MULTICOMPONENT ION EXCHANGE ON ZEOLITE 4A

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ABSTRACT

MULTICOMPONENT ION EXCHANGE ON ZEOLITE 4A

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In this study binary and ternary ion exchange on Zeolite NaA using silver and cadmium ions were investigated. Ion exchange were conducted at constant temperature (25^{o}C) and normality (0.1N) in a batch system for both binary and ternary experiments. Zeolite weights were varied between 0.1 and 1 g for binary experiments.

Thermodynamic analysis of binary ion exchange between Cd^{2+}-Na^{+} and Ag^{+}-Na^{+} were examined and thermodynamic equilibrium constant and Gibbs free energy were calculated. Thermodynamic equilibrium constants were found as respectively 28.2 and 300.4 for Cd^{2+}-Na^{+} and Ag^{+}-Na^{+} binary system. Standart free energy of Cd^{2+}-Na^{+} and Ag^{+}-Na^{+} binary exchange were calculated as -4.1 kJ/mol and -14.1 kJ/mol respectively. In literature Ay (2008) calculated the Gibbs free energy for Ag^{+}-Na^{+} binary system as -14.4 kJ/mol and Biskup and Subotic (2010) and Gal et al. (1970) calculated the Gibbs free energy for Cd^{2+}-Na^{+} binary system as -3.7 kJ/mol and -4.4 kJ/mol respectively. It is concluded Zeolite 4A has higher affinity to silver than cadmium and selectivity sequence was found as; $Ag^{+}>Cd^{2+}>Na^{+}$.

Langmuir and Freundlich isotherms were drawn to describe experimental data. As compared the R^2 of isotherms, it is clearly seen that Freundlich isotherm provides better fit for Cd^{2+}-Na^+ binary ion exchange and Ag^+-Na^+ binary ion exchange.

The ternary ion exchange isotherms were plotted using equivalent fraction of three ions (Ag^+,Na^+,Cd^{2+}) which participated in ion exchange experiments to determine selectivity of zeolite 4A for cadmium and silver. Selectivity sequence was determined as $Ag^+ > Cd^{2+} > Na^+$ for ternary ion exchange.

Keywords: Zeolite 4A, ion exchange, silver, cadmium, binary and ternary equilibrium isotherms.

ÖZ

ZEOLİT 4A ÜZERİNDE ÇOKLU İYON DEĞİŞİMİ

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Bu çalışmada, gümüş ve kadmiyum iyonlarının zeolit NaA üzerinde ikili ve üçlü iyon değişimleri incelenmiştir. İkili ve üçlü iyon değişim deneyleri 25 ^{o}C sabit sıcaklık ve 0.1 N sabit normalitede kesikli sistem kullanılarak gerçekleştirilmiştir. İkili iyon değişim deneylerinde zeolit ağırlıkları 0.1g ve 1g arasında olmak üzere değiştirilmiştir.

Gümüş-sodyum ve kadmiyum-sodyum arasındaki ikili iyon değişim deneylerinin termodinamik analizleri yapılarak, Gibbs serbest enerjileri ve termodinamik denge katsayıları hesaplanmıştır. Termodinamik denge sabitleri kadmiyum-sodyum ve gümüş-sodyum ikili deneyleri için sırasıyla 28.2 ve 300.4 olarak hesaplanmıştır. Gibbs serbest enerjileri ise kadmiyum-sodyum ve gümüş-sodyum ikili deneyleri için sırasıyla -4.1 kJ/mol ve -14.1 kJ/mol olarak hesaplanmıştır. Literatüre göre Ay(2008) Ag^+-Na^+ ikili sistemi için Gibbs serbest enerjiyi -14,4 kJ/mol olarak hesaplamış, Biskup ve Subotic (2010) ve Gal ve arkadaşları (1970) Cd^{2+}-Na^+ ikili sistemi için Gibss serbest enerjiyi sırasıyla -3.7 kJ/mol ve -4.4 kJ/mol olarak hesaplamışlardır. Termodinamik analiz sonuçlarına göre zeolit 4A'nın gümüşe kadmiyumdan daha çok eğilimi olduğu saptanmış olup seçicilik sırasıyla $Ag^+ > Cd^{2+} > Na^+$ olarak bulunmuştur.

Langmuir ve Freundlich izotermleri deneysel verileri tanımlamak amacıyla çizilmiştir. Çizilen izotermlerin R^2 değerleri karşılaştırılarak, Freundlich izoterminin Cd^{2+}-Na^{+} ve Ag^{+}-Na^{+} ikili sistemiyle uyumluluk gösterdiği görülmüştür.

Zeolit 4A'nın gümüş ve kadmiyuma olan seçimliliğini belirlemek için, iyon değişim deneylerinde yer alan üç iyonunda (gümüş,kadmiyum ve sodyum) eşdeğer katsayıları kullanılarak üçlü iyon değişim izotermleri çizilmiştir. Üçlü iyon değişim deneyleri için zeolit 4A'nın seçiciliği sırasıyla $Ag^{+}>Cd^{2+}>Na^{+}$ olarak bulunmuştur.

Anahtar kelimeler: Zeolit 4A, iyon değişimi, gümüş, kadmiyum, ikili ve üçlü iyon değişim denge izotermleri

To My Family…

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a : The distance of closest approach of the ions,cm

A : Debye Hückel Parameter at constant temperature, $l^{-1/2}$/mole$^{-1/2}$

A_s : Equivalent fraction of cation A in solution

As : Equivalent fraction of cation A in zeolite

b : A constant adjustable to suit experimental curve

B : Debye Hückel Parameter at constant temperature, $l^{-1/2}$/mole$^{-1/2}$

B_s : Equivalent fraction of cation B in solution

B_z : Equivalent fraction of cation B in zeolite

Ce : The liquid phase metal ion concentration at equilibrium,mg/l

E_c : Exchange capacity,meq/g

ΔG : Gibbs free energy change of the reaction, kj/mole

I : Ionic Strength

K : Equilibrium constant,l/mg

K_a : Thermodynamic equilibrium constant

K_c : Kielland quotient

K_f : Adsorption capacity

m_A : Cation concentration in solution phase,mol/dm^3

M_A : Cation concentration in zeolite phase,mol/dm^3

M_{Ai} : Molecular Weight of Zeolite 4A, g/mol

MeAPO : Metal substituted aluminophosphate based molecular sieves

n : Constant in Freundlich equation.

q_e : The solid-phase concentration in equilibrium,mg/g

qmax : Maximum adsorption capacity,mg/mg

R : Gas constant, 8.314 j/molK

s : Subscript which indicates the solution phase

SAPO : A silico-alumino-phosphate zeolite

T : Temperature,25 ^{o}C.

z : Subscript which indicates the zeolite phase

Z_A : The charge of the cation A.

Z_B : The charge of the cation B.

Greek Letters

α_B^A : Separation factor

$\gamma\pm_{(Bx)}^{(Ax)}$: Activity coefficient of cation AX in mixed salt solution

$\gamma_A x$: Acitivity coefficient of AX in single salt solution

Γ : Solution non ideality correction factor

CHAPTER 1

INTRODUCTION

Heavy metals are undesirable ions because of their toxicity. The sources of heavy metals in the environment are metal extraction, metal fabrication and surface finishing, paints and pigments, as well as the manufacture of batteries. They have crucial effect on human health and living organisms. For this reason removal of heavy metals from industrial waste water is important [Biškup and Subotic,2004].

Silver has higher electrical conductivity and thermal conductivity than other all metals [Sha et al.,2010]. It is a useful raw material in industries due to its malleability, ductility, photosensitivity and antibacterial properties. The removal of this element from wastewater is important because of the toxicity property of silver to living organisms [Ghassabzadeh et al., 2010].

Cadmium is one of the most harmful elements. Metal plating, cadmium–nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, and alloys cause to cadmium discharged into wastewater [Biskup and Subotic, 2010]. These industries are the main source of increasing cadmium concentration in the environment. It can be taken up by plant and cadmium accumulation in plants leads to heavy metal entering in food chain [Street et al., 2009]. Because of these reasons, cadmium causes detrimental effect on human body such as hypertension, respiratory disorder, and damages to the kidneys and liver [Rao et al., 2006].

Removal of heavy metals from aqueous media can be achieved by different technologies such as electrodialysis, chemical precipitation, adsorption, solvent extraction, reverse osmosis, ultrafiltration or ion exchange [Ahmed et al., 1998]. Although some of these methods may be more effective than ion exchange, due to simplicity of its application and low cost of exchangers using in ion exchange processes, ion exchange seems to be an attractive method [Biskup and Subotic, 2010]. Zeolites are widely used in ion exchange processes and antibacterial zeolites are generally prepared by ion exchange.

Zeolites are hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally Na, K, Ca and Mg) as well as water in their channels and pores. They contain silica and alumina tetrahedral units in their three-dimensional framework linked by shared four oxygen atoms. Alumina tetrahaedral units in the framework results in a negative charge. Negative charge is balanced by alkaline and alkaline earth metal cations [Pitcher et al., 2004]. These exchangable cations are mobile and they provide ion exchange ability to zeolites exchanging with heavy metals.

Among metallic elements, heavy metals such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium, and thallium provide antibacterial activity to the zeolites. Silver exchanged synthetic Zeolite A, has been used as a sterilizing and antibacterial agent in paper, plastic, paint, ceramics and several industries [Top and Ülkü,2004]. Silver-exchanged zeolites are used as coatings. There are lots of application area of these materials such as portland cement mortars, food packaging, stainless steel, paper, paints and plastic products. The antibacterial properties of silver have been also utilized by its incorporation into ceramic and glass materials for prosthesis and tissue regeneration [Coleman et al., 2009].

Antibacterial zeolites are generally obtained using silver, zinc and copper ion due to their high antibacterial properties. Silver ion is widely used as an disinfectant in the form of silver nitrate solution. However, silver nitrate solution has some disadvantages such as handling. Metal ion supported Zeolite, silver-exchanged Zeolite A was developed to eliminate these disadvantages [Maeda and Nose, 1999].

This antibacterial agent, zeolite looks like a plain white powder and it provides antiseptic and nontoxic effect. It is an inorganic compound and it is very different from other antibacterial agents due to its chemical stability such as melting point. Furthermore, the use of antibacterial zeolite has been widely used rather than other agents because of its advantages such as effective cost and no toxicity to the human [Maeda and Nose, 1999].

The aim of this study is to investigate Ag^+-Na^+ and Cd^{2+}-Na^+ binary ion exchange experiments and Ag^+-Cd^{2+}-Na^+ ternary ion exchange in a batch system at constant temperature and normality and thermodynamics of binary ion exchange process.

In industrial areas, this study is crucial because heavy metals such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium, and thallium imparts antibacterial activity to the zeolites. Zeolites gain antibacterial property using these metal alone or combination of these by ion exchange process.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 THE ZEOLITES

2.1.1 Early History of Zeolites

The first zeolite mineral, stilbite was discovered by the Swedish mineralogist Cronstedt in 1756. He realized that this is a new class mineral which contain hydrated aluminosilicates of the alkali and alkaline earth metals. Cronstedt called this mineral as zeolite because when he heated this mineral in a blowpipe flame, intumescence occured. Zeolite is the combination of two words which are ‘zeo’ and ‘lithos’. The meaning of ‘zeo’ and ‘lithos’ words are ‘to boil’ and ‘a stone’ respectively.

McBain named the zeolite as “molecular sieve” in order to **characterize** porous solid materials which act as sieves in 1932. By the mid-1930's, there were a lot of reports about synthesis of zeolites and the term of ion exchange, adsorption, molecular sieving and structural properties of zeolite minerals were described in the literature [Bekkum et al., 2001].

The major discoveries and advances in zeolite materials are summarized in Table 2.1

Table 2.1. Evolution of Molecular Sieve Materials [Bekkum et al., 2001].

Time of Initial Discovery	Composition
Late 40's to Early 50's	Low Si/A1 Ratio Zeolites
Mid 50's to late 60's	High Si/A1 Ratio Zeolites
Early 70's	SiO_2 Molecular Sieves
Late 70's	$AlPO_4$ Molecular Sieves
Late 70's to Early 80's	SAPO and MeAPO Molecular Sieves
Late 70's	Metallo-silicates, -aluminosilicates
Early to Mid 80's	$A1PO_4$-based Molecular Sieves
Early to Mid 90's	Metallophosphates

MeAPO indicates metal substituted aluminophosphate based molecular sieves, SAPO is a silico-alumino-phosphate based molecular sieves and AlPO4 is aluminophosphate zeolite.

2.1.2 Zeolite Structure

Zeolites are crystalline hydrated aluminosilicates of alkali and alkali earth metals, such as sodium, potassium, magnesium and calcium. They are represented by the formula given below:

$M_{2/n}O.Al_2O_3.ySiO_2.wH_2O$

where y is 2 – 200, n is the charge of the cation, M is an exchangable cation and w indicates the water in the voids of the zeolite. Structurally, zeolites are three dimensional, four connected framework of TO_4 tetrahedra (T = Si, Al) linked through oxygen atoms. AlO_4 framework of zeolite bears a net negative charge which is balanced by an extraframework cation. Zeolites are porous materials which contain voids and channels in their structure. These interconnected voids and channels are occupied by extraframework cations and water molecules [Kulprathipanja, 2010].

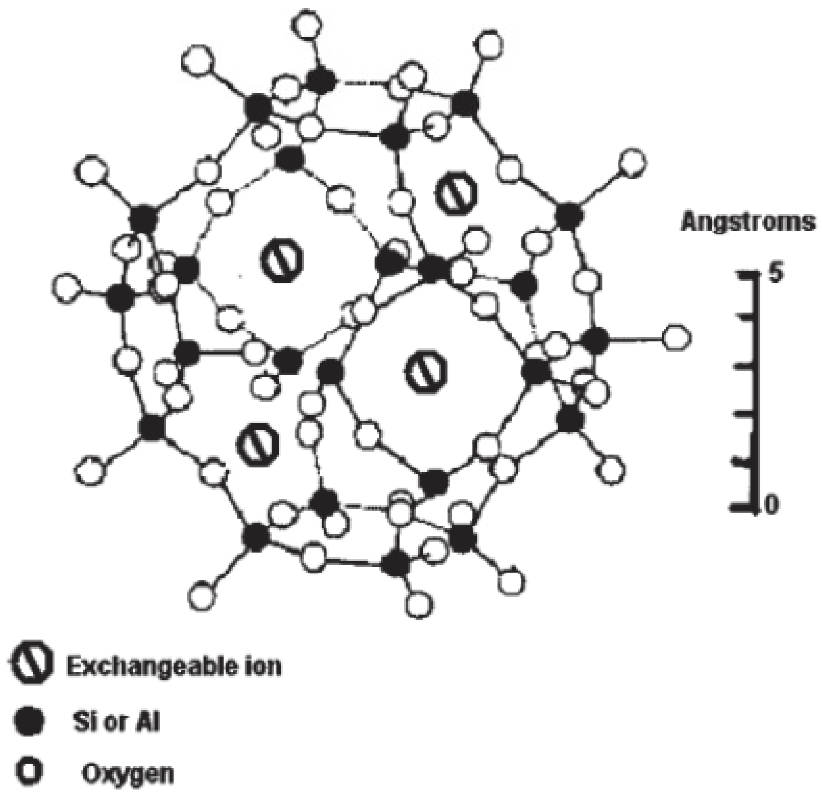

Figure 2.1 Sodalite Cage [Inglezakis, 2006]

2.1.2.1 Building Units of Zeolites

All zeolite frameworks occur by linking in a basic building unit (BBU) which is called the tetrahedron. The center of the tetrahedra are generally surrounded by Si, Al, P atoms and in the corners there are oxygen atoms. As a result of this combination, [SiO_4], [AlO_4], [PO_4] tetrahedrals occur. In order to describe these tetrahedrals, in general the term TO_4 is used where T indicates for any tetrahedral species.

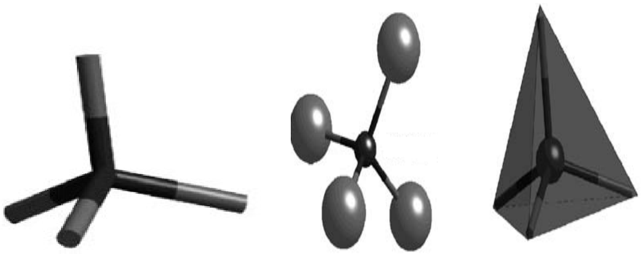

Figure 2.2 Different Representation of Tetrahedral Units[Auerbach, 2003].

Each oxygen atom is shared by metal ions, as a consequence, the ratio of oxygen to metal ions is always equal to two in the zeolite framework. T-O-T bond angle is quite flexible thus this property allows the formation of rings and other more complex building units may be formed [Auerbach et al., 2003].

When basic building units come together, complex building units occur. The simplest complex building units are called rings. The name of 'n rings' comes from the number of 'n tetrahedral units'.

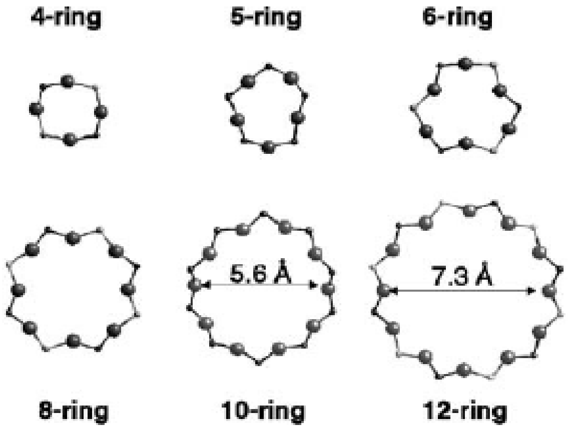

Figure 2.3 Most Commonly Used n-rings in Zeolites[Auerbach et al., 2003].

A ring defines a face of a polyhedral unit and polyhedral unit whose largest rings are to allow the passage of molecules larger than water is called cage. Two most common cages used in zeolites are cancrinite (CAN) and sodalite (SOD) [Auerbach et al., 2003].

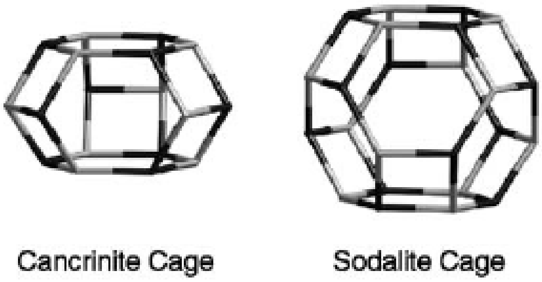

Figure 2.4 Two Different Cages Types Most Commonly Used in Zeolites [Auerbach et.al., 2003].

2.1.2.2 Extraframework Cations

Extraframework cations have large influence on ion exchange properties of zeolites [Pirngrube et al., 2010]. Extraframework cations make the zeolite framework neutral. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution [Helfferich, 1962].

Each AlO_4 tetrahedra bears a negative charge. Tetrahedral units are linked at their corners via a common oxygen atom. The charge of alumina is +3 and the charge of sharing oxygen molecules is -4. As a result of these, the overall framework will be negatively charged. In order to make overall framework neutral, water molecules and extraframework cations (alkali and alkali earth metals) are connected to alumina tetrahedral unit.

Extraframework cations are mobile and they are free to move to gain the zeolite ion exchange property [Inglezakis, 2006].

These exchangable ions are generally Ca, K and Na atoms. The sodium form of zeolite A is called zeolite 4A because its pore size is 4A°. Sodium can be exchanged by the other cationic ions such as calcium and potassium. When the sodium ion is replaced by the calcium ion, the pore size of zeolite A will be 5A° and it is called zeolite 5A; when the sodium ion is replaced by the potassium ion, the zeolite A will have a size of 3A° and it is called zeolite 3A [Huang et al., 2006]. As a consequence, zeolite 3A and 5A are very similar to zeolite 4A, except they have different exchangable cations in the zeolite and pore sizes [Li et al., 2005].

2.1.3 Types of Zeolites

There are about a hundred zeolite framework types and some of these are found in nature and specified as minerals such as chabazite, erionite, mordenite and clinoptilolite. However, most zeolite framework types are not found in nature but they are synthetic like Zeolite A [Seff, 1996].

Zeolites are classified according to Si/Al ratio in their framework. If this ratio is between 1-1.5, zeolite is called low silica zeolite. As the Si/Al ratio increases between 2-5, it is called intermediate silica zeolite. In high silica zeolites, this ratio is between 10-100.

