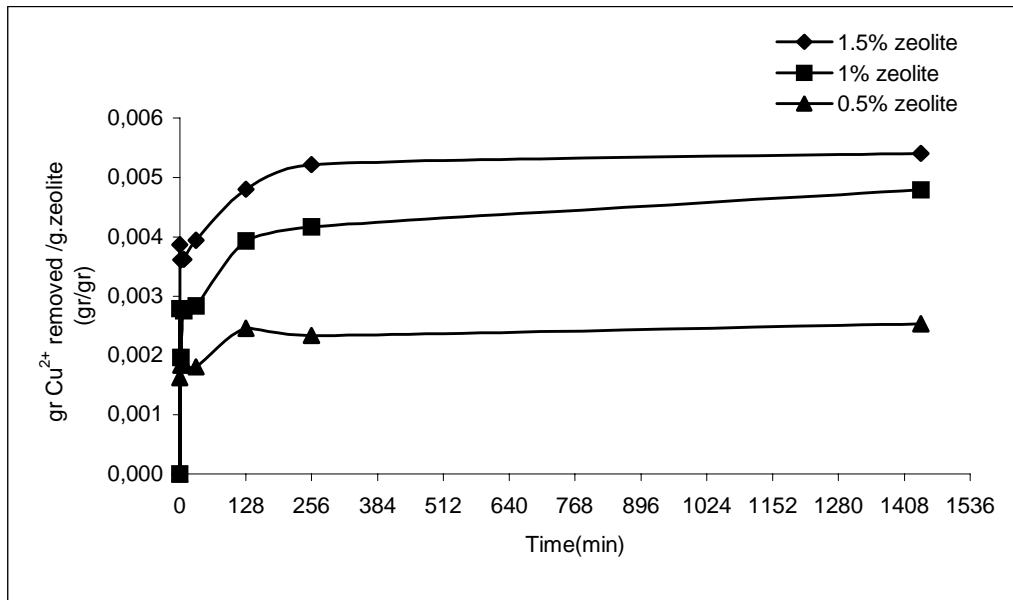


Figure 19. Cu²⁺ Removal per gram of zeolite. Co=346 ppm, D_p=87 μm,
Shaking Rate=450 rpm, pH=3.5

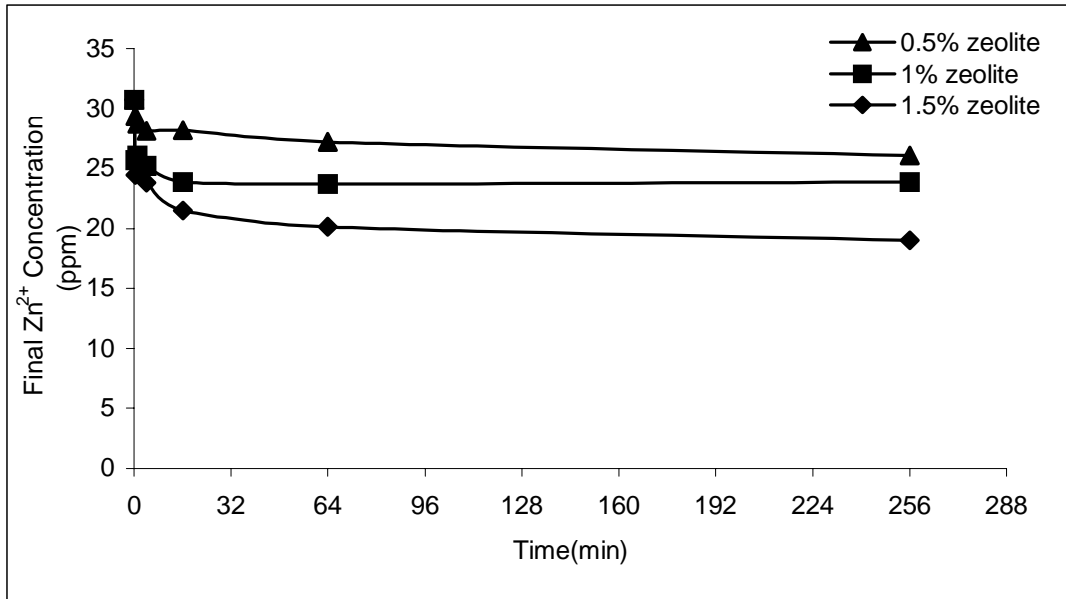


Figure 20. Change in Zn²⁺ concentration with time. Co=30ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

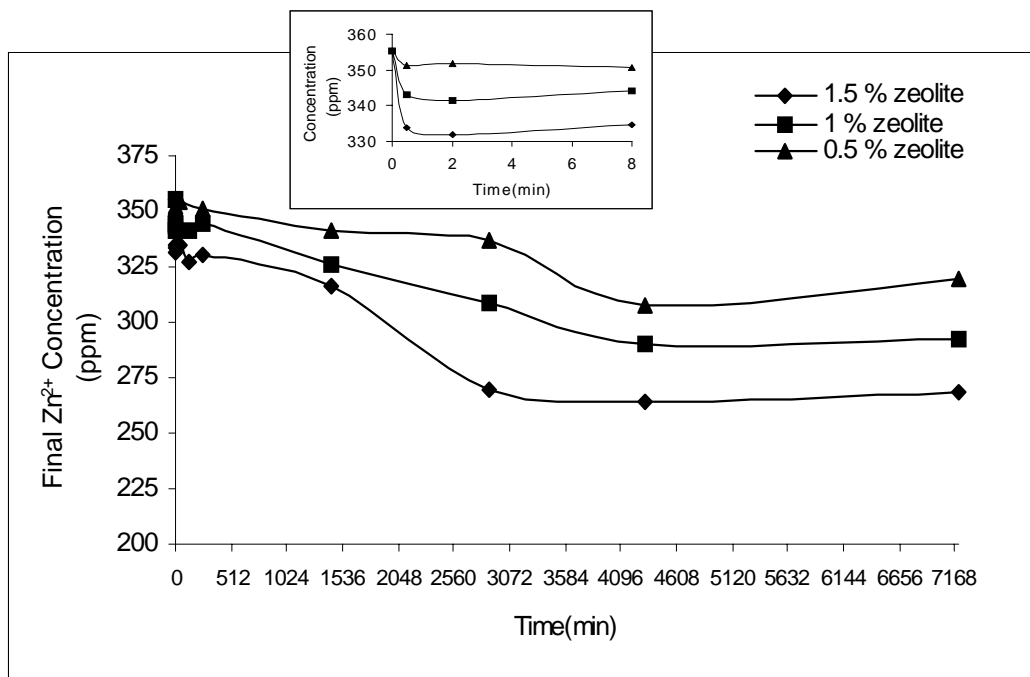


Figure 21. Change in Zn²⁺ concentration with time, D_p=87 μm, Co=355 ppm, Shaking Rate=450 rpm, pH=3.5.

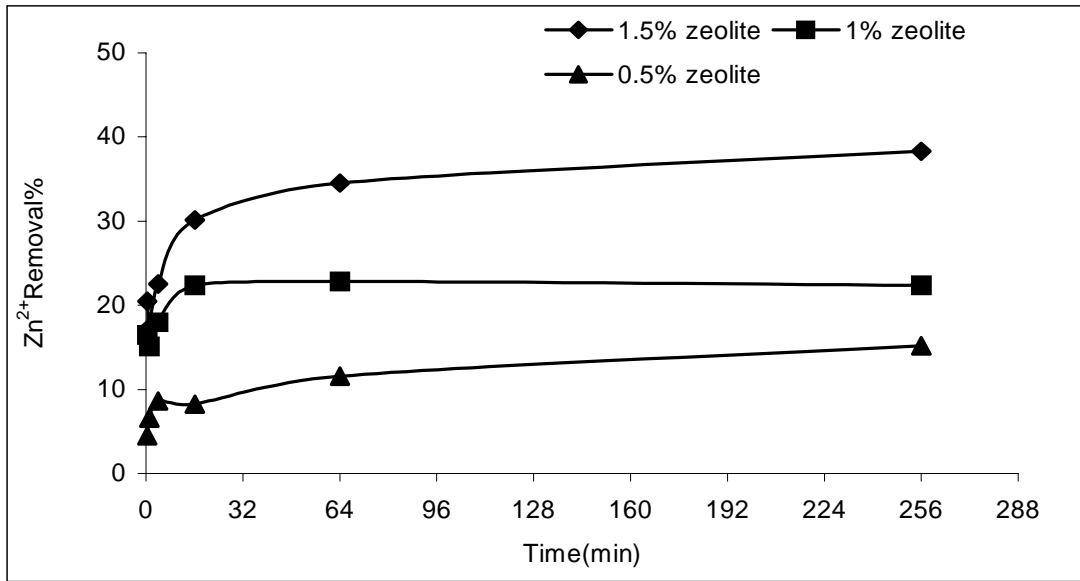


Figure 22. Change in % removal of Zn²⁺ with time. Co=30ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5

