MULTICOMPONENT ION EXCHANGE ON CLINOPTILOLITE

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ABSTRACT

MULTICOMPONENT ION EXCHANGE ON CLINOPTILOLITE

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Zeolites are crystalline, hydrated aluminosilicate minerals that are characterized by their ability to exchange some of their constituent cations with cations in aqueous solutions, without a major change in their crystalline structure. Clinoptilolite is the most abundant type of zeolite and it has received extensive attention due to its favorable selectivity for ammonium and certain heavy metal cations.

The aim of this study is to investigate the binary and ternary (multicomponent) ion exchange behavior of sodium form of Gördes type clinoptilolite for ammonium, cadmium and sodium ions.

For this purpose, NH_4^+-Na^+,Cd^{2+}-Na^+ binary systems and NH_4^+-Cd^{2+}-Na^+ multicomponent system were investigated both in batch and column systems at 0.1 and 0.01 constant total normality respectively and at 25^0C constant temperature. As a result of binary and ternary experiments, clinoptilolite's affinity for both ions but greater affinity to NH_4^+ ion than Cd^{2+} ion was observed and the selectivity sequence of Gördes clinoptilolite was determined as NH_4^+>Cd^{2+}>Na^+ in binary and multicomponent batch and column operations.

Additionally, total ion exchange capacities and maximum exchange levels of Gördes clinoptilolite for both ions were determined in batch systems whereas breakthrough capacities and column efficiencies (for three different flow rates) were determined in column systems. Finally, it was concluded that the increase of the flow rate reduced the breakthrough capacities and column efficiencies of Gördes clinoptilolite for ammonium and cadmium ions in multicomponent column systems involving more than one cation.

Keywords: Clinoptilolite, Cadmium, Ammonium, Removal, Binary, Ternary

ÖZ

KLİNOPTİLOLİT ÜZERİNE COK BİLEŞENLİ İYON DEĞİŞİMİ

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Zeolitler, alkali ve toprak alkali metallerin kristal yapıya sahip sulu aluminyum silikatları olup kristal yapılarını bozmadan kendi içlerinde bulunan katyonları sulu çözelti içindeki katyonlarla değiştirme özelliklerine sahip minerallerdir. Klinoptilolit, en fazla bulunan zeolit tipidir ve ağır metallere ve amonyum iyonuna olan yüksek seçiciliği sebebiyle kendisine olan ilgi günden güne artmaktadır.

Bu çalışmanın amacı, sodyum formuna çevrilmiş Gördes tipi klinoptilolitinin amonyum, kadmiyum ve kurşun iyonları için ikili ve çok bileşenli iyon değişim davranışının incelenmesidir. Bu amaç için, NH_4^+-Na^+, Cd^{2+}-Na^+ ikili sistemleri ve NH_4^+-Cd^{2+}-Na^+ üçlü sistemi, kesikli sistem ve kolon operasyonlarıyla, sırasıyla 0.1 ve 0.01 sabit toplam konsantrasyonlarında ve 25^0C sabit sıcaklıkta incelenmiştir. İkili ve üçlü sistem çalışmalarında, Gördes klinoptilolitinin, iki iyona da ilgisinin bulunduğu fakat amonyum iyonuna, kadmiyum iyonundan daha fazla ilgisinin olduğu gözlemlenmiş ve bu sonuçlar ışığında klinoptilolitin seçicilik sırası her iki sistem için de, $NH_4^+ > Cd^{2+} > Na^+$ olarak belirlenmiştir.

Buna ek olarak, Gördes klinoptilolitinin, hem amonyum hem de kadmiyum iyonu için maksimum iyon değişim seviyeleri ve iyon değişim kapasiteleri kesikli sistemlerde tespit edilirken, salıverme eğrileri ve kolon verimleri (üç farklı akış hızı için) ise kolon sistemlerinde elde edilmiştir. Sonuç olarak, çok bileşenli kolon sisteminde akış hızının artması ile klinoptilolitin amonyum ve kadmiyum iyonları için salıverme kapasitelerinin ve kolon verimlerinin azaldığı anlaşılmıştır.

Anahtar Kelimeler: Klinoptilolit, Kadmiyum, Amonyum, Arıtım, İkili, Üçlü, Sistem

To My Dear Grandmother...

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A_s : Fraction of the exchanging cation in the solution

A_z : Fraction of the exchanging cation in the zeolite

C : Ion concentration in effluent

Co : Ion concentration in influent

CEC : Cation exchange capacity

h_T : Height of the packed bed

hz : Exchange zone height

Meq : Miliequivalent

M_{Aif} : Initial and final molarities of exchanging cations

S : Surface area

T.N : Total normality

V : Total Volume

V_B : Effluent volume collected up to the breakthrough point

V_t : Effluent volume collected up to the exhaustion

W : Weight of clinoptilolite

Z : Charges of cations

CHAPTER 1

INTRODUCTION

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter to human body via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Pb^{2+}, Cd^{2+} Cu^{2+}, Fe^{3+}, and Cr^{3+} are especially common metals that tend to accumulate, causing numerous diseases and disorders. They are also common groundwater contaminants such as ammonium, at industrial and military installations. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis. The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently.

Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities; however, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. Various treatment processes are available, among which ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used.

Zeolites are naturally occurring hydrated aluminosilicate minerals and they contain some cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} in their structure. These cations are exchangeable with certain heavy metal cations in solutions like lead, cadmium, zinc, and also ammonium ion. Due to favorable ion exchange selectivity for the specific heavy metal cations, natural zeolites (especially clinoptilolite) have been studied for potential use in the treatment of nuclear, municipal and industrial wastewaters. Also, there exists many studies for the removal of ammonium ion, again related to clinoptilolite's favorable selectivity in the presence of heavy metal cations. However, most theoretical and experimental studies of ion exchange equilibria on clinoptilolite are focused on ion exchange reactions involving only two cations (binary exchange) and little attention has been paid to ternary ion exchange equilibria.

The aim of this study is to determine the binary and multicomponent ion exchange behaviour of sodium form of Gördes type clinoptilolite for ammonium,cadmium and sodium ions. For this purpose, NH_4^+-Na^+, Cd^{2+}-Na^+ binary systems and NH_4^+-Cd^{2+}-Na^+ ternary system were investigated both in batch and column systems at 0.1 and 0.01 constant total normality respectively and at 25^0C constant temperature experimental conditions. Studies focused on the behaviour of clinoptilolite for ammonium and cadmium ions in the presence of each other (multicomponent operation) for both systems.

CHAPTER 2

THEROTICAL BACKGROUND

2.1 THE ZEOLITES

2.1.1 Definition of Zeolites

The zeolite word is a Greek originated word. It means "boiling stone", in allusion to the visible water loss when natural zeolites are heated. This property illustrates zeolites' easy water loss when they are heated. This property is known as "intumessence" property of zeolites.

A zeolite is an alumino-silicate, whose framework structure of $(Si,Al)O_4$ tetrahedra contains pores filled with water molecules and exchangeable cations.

They are mainly aluminosilicate minerals which has got crystal structure. Their both synthetic and natural forms exist. The skeletal structure of the zeolite contains voids occupied by exchangeable ions and water molecules which have a considerable freedom of movement leads to ion exchange and reversible dehydration, this account for the well known desiccant properties of zeolites.

2.1.2 Crystal Structure of the Zeolites

Zeolites have a framework structure arising from $[SiO]^{-4}$ and $[AIO_4]^{+5}$ tetrahedron. Tetrahedron is the primary building block of zeolite framework and it is shown in Figure 2.1. The center of the tetrahedron is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices.

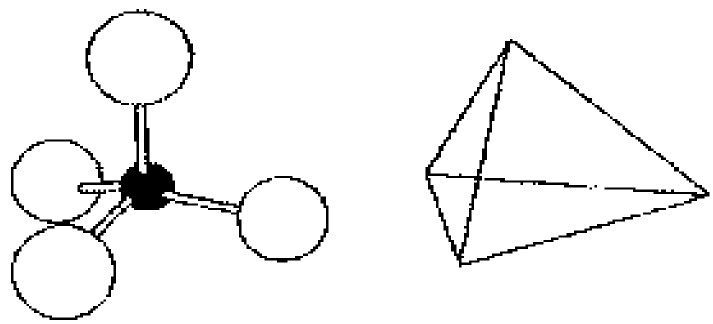


Figure 2.1. Representation of Primary Building Block of Zeolite Framework Structure : $[SiO_4]^{-4}$ or $[AIO_4]^{+5}$ Tetrahedral

Each oxygen atom is shared between two tetrahedra. In this way, the tetrahedral forms a continuous framework. Substitution of Si^{+4} and Al^{+3} defines the negative charge of the framework, this negative charge is balanced by monovalent or divalent cations located together with water molecules in structural channels.

Cations which reside in the channels are substituted easily, for this reason they are termed exchangeable cations or extra-framework cations, unlike Si and Al which are not exchanged under ordinary conditions; the others are termed framework cations.

The generalized chemical formula of the zeolites is of the type $M_x/_n$ $[Al_xSi_yO_{2(x+y)}].wH_20$ where M is Na, K, Li and/or Ca, Mg, Ba, Sr; n is cation charge; y/x = 1 to 6; w/x = 1 to 4 and (x + y) is the total number of tetrahedrals in the unit cell. The composition of the tetrahedral framework is generally given in square brackets. It may also be convenient to express the zeolite composition by so-called oxide formulas of the type $M_{2}/n\ O.Al_2O_3.xSiO_2.yH2O$.

The Si/Al ratio in natural zeolites ranges within the limits of 1 to 6. The lower limit is determined by Lowenstein's rule, which states that an AlO_4 tetrahedron can not associate with another AlO_4 tetrahedron by a common oxygen atom; at Si/Al =1, the silicon and aluminum tetrahedral alternate to form the ordered framework. Ordered locations of Si and Al, is also possible at other Si/Al ratios. The upper limit of the Si/Al ratio in the natural zeolites reaches to 5 to 6. (e.g., clinoptilolite, mordenite, ferrierite).

In synthetic zeolites the silicon can be substituted by germanium, and aluminum can be substituted by gallium, iron, chromium, boron etc., but in natural specimens only Be and Fe is observed in tetrahedral sites, in addition to Si and Al (Tsitsishvili, 1992)

2.1.3 The Aluminosilicate Framework

As stated above, all zeolites have 3-D structures constructed by joining together $[SiO_4]^{-4}$ and $[AlO_4]^{+5}$ coordination polyhedral. The most conserved and stable component is the aluminosilicate framework and it defines the structure type. The topological structure of the framework, the numbers and distribution of charges and stacking faults are basically formed at the crystal growth stage and define a series of technologically important properties of zeolites. Framework topology forms the basis of contemporary classification of the zeolites.

The Si/Al distribution can be estimated confidently, by the distance between the tetrahedron center and the oxygen atom. In ordered structures one can distinguish two groups of distances, for silicate tetrahedra it is close to 0.162 nm and for aluminate tetrahedra it is close to 0.174 nm.

A remarkable characteristic zeolite property arising from their molecules framework structure is the assemblages of tetrahedral such that creating their porous structure which happen to form regular arrays of apertures. These aperture have such a size that, they are selectively take up some molecules into their porous structure, while rejecting others on the basis of their larger effective molecular dimensions. For sorption and catalysis, the dimensions and locations of these channels, through which the molecules diffuse into the inter crystalline free volume are very important. This property is known as "molecular sieving".

2.1.4 Exchangeable Cations and Water Molecules in Zeolite Structure

All zeolites have 3-D framework structures constructed by joining together $[SiO_4]^{-4}$ and $[A1O_4]^{+5}$ coordination polyhedral.The negative charge is balanced by ions found in the interstices of zeolites; generally alkaline or alkaline-earth cations, such as Na^+, K^+, Ca^{+2}, Mg^{+2} or Sr^{+2}.

The channels and voids in zeolite framework are filled with exchangeable cations and water molecules. Ease of water removal and ion exchange creates an impression of disordered location of cations and water molecules in their structure. The truth of the matter is, as recent determinations of zeolite structures show, most of the water molecules and cations occupy rather definite sites in the lattice structure. (Tsitsishvili, 1992).

In the structure, exchangable cations are surrounded by water molecules and oxygen atoms. Distances to the nearest neighbours are very different and cations lie at the centers of irregular polyhedra. Cation-oxygen atom and cation-water molecule distances mainly depend on the size of the cation and cover wide ranges as compared with tetrahedral interactions. Magnesium ions are coordinated only by water molecules, but potassium and barium ions are surrounded generally by oxygen atoms of the lattice. Coordination of Ca^{+2} and Na^+ ions depend strongly on the cavity geometry.

The characteristic property for zeolites containing large cavities is the presence of large complexes of water molecules in voids and bonding between framework ions and exchangable ions by means of aqueous bridges. Water molecules can also serve as bridges between exchangeable cations. The most typical case involves a cation bound to the channel wall on one side and to a water molecule on the other. Structural refinements show that each cation occupies its own specific site in natural or exchanged form. Most of the time, the decisive factor is not the charge but the size of the cation.

2.1.5 Classification of Zeolites

Zeolites can be classified into groups considering common features of the aluminosilicate framework structures. The most important properties of zeolites which are structure related can be determined as follows:

- High degree of hydration and behaviour as zeolitic water
- Low density and void volume after dehydration
- Exhibition of high stability of the crystal structure during dehydration
- Cation exchange properties
- Various physical properties (e.g. electrical conductivity)
- Uniform molecular-sized channels in the dehydrated crystals
- Adsorption of gases and vapors
- Catalytic properties.

The classification includes mainly seven groups; for each group, zeolites have a common subunit structure which is a specific array of $(Al,Si)O_4$ tetrahedra (Breck,1974).The groups and some examples for each group can be summarized as follows:

Group 1 : Analcime, Philipsite

Group 2 : Erionite, Offreite

Group 3 : Zeolite A

Group 4 : Faujasite, Chabazite

Group 5 : Natrolite, Mesolite

Group 6 : Mordenite, Ferrierite

Group 7 : Heulandite, Clinoptilolite

The members of group 7, heulandite and clinoptilolite, are the most abundant zeolites in nature. In many countries, huge occurrences of clinoptilolite is mined and its interesting properties are investigated and clinoptilolite finds itself a wide variety of application areas.

2.1.6 Structure of Heulandite and Clinoptilolite

The chemical composition of the Heulandite-Clinoptilolite series is characterized according to their remarkable changes in the Si/Al ratio and depending upon composition of exchangable cations in their structure. Main components in the clinoptilolite structure are represented in Figure 2.2.

It is observed that all structural determinations of heulandite and clinoptilolite justify the structural scheme offered by Merkle & Slaughter (1968). In this structural scheme, $(Si,Al)O_4^-$ tetrahedra are bound in layers in Figure 2.3. These layers are in turn bound by oxygen atoms in the symmetry plane and they form a 3-D framework as shown in Figure 2.4.

Framework units are joined in a layer like array which cause the characteristic perfect cleavage of the mineral. The channel system is 2-D, including 8 to 10 membered channels, parallel [001] and 8-tetrahedra channels channels along [100], termed by Koyama et al. (1977) as A, B and C channels respectively as seen in Figure 2.2.. Calcium and sodium ions both occupy two sites (Ml and M2) in channels A and B of heulandite and clinoptilolite. In addition, in clinoptilolite structure, there are two sites, M3 occupied by potassium and M4 occupied by magnesium ions.

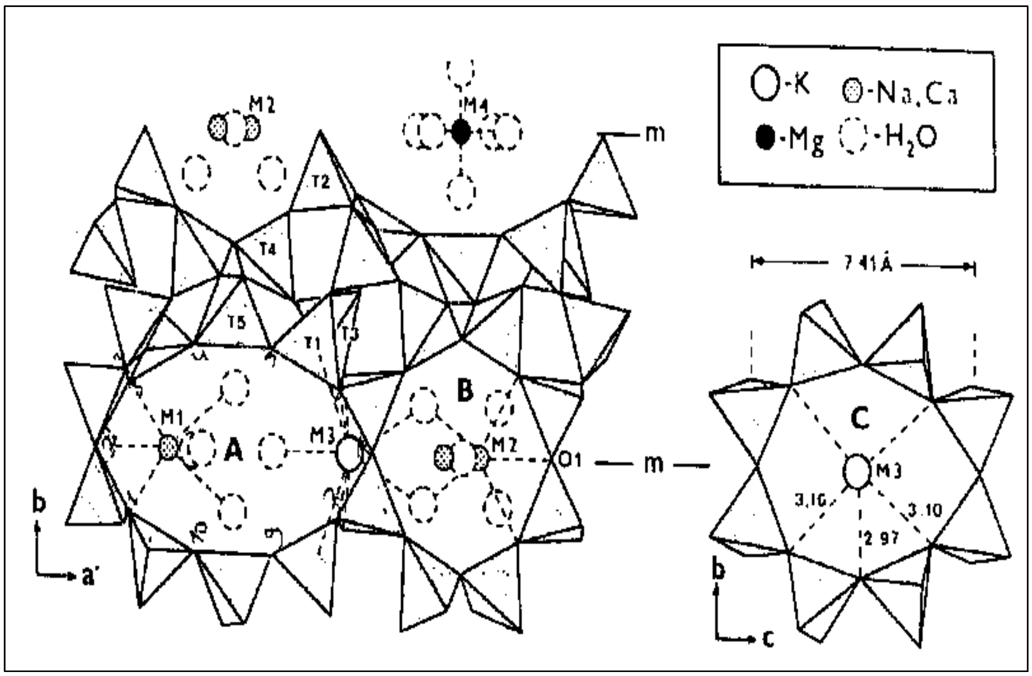


Figure 2.2. Main Components in the Clinoptilolite Structucture (Koyama 1977)

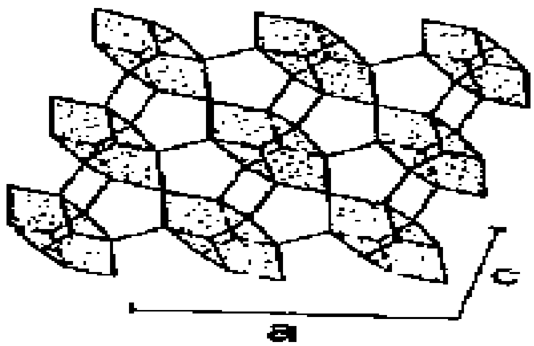


Figure 2.3. Arrangement of the 4-4-1 Units in the Framework Structure of Heulandite (Merkle and Slaughter, 1968)

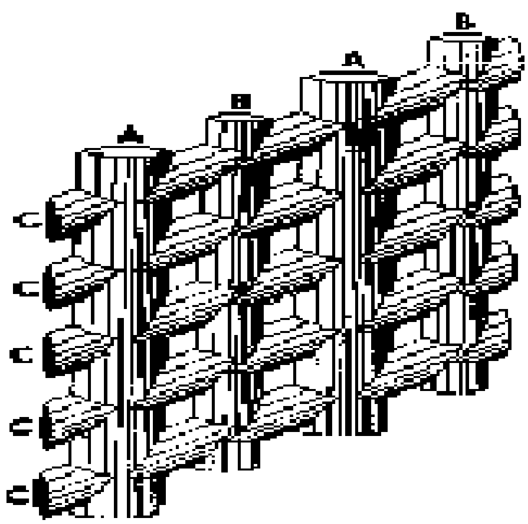


Figure 2.4. System of Channels in the ac Plane in Heulandite Structure (Koyama and Takeuchi, 1977)

2.1.7 Occurrence of Natural Zeolites

The rock forming zeolites are primarily found as products of the alteration of glasses of volcanic or impact origin. Fine grained volcanic glass is the basic source of natural zeolites due to their high reactive capacities, chemical compositions and large surface areas (Tsitsishvili, 1992).