The low silica zeolites are zeolite A and X. These zeolites are aluminum-saturated, have the highest cation concentration and give optimum adsorption properties in terms of capacity, pore size and three dimensional channel systems. They have highly heterogeneous surfaces with a strongly hydrophilic surface selectivity. The intermediate silica zeolites (Si/Al ratio is 2–5) include the natural zeolites such as erionite, chabazite, clinoptilolite and mordenite. The high silica zeolites with Si/Al of 10–100 are zeolite Y, mordenite, erionite, ZSM-5 which can be generated by either thermochemical framework modification of hydrophilic zeolites or by direct synthesis [Kulprathipanja, 2010].

2.1.4 Zeolite A

Zeolite A has the anionic aluminosilicate framework which is balanced by extraframework cation and it has large channels of spherical voids [Mohameda et al., 2009].

Tetrahedral unit of alumina or silica composed of oxygen atoms in the corners is the basic unit of Zeolite A. Sodalite cage is formed by 24 tetrahedra. Sodalite cages are the secondary building units for different types of zeolites. Sodalite cage contains six 4-membered rings and eight 6-membered rings [Huang, 1980].

The aluminosilicate framework of zeolite A is generated by placing cubic double four rings in the centers of the edges of a cube is 12.3 A which is connected by oxygen bridges. Half of the T atoms are Si and the other half are Al according to Löwenstein's rule [Bartsch et al., 1990].

Löwenstein's rule indicates that two contiguous tetrahedra contain aluminum on tetrahedral positions, i.e. Al–O–Al linkages are forbidden [Weitkamp, 1999].

The center of the unit cell is a large cavity and its diameter is 11 A^o and diameter of 8-membered rings is 4.1 A^o which give access to the large cavity.

Zeolite A is used as a desiccant in the laboratory and as an ion-exchanger in detergent industry [Bekkum et al., 2001].

Zeolite 4A, with an approximate pore diameter of 4Å, is one of the more commonly encountered molecular sieves. The basic composition of unit cell of Zeolite 4A is as given below [Gal et al., 1970];

$Na_{12}(12\ Al0_2.12SiO_2)27H_2O$

2.1.4.1 Zeolite 4A

Zeolite structures consist of SiO_4 and AlO_4 primary building units. About 100 different architectures are known which are based on vertex-sharing SiO_4 and AlO_4 tetrahedra and these units into truncated octahedra. If these octahedra are linked by double rings of four oxygen atoms each is called as zeolite 4A (also known as LTA, Linde Type A and sodium zeolite A). The negatively charged framework of zeolite 4A is balanced by the presence of cations. This cations is sodium ions for zeolite 4A.

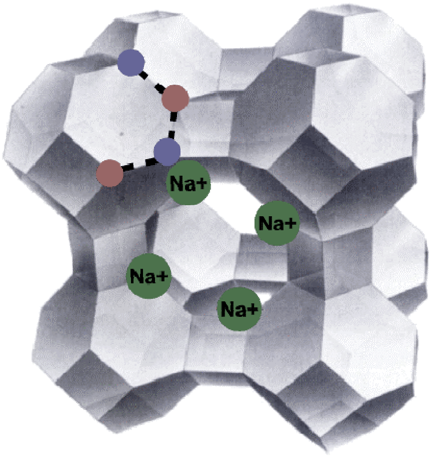

Figure 2.5 Schematic Three Dimensional Framework of Zeolite 4A

2.1.5 Chemical and Physical Properties of Zeolites

Aluminium content of zeolite structure determined the most of the physical and chemical properties and their areas of use. This is described as Si/Al or SiO_2/Al_2O_3 in the literature.

Synthetic zeolites are generally colorless material. However, when its own ions, alkali and alkali earth metals are exchanged with heavy metals during ion exchange process, color occurs.

According to types of cations and zeolite framework, densities change. When zeolites include heavy metals, densities can be higher. As it is known, heavy metals are mobile and so zeolites display ionic conductivity which depends on channel diameter, concentration of the cations, and the water content.

Zeolites have generally thermal stability however this property of zeolites can be varied according to their silica to alumina ratio and the nature of cations. Besides, they have ability to retain their structure without undergoing a phase change in the presence of water vapor.

Low-silica zeolites such as NaA and NaX are decomposed by strong acids which dissolve the aluminum atoms out of the framework, with consequent breakdown of the crystal structure. As silica to alumina ratio increases, the zeolites become less sensitive to dealumination by acids so high-silica zeolites are structurally stable even in strong mineral acids [Ullman, 2005].

2.1.6 Application of Zeolites

Zeolites are used in several industries. These are laundry detergents, oil refining and petrochemical industries, adsorbents, gas separations, agriculture and major

application areas as adsorbents, catalysts, and ion exchange materials. [Bekkum et al., 2001]. Zeolites are especially used as drying agent like silica gel and aluminum oxide. Zeolites have higher ability to adsorb water and when the temperature increases, adsorption capacity decreases but not as sharp as with silica gel and aluminum oxide.

Fluid catalytic cracking is a conversion process of high boiling and molecular weight hydrocarbon fractions of petrolium oils to more valuable gasoline and other molecules. Zeolites are used as catalysts. Hydrocarbon molecules can enter the lattice. The catalytic size in zeolites is strong acids. The acid sites are provided by alumina tetrahedra. Ammonium ion is replaced by sodium ion and forms Bronsted and Lewis acid sites and these sites can be exchanged with rare earth metals.

Zeolites are selective ion exchangers as water softeners and for radioactive waste treatment purposes.

Zeolite 4A is used in detergent industry due to its antibacterial property. As we know that heavy metals are very toxic elements and when they are exchanged with sodium ions in zeolite 4A, zeolite 4A gains antibacterial property and it can be used as an antibacterial agents.

2.2 HEAVY METALS

The pollution and toxicity associated with heavy metals are well known. The presence of heavy metals in water has a crucial effect on acidity and the result of decrease of pH is known to adversely effect fish stocks and vegetation. Metal ions in solution are toxic to humans if the concentration is very high [Ahmed et al., 1998].

These heavy metals are Ag^+, Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , and Ba^{2+} etc. A high concentration of cadmium, copper and silver in water is identified as a potential health and environmental hazard [Hanzlík et al., 2004].

Cadmium is classed as a highly toxic metal that affects the action of enzymes and impedes respiration, photosynthesis, transpiration and chlorosis [Ahmed et al., 1998]. Cadmium ion is a hazardous pollutant which is available in wastewater released by many activities, like mining, mineral processing, metallurgy, electroplating, and batteries' production and recycling [Panayotova, 2010]. Due to these reasons, removal of cadmium ions from wastewater is a must.

One of the most crucial heavy metals is silver. It is generally found in the combined state in nature. The major usage area of silver is as silver halide in the manufacture of photographic film. Other industrial uses of silver include of the production of electrical contacts and switching gear, batteries catalysts and mirrors. The main technologies used for silver removal from wastewaters are precipitation, ion exchange, membrane processes, solvent extraction, cementation, electro coagulation, coagulation–flocculation, adsorption, reductive exchange and electrolytic recovery [Çoruh et al., 2010].

Although these methods are all rather expensive, involving high-priced equipment and energy requirements, ion exchange is an easy and quick method including low-priced equipment [Hanzlík et al., 2004].

2.3 ION EXCHANGE

Ion exchange is a reversible chemical reaction and an exchange of ions between a solid (ion exchange material) and a liquid in which there is no change in the structure of the solid [Wheaton and Lefevre, 2000].

A is a cation which is in solution, B is the cation which is in the zeolite. Z_A and Z_B are charges of the cations A and B, respectively in ion exchange process. The ion exchange between these two ions is described as;

$$Z_B A^{Z_A} + Z_A B^{Z_B} \leftrightarrow Z_B \bar{A}^{Z_A} + Z_A \bar{B}^{Z_B}$$

When the zeolite is contacted with solution, A and B ions are exchanged until the equilibrium has been reached. This results the distribution of cations between zeolite and solution phase and ion exchange isotherms can be constructed at a constant temperature [Dyer, 2007].

2.3.1 Ion Exchange Isotherm

The term of "isotherm" implies that the temperature must be constant. The aim of ion exchange isotherm is to determine the preference which Zeolite exhibits for one ion over other ion. For this purpose, equivalent fractions of ions are calculated to plot an ion exchange isotherm. This isotherm is plotted as equivalent fraction of cation in solution phase versus equivalent fraction of the same cation in zeolite phase [Townsend and Coker, 2001].

Equivalent fractions are defined as;

$$A_S = \frac{z_A m_A}{z_A m_A + z_B m_B} \tag{2.1}$$

$$A_Z = \frac{z_A M_A}{z_A M_A + z_B M_B} \tag{2.2}$$

Z_A and Z_B are charge of the cations, where M_A and M_B are molalities of A and B (mol/kg), m_A and m_B are molarities of A and B (mol/dm^3) in solution phase and zeolite phase. The subscript “s” and “z” indicates the solution phase and zeolite phase respectively [Dyer, 2007].

Ion exchange isotherms are classified into four kinds according to Townsend (2001). The isotherms of the first type are presented in Figure 2.6 and it is for simple systems.

Isotherm of the first type (Figure 2.6a);

Case 1 indicates that the zeolite does not prefer the ion that enters.
Case 2 shows that the zeolite is not selective for the ingoing ion.
Case 3 is obtained as zeolite is selective for the ion that enters.

Isotherm of the second type (Figure 2.6b) ;

The plot is a sigmoid shape and indicates an alteration in the selectivity as a function of X_{AZ}.

Isotherms of the third type (Figure 2.6c);

It is a plateau in the hysteresis region. There is a formation of a new crystalline phase that occurred during the exchanging process.

Isotherms of the fourth type (Figure 2.6d)

It is generally observed for the zeolites. The effect of zeolites due to cation volume may be responsible for such a limit [Townsend and Coker, 2001].

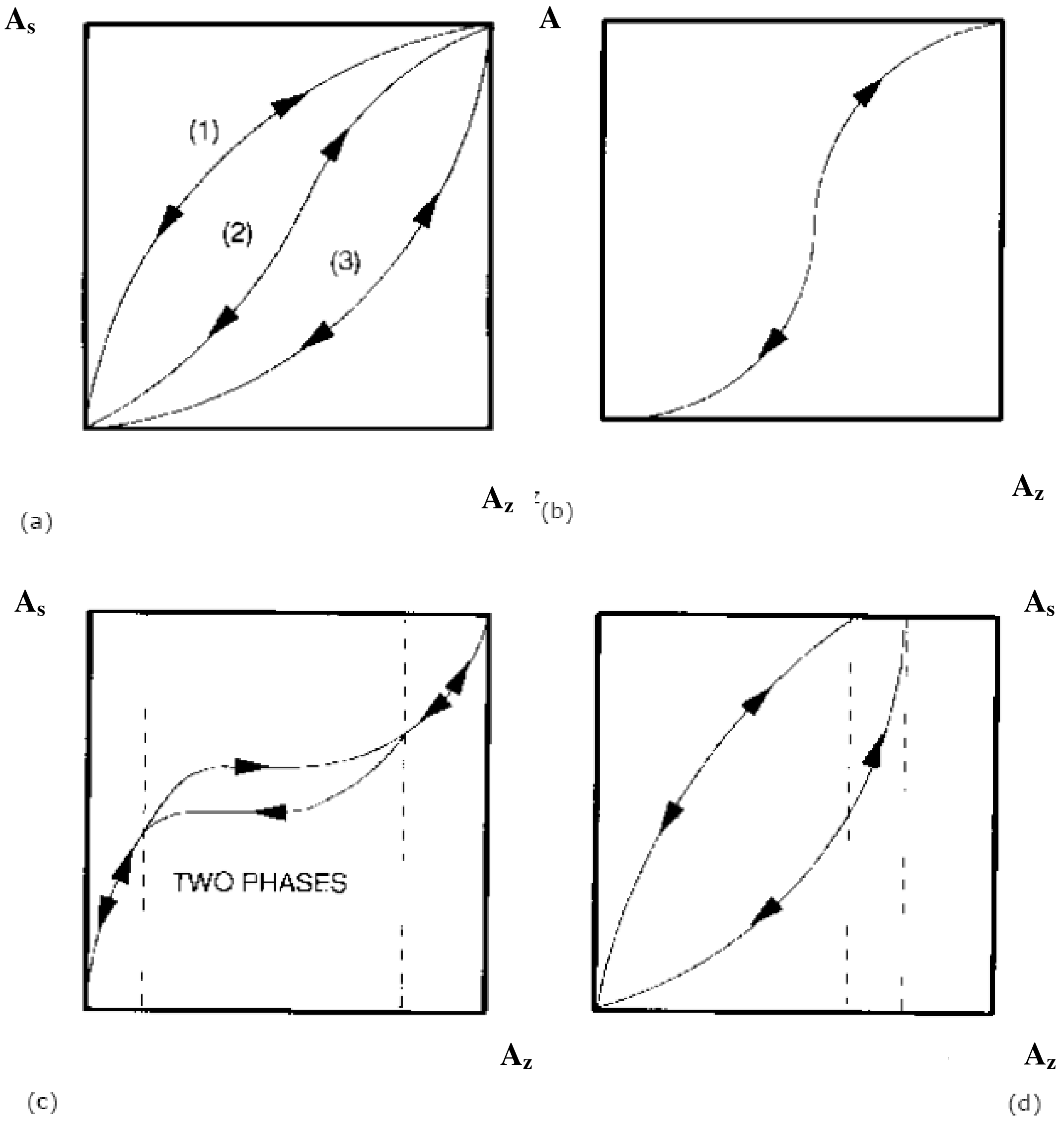

Figure 2.6 Ion Exchange Isotherms Described by Townsend; a: First Type, b: Second Type, c: Third Type, d: Fourth Type [Barros et al., 1997].

There is another classification of isotherms defined by Breck (1984) shown in Figure 2.7 [Barros et al., 1997]. This classification includes five isotherms types. In Type a; zeolite is selective for the entering cation over the entire range of the zeolite. In type b; the entering cation has a selectivity reversal with an increasing equivalent fraction in the zeolite. In type c; there is a selectivity for the cation A over the entire range of the zeolite composition. In type d; zeolite is selective for the entering ion initially however exchange is not completed. Finally in type e; there is hysteresis loop which may result from the formation of two zeolite phases [Barros et al., 1997].

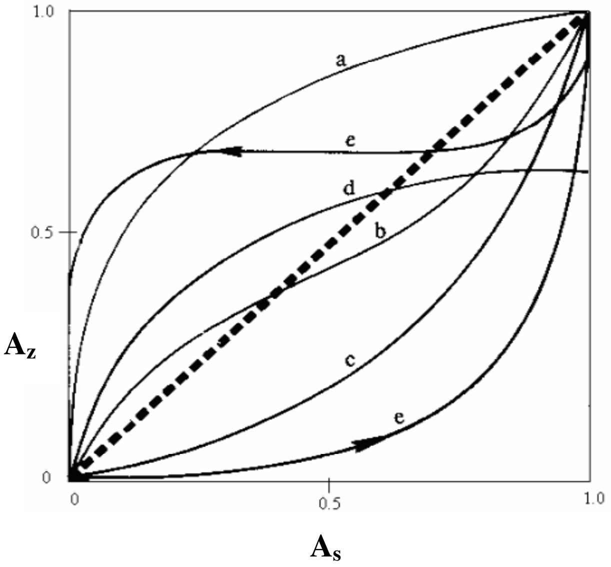

Figure 2.7 Ion Exchange Isotherms for Breck’s Classification [Barros et al.,1997]

2.3.2 Selectivity and Affinity in Ion Exchange

There is an apparent difference between the terms “selectivity” ,“affinity” and “preference”. The value of preference depends on several system conditions such as temperature, pressure, solution pH, composition of solution and zeolite phase etc.In order to determine the preference which zeolite exhibits one ion over other ion, the equation can be used given below [Townsend and Coker, 2001];

$$\alpha_B^A = \frac{A_Z * B_S}{B_Z * A_S} \tag{2.3}$$

This is the separation factor. If separation factor is greater than 1, it means that zeolite has affinity to ion A (which is present in solution). If it is smaller than 1, zeolite has affinity to its own ion B. When this ratio is equal to 1, zeolite shows no preference for ion A or B. Separation factors for Ag^+-Na^+ binary ion exchange and Cd^{2+}-Na^+ binary ion exchange are given in Appendix H.

There is another calculation method is known as a graphical representation of the separation factor.

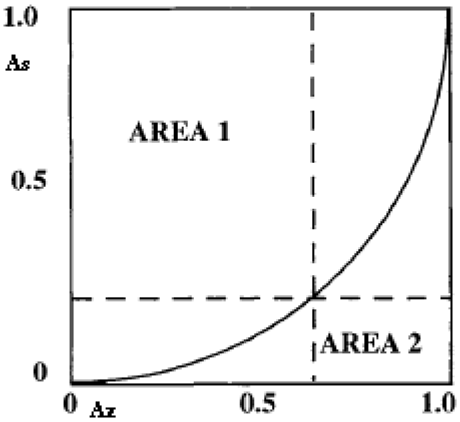

Figure 2.8 Graphical Representation of Separation Factor

$$\alpha_B^A = \frac{AREA\ 1}{AREA\ 2} \tag{2.4}$$

Selectivity of the resins for ions having the same charge usually increases when the atomic weight increases as well and selectivities for divalent ions are greater than for monovalents [Kirk Othmer, 1998].

The term of “Affinity” in ion exchange has a thermodynamic meaning and it is qualified by thermodynamic equations which gives chemical potential of components at equilibrium [Townsend and Coker, 2001].

2.3.3 Thermodynamic Analyses of Ion Exchange

Ion exchange is a reversible reaction. If we consider an ion exchange reaction between two cations A^+ and B^+, mass action quotient describes the equilibrium distribution and is expressed by an equation given below [Lewis, 1952];

$$K_m = {A_Z}^{Z_B} {m_B}^{Z_A} / {B_Z}^{Z_A} {m_A}^{Z_B} \tag{2.5}$$

Mass action quotient is defined in terms of concentration because it depends on exchanger composition in contrast to thermodynamic equilibrium constant which is related to activities of cations. Let’s imagine an ion exchange reaction between A^+ cation in solution and an exchanger which is fully in B^+ cationic form. The system has given amount of energy which is required to neutralise one B cation until the system is reached to equilibrium. Within this period there is interaction between water, A^+ and B^+ cations because of these new interactions, the behaviour of the system will not be predictable simply on the basis of the concentrations of A, B.

Consequently, each of these concentrations should be multiplied by a correction factor. When we multiply each component concentration by its own correction factor, activities of each components, the magnitudes of which take into account these new interactions are obtained. Thus the thermodynamic equilibrium constant is defined in terms of activities [Townsend and Coker, 2001].

Mass action quotient and correction factor (Γ) are related to Kielland coefficient (K_c) which is required to determine thermodynamic equilibrium constant (K_a) by Gaines and Thomas equation given in Equation 2.7. In order to calculate Kielland quotient, Kielland plot (ln K_c versus A_z) is drawn using the Equation 2.8. Whether the energy of exchange sites in ion exchange are the same or not is observed by analysing the Kielland plot [Barros et al., 2004].

$$\Gamma = \frac{{\gamma_B}^{Z_A}}{{\gamma_A}^{Z_B}} = \frac{\left[\gamma\pm^{(Ax)}_{(Bx)}\right]^{Z_A(Z_B+Z_X)/Z_X}}{\left[\gamma\pm^{(Bx)}_{(Ax)}\right]^{Z_B(Z_A+Z_X)/Z_X}} \tag{2.6}$$

$$K_C = \Gamma K_m \tag{2.7}$$

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_C \, dA_z \tag{2.8}$$

Activity coefficients of A and B cations in correction factor can not be determined so we can calculate these values using Debye-Huckel equation.

Debye and Hückel is an expression which is derived for the activity coefficient of an electrolyte in which allowance is made for the finite size of the ions, an equation which, in the case of an aqueous solution at 25 ^{o}C, takes the form:

$$\log \gamma_{\pm\,Ax} = \frac{A\,|Z_1 Z_2|\sqrt{I}}{1+Ba\sqrt{I}} + bI \tag{2.9}$$

A and B are Debye Hückel Parameters at constant temperature. The symbol ”a” is interpreted as a mean ionic diameter, or the closest distance of approach of the ions. The symbol “b” is an adjustable constant in order to suit experimental curve.