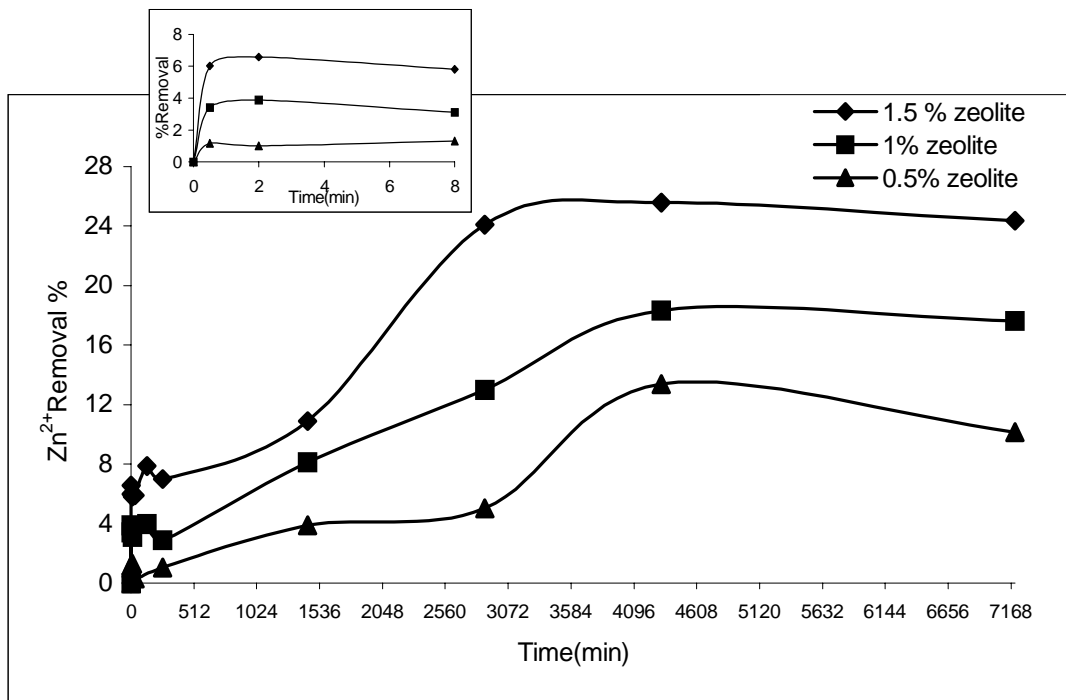


Figure 23. Change in % removal of Zn²⁺ with time. Co=355 ppm, D_p=87 μm, Shaking Rate=450 rpm, pH=3.5, Shaking Period= 5 Days.

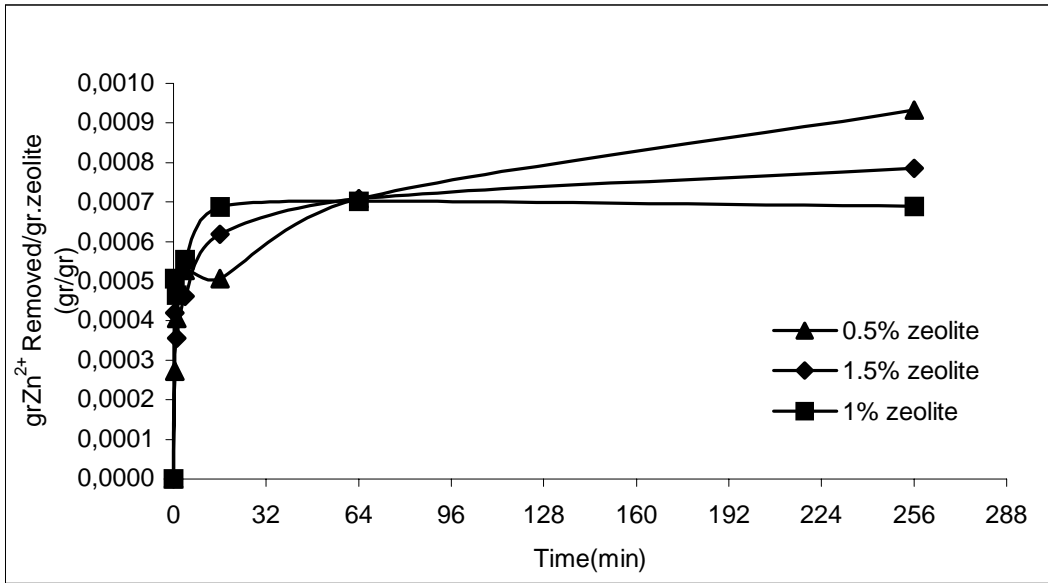


Figure 24. Zn²⁺ Removal per gram of zeolite. Co=30ppm, D_p=87 μm,
Shaking Rate=450 rpm, pH=3.5

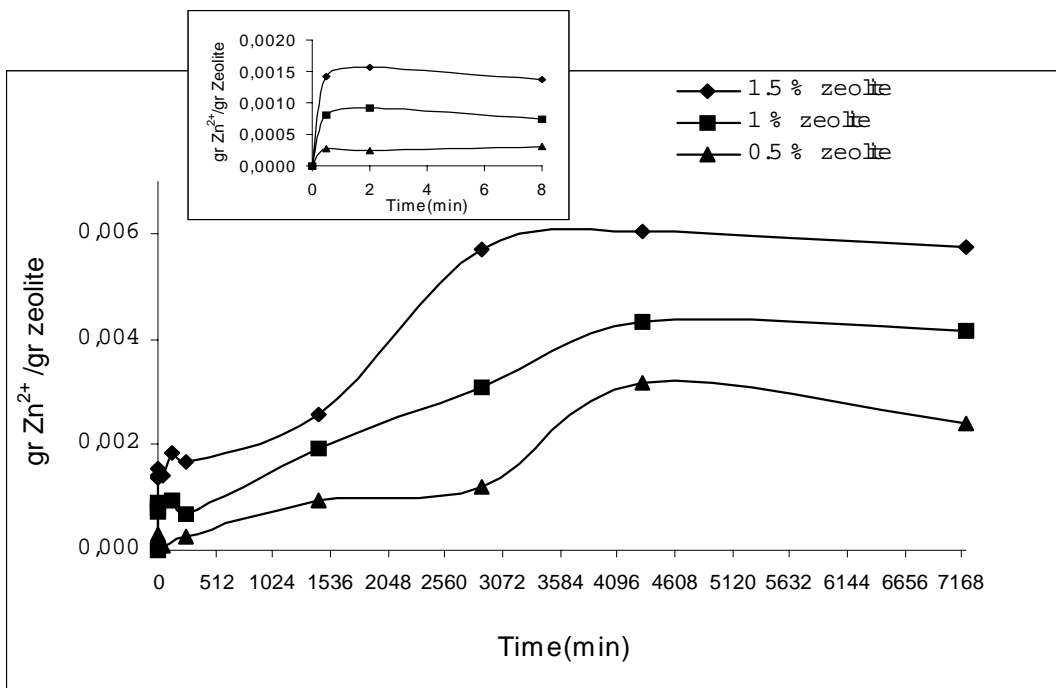


Figure 25. Zn²⁺ Removal per gram of zeolite. Co=355 ppm, D_p=87 μm,
Shaking Rate=450 rpm, pH=3.5, Shaking Period= 5 Days.

These first group of ion-exchange studies were performed for Pb^{2+} , Cu^{2+} and Zn^{2+} . They included preliminary kinetic experiments performed in static conditions. In the experiments, initial metal concentrations, zeolite content of the solutions and contact time were the parameters in concern.

According to the results, zeolite has a higher removal efficiency for lead than for copper and zinc ions regardless of the operating conditions. For lead, at the low initial concentration, added Pb^{2+} was almost completely exchanged by the zeolite in a very short contact time. In this study, lower copper removal efficiencies and much lower zinc removal efficiencies were obtained in compare to lead removal. Results demonstrated that more than 90% of the removal was achieved in 256 minutes even for higher Cu^{2+} concentrations. Results of the experiments also indicate that, as the initial concentration of metals increases, the exchanged metal amount also increases. However, the percentage of metal removed by zeolite decreased. On the other hand, being dependent on the initial metal concentration and the zeolite/solution ratio, removal efficiency decrease as the metal concentration increases and the zeolite/solution ratio decreases.