Huge zeolite occurences are found in belts of recent volcanism, frequently in rocks of Cretaceous, Paleogenic and Neogenic age. Clinoptilolite, mordenite, chabazite, erionite, philipsite, laumontite, analcime and ferrierite form large deposites. Six of them are used in industrial applications whereas analcime and laumontite are not utilized in industry yet.

The most important occurences of clinoptilolite are formed in lake or marin basins. Zeolitization is the result of burial diagenesis or hydrothermal metamorphism at shallow depths. Due to mechanical strength, heat insulating and decorative properties, clinoptilolite tuffs have been used for ancient times.

Clinoptilolite tuffs contain 70-90 % of clinoptilolite in association with authigenic species such as montmorillonite, celadonite, chlorite, low cristobalite and sometimes mordenite, as well as with the high temperature minerals quartz, plagioclase, biotite and potassium feldspar.

2.1.8 Applications of Zeolites

Properties such as structural chemistry, availability, cost determines the industrial use of zeolites. Applications and uses of zeolites have attracted much attention and considerable progress has been made in utilization of zeolites in many industrial, agricultural areas in many countries.

The major industrial applications which make use of zeolites can be summarized as follows:

- Treatment of nuclear effluents
- Waste water treatment
- Use of zeolites in gas purification
- Zeolites as catalysts
- Adsorbent applications

2.2 Ion Exchange Properties of Clinoptilolite

Zeolite structures have unique features that lead to unusual types of cation selectivity and sieving. Therefore, cation selectivities in zeolites do not follow the typical rules which are evidenced by other inorganic and organic exchangers.

Substitution of trivalent Al for quadrivalent Si in the silicate tetrahedral of clinoptilolite structures create fixed, negatively charge sites throughout the structure. To maintain electrical neutrality the negative charges are neutralized by the presence of an equivalent number of mobile cations and these mobile cations are loosely bonded in the crystal structure and they are free to exchange with cations in the solution. The cation exchange occurs when ions from solution replace counter ions within the crystal structure.

The unusual selectivity of clinoptilolite that make it attractive for ion exchange applications is caused by structure related ion sieve properties. Many different mechanisms exist which are responsible for the cation sieve properties exhibited by natural zeolites.

One of them is the positive exclusion of certain cations due to the inability of these larger cations to enter the zeolite lattice in considerable amounts. An example of this mechanism is the sieve effect shown by analcite for Cs. The second mechanism for a cation sieve effect is the inability of the negative charge distribution on the zeolite structure to accomodate a given cation (Mumpton, 1960).

2.3 Ion Exchange Theory

The ion exchange process can be represented by the equation 2.3.1 as follows;

$$Z_A B^{Z_B^+}_{(Z)} + Z_B A^{Z_A^+}_{(S)} \Leftrightarrow Z_A B^{Z_B^+}_{(S)} + Z_B A^{Z_A^+}_{(Z)}$$

where Z_A and Z_B are charges of the exchanging cations A and B, subscripts z and s refer to the zeolite and solution, respectively. The equivalent fractions of the exchanging cation in the solution and zeolite are defined by:

$$A_s = \frac{\text{Normality of exchanging cation A}}{\text{Total Normality}} \qquad 2.3.2$$

$$A_Z = \frac{\text{number of equivalents of exchanging cation A}}{\text{total equivalents of cations in the zeolite}} \qquad 2.3.3$$

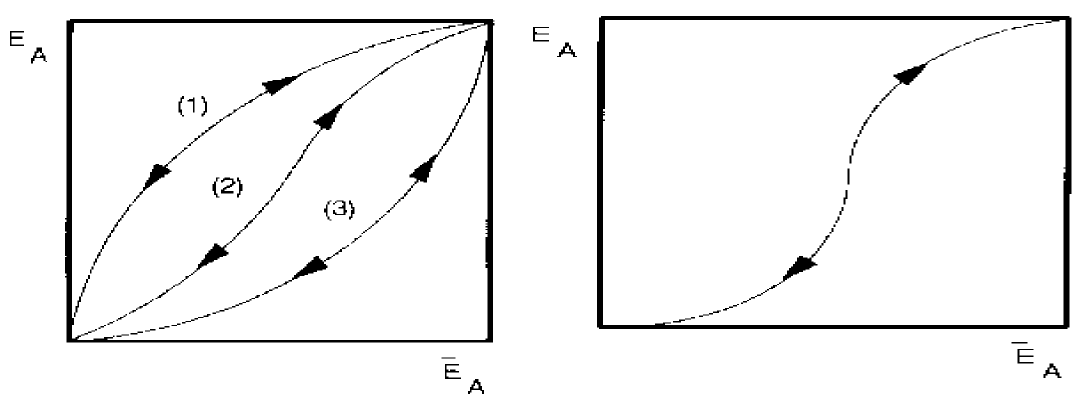
also $A_s + B_s = 1$ and $A_z + B_z = 1$ (Bhatia S,1990)

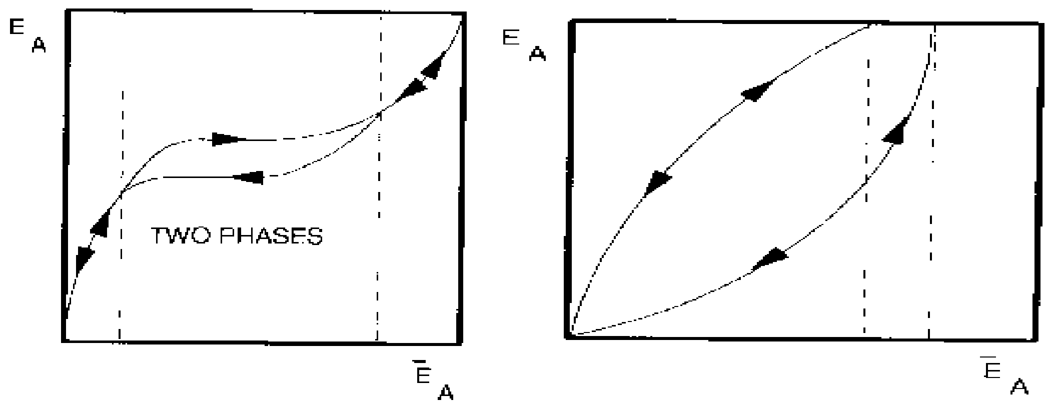
2.4 Ion Exchange Isotherms

A plot of solute concentration in the zeolite versus concentration in the solution as a function of the experimental conditions is called an isotherm. Considering above definitions, the ion exchange isotherm is a plot of A_z (or E_A) as a function of A_s (or $\underline{E}_A$) at a given total concentration in the equilibrium solution and at constant temperature.

The isotherms are classified in four types (Townsend, 1991). The isotherms of the first type are presented in Figure 2.5.a and represent relatively simple systems. Case 1 shows that the zeolite does not prefer the ion that enters. Case 2 is obtained when the zeolite is not selective. Case 3 occurs when it is selective. Isotherms of the second type (Figure 2.5.b) show a sigmoid shape and indicate a change in the selectivity. Isotherms of the third type (Figure 2.5.c) present a plateau in the hysteresis region.

This kind of behaviour is due to the formation of a new crystalline phase that occurred during the exchanging process, as in the isotherms type "e." Finally, isotherms of the fourth type (Figure 2.5.d) are frequently observed for the zeolites.





(c) (d)

Figure 2.5: Arrangement of Isotherms described by Townsend (1991).

2.5 Ion Exchange in Column Operation

Ion exchange replacement is usually carried out in columns. Ion exchange process can be used for replacement, removal and separation of ions and non-electrolytes. The simplest column operation is the replacement of counter ion in feed by another counter ion which is initially in the ion exchanger. The counter ion from the feed is removed by ion exchange process and it is absent in the effluent until breakthrough occurs.

2.6 Calculation of Breakthrough Capacity

Breakthrough curves are obtained by plotting the effluent concentration of the exchangable cations as a function of the volume of effluent collected. These curves are quite useful so as to calculate the dynamic parameters affecting the ion exchange process.

The breakthrough curves are also suitable so as to determine the exchange capacity of the packed bed. For any fixed bed operating at constant flow rate, it is clear that the total exchange capacity of the bed can be calculated by integration of the area above the breakthrough up to exhaustion, according to the equation 2.6.1;

$$Q_t = \frac{\int_0^{V_t} (C_0 - C).dV}{\rho_b h_T a_s}$$

where Q_t is the total clinoptilolite capacity for the influent ions, and ρb is packed bed density.

In the same way, the breakthrough capacity of the clinoptilolite may be calculated from the relation:

$$Q_B = \frac{\int_0^{V_B} (C_0 - C).dV}{\rho_b h_T a_s} \qquad 2.6.2$$

The column efficiency, is the fraction of the exchange capacity defined as :

$$\eta_c = \frac{Q_B}{Q_t} \qquad 2.6.3$$

CHAPTER 3

LITERATURE SURVEY

In 1978, Semmens and Seyfarth examined occurrence and properties of sodium formed clinoptilolite as well as removal of heavy metals like Pb^{2+} and Cd^{2+} at 28^0C and 0.26-0.32 total solution normality. They obtained very high selectivities and maximum exchange levels (expressed as the percentage of the theoretical exchange capacity) for both cations; 100% for lead and 85% for cadmium respectively. This result showed that sodium formed clinoptilolite has affinity for lead and cadmium ion.

Blanchard et al. (1984) studied removal of heavy metals and ammonia from wastewaters by means of natural zeolites. They converted clinoptilolite to sodium form and they found the selectivity sequence as $Pb^{2+} > NH_4^{+} > Cu^{2+}$, $Cd^{2+} > Zn^{2+}$, $Co^{2+} > Ni^{2+} > Hg^{2+}$.

Czaran et al. (1988) examined the cation exchange properties of a Hungarian clinoptilolite. They found the exhausted clinoptilolite could be regenerated more efficiently by potassium ions than by the sodium ions commonly used. Also, their study suggested that the rate of NH_4^+ removed is not so strongly dependent on the pH in the range of 7-12.

El Akrami (1991) studied effects of feed composition, particle size, flow rate, and accompanying cation concentration on the ion exchange properties of Bigadic clinoptilolite. Particle sizes were taken as 6/16, 16/30, and 30/50 mesh. Flow rates were chosen in the range of 22-78 BV/h. The optimal exchange conditions found are as follows: 30/50 mesh in particle size and about 30 BV/h loading flowrate.

He found that under different conditions breakthrough capacity was varied from 0.085 to 0.891 meq/ml depending on the influent NH_4^+ ion concentration in the range of 23-178 mg/L.

Malliou et al. (1994) investigated uptake of lead and cadmium by clinoptilolite. They found the removal of Pb^{2+} is increased by decreasing the particle size, but at equilibrium the difference is minimized. In addition, they observed the uptake of Pb^{2+} and Cd^{2+} is favored at higher temperatures.

Abusafa (1995) examined the performance of local clinoptilolite from Bigadic in column system for ammonium and cesium removal. He found that the breakthrough capacity varied between 0.036-1.08 meq/g. He also concluded that the optimum particle size for ion removal was 30/50 mesh.

Curkovic et al. (1997) examined lead and cadmium removal from wastewaters by natural and pretreatment zeolites using a batch-type method. The results demonstrated that the natural zeolites contained a complement of exchangeable Na, K and Ca ions and they exposed them to 2 M NaCl solution at 22 and 70^0C. Removal results showed that pretreatment improved both the exchange capacity and the removal efficiency. They also concluded that the metal uptake was increased with increasing temperature during the ion-exchange process.

Komarowski and Yu (1997) performed batch equilibrium studies for ammonium ion removal from wastewater using Austrialian clinoptilolite. They achieved 90% ammonium removal as a result of their experiments. They also found that removal efficiency increased with higher initial ammonium ion concentration and was highest for pH 5.5 .

However, inreasing the amount of zeolite added, decreased the uptake capacity and uptake rate whereas increasing inital ammmonium ion concentration resulted in more rapid uptake.

Ouki and Kavannagh (1999) evaluated two natural zeolites, clinoptilolite and chabazite, with respect to their selectivity and removal performance for the treatment of effluents containated with mixed heavy metals, namely Pb, Cd, Cu, Zn, Cr, Ni and Co. Parameters such as metal concentration, pH and presence of competing ions were examined and removal performance was determined. Their study showed that clinoptilolite and chabazite exhibited different selectivity profiles for all metals studied except Pb for which both zeolites performed exceptionally well. Additionally, metal removal efficiencies exceeding 99% was achieved by both clinoptilolite and chabazite and optimum pH range was reported between 4 and 5. Moreover, the selectivity sequence was determined as $Pb^{2+}>Cu^{2+}>Cd^{2+}> Zn^{2+}> Cr^{3+}>Co^{2+}$.

Faghihian et al. (1999) investigated the use of Iranian clinoptilolite and its sodium form for removal of radioactive cesium and stronsium from nuclear wastewater and $Pb^{2+,}$ Ni^{2+}, Cd^{2+}, Ba^{2+} from municipal wastewater at 25^0C and 0.1 total normality . They determined the selectivity sequence as $Pb^{2+}>Cd^{2+}>Ba^{2+}>Sr^{2+}>Cs^{+}>Ni^{2+}$ and $Pb^{2+}>Ba^{2+}>Cd^{2+}>Sr^{2+}>Cs^{+}>Ni^{2+}$ for natural and sodium-exchanged clinoptilolite. Results showed that clinoptilolite had high affinity for all the cations, and they recommended Iranian clinoptilolite can be used either in natural or sodium form for removal of all these cations from radioactive or municipal wastewater.

Rozic et al. (2000) studied on the removal of ammonium from aqueous solutions with Croatian zeolite. They performed alkaline and acid modification on clinoptilolite. It was found that by increasing the initial ammonia nitrogen concentration, the removal efficiencies decreased on all samples. It was also resulted that the acid modification of zeolite decreases the efficiency of ammonium removal.

Panayotova (2000) examined kinetics and thermodynamics of uptake of Cd^{2+} by natural and modified Bulgarian zeolite. He found that the ratio of wastewater to zeolite equal to 0.1 $dm^3/1$ g was the optimum and Cd^{2+} removal due to zeolite's uptake was the highest if the pH value of water to be treated was in the range of pH 5-7. However, the uptake of Cd^{2+} was considerably decreased in presence of other cations such as Ca^{2+} and Mg^{2+}.

Singh et al. (2000) studied the sorptive properties of natural and synthetic clinoptilolite zeolites for Cd^{2+} with the intention of selecting suitable materials, for use as amendment in contaminated soils, to reduce the uptake of Cd by field crops at 20^0C constant temperature. They observed the cadmium sorption increased with decreasing particle size and sorption of cadmium reached near maximum at pH between 4.5 and 6. At the end of the study, their results showed that both natural and synthetic zeolites preferentially adsorbed Cd and Cd sorption was extremely high for synthetic zeolites.

Langella et al. (2000) investigated Sardinia clinoptilolite with the aim of evaluating the cation exchange properties of this zeolite. They obtained NH_4^+-Na^+, Cu^{2+}-Na^+ , Cd^{2+}-Na^+, Zn^{2+}-Na^+ and Pb^{2+}-Na^+ ion exchange isotherms at 25^0C and 0.1 total normality. In the light of these isotherms, the selectivity sequence was achieved as $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} = Zn^{2+}$. This result showed that clinoptilolte has higher affinity for NH_4^+ and Pb^{2+} and lower affinity for Cu^{2+}, Zn^{2+} and Cd^{2+}.

Cincotti et al. (2001) examined Sardinian natural clinoptilolite at 25^0C and 0.1 M to evaluate its adsorption for the metals, Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}, as well as ammonium removal. They converted natural clinoptilolite to sodium form and observed that the natural material converted into the sodium form gives rise to better capacity for all ions investigated.

Moreover, the selectivity order was evaluated as Pb^{2+} > NH_4^+> Cd^{2+}, Cu^{2+}, Sr^{2+} > Zn^{2+} > Co^{2+} and they concluded that Sardinian natural clinoptilolite considered in the study is a potential adsorbent, especially for lead removal.

Demir et al. (2002) examined ammonium ion removal from aqueous solution by ion exchange using packed bed Bigadiç clinoptilolite. Their results indicated that conditioning of the zeolite with ammonium chloride impoved the ion exchange capacity and the smaller particle size also caused a higher ion exchange capacity due to greater available surface area. The actual ion-exchange capacity of the clinoptilolite was found to be 0.57 meq/g zeolite. Moreover, after column operations, they stated the columns could be regenerated number of times without loss of ammonium ion exchange capacity

Panayotova and Velikov (2002) examined kinetics of heavy metal ions removal by use of natural Bulgarian clinoptilolite. They observed that Pb^{2+} ions are strongly bound to zeolite and immobilization of the other heavy metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) is relatively weaker. They also stated that Pb^{2+} uptake was not influenced by the presence of Ca^{2+} and Mg^{2+}, whereas lower uptakes were attained for Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} in the presence of Ca^{2+}. Also, the selectivity sequence was obtained as Pb^{2+}> Cd^{2+}> Cu^{2+}> Zn^{2+}>Ni^{2+}.

