INVESTIGATION OF CADMIUM REMOVAL MECHANISMS
BY
CLINOPTILOLITE

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ABSTRACT

INVESTIGATION OF CADMIUM REMOVAL MECHANISMS BY CLINOPTILOLITE

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Clinoptilolite is a natural zeolite which can be used favorably in heavy metal removal. The main mechanisms for metal removal via clinoptilolite are adsorption and ion exchange. Several sources propose to keep the normality constant to obtain equilibrium isotherms for ion exchange systems, while many studies use constant sorbent mass with varying normalities of the sorbate. The objective of this study is to investigate the prevailing mechanisms of clinoptilolite during cadmium removal and the impact of the methodology for obtaining equilibrium isotherms.

Batch Cd^{2+} removal experiments were conducted by using the two different methodologies (i.e. keeping the sorbent mass constant vs. keeping the normality constant) with clinoptilolite in as-received (AsC) and conditioned form (CnC), an ion exchange resin and granulated activated carbon. Exchangeable and framework cations, conductivity and pH were monitored during experiments. The equilibrium results were then fitted to isotherm models.

The prevailing mechanisms for Cd^{2+} removal with clinoptilolite are discussed considering all monitored parameters and isotherm model fits. Use of the methodology was seen to have an effect on the overall Cd^{2+}-clinoptilolite interaction. For example, differences between methodologies are observed regarding maximum sorbed Cd^{2+} and the distribution of exchangeable cations. Conductivity profiles provided a good indication of presence of ion exchange and demonstrated that it is more dominating for CnC than for AsC. The Cd^{2+} removal capacities observed in this study (0.65 meq/g for AsC and 1.46 meq/g for CnC) are the highest recorded for a clinoptilolite sample, as can be found in the literature.

Keywords: Clinoptilolite; mechanism; cadmium; exchangeable cation; conductivity

ÖZ

KLİNOPTİLOLİTİN KADMİYUM GİDERİMİNDEKİ MEKANİZMALARININ ARAŞTIRILMASI

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Klinoptilolit ağır metal gideriminde avantajlı olarak kullanılabilen bir doğal zeolittir. Klinoptilolit ile metal gideriminin başlıca mekanizmaları iyon değiştirme ve adsorpsiyondur. Çok sayıda kaynak, iyon değiştirme sistemlerinde izoterm elde etmek için normaliteyi sabit tutmayı ileri sürerken, birçok çalışma sabit sorbent miktarı ve farklı normalite kullanır. Bu çalışmanın amacı, kadmiyum gideriminde klinoptilolitin ana mekanizmalarını ve denge izotermleri elde etmede yöntemin etkisini araştırmaktır.

Cd^{2+} giderim deneyleri kesikli test reaktörlerinde iki farklı yöntem kullanılarak (sorbent miktarını ya da normaliteyi sabit tutarak) şartlandırılmamış (AsC) ve şartlandırılmış (CnC) klinoptilolit, bir iyon değiştirici reçine ve granüler aktif karbon kullanarak gerçekleştirilmiştir. Deney sıradında değişebilir ve yapı katyonları, iletkenlik ve pH izlenmiştir.

Denge deneylerinden elde edilen sonuçlar birçok izoterm modeline uygulanmıştır.

İzlenen tüm parametreler ve izoterm model uygulamaları göz önünde bulundurularak klinoptilolitin Cd^{2+} giderimindeki ana mekanizmaları tartışılmıştır. Kullanılan yöntemin genel olarak Cd^{2+}-klinoptilolit etkileşimine etkisi olduğu görülmüştür. Örneğin, maksimum giderilen Cd miktarları ve değişebilir katyonların dağılımında iki yöntem arasında farklar gözlenmiştir. İletkenliğin iyon değiştirmenin varlığına yönelik iyi bir gösterge olduğu ve bunun AsC'ye oranla CnC ile Cd^{2+} gideriminde daha baskın olduğunu göstermiştir. Bu çalışmada gözlenen Cd^{2+} giderim kapasiteleri (AsC için 0.65 meq/g ve CnC için 1.46 meq/g) bir klinoptilolit örneği için literatürde bulunabildiği kadarıyla kaydedilmiş en yüksek değerlerdir.