Debye-Hückel Equation is generally used for the analytical represantation of activity coefficients. However, ionic strength is required in order to calculate activity coefficients. Ionic strength is given as follows [Robinson and Stokes, 1959];

$$I = \frac{1}{2} \sum m_i \, {z_i}^2 \tag{2.10}$$

where m_i is the concentration of each ion present in solution and z_i is the charge of the ions.

The activity coeffient is affected by the electrostatic interactions between cations and these interactions is described by ionic strenth equation for an electrolyte solution [Pitzer, 1984].

At the end of the thermodynamic anaylsis after determining all thermodynamic quantities standard Gibbs free energy (ΔG) can be calculated in order to predict free energy change in ion exchange equilibria and also physical meaning of negative or positive value of standart free energy indicates whether zeolite has affinity or not to exchanging ions. Standard Gibbs free energy is expressed by Equation 2.11;

$$\Delta G^o = \frac{(-RT \ln K_a)}{z_A z_B} \tag{2.11}$$

2.3.4 Adsorption Isotherms

Adsorption isotherms are required to define the removal of metal ions at equilibrium mathematically. Two types of isotherms commonly used are Langmuir and Freundlich isotherms [Ali and Bishtawi, 1997].

2.3.4.1 Langmuir Isotherm

Langmuir isotherm is the result of a theory including a process of bombardment of molecules on the surface and desorption of molecules from the surface to keep zero rate of accumulation at surface at equilibrium. Langmuir model's assumptions are as follows [Do, 1998];

- Homogeneous surface and adsorption energy is constant for all sites
- Adsorption occurs on the surface by atoms and molecules are adsorbed at localised sites.
- One molecule or atom is only accommodated in each site

Langmuir isotherm is defined by Equation 2.12 [Townsend and Coker, 2001];

$$q_e = \frac{q_{max}*K*C_e}{1+K*C_e} \qquad (2.12)$$

where,

q_e is the solid-phase concentration in equilibrium with the liquid-phase concentration

q_{max} is maximum adsorption capacity (mg/mg)

K is an equilibrium constant (l/mg)

C_e is the liquid phase metal ion concentration at equilibrium(mg/l)

The linearized form of Langmuir equation is ;

$$\frac{1}{q_e} = \frac{1}{K*q_{max}*C_e} + \frac{1}{q_{max}} \qquad (2.13)$$

Langmuir isotherm is plotted $1/q_e$ versus $1/C_e$ in order to find equilibrium constant (K). The slope of the graph is equal to $1/K*q_{max}$ and intercept is equal to $1/q_{max}$.

2.3.4.2 Freundlich Isotherm

Freundlich isotherm is used to define equilibrium data. The name of the isotherm comes from the “Freundlich” who is a researcher used this equation. [Do, 1998]. It is used for the description of adsorption of ions from solution onto the adsorbent surface where there is a heterogeneous valance distribution [Al-Asheh et al., 2000]. The equation is;

$$q_e = K_f * C_e^{1/n} \qquad (2.14)$$

where, n is a constant, K_f is adsorption capacity.

Linearized form of Freundlich Isotherm;

$$\ln q_e = \ln K_f + (\frac{1}{n}) * \ln C_e \qquad (2.15)$$

The Freundlich isotherm is plotted as $\ln C_e$ versus $\ln q_e$. The slope of the graph is equal to 1/n and intercept is equal to $\ln K_f$.

CHAPTER 3

LITERATURE SURVEY

Gal et al. (1970) investigated the ion exchange equilibria of synthetic zeolite 4A with nickel, cobalt, cadmium and zinc ions. They used in this study zeolite 4A as an ion exchanger and exchanging metals were cobalt, nickel, cadmium and zinc. The ion exchange experiments were conducted by using 0.1 N solutions of metal chlorides at room temperature. According to isotherm they plotted using equivalent fractions, zinc and cadmium replaced all sodium ions. Thermodynamic analyses was done calculating free energy of exchange. Free energy of exchange between zinc and sodium ion was calculated as -3.94 kJ per equivalent.It means that, ion exchange reaction occur simultaneously. According to differential thermal analyses results, they found that Co-Zn and Cd zeolites are stable when they are dehydrated up to 750-800 ^{o}C. Nickel is just stable up to 70 ^{o}C due to its crystal structure and it destroyed above this temperature. They found that the main factor affecting the ion exchange equilibria was the size of the divalent metal cations after analyzing the thermodynamic data.

Heo and Kim (1990) examined the binary ion exchange isotherms between Cs^+-Ag^+, Ag^+-Na^+ and NH_4^+-Na^+ for three system. Binary ion exchange isotherms were determined using 0.1 M solutions of aqueous nitrates of metals at 21 ^{o}C. For ion exchange experiment between Ag^+-Na^+, 0.1 g zeolite A and 30 ml of exchange solution which was prepared by silver nitrate were used. Binary ion exchange between Cs^+ and Ag^+ ions was performed to obtain Ag^+-A zeolite firstly and after that Ag^+ ions in zeolite A were exchanged with Cs^+ ions contacting 75 ml of exchange solution with 0.4 g Ag^+-A zeolite. Analyses of experiments were done by using flame emission spectrometry. Ion exchange isotherm for NH_4^+-Na^+ exchange indicates that selectivity for the entering ion NH_4^+ was reversed when the equivalent fraction of NH_4^+ ions increased. Isotherm for Ag^+-Na^+ demostrated that zeolite A has great preference for Ag^+ ions. Cs^+-Ag^+ exchange isotherm shows that the entering Cs^+ ion can not fully displace all of the Ag^+ due to the greater ion size of Cs^+ ions.

Curkovic et al. (1996) examined the removal of lead and cadmium ions using natural and modified zeolites. They used three different forms of clinoptilolite (Croatian Zeolite). One of these zeolites has no pretreatment and the others have pretreatment with NaCl at different temperatures. The experiments were conducted in batch mode. Zeolite weights were kept constant as 1 g and metal ion concentrations were varied between 1 and 10 mmol/l at five different temperatures 4, 22, 50, 60, 70 ^{o}C. Exchange of potassium and calcium ions increased with increasing temperature. All zeolite samples are more selective to lead than cadmium ion. It was seen that the croatian zeolites can be used as an ion exchanger for lead and cadmium removal.

Ahmed et al.(1998) investigated the removal of cadmium and lead from aqueous solution using ion exchange method with Na-Y zeolite. Ion exchange process was carried out in batch mode at constant room temperature and 0.1 N normality. Binary and ternary ion exchange isotherms were drawn for Cd^{2+}-Na^+, Pb^{2+}-Na^+ and Cd^{2+}-Pb^{2+}-Na^+ exchange. In this study, separation factor, removal efficiency of ions were calculated and preference of Na^+-Y zeolite was determined. According to binary ion exchange experiments between Pb^{2+}-Na^+ and Cd^{2+}-Na^+, Na^+-Y zeolite showed a great preference for Pb ions. However, an increase in heavy metal concentration results a decrease in selectivity of ions for both heavy metals. Comparing ion exchange isotherms plotted in this study with ion exchange isotherms for Ni^{2+} and Cu^{2+} ions, selectivity sequence was found as $Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+}$. As a results of ternary ion exchange experiments it is found that Na-Y zeolite is more selective to

Pb ions than Cd and Na ions. For binary and ternary ion exchange experiments, Na-Y zeolite showed the highest selectivity to lead ions.

Biskup and Subotic (2010) examined the thermodynamics of ion exchange between cadmium and sodium ion on zeolite A. They used appropriate weight of zeolite 4A as an exchanger. The total concentrations of sodium and cadmium ions were 0.02, 0.05 and 0.1 meqv/dm^3. The ion exchange experiments were carried out at three different temperatures, 20, 40 and 60 ^{o}C using water bath which keep the temperature constant throughtout the experiment. According to all isotherms plotted, cadmium isotherm is a sigmoidal type isotherm which means that the entering cation has a selectivity reversal with an increasing equivalent fraction in the zeolite. Kielland plots were drawn and Kielland coefficient, standart free energy of exchange, thermodynamic equilibrium constant were calculated at three different temperatures. They observed that the thermodynamic equilibrium constant increased with temperature of exchange process but it doesn’t change with solution normality. Standard free energy was calculated as -3.76, -4.06 and -6.62 kJ/eq. for three different temperature 293, 313 and 333 K respectively. It can be said that ion exchange reactions occur simultaneously for all temperature ranges and concluded that zeolite A has higher affinity to cadmium ion than sodium ion.

Çulfaz and Yağız (2004) studied on the removal of lead and cadmium ions using clinoptilolite. Ion exchange experiments were carried out at 25 ^{o}C and 0.1 total normality. According to their experimental study, selectivity sequence was found as $Pb^{2+} > Na^{+} > Cd^{2+}$. Thermodynamic analyses of ion exchange between Cd-Na and Pb-Na binary system were carried out calculating thermodynamic equilibrium constants and standart free energy of system for each pair. Thermodynamic equilibrium constant was found as 16.6 and 0.16 for Pb^{2+}- Na^{+} binary system and Cd^{2+}- Na^{+} binary system respectively. Standart free energies of exchange were calculated as -3.48 and +2.27 kJ/eq. for Pb^{2+}-Na^{+} binary system and Cd^{2+}-Na^{+} binary system respectively. According to Gibbs Free Energy results, ion exchange reaction between cadmium and sodium ion does not occur simultaneously and there is need to extra energy from outer space and it is concluded that clinoptilolite has no selectivity to cadmium ion.

Top and Ülkü (2004) studied on silver, zinc and copper exchange in a Na-cliniotilolite. Antibacterial activities of ions were investigated. Na form of Gördes clinoptilolite and salt solution of silver, zinc and copper were used. To examine antibacterial activity of metal exchanged zeolite, they used two different strains. These experiments were conducted by treating Na-Clinoptilolite with a series of different proportions of two competiting cations in a shaker at 25 ^{o}C for two days. The masses of clinoptilolite were varied between 0.1 and 1 g. Solution volume was changed from 5 to 25 ml. Silver solution was kept in dark because it is sensentive to light. After these experiments selectivity sequence was found as follows $Ag^{+}>Na^{+}>Zn^{2+}>Cu^{2+}$. Na-clinoptilolite has higher affinity to silver and lower affinity to copper. Silver was favorable at whole concentration range however copper and zinc is favorable at low concentrations. Standard free energies of the pair of the Ag^{+}, Zn^{2+}, Cu^{2+} ions with sodium ion in binary experiments was calculated as -6.0, 2.03 and 3.09 kJ/equiv. respectively and Na-clinoptilolite has no selectivity to zinc and copper ion. Original clinoptilolite has not antibacterial activity. Silver clinoptilolite gains antibacterial property at low loadings, at high loadings due to increase in the disordered Ag, antibacterial activity of silver is reduced.

Pitcher et al. (2004) used two different types of zeolites to remove heavy metals from motorway stormwater in this study. They used synthetic MAP (Maximum aluminum zeolite P) and natural mordenite as an exchanger and heavy metals were chosen as lead, copper, zinc and cadmium. Zeolites were used with no pretreatment due to make sure that this method is economical. Heavy metal concentrations were as 25, 50, 250 and 500 mg per liter of cadmium, lead, copper and zinc respectively. Batch experiments were carried out due to it is a quick and simple method. 0.5 g of zeolite was mixed with 50 ml of solution and shaken for 10 minutes using a mechanical shaker in the experiment. As a result of experiments, the selectivity sequence was determined as Pb>Cu>Zn~Cd. Mordenite has high affinity to lead however it has lower affinity to zinc and cadmium. On the other hand all heavy metals were removed by MAP (maximum aluminum P) which means MAP is more effective than natural mordenite because MAP releases more sodium ions.

El-Kamash et al. (2005) analysed the batch kinetics and thermodynamics of removal mechanism of zinc and cadmium ion using zeolite A. Metal concentration and temperature change were experimental parameters and they were varied between 100-2000 mg/l and 298, 313 and 333 K respectively in a batch experiment mode. Zeolite weight was kept constant as 25 mg contacting with 25 ml of metal ion solution. Standard free energies of cadmium and zinc ion were calculated as 39.46 and 39.45 kJ/mol respectively as a result of thermodynamic analyses. Kinetic analyses showed that sorbed amount of zinc and cadmium ions increased with increase in temperature. Three different types of adsorption isotherm, Langmuir, Freundlich and Dubinin-Radushkevich, were examined to determine which isotherm model give the best fit for cadmium and zinc ions. As a consequence, Freundlich isotherm gave best fit to cadmium ions in all temperature range and there are heterogeneous distribution of ions on the exchanger surface however, both Langmuir and Freundlich isotherm gave best fit to zinc ions.

Akgül et al.(2006) studied on removal mechanism of silver ion using clinoptilolite. Batch adsorption experiments were carried out using 50 mg zeolite sample and 25 ml of stock solution of silver nitrate whose concentration range is varied between 10-150 ppm at 25 ^{o}C constant temperature. It was found that clinoptilolite has great preference for silver ion due to its short equilibrium time which is related to minumum energy consumption. However, when clinoptilolite was treated with acid solution, adsorption capacity decreased. For maximum adsorption capacity it was observed that the initial metal concentration should be low because when initial concentration was increased, adsorption capacity for Ag ion decreased.

Thermodynamics of adsorption process was examined in terms of Langmuir and Freundlich isotherms. The correlation coefficient (R^2) was found for Langmuir and Freundlich model as 0.99 and 0.98 respectively. These results indicated that the Langmuir model can be applied to the this adsorption system.

Ay (2008) studied on single and multicomponent ion exchange of silver, zinc and copper using zeolite 4A. Zeolite 4A was used as an ion exchanger and silver, copper and zinc were used as heavy metals. Binary and ternary experiments were performed at batch mode at constant temperature 25 ^{o}C and 0.1 normality. Amount of zeolites were chosen between 0.1 and 1g for binary ion exchange and zeolite amounts were chosen as 0.25 g, 0.50 g and 1 g for ternary ion exchange. 20 ml of 0.1 N solution was used to examine ion exchange ability of metal ions on zeolite 4A. As a result of experiments, selectivity sequence was determined as follows; $Ag^+ > Cu^{2+} > Zn^{2+}$ for both binary and ternary ion exchange experiments analyzing the ion exchange isotherms. Thermodynamic analyses gave the same result and ion exchange reactions occurs simultaneously. As a consequence, it was observed that silver, copper and zinc could be used for waste water treatment and antibacterial applications. Silver-zinc exchanged zeolite gave the best result by means of antibacterial activity.

CHAPTER 4

EXPERIMENTAL WORK

4.1 CHARACTERIZATION OF ZEOLITE 4A

In this study commercial Zeolite 4A was used as an exchanger in ion exchange experiments. The ion exchanger, commercial zeolite 4A was supplied by Sigma Aldrich Company and its chemical formula is given as;

$Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]nH_2O$

As it is seen from the formula, water content of zeolite 4A is variable. In order to obtain constant relative humidity in all experiments, zeolite 4A powder was kept in desiccator which contained saturated sodium chloride solution. The additional methods to characterize of zeolite 4A were scanning electron microscopy (SEM) thermogravimetric analyses (TGA) and X ray diffraction (XRD). In order to determine surface morphology scanning electron microscopy analyses was done. The sample was identified by X ray diffraction method in a previous study [Ay, 2008]

4.1.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy analyses was done in Central Laboratory of METU using Quanta 400 FE-SEM.

4.1.2 Thermogravimetric Analyses (TGA)

Thermogravimetric analyses were done to determine water content of zeolite 4A. Shimadzu DTG 60-H was used for the measurements in chemical engineering department of METU.

The measurements were conducted in the temperature range of 20-750 ^oC under the nitrogen atmosphere at the flow rate of 75 ml/ min. Water content of commercial zeolite 4A was calculated from TGA graph.

4.2 CHEMICAL REAGENTS

In this study nitrate forms of silver and cadmium ions were used as reagents. Stock solutions of the reagents were prepared using deionized water. $Ag(NO_3)$ and $Cd(NO_3)_2 4H_2O$ with purity 99+% were supplied by Merck and Acros Organics respectively.

4.3 CHEMICAL ANALYSES OF THE SAMPLES

4.3.1 Atomic Absorption Spectrophotometry (AAS)

The concentration of silver and cadmium ions in aqueous solution were determined with the method of Atomic Absorption Spectrophotometry (AAS). To determine the concentrations of Ag^+, Cd^{2+}, hallow cathode lamps were used for each metal ions.

Commercial standard solutions which are prepeared from 1000 ppm stock solutions of silver and cadmium were used for calibration of atomic absorption spectrophotometry. Dilution of aqueous solutions were done in the appropriate range of concentration of standard solutions of each metal ions.

The Atomic Absorption Spectrophotometry measurements were performed at the wavelengths 328.1 nm and 228.8 nm for silver and cadmium respectively using Shimadzu AA-6300.

4.4 BINARY ION EXCHANGE EXPERIMENTS

Powder form of commercial zeolite 4A was used after keeping it in desiccator filled with saturated NaCl solution for 2 days before use. The experiments were carried out at 0.1 N constant normality and 25 ^{o}C temperature in batch system. The aqueous solutions of metals were prepared by dissolving nitrate forms of silver and cadmium in deionized water. Zeolite weights were varied between 0.1 g and 1 g. Solution volume was kept constant as 20 ml.

Appropriate amount of commercial zeolite 4A was added to sample vessels and 20 ml of stock solutions of metal ions were added to the same vessels. All sample vessels were placed in a water bath. Samples were shaken in water bath at constant temperature and stroke length. The samples (there are six samples and their concentration are the same) taken from water bath for every two hours in order to find the equilibrium time of exchange process and equilibrium time was determined as 6 hours. ST 402 shaking water bath used in experiments given in Figure 4.1.

Figure 4.1 ST 402 Shaking Water Bath

After taking the sample vessels from the water bath, solution and solid parts were separated by centrifuging at 3000 rpm. Final concentrations of exchanging cations were determined using Atomic absorption spectrophotometry after appropriate dilutions. Equivalent fractions of metal ion were calculated in order to plot the ion exchange isotherms which were plotted as equivalent fraction of the exchanging ion in solution phase versus the equivalent fraction of the same ion in the zeolite phase for binary ion exchange system between Ag^+-Na^+ and Cd^{2+}-Na^+.

Table 4.1 Experimental Conditions and Parameters for Binary Ion Exchange Experiments

Temperature	25 °C
Total Normality	0.1 N
Solution Volume	20 ml
Zeolite Weight	0.1-1g
Equilibrium Time	6 h

4.5 TERNARY ION EXCHANGE EXPERIMENTS

Multicomponent ion exchange experiments were done between Ag^+-Cd^{2+}-Na^+ ion in ternary system. The aqueous solutions of silver and cadmium ions were prepared with the same procedure in binary ion exchange experiments. A weighed amount of zeolite 4A after keeping in desiccator filled with saturated NaCl solution was placed in sample vessels in which the aqueous solutions containing different proportions of two competing cations at constant concentration of 0.1N constant total normality and was stirred to reach equilibrium in water bath at 25 ^{o}C constant temperature. Zeolite amount was kept constant as 0.4, 0.5 and 0.75 g while the concentrations of aqueous solutions were varied from 0.01 N to 0.09 N.

The samples were taken from water bath for every two hours in order to find equilibrium time of exchange process. When the final concentrations of exchanging ions were equal to each other, equilibrium time was determined as 24 hours. The samples were centrifuged at 3000 rpm in order to separate as solution and solid part. Solution part was analyzed with AAS. Final concentration of silver and cadmium ions in solution part were determined by AAS.

Sample calculation of equivalent fractions of exchanging ions in solution and solid phase is given in Appendix B. Ion exchange isotherms were drawn as equivalent fraction of exchanging ion in solution phase versus the equivalent fraction of the same exchanging ion in zeolite phase for Ag^+-Cd^{2+}-Na^+ ternary system.

Silver is sensitive to light and due to this fact, it was stored in the dark and maintaned in the dark vessels during both binary and ternary ion exchange experiments.

Table 4.2 Experimental Conditions and Parameters for Ternary Ion Exchange Experiments

Temperature	25 ^oC
Total Normality	0.1 N
Solution Volume	0.01N-0.09N
Zeolite Weight	0.4-0.75g
Equilibrium Time	24 h

CHAPTER 5

RESULTS AND DISCUSSION

5.1 THERMOGRAVIMETRIC ANALYSES (TGA)

Thermogravimetric analyses was done to determine the water content of zeolite 4A. TGA graph is given in Figure 5.1.