Çulfaz and Yağız (2004) examined ion exchange of Pb^{2+} and Cd^{2+} on the sodium form of Bigadiç clinoptilolite at 25^0C and 0.1 total normality. According to the equilibrium studies, the selectivity sequence was obtained as Pb^{2+}> Na^+>Cd^{2+} Therefore, they stated that this clinoptilolite can be used for the treatment of wastewaters containing lead, but not cadmium.

CHAPTER 4

MATERIALS AND METHODS

4.1 Preparation and Characterization of Clinoptilolite Samples

4.1.1 Clinoptilolite Samples

The clinoptilolite sample used throughout the studies is originated from Gördes (Manisa) and obtained from Mineral Research and Exploration Institute (MTA).This batch (about 50 kg) contained particles that were in 4-5 cm diameter. About 10 kg of clinoptilolite were crushed and sieved into 35/60 mesh (0.5-0.25 mm) size range considering previous exchange studies (Tufan, 2002).

4.1.2 Mineral Identity

For verifying mineral identity, Scanning Electron Microscopy (SEM) analysis was performed via Scanning Electron Microscopy instrument for morphology in Turkish Cement Manufacturer's Association. In addition to that, Tufan's X-ray Diffraction (XRD) and thin section analysis were taken into consideration since clinoptilolite samples and clinoptilolite particle size range used in this study were from the same batch of Tufan's study (Tufan, M.Sc. Thesis, METU, 2002).

4.1.3 Pretreatment of Clinoptilolite

The original form of Gördes clinoptilolite contains exchangeable cations such as K^+, Na^+, Mg^{2+}, Ca^{2+}. It was attempted to replace these cations by Na^+ ion to prepare a near homoionic form of clinoptilolite and to improve effective ion exchange capacity.

The near homoionic form was obtained by treating each 50 grams of original clinoptilolite sample with 500 ml of 1 N NaCl solution in a vessel with stirring by a wrist-action shaker at ambient temperature for 10 days. The exchange solution was replaced with fresh NaCl solution every 24 hours. Each day, all exchangeable cations were measured with AAS and flame photometer until their concentrations decreased to sufficiently low values (5-10 ppm).

After treatment, near homoionic Na form of clinoptilolite was washed by deionized water until chloride ion was not detected when a drop of 0.1 % $AgNO_3$ was introduced. Sample was then dried at 70^0C for 24 hours. Finally, it was kept in a dessicator, containing saturated NaCl solution for further use.

4.1.4 Chemical Composition of Clinoptilolite Samples

Chemical composition of original and Na form of clinoptilolite was determined with X-ray Fluorescence (XRF) analysis performed at MTA laboratories. Based on chemical composition, theoretical cation exchange capacity and Si/Al ratio of Gördes clinoptilolite were estimated.

4.2 Reagents

All chemicals used in the experiments were analytical grade reagents and obtained from Merck. The aqueous solutions of Cd^{2+}, NH_4^+ and Na ions were prepared by dissolving $Cd(NO_3)_2.4H_2O$, NH_4Cl and NaCl in deionised water.

4.3 Batch Studies for Ion Exchange Process

4.3.1 Binary Experiments

Binary ion-exchange experiments were conducted by reacting weighed amounts of near homoionic clinoptilolite with known volumes of solution mixtures of the cations of interest. Before performing the experiments, first, initial solutions of Cd^{2+} and NH_4^+ cations were prepared from $Cd(NO_3)_2.4H_2O$ and NH_4Cl salts. Total solution concentrations and total volumes of solution mixtures were held constant at 0.1 N and 50 mL while the concentration of each cation was varied between in the range of 0.01-0.1 N. The solutions were then dispensed and mixed with 0.5, 1 and 1.5 grams of clinoptilolite powder. After that, mixtures containing clinoptilolite and salt solution were put in polypropylene bottles and were agitated on water bath for 24 hours (Curkovic et al. 1997) at constant temperature (25°C). After the equilibrium is reached, the mixtures were separated by filtration, and the solution parts were analyzed using Atomic Absorption Spectrophotometer for Cd^{2+}, flame photometry (Jenway Model PFP7) for Na^+ and ammonium electrode (Russel Model 95-5129) for NH_4^+ ion. Following the ion analysis and measuring final equilibrium concentrations, ion exchange isotherms (representing the ion-exchange equilibrium of the system at the specified concentration and temperature) were plotted as equivalent fractions of exchanging cation in solution versus equivalent fractions of exchanging cation in zeolite .

4.3.2 Ternary Experiments

Ternary ion-exchange experiments were conducted in a fashion similar to the binary experiments. 0.5, 1 and 1.5 grams of clinoptilolite powder were reacted with 50 mL total volume and 0.1 N total concentration of solution mixtures of the cations of interest. Cation solutions were once again prepared from $Cd(NO_3)_2.4H_2O$ and NH_4Cl salts. After mixing solutions and clinoptilolite powder, samples were shaken in water bath. After the equilibrium is reached, the mixtures were separated and the solution parts were analyzed in the same manner as in binary experiments. The only difference between binary and ternary batch studies is that after following the ion analysis and measuring final equilibrium concentrations, ternary ion exchange isotherms were plotted in equilateral triangle graphs unlike binary studies since three ions involve in ion exchange process (in the presence of each other) at ternary experiments (Cd^{2+}-NH_4^+-Na system). The experimental parameters of batch studies are listed in Table 4.1.

Table 4.1. Experimental Parameters for Batch Studies

Weight of Clinoptilolite Sample	0.5, 1, 1.5 gram
Particle Size	0.25-0.5 mm
Natural pH	4 – 6
Temperature	25^0C
Total Normality	0.1 N

4.4 Column Studies for Ion Exchange Process

4.4.1 Binary Column Studies

Binary column studies were conducted using columns of 1.0 cm diameter and 15 cm height. The column was filled with 5 g, 0.5-0.25 mm Na form of clinoptilolite sample. The packed bed height was 5.5 cm. The examination of Cd^{2+} and NH_4^+ removal on the zeolite was carried out on the solutions, keeping initial concentration constant. The solutions used in the experiments were prepared by dissolving $Cd(NO_3)_2.4H_2O$ and NH_4Cl salts in deionized water. The experiments were carried out at isothermal conditions ($T=25 \pm 2^{O}C$) with 8 mL/min flow rate through the column for Cd^{2+}-Na^+ and NH_4^+-Na^+ systems. The solution was brought to the top of column, passed through the zeolite loaded column, and the samples from effluent solution were collected in 50 ml test tube so as to determine the concentration of ions in the effluent.

Constant flow was maintained using Cole Parmer Masterflex L/S model peristaltic pump. The process was stopped when the ion concentration in the effluent became equal to the initial concentration in the influent and the breakthrough curves were established. It should be noted that, during breakthrough analysis, the breakthrough concentration was taken as 5% of the influent ion concentration.

4.4.2 Ternary Column Studies

Ternary column experiments were carried out just like in binary column experiments. However, main difference between binary and ternary column experiments is that feed solution used in ternary system contained two species (Cd^{2+} and NH_4^+) and loading flow rate was varied 8, 15, 30 mL/min to observe the effect of flow rate on breakthrough capacity. Equipment used in column experiments is presented in Figure 4.1 and the experimental parameters of column studies are listed in Table 4.2.

Table 4.2 Experimental Parameters for Column System

Equipment Specifications	
Inside Column Diameter	1.0 cm
Weight of Clinoptilolite	5.0 grams
Packed Height	5.5 cm
Particle Size	35/60 mesh (0.25-0.5 mm)
Operating Conditions	
Feed Concentration	0.01 N
Flow Rate	8,15,30 mL/min
Natural pH	4-6

Figure 4.1. Experimental Setup of Column Systems

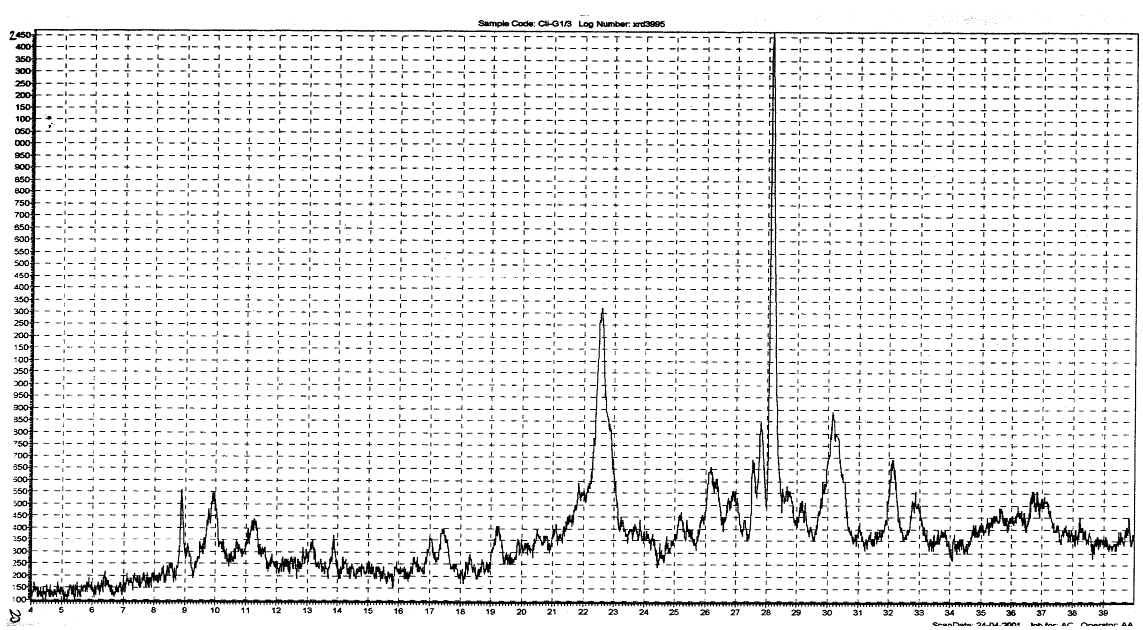
CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characterization of Clinoptilolite Samples

5.1.1 Mineral Characterization

X-ray diffraction (XRD) pattern given by Tufan (Tufan, 2002) is shown in Figure 5.1.



Bragg Angle, 2 Theta (Cu Anode)

Figure 5.1. X-Ray Diffraction Patterns of Gördes Clinoptilolite for 0.5-0.25 mm (Tufan, 2002)

According to X-ray pattern (Figure 5.1) although there are some crystalline impurities (indicated by small peaks), the zeolite consisted mainly of clinoptilolite. The approximate percentages of these species were determined by thin section analysis (Tufan, 2002) and seen that 90±5 % of the sample is composed of clinoptilolite, the rest is small amounts of quartz, feldspar, biotite and rock fragments (3±1 % quartz, 2±0.5 % feldspar, 1±0.5 % biotite and 0.3 % rock fragments).

In addition to X-ray diffraction, SEM analysis was also performed to analyze the morphology of clinoptilolite sample. As a result, typical coffin-shaped crystal structure was observed. Scanning electron micrograph of original Gördes clinoptilolite is given in Figure 5.2.

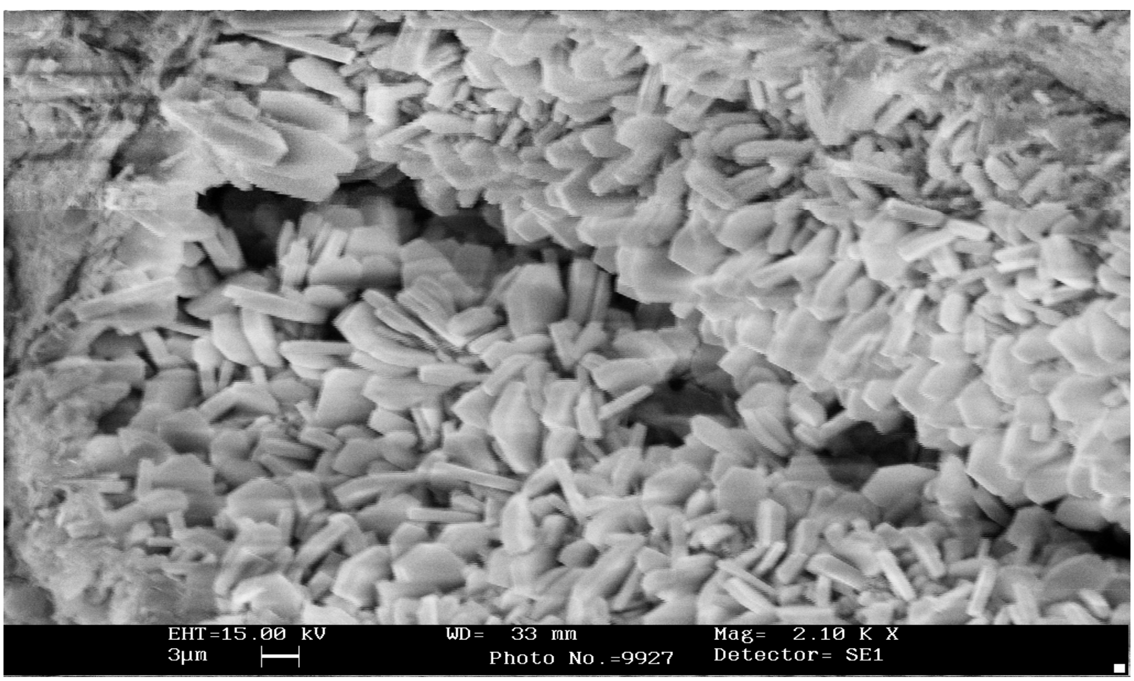


Figure 5.2. Scanning Electron Micrograph of Original Gördes Clinoptilolite

5.1.2 Chemical Composition

Chemical composition of original and Na form of clinoptilolite sample obtained with XRF analysis is presented in Table 5.1 and Table 5.2. respectively. According to the tables, Si/Al ratio of original sample was calculated as 5.2, and Si/Al ratio of Na form of clinoptilolite was determined as 5.3 . This means that Si/Al ratios of both samples are in typical ranges (5-6) for clinoptilolite zeolite (Tsitsishvili, 1992). Theoretical exchange capacities based on ammonium content were calculated as 2.36 meq/g and 2.28 meq/g for original and Na form of clinoptilolite samples, respectively . However it should be noted that these values ignore the elements coming from the impurities.

Table 5.1. Chemical Composition of Original Clinoptilolite Sample

	% Weight	Moles/100 g	Exchangeable Cations meq/g
SiO_2	68.200	1.137	
Al_2O_3	11.200	0.11	
Fe_20_3	2.400	0.015	
MgO	1.000	0.025	0.500
CaO	2.100	0.037	0.740
Na_2O	0.600	0.010	0.200
K_2O	4.400	0.046	0.920
MnO	0.100	0.001	
TiO_2	0.100	0.001	
P_2O_5	<0.100	<0.001	
Total	90.100		2.360

Table 5.2. Chemical Composition of Na-form of Clinoptilolite Sample

	% Weight	Moles/100 g	Exchangeable Cations meq/g
SiO_2	68.900	1.148	
Al_2O_3	11.100	0.11	
Fe_20_3	2.200	0.014	
MgO	0.800	0.020	0.400
CaO	0.600	0.011	0.220
Na_2O	3.600	0.058	1.160
K_2O	2.400	0.025	0.500
MnO	0.100	0.001	
TiO_2	0.100	0.001	
P_2O_5	<0.100	<0.001	
Total	89.700		2.280

5.2 Effect of Pretreatment

As it is stated in the experimental part, before starting the experiments, for the aim of improving ion exchange ability, pretreatment applied to natural clinoptilolite. Since the selectivity of clinoptilolite for Na^+ ion is very low among other exchangeable ions, clinoptilolite was conditioned with 1M NaCl solution for 10 days by replacing NaCl solution in every 24 hours. The contribution of exchangeable cations calculated from Table 5.1 and 5.2 for original and treated clinoptilolite samples are shown in Table 5.3

Table 5.3. Contribution of Exchangeable Ions to Theoretical Exchange Capacity

Clinoptilolite	Na^+ (eq/eq%)	K^+ (eq/eq%)	Ca^{2+} (eq/eq%)	Mg^{2+} (eq/eq%)	TEC (meq/g)
original	8.5	38.9	31.4	21.2	2.36
Na form (treated)	50.9	21.9	9.6	17.6	2.28

From the results in Table 5.3, the increase of Na^+ content of the clinoptilolite by displacing other exchangeable cations (K^+, Ca^{2+}, Mg^{2+}) from zeolite structure was obvious. Also, results show that although Ca^{2+} was exchanged successfully, it was very difficult to replace K^+ and Mg^{2+} ions. This is because Mg^{2+} ions are strongly bonded to clinoptilolite structure.

It is proposed that potassium is located at a specific site which is situated in an eight-membered ring and has the highest coordination (six framework oxygen and three water molecules) among all the cation sites in the unit cell

(Yücel and Jama, 1990). Because of this location and strong bonding to the zeolite structure, potassium ion has low ion exchange ability. Therefore, it was decided to use sodium content of clinoptilolite (1.16 meq/g) as the total ion exchange capacity of clinoptilolite after pretreatment.

5.3 Particle Size Selection

Selection of suitable particle size is an important parameter for ion exchange studies in both batch and column systems. After crushing the samples, one should be very careful when selecting the suitable particle size for ion exchange experiments. Very high particle sizes lead to lower ion exchange capacities in batch and column systems and very small particle sizes cause high flow resistance within the column. Also, channelling and high pressure drops may occur in column operations. On the contrary, smaller particle sizes result in higher removal performance. In previous thesis studies Abusafa (1995) and Tufan (2002) determined the most suitable particle size range (0.5-0.25 mm) for column systems, so, this particle range of clinoptilolite was selected and used in both batch and column studies.

5.4 Batch Studies

5.4.1 Binary System Ion Exchange Isotherms

To investigate the multicomponent ion exchange behaviour of Gördes type clinoptilolite, firstly, binary system experiments of both ions (Cd^{2+}, NH_4^+) took part in this study. Cd^{2+}-Na^+ and NH_4^+-Na^+ ion exchange systems were examined.

In binary system studies, experimental isotherms of NH_4^+-Na^+ and Cd^{2+}-Na^+ systems for 0.5, 1, 1.5 grams of clinoptilolite were as equivalent fractions of exchanging cation in solution versus equivalent fractions of cation in clinoptilolite. These isotherms are shown in Figures 5.3, 5.4 and 5.5. The experimental data for the isotherms are given in Appendix B. As seen in the figures, ion exchange isotherms for all three cations are above the diagonal. This result shows that Gördes type of clinoptilolite is selective for both cations in the studied experimental ranges.