Anahtar kelimeler: Klinoptilolit; mekanizma; kadmiyum; değişebilir katyon; iletkenlik

To My Family…

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TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

ABBREVIATIONS

AsC: As-received Clinoptilolite

CnC: Conditioned Clinoptilolite

IR: Ion-exchange Resin

GAC: Granulated Activated Carbon

P1: Procedure 1

P2: Procedure 2

L: Langmuir isotherm

F: Freundlich isotherm

RP: Redlich-Peterson isotherm

T: Toth isotherm

DA: Dubinin-Astakhov isotherm

R^2: Correlation coefficient

SSE: Sum of Squares of Errors

HYBRID: Hybrid fractional error function

MEL: Maximum Exchange Level

CHAPTER 1

INTRODUCTION

Zeolites are crystalline, hydrated aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens. Although there are 34 species of zeolite minerals, only a few have practical significance (Breck, 1974). Clinoptilolite is a natural zeolite belonging to the heulandite group of minerals. High cation exchange capability of clinoptilolite makes it a potential candidate in the removal of heavy metals from water and wastewater (Ersoy and Celik, 2002).

There are many mechanisms involved in the removal of heavy metals by clinoptilolite. The two main mechanisms are attributed to ion exchange and adsorption (Doula and Ioannou, 2003). Others are; surface precipitation (Trgo and Peric, 2003), surface protonation (Doula and Ioannou, 2003) and co-precipitation. In addition to those, hydrolysis of metal ions and dissolution of the clinoptilolite structure are other mechanisms that have an effect on the removal of heavy metals.

Equilibrium isotherm is a common way to represent the equilibrium in adsorption and ion-exchange systems. The equilibrium isotherm represents the distribution of the adsorbed material between the adsorbed phase and the solution phase at equilibrium at a constant temperature. The basic difference between adsorption and ion exchange is that while there is only one isotherm at a specified temperature for adsorption, more than one isotherm can exist at a specified temperature for different normalities of the solution in the exchange of ions of different valences due to the concentration–valence effect (Inglezakis and Poulopoulos, 2006). Therefore, it is proposed to keep the normality constant to obtain isotherms for ion exchange systems (Auerbach et al., 2003; Cremers, 1977; Dyer and Enamy, 1981).

The objective of this study is to investigate the prevailing mechanisms of clinoptilolite in cadmium removal and the impact of the methodology for obtaining equilibrium isotherms for clinoptilolite systems accordingly. This will be accomplished by:

i. Conducting equilibrium experiments: Comparison of the two different experimental procedures (i.e. by keeping the sorbent mass constant vs. by keeping the metal concentration constant) for as-received and conditioned forms of clinoptilolite as well as for an ion exchange resin and a granulated activated carbon
ii. Monitoring exchangeable (for all sorbents) and framework (for clinoptilolite) cations as well as pH and conductivity during equilibrium experiments
iii. Modeling results using various frequently used isotherm models

CHAPTER 2

THEORETICAL BACKGROUND

2.1. SORPTION PHENOMENA: SORBATE AND SORBENT

2.2.1. Adsorption

Adsorption is the accumulation of substances at a surface or interface. It can occur between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being adsorbed is called the *adsorbate*, and the adsorbing phase is termed as the *adsorbent*.

There are three kinds of adsorption: *exchange adsorption, physical adsorption* and *chemical adsorption. Exchange adsorption* is referred as ion exchange in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface.

Physical adsorption is the adsorption which occurs as a result of van der Waals forces. In this kind of adsorption, the adsorbed molecule is not affixed to a specific site and free to undergo translational movement within the interface.

If the adsorbate undergoes chemical interaction with the adsorbent, then this kind of adsorption is called as *chemical adsorption*. Chemically adsorbed molecules are affixed to a site and they are not free to move on the surface, or within the interface (Walter J. Weber, 1972).

2.2.2. Ion Exchange

Weber (1972) defined ion exchange as: “A process in which ions held by electrostatic forces to charged functional groups on the surface of a solid are exchanged for ions of similar charge in solution in which the solid is immersed” and classified ion exchange as an adsorption process since the exchanging ions undergo a phase transfer from solution phase to surface phase. Helfferich (1995) made a distinction between those two process emphasizing that ion exchange is a stoichiometric process in which every ion removed from the solution is replaced by an equivalent amount of another ionic species of the same sign. In sorption, on the other hand, a solute is taken up without being replaced by other species (Helfferich, 1995).