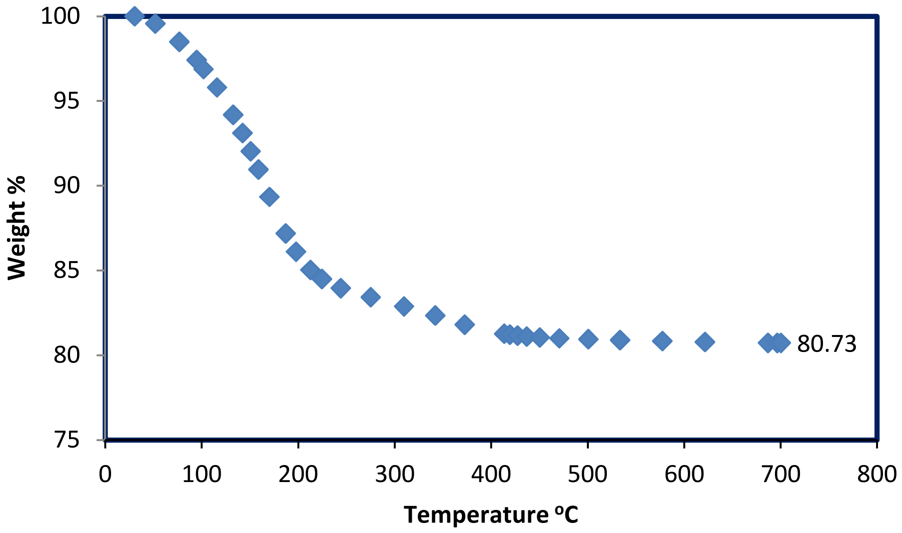

Figure 5.1 TGA Graph of Zeolite 4A

Water content of zeolite 4A was found as 19.27 wt %. Using this water content value ion exchange capacity of zeolite 4A was calculated. In order to determine the water content of zeolite 4A, TGA analyses is required due to the uncertainty in water content under the laboratory atmosphere. The chemical formula of zeolite 4A varies with the water content which depends on relative humidity. After finding the chemical formula using percentage of water content, ion exchange capacity was calculated. Ion exchange capacity was found as 5.7 meq/g of wet resin and 7.0 meq/g of dry resin. Calculations are given in Appendix A.

5.2 SCANNING ELECTRON MICROSCOPY (SEM)

Scanning electron microscopy is required to examine the morphology of commercial zeolite 4A. As it is seen from the figure given below, zeolite 4A has cubic shape. Although it is commercial zeolite 4A, it did not show well-defined crystals and they have different sizes varied between 2-8 μm.

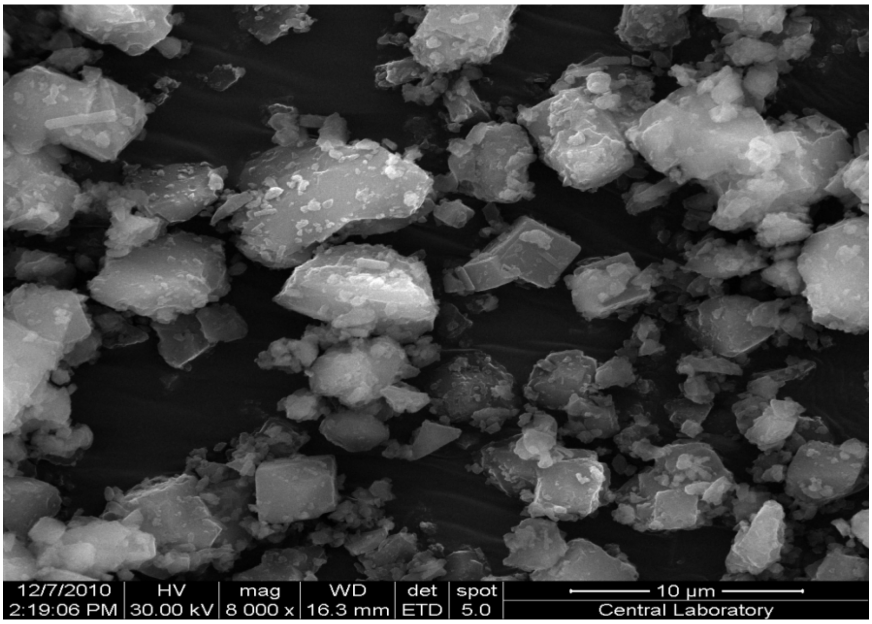

Figure 5.2 SEM Micrograph of Zeolite 4A.

5.3 BINARY ION EXCHANGE EXPERIMENTS

Binary ion exchange experiments were done for Ag^+-Na^+ and Cd^{2+}-Na^+ exchanges. Experiments were carried out at a constant temperature of 25 ^oC and constant normality of 0.1N. Zeolite weights were varied between 0.1 and 1 g for binary experiments Equilibrium time was found as 6 hours for both binary ion exchange systems. After the samples reached the equilibrium, the ion exchange isotherms were drawn using calculated equivalent fractions of each ions from their concentration values. Ion exchange isotherms were drawn as equivalent fraction of exchanging cation in solution versus equivalent fraction of exchanging cation in zeolite to determine selectivity of zeolite 4A to cadmium and silver ions. Calculations of equivalent fractions are given in Appendix B. Ion exchange isotherms for each binary system is given in Figure 5.3-5.8.

According to binary ion exchange isotherm for Ag^+-Na^+ system, zeolite 4A has higher selectivity to silver ions. This is in accordance with previous results [Ay, 2008 ;Heo and Kim, 1990]. All silver ions are almost exchanged with sodium ions in zeolite 4A. Exchange of silver ions has been completed and it may results from the similar ionic radii of silver and sodium ions and the high polarisability property of silver ions.

Ion exchange isotherms for Cd^{+2}–Na^+ binary system indicates that the zeolite 4A has selectivity for cadmium ions as well. In this system almost complete exchange was not obtained in contrast to Ag^+-Na^+ exchange. Repeatability of Cd^{2+}-Na^+ binary ion exchange experiment was done to make sure that the experiments always give the same results and it is given in Appendix I.

Cd^{+2}–Na^+ binary ion exchange isotherms for isotherm classifications (Breck's classification), cadmium has a selectivity reversal with an increasing equivalent fraction in the zeolite.

According to the ion exchange isotherms for Cd^{+2}–Na^+ binary exchange on zeolite 4A in previous studies which shows the similarity with these results, zeolite 4A has higher selectivity to cadmium ion than sodium ions [Gal et al., 1970; Biskup and Subotic, 2004].

For these binary ion exchange experiments between Ag^+-Na^+ and Cd^{2+}–Na^+ on zeolite 4A, total exchange capacities for silver-exchanged zeolite and cadmium exchanged zeolite were calculated. Calculations are given in Table C.1 in Appendix C.

Total exchange capacity was found as 5.6 meq/g for Ag^+-Na^+ binary ion exchange for 0.1 g zeolite. Total exchange capacity decreases with increasing zeolite weight. Therefore, the greatest value of total exchange capacity was found at low zeolite weight values. This result is valid for Cd^{2+}-Na^+ binary ion exchange system as well however, total exchange capacity was found as 4.6 meq/g for 0.1 g zeolite. Total ion exchange capacity of zeolite 4A was calculated as 5.7 meq/g from chemical Formula of zeolite 4A. Therefore, calculated total exchange capacities of silver and cadmium exchanged zeolite were acceptable.

Comparison of these two binary ion exchange isotherms in this study, silver and cadmium isotherms lie above the diagonal however, sodium isotherm lies below the diagonal. Therefore, zeolite 4A has higher selectivity to silver and cadmium ions. Selectivity sequence was determined after thermodynamic analyses were done.

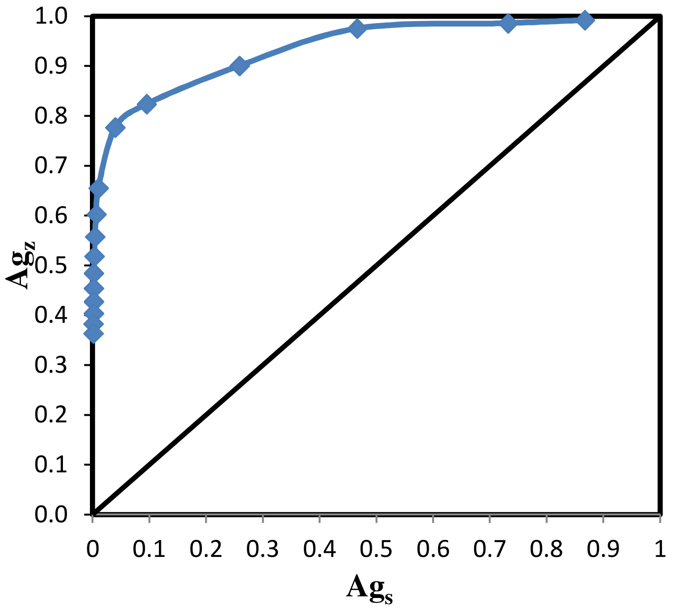

Figure 5.3 Ion exchange isotherm for Ag^+-Na^+ Binary exchange on Zeolite 4A at 25 ^OC and 0.1 N.

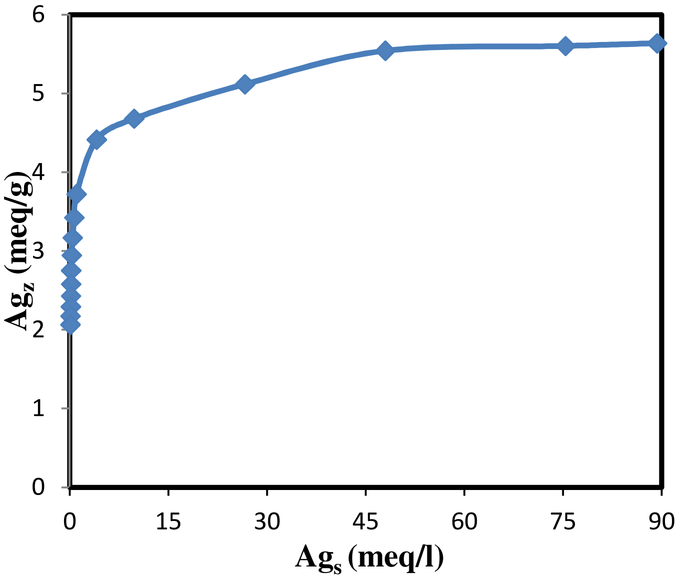

Figure 5.4 Ion exchange isotherm for Ag^+-Na^+ Binary exchange on Zeolite 4A at 25 ^OC and 0.1 N (meq/l vs. meq/g)

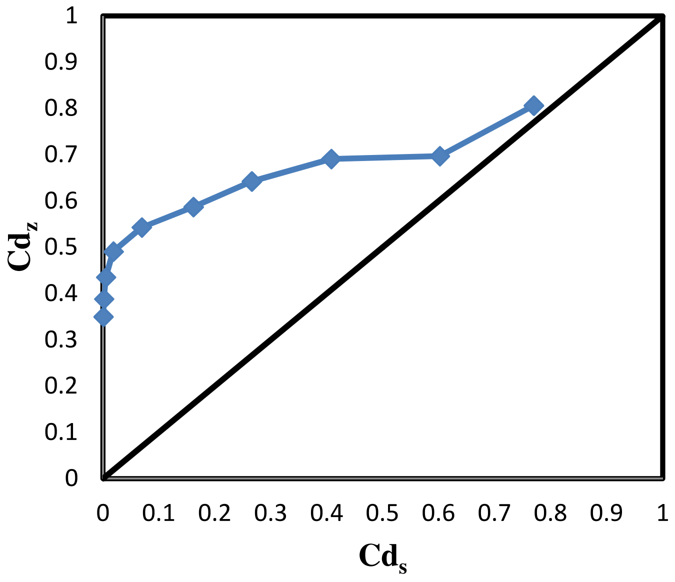

Figure 5.5 Ion exchange isotherm for Cd^{2+}-Na^+ Binary Exchange on Zeolite 4A at 25 ^OC and 0.1 N.

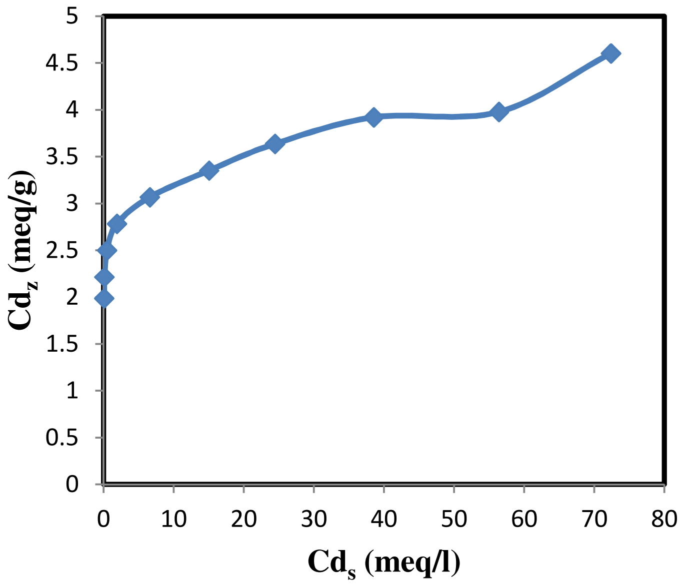

Figure 5.6 Ion Exchange Isotherm for Cd^{2+}-Na^+ Binary Exchange on Zeolite 4A at 25 ^OC and 0.1 N (meq/l vs. meq/g)

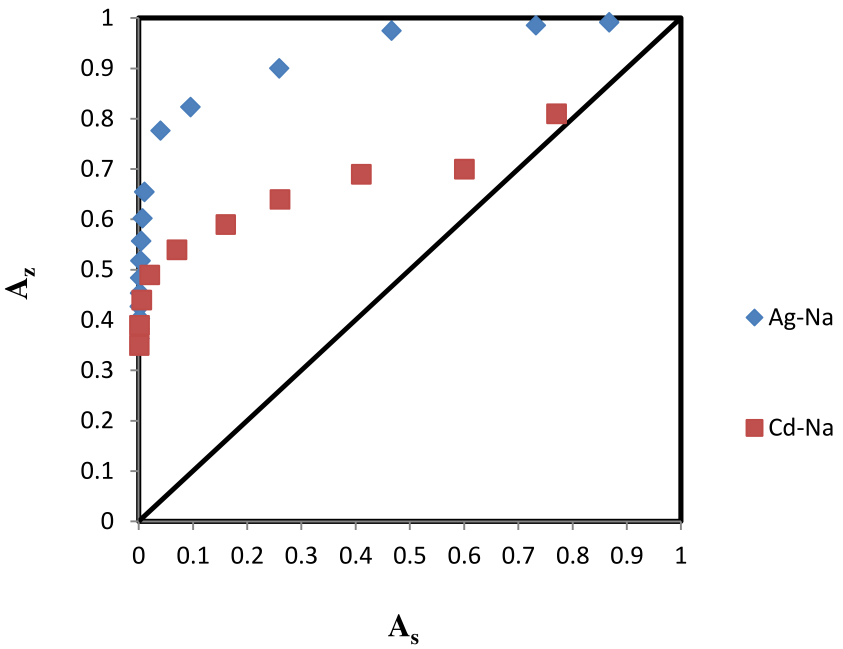

Figure 5.7 Comparison of Ion Exchange Isotherms for Ag^+-Na^+ and Cd^{2+}-Na^+ Binary Exchange on Zeolite 4A at 25 ^{O}C and 0.1 N.

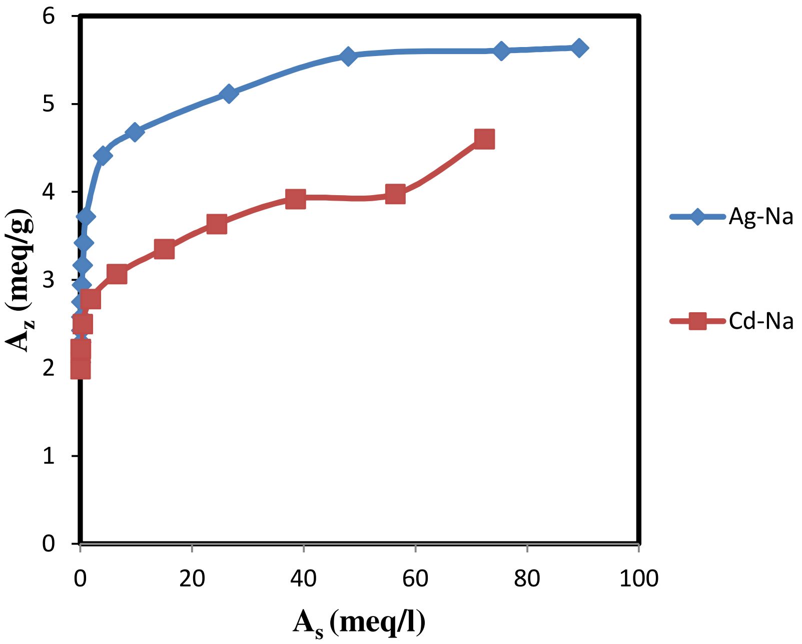

Figure 5.8 Comparison of Ion Exchange Isotherms for Ag^+-Na^+ and Cd^{2+}-Na^+ Binary Exchange on Zeolite 4A at 25 ^{O}C and 0.1 N (meq/l vs. meq/g).

5.4 TERNARY ION EXCHANGE EXPERIMENTS

Ternary ion exchange experiments were done for Ag^+-Cd^{2+}-Na^+ system. Experiments were carried out at 25 °C constant temperature and 0.1 N constant total normality. Zeolite weights were kept constant as 0.4, 0.5 and 0.75 g. Equilibrium time was found as 24 hours for ternary ion exchange system.

Zeolite weight was tried to be kept minumum because at lower zeolite weight total exchange capacity would be maximum and more ions can be exchanged. Trial experiments were performed for different zeolite weights (0.4-0.75g of zeolite).

Triangular ternary ion exchange diagrams are important to determine the weight percent ratio of exchanging ions. Triangular ternary ion exchange diagrams are given in Figure 5.9-5.11. Antibacterial zeolites are prepared using appropriate amount of exchanging ions. As it is known that silver imparts the antibacterial property to zeolite 4A while exchanging sodium ion in zeolite. In ternary experiments, silver which is in mixed solution containing different proportions of cadmium and silver cations can be exchanged with most of sodium ions and the rest of sodium ion can be exchanged with cadmium ion in this mixed solution forming the silver-cadmium exchanged zeolite. In order to obtain these antibacterial zeolites, it is required to know the weight percent of exchanging ions.

Triangular ternary ion exchange diagrams were used to explain which ion is preffered by zeolite 4A. For instance while the concentration proportions of exchanging ions are the same (0.05 N) for 0.5 g zeolite, equivalent fraction of exchanging ions were 0.368, 0.354, 0.278 for Ag^+, Cd^{2+} and Na^+ ions respectively. Consequently, zeolite 4A has higher selectivity to silver ion as the cadmium ion presented in solution.

As a consequence of ternary experiment results, selectivity sequence of zeolite 4A was found as $Ag^+ > Cd^{2+}$ for ternary ion exchange experiments. The amounts of zeolite were chosen greater than 0.4 g due to cadmium ions were inactive in ion exchange at low zeolite weight. At low zeolite weights (in the range between 0.1 g and 0.4 g zeolite) silver ions exchanged with all sodium ions and cadmium ions could not affect the exchange process as expected because of the high selectivity of zeolite 4A to silver ions. The total amount of exchange increases with the decrease in zeolite weight like binary ion exchange experiments.

Exchange capacities of ions were calculated and given in Appendix D and E.