For the same experimental conditions and the same initial concentration of Pb^{2+} , Cu^{2+} and Zn^{2+} (10^{-3} N), a lower C_i/C_o concentration ratio is indicative of a higher preference for one over another [Yuan and Seyama 1999]. Based on this, selectivity sequence for these three metals was found as follows: $\text{Pb} > \text{Cu} > \text{Zn}$ since the C_i/C_o ratios were found for 10^{-3} N initial metal concentrations, 256 minutes shaking time with 1.5% zeolite content as; 0.0097 for Pb^{2+} , 0.532 for Cu^{2+} , and 0.617 for Zn^{2+} . On the other hand, this sequence has changed at higher initial metal concentration (10^{-2} N) of these metals since the concentration ratios have changed as 0.7975 for Pb^{2+} , 0.7744 for Cu^{2+} , and 0.9299 for Zn^{2+} . According to these values, selectivity sequence can be expressed as $\text{Cu} > \text{Pb} > \text{Zn}$ at higher initial metal concentrations.

The selectivity series can be the result of various factors which influence ion exchange behaviour of zeolites. For instance, dimensions of the channels are expected to be large enough to allow passage of a hydrated metal ion. It is hard to explain the ion exchange phenomena in clinoptilolite in terms of hydrated radii of these three metals of interest since their hydrated radii are almost at the same size with the channel dimensions of the clinoptilolite. Hydrated radii of Pb^{2+} , Cu^{2+} and Zn^{2+} are 4.01, 4.19 and 4.30 Å, respectively [Semmens 1974]. However, pore opening of clinoptilolite is (4.0 x 5.5-4.4 x 7.2 Å) [Tsitsishvili 1992]. Semmens (1974) states that, at least some of

the waters of hydration must be stripped from the solvated ions for exchange to take place. Similar to Semmens, Kühl (1999) has also indicated that, large hydrated cations can vary their size by temporarily losing some water molecules, and the smaller, less hydrated ions may be able to penetrate through pore openings. Selectivity series that was found from current study coincides with the literature in terms of the sequence in hydrated radii of metals in concern.

Eisenman (1962) developed a model to predict selectivity sequences. According to this model, the preference of the exchanger for ion A^+ or ion B^+ depends on whether the difference in their hydration free energies or their coulombic energies interaction with the fixed anionic exchange sites predominates. Hydration free energies of Pb^{2+} , Cu^{2+} and Zn^{2+} are -357.8 , -498.7 and -484.6 kcal/g-ion, respectively. These values indicate that copper, with the largest hydration energy, prefers the solution phase where it may satisfy its hydration requirements. Therefore the hydration free energy values should give the following selectivity series: $Pb > Zn > Cu$. However, observed selectivity sequences show $Pb > Cu > Zn$.

4.2.1.2. Effect of pH and Particle Size

pH effect was determined at fixed experimental conditions such that, 10^{-3} N metal solutions, 1.5% zeolite and 256 minutes contact time, at a shaking rate of 450 rpm.. pH of metal solutions was adjusted to 2.5, 4.5, 6 and 10 by adding 0.1 N NaOH or 0.1 N HNO_3 . Three different particle size of zeolite (122 , 87 and 68 μm) were used in the experiments.

The results were given in Figure 26, 27 and 28 to show the changes in percent Pb^{2+} removal, Pb^{2+} removal per gram of zeolite as a function of pH and particle size of the zeolite. According to the Figure 26, especially at pH 2.5, there is a significant difference in the final Pb^{2+} concentrations between the zeolite having 122 μm particle size and the other two sizes. That can be explained by the change in the exchange rate with the change in the zeolite size. Since metal uptake takes place at the exterior surface of the particle as well as the sites within the particle, decreasing the particle size increases the external surface area, which means increase in the number of available sites for metal uptake. Low pH levels, especially below 4.0, are reported as undesirable in zeolite applications because this would adversely affect the chemical structure of the mineral [Ali 1996]. Decrease in removal efficiency in lower pH values

can also be explained by the competition between the protons and the metal cation for sites in the zeolite particle.

As the pH value increased in Figure 26, the difference between the final metal concentrations in terms of the zeolite particle size decreased. However, ion-exchange is not the only reason of the decrease in the final Pb^{2+} concentration as the pH value increases. Precipitation of metal hydroxide is the main factor in the decrease in final metal concentration at the pH values higher than 4-4.5. The precipitates are responsible for the observed removal of a number of metal ions from the solution.

Similar to the experiments performed for lead, they were performed also for both copper and zinc. In the experiments, 10^{-3} N initial metal concentration, 1.5% zeolite content, 256 minutes contact time, 450 rpm shaking rate, four different pH and three different zeolite particle size were used to see the effect of pH and particle size on the metal removal efficiency of zeolites.

Change in final Cu^{2+} concentration with change in pH and the change in zeolite particle size were presented in Figure 29. Change in Cu^{2+} removal percent and change in amount of Cu^{2+} exchanged per gram of zeolite with the change in pH and the zeolite particle size are given in Figure 30 and Figure 31 respectively. Experimental results of change in Zn^{2+} concentration with the change in pH and particle size of the zeolite are in Figure 32. Change in Zn^{2+} removal percentage and the change in the amount of Zn^{2+} exchanged per gram of zeolite are given in Figure 33 and Figure 34 respectively. According to the figures, it can be concluded that as the zeolite particle size decreases, final metal concentration decreases and removal percent increases. Moreover, amount of metal removed per gram of zeolite increases as the particle size decreases. These results are coinciding with the literature by proving the increase in the cation exchange rate with the increase in the external surface area. On the other hand, if results are compared in terms of the change in pH of the solutions, maximum removal percentages are 41% for Cu^{2+} and 25% for Zn^{2+} at highly acidic pH 2.5. However, removal efficiency seems to increase with the increase in pH, in fact that is due to the beginning of the precipitation after pH of 4-4.5. The Cu^{2+} at ordinary concentrations begins to hydrolyze above pH 4 and precipitates the oxide or hydroxide soon thereafter [Baes and Mesmer 1986].

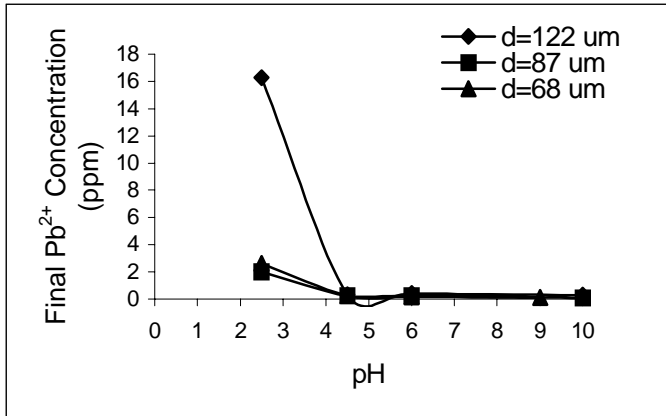


Figure 26. Change in Pb²⁺ Concentration with pH and particle size of the zeolite. Co=119 ppm, 1.5% zeolite, Contact time=256 minutes

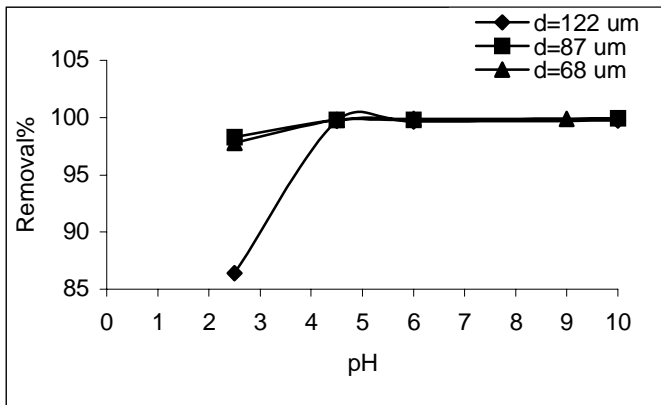


Figure 27. Change in Pb²⁺ Removal with pH and particle size of the zeolite. Co=119 ppm, 1.5% zeolite, Contact time=256 minutes

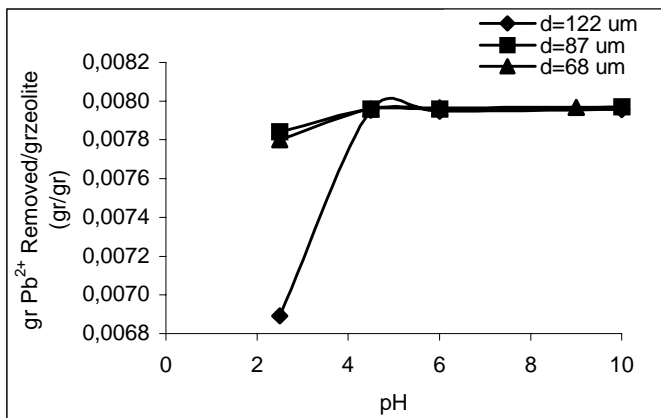


Figure 28. Change in Pb²⁺ removal per gram of zeolite with the change in pH and particle size of the zeolite. Co=119 ppm, 1.5% Zeolite, ContactTime=256 minutes.