2.2.3. Concentration Valence Effect (Donnan Potential)

In ion exchange systems, the ion exchanger always prefers the counter ion that have *higher valence.* This preference arises from electrostatic factors and is termed as “electroselectivity” (Helfferich, 1995). Electroselectivity increases with *dilution of the solution*. Therefore, valences of the counter ions have an effect on the ion exchange equilibria. When the exchange is between the counter ions of the same valence, no difference is observed. However when the exchange is between the counter ions of different valences, different equilibrium isotherms are obtained for different normalities. This is known as **concentration valence effect** studied by many researchers (Barrer and Klinowski, 1974; Barri and Rees, 1980; Loizidou and Townsend, 1987; Subba Rao and David, 1957).

For this reason, Inglezakis (2006) made a distinction between adsorption and ion exchange systems declaring that there is only one isotherm at a specified temperature for adsorption but a specific ion-exchange system presents one isotherm only under constant temperature *and* normality. Then he suggested using the term "isotherm–isonormal" for the equilibrium curves in the case of ion exchange while "isotherms" is being used for adsorption systems.

Concentration valence effect is as a result of the *Donnan potential*. Donnan potential is explained by Helfferich (1995) as:

> When a cation exchanger (containing no sorbed electrolyte) is placed in a dilute solution of a strong electrolyte there are considerable concentration differences between the two phases; the cation concentration is larger in the ion exchanger, whereas the (mobile) anion concentration is larger in the solution. Migration both of cations into the solution and of anions into the ion exchanger results in an accumulation of positive charge in the solution and of negative charge in the ion exchanger. The first few ions which diffuse build up an electric potential difference between the two phases. This is called as 'Donnan potential'.

Because of that potential, cations are pulled back into the (negatively charged) ion exchanger and anions back into the (positively charged) solution (Helfferich, 1995). Equilibrium is established when the tendency of the ions to level out the concentration differences is balanced by the action of the electric field.

Consequently, the Donnan potential attracts counter ions into the ion exchanger preventing their tendency to diffuse out into the solution. The force (with which the Donnan potential acts on an ion) is proportional to the ionic charge so that the counter ion of higher charge is more strongly attracted and preferred by the ion exchanger; termed as “electroselectivity”. And the value of the Donnan potential increases with dilution of the solution, hence the preference increases with dilution of the solution; known as “concentration valence effect” (Helfferich, 1995).

That condition creates a necessity to keep the solution normality constant in order to obtain an isotherm for ion exchange systems. This necessity is also stated by some of the authors in the literature (Auerbach et al., 2003; Cremers, 1977; Dyer and Enamy, 1981). A cation removal study of Robinson et al. (1993) by a natural zeolite, chabazite, involves a comparison between the two different experimental procedures (i.e. by keeping the metal concentration constant vs. by keeping the sorbent mass constant). By that way, they demonstrated that there is a difference in the results of the two procedures and that the solution concentration affects the equilibrium results.

Though the situation for ion exchange systems is as described above, the number of equilibrium studies keeping the solution normality constant is scarce. Comparison of heavy metal removal studies by natural zeolite from literature that keep the sorbent mass constant and solution normality constant are given in Table 2.1. Although more examples can be given that keep the sorbent mass constant, only the studies given in Table 2.1 could be found that keep the solution normality constant.

Table 2. 1. Metal removal studies by natural zeolites from literature that
A. keeps the sorbent mass constant
B. keeps the solution normality constant during batch equilibrium tests

A	*B*
Akgül et al. (2006)	Blanchard et al. (1984)
Al-Anber and Al-Anber (2008)	Cincotti et al. (2001), (2006)
Arambula-Villazana et al. (2006)	Çulfaz and Yağız (2004)
Athanasiadis and Helmreich (2005)	Inglezakis (2002), (2007)
Bektas and Kara (2004)	Langella et al. (2000)
Berber-Mendoza et al. (2006a)	Semmens and Martin (1988)
Castaldi et al. (2008)	
Curkovic et al. (1997)	
Çoruh (2008)	
Doula (2006)	
Doula et al. (2002)	
Doula and Dimirkou (2008)	
Doula and Ioannou (2003)	
Englert and Rubio (2005)	
Genc et al. (2007)	
Kocaoba et al. (2007)	
Langwaldt (2008)	
Lee and Moon (2001)	
Llanes-Monter et al. (2007)	
Ouki et al. (1993)	
Ouki and Kavannagh (1999)	
Petrus and Warchol (2003; 2005)	
Peric et al. (2004)	
Sheta et al. (2003)	
Weatherley and Miladinovic (2004)	