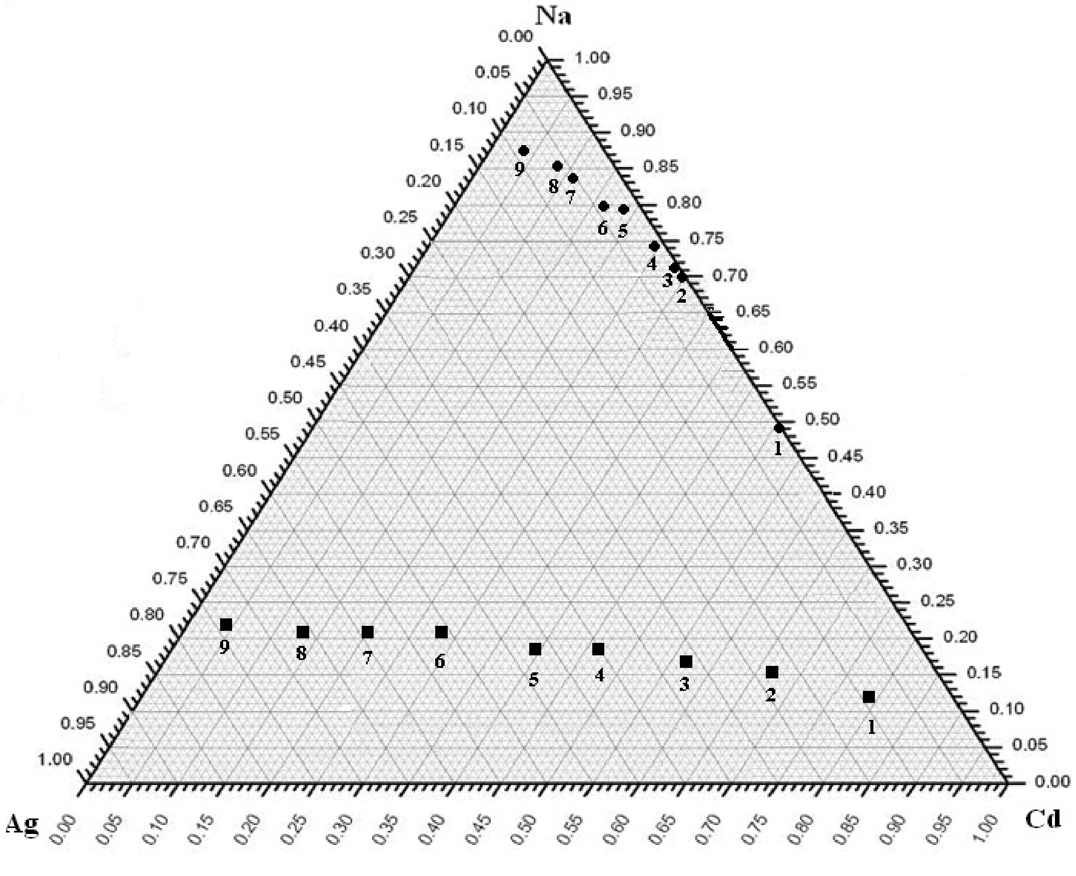

Figure 5.9 Ternary Ion Exchange Isotherm of Ag^+-Cd^{2+}-Na^+ System at Constant Temperature 25 °C and Constant Normality 0.1 N for 0.4 g Zeolite 4A (Squares indicate the equivalent fraction of exchanging ion in zeolite phase (A_z), circles indicate the equivalent fraction of exchanging ion in solution phase (A_s)).

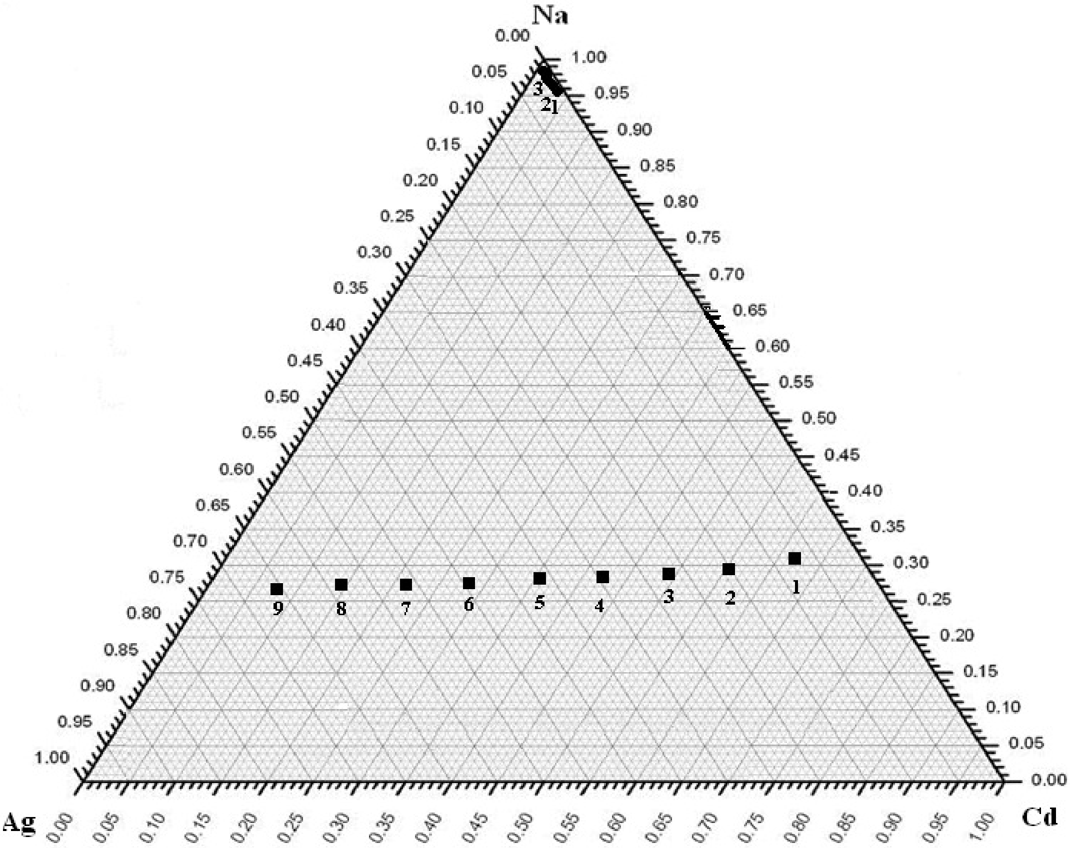

Figure 5.10 Ternary Ion Exchange Isotherm of Ag^+-Cd^{2+}-Na^+ System at Constant Temperature 25 °C and Constant Normality 0.1 N for 0.5 g Zeolite 4A (Squares indicate the equivalent fraction of exchanging ion in zeolite phase (A_z), circles indicate the equivalent fraction of exchanging ion in solution phase (A_s)).

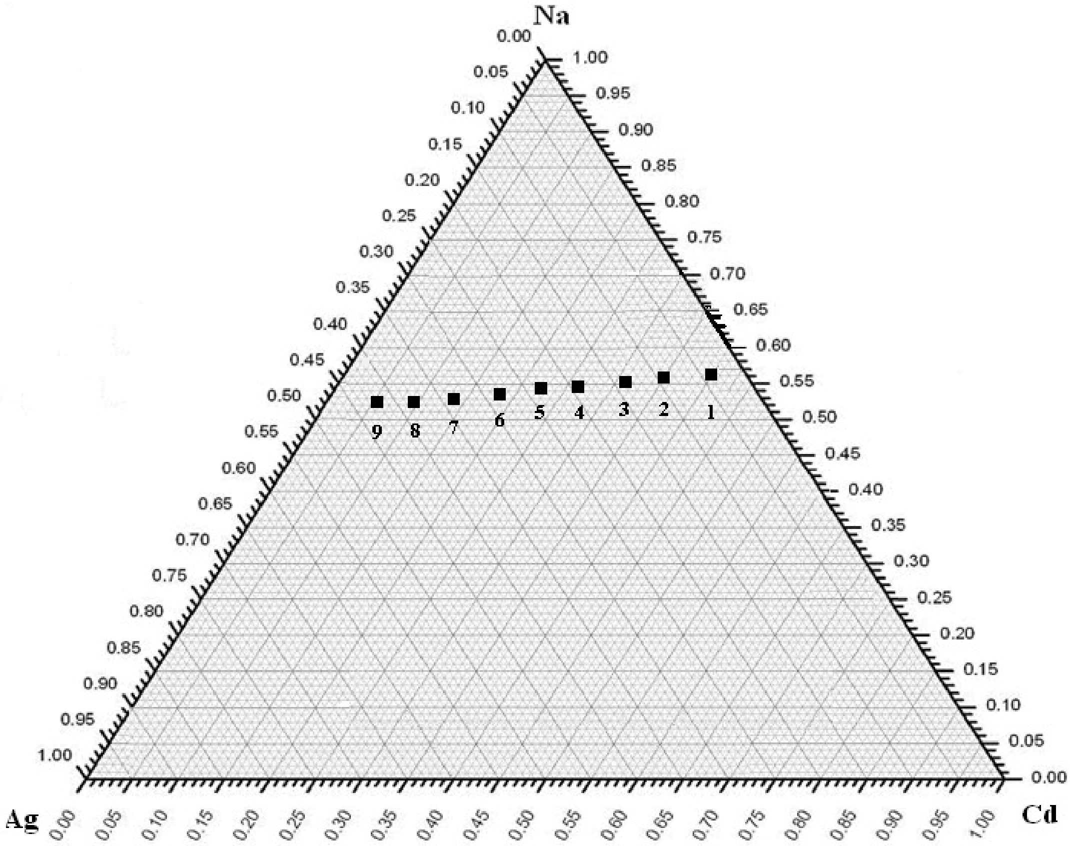

Figure 5.11 Ternary Ion Exchange Isotherm of Ag^+-Cd^{2+}-Na^+ System at Constant Temperature 25 °C and Constant Normality 0.1 N for 0.75 g Zeolite 4A (Squares indicate the equivalent fraction of exchanging ion in zeolite phase (A_z)).

5.5 ADSORPTION ISOTHERMS FOR BINARY ION EXCHANGE

5.5.1 Langmuir Adsorption Isotherm

In order to plot adsorption isotherms of binary ion exchange systems, linearized form of Langmuir equation was used. Langmuir isotherm was plotted $1/q_e$ versus $1/C_e$ and equilibrium constant (K) was found. The slope of the graph was equal to $1/K*q_{max}$ and intercept was equal to $1/q_{max}$.

Calculations are given in Appendix F. Isotherm parameters calculated using linearized adsorption isotherm are given in Table 5.1. In Figure 5.12 and 5.13 Langmuir adsorption isotherms for Ag^+-Na^+ and Cd^{2+}-Na^+ binary ion exchange are given respectively.

Table 5.1 Langmuir Isotherm Parameters for Binary Ion Exchange Systems

Langmuir Isotherm Parameters	Ag^+-Na^+ Binary Ion Exchange System	Cd^{2+}-Na^+ Binary Ion Exchange System
q_{max} (mg/g)	500.00	188.60
K (l/mg)	0.06	0.31
R^2	0.94	0.68

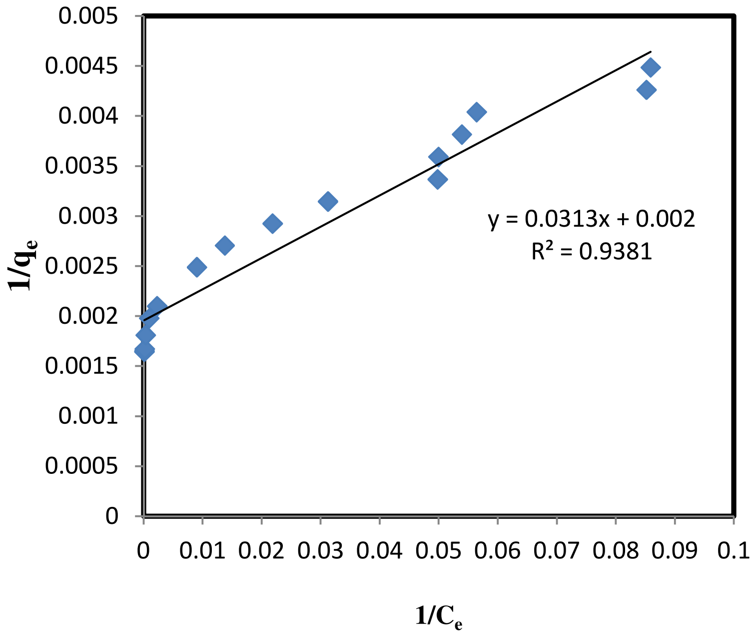

Figure 5.12 Langmuir isotherm of Ag^+-Na^+ Binary Ion Exchange

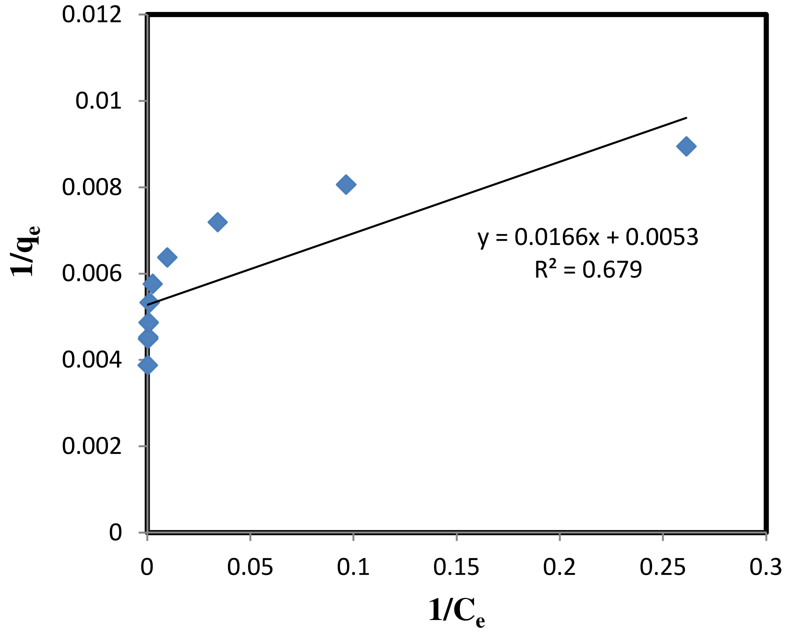

Figure 5.13 Langmuir Isotherm of Cd^{2+}-Na^+ Binary Ion Exchange

5.5.2 Freundlich Adsorption Isotherms

Linearized form of Freundlich equation was used to plot Freundlich adsorption isotherms for binary ion exchange systems. According to this form of equation, the graphs were drawn as ln q_e versus ln C_e and 1/n is constant, K_f is adsorption capacity.

Calculations are given in Appendix F. Isotherm parameters calculated using Freundlich isotherm are given in Table 5.2. Freundlich adsorption isotherms for Ag^+-Na^+ and Cd^{2+}-Na^+ binary ion exchange are given in Figure 5.14 and 5.15 respectively.

Table 5.2 Freundlich Isotherm Parameters for Binary Ion Exchange Systems

Freundlich Isotherm Parameters	**Ag^+-Na^+ Binary Ion Exchange System**	**Cd^{2+}-Na^+ Binary Ion Exchange System**
K_f (l/g)	183.300	95.500
n	7.147	9.345
R^2	0.943	0.977

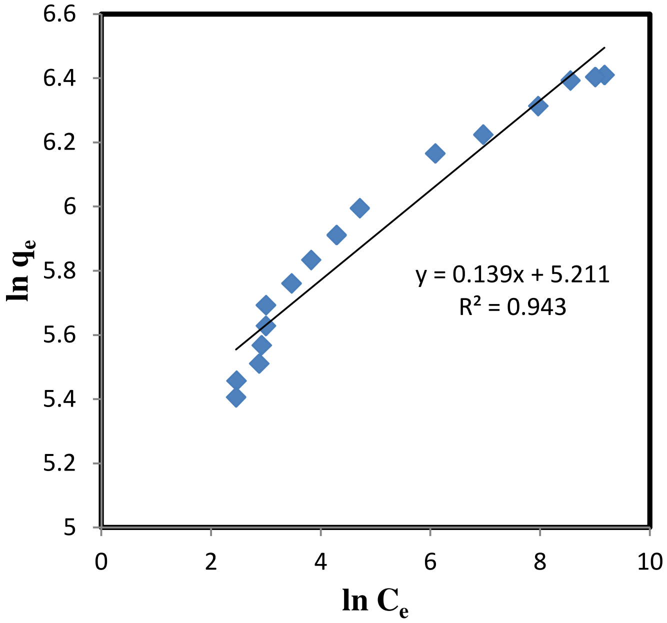

Figure 5.14 Freundlich Isotherm for Ag^+-Na^+ Binary Ion Exchange

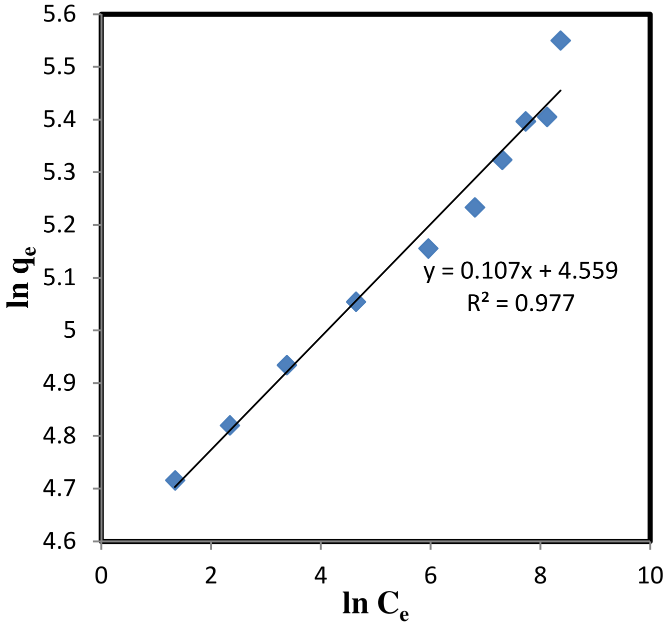

Figure 5.15 Freundlich Isotherm for Cd^{2+}-Na^+ Binary System

When the R^2 values of isotherms are compared, it is clearly seen that Freundlich isotherm appears to provide better fit for Cd^{2+}-Na^+ binary ion exchange system and Ag^+-Na^+ binary ion exchange system.

Langmuir isotherm model indicated that binding sites are homogeneously distributed over the adsorbent surface. These binding sites have the same selectivity for adsorption of a single molecular layer. This model shows that there is no interaction between adsorbed molecules. This model does not appear to provide better fit for both binary ion exchange systems. As a result of this, there is no homogeneous distribution over the exchanger surface in both ion exchange systems between Ag^+-Na^+ and Cd^{2+} -Na^+.

Freundlich model is the better model for binary ion exchange system between Cd^{2+}-Na^+ and Ag^+-Na^+. This model indicates that the binding sites are heterogeneously distributed over the exchanger surface.

El-Kamash et al.(2005) studied on “Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A”. Freundlich isotherm provided best fit for cadmium ion in this study.

Papageorgiou et al.(2009) studied on “Prediction of binary adsorption isotherms of Cu^{2+}, Cd^{2+} and Pb^{2+} on calcium alginate beads from single adsorption data.In this study, they found that Freundlich isotherm provides best fit for cadmium ions.

It’s seen from the results of these two studies, Freundlich isotherm appears to provide best fit for cadmium ion. As it is seen from table 5.1, correlation coefficient of Langmuir isotherm for Cd^{2+}-Na^+ exchange is very low so Langmuir isotherm does not appears to provide better fit for this system due to the heteregenity on the exchanger surface during ion exchange process.

5.6 THERMODYNAMIC ANALYSES OF BINARY ION EXCHANGE SYSTEMS

Activity coefficients of salt solutions were calculated using Debye-Hückel and Glueckauf's equations. Debye-Hückel equation includes some variables. These are constants a and b and ionic strength. Analytical activity coefficients were used and taken from a table which was given by Stokes and Robinson (1959). [Stokes and Robinson, 1959].

In the Debye-Hückel equation, A and B are the Debye-Hückel constants. These variables change with respect to temperature. I is the ionic strength and it's related to concentration of each ion present in solution and charge of the ions.

Appropriate values of concentration, analytical activity coefficients and ionic strengths which were given by Stokes and Robinson (1959) for 25 ^{o}C were used in Debye-Hückel equation in order to mean activity coefficients of cation in single salt solution. In this equation there are two variables, a and b. Two equation were obtained for two different ionic strength and activity coefficient value. In the first equation obtained, a is expressed in terms of b. This expression was put into second equation obtained and second equation contains a variable "a" and it's solved in terms of "a". After this solution, "b" was found. These constants were found for each ion present in solution.

After calculating all ion concentrations; ionic strengths and activity coefficients were found using Debye-Hückel equation. For binary ion exchange systems, in order to calculate activity coefficient of mixed salt solutions Glueckauf's equation was used. Solution non-ideality factor was determined using activity coefficient of salt solutions. All thermodynamic calculations and data are given Appendix G.

As it is seen from the Figure 5.16 and Figure 5.17 solution non-ideality correction factor increases with the increase in concentration of ions in solution for divalent-univalent exchange. However, univalent-univalent exchange this factor does not change and does not affect the selectivity coefficient (K_c).