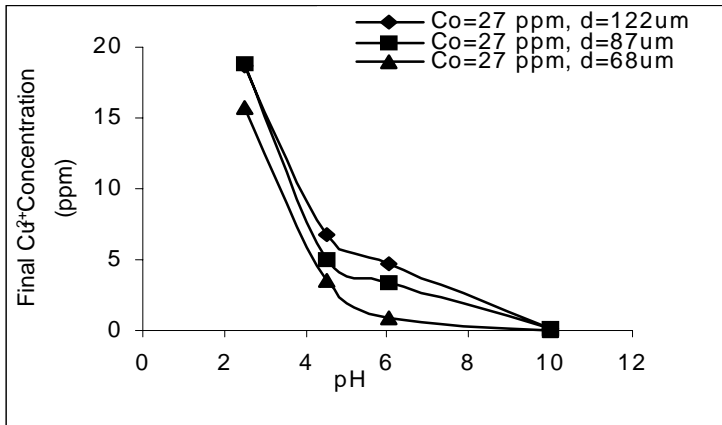


Figure 29. Change in Cu²⁺ Concentration with pH and the particle size of the zeolite. Co=27 ppm, 1.5% zeolite, Contact time=256 minutes

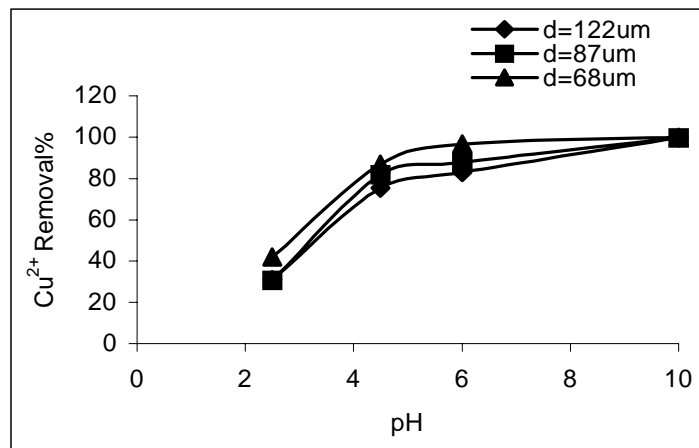


Figure 30. Change in Cu²⁺ removal with pH and the particle size of the zeolite. Co=27 ppm, 1.5% zeolite, Contact time=256 minutes

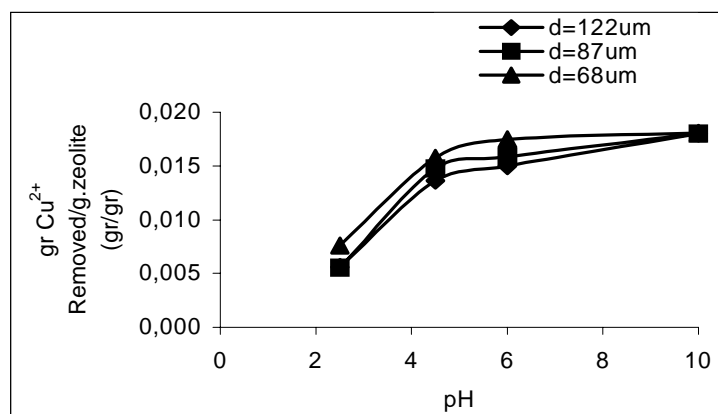


Figure 31. Change in Cu²⁺ removal per gram of zeolite, with pH and particle size of the zeolite. Co=27 ppm, 1.5% zeolite, Contact time=256 minutes

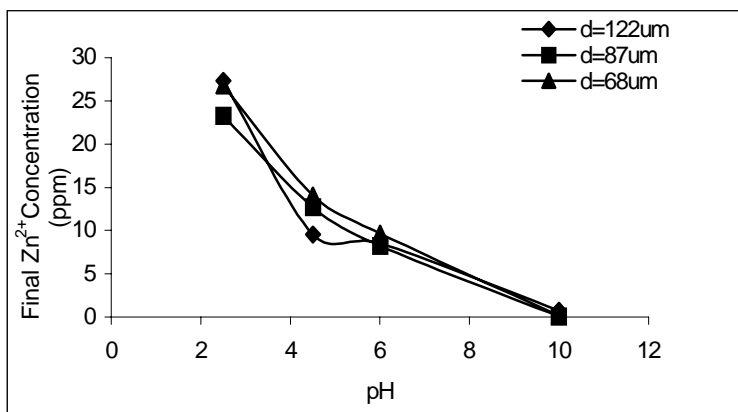


Figure 32. Change in Zn²⁺ Concentration with pH and the particle size of the zeolite. Co=31 ppm, 1.5% zeolite, Contact time=256 minutes

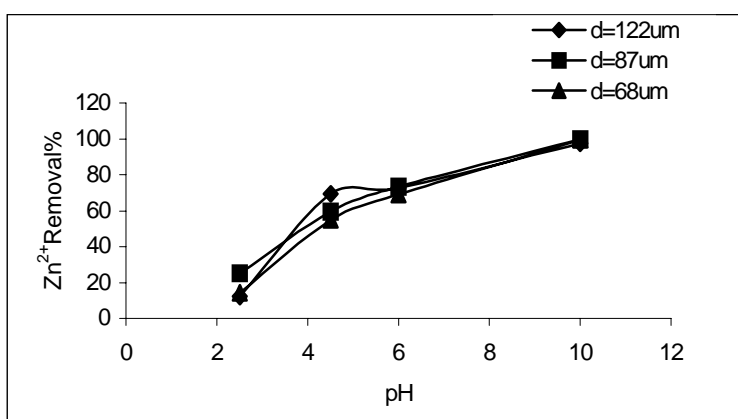


Figure 33. Change in Zn²⁺ removal with pH and the particle size of the zeolite. Co=31 ppm, 1.5% zeolite, Contact time=256 minutes

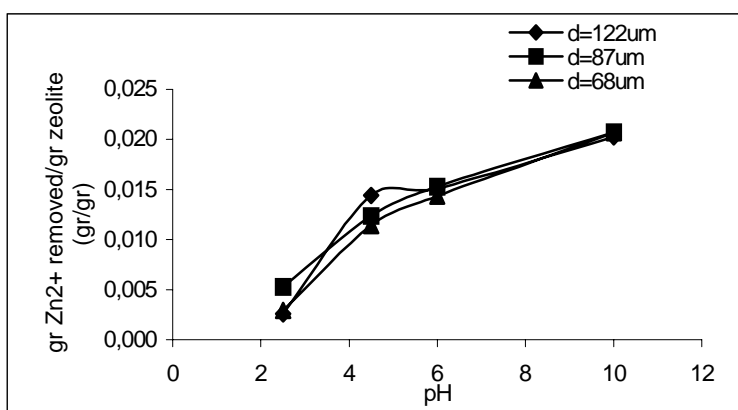


Figure 34. Change in Zn²⁺ removal per gram of zeolite, with pH and particle size of the zeolite. Co=31 ppm, 1.5% zeolite, Contact time=256 minutes

Natural zeolites such as clinoptilolite is not only influenced by pH but in turn is capable of affecting solution pH especially in batch systems. Calcium and sodium are the major cations released in solution and bicarbonates/carbonates are the major anions. This points the major problem in researching natural zeolites; they are not pure products. They usually contain a variety of impurities such as calcium carbonate, unaltered glass, clays, etc., which are occluded during the formation of the zeolite. Unlike synthetic ion exchange resins which tend to have an internal pH slightly lower than that measured in solution, natural zeolites tend to have higher internal pH. The influence of the zeolite on pH must be recognized when metal removal behavior is interpreted and in certain cases it makes data analysis difficult. The solution must be kept to the original desired value manually. The higher internal pH of the zeolite combined with high internal metal concentrations may cause hydroxide or carbonate precipitation within the channels of the zeolite and at the zeolite surface [Ouki and Kavannagh 1997].

pH is known to have a significant impact on metals removal by zeolite since it can influence both the character of the exchanging ions and the character of the zeolite itself. Kinetic studies conducted at various pH values showed that optimum removal is achieved when operating at pH between 4 and 6. Ion-exchange performance of zeolite is very sensitive to pH especially between pH values of 2.5 and 4.5. For instance, between this pH range, Cu^{2+} removal changes from 30% to 75%.

Experimental results indicated that the actual removal was adversely affected by decreasing the solution pH. Literature and experimental studies also showed that precipitation begins at pH 6. Stability experiments were performed by shaking metal solutions for a certain period in the absence of zeolite to observe the precipitation of metal hydroxides at higher pH values. Final concentrations of Pb, Cu and Zn salts at different pH values are given in Figures 35-36-37, respectively. According to the experimental results, precipitation begins around pH 6 and metal hydroxide completely precipitates at pH 10. Although precipitation was not observed at pH 2.5, due to its negative effect on both the structure of the zeolite and the removal efficiency, pH around 4-4.5 was found optimum for exchange studies.