2.3. SORBATE: CADMIUM

Cadmium is a heavy metal belonging to Group IIB in Periodic Table. It is a naturally found component in surface and groundwater in minor quantities (Ahmad et al., 2007). However, discharge of cadmium from industrial operations such as metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys can cause environmental pollution (Balkaya and Cesur, 2008). Turkish Legislation sets a discharge standard to sewerage systems of 2 mg/L for cadmium in the Water Pollution Control Regulation. Cadmium ions are very toxic and cause serious health problems. Lung cancer, kidney failure, bone diseases (such as osteomalacia), emphysema and hypertension are some of the harmful effects of cadmium (Balkaya and Cesur, 2008; Hizal and Apak, 2006). Because of these, many studies are performed for its removal (Arambula-Villazana et al., 2006; Balkaya and Cesur, 2008; Deng et al., 2007; Ennigrou et al., 2009; Wang et al., 2009) .

Thus removal of cadmium from wastewaters is necessary. Techniques used in the removal of the heavy metal ions can be listed as chemical precipitation, adsorption, ion exchange, coagulation, reverse osmosis, electrodialysis, solvent extraction, vacuum evaporation, ultrafiltration, etc. (Balkaya and Cesur, 2008; Minceva et al., 2008). Among them ion exchange is a convenient and an attractive method with its relatively simple and safe application (Inglezakis et al., 2004).

2.4. SORBENT

2.4.1. Natural Zeolites

Natural zeolites are naturally occurring minerals composed of AlO_4 and SiO_4 tetrahedra that are linked to each other by sharing the oxygen atoms. They are hydrated aluminosilicates that have crystalline porous structure. The isomorphous replacement of aluminum atom for silicon atom creates a charge deficiency because the aluminum atom has a formal charge of 3+ whereas the silicon atom has 4+. This charge deficiency is compensated by additional cations generally by alkali (mainly Na^+ and K^+) and alkaline earth metals (mainly Ca^{2+} and Mg^{2+}). These cations are generally free to move in the framework and are responsible for the ion exchange properties of zeolites by exchanging their sites with other cations in solution (Breck, 1974).

Natural zeolites have a general formula of:

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O \tag{2.1}$$

Where; M is the exchangeable cation and n is the valance of the cation. In general, x has a value equal to or greater than 2 (Breck, 1974).

Natural zeolites have a wide variety of applications. Their applications in industrial area are purification of gas streams, water softening, wastewater treatment, heavy metal removal, ammonia removal, sewage treatment, radioactive waste treatment, etc. (Englert and Rubio, 2005; Kesraouiouki et al., 1994). The reason for the preference of natural zeolites especially for water treatment is due to their low cost, wide availability on the earth and their regeneration potential (Cincotti et al., 2001; Gedik and Imamoglu, 2008). Besides, they are the most important inorganic cation exchangers that have high removal capacity, selectivity and compability with the natural environment (Petrus and Warchol, 2003). Moreover, their relatively harmless exchangeable cations which are mainly sodium, potassium, calcium and magnesium makes them especially attractive alternatives (Kesraouiouki et al., 1994).

There are 34 species of zeolite minerals but only a few of them have practical significance and are available in sufficient quantity (Breck, 1974; Cincotti et al., 2001). Those include chabazite, clinoptilolite, erionite, ferrierite, phillipsite, mordenite and analcime (Cincotti et al., 2001; Kesraouiouki et al., 1994).

a. Clinoptilolite

Clinoptilolite is a natural zeolite that belongs to the heulandite group of minerals which occur in sedimentary rocks. They are the most widely distributed zeolites in nature (Tsitsishvili et al., 1992). Volcanic ash particles which are carried by the wind to the lakes participate in the formation of clinoptilolite therefore they contain quartz, feldspar, montmorillonite, cristobalite and unaltered ash particles to some extent (Breck, 1974).

Clinoptilolite is a high-silica containing zeolite (Tsitsishvili et al., 1992). Its mineral content depends to some extend on the characteristic of the environment during its formation such as pH, salinity and the dissolved ion composition of the surrounding water (Breck, 1974). This makes a variation in the composition, purity and mineralogical characteristics of clinoptilolite from one deposit to another and even within the same deposit (Abusafa and Yucel, 2002).