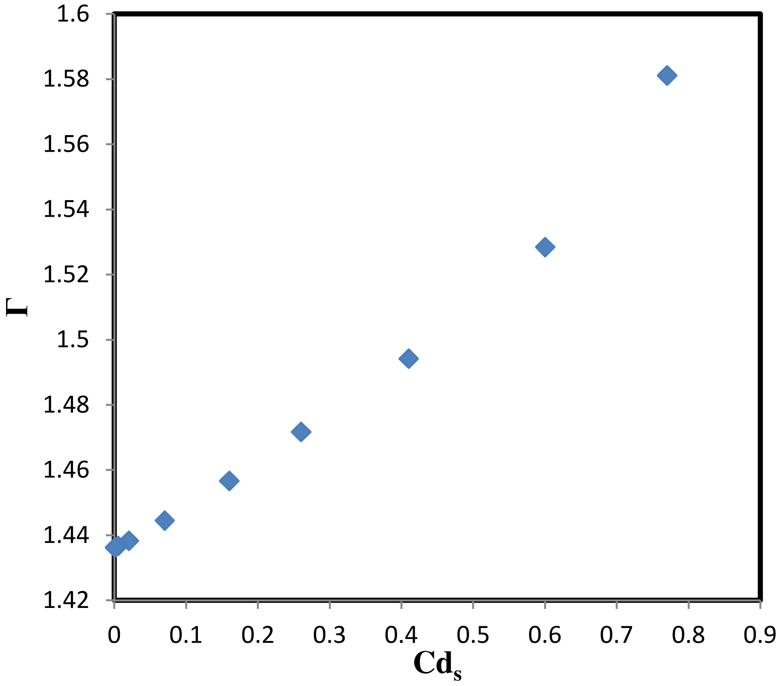

Figure 5.16 Change in Solution Non-Ideality Correction Factor with respect to Equivalent Fraction of Cadmium Ion in Solution for Cd^{2+}-Na^{+} Binary Ion Exchange System.

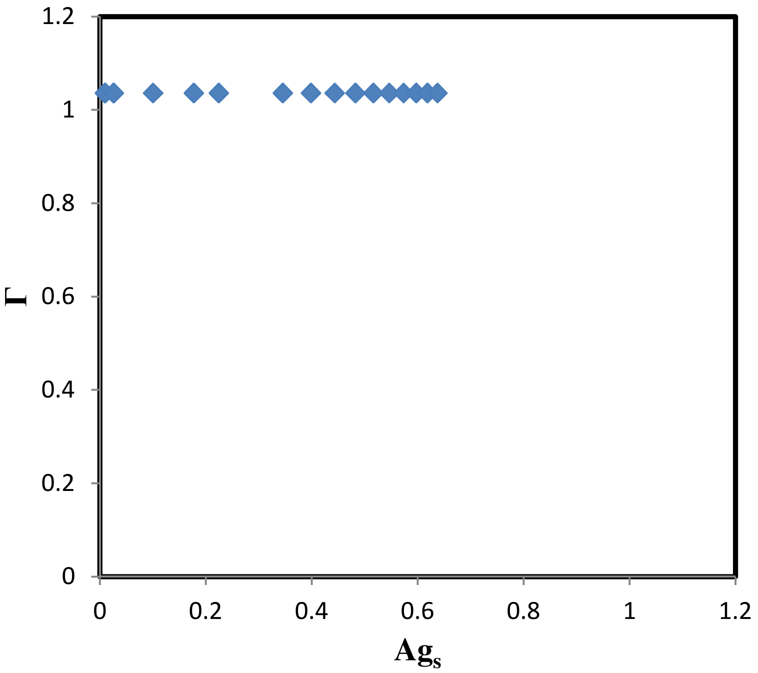

Figure 5.17 Change in Solution Non-Ideality Correction Factor with respect to Equivalent Fraction of Silver Ion in Solution for Ag^+-Na^+ Binary Ion Exchange System.

In order to calculate Gibbs free energy of binary ion exchange, thermodynamic equilibrium constant which is related to mass action quotient and Kielland quotient was found. Thermodynamic equilibrium constant was calculated with the help of Kielland plot which was drawn as ln K_c (selectivity coefficient) versus A_z (equivalent fraction of the exchanging ion in zeolite phase).

For binary ion exchange between Ag^+-Na^+ and Cd^{2+}-Na^+, Kielland plot shows straight line. Both ions have the same energy during ion exchange. As a result, majority sites which participated in ion exchange reactions have the same energy and there are same exchange sites in all cages [Barros and Arroya, 2004].
Kielland plots for binary ion exchange systems between Cd^{2+}-Na^+ and Ag^+-Na^+ was given in Figure 5.18 and Figure 5.19.

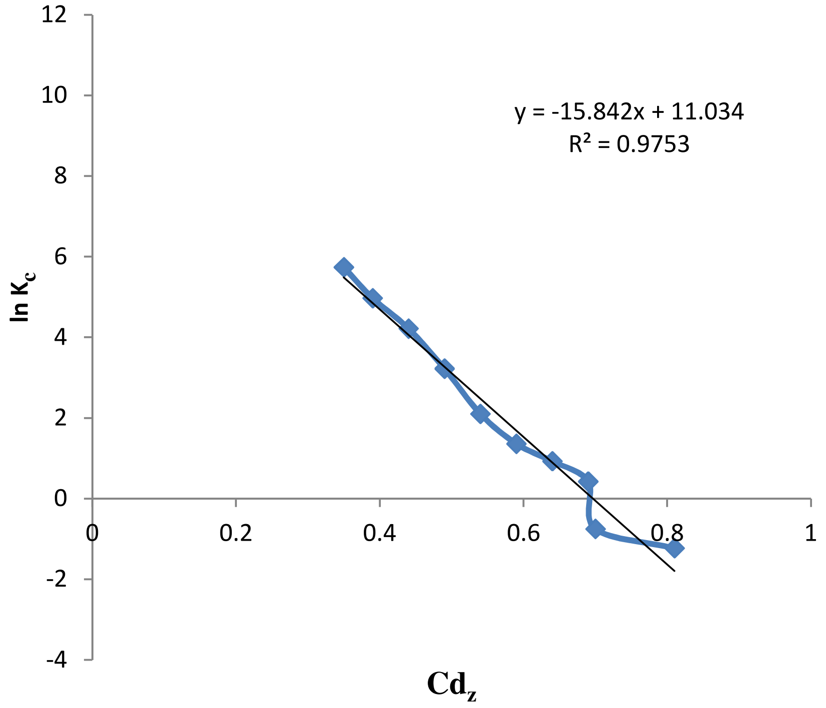

Figure 5.18 Kielland Plot for Cd^{2+}-Na^{+} Binary Ion Exchange System

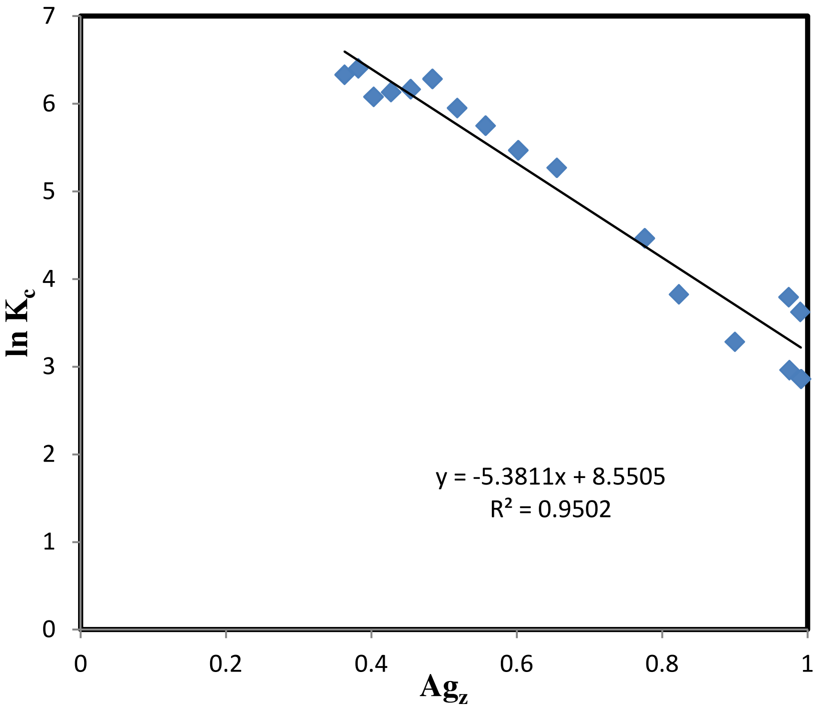

Figure 5.19 Kielland Plot for Ag^+-Na^+ Binary Ion Exchange System

Thermodynamic equilibrium constants were found as 28.22 and 300.44 for binary ion exchange between Cd^{2+}-Na^+ and Ag^+-Na^+ ions respectively at constant 25 °C temperature.

Gibbs free energies for binary ion exchange between Cd^{2+}-Na^+ and Ag^+-Na^+ ions were found as -4.139 kj/mol and -14.141 kj/mol respectively. If ΔG^O is negative, it means that ion exchange reaction is spontaneous and there is a sufficient amount of molecular interactions such that there is no energy required to increase the interactions. According to calculated Gibbs free energy value for binary ion exchange between Cd^{2+}-Na^+ ions and Ag^+-Na^+ ions, zeolite 4A has higher affinity to silver ions than cadmium ions. As a result for both binary ion exchange systems the physical meaning of negative value of standard free energy is related to the higher affinity of Zeolite 4A to Cd^{2+} and Ag^+ ions.

Biskup and Subotic (2010) and Gal et al.(1970) studied on thermodynamics of the exchange processes between Cd^{2+}-Na^{+} ions. In this study they investigated thermodynamics of ion exchange between Cd^{2+}-Na^{+} ions. The results found in their study and this study are given in Table 5.3.

Table 5.3 Comparison of Thermodynamic Data Between Previous Studies and Present Study at Constant Normality 0.1 N for Cd^{2+}-Na^{+} Binary Ion Exchange System.

Thermodynamic Data	**Present Study**	**Biskup et al., 2010**	**Gal et al., 1970**
Temperature (K)	298	293	298
K_a	28.22	21.89	38.54
ΔG^{O} (kj/mol)	-4.139	-3.76	-4.463

In a previous study, Ay (2008) investigated the thermodynamic properties of binary ion exchange between Ag^{+}-Na^{+} ions. The comparison of thermodynamics results is given in Table 5.4.

Table 5.4 Comparison of Thermodynamic Data Between Present Study and Previous Study at Constant Temperature 25 °C and Constant Normality 0.1 N for Ag^+-Na^+ Binary Ion Exchange.

Thermodynamic Data	**Present Study**	**Ay 2008**
Temperature (K)	298.00	298.00
K_a	300.44	340.89
ΔG^O (kj/mol)	-14.14	-14.46

According to thermodynamic analyses results, the largest free energy decrease was observed in Ag^+-Na^+ binary ion exchange and as a result of this selectivity sequence of zeolite 4A was found as follows; $Ag^+ > Cd^{+2}$.

The another important point in ion exchange is to determine preference the zeolite 4A exhibits one ion over other ion In general hydrated radius is inversely related to cation radius and divalent cations usually have smaller cation radius than univalent cations.

Exchangable alkaline cations are required to balance the framework charge. When these cations encounter water molecules, hydration spheres occur. Divalent alkaline cations have smaller cation radius. Due to the hydration radius is inversely proportional to cation radius, these divalent cations can not move out of the channels easily [Top and Ülkü, 2004].

The pore size of zeolite 4A is 4A°. If the hydrated pore size of the exchangable cations in solution is less than the pore size of zeolite 4A, these cations can enter the pores easily and quickly than other ions. As it is seen from the Table 5.5, the hydrated radius of silver ions is less than the pore size of zeolite 4A and besides, its hydrated radius is less than the hydrated radius of cadmium ions as well. On the other hand, the hydrated radius of cadmium ions are greater than the pore size of zeolite 4A, so they can not enter the pores easily such as silver ions.

In order to determine the selectivity sequence according to radius of ions. the hydrated radius is considered because metals always interact with water molecules in solution phase and hydration spheres occur before they enter in the pores. According to results given in Table 5.5, selectivity sequence can be given as Ag^+>Cd^{+2}. The same result obtained as a result of thermodynamic analyses and binary ion exchange experiments as well.

Table 5.5 Cation Radius and Hydrated Radius of Ions [Volkov et al., 1997]

Ions	**Cation Radius (A^o)**	**Hydrated Radius(A^o)**
Ag^+	1.26	3.41
Cd^{2+}	0.97	4.26

CHAPTER 6

CONCLUSIONS

Binary and ternary ion exchange experiments for silver and cadmium ions on zeolite 4A were investigated. Both experiments were conducted at constant temperature 25 ^{o}C and constant total normality 0.1N in batch system.

Zeolite 4A was chosen as ion exchanger in this study because Si/Al ratio of zeolite 4A is low, it means that more sodium ions release and zeolite 4A has higher cation exchange capacity than other types of zeolites as a results of these property of zeolite 4A, ion exchange will be better.

According to binary ion exchange experiments results, zeolite 4A has higher selectivity to silver than cadmium. Examining Townsend and Breck's isotherm classifications, zeolite 4A has selectivity to silver ion due to the isotherms lie above the diagonal. Zeolite 4A has selectivity to cadmium ion as well however, zeolite 4A has not selectivity to cadmium as much as silver due to isotherm classification because silver isotherm lies above the isotherm of cadmium.

In ternary ion exchange experiments, zeolite weights were kept constant, however, solution volume was changed. It is known that, zeolite 4A has higher selectivity to silver ion than cadmium ion and as a result of this, silver exchanged zeolite can be used in antibacterial agents. In this applications, all silver can not be exchanged and trace ions can be left in solution. These trace elements can be exchanged with other ions participated in solution phase such as cadmium. Ternary ion exchange results showed that when the stock solution volume of both ions are equal to each other, zeolite 4A has showed higher selectivity to silver ion than cadmium ion. This phenomena can be concluded that cadmium ions can be exchanged with trace elements left in solution phase and silver-cadmium exchanged zeolite for using antibacterial purposes can be obtained. On the other hand, silver can not kill all types of bacterias and in this situation, the rest of bacterias in solution can be killed by cadmium ions.

Equlibrium experiment data were used to plot adsorption isotherms such as Langmuir and Freundlich isotherms. Examining the R^2 values of isotherms, Freundlich isotherm appears to provide better fit for both Cd^{2+}-Na^+ binary ion exchange system and Ag^+-Na^+ binary ion exchange system. From these results, heteregeneous distribution on exchanger surface was obtained in Cd^{2+}-Na^+ and Ag^+-Na^+ binary ion exchange experiments.However, correlation factor of Langmuir and Freundlich isotherm for Ag^+-Na^+ binary ion exchange are close to each other and it can be said that Langmuir isotherm appears to provide better fit to Ag^+-Na^+ binary system as well.

Solution non ideality correction factor does not change with respect to equivalent fraction of silver in solution phase. Actually, solution is not ideal for electrolyte solutions due to the non-ideal nature of ions in solution. However, in this study solution behaves like ideal solution because there is an univalent-univalent exchange between silver and sodium ion.

Thermodynamic analyses was done for binary ion exchange experiments. Thermodynamic equilibrium constants and Gibbs free energies for both system were calculated. The largest decrease in Gibbs free energy was examined in Ag^+-Na^+ binary ion exchange as compared to Cd^{2+}-Na^+ binary results. As a result of thermodynamic analyses, zeolite 4A has higher affinity to silver ion than cadmium ion. Ion exchange reactions between Ag^+-Na^+ and Cd^{2+}-Na^+ occur simultaneously and there is no need to extra energy from outer space due to the Gibbs Free Energy values. In addition to thermodynamic analyses, since the hydrated cation radius of silver ion is smaller than pore size of zeolite 4A, zeolite 4A has showed higher affinity to silver ion than cadmium ion as well and silver can enter the pores easily.

Separation factors were determined for both Ag^+-Na^+ and Cd^{2+}-Na^+ binary ion exchange and as a result of this, zeolite 4A shows higher selectivity to silver than cadmium because separation factor was found as greater than 1 for Ag^+-Na^+ binary system. As a consequence of all analyses selectivity sequence of zeolite 4A was determined as $Ag^+>Cd^{2+}$.

CHAPTER 7

RECOMMENDATIONS

In this study, ion exchange behaviour of silver and cadmium ion on zeolite 4A was determined in ternary and binary ion exchange experiments at constant temperature and constant normality. Besides, thermodynamic analyses of binary ion exchange systems was investigated. As a result of this study, zeolite 4A showed the higher selectivity to these heavy metals and they impart the antibacterial property to zeolite 4A.

There are several heavy metals which can impart antibacterial property to zeolite 4A such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium, and thallium. The ion exchange behaviour of these heavy metals in single or mixed solution can be investigated.

Experiments were carried out at constant temperature 25 ^{o}C and constant normality 0.1N. The effect of solution volume on ion exchange can be investigated. Temperature and normality effect on ion exchange can be examined.

Biological tests can be applied on metal exchanged zeolite 4A and antibacterial activity of zeolite can be determined with regard to different composition.

In this study, thermodynamic analyses was done only for binary ion exchange systems and this analyses can be extended to ternary ion exchange experiments.

The kinetic analyses of ion exchange processes can be done in order to understand the ion exchange mechanism and design the systems including the ion exchange processes. Different adsorption isotherm models which can be applied for silver and cadmium ion exchange on zeolite 4A can be investigated to find the best model which describes the observed equilibrium data.

The ion exchange behaviour of these heavy metals on different types of zeolites can be examined.

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APPENDIX A

EXCHANGE CAPACITY

The commercial zeolite 4A has the following chemical formula;

$Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]nH_2O$

Molecular weights of the atoms in the zeolite content

Na = 22.9898 g/mol
Si = 28.0855 g/mol
Al = 26.9815 g/mol
O = 15.9994 g/mol
H = 1.0079 g/mol

Molecular weight of the zeolite 4A;

$= 12*Na + 12*Si + 12*Al + 48*O + n*(2*H + O)$
$= 12*22.9898 + 12*28.0855 + 12*26.9815 + 48*15.9994 + n*(2*1.0079 + 15.9994)$
$= 1704.6528 + n*18.0528$

TGA analyses was done in order to find out the water content of the zeolite. Moisture content of the zeolite was found as 19.27 wt % from TGA analyses.

$((14.31-11.58)/14.31)*100=19.268$ wt%
$n*18.0152/(1704.6528+n*18.0152)*100=19.268$
$n=22.583$

Molecular weight of zeolite = 1704.6528 + 22.583x18.0512 = 2111.49 g/mol

Molecular weight of hydrated 4A zeolite = 2111.49 g/mol

Molecular weight of unhydrated 4A zeolite = 1704.65 g/mol

Exchange Capacity=($12*10^3$ meq/mol Na)/(2111.49g/mol)=5.7 meq/g hydrated 4A zeolite

Exchange Capacity=($12*10^3$ meq/mol Na)/(1704.65g/mol)=7.0 meq/g unhydrated 4A zeolite

APPENDIX B

CALCULATIONS OF EQUIVALENT FRACTIONS FOR BINARY ION EXCHANGE

Sample calculation for silver nitrate is given below in order to find the amount of Ag(NO3) to prepare for stock solution;

$M_{AiAg(NO3)}$= 169.87 g/mol **.** M_{AAg}=107.868 g/mol

$$0.1\frac{eq}{L}*\frac{1mol}{1eq}*\frac{107.868*10^{+3}mg\ \mathrm{Ag}^{+}}{1mol}=10786.8\frac{mg}{L}=10786.8ppm$$

$$x\frac{g\ \mathrm{Ag(NO_3)}}{L}*\frac{107.868g\ \mathrm{Ag}}{169.87g\ \mathrm{Ag(NO_3)}}*\frac{1000mg}{1g}=10786.8\frac{mg}{L}$$

$$x=16.987g\ \mathrm{Ag(NO_3)}$$

16.987 g of Ag(NO3) should be added into the 1 lt of solution in order to prepare 10787 ppm of stock solution. However prepared stock solution is found as 11153.7 ppm and 0.103 N.