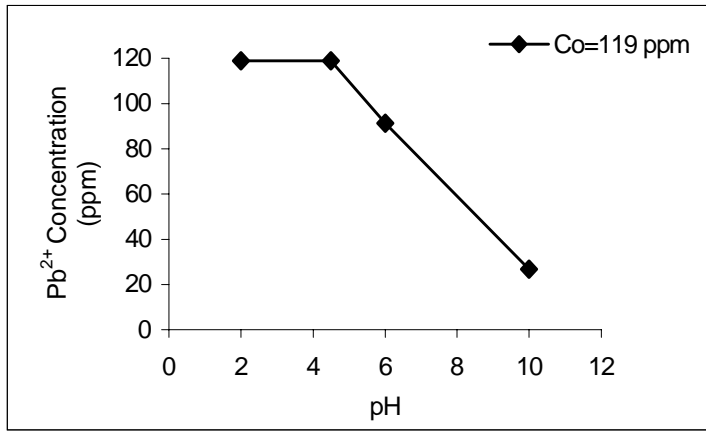


Figure 35. Stability of $\text{Pb}(\text{OH})_2$ at different pH's. ($K_{sp}=1.42 \times 10^{-20}$)

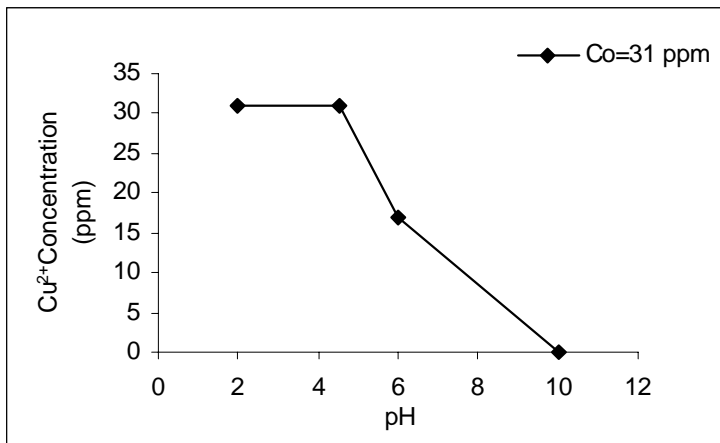


Figure 36. Stability of $\text{Cu}(\text{OH})_2$ at different pH's. ($K_{sp}=5.6 \times 10^{-20}$)

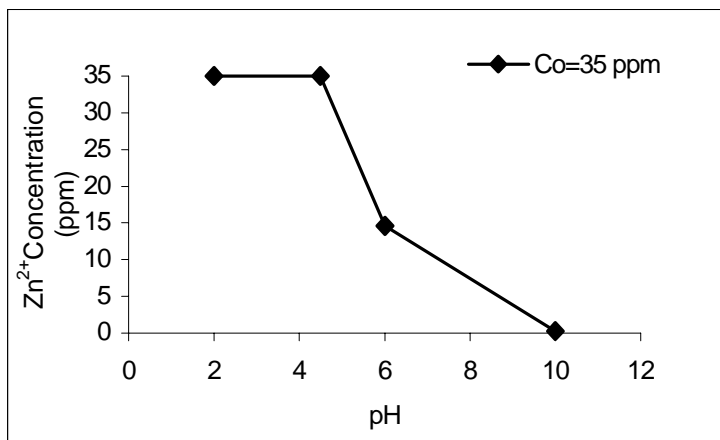


Figure 37. Stability of $\text{Zn}(\text{OH})_2$ at different pH's. ($K_{sp}=4.12 \times 10^{-17}$)

4.2.2. Removal of Heavy Metals in Single Component and Multi-component Systems in the Absence and Presence of Electrolytes

Usually, there are more than one type of metal in metal containing wastewaters. In a natural setting, the presence of multiple competing ions is more frequent than the existence of only one contaminant. Therefore the efficiency of heavy metal removal (lead, copper and zinc) by local natural zeolite in single, binary, ternary and competing ion (Na, Ca) containing solutions were investigated.

Metal solutions were prepared to contain 30 mg/L total metal concentration. Concentration of each metal was 30 mg/L for single metal solutions, 15 mg/L for binary solutions, and 10 mg/L for ternary metal solutions. In other words, there is 0.0029 gr of each metal in its single component solution. In binary and ternary solutions, there is 0.0015 gram and in 0.001 gram of each metal, respectively. Due to low initial metal concentrations, contact time with zeolite was fixed at 128 minutes. In the experiments, 1.5% (weight/volume) zeolite and 450 rpm shaking speed were used. Based on the results of previous studies, pH of the solutions were adjusted to 4-4.5 by adding 0.1 N NaOH or 0.1 N HNO₃. For the investigation of competing cation effect, NaCl₂, CaCl₂ and Na₂SO₄ were used at different concentrations as 1, 0.1, 0.01% (weight/volume). Na⁺ and Ca²⁺ are two of the main cations present in the interstices of the zeolite framework to make the crystal neutral, and they are usually mobile and are responsible for the ion-exchange properties of zeolites. Presence of these cations in the solution is expected to cause a decrease in metal removal efficiency due to higher affinity of zeolite towards Na⁺ and Ca²⁺. Therefore, Na⁺ and Ca²⁺ containing electrolytes were selected to investigate their effects on the metal removal efficiency of zeolite.

Experimental results were summarized in three different sections according to the components of metal solutions, such as single, binary and ternary solutions. Removal percentages of metals from the single, binary and ternary metal solutions and effects of NaCl, CaCl₂ and Na₂SO₄ on the metal removal performance are presented in Figure 38. Removal percentage values are summarized in Table 8. Amount of metal removed per gram of zeolite was summarised in Table 9.

Single Systems

According to the results, in the absence of competing cations (Na⁺, Ca²⁺), Pb²⁺, Cu²⁺, and Zn²⁺ removals in their single solutions were achieved as 100%, 88% and 73%

respectively. Results resembled with the results obtained from kinetic studies by exhibiting same preference order such as $Pb > Cu > Zn$. However, difference in removal % values between kinetic studies and single component studies could be resulted from the difference in the solution pH's which were adjusted to 4.5 in single component cation exchange studies. Increase in removal efficiency at pH 4.5 is in accordance with the results obtained from the "pH effect" studies in 4.2.1.2.

In single system, metal removal efficiency decreased with the increasing NaCl addition as a function of concentration. As can be seen from the Figure 38a, 38b and 38c that, in the presence of 1% NaCl, Pb^{2+} removal decreased from 100% to 88%, Cu^{2+} removal decreased from 88% to 53.8% and Zn^{2+} removal decreased from 73% to 11.8%. In the presence of 0.01% NaCl, efficiency did not change.

Addition of $CaCl_2$ showed the similar effect and decreased the removal efficiency as a function of concentration. However, it is seen that Ca^{2+} has a higher interfering effect than Na^+ especially in the removal of Zn^{2+} and Cu^{2+} . For example, at 0.1%, Zn^{2+} removal decreased from 73% to 29% in the presence of NaCl and decreased to 18.6% in the presence of $CaCl_2$. Their charges could be one reason for this difference. Since sodium has one positive charge, and the calcium has two, in case of competition with a metal ion having two positive charges, two Na ions are needed to compete with a metal ion, whereas one Ca ion is enough for that competition. Therefore, although same percentage of salts has been added to the solutions, $CaCl_2$ addition made more negative effect on metal removal efficiency than NaCl.

In contrast to previous results, Na_2SO_4 addition to a single metal solution increased the removal efficiency of zeolite for all the metals tested. This was most probably due to SO_4 anion. This effect was however true for single systems where metal concentrations are higher. Effect of SO_4 ion was different in binary and ternary systems and its effect was similar to other electrolytes.

Binary Systems

In binary metal exchange studies with natural zeolite, different electrolytes were added to the solutions in different percentages to test the effect of other competitive cations in metal removal efficiency of zeolite.

Lead removal efficiencies are summarized in Figures 38a, Figure 38d, and Figure 38g. in presence of NaCl, $CaCl_2$ and Na_2SO_4 respectively. Copper removal efficiencies and zinc removal efficiencies are also given as a function of the type and

the amount of the electrolyte added to the solution. Copper removal efficiencies are presented in Figures 38b, Figure 38e, and Figure 38h and zinc removal efficiencies from binary metal solutions are in Figures 38c, Figure 38f, and Figure 38i, in presence and absence of NaCl, CaCl₂ and Na₂SO₄ respectively.