It should also be noted that although the sodium form of clinoptilolite contains some calcium, magnesium and potassium, no significant amount of these cations was observed in the liquid phase after cadmium-sodium and ammonium-sodium exchange reached equilibrium. Therefore, all the systems are considered as bicationic.

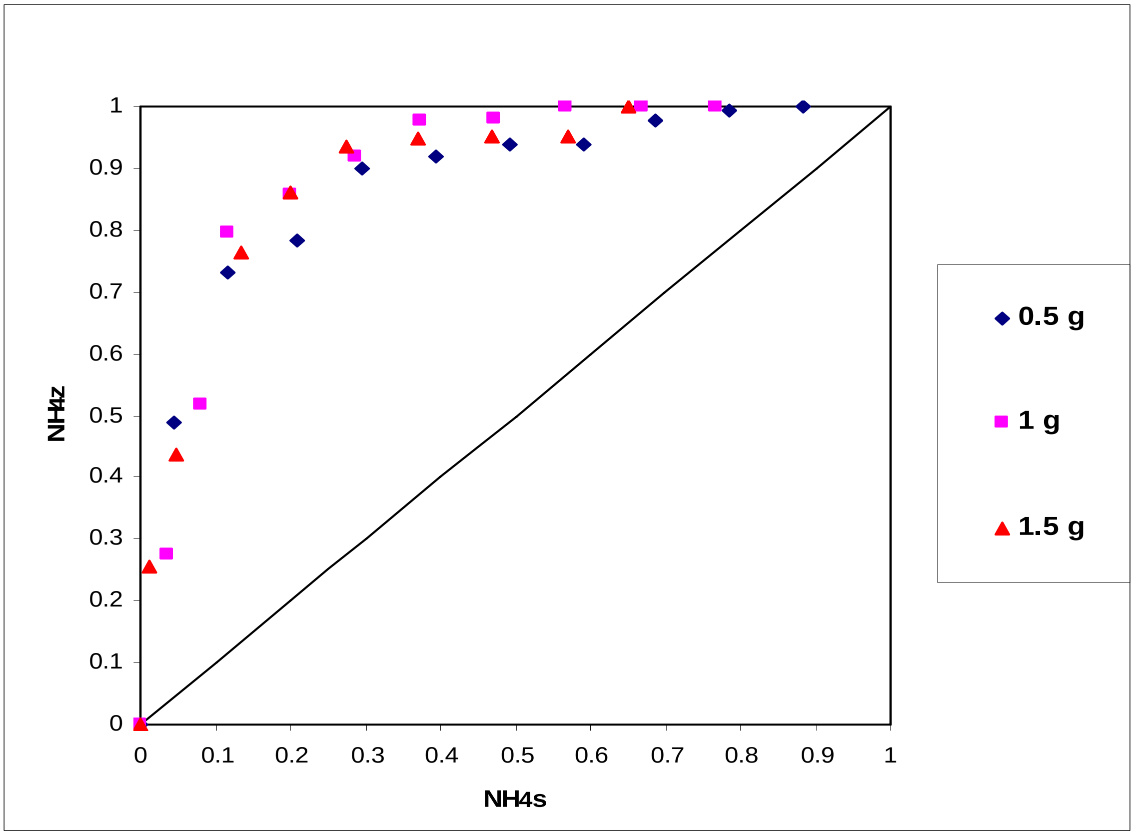


Figure 5.3. Ion Exchange Isotherms of NH_4^+-Na^+ Binary System for 0.5, 1, 1.5 grams of Clinoptilolite at 25^0C and 0.1 N Total Normality

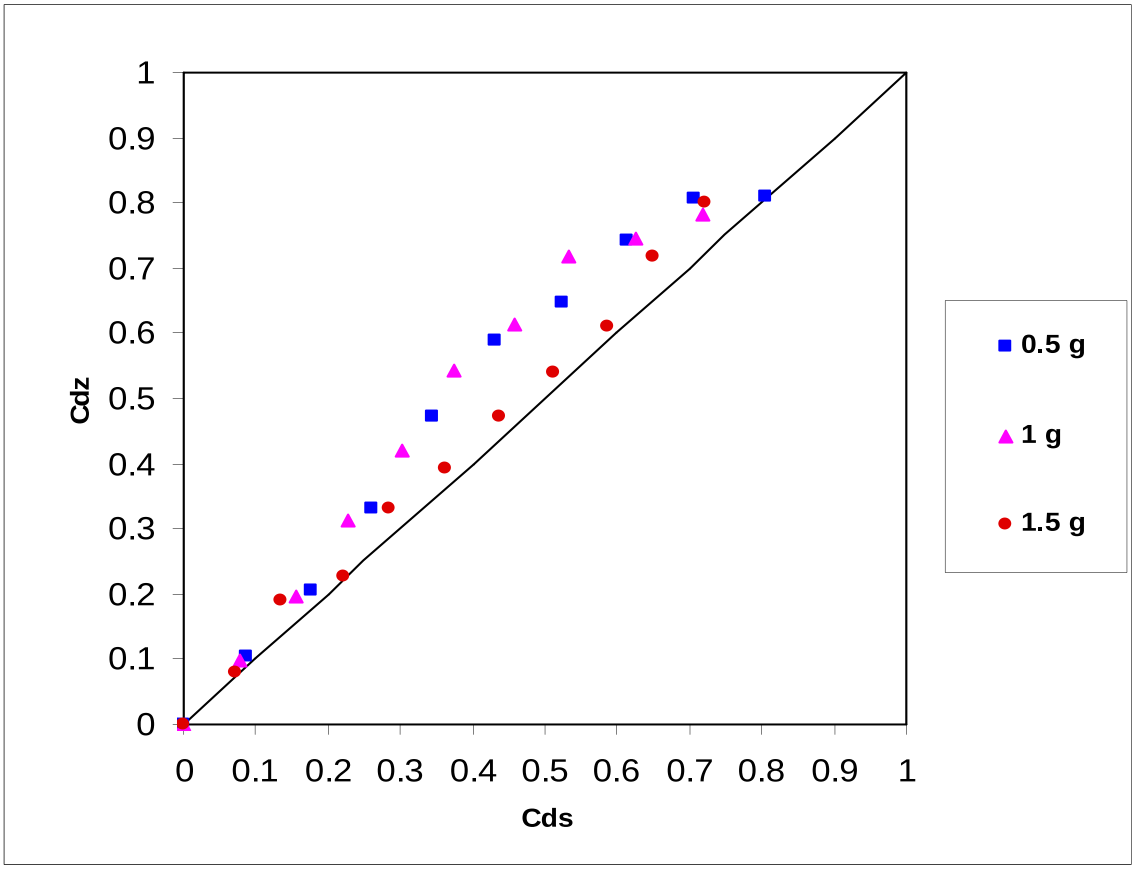


Figure 5.4. Ion Exchange Isotherms of Cd^{2+}-Na^{+} Binary System for 0.5, 1, 1.5 grams of Clinoptilolite at $25^{0}C$ and 0.1 N Total Normality

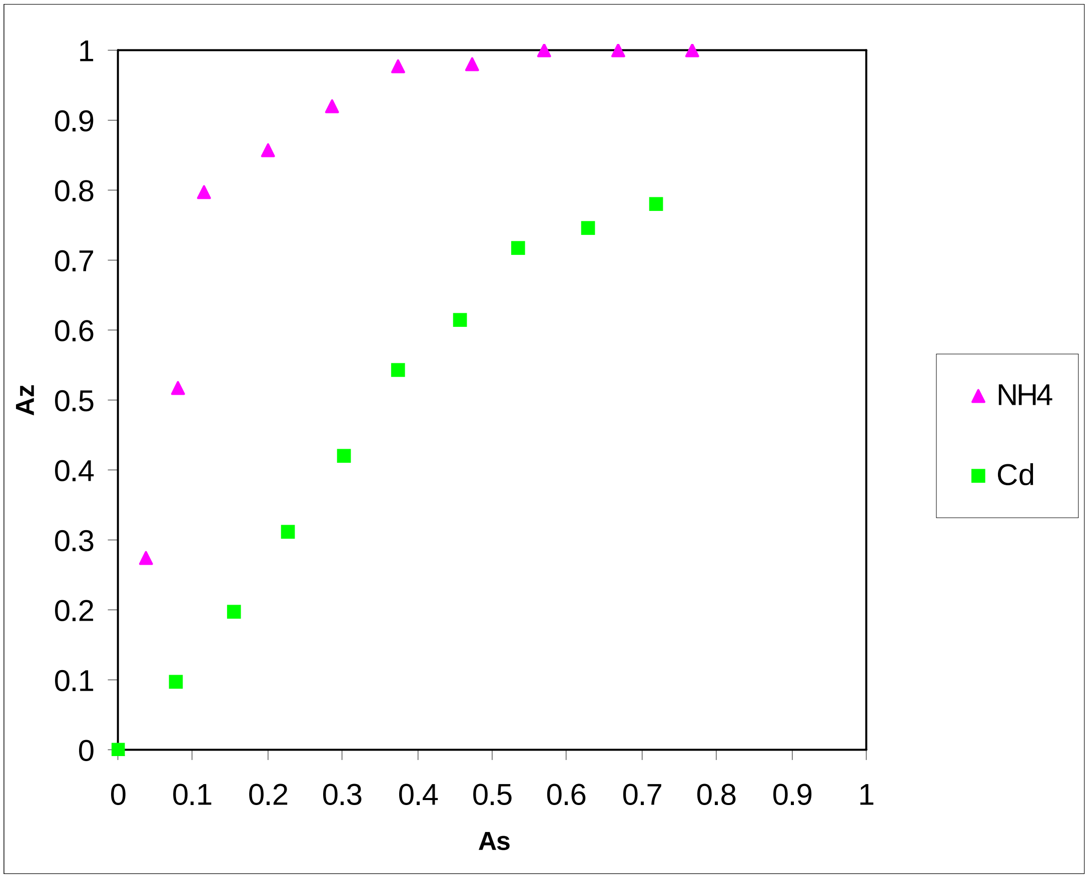


Figure 5.5. Comparison of NH_4 and Cd Ion Exchange Isotherms for 1 grams of Clinoptilolite at 25^0C and 0.1 N Total Normality

Ion exchange isotherms in Figure 5.3 and 5.4 show the maximum exchange levels (based on sodium content) for ammonium and cadmium cations attained were 100% and 80% of the cation exchange capacity respectively. Also, when both ion exchange isotherms were examined together (Figure 5.5.), it is determined that clinoptilolite has higher affinity to NH_4^+ than Cd^{2+} ion. According to these observations and analysis of isotherms, the selectivity sequence of Gördes clinoptilolite was obtained as,
$NH_4^+ > Cd^{2+} > Na^+$ at 25^0C and 0.1 N total normality. This result was compared with the the previous studies and shown in Table 5.4.

Table 5.4. Selectivity Series for Various Heavy Metal Ions on Literature

Researchers	**Selectivity Series**
Blanchard et al. (1984)	$Pb^{2+} > NH_4^+ > Cu^{2+}, Cd^{2+}, Sr^{2+} > Zn^{2+}$
Komarowski and Yu (1997)	$NH_4^+ > Na^+$
Langella et al. (2000)	$NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} = Zn^{2+}$
Panayotova (2000)	$Cd^{2+} > Na^+$
Çulfaz and Yağız (2004)	$Pb^{2+} > Na^+ > Cd^{2+}$
Present Study	$NH_4^+ > Cd^{2+} > Na^+$

On the other hand two more isotherms were obtained as the amount of exchanging cation in solution versus the amount of exchanging cation in zeolite. These isotherms are shown in Figures 5.6 and 5.7. In figure 5.6, maximum exchange levels were 1.16 meq/g, which is 100% of cation exchange capacity (same as figure 5.3) based on sodium content . However, in Figure 5.7, these values were decreased and determined as 0.93

meq/g , approximately 80% of cation exchange capacity of clinoptilolite (again based on sodium content).

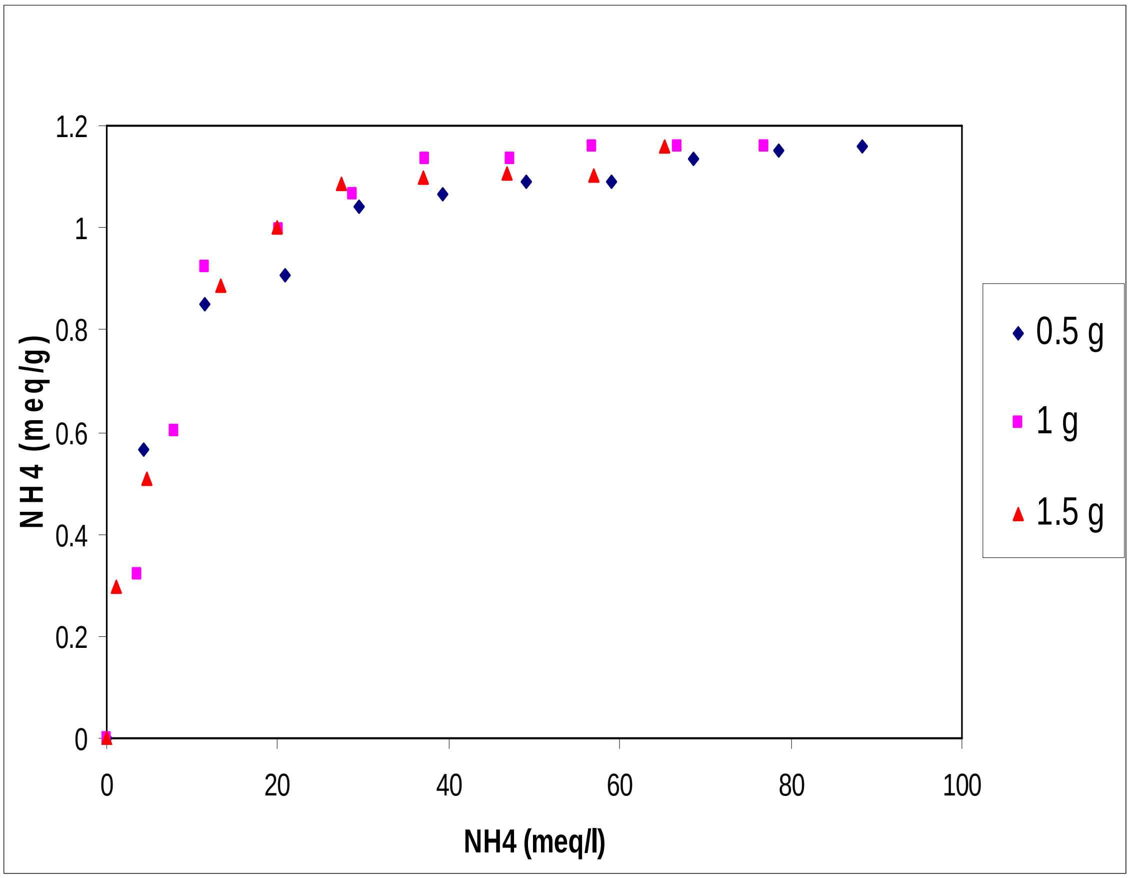


Figure 5.6. Ion Exchange Isotherms of NH_4^+-Na^+ Binary System (meq/g versus meq/l) for 0.5, 1, 1.5 grams of clinoptilolite at 25^0C and 0.1 N Total Normality

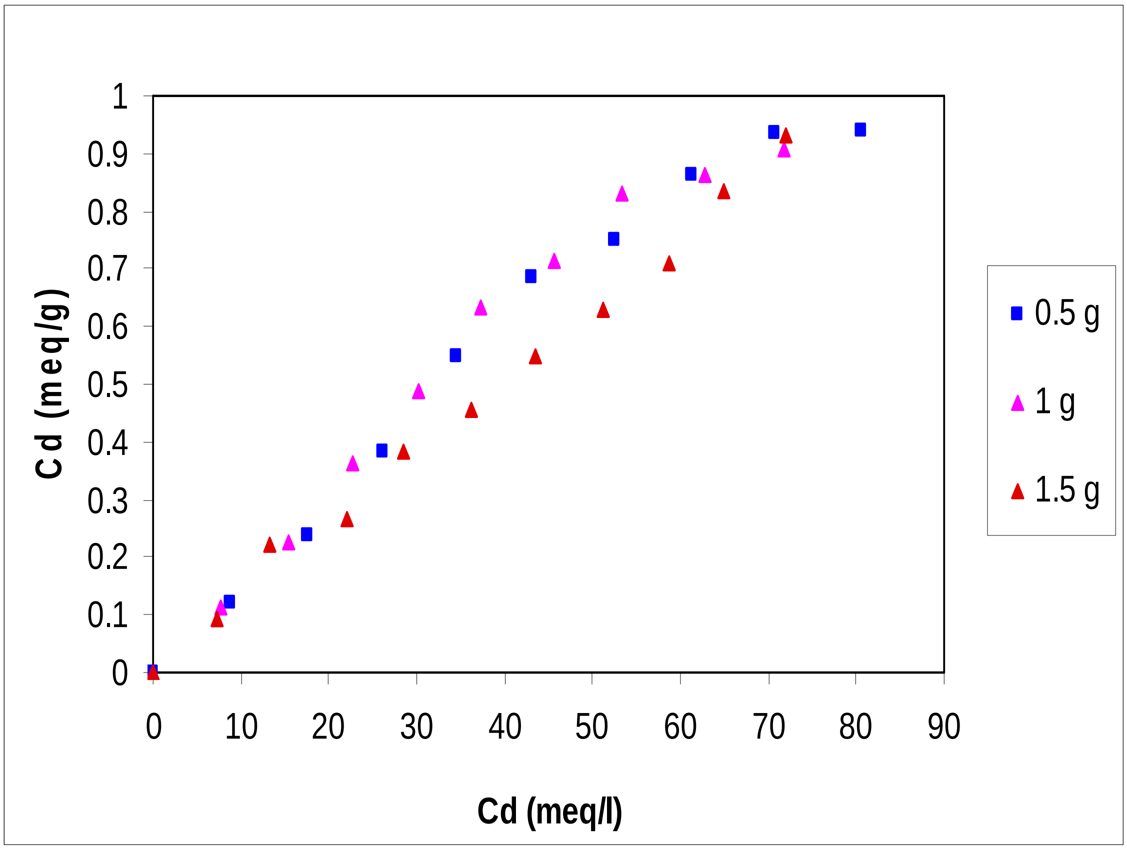


Figure 5.7. Ion Exchange Isotherms of Cd^{2+}-Na^{+} Binary System (meq/g versus meq/l) for 0.5, 1, 1.5 grams of clinoptilolite at 25^{0}C and 0.1 N Total Normality

5.4.2 Ternary System Ion Exchange Isotherms

In ternary systems, experimental isotherms of NH_4^+-Cd^{2+}-Na^+ multicomponent system for 0.5, 1, 1.5 grams of clinoptilolite were plotted in equilateral triangle graphs. Similar to binary experiments, isotherms were obtained again as equivalent fractions of exchanging cations in solution and equivalent fractions of exchanging cations in zeolite. With the help of these isotherms, the affinity and selectivity of Gördes clinoptilolite for NH_4^+ and Cd^{2+} ions were determined in the presence of each other. The results are explained below:

NH_4^+- Cd^{2+}-Na^+ ternary system isotherms are shown from Figure 5.8 to Figure 5.10. The experimental data for the isotherms are given in Appendix B. In the figures, filled symbols are the equivalent fractions of exchanging cations in solution and empty sembols are the equivalent fractions of exchanging cations in zeolite at 0.1 N constant total normality whereas concentration of NH_4^+ and Cd^{2+} ions vary. Each symbol represents three fractional amounts, one for NH_4^+ ion, one for Cd^{2+} ion and one for Na^+ ion. As an example, fractional amounts of cations in zeolite for the fifth empty symbol of Figure 5.8 is; 0.736 for NH_4^+ , 0.202 for Cd^{2+}, and 0.062 for Na^+. This fractions mean both Cd^{2+} and NH_4^+ ions are adsorbed into clinoptilolite. In other words, clinoptilolite has affinity for both ions.