This is the sample calculation for Ag^+-Na^+ binary system at constant normality 0.103 N and constant temperature 25 ^{o}C. Zeolite weight is 0.2 g and solution volume was 20 ml. Equilibrium concentration of silver was 5175 ppm.

$$A_s=\frac{Normality\ of\ Exchanging\ Cation\ A}{Total\ Normality}$$

$$\mathrm{Ag_s}\frac{\dfrac{5175\ \dfrac{\mathrm{mg}}{\mathrm{L}} * \dfrac{1\mathrm{g}}{1000\mathrm{mg}}}{107.868\dfrac{\mathrm{g}}{\mathrm{mol}} * \dfrac{1\mathrm{mol}}{1\mathrm{eq}}} * 0.02\mathrm{L}}{0.103\dfrac{\mathrm{eq}}{\mathrm{L}} * 0.02\mathrm{L}} = 0.466$$

$$A_z = \frac{Equivalent\ of\ Exchanging\ Cation\ A\ in\ Zeolite}{Total\ Equivalents\ of\ Cations\ \ in\ Zeolite}$$

$$\mathrm{Ag_z} = \frac{(11153.8 - 5175)\dfrac{\mathrm{mg}}{\mathrm{L}} * 0.02\mathrm{l} * \dfrac{1\mathrm{mol}}{107868\mathrm{mg}} * \dfrac{1\mathrm{eq}}{1\mathrm{mol}} * \dfrac{1000\mathrm{meq}}{1\mathrm{eq}}}{0.2\mathrm{g} * \dfrac{5.687\mathrm{meq}}{\mathrm{g}}}$$

=0.975

$$\mathrm{E_{c_{Ag}}} = \frac{(11153.8 - 5175)\dfrac{\mathrm{mg}}{\mathrm{L}} * 0.02\mathrm{l} * \dfrac{1\mathrm{mol}}{107868\mathrm{mg}} ** \dfrac{1\mathrm{eq}}{1\mathrm{mol}} * \dfrac{1000\mathrm{meq}}{1\mathrm{eq}}}{0.2\mathrm{g}}$$

=5.543 meq/g

APPENDIX C

Ag^+-Na^+ and Cd^{2+}-Na^+ BINARY ION EXCHANGE DATA

Table C.1 Experimental Data for Ag^+-Na^+ Binary Ion Exchange on Zeolite 4A at constant Normality 0.1 N and constant Temperature 25 °C.

Zeolite Weight(g)	**m_{Ag}(ppm)**	**Ag_z**	**Ag_s**	**E_c (meq/g)**	**pH**
0.05	9633.300	0.992	0.867	5.638	5.94
0.10	8131.600	0.986	0.732	5.603	6.73
0.20	5175.000	0.975	0.466	5.543	6.63
0.30	2872.800	0.901	0.259	5.118	6.65
0.40	1055.000	0.824	0.095	4.681	6.38
0.45	440.000	0.777	0.040	4.414	6.93
0.55	111.088	0.655	0.010	3.723	8.13
0.60	72.752	0.603	0.007	3.424	8.45
0.65	45.800	0.558	0.004	3.169	8.99
0.70	32.031	0.518	0.003	2.946	8.91
0.75	20.080	0.484	0.002	2.752	9.28
0.80	20.027	0.454	0.002	2.580	9.23
0.85	18.550	0.427	0.002	2.429	9.44
0.90	17.728	0.404	0.002	2.294	9.33
0.95	11.740	0.383	0.001	2.175	9.56
1.00	11.643	0.364	0.001	2.066	9.56

Table C.2 Experimental Data for Cd^{2+}-Na^{+} Binary Ion Exchange on Zeolite 4A at constant Normality 0.1 N and constant Temperature 25 °C.

Zeolite Weight (g)	**m_{Cd} (ppm)**	**Cd_z**	**Cd_s**	**E_c (meq/g)**	**pH**
0.1	4301.00	0.806	0.770	4.580	6.73
0.2	3362.75	0.697	0.602	3.961	6.63
0.3	2278.80	0.691	0.408	3.927	6.65
0.4	1485.00	0.642	0.266	3.648	6.88
0.5	902.35	0.587	0.161	3.336	8.13
0.6	386.45	0.543	0.069	3.086	8.45
0.7	103.44	0.491	0.019	2.790	8.91
0.8	29.33	0.435	0.005	2.472	9.23
0.9	10.38	0.388	0.002	2.205	9.33
1.0	3.82	0.350	0.001	1.989	9.56

APPENDIX D

CALCULATIONS OF EQUIVALENT FRACTIONS FOR TERNARY ION EXCHANGE

This is a sample calculation for equivalent fraction of silver in zeolite phase for Ag^+-Cd^{2+}-Na^+ ternary ion exchange experiment at constant normality 0.1 N and constant temperature 25 °C. Zeolite weight was 0.5 g. When the normality of silver was 0.02N. normality of cadmium was 0.08N and total normality was still 0.1N. Equilibrium concentration of silver was 20.02 ppm. Stock solution of silver was 11350 ppm.

The equations which are given in Appendix B were used in order to calculate equivalent fractions for ternary ion exchange.

$$Ag_s = \frac{\frac{20.02\,mg}{L} * 0.002\,L * \frac{1mol}{107.868\,g} * \frac{1g}{1000mg} * \frac{1\,eq}{1mol}}{0.105\frac{eq}{L} * 0.002L} = 0.001$$

$$Ag_z = \frac{(11350 - 20.09)\frac{mg}{L} * 0.004L * \frac{1mol}{107.868g} * \frac{1g}{1000mg} * \frac{1eq}{1mol} * \frac{1000meq}{1eq}}{0.5\,g * \frac{5.683meq}{g}}$$
$$= 0.15$$

APPENDIX E

Ag^+-Cd^{2+}-Na^+ TERNARY ION EXCHANGE DATA

Table E.1 Ternary Ion Exchange Data for Ag^+-Cd^{2+}-Na^+ system at constant normality 0.1 N and constant temperature 25 °C(Zeolite weight=0.4 g).

Normality Ag (N)	**Normality Cd(N)**	**m_{Ag} (ppm)**	**m_{Cd} (ppm)**	**E_{CAg} (meq/g)**	**E_{CCd} (meq/g)**
0.01	0.09	18.43	2941.7	0.51	4.48
0.02	0.08	49.91	1674.6	1.01	3.79
0.03	0.07	114.55	1615.6	1.50	3.22
0.04	0.06	157.67	1369.6	2.00	2.60
0.05	0.05	266.15	1086.05	2.47	2.10
0.06	0.04	479.30	935.35	2.90	1.58
0.07	0.03	603.10	625.8	3.35	1.12
0.08	0.02	720.00	470.55	3.78	0.73
0.09	0.01	983.80	205.47	4.15	0.25

Table E.2 Equivalent Fractions of Silver and Cadmium in Zeolite and Solution Phase for Ag^+-Cd^{2+}-Na^+ Ternary Ion Exchange (Zeolite weight=0.4 g).

Ag_z	Cd_z	Na_z	Ag_s	Cd_s	Na_s
0.089	0.788	0.123	0.002	0.507	0.491
0.177	0.667	0.155	0.005	0.289	0.706
0.265	0.567	0.168	0.010	0.279	0.711
0.351	0.457	0.192	0.014	0.236	0.75
0.435	0.369	0.196	0.024	0.187	0.789
0.511	0.277	0.211	0.044	0.161	0.795
0.589	0.197	0.214	0.055	0.108	0.837
0.666	0.129	0.205	0.066	0.081	0.853
0.730	0.045	0.226	0.090	0.035	0.875

Table E.3 Ternary Ion Exchange Data for Ag^+-Cd^{2+}-Na^+ system at constant normality 0.1 N and constant temperature 25 °C (Zeolite weight=0.5 g).

Normality Ag (N)	**Normality Cd(N)**	**m_{Ag} (ppm)**	**m_{Cd} (ppm)**	**E_{CAg} (meq/g)**	**E_{CCd} (meq/g)**
0.01	0.09	8.11	252.70	0.42	3.52
0.02	0.08	20.02	209.79	0.84	3.15
0.03	0.07	30.99	181.90	1.26	2.77
0.04	0.06	30.71	112.06	1.68	2.41
0.05	0.05	69.41	95.41	2.09	2.01
0.06	0.04	92.41	57.83	2.50	1.62
0.07	0.03	129.46	36.82	2.91	1.22
0.08	0.02	148.19	16.02	3.32	0.82
0.09	0.01	159.75	11.44	3.73	0.41

Table E.4 Equivalent Fractions of Silver and Cadmium in Zeolite and Solution Phase for Ag^+-Cd^{2+}-Na^+ Ternary Ion Exchange (Zeolite weight=0.5 g).

Ag_z	Cd_z	Na_z	Ag_s	Cd_s	Na_s
0.074	0.620	0.306	0.001	0.044	0.955
0.148	0.555	0.297	0.002	0.036	0.962
0.222	0.488	0.290	0.003	0.032	0.966
0.295	0.424	0.281	0.003	0.019	0.978
0.368	0.354	0.278	0.006	0.017	0.977
0.441	0.285	0.274	0.008	0.010	0.982
0.513	0.215	0.273	0.011	0.006	0.982
0.585	0.144	0.272	0.013	0.003	0.984
0.657	0.072	0.271	0.014	0.002	0.984

Table E.5 Ternary Ion Exchange Data for Ag^+-Cd^{2+}-Na^+ system at constant normality 0.1 N and constant temperature 25 °C (Zeolite weight=0.75 g).

Normality Ag (N)	**Normality Cd(N)**	**m_{Ag} (ppm)**	**m_{Cd} (ppm)**	**E_{CAg} (meq/g)**	**E_{CCd} (meq/g)**
0.01	0.09	1.31	17.75	0.42	3.52
0.02	0.08	4.41	13.54	0.84	3.15
0.03	0.07	7.08	8.81	1.26	2.77
0.04	0.06	8.52	4.98	1.68	2.41
0.05	0.05	11.67	2.36	2.09	2.01
0.06	0.04	14.90	1.75	2.50	1.62
0.07	0.03	15.57	1.10	2.91	1.22
0.08	0.02	16.45	0.58	3.32	0.82
0.09	0.01	16.64	0.33	3.73	0.41

Table E.6 Equivalent Fractions of Silver and Cadmium in Zeolite and Solution Phase for Ag^+-Cd^+-Na^+ Ternary Ion Exchange (Zeolite weight=0.75 g).

Ag_z	Cd_z	Na_z	Ag_s	Cd_s	Na_s
0.047	0.396	0.557	0.000	0.003	0.997
0.094	0.352	0.554	0.000	0.003	0.997
0.141	0.308	0.550	0.001	0.002	0.998
0.188	0.265	0.547	0.001	0.001	0.998
0.235	0.221	0.544	0.001	0.000	0.998
0.282	0.177	0.541	0.001	0.000	0.998
0.329	0.132	0.538	0.001	0.000	0.998
0.377	0.088	0.535	0.002	0.000	0.998
0.424	0.044	0.532	0.002	0.000	0.998

APPENDIX F

ADSORPTION ISOTHERMS FOR BINARY ION EXCHANGE

Langmuir isotherm equation and its linear form is given in below;

$$q_e = \frac{q_{max}*K*C_e}{1+K*C_e} \tag{F.1}$$

$$\frac{1}{q_e} = \frac{1}{K*q_{max}*C_e} + \frac{1}{q_{max}} \tag{F.2}$$

The graph is plotted $1/q_e$ versus $1/C_e$ in order to find energy of adsorption (K).The slope of the graph is equal to $1/K*q_{max}$ and intercept is equal to $1/q_{max}$.

q_e = (Initial concentration – equilibrium concentration) * Solution volume / Absorbate weight (F.3)

q_e = mass of material adsorbed at equilibrium per mass of adsorbent (mg/g)

C_e = equilibrium concentration in solution (mg/L)

K = energy of adsorption (L/mg)

q_{max} = maximum adsorption capacity (mg/g)

Sample Calculations are given below;

$1/q_{max}$=0.002 (from Figure 5.12) q_{max}=500 mg/g

$1/q_{max}$= 0.0053 (from Figure 5.13) q_{max}=188.679 mg/g

$1/K*q_{max}$= 0.0313 (from Figure 5.12) K=0.0638 L/mg

$1/K*q_{max}$= 0.0166 (from Figure 5.13) K=0.319 L/mg

Table F.1 Adsorption Data for Ag^+-Na^+ Binary Ion Exchange for Langmuir Isotherm

Zeolite Weight (g)	**C_e (mg/L)**	**q_e (mg/g)**	**$1/C_e$ (L/mg)**	**$1/q_e$ (g/mg)**
0.05	9633.30	608.20	0.0001	0.0016
0.10	8131.60	604.44	0.0001	0.0016
0.20	5175.00	597.88	0.0001	0.0016
0.30	2872.80	552.06	0.0003	0.0018
0.40	1055.00	504.94	0.0009	0.0019
0.45	440.00	476.16	0.0022	0.0021
0.55	111.08	401.55	0.0090	0.0024
0.60	72.75	369.36	0.0137	0.0027
0.65	45.80	341.78	0.0218	0.0029
0.70	32.03	317.76	0.0312	0.0031
0.75	20.08	296.89	0.0498	0.0033
0.80	20.02	278.34	0.0499	0.0035
0.85	18.55	262.00	0.0539	0.0038
0.90	17.72	247.46	0.0564	0.0040
0.95	11.74	234.56	0.0851	0.0042
1.00	11.64	222.84	0.0858	0.0044

Table F.2 Adsorption Data for Cd^{2+}-Na^{+} Binary Ion Exchange for Langmuir Isotherm

Zeolite Weight (g)	C_e(mg/L)	q_e(mg/g)	1/C_e(L/mg)	1/q_e(g/mg)
0.1	4301.00	257.45	0.0002	0.0038
0.2	3362.70	222.55	0.0002	0.0044
0.3	2278.80	220.63	0.0004	0.0045
0.4	1485.00	205.16	0.0006	0.0048
0.5	902.35	187.43	0.0011	0.0053
0.6	386.45	173.39	0.0025	0.0057
0.7	103.44	156.70	0.0096	0.0063
0.8	29.33	138.97	0.0340	0.0071
0.9	10.38	123.95	0.0963	0.0080
1.0	3.82	111.68	0.2613	0.0089

Freundlich Isotherm equation and linearized form of Freundlich Isotherm equation are given below;

$$q_e = K_f * C_e^{1/n} \qquad (F.4)$$

1/n and K_f are constants.

Linearized form of Freundlich Isotherm;

$$\ln q_e = \ln K_f + (\frac{1}{n}) * \ln C_e \qquad (F.5)$$

Freundlich isotherms were drawn as ln q_e versus ln C_e

Sample Calculations ;

ln K_f= 5.2114 K_f=183.350 L/g 1/n=0.1399 n=7.147 (from Figure 5.14)
ln K_f= 4.5596 K_f=95.545 L/g 1/n=0.107 n=9.345 (from Figure 5.15)

Table F.3 Adsorption data for Ag^+-Na^+ Binary Ion Exchange for Freundlich Isotherm

Zeolite Weight (g)	**C_e (mg/L)**	**q_e (mg/g)**	**$1/C_e$ (L/mg)**	**$1/q_e$ (g/mg)**	**ln C_e**	**ln q_e**
0.05	9633.30	608.20	0.0001	0.0016	9.1729	6.4105
0.10	8131.60	604.44	0.0001	0.0016	9.0035	6.4043
0.20	5175.00	597.88	0.0001	0.0016	8.5515	6.3933
0.30	2872.80	552.06	0.0003	0.0018	7.9630	6.3136
0.40	1055.00	504.94	0.0009	0.0019	6.9612	6.2244
0.45	440.00	476.16	0.0022	0.0021	6.0867	6.1657
0.55	111.08	401.55	0.0090	0.0024	4.7103	5.9953
0.60	72.752	369.36	0.0137	0.0027	4.2870	5.9117
0.65	45.80	341.78	0.0218	0.0029	3.8242	5.8341
0.70	32.03	317.76	0.0312	0.0031	3.4667	5.7613
0.75	20.08	296.89	0.0498	0.0033	2.9997	5.6933
0.80	20.02	278.34	0.0499	0.0035	2.9970	5.6288
0.85	18.55	262.00	0.0539	0.0038	2.9204	5.5683
0.90	17.72	247.46	0.0564	0.0040	2.8751	5.5112
0.95	11.74	234.56	0.0851	0.0042	2.4630	5.4577
1.00	11.64	222.84	0.0858	0.0044	2.4547	5.4064

Table F.4 Adsorption Data for Cd^{2+}-Na^{+} Binary Ion Exchange for Freundlich Isotherm

Zeolite Weight (g)	**C_e (mg/L)**	**q_e (mg/g)**	**$1/C_e$ (L/mg)**	**$1/q_e$ (g/mg)**	**ln C_e**	**ln q_e**
0.1	4301.00	257.45	0.0002	0.0038	8.3666	5.5500
0.2	3362.75	222.55	0.0002	0.0044	8.1205	5.4051
0.3	2278.80	220.63	0.0004	0.0045	7.7314	5.3964
0.4	1485.00	205.16	0.0006	0.0048	7.3030	5.3238
0.5	902.35	187.43	0.0011	0.0053	6.8050	5.2334
0.6	386.45	173.39	0.0025	0.0057	5.9570	5.1555
0.7	103.44	156.70	0.0096	0.0063	4.6389	5.0543
0.8	29.33	138.97	0.0340	0.0071	3.3788	4.9342
0.9	10.38	123.95	0.0963	0.0080	2.3400	4.8198
1.0	3.82	111.68	0.2613	0.0089	1.3420	4.7157

APPENDIX G

THERMODYNAMIC ANALYSES OF BINARY ION EXCHANGE

The equation given below was used for the analytical representation of activity coefficients. Activity coefficients of single salt solution was calculated using Debye-Hückel Equation.

$$\log \gamma_{\pm\, Ax} = \frac{A\,|Z_1 Z_2|\sqrt{I}}{1+Ba\sqrt{I}} + bI \qquad \text{(G.1)}$$

A and B are Debye Hückel Parameters at constant temperature.

a is the distance of closest approach of the ions.

b is a constant adjustable to suit experimental curve.

I is the ionic strength of the solution.

z_1 and z_2 are the charge of the ions.

γ is the activity coefficient

A and B is taken as 0.5115 $l^{-1/2}$/mole$^{-1/2}$ and 0.3291×10^8 $l^{-1/2}$/mole$^{-1/2}$ respectively at constant temperature 25 ^{o}C [Robinson and Stokes. 1959].

I is defined as ionic strength ;

$$I = \frac{1}{2} \sum m_i \, {z_i}^2 \tag{G.2}$$

m_i: Concentration of each ion present in solution.

To calculate constant a and b given values of activity coefficient by Robinson and Stokes at 25 °C was used and two equations were obtained. Using these two equations, a is expressed in terms of b and equations were solved simultaneously. Equations are given in calculation part of this Appendix.

After calculating all data in Debye-Hückel equation to evaluate activity coefficients of mixed salt solution Glueckauf's equation was used.

$$\log \gamma \pm_{(Ax)}^{(Bx)} = \log \gamma \pm_{(Ax)} - \frac{m_B}{4I} \left\{ K_1 \log \gamma \pm_{(Ax)} - K_2 \log \gamma \pm_{(Bx)} - \frac{K_3}{(1+ I^{-\frac{1}{2}})} \right\} \tag{G.3}$$

$$\log \gamma \pm_{(Bx)}^{(Ax)} = \log \gamma \pm_{(Bx)} - \frac{m_A}{4I} \left\{ K_4 \log \gamma \pm_{(Bx)} - K_5 \log \gamma \pm_{(Ax)} - \frac{K_6}{(1+ I^{-\frac{1}{2}})} \right\} \tag{G.4}$$

K_1.K_2.K_3.K_4.K_5 and K_6 are defined as;

$$K_1 = Z_B(2Z_B - Z_A + 2Z_X) \tag{G.5}$$

$$K_2 = Z_A(Z_B + Z_X)^2(Z_A + Z_X)^{-1} \tag{G.6}$$

$$K_3 = 0.5 \, [Z_A Z_B Z_X (Z_A - Z_B)^2 (Z_A + Z_X)^{-1}] \tag{G.7}$$

$$K_4 = Z_A(2Z_A - Z_B + Z_X) \tag{G.8}$$

$$K_5 = Z_B(Z_A + Z_X)^2(Z_B + Z_X)^{-1} \tag{G.9}$$

$$K_6 = 0.5[(Z_A Z_B Z_X)(Z_B - Z_A)^2(Z_B + Z_X)^{-1}] \tag{G.10}$$

The solution non-ideality factor was calculated using by equation given below

$$\Gamma = \frac{{\gamma_B}^{Z_A}}{{\gamma_A}^{Z_B}} = \frac{\left[\gamma\pm_{(Bx)}^{(Ax)}\right]^{Z_A(Z_B+Z_X)/Z_X}}{\left[\gamma\pm_{(Ax)}^{(Bx)}\right]^{Z_B(Z_A+Z_X)/Z_X}} \qquad \text{(G.11)}$$

Thermodynamic equilibrium constant is related to mass action quotient and kielland quotient. Thermodynamic equilibrium constant is needed to evaluate Gibbs free energy. These variables were calculated by Equation G.12, G.13, and G.14 respectively.

$$K_m = \frac{{A_z}^{Z_B}{m_B}^{Z_A}}{{B_Z}^{Z_A}{m_A}^{Z_B}} \qquad \text{(G.12)}$$

$$K_C = \Gamma\, K_m \qquad \text{(G.13)}$$

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_C \, dA_z \qquad \text{(G.14)}$$

The second term of Equation G.14 was calculated from the area under the curve in ln K_c versus A_z graph.