Both in binary and ternary systems of lead (Pb-Cu, Pb-Zn, Pb-Cu-Zn), in the absence of electrolytes, zeolite always exhibited higher affinity for Pb²⁺ when this metal is present in the system. The removal of Pb²⁺ is always high. Lead was removed at nearly 100% efficiency from binary and ternary solutions containing copper and zinc. According to the results, Pb²⁺ removal is highly favorable even at high concentrations of Na⁺ and Ca²⁺.

Copper removal increased in all binary solutions in comparison with its single solutions. For instance, while copper removal is 88.3% in single solution, it is 96.4% in Pb-Cu binary solution, and 91.5% in Cu-Zn binary solution. Copper was more effectively removed from Pb-Cu solutions than Cu-Zn solutions independent from the absence or presence of competitive cations (Na⁺, Ca²⁺).

Zinc removal was higher only in Pb-Zn binary solution (76.6%) than it was in single solution (73.4%). However, its removal decreased to 61.3% in presence of copper. Unlike copper, zinc was adversely affected in presence of copper in the solution.

In case of salt addition, minimum removal percentage was obtained by CaCl₂ addition either in Pb-Cu or Cu-Zn binary solutions. For instance, copper removal in the binary solution of Cu-Zn decreased to 47.4% in presence of 0.1% CaCl₂, while it was 91.5% in absence of Ca²⁺ salt. For all combinations (Pb-Zn, Cu-Zn), minimum zinc removals were obtained in case of CaCl₂ addition to the solution. Especially for Cu-Zn binary solution, presence of 0.1% CaCl₂ cause a decrease from 61.3% to 3.7% in zinc removal. Addition of NaCl and Na₂SO₄ also decreased zinc removal from both Pb-Zn and Cu-Zn binary solutions.

Ternary Systems

In ternary metal exchange studies with zeolite, similar to single and binary exchange studies, three different electrolytes were put into the solutions in different percentages to measure the effect of competing ion on the metal removal efficiencies of natural zeolite

Lead removal efficiency of natural zeolite remained unchanged with the presence of other two metals (Cu, Zn). Mier and Callejas [2001] have also indicated that in all combinations of Pb^{2+} with Cr^{6+} and Cd^{2+} (binary and single) more than 97% of Pb^{2+} was removed especially at slightly acidic pH's. Considering copper removal efficiency of zeolite, the highest Cu^{2+} removal was measured in binary Pb-Cu solution (96.4%) and in ternary solution (95%). In its single solution, copper removal percentage has been found as 88% which is lower than the removal values obtained from its binary and ternary solutions.

Presence of lead and copper together with zinc, made almost no effect on zinc removal efficiency of natural zeolite. Zinc removal percentage from single metal solution was 73.4%, it increased to 76.6% with the presence of lead, and decreased to 61.3% with the presence of copper. In ternary metal solutions, zinc removal was measured as 75%. If the results obtained from ternary solutions were compared with the these obtained from binary solutions, it can be concluded that presence of lead in the solution decreased the adverse effect of copper on the removal efficiency of zeolite toward zinc.

Minimum lead removal was reported as 85.7% with the addition of 1% NaCl into the ternary metal solution. However it has been found as 88.7% in single metal solution with 1% NaCl content. Copper removal was measured as 68.4% in case of 0.1% CaCl_2 addition into the ternary metal solution, whereas these values were 56.65% for Pb-Cu and 47.4% for Cu-Zn binary solutions. On the other hand, in case of 1% NaCl addition, lower removal percentage (57.5%) was obtained for copper in ternary metal solution than it was for binary solutions (60.6% for Pb-Cu and 70.8% for Cu-Zn). Minimum zinc removal was again obtained with the presence of CaCl_2 . Addition of electrolytes has more negatively affected zinc removal from ternary solutions.

Mohan and Chander [2001] have investigated the effect of interfering ions (Ca^{2+} , Zn^{2+}) on Fe^{2+} and Mn^{2+} adsorption efficiency of activated carbon. In their study, single, binary, ternary and quaternary systems were used to determine the competitive adsorption of metal ions. They found that, Ca^{2+} , Mn^{2+} and Zn^{2+} compete with Fe^{2+} adsorption. It was observed that Ca^{2+} has the highest interfering capacity. However, due to the variations of the results from carbon to carbon, they have stated that adsorption in multi-components systems is complicated because of the fact that the solute-solute competition and the solute-surface interactions are involved. They have

also indicated that due to large number of variables involved in the adsorption of metal ions by activated carbon and the complexity of the surface and water chemistry, no single mechanism can explain the adsorption of metal ions from aqueous solutions.

Christophi and Axe [2000] have studied on the competition of copper, lead and cadmium on goethite at constant pH and temperature. In the case of Cd-Pb competition studies, 97.5% of cadmium was displaced by lead. In the case of Cu-Pb competition studies, 60% of lead was displaced by copper when lead was introduced first to the system. They indicated that, copper and lead compete for the same type of sites in goethite and copper, which has smaller hydrated and ionic radii and greater electronegativity than cadmium, displaced cadmium in all studies.

In our study, to avoid complexity, variables were tried to be minimized by fixing the contact time period, pH, total metal concentration and the amount of natural zeolite added to the solutions. Therefore, comparative interactions between the cations could be measured more properly. However, ionic composition of system got more complex due to the addition of NaOH or HNO₃ in order to adjust the solution pH to a certain value (pH 4-4.5). Since zeolite has a greater affinity towards Na⁺ than it is for other metal cations, Na ions coming from NaOH might change the cationic composition of the natural zeolite.

Results showed that, presence of other cations does not affect lead removal. Lead also makes a positive effect in the removal of copper and zinc both in binary and ternary solutions. On the other hand, zinc negatively affects copper removal in their binary solutions. Among three metals, the least removal efficiency was measured for zinc. Electrolyte addition decreased the removal of heavy metals. Since there occurred some interference problems in ICP-AES analysis of samples having 1% CaCl₂ and 1% Na₂SO₄, analysis results only for the samples containing 0.1% and 0.01% CaCl₂ and Na₂SO₄ could be presented.

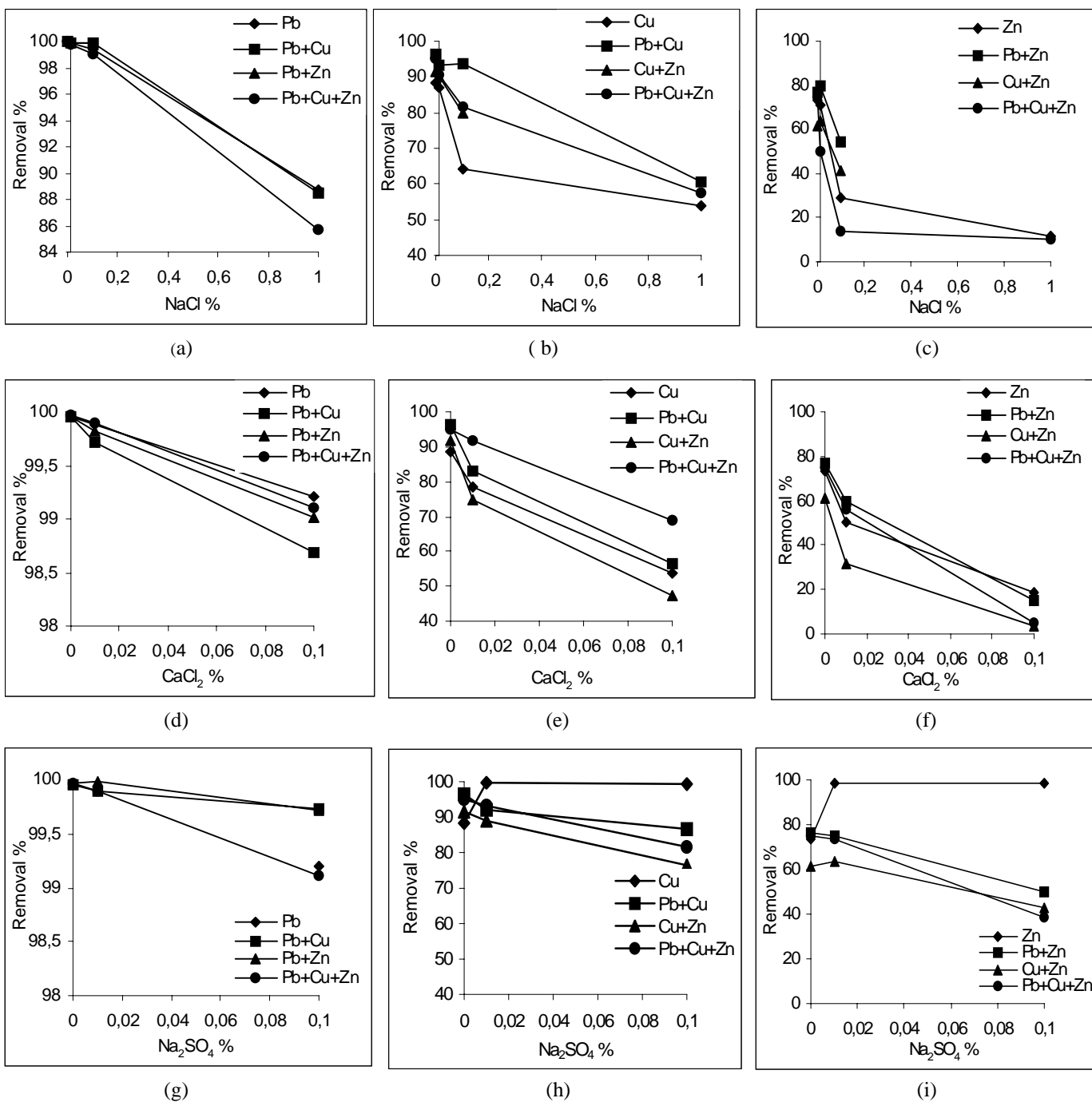


Figure 38. Comparative evaluation of removal of Pb²⁺, Cu²⁺ and Zn²⁺ by zeolite from their single, and multi-component solutions in absence and the presence of electrolytes (NaCl, CaCl₂, Na₂SO₄).