The reason for especially observing the fifth empty symbol of each isotherm is that experiments were performed at varying concentrations for each cation respectively (except sodium ion since it is in zeolite phase) at 0.1 total constant normality and fifth empty symbol is the point where concentrations of Cd^{2+} and NH_4^+ ions are equal (0.05N). In other words, the equivalent fractions at fifth empty symbol shows which ion is more favoured by clinoptilolite where cadmium and ammonium ions were prepared at equal concentrations.

As a result, in all NH_4^+- Cd^{2+}- Na^+ isotherms , it could easily be seen that clinoptilolite has more affinity to NH_4^+ ion than Cd^{2+} ion. Finally, the selectivity sequence of Gördes clinoptilolite was determined as;

$NH_4^+ > Cd^{2+} > Na^+$ at 25^0C and 0.1 N total normality which is exactly the same result obtained in binary systems.

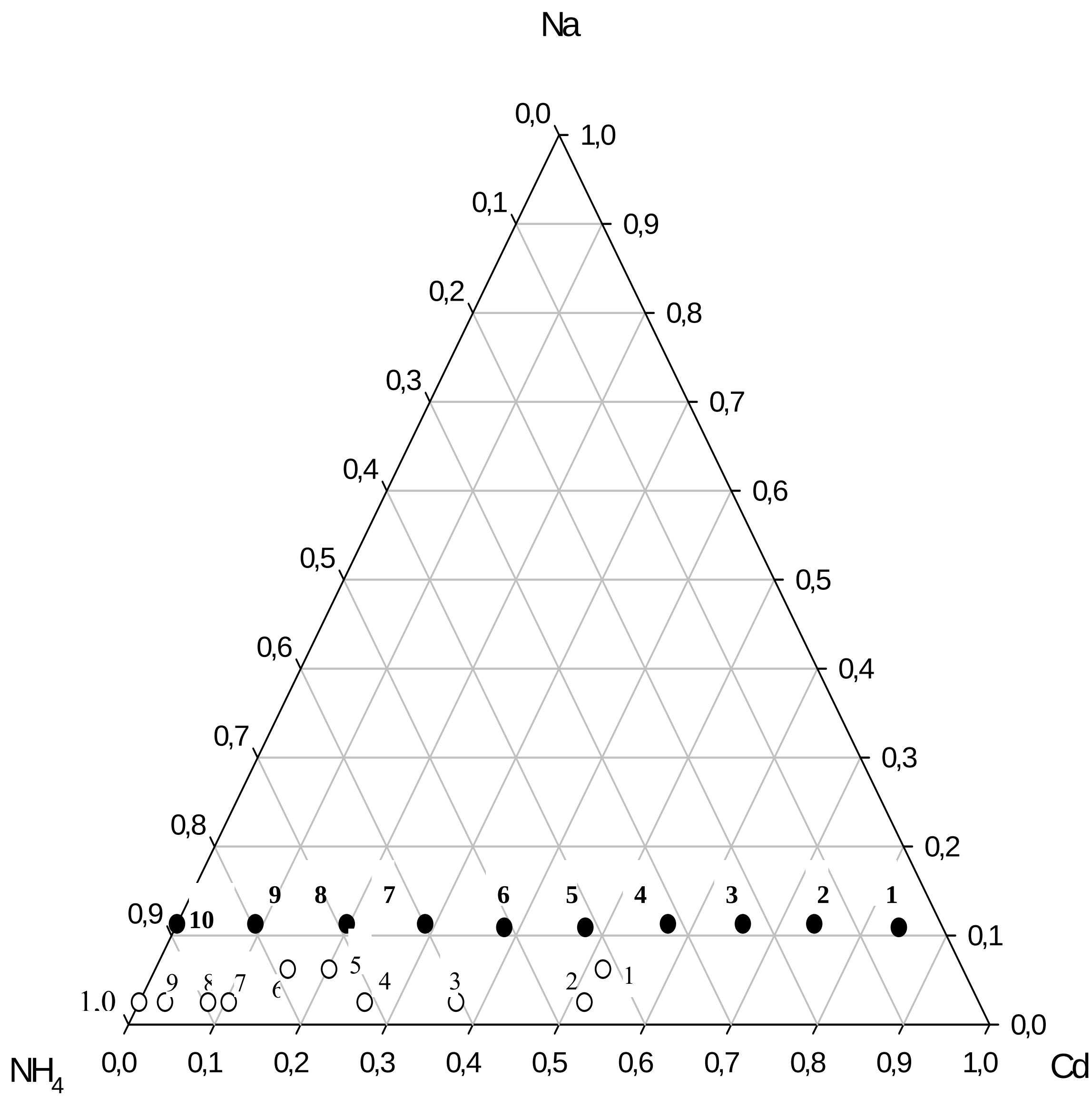


Figure 5.8. Ion Exchange Isotherm of NH_4^+-Cd^{2+}-Na^+ Ternary System for 0.5 g Clinoptilolite at 25^0C and 0.1 N Total Normality

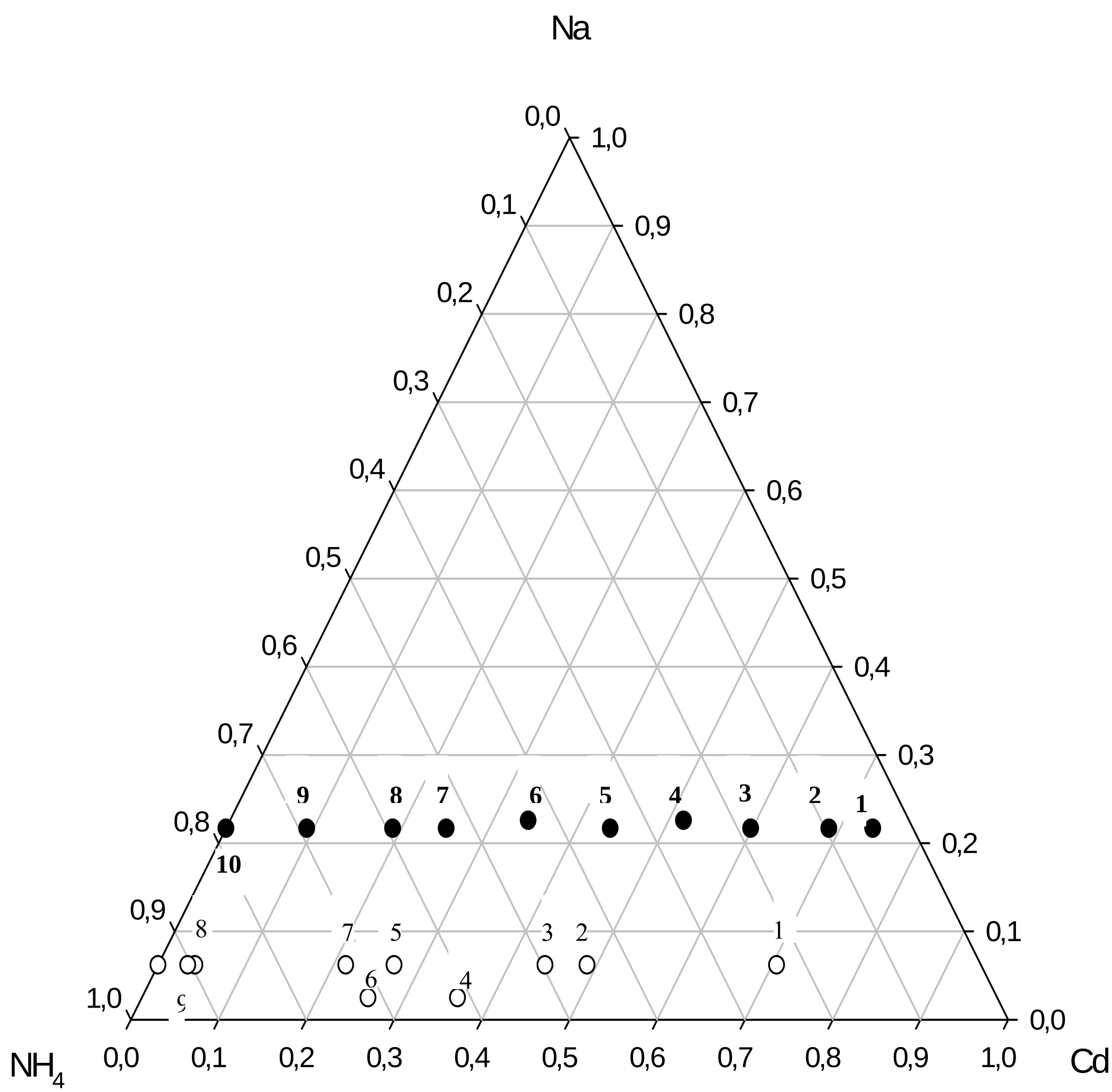


Figure 5.9. Ion Exchange Isotherm of NH_4^+-Cd^{2+}-Na^+ Ternary System for 1 g Clinoptilolite at 25^0C and 0.1 N Total Normality

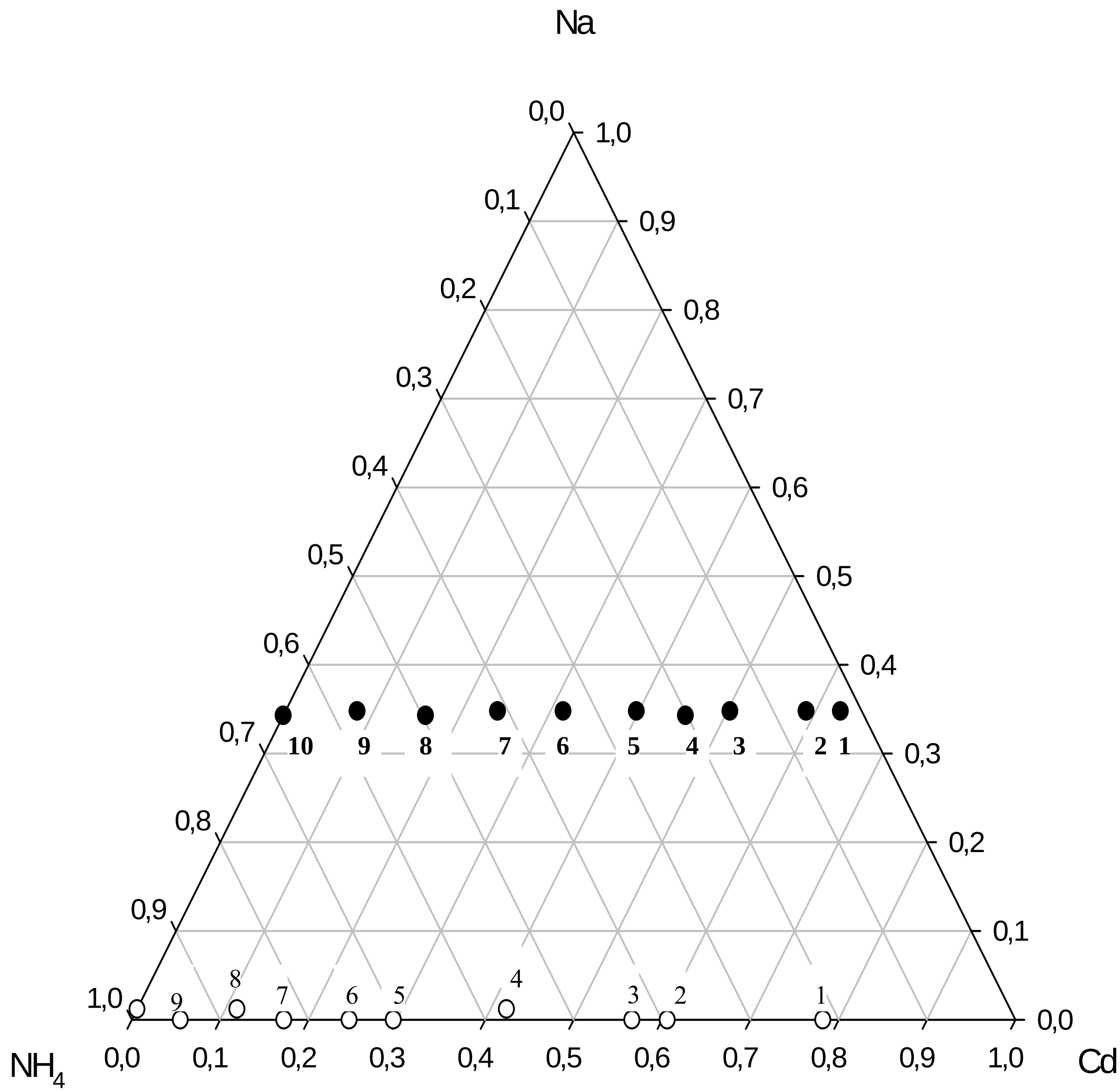


Figure 5.10. Ion Exchange Isotherm of NH_4^+-Cd^{2+}-Na^+ Ternary System for 1.5 g Clinoptilolite at 25^0C and 0.1 N Total Normality

On the other hand, when all figures were examined, the increase in equivalent fractions of sodium in the solution phase for bigger particle weights were observed. It was an expected result because the concentration amount of sodium in 1.5 grams of clinoptilolite is greater than the amount in 0.5 grams of clinoptilolite. In addition to that, again in all figures, it was observed that the percentage of sodium in zeolite phase is between 0% and 10 % and this result clearly proves the complete ion exchange of clinoptilolite with NH_4^+ and Cd^{2+} since nearly all the sodium in the zeolite was replaced with these ions.

5.5 pH Observation

Normally, pH has a significant impact on heavy metal removal by zeolites since it can influence the metal speciation. In addition to that, pH should be high enough to prevent competition of H^+ ions with metal ions for the same exchange and it should also be acidic, since metal bearing wastewaters are usually acidic. Because of all these reasons, in ion exchange processes, pH values were adjusted during the experıments.

In literature, for heavy metal-clinoptilolite interactions, pH was adjusted to low values (mainly pH range around 4-7 was studied) and high removal efficiencies were obtained. pH ranges of previous studies are shown in Table 5.5.

Table 5.5. Summary of Literature on Adjusted pH Ranges for Cd^{2+} and NH_4^+ Removal

Researchers	**Study**	**Adjusted pH**
Komarowski and Yu (1997)	NH_4^+ removal	4 - 5.5
Panayotova (2000)	Cd^{2+} removal	5 – 7
Singh et al. (2000)	Cd^{2+} removal	4.5 - 6
Sarıoğlu (2005)	NH_4^+ removal	4 - 4.5

Initial and final pH values of cations were observed between pH 4 – 6 in experiments. Between this pH range, high removal efficiencies for NH_4^+ and Cd^{2+} ions were obtained. Additionaly, no precipitation occurred at the end of experiments. Considering these observations and previous studies, for all ions tested, results indicate that pH adjustment was not necessary and metal removal is independent of solution pH at observed pH range.

5.6 COLUMN STUDIES

5.6.1 Removal Studies of Cadmium and Ammonium Ions in Column Operation

In this study, performance of Na-form of Gördes clinoptilolite for the removal of cadmium and ammonium ions was investigated. Cadmium and ammonium removal efficiencies of clinoptilolite depend on the solution characteristics (such as initial ion concentration, presence of other competing ions in influent), experimental conditions (type of the exchangeable cations, particle size). In column experiments, influent cadmium and ammonium concentrations were kept constant. A number of column runs were conducted to investigate ion exchange features of Gördes clinoptilolite. Simultaneous removal of cadmium-ammonium solution was also investigated while keeping their initial ratio concentration constant.

The loading conditions and breakthrough results are presented in Table 5.6. The breakthrough curves of clinoptilolite for cadmium and ammonium removal are shown in Figures 5.11 and 5.12 and the experimental data for the isotherms are given in Appendix B.