Gibbs free energy was evaluated by the equation which is given as;

$$\Delta G^o = \frac{(-RT \ln K_a)}{Z_A Z_B} \qquad \text{(G.15)}$$

Sample calculation was done for Cd^{2+}-Na^{+} binary ion exchange system.

Debye-Hückel equation contains some variables. These are constant a and b and ionic strength. Activity coefficients were taken from Stokes and Robinson.

$$I = 0.5 * \sum(0.1 * 4 + 0.2) = 0.3\ (When\ the\ activity\ coefficient\ was\ taken\ as\ 0.516)$$

$$\log 0.516 = \frac{-0.5115 * 2 * \sqrt{0.3}}{1+0.3291*10^{8}*a*\sqrt{0.3}} + b * 0.3$$

a is expressed in terms of b.

$$a = \frac{(0.273 - 0.3b)}{(5.173 * 10^{6} + 5.407 * 10^{6}b}$$

$$I = 0.5 * \sum(0.2 * 4 + 0.4) = 0.6\ (When\ the\ activity\ coefficient\ was\ taken\ as\ 0.467)$$

$$\log 0.467 = \frac{-0.5115 * 2 * \sqrt{0.6}}{1 + 0.3291 * 10^{8} * a * \sqrt{0.6}} + b * 0.6$$

a was put into equation given above and b is found as 0.04224 and a is found as $4.819x10^{-8}$. These constants were found as -0.4951 and $12.482*10^{-8}$ respectively for sodium ion.

Table G.1 Debye Huckel Constants

Constants	$Cd(NO_3)_2$	$Ag(NO_3)$	$Na(NO_3)$
A $(L/mol)^{0.5}$	-0.5115	-0.5115	-0.5115
B$(L/mol)^{0.5}$ cm^{-1}	$0.32*10^{-8}$	$0.32*10^{-8}$	$0.32*10^{-8}$
a (cm)	$4.81*10^{-8}$	$1.94*10^{-8}$	$12.48*10^{-8}$
b	0.0400	-0.0100	-0.4900

Concentration of stock solution is 5588.25 ppm. Zeolite weight is 0.1 gram. At the end of the experiment equilibrium concentration of cadmium ions are 4301 ppm.

According to these values total normality of solution;

$$Total\ Normality = 5588.25\frac{mg}{L} * \frac{1\ mol}{112400\ mg} * \frac{2\ eq}{1\ mol} = 0.0994\ eq/L$$

$$m_{Cdi} = 5588.25\ \frac{mg}{L} * \frac{1\ mol}{112400\ mg} = 0.0497\ mol\ /L$$

$$m_{Cdi} = 4301\ \frac{mg}{L} * \frac{1\ mol}{112400\ mg} = 0.0382\ mol\ /L$$

$$m_{Na} = 0.0994\ \frac{eq}{L} - 0.0382\ \frac{mol}{L} * \frac{2eq}{1mol} = 0.0228\frac{eq}{L}(\frac{mol}{L})$$

$$m_{NO_3} = 0.0994\frac{mol}{L}\ (Sodium\ concentration\ doesn't\ change\ through\ out\ to\ experiment)$$

$$I = 0.5 * (4 * 0.0382 + 0.0994 + 0.0228\,) = 0.1375$$

$$\log \gamma_{\pm Cd(NO)_3} = \frac{-0.5115 * 2 * \sqrt{0.1375}}{1 + 0.3291 * 10^8 * 4.819\ 10^{-8} * \sqrt{0.1375}} + 0.1375 * 0.0424 = -0.244$$

$$\gamma_{\pm Cd(NO)_3} = 0.570$$

$$\log\gamma_{\pm Na(NO)_3} = \frac{-0.5115 * 1 * \sqrt{0.1375}}{1 + 0.3291 * 10^8 * 12.482 * \ 10^{-8} * \sqrt{0.1375}} + 0.1375 * -0.4951 = -0.143$$

$$\gamma_{\pm Na(NO)_3} = 0.719$$

The constants which are in Glueckauf's equation were calculated as ;

$$K_1 = 1 * (2 * 1 - 2 + 1) = 1$$

$$K_2 = 2 * (1 + 1)^2 * (1 + 2)^{-1} = 2.667$$

$$K_3 = 0.5 * [2 * (1)^2 * (3)^{-1}] = 0.333$$

$$K_4 = 2 * (2 * 2 - 1 + 1) = 8$$

$$K_5 = 1 * (2 + 1)^2 (1 + 1)^{-1} = 4.5$$

$$K_6 = 0.5 * (2 * 1 * (2)^{-1} = 0.5$$

These constants were put into Gleuckauf's equation and activity coefficients of salt solutions were calculated as follows;

$$\log\gamma\pm^{(NaNO_3)}_{(Cd(NO_3)_2)} = -0.244 - \frac{0.0228}{4 * 0.1375} * [1 * (-0.244) - 2.667 * (-0.143)$$

$$\gamma\pm^{(NaNO_3)}_{(Cd(NO_3)_2)} = 0.5701$$

$$\log \gamma \pm_{(NaNO_3)}^{(Cd(NO_3)_2} = -0.143 - \frac{0.0382}{4 * 0.1375} * [8 * (-0.143) - 4.5 * (-0.244)$$

$$-\frac{0.5}{(1+0.1375^{-0.5})}]=\text{-}0.1304$$

$$\gamma \pm_{(NaNO_3)}^{(Cd(NO_3)_2)} = 0.7403$$

The solution non ideality correction factor. mass action quotient and kielland quotient were calculated as respectively;

$$\Gamma = \frac{0.7403^{\frac{2(1+1)}{1}}}{0.5701^{\frac{1(2+1)}{1}}} = 1.6216$$

$$\mathrm{K_m} = \frac{0.81^1 * 0.0228^2}{0.19^2 * 0.0382^1} = 0.3053$$

$$\mathrm{K_c} = 0.3053 * 1.6216 = 0.4951$$

In order to determine thermodynamic equilibrium constant, ln K_c versus A_z plot was drawn and area under the curve was calculated as;

$$\ln K_a = (z_{Na} - z_{Cd}) + \int \ln K_c \, dA_z$$

$$\ln Ka = \frac{\big((10.798 + 0.481) + (0.481 + 0.606)\big) * 0.7}{2} + \frac{(0.702 - 0.481) * (0.81 - 0.7)}{2} = 4.34$$

$$\ln K_a = ((1 - 2) + 4.34) = 3.34$$

$$K_a = 28.22$$

Consequently, as all variables were found. gibbs free energy of ion exchange process was calculated as given below and all values which were calculated above are given in following tables.

$$\Delta G^{o} = \frac{-8.314 * 10^{-3} \frac{kj}{mol.K} * 298.15\ K * 3.34}{2 * 1} = -4.139 \frac{kj}{mol}$$

Table G.2 Thermodynamic data for Cd^{2+}- Na^{+} Binary Ion Exchange at 25 °C and 0.1 N.

$M_{Na}{}^{+}$(mol/L)	$M_{Cd}{}^{2+}$(mol/L)	Ionic Strength (mol/L)
0.022	0.03820	0.1375
0.039	0.02990	0.1293
0.059	0.02020	0.1196
0.073	0.01320	0.1126
0.083	0.00802	0.1070
0.092	0.00343	0.1020
0.097	0.00092	0.1000
0.098	0.00026	0.0990
0.099	0.00009	0.0995
0.099	0.00003	0.0990

Table G.3 Activity Coefficients for Cd^{2+}- Na^{+} Binary Ion Exchange at 25 °C and 0.1 N (cont'd).

$\log \gamma_{\pm Cd(NO_3)_2}$	$\gamma_{\pm Cd(NO_3)_2}$	$\log \gamma_{\pm Na(NO)_3}$	$\gamma_{\pm Na(NO)_3}$
-0.24404	0.5701	-0.14327	0.719
-0.22841	0.5910	-0.13846	0.727
-0.22329	0.5980	-0.13253	0.737
-0.21968	0.6030	-0.12842	0.744
-0.21609	0.6080	-0.12436	0.751
-0.21253	0.6130	-0.12147	0.756
-0.21112	0.6150	-0.11975	0.759
-0.21063	0.6157	-0.11918	0.760
-0.21041	0.6160	-0.11912	0.760
-0.21038	0.6161	-0.11907	0.760

Table G.4 Thermodynamic data for Cd^{2+}- Na^{+} Binary Ion Exchange at 25 °C and 0.1 N (cont'd).

$\log\gamma\pm^{(NaNO_3)}_{(Cd(NO_3)_2}$	$\log\gamma\pm^{(Cd(NO_3)}_{(NaNO_3)}$	$\gamma\pm^{(Cd(NO_3)_2}_{[\![(NaNO]\!]_3)}$	$\gamma\pm^{(NaNO_3)}_{(Cd(NO)_3)_2}$	**Γ**	**K_m**	**K_c**	**ln K_c**
-0.1305	-0.2460	0.7403	0.570	1.62	0.3	0.49	-0.70
-0.1262	-0.2284	0.7478	0.591	1.51	0.4	0.61	-0.48
-0.1247	-0.2232	0.7502	0.598	1.48	1.2	1.83	0.60
-0.1236	-0.2196	0.7523	0.603	1.46	1.9	2.91	1.06
-0.1216	-0.2160	0.7557	0.608	1.45	3.0	4.37	1.47
-0.1203	-0.2125	0.7579	0.613	1.43	6.2	9.02	2.20
-0.1194	-0.2111	0.7595	0.615	1.43	19.2	27.56	3.31
-0.1191	-0.2106	0.7601	0.615	1.43	52.4	75.06	4.31
-0.1191	-0.2104	0.7601	0.616	1.42	111.7	159.61	5.07
-0.1190	-0.2103	0.7602	0.616	1.42	238.5	340.66	5.83

Table G.5 Thermodynamic data for Ag^+-Na^+ Binary Ion Exchange System at 25 °C and 0.1 N.

M_{Na^+}(mol/L)	M_{Ag^+}(mol/L)	Ionic Strength (mol/L)
0.0136	0.08931	0.103
0.0276	0.07538	0.103
0.0333	0.06962	0.103
0.0550	0.04798	0.103
0.0763	0.02663	0.103
0.0932	0.00978	0.103
0.0989	0.00408	0.103
0.1019	0.00103	0.103
0.1023	0.00067	0.103
0.1025	0.00042	0.103
0.1027	0.0003	0.103
0.1028	0.00019	0.103
0.1028	0.00019	0.103
0.1028	0.00017	0.103
0.1028	0.00016	0.103
0.1028	0.00011	0.103
0.1028	0.00011	0.103

Table G.6 Activity Coefficients for Ag^+- Na^+ Binary Ion Exchange at 25 ^oC and 0.1 N (cont'd).

$\log \gamma_{\pm Ag(NO_3}$	$\gamma_{\pm Ag(NO_3)}$	$\log \gamma_{\pm Na(NO)_3}$	$\gamma_{\pm Na(NO)_3}$
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554
-0.13739	0.7288	-0.1218	0.7554

Table G.7 Thermodynamic data for Ag^+- Na^+ Binary Ion Exchange at 25 ^oC and 0.1 N (cont'd).

$\log \gamma \pm_{(Ag(NO_3)}^{(NaNO_3)}$	$\log \gamma \pm_{(NaNO_3)}^{(Ag(NO_3)_2}$	$\gamma \pm_{\llbracket(NaNO\rrbracket_3)}^{(Ag(NO_3)}$	$\gamma \pm_{(Ag(NO)_3)}^{(NaNO_3)}$	**Γ**	**K_m**	**K_c**	**ln K_c**
-0.13635694	-0.12856222	0.74377	0.73054	1.03	16.8	17.50	2.86
-0.1353034	-0.12750867	0.74557	0.73231	1.03	36.2	37.59	3.62
-0.13486747	-0.12707275	0.74632	0.73305	1.03	18.6	19.37	2.96
-0.13322913	-0.12543441	0.74914	0.73582	1.03	42.9	44.53	3.79
-0.13161398	-0.12381925	0.75194	0.73856	1.03	25.8	26.75	3.28
-0.13033866	-0.12254394	0.75415	0.74073	1.03	44.3	45.93	3.82
-0.1299072	-0.12211247	0.7549	0.74147	1.03	84.0	87.08	4.46
-0.12967644	-0.12188172	0.7553	0.74186	1.03	187.8	194.85	5.27
-0.12964955	-0.12185482	0.75534	0.74191	1.03	229.4	237.86	5.47
-0.12963064	-0.12183591	0.75538	0.74194	1.03	303.7	314.85	5.75
-0.12962098	-0.12182625	0.75539	0.74196	1.03	371.6	385.28	5.95
-0.1296126	-0.12181787	0.75541	0.74197	1.03	518.0	536.98	6.28
-0.12961256	-0.12181783	0.75541	0.74197	1.03	460.4	477.29	6.16
-0.12961152	-0.1218168	0.75541	0.74197	1.03	445.5	461.87	6.13
-0.12961095	-0.12181622	0.75541	0.74197	1.03	422.3	437.82	6.08
-0.12960674	-0.12181202	0.75542	0.74198	1.03	584.3	605.71	6.40
-0.12960668	-0.12181195	0.75542	0.74198	1.03	543.2	563.07	6.33

APPENDIX H

SEPARATION FACTOR

Separation factor is defined as ;

$$\alpha_B^A = \frac{A_Z * B_S}{B_Z * A_S} \qquad \text{(H.1)}$$

$$\alpha_A^B = \frac{B_Z * A_S}{A_Z * B_S} \qquad \text{(H.2)}$$

Sample Calculation;

For 0.05 g zeolite;

$$\alpha_{Na}^{Ag} = \frac{0.992 * 0.133}{0.008 * 0.867} = 19.022$$

$$\alpha_{Ag}^{Na} = \frac{0.867 * 0.008}{0.992 * 0.133} = 0.053$$

Table H.1 Separation Factor for Binary Ion Exchange for Ag^+-Na^+ at Constant Normality 0.1 N and Temperature 25°C for Different Zeolite Weights.

Zeolite Weight (g)	Ag_s	Ag_z	Na_z	Na_s	α_{Na}^{Ag}	α_{Ag}^{Na}
0.05	0.867	0.992	0.008	0.133	19.022	0.053
0.10	0.732	0.986	0.014	0.268	25.785	0.039
0.20	0.466	0.975	0.025	0.534	44.691	0.022
0.30	0.259	0.901	0.099	0.741	26.038	0.038
0.40	0.095	0.824	0.176	0.905	44.600	0.022
0.45	0.040	0.777	0.223	0.960	83.623	0.012
0.55	0.010	0.655	0.345	0.990	187.957	0.005
0.60	0.007	0.603	0.397	0.993	215.466	0.005
0.65	0.004	0.558	0.442	0.996	314.348	0.003
0.70	0.003	0.518	0.482	0.997	357.155	0.003
0.75	0.002	0.484	0.516	0.998	468.054	0.002
0.80	0.002	0.454	0.546	0.998	414.919	0.002
0.85	0.002	0.427	0.573	0.998	371.855	0.003
0.90	0.002	0.404	0.596	0.998	338.248	0.003
0.95	0.001	0.383	0.617	0.999	620.125	0.002
1.00	0.001	0.364	0.636	0.999	571.755	0.002

Table H.2 Separation Factor for Binary Ion Exchange for Cd^{2+}-Na^{+} at Constant Normality 0.1 N and Temperature 25°C for Different Zeolite Weights.

Zeolite Weight (g)	**Cd_z**	**Cd_s**	**Na_z**	**Na_s**	α_{Na}^{Cd}	α_{Cd}^{Na}
0.1	0.806	0.770	0.194	0.230	1.244	0.804
0.2	0.697	0.602	0.303	0.398	1.521	0.657
0.3	0.691	0.408	0.309	0.592	3.245	0.308
0.4	0.642	0.266	0.358	0.734	4.963	0.201
0.5	0.587	0.161	0.413	0.839	7.377	0.136
0.6	0.543	0.069	0.457	0.931	15.987	0.063
0.7	0.491	0.019	0.509	0.981	51.079	0.020
0.8	0.435	0.005	0.565	0.995	145.997	0.007
0.9	0.388	0.002	0.612	0.998	340.825	0.003
1.0	0.350	0.001	0.650	0.999	786.133	0.001

APPENDIX I

REPEATABILITY

Repeatability of the experiment is important to make sure that the experiments always give the same results. On this purpose the experiment of binary ion exchange between cadmium and sodium ion was done three times.

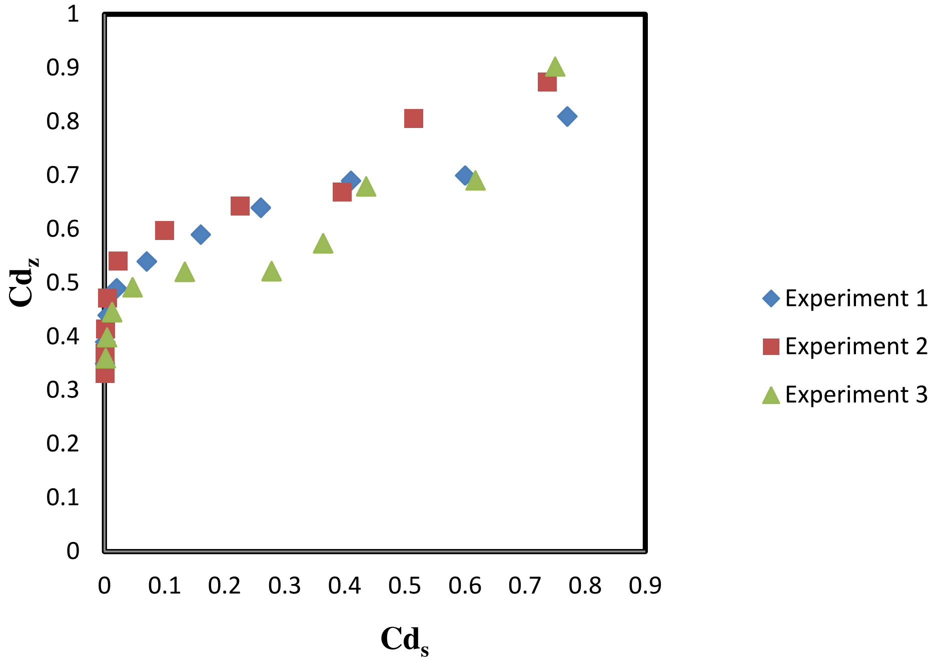

Figure I.1 Binary Ion Exchange Isotherms of Cd^{2+}-Na^{+} at Constant Normality 0.1 N and Temperature 25 °C.

As it is seen from the isotherms given above, three isotherms are not very similar to each other.

Differences between three experiments can result from;

- Stock solution of heavy metals were prepared again for every experiments and their concentrations were a little bit different from each other due to dilutions. Concentration of stock solutions were 5588.25 ppm, 5300.00 ppm and 5768.90 ppm for experiment 1,2 and 3 respectively. Experiment 1 was chosen for binary ion exchange, thermodynamic and adsorption isotherm calculations. Deviations between experiment 1-experiment 2 and experiment 1-experiment 3 were calculated as 3% and 5% respectively.

- A lot of dilutions were done for every sample in three experiments and the measured concentration results can be different due to the differences between dilutions. In order to calculate final concentration of a sample, dilution was done for three times and the deviation between these three final concentration of a sample was calculated between 1%-2%.