Clinoptilolite has high cation exchange capability which enables it to be used in the removal of inorganic contaminants from water and wastewater (Ersoy and Celik, 2002). Besides, it shows high selectivities for several cations and especially for heavy metals (Inglezakis et al., 2005).

Clinoptilolite tuffs are widely spread all over the world, and new reserves are continuously being discovered. Reserves exploited or in exploitation are in Europe (Bulgaria, Greece, Hungary, Italy, Romania, Slovakia, Slovenia, Turkey, Yugoslavia), in Russia and several states of former Soviet Union (Georgia, Ukraine, Azerbaijan) in Asia (China, Iran, Japan, Korea), in Africa (South Africa), in Australia and New Zealand and in many countries of America, such as Argentina, Cuba, Mexico and the United States (Colella, 2005).

Turkey is rich country for its clinoptilolite reserves (DPT, 1996). Most important reserves in are found in Manisa-Gördes region (20 million tons) and in Balıkesir-Bigadiç region (500 million tons).

b. Clinoptilolite-Metal interaction mechanisms

Many interaction mechanisms occur when clinoptilolite is in contact with a metal solution because sorption on zeolitic particles is a complicated process. This is because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface (Peric et al., 2004). Mechanisms take place can be listed as:

Ion exchange

Ion exchange is the prominent characteristic property of natural zeolites, hence clinoptilolite (Tsitsishvili et al., 1992). Exchangeable cations in the structure of clinoptilolite exchange their sites stoichiometrically with the cations present in the solution. Doula and Ioannou (2003) classify ion exchange as a sorption process and refer it as "outer-sphere complexation" mechanism. Ion exchange is a rapid and reversible process expressed by the reaction:

$$(\equiv S - O^-)_z + M^{z+} \leftrightarrow (\equiv S - O^-)_z ... M^{z+} \tag{2.2}$$

Where; S is the surface central metal (Si or Al), and M is the cation in the solution with a valence of z.

Adsorption

- *Physical adsorption*

Porous structures in a solid body are grouped in three depending on their sizes: micropores, transitional (meso) pores and macropores. Micropores are less than 1.5 – 1.6 nm (15 – 16 A), mesopores range from 1.5 – 1.6 nm (15 – 16 A) to 100 – 200 nm (1000 – 2000 A) and macropores are greater than 200 nm (2000 A) in size. Physical adsorption occurs by the attractive forces between the adsorbent and adsorbate. It is primarily related with the microporous structure of the adsorbent since micropores have greater adsorption energy compared to larger pores or smooth surfaces. It is primarily the micro- and secondarily the mesopores which are responsible for adsorption (Seader and Henley, 1998; Tsitsishvili et al., 1992).

Natural zeolites have uniform pore widths about 3 to 10 A which are characterized as microporous crystallines (Breck, 1974; Helfferich, 1995; Seader and Henley, 1998). Of all zeolites, clinoptilolite is the one that has taken the most attention with its large pore sizes and wide inner volumes (Clinoptilolite has three channels having dimensions (in units of A): 4.4x7.2, 4.7x4.1 and 5.5x4.0, making up of 34 % total pore volume) (Ackley and Yang, 1991; Barrer, 1982; Colella, 2005; Tsitsishvili et al., 1992). It is the most widely used zeolite for adsorption purposes of both gas and liquid systems. Yet already, their adsorptive properties are mainly concentrated on sorption of gases because their dehydrated forms are effective in the removal of gas molecules (Colella, 2005; Vaughan, 1978).

- *Chemical adsorption*

Chemical adsorption, also referred to as inner-sphere complexation, is the formation of covalent bonds between metal ions and surface groups. Metal ions are forced into internal surface sites due to the increase in concentration. As a result more stable complexes are formed and hydrogen is released as the product which may cause a decrease in the pH of the solution. Inner-sphere complexation reactions are slower and usually irreversible (Doula and Ioannou, 2003):

$$\equiv S-OH+M^{z+}\leftrightarrow\equiv S-OM^{+}+H^{+} \tag{2.3}$$

$$\equiv zS - OH + M^{z+} \leftrightarrow \equiv (S - O)_z M + zH^{+} \tag{2.4}$$

Where; S is the surface central metal (Si or Al), and M is the cation in the solution with a valence of z.