Table 8. Change in Removal% of Pb²⁺, Cu²⁺ and Zn²⁺ from Their Single and Multicomponent Solutions By Ion-Exchange with Zeolite

	Pb Removal %				Cu Removal %				Zn Removal %			
	Pb	Pb-Cu	Pb-Zn	Pb-Cu-Zn	Cu	Pb-Cu	Cu-Zn	Pb-Cu-Zn	Zn	Pb-Zn	Cu-Zn	Pb-Cu-Zn
No Salt	99.96	99.96	99.95	99.97	88.34	96.49	91.53	95.08	73.40	76.62	61.35	74.88
1% NaCl	88.72	88.51	-	85.74	53.87	60.64	-	57.54	11.86	-	-	10.00
0.1%NaCl	99.45	99.86	99.88	99.09	64.38	93.71	79.87	81.73	28.98	54.40	40.95	14.03
0.01%NaCl	99.93	99.92	99.92	99.80	87.15	93.33	90.29	90.46	71.00	70.78	64.02	49.78
0.1% CaCl₂	99.21	98.69	99.01	99.11	53.54	56.61	47.43	68.44	18.68	15.01	3.77	4.92
0.01%CaCl₂	99.88	99.72	99.82	99.89	78.70	82.88	74.95	91.86	50.10	59.39	31.98	56.27
0.1%Na₂SO₄	99.20	99.73	99.92	99.72	99.32	86.71	76.46	81.62	98.88	50.21	43.20	38.57
0.01%Na₂SO₄	-	99.89	99.88	99.99	99.75	92.10	88.96	93.25	98.66	74.81	63.85	73.11

4.2.3. Using Natural Zeolite to Treat Acid Mine Drainage(AMD)

In the study, simulated wastewater, having a content of 13 mg/L Pb^{2+} , 112 mg/L Cu^{2+} , 84 mg/L Zn^{2+} , 665 mg/L Fe^{2+} and 150 mg/L Al^{3+} at pH 2.5, was used to determine the efficiency of zeolite in treating such kind of highly acidic mixed-metal solutions. In these experiments different time periods (10 min., 30 min., 1 hr, 2 hrs, 4 hrs and 8 hrs) were used to see the change in metal concentrations and also in the pH. Zeolite content of the solutions was 1.5 g. Shaking speed was chosen as 450 rpm. pH adjustment was performed by adding 0.1 N NaOH or 0.1 N HNO_3 . Final pH values of each solution were recorded at the end of the each time period, to test whether natural zeolite, having a slightly basic structure, would result any increment in pH of these highly acidic solutions.

Experimental results for each element are presented in following figures. Change in Pb^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} and Al^{3+} concentrations with time are given in Figures 39, 40, 41, 42 and 43 respectively. Amounts of metal removed per gram of zeolite are given in Figure 44. pH was also monitored during the ion-exchange tests and the results are shown in Figure 45.

According to the results, highest metal removal per gram of zeolite was obtained for Fe. Almost all Pb^{2+} in the solution was removed. On the other hand, if the results were compared with the previous results obtained in kinetic and mixed-metal studies, a sharp decrease in removal of copper and zinc can be observed. As mentioned before in pH effect studies, this decrease in efficiency can be explained by the deformation of zeolite structure due to the extremely low pH. In Figure 43, increase in Al concentration with time can be taken as another proof of that deformation in the zeolite structure. Decrease in pH to lower values especially below 4.0, results in direct attack in aluminosilicate framework of the zeolite and triggers the dealumination process. As can be seen from the Figure 43, almost 10% increase in aluminum concentration was measured after the exchange process. On the other hand, similar to the results obtained previously, zeolite exhibited minimum affinity to Zn^{2+} relative to other elements.

Although another aim was to obtain an increase in solution pH at the beginning of this study, just a slight increase could be obtained due to the high acidity of the simulated AMD solutions. Therefore, it can be concluded that zeolite can be used effectively to treat such wastewaters at proper pH values, especially around 4.0-4.5.

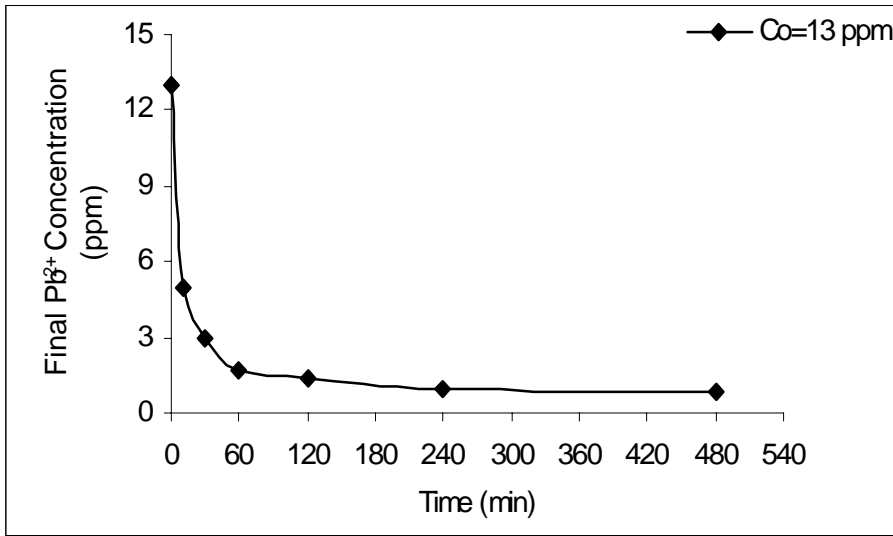


Figure 39. Change in Pb²⁺ concentration with time.

Co=13 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

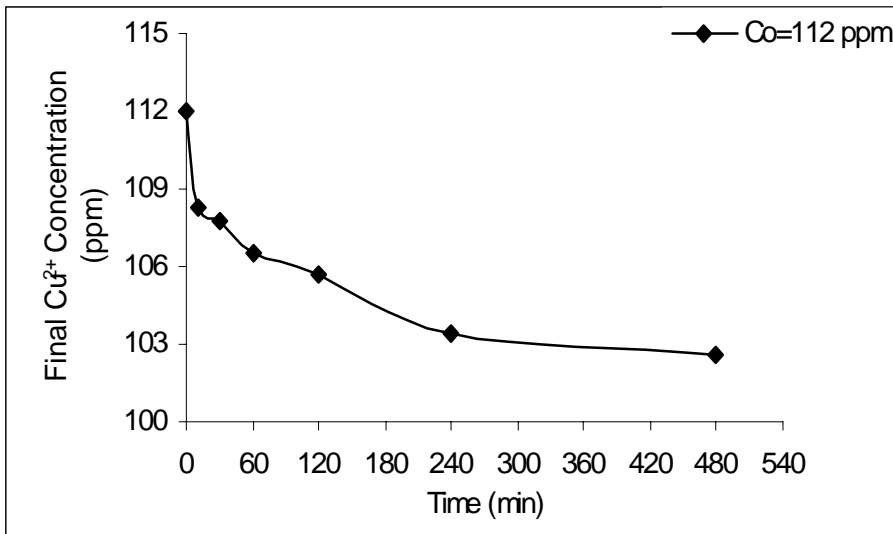


Figure 40. Change in Cu²⁺ concentration with time.