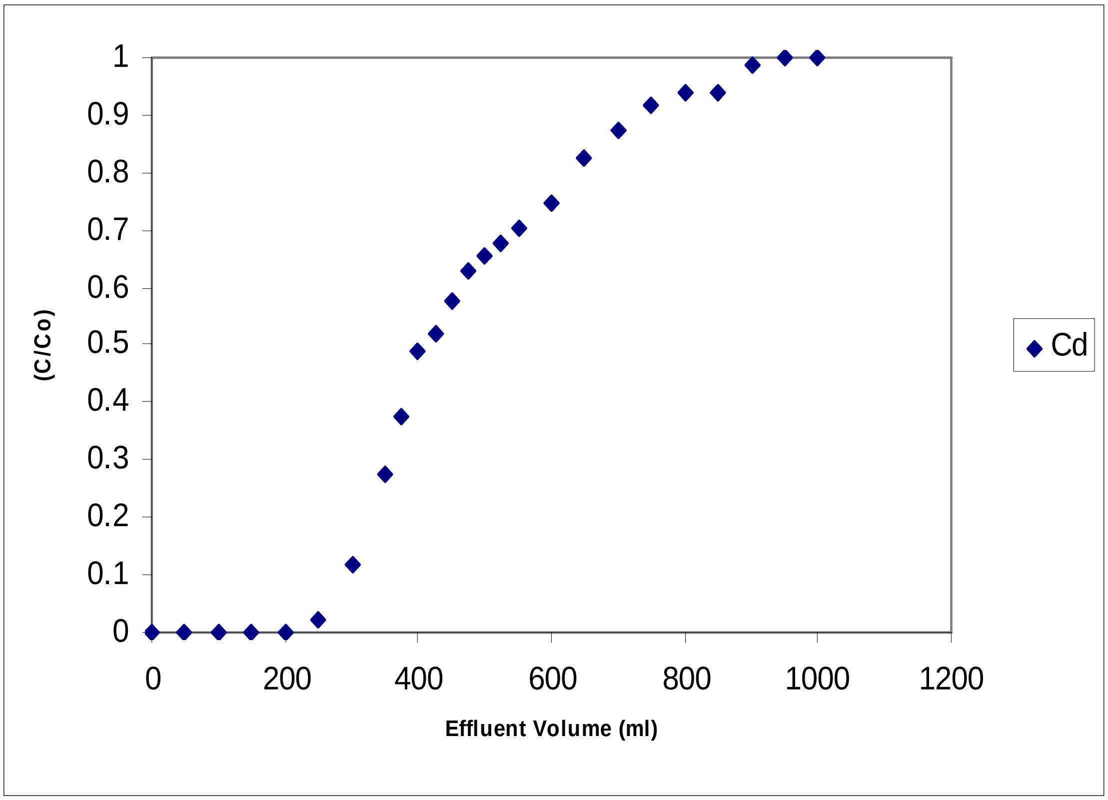


Figure 5.11. Breakthrough Graph of Cd^{2+} at 8 ml/min Flow Rate, 0.01 N Total Normality, 25°C Constant Temperature

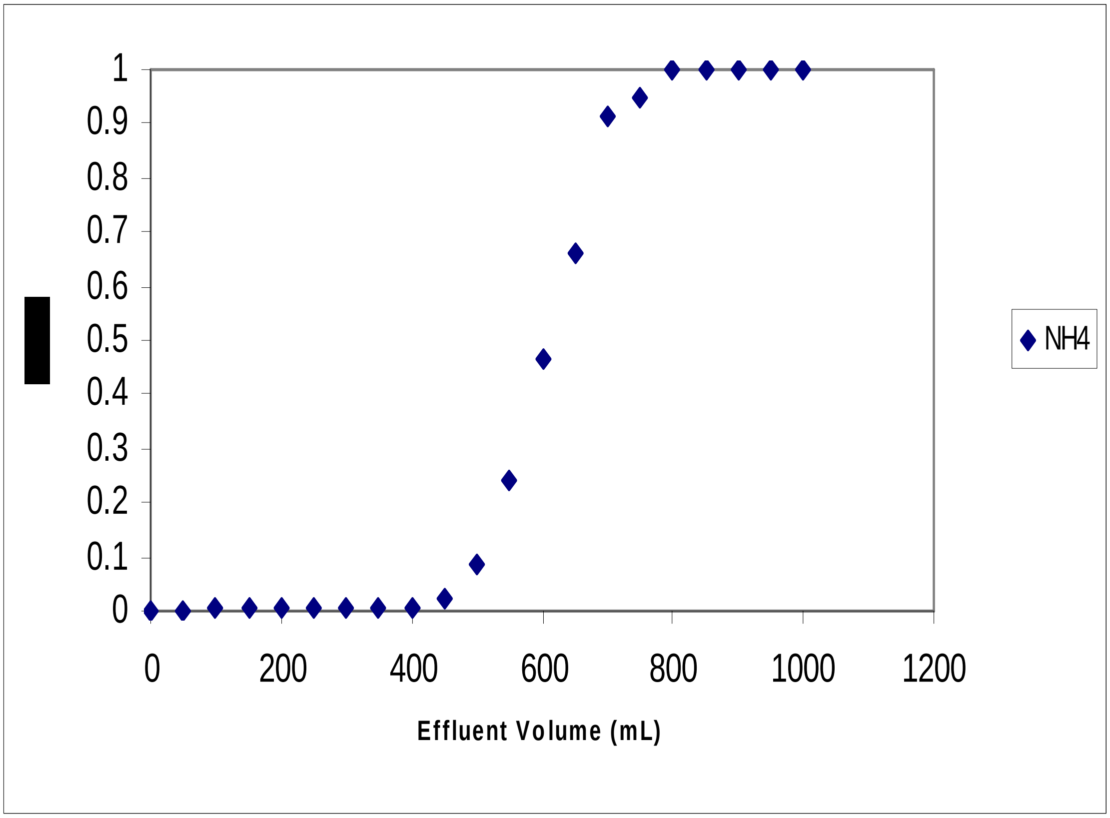


Figure 5.12 Breakthrough Graph of NH_4^+ at 8 ml/min Flow Rate, 0.01 N Total Normality, 25°C Constant Temperature

Table 5.6. Results of Column Experiment for Solutions Containing Only One Cation

Influent Conc. (N)	System	Flow Rate (ml/min)	Total Capacity (meq/)	Breakthrough Capacity (meq/g)	Column Efficiency (%)	Volume of solution treated up to break through point (mL)
0.01	Cd^{2+}	8	0.716	0.465	65.0	250
0.01	NH_4^+	8	1.160	0.895	77.1	450

A breakthrough curve represents the effluent concentration versus time or effluent volume. The effluent concentration can be expressed as absolute concentration (c), or normalized to inlet concentration (C/Co). The breakthrough is the point on the S-shaped curve at which the effluent concentration reaches its maximum allowed value (5% of its influent value), and the point of column exhaustion is the point where the effluent concentration reaches 95% of its influent value. In experiments, when the normalized effluent concentration (C/Co) (that is the ratio of the effluent concentration in treated water to influent cadmium and ammonium concentration) approached to 1.0, it was realized that clinoptilolite was saturated and experiments were terminated. The breakthrough curves were constructed by plotting C/Co versus effluent volume. Breakthrough curves are quite useful so as to calculate the dynamic parameters affecting the ion exchange process. They are also suitable in order to calculate the equilibrium capacity of packed bed and column efficiency since column efficiency is the ratio of breakthrough capacity to total capacity.

The breakthrough capacities for cadmium-sodium and ammonium-sodium systems were determined as 0.465 meq/g, 0.895 meq/g, respectively. Besides, total capacity was found 0.716 meq/g for cadmium-sodium system whereas this value was 1.160 meq/g for ammonium-sodium system. These result indicate that nearly all ion exchange channels presenting in the structure of zeolite were occupied by ammonium ions due to higher affinity of zeolite for ammonium ion in binary column systems .

5.6.2 Simultaneous Removal of Cadmium and Ammonium Ions in Column Operation (Multicomponent Ion Exchange)

In order to determine the performance of Gördes clinoptilolite for simultaneous removal of cadmium and ammonium ions (multicomponent removal), a number of column runs were performed using packed bed column loaded with 5 g of Na form of zeolite. Different flow rates (8, 15, 30 ml/min) were selected to understand the effect of flow rates on ion exchange. The influent concentrations were kept constant. Breakthrough capacity and breakthrough point were determined with respect to ion that first emerged from column.

Breakthrough curves become more complicated if several components have to be removed simultaneously. Ion that zeolite has more affinity will be held more strongly than other ion. Therefore, at the exit of the column, the ion ion that zeolite has less affinity will break through first.

Experimental results are summarized in Table 5.7 and they are shown in graphical form in Figures 5.13 to 5.15. Figures are given as C/Co versus effluent volume . The experimental data for the isotherms are given in Appendix B.

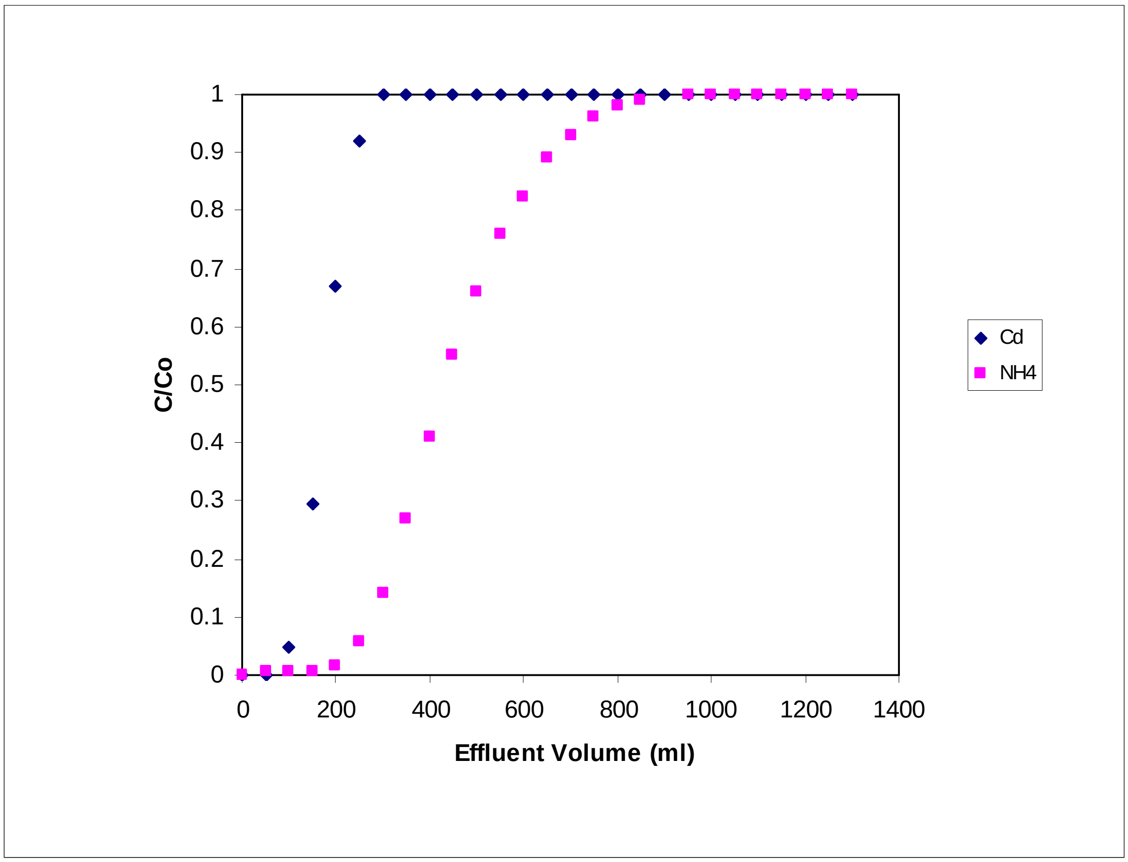


Figure 5.13 Simultaneous Removal of Cadmium and Ammonium at 8 ml/min Flow Rate, 0.01 N Total Normality, 25^{o}C Constant Temperature

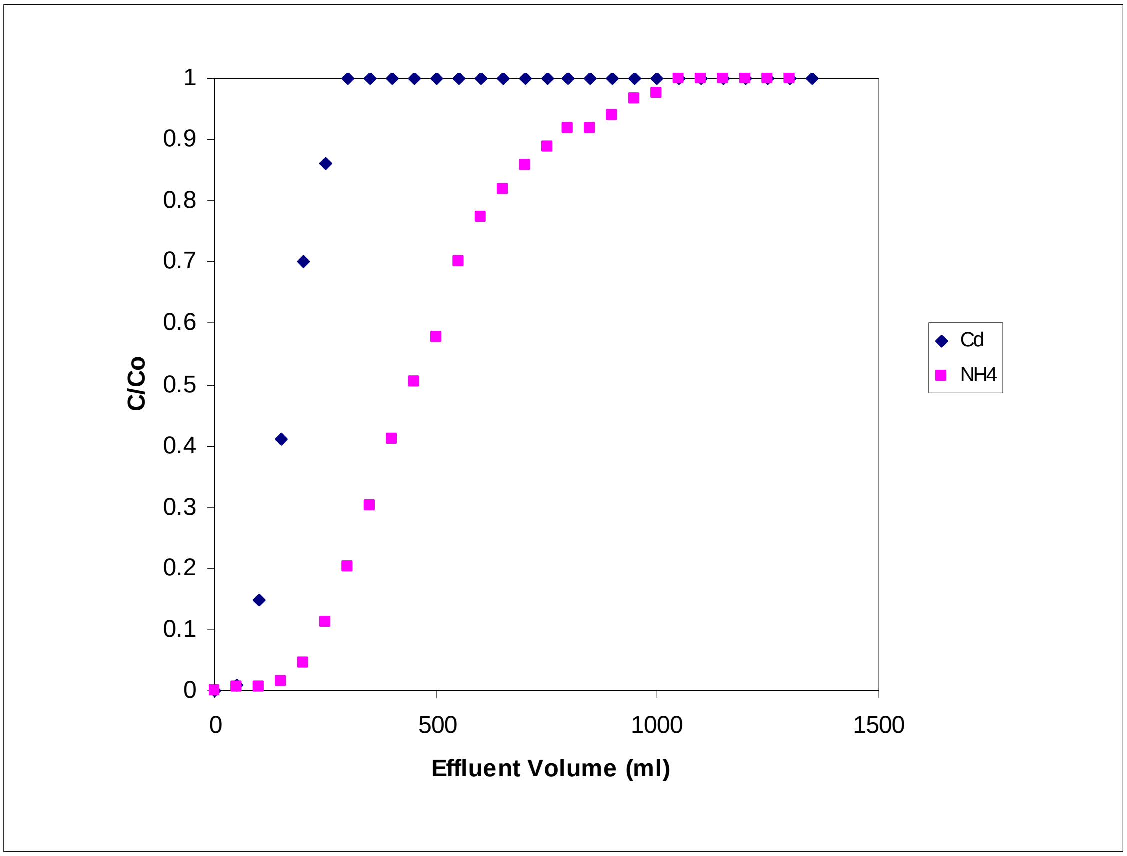


Figure 5.14 Simultaneous Removal of Cadmium and Ammonium at 15 ml/min Flow Rate, 0.01 N Total Normality, 25°C Constant Temperature

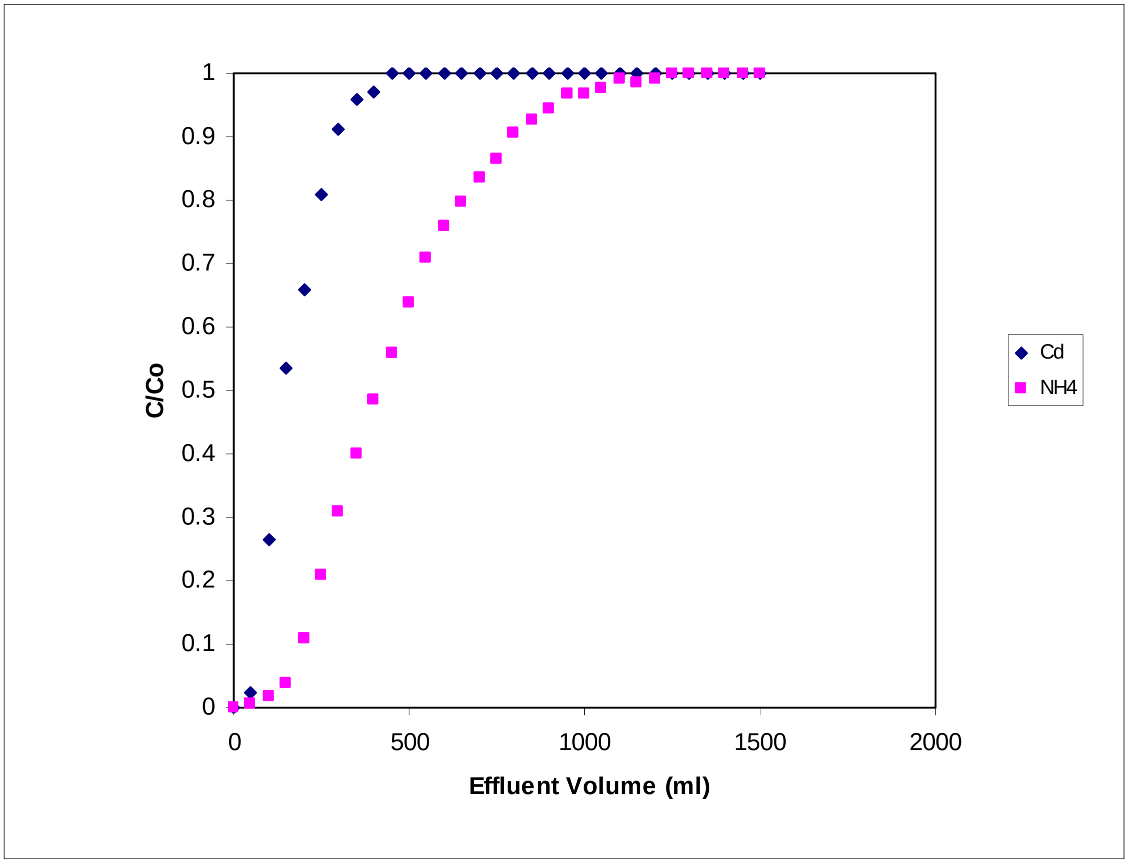


Figure 5.15 Simultaneous Removal of Cadmium and Ammonium at 30 ml/min Flow Rate, 0.01 N Total Normality, 25^{o}C Constant Temperature

Table 5.7. Results of Cadmium-Ammonium System

Flow Rate (ml/min)	**System**	**Breakthrough Capacity (meq/g)**	**Column Efficiency (%)**
8	Na^{+}-Zeolite-Cd^{2+}- NH_4^{+}	0.198 (Cd^{2+})	34.200
		0.199(NH_4^{+})	
	Total	0.391	
15	Na^{+}-Zeolite-Cd^{2+}- NH_4^{+}	0.149 (Cd^{2+})	23.010
		0.118 (NH_4^{+})	
	Total	0.267	
30	Na^{+}-Zeolite-Cd^{2+}- NH_4^{+}	0.098 (Cd^{2+})	16.980
		0.099 (NH_4^{+})	
	Total	0.197	

For cadmium-ammonium system at flow rates 8,15,30 ml/min breakthrough capacity were found as 0.198 meq/g (Cd^{2+}) and 0.199 meq/g (NH_4^+), 0.149 meq/g (Cd^{2+}) and 0.118 meq/g (NH_4^+), 0.098 meq/g (Cd^{2+}) and 0.099 meq/g (NH_4^+) and corresponding column efficiencies were 34.20%, 23.01%, 16.98%, respectively.