Surface precipitation

Surface precipitation is the precipitation of the metal cations on the surface of clinoptilolite. Surface precipitation and surface complexation (inner and outer) follows a continuous sequence triggering each other. According to Doula and Iannou (2003), surface precipitation increases as more metal cations and anions accumulate on the surface of clinoptilolite. Surface complexation is the dominating mechanism at low surface coverage while it becomes surface precipitation at high surface coverage (Doula and Ioannou, 2003). Surface coverage is the number of adsorbed molecules on a surface divided by the number of molecules in a filled monolayer on that surface (IUPAC, 1997).

According to Semmens and Seyfarth (1978), the increase in the solubility products when the metal is concentrated on the zeolite surface might be the reason for the precipitation of metal species on the surface of the clinoptilolite. Another reason may be related to the surface properties of the zeolites. That is; natural zeolites have an internal pH higher than their surrounding solutions (Ouki and Kavannagh, 1999). That may be another explanation for surface precipitation.

Surface protonation

Surface protonation is the bonding of the hydrogen ions to surface sites of the clinoptilolite (Doula and Ioannou, 2003):

$$\equiv S - O^{-} + H_{aq}^{+} \leftrightarrow \equiv S - OH \tag{2.5}$$

$$\equiv S - OH + H_{aq}^{+} \leftrightarrow \equiv S - OH_{2}^{+} \tag{2.6}$$

Surface protonation provokes the exchange of ligands with hydroxyl ions on surface sites (Eqn 2.7) and polarization of the atomic bonds. Polarization of the atomic bonds causes detachment of the central metal ions (Al and Si), which is the dissolution of the framework. Surface protonation also increases the pH of the solution. For those reasons it is considered as one of the important mechanisms.

$$\equiv S - OH_{2}^{+} + L^{n-} \leftrightarrow \equiv S - L^{(-n+1)} \tag{2.7}$$

Dissolution of the framework

Zeolites are not very abrasion resistant materials since they have a quite soft structure (Helfferich, 1995). Therefore dissolution of the framework is another relevant mechanism which is the detachment of the central metal ion(s) (Al and/or Si) from the clinoptilolite's structure. Main factors that provoke dissolution are; metal ions and ligands, surface protonation and the solution pH (Doula and Ioannou, 2003).

Swelling

Swelling is the expansion of the adsorbent by taking up solvent. It is a basic property of ion exchange resins. However, zeolites have frameworks that are rather rigid and less open. Therefore the volume change in the crystals is very small. As a result, swelling takes place very little in zeolites that can be ignored and not to be considered (Helfferich, 1995).

2.4.2. Ion Exchange Resin

Ion exchange resins are typical gels which are organic. They have an irregular, macromolecular, three-dimensional framework consisting of hydrocarbon chains. The matrix carries ionic groups such as $—SO_3^-$, $—COO^-$, $—PO_3^{2-}$, $—AsO_3^2$ for cation exchangers. Ion exchange resins thus can simply be defined as crosslinked polyelectrolytes (Helfferich, 1995).

Amberlite IR 120, the ion exchange resin used in this study, is a cation exchange resin with sulfonic acid groups crosslinked by polystyrenes (Figure 2.1). Divinylbenzene is used for the crosslinking agent (Helfferich, 1995). It can be found either in hydrogen (H^+) or in sodium (Na^+) form. The sodium (Na^+) form is used in this study.

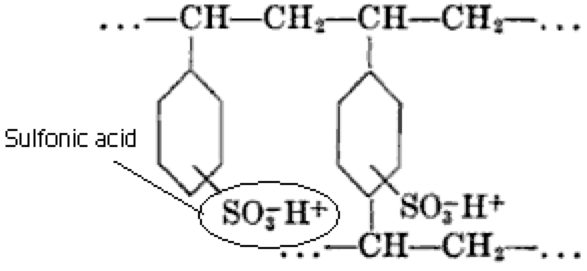

Figure 2. 1. Structure of Amberlite IR 120 in H^+ form

2.4.3. Granulated Activated Carbon

Activated carbons are microporous carbonaceous adsorbents. They can be prepared from various carbon-containing source materials such as coal, lignite, wood, nut shell, petroleum, etc. They also contain to some extent ashes mainly of silica, alumina, iron, alkali and alkaline earth metals derived from their starting materials. The amount of ash ranges from 1 % to 12 %. (Suzuki, 1990).