Co=112 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

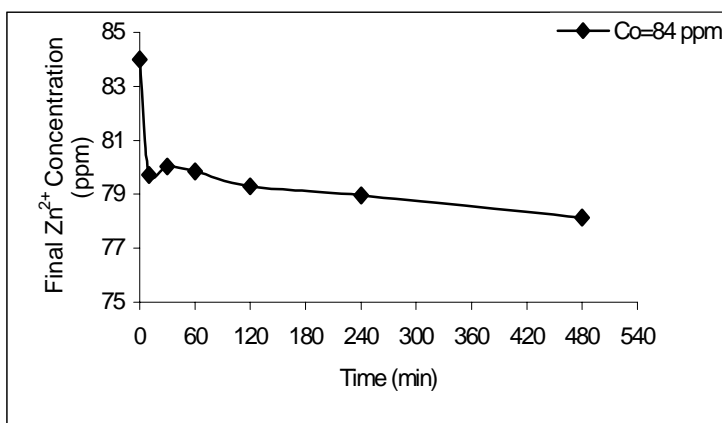


Figure 41. Change in Zn²⁺ concentration with time.
Co=84 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

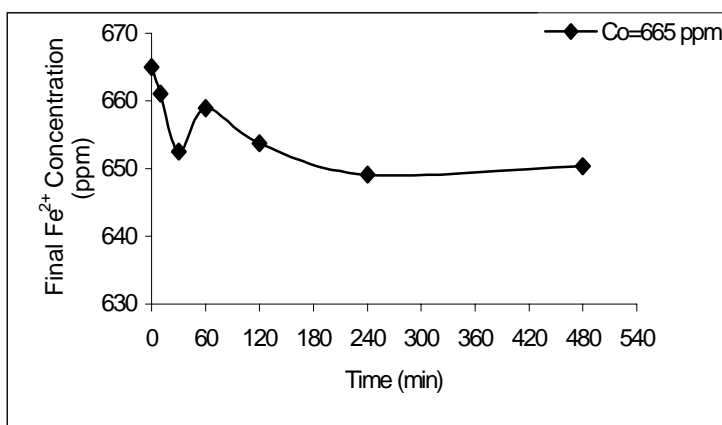


Figure 42. Change in Fe²⁺ concentration with time.
Co=665 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

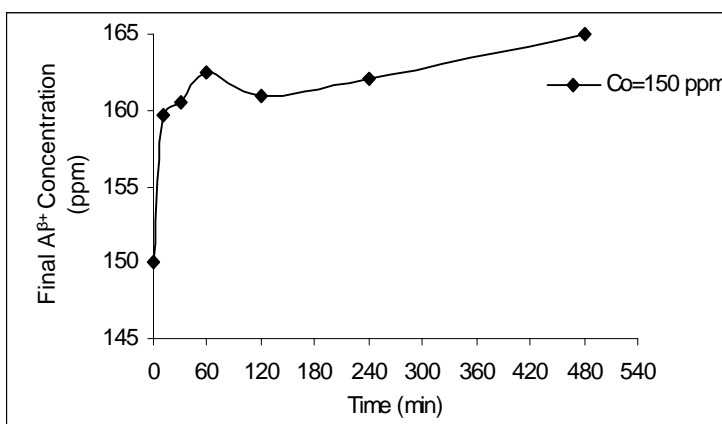


Figure 43. Change in Al³⁺ concentration with time.
Co=150 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

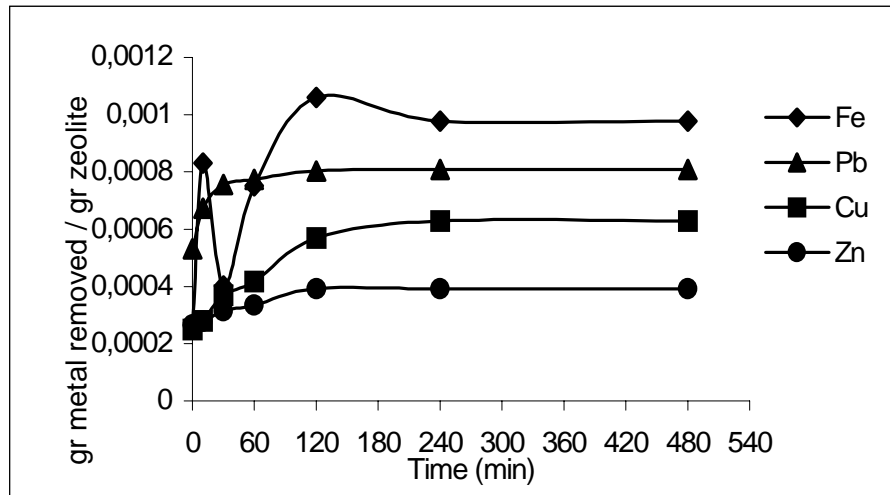


Figure 44. Change in amount of metal removed/gram zeolite (gr/gr) with time.

Co(Fe^{2+})=665 ppm, Co(Pb^{2+})=13 ppm, Co(Cu^{2+})=112 ppm,
 Co(Zn^{2+})=84 ppm, 1.5% Zeolite, pH=2.5, Shaking Rate=450 rpm

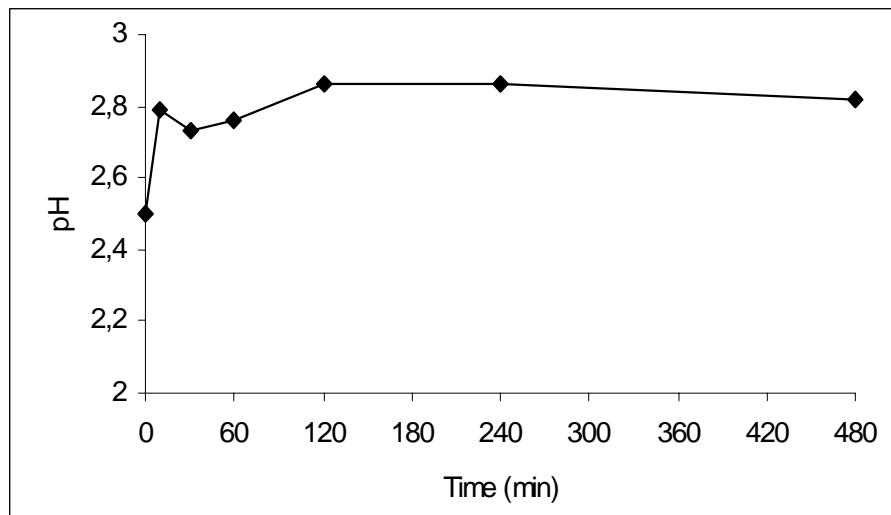


Figure 45. Change in pH of simulated AMD solutions with time.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

Ion exchange efficiency of clinoptilolite rich local natural zeolite in removal of heavy metals (Pb^{2+} , Cu^{2+} , Zn^{2+}) was investigated. Local mineral zeolite has a higher removal efficiency for lead than for copper and zinc ions regardless of the operating conditions. The more the zeolite amount put into the solution, the higher the metal ion removal.

Ion exchange studies indicated that, there is a strong relationship between ion-exchange efficiency of zeolite and the pH of the solution. Zeolite exhibited an higher performance at slightly acidic pH's, especially around 4-5. High metal removal can be achieved using an initial solution pH of 4.0-4.5 with careful selection of other conditions, especially initial metal ion concentrations and the amount of zeolite in the solution to avoid masking of ion exchange by chemical precipitation. It was proved that precipitation of metal hydroxides took place at around pH 6, and structural deformation in zeolite began at lower pHs such as pH 2-2.5. Therefore, extremely low pH values should be avoided during the ion-exchange processes with zeolites.

Natural zeolite exhibited a high affinity to Pb^{2+} even in presence of interfering ions (Cu^{2+} , Zn^{2+} , Na^+ , Ca^{2+}). Cu^{2+} removal decreased in the presence of Zn^{2+} in their binary solutions and vice versa. In addition, the presence of competing cations (Na^+ , Ca^{2+}) decreased the Cu^{2+} and Zn^{2+} removal efficiencies of zeolite. It was observed that Ca^{2+} has a higher interfering capacity than Na^+ in ion exchange process. Therefore, it was concluded that depending on the chemistry of the system, metal species are predominant in the aqueous phase and compete with each other in solution for the exchange sites in the zeolite

A decrease in removal efficiency of zeolite has been observed in ion-exchange studies with simulated acid mine drainage solutions. Extremely low pH (pH=2.5) of the AMD solution was thought as the main reason of the decrease. Nevertheless, Pb^{2+} was totally removed from the solution, even at such a low pH.

Since very little experimental work has been carried out to investigate the interaction of metal cations with each other in the literature, detailed studies are recommended for further evaluation of the phenomenon. Further studies are thought to

be useful in pollution control with this cost-effective ion-exchanger, especially in natural systems which usually consists not only inorganic compounds but also organic compounds. In addition, conducting column studies simultaneously with batch studies will make easy to compare the efficiencies of these two methods and select the most efficient one for the proper application of natural zeolites in the treatment of industrial wastewaters.

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