As it can be observed from the cadmium-ammonium system in Figure 5.13, 5.14, and 5.15, cadmium ion was first detected in the effluent; so breakthrough capacity and breakthrough point were calculated with respect to Cd^{2+} ion. As apparent from the data there was relatively significant difference between the behaviors of breakthrough capacities when flow rate was increased. Breakthrough curve results clearly show that the removal of ions is dependent upon flow rate. A comparatively lower flow rate yielded a higher ion exchange capacity. At higher flow rates, the retention time was insufficient for the ion exchange to take place completely between zeolite and ions. Breakthrough graphs of cadmium and ammonium ions (Figure 5.13 to 5.15) show the competition for exchange sites between cadmium and ammonium and this competition is in favor for ammonium ion. With this observation, it was concluded that the affinity of zeolite for ammonium ion is higher than that for cadmium ion in cadmium-ammonium-sodium multicomponent column system just like in cadmium-ammonium-sodium multicomponent batch system, and selectivity sequence of clinoptilolite was determined as $NH_4^+ > Cd^{2+} > Na^+$.

CHAPTER 6

CONCLUSIONS

According to the results of binary and multicomponent ion exchange studies, following conclusions were reached:

1. 100% removal efficiency of Gördes clinoptilolite for NH_4^+ ion and 80% removal efficiency of Gördes clinoptilolite for Cd^{2+} ion were obtained in batch binary systems (based on sodium content).

2. Selectivity sequence of Gördes clinoptilolite was determined as $NH_4^+ > Cd^{2+} > Na^+$ in batch and column binary sytems.

3. Clinoptilolite had more affinity to NH_4^+ than Cd^{2+} ion when they are present together both in batch and column ternary systems, so the selectivity sequence was concluded as $NH_4^+ > Cd^{2+} > Na^+$ in multicomponent systems, similar to binary systems.

4. Breakthrough capacities of Gördes clinoptilolite for ammonium and cadmium ions decreased with increasing flow rate in multicomponent column operations.

5. Column efficiencies for NH_4^+ and Cd^{2+} ions decreased in column systems involving more than one cation (multicomponent systems) compared to column systems involving only one cation (binary systems).

6. Ion exchange was independent of solution pH at observed pH range and pH wasn't adjusted since no precipitation occurred during the experiments.

CHAPTER 7

RECOMMENDATIONS

For the further investigation, ternary ion exchange equilibria of different heavy metals can be investigated on Gördes clinoptilolite. Additionally, it will also be useful to perform a quaternary ion exchange study including ammonium, lead and cadmium in the presence of each other both in batch and column operations.

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REFERENCES

Abusafa A. (1995). Column Studies of Ammonium and Cesium Exchanges on Bigadic Clinoptilolite, MSc. Thesis, METU, Ankara.

Barrer R.M., Papadopoulos R., Rees L.V.C. (1967). *Journal of Inorg. Nuclear Chemistry*, 29, 1967.

Bhatia S. (1990). Zeolite Catalysis; Principles and Applications. CRC Press Inc. United States

Bilba N., Mihaila G., Onu P., Dranga D., Luca C. (1983) Rev. Roum. Chim. 28 ,1009.

Blanchard G., Maunaye M., Martin G. (1984). Removal of Heavy Metals from Waters by means of Natural Zeolites. *Water Research*, 18(12), 1501 – 1507.

Breck T.W., 1974, Zeolites Molecular Sieves: Structure, Chemistry and Use, John Wiley and Sons, New York.

Czaran E., Meszaros-Kis A., Domokos E, and Papp J. (1988). Separation of Ammonia from Wastewater Using Clinoptilolite as Ion Exchange, *Nuclear and Chemical Waste Management*, 8, 107-113.

Cincotti A., Lai N., Orrù R., Cao G. (2001). Sardinian Natural Clinoptilolites for Heavy Metals and Ammonium Removal: Experimental and Modeling. *Chemical Engineering Journal,* 84, 275 - 282.

Ćurković L., Cerjan - Stefanović Š., Filipan T. (1997). Metal Ion Exchange by Natural and Modified Zeolites. *Water Research,* 31(6), 1379 - 1382.

Çulfaz M., Yağız M. (2004). Ion Exchange Properties of Natural Clinoptilolite: Lead-Sodium and Cadmium-Sodium Equilibria. *Separation and Purification Technology,* 37(2), 93 - 105.

Demir A., Günay A., Debik E. (2002). Ammonium Removal from Aqueous Solution by Using Packed Bed Natural Zeolite, *Water SA*, 28(3), 329-336.

El Akrami H.A. (1991). Column Studies of Ammonium Ion Exchange on Clinoptilolite, MS. Thesis, METU, Ankara.

Faghihian H., Marageh M.G., Kazemian H. (1999). The Use of Clinoptilolite and Its Sodium Form for Removal of Cesium and Strontium from Nuclear Wastewater and Pb^{2+}, Ni^{2+}, Cd^{2+}, Ba^{2+} from Municipal Wastewater. *Applied Radiation and Isotopes,* 50, 655 - 660.

Helfferich F.G, 1962, Ion Exchange, McGraw-Hill, New York.

Inglezakis V.J., Hadjiandreu K.J., Loizidou M.D., Grigoropoulou H.P. (2001). Pretreatment of Natural Clinoptilolite in a Laboratory-Scale Ion Exchange Packed Bed. *Water Research,* 35(9), 2161 - 2166.

Inglezakis V.J., Loizidou M.M., Grigoropoulou H.P. (2004). Ion Exchange Studies on Natural and Modified Zeolites and the Concept of Exchange Site Accessibility. *Journal of Colloid and Interface Science,* 275, 570 - 576.

Komarovski S., Yu Q. (1997). Ammonium Ion Removal from Wastewater Using Australian Natural Zeolite: Batch Equilibrium and Kinetic Studies. *Environmental Technology*, 1085 – 1097.

Koyama K., Takeuchi Y.(1977). Clinoptilolite: The Distribution of Potassium Atoms and Its Role in Thermal Stability, *Zeitschrift Fur Kristallographie*, Vol. 145, pp. 216-249.

Langella A., Pansini M., Cappelletti P., Gennaro B., Gennaro M., Colella C. (2000). NH_4^+, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} Exchange for Na^+ in a Sedimentary Clinoptilolite, North Sardinia, Italy. *Microporous and Mesoporous Materials,* 37, 337 - 343.

Loizidou M., Townsend R.P. (1984). *Zeolites,* 4 , 191.

Loizidou M., Townsend R.P. (1987). *Zeolites,* 7 (3), 153.

Malliou E., Loizidou M., Spyrellis N. (1994). Uptake of Lead and Cadmium by Clinoptilolite. *The Science of the Total Environment,* 149, 139 - 144.

Mercer B.W., Ames L.L., Touhill C.J., Slyke W.J.V, and Dean R.B. 1970. Ammonia Removal from Secondary Efluents by Selective Ion Exchange, *Journal WPCF*, 42(42), 95-107.

Merkle A.B., Slaughter M. (1968). Determination and Refinement of the Structure of Heulandite. *Am. Mia*, 53, 1120-1138.

Michaels A.S. (1952). Simplified Method of Interpreting Kinetic Data in Fixed Bed Ion Exchange. *Industrial and Engineering Chemistry*, 44(8),1922-1930.

Mumpton F.A. (1960). Clinoptilolite Redefined. *Am. Min*., 47, 351-369.

Ouki S.K., Kavannagh M. (1999). Treatment of Metals-Contaminated Wastewaters by Use of Natural Zeolites. *Water Science and Technology,* 39(10-11), 115 - 122.

Panayotova M. (2000). Use of Zeolite for Cadmium Removal from Wastewater. *Journal of Environmental Science and Health*, A35(9), 1591 – 1601.

Panayotova M., Velikov B. (2002). Kinetics of Heavy Metal Ions Removal by Use of Natural Zeolite. *Journal of Env. Science and Health,* A37(2), 139 - 147.

Rozic M., Cerjan-Stefanovic S., Kurajica S., Vancina V. And Hodzic E. (2000). Ammoniacal Nitrogen Removal from Water by Treatment with Clays and zeolites, *Water Resources*, 34(14), 3675-3681.

Sand L.B., Mumpton F.A. (1976). Natural Zeolites: Occurance, Properties, Use, Pergamon Press, New York

Sarioglu M. (2005). Removal of Ammonium from Municipal Wastewater Using Natural Turkish (Dogantepe) Zeolite, Seperation and Purification Technology , 41, 1-11

Semmens M.J., Seyfarth M. (1978). Natural Zeolites, Occurence, Properties and Use, Pergamon Press, New York.

Semmens M.J., Klieve J., Schnobrich D., and Tauxe W. (1981). Modeling Ammonium Exchange and Regeneration on Clinoptilolite, *Water Research*, 15, 655-666.

Suzuki M., Ha K. S. (1984). *Journal of Chemical Engineering in Japan*. 17, 139.

Townsend R.P. (1991). Ion Exchange in Zeolites, In Flanigen, E. M. and Janson, J.C., Studies in Surface Science and Catalysis, vol. 58: Introduction to Zeolite Science and Practice, 15, 359-390.

Tsitsishvili G.V., Andronikashvili T.G, Kirov G.N., Filizova L.D. (1992). Natural Zeolites, Ellis Horwood Limited, London.

Tufan E.Ö. (2002). Ion Exchange Properties of Gördes Clinoptilolite: Ammonium Exchange, MSc. Thesis, METU, Ankara.

Turan M., Arslan R., Benligönül B., Çelik M.S. (2000). Ammonia Removal from a Contaminated Drinking Water Reservoir by Clinoptilolite, *World Filtration Congress and Proceedings European Federation of Chemical Event*, No. 667

APPENDIX A

CALIBRATION CURVE for AMMONIUM ION

mV	ppm
209.7	1
258	10
307	100
356.1	1000
371	2000

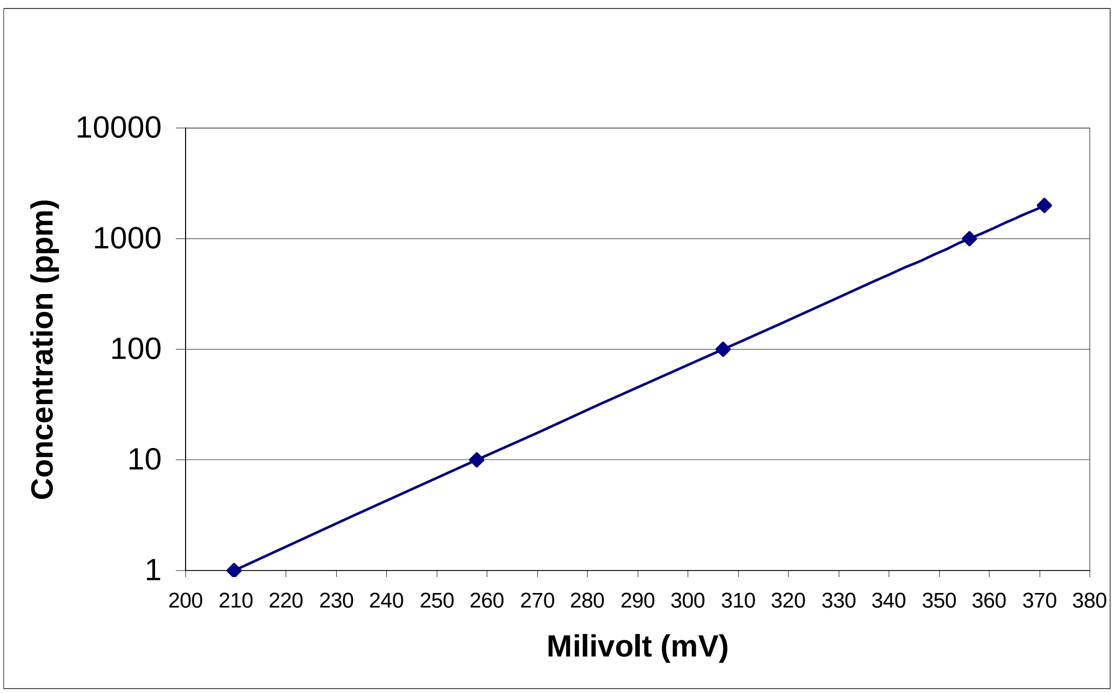

Figure A.1. Ammonium Calibration Curve (semi logarithmic scale)

APPENDIX B

EXPERIMENTAL EQUILIBRIUM DATA for ION EXCHANGE ISOTHERMS

Batch Systems

$$A_s = \frac{\text{Normality of exchanging cation A}}{\text{Total Normality}}$$

$$A_z = \frac{\text{Number of equivalent of exchanging cation A}}{\text{Total equivalent of cations in zeolite}}$$

$$A_s = \frac{Z_A \times M_{A}f}{T.N}$$

$$A_z = \frac{Z_A \times \left(M_{Ai} - M_{Af}\right) \times V}{CEC \times W}$$

M_{Aif} = Initial and final molarities of exchanging cations in solution phase at equilibrium

Z = Charges of cations

CEC = Cation exchange capacity

T.N = Total normality

V = Total volume

W = Weight of clinoptilolite

Equilibrium data and A_s, A_z values for all batch studies are shown in table B.1 to B.9.

Table B.1 Equilibrium Data for NH_4^+-Na^+ System at 25^0C and 0.1N Total Normality Using 0.5 g Clinoptilolite

Mix. No	Normality of NH_4	Normality of Na	Na_f (mg/L)	NH_{4f} (mg/L)	NH_4 (Meq/L)	NH_4 (Meq/g)	NH_4s	NH_4z
1	0.010	0.090	2197	78.30	4.350	0.565	0.044	0.487
2	0.020	0.080	1910	207.0	11.50	0.850	0.115	0.733
3	0.030	0.070	1675	376.7	20.93	0.907	0.209	0.782
4	0.040	0.060	1450	532.3	29.57	1.043	0.296	0.899
5	0.050	0.050	1200	708.3	39.35	1.065	0.394	0.918
6	0.060	0.040	1130	884	49.11	1.089	0.491	0.939
7	0.070	0.030	705	1064	59.11	1.089	0.591	0.939
8	0.080	0.020	485	1236	68.67	1.133	0.687	0.977
9	0.090	0.010	500	1413	78.48	1.151	0.785	0.992
10	0.100	0	258	1591	88.41	1.159	0.884	0.999

Table B.2 Equilibrium Data for NH_4^+-Na^+ System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

Mix. No	Normality of NH_4	Normality of Na	Na_f (mg/L)	NH_{4f} (mg/L)	NH_4 (Meq/L)	NH_4 (Meq/g)	NH_4s	NH_4z
1	0.010	0.090	2450	65	3.611	0.319	0.036	0.275
2	0.020	0.080	2100	143.6	7.978	0.601	0.080	0.518
3	0.030	0.070	1760	207.5	11.53	0.924	0.115	0.796
4	0.040	0.060	1450	361.6	20.09	0.996	0.201	0.858
5	0.050	0.050	1200	516.2	28.68	1.066	0.287	0.919
6	0.060	0.040	940	671.4	37.30	1.135	0.373	0.978
7	0.070	0.030	780	850.8	47.27	1.137	0.473	0.980
8	0.080	0.020	460	1022.8	56.82	1.159	0.568	0.999
9	0.090	0.010	230	1202.4	66.80	1.160	0.668	1.000
10	0.100	0	60	1382.8	76.82	1.159	0.768	0.999

Table B.3 Equilibrium Data for NH_4^+-Na^+ System at 25^0C and 0.1N Total Normality Using 1.5 g Clinoptilolite

Mix. No	Normality of NH_4	Normality of Na	Na_f (mg/L)	NH_{4f} (mg/L)	NH_4 (Meq/L)	NH_4 (Meq/g)	NH_4s	NH_4z
1	0.010	0.090	2550	19.5	1.083	0.297	0.011	0.256
2	0.020	0.080	2250	86	4.778	0.507	0.048	0.437
3	0.030	0.070	1850	77.5	4.306	0.856	0.043	0.738
4	0.040	0.060	1580	241.8	13.433	0.886	0.134	0.763
5	0.050	0.050	1300	359.9	19.994	1.000	0.200	0.862
6	0.060	0.040	970	493.7	27.428	1.086	0.274	0.936
7	0.070	0.030	800	666	37.000	1.100	0.370	0.948
8	0.080	0.020	520	843	46.833	1.106	0.468	0.953
9	0.090	0.010	280	1025	56.944	1.102	0.569	0.950
10	0.100	0	70	1174	65.222	1.159	0.652	0.999

Table B.4 Equilibrium Data for Cd^{2+}-Na^{+} System at $25^{0}C$ and 0.1N Total Normality Using 0.5 g Clinoptilolite

Mix. No	Normality of Cd	Normality of Na	Na_f (mg/L)	Cd_f (mg/L)	Cd (Meq/L)	Cd (Meq/g)	Cds	Cdz
1	0.010	0.090	2300	495.0	8.808	0.119	0.088	0.103
2	0.020	0.080	2050	990.0	17.62	0.238	0.176	0.205
3	0.030	0.070	1780	1470	26.16	0.384	0.262	0.331
4	0.040	0.060	1520	1940	34.52	0.548	0.345	0.472
5	0.050	0.050	1260	2425	43.15	0.685	0.432	0.590
6	0.060	0.040	1020	2950	52.49	0.751	0.525	0.647
7	0.070	0.030	770	3450	61.39	0.861	0.614	0.742
8	0.080	0.020	505	3970	70.65	0.936	0.706	0.806
9	0.090	0.010	300	4530	80.61	0.939	0.806	0.809

Table B.5 Equilibrium Data for Cd^{2+}-Na^{+} System at $25^{0}C$ and 0.1N Total Normality Using 1 g Clinoptilolite