Granulated activated carbons (GAC) are in the form of crushed granules or in their pelletized form. Size of the granules vary depending on their application (Suzuki, 1990). They are mainly used in the removal of toxic organic compounds from water, groundwater, wastewater and industrial wastewater. Basically, they are effective in removing large organic molecules and nonpolar compounds. Inorganic compounds, like heavy metals, are not effectively removed by activated carbons (Inglezakis and Poulopoulos, 2006).

2.5. ION EXCHANGE EQUILIBRIUM MODELING

A proper and exact modeling does not exist for ion exchange equilibria (Helfferich, 1995). Efforts for solving the relationship between the extent of exchange and concentration fall mainly into three categories; assuming a simple phase adsorption process, using the Dubinin-Polanyi theory and applying the law of mass action (Inglezakis, 2007; Mumford et al., 2008; Petrus and Warchol, 2005; Robinson et al., 1993). Adsorption isotherms in the first group of models are empirical equations which are extension of gaseous adsorption isotherm equations. Isotherms in the second group are based on the potential theory of Polanyi which is a model for microporous adsorption. The third group of isotherms are basically the application of thermodynamic relations that is derived from the mass action law.

2.5.1. Adsorption Relations

In a solid-liquid system, adsorption occurs when an adsorbent is brought in contact with a surrounding solution. After a sufficiently long time, concentration of the solutes in the solution and at the surface of the adsorbent reach equilibrium. At that point of equilibrium, there exist a defined distribution of the solute between the liquid and solid phases. *Adsorption isotherm* is used in order to express this distribution which is the relation between the amount of adsorbed solute, q, and the concentration of the solute in the liquid phase, C, at temperature, T. Adsorption isotherm provides a functional expression for the change in the quantity of adsorption with respect to concentration of the adsorbate in solution at constant temperature (Suzuki, 1990; Walter J. Weber, 1972).

There are many types of adsorption isotherms. Brunauer (1943) classified these isotherms into five for pure gases (Figure 2.2).

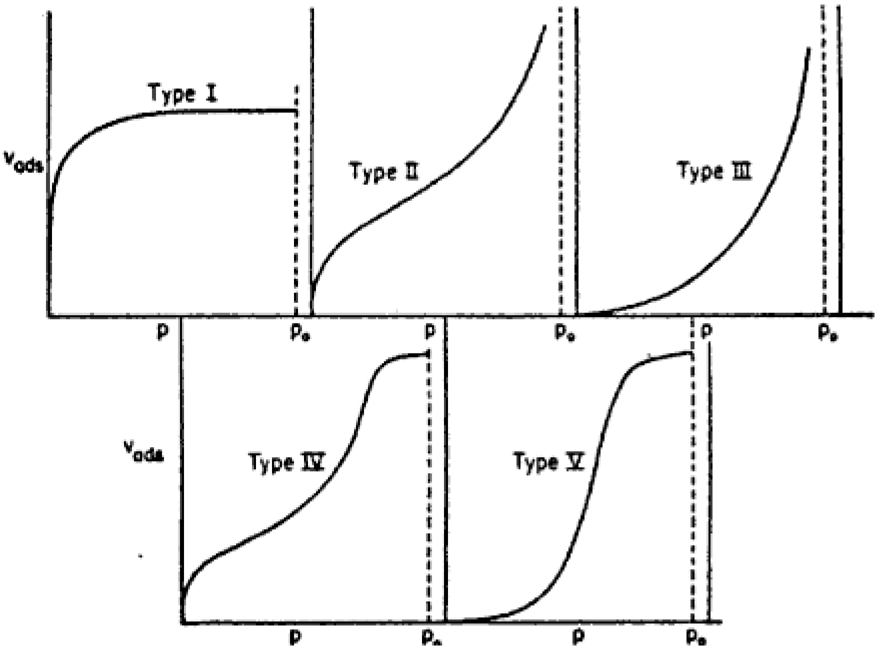

Figure 2. 2. Five types of adsorption isotherms according to Brunauer's classification

Most common isotherms are Type I (simplest isotherm, unimolecular adsorption) and Type II (more complex, multimolecular adsorption) isotherms. Models have been developed from empirical relations in order to describe the adsorption process. No valid theory has been developed when the adsorbent phase is solid. Relations derived for gaseous isotherms are implemented for liquid-solid systems (Seader and Henley, 1998).

Some of the common isotherm models are briefly described below and equations of those which are used in this study are given in Table 2.2.