Mix. No	Normality of Cd	Normality of Na	Na_f (mg/L)	Cd_f (mg/L)	Cd (Meq/L)	Cd (Meq/g)	Cds	Cdz
1	0.010	0.090	2400	436	7.758	0.112	0.077	0.097
2	0.020	0.080	2240	868	15.44	0.227	0.154	0.196
3	0.030	0.070	1950	1280	22.77	0.361	0.228	0.311
4	0.040	0.060	1650	1700	30.25	0.487	0.302	0.420
5	0.050	0.050	1400	2100	37.37	0.631	0.374	0.544
6	0.060	0.040	1120	2571	45.75	0.712	0.458	0.614
7	0.070	0.030	900	3000	53.38	0.831	0.534	0.716
8	0.080	0.020	610	3525	62.72	0.864	0.627	0.745
9	0.090	0.010	400	4040	71.89	0.906	0.719	0.781

Table B.6 Equilibrium Data for Cd^{2+}-Na^{+} System at $25^{0}C$ and 0.1N Total Normality Using 1.5 g Clinoptilolite

Mix. No	Normality of Cd	Normality of Na	Na_f (mg/L)	Cd_f (mg/L)	Cd (Meq/L)	Cd (Meq/g)	Cds	Cdz
1	0.010	0.090	2690	405	7.20	0.093	0.072	0.080
2	0.020	0.080	2360	750	13.3	0.222	0.133	0.191
3	0.030	0.070	2210	1240	22.1	0.265	0.221	0.228
4	0.040	0.060	1780	1600	28.5	0.384	0.285	0.331
5	0.050	0.050	1520	2040	36.3	0.457	0.363	0.393
6	0.060	0.040	1235	2450	43.6	0.547	0.436	0.471
7	0.070	0.030	1120	2875	51.2	0.628	0.512	0.541
8	0.080	0.020	800	3300	58.7	0.709	0.587	0.611
9	0.090	0.010	600	3650	64.9	0.835	0.649	0.719
10	0.010	0	150	4050	72.1	0.931	0.721	0.802

Table B.7. Equilibrium Data for NH_4^+- Cd^{2+}-Na^+ System at 25^0C and 0.1N Total Normality Using 0.5 g Clinoptilolite

No	Normality of NH_4	Normality of Cd	Final NH_4 in Solution (mg/L)	Final Cd in Solution (mg/L)	Final Na in Solution (mg/L)	NH_4s	Cds	Nas	NH_4z	Cdz	Naz
1	0.010	0.090	92.79	4719	250.0	0.051	0.840	0.109	0.418	0.520	0.062
2	0.020	0.080	264.3	4159	260.0	0.147	0.740	0.113	0.458	0.517	0.025
3	0.030	0.070	413.3	3694	260.0	0.230	0.657	0.113	0.607	0.368	0.025
4	0.040	0.060	571.1	3201	260.0	0.317	0.570	0.113	0.713	0.262	0.025
5	0.050	0.050	746.4	2679	250.0	0.415	0.476	0.109	0.736	0.202	0.062
6	0.060	0.040	916.3	2148	250.0	0.509	0.382	0.109	0.784	0.154	0.062
7	0.070	0.030	1078	1618	260.0	0.599	0.288	0.113	0.871	0.104	0.025
8	0.080	0.020	1243	1104	260.0	0.690	0.197	0.113	0.945	0.030	0.025
9	0.090	0.010	1433	509.8	260.0	0.796	0.091	0.113	0.895	0.080	0.025
10	0.100	0	1596	0	260.0	0.887	0.000	0.113	0.975	0.000	0.025

Table B.8. Equilibrium Data for NH_4^+- Cd^{2+}-Na^+ System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

No	Normality of NH_4	Normality of Cd	Final NH_4 in Solution (mg/L)	Final Cd in Solution (mg/L)	Final Na in Solution (mg/L)	NH_4s	Cds	Nas	NH_4z	Cdz	Naz
1	0.010	0.090	82.79	4139	500.0	0.046	0.737	0.217	0.233	0.705	0.062
2	0.020	0.080	172.6	3859	500.0	0.096	0.687	0.217	0.449	0.489	0.062
3	0.030	0.070	332.6	3359	500.0	0.185	0.598	0.217	0.497	0.441	0.062
4	0.040	0.060	463.1	2903	520.0	0.257	0.517	0.226	0.615	0.360	0.025
5	0.050	0.050	620.7	2460	500.0	0.345	0.438	0.217	0.669	0.269	0.062
6	0.060	0.040	780.8	1911	520.0	0.434	0.340	0.226	0.717	0.258	0.025
7	0.070	0.030	957.7	1408	500.0	0.532	0.251	0.217	0.724	0.214	0.062
8	0.080	0.020	1066	1069	500.0	0.593	0.190	0.217	0.896	0.042	0.062
9	0.090	0.010	1243	517.6	500.0	0.691	0.092	0.217	0.904	0.034	0.062
10	0.100	0	1409	0	500.0	0.783	0.000	0.217	0.938	0.000	0.062

Table B.9. Equilibrium Data for NH_4^+- Cd^{2+}-Na^+ System at 25^0C and 0.1N Total Normality Using 1.5 g Clinoptilolite

No	Normality of NH_4	Normality of Cd	Final NH_4 in Solution (mg/L)	Final Cd in Solution (mg/L)	Final Na in Solution (mg/L)	NH_4s	Cds	Nas	NH_4z	Cdz	Naz
1	0.010	0.090	43.53	3528	800.0	0.024	0.628	0.348	0.218	0.782	0.000
2	0.020	0.080	112.9	3312	800.0	0.063	0.589	0.348	0.394	0.606	0.000
3	0.030	0.070	267.8	2828	800.0	0.149	0.503	0.348	0.434	0.566	0.000
4	0.040	0.060	363.1	2555	790.0	0.202	0.455	0.343	0.570	0.418	0.012
5	0.050	0.050	458.8	2232	800.0	0.255	0.397	0.348	0.704	0.296	0.000
6	0.060	0.040	607.6	1767	800.0	0.338	0.314	0.348	0.754	0.246	0.000
7	0.070	0.030	741.1	1350	800.0	0.412	0.240	0.348	0.828	0.172	0.000
8	0.080	0.020	892.1	903	790.0	0.496	0.161	0.343	0.875	0.113	0.012
9	0.090	0.010	1028	455	800.0	0.571	0.081	0.348	0.945	0.055	0.000
10	0.100	0	1181	0	790.0	0.657	0.000	0.343	0.988	0.000	0.012

Column Systems

Table B.10 Equilibrium Data for Ammonium Analysis at 25^0C and 0.1N Total Normality Using 5 g Clinoptilolite

Sample No	C/Co	Volume of Effluent (mL)
1	0.000	0
2	0.004	50
3	0.004	100
4	0.004	150
5	0.004	200
6	0.004	250
7	0.004	300
8	0.006	350
9	0.006	400
10	0.022	450
11	0.089	500
12	0.240	550
13	0.463	600

Table B.11 Equilibrium Data for Cadmium Analysis at 25^0C and 0.1N Total Normality Using 5 g Clinoptilolite

Sample No	C/Co	Volume of Effluent (mL)
1	0.000	0
2	0.000	50
3	0.000	100
4	0.000	150
5	0.001	200
6	0.021	250
7	0.118	300
8	0.273	350
9	0.376	375
10	0.491	400
11	0.518	425
12	0.578	450

Table B.12 Equilibrium Data for Cadmium-Ammonium Analysis at 25^0C and 0.1N Total Normality Using 5 g Clinoptilolite at 8 ml/min Flow Rate

Sample No	C/Co for Cd^{2+}	C/Co for NH_4^+	Volume of Effluent (mL)
1	0	0	0
2	0	0.006	50
3	0.046	0.006	100
4	0.296	0.008	150
5	0.670	0.017	200
6	0.920	0.056	250
7	1	0.142	300
8	1	0.269	350
9	1	0.411	400
10	1	0.551	450
11	1	0.660	500
12	1	0.760	550
13	1	0.824	600
14	1	0.892	650
15	1	0.931	700
16	1	0.962	750
17	1	0.981	800
18	1	0.990	850
19	1	1	900
20	1	1	950
21	1	1	1000
22	1	1	1050
23	1	1	1100
24	1	1	1150
25	1	1	1200
26	1	1	1250
27	1	1	1300

Table B.13 Equilibrium Data for Cadmium-Ammonium Analysis at 25^0C and 0.1N Total Normality Using 5 g Clinoptilolite at 15 ml/min Flow Rate

Sample No	C/Co for Cd^{2+}	C/Co for NH_4^+	Volume of Effluent (mL)
1	0	0	0
2	0.009	0.005	50
3	0.149	0.007	100
4	0.410	0.015	150
5	0.700	0.046	200
6	0.860	0.113	250
7	1	0.202	300
8	1	0.303	350
9	1	0.410	400
10	1	0.504	450
11	1	0.578	500
12	1	0.701	550
13	1	0.774	600
14	1	0.820	650
15	1	0.859	700
16	1	0.888	750
17	1	0.918	800
18	1	0.918	850
19	1	0.940	900
20	1	0.967	950
21	1	0.976	1000
22	1	1	1050
23	1	1	1100
24	1	1	1150
25	1	1	1200
26	1	1	1250
27	1	1	1300
28	1	1	1350

Table B.14 Equilibrium Data for Cadmium-Ammonium Analysis at 25^0C and 0.1N Total Normality Using 5 g Clinoptilolite at 30 ml/min Flow Rate

Sample No	C/Co for Cd^{2+}	C/Co for NH_4^+	Volume of Effluent (mL)
1	0	0	0
2	0.023	0.007	50
3	0.264	0.017	100
4	0.536	0.037	150
5	0.660	0.110	200
6	0.810	0.208	250
7	0.912	0.310	300
8	0.960	0.400	350
9	0.972	0.485	400
10	1	0.559	450
11	1	0.638	500
12	1	0.708	550
13	1	0.760	600
14	1	0.797	650
15	1	0.835	700
16	1	0.863	750
17	1	0.905	800
18	1	0.927	850
19	1	0.944	900
20	1	0.967	950
21	1	0.967	1000
22	1	0.976	1050
23	1	0.990	1100
24	1	0.985	1150
25	1	0.990	1200
26	1	1	1250
27	1	1	1300
28	1	1	1350
29	1	1	1400
30	1	1	1450

APPENDIX C

SAMPLE CALCULATION of NH_4-Cd-Na TERNARY SYSTEM for BATCH STUDIES

$$A_s = \frac{\text{Normality of exchanging cation A}}{\text{Total Normality}}$$

$$A_z = \frac{\text{Number of equivalent of exchanging cation A}}{\text{Total equivalent of cations in zeolite}}$$

$$A_s = \frac{Z_A * M_{Af}}{T.N}$$

$$A_z = \frac{Z_A * (M_{Ai} - M_{Af}) * V}{CEC * W}$$

M_{if} = Initial and final molarities of exchanging cations

Z = Charges of cations

CEC = Cation exchange capacity

T.N = Total normality

V = Total volume

W = Weight of clinoptilolite

A = NH_4^+, Cd^{2+} or Na^+

First, ammonium concentrations were calculated by using Russel Model ammonium electrode.

mV	ppm
209.7	1
258	10
307	100
356.1	1000
371	2000

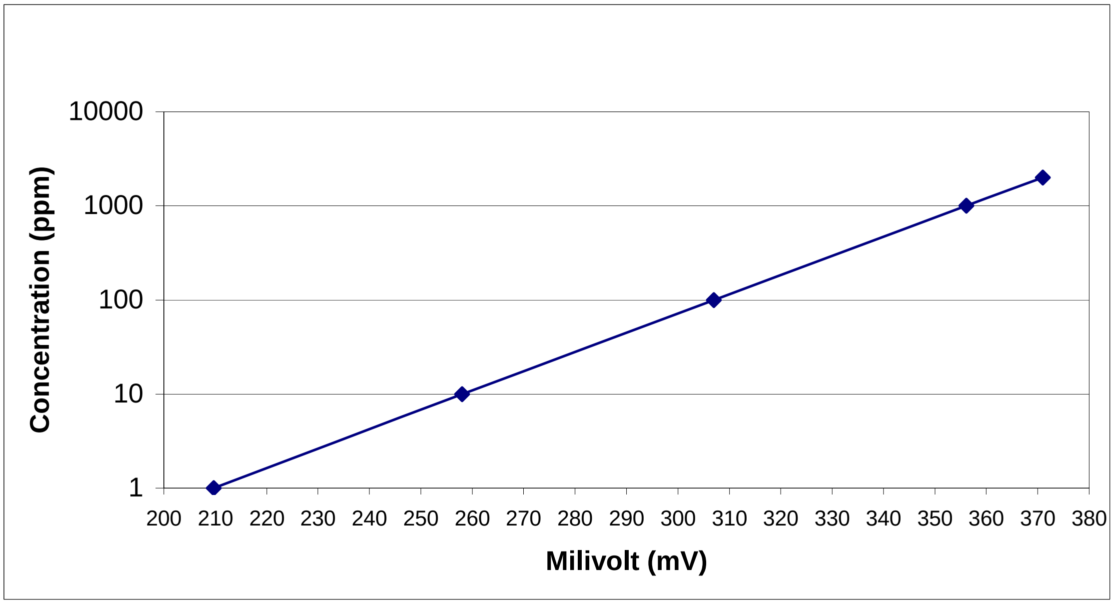

Figure C.1. Ammonium Calibration Curve (semi logarithmic scale)

Now, ammonium measurements can be converted from mV to mg/L.

Table C.1. Ammonium Concentration for NH_4^+-Cd^{2+}-Na^+ System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

Sample No	mV	NH_4 Concentration (mg/l)
1	303.3	82.50
2	318.8	172.1
3	332.7	332.0
4	339.7	462.4
5	346.0	619.9
6	350.8	780.0
7	355.2	956.9
8	357.4	1065
9	360.8	1249
10	363.3	1407

After determining ammonium concentrations, cadmium and sodium concentrations in solution phase (at equilibrium) were measured with AAS.

Table C.2. Cadmium and Sodium Concentrations for NH_4-Cd-Na System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

Sample No	Cd Concentration (mg/l)	Na Concentration (mg/l)
1	4137	500.0
2	3857	500.0
3	3358	500.0
4	2902	520.0
5	2459	500.0
6	1910	520.0
7	1407	500.0
8	1069	500.0
9	517.0	500.0
10	0	500.0

As and Az values were then calculated for the first sample.

$$NH_4s = \frac{Z_A * M_Af}{T.N}$$

$$M_{f\ NH4} = \frac{82.5\ mg}{L} * \frac{1\ mole\ NH_4}{18000\ mg\ NH_4} = 0.0046\ M$$

$$NH_4s = \frac{1 * 0.0046}{0.1} = 0.046$$

By the same way, Cd_s and Na_s were determined.

$Cd_s = 0.737$ $Na_s = 0.217$

Table C.3. A_s values of all cations for NH_4-Cd-Na System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

Sample No	NH_{4s}	Cd_s	Na_s
1	0.046	0.737	0.217
2	0.096	0.687	0.217
3	0.185	0.598	0.217
4	0.257	0.517	0.226
5	0.345	0.438	0.217
6	0.434	0.340	0.226
7	0.532	0.251	0.217
8	0.593	0.190	0.217
9	0.691	0.092	0.217
10	0.783	0.000	0.217

$$A_z = \frac{Z_A * (M_{Ai} - M_{Af}) * V}{CEC * W}$$

N= Molarity * valence of cation

$$M_{NH4}i = 0.01N * \frac{1M\ NH_4}{1N\ NH_4 * (1)} = 0.01M$$

$$M_{f\ NH4} = \frac{82.5\ mg}{L} * \frac{1\ mole\ NH_4}{18000\ mg\ NH_4} = 0.0046\ M$$

V = 0.05 L

CEC = 1.16meq/g

W = 1 g of clinoptilolite

$$NH_{4z} = \frac{1*(0.01-0.0046)*0.05}{1.16\frac{meq}{g}*1g*\frac{1eq}{1000meq}} = 0.233$$

By the same way, Cd_z and Na_z were determined.

$Cd_z = 0.705$ $Na_z = 0.062$

Table C.4. A_z values of all cations for NH_4-Cd-Na System at 25^0C and 0.1N Total Normality Using 1 g Clinoptilolite

Sample No	NH_{4z}	Cd_z	Na_z
1	0.233	0.705	0.062
2	0.449	0.489	0.062
3	0.497	0.441	0.062
4	0.615	0.360	0.025
5	0.669	0.269	0.062
6	0.717	0.258	0.025
7	0.724	0.214	0.062
8	0.896	0.042	0.062
9	0.904	0.034	0.062
10	0.938	0.000	0.062

APPENDIX D

SAMPLE CALCULATION for DETERMINATION of BREAKTHROUGH CAPACITY and COLUMN EFFICIENCY from BREAKTHROUGH CURVES

Operating Conditions

Influent NH_4^+ Concentration : 0.01N (180 ppm)

Temperature: 25^0C

Total Normality: 0.1 N

The experimental breakthrough curve (Figure 5.11) obtained by plotting ammonium ion concentration versus the volume of solution treated. In determining the breakthrough capacity of clinoptilolite, Simpson rule was used. Experimental data is shown on Table B.10

From Figure 5.11, it is seen that breakthrough point is sample 10 which is obtained at 450 ml effluent volume.

Total area up to breakthrough point = $(1) * (450 \text{ ml}) = 450$ ml

Area under the curve = Simpson Rule is used.

$$\frac{1}{3}\left(\frac{400-0}{8}\right)[0+4(0.004)+2(0.004)+....+(0.006)]+\frac{1}{2}\left(\frac{450-400}{2}\right)[0.006+0.022]$$

Area under the curve = 1.7 + 0.7 = 2.4 ml.

Area above the curve = 450 – 2.4 = 447.6 ml

Breakthrough Capacity = $447.6\,\text{ml} * \frac{0.01\,\text{meq}}{\text{ml}} * \frac{1}{5\text{g}}$ = 0.895 meq/g

Total Capacity was calculated in similar way.

Total Area = $(1) * (1000\,\text{ml})$ = 1000 ml

Area under the curve = 421.1 ml

Area above the curve = $1000 - 421.1$ = 578.9 ml

Total Capacity = $578.9\,\text{ml} * \frac{0.01\,\text{meq}}{\text{ml}} * \frac{1}{5\text{g}}$ = 1.16 meq/g

Column Efficiency = $\frac{\text{Breakthrough Capacity}}{\text{Total Capacity}} = \frac{0.895}{1.16}$

Column Efficiency = 77.1 %