Langmuir Isotherm

Langmuir isotherm is derived from mass-action kinetics and it is a Type I isotherm. Adsorption is single-layer and the assumptions made are (Seader and Henley, 1998; Walter J. Weber, 1972):

- Surface of the adsorbent is homogeneous.
- There is no interaction between adsorbed molecules.
- Energy of adsorption is constant and uniform on the surface.
- Saturation level is limited.
- Maximum adsorption level corresponds to a saturated monolayer on the adsorbent surface.
- Adsorbate is affixed to the site on the surface (no migration).

There are some limitations of the Langmuir isotherm. First of all, in most of the real systems, surface of the adsorbents are heterogeneous. Secondly, no interaction between the molecules and constant energy on the adsorption surface are not realistic assumptions. And lastly, monolayer adsorption and ideal behavior is achieved only at low concentrations thus Langmuir Equation is valid under low concentrations only.

Freundlich Isotherm

Freundlich isotherm is derived for heterogeneous surfaces with heterogeneous surface energies. It is an empirical equation and in general agrees well with the Langmuir equation for moderate ranges of concentration (Seader and Henley, 1998; Walter J. Weber, 1972). The limitation of the isotherm is not being an appropriate relation for low concentrations (Ho et al., 2001).

General Purpose Adsorption Isotherms

Langmuir and Freundlich models are the earliest isotherms that have been used for many years (Kinniburgh, 1986). Although there are some limitations in both of them, they are still the most commonly used isotherms. This is beause they are simple to use and have an ability to fit over wide concentration ranges (Altın et al., 1998; Balci, 2004; Kinniburgh, 1986). Besides, both can be expressed in linearized form which provides ease of fitting.

In order to compensate the limitations of the two isotherms, new relations are derived originating from the two of them. They are three parameter isotherms and nonlinear regression analysis is necessary to be applied to fit those isotherms into experimental data (Altın et al., 1998; Balci, 2004; Kinniburgh, 1986). Kinniburgh (1986) called them "General Purpose Adsorption Isotherms" because they are able to fit a wide variety of adsorption data by their adjustable parameters. Also they are suitable for heterogeneous surfaces by including the heterogeneity factor, β. Some examples of the general purpose adsorption isotherms are; Redlich-Peterson, Toth, Sips, Multisite Langmuir, Lineweaver-Burk, Linear Freundlich, Khan, etc. Redlich-Peterson and Toth isotherms take place in this study.

Redlich-Peterson Isotherm Redlich-Peterson isotherm describes the experimental data over a wide concentration range by eliminating the limitations of Freundlich equation for low concentrations and Langmuir equation for high concentrations (Redlich and Peterson, 1959). It approaches Freundlich isotherm at high concentrations and Langmuir isotherm at low concentrations (Foo and Hameed, 2009).

Toth Isotherm The important difference of Toth Isotherm from Redlich-Peterson isotherm is that it predicts a Gaussian type energy distribution.

Multilayer Adsorption Isotherms

BET Isotherm BET Isotherm is basically an extension of the Langmuir equation which is derived for multilayer adsorption. It is a Type II isotherm and the assumptions that the model makes are (Walter J. Weber, 1972):

- Energy of adsorption is uniform on the surface.
- Adsorption is layer-by-layer (i.e. A number of layers of adsorbate form at the surface).
- Langmuir equation is applied to each layer.
- New layers can start to form without completion of other layers.
- Capacity (q) is not limited; there is no maximum adsorption level. Hence q extends asymptotically toward infinity.

The model is not adequately describing the adsorption in porous adsorbents. This is because the adsorption is enhanced by pore filling, in the micropores of the porous adsorbents. Thus, the assumption that monolayer formation must be completed before multilayer adsorption begins is not appropriate for them.

Also the same limitations (except the one coming for monolayer coverage) as in Langmuir isotherm are valid in BET isotherm as well.

2.5.2. Dubinin-Polanyi Theory

Models derived from Dubinin-Polanyi Theory are based on microporous adsorption rather than physical adsorption. In micropores, adsorption occurs by the attractive forces of the wall surrounding the micropores, and adsorption takes place by micropore volume filling (Inglezakis, 2007; Suzuki, 1990).

The isotherms based on Dubinin-Polanyi theory defines an adsorption potential equal to change of the free energy of a substance from the fluid state to the adsorbed state. Dubinin-Astakhov (DA) and Dubinin-Radushkevich (DR) equations are derived according to this theory. They are originally derived for adsorption of vapors on porous solids and used especially for adsorption of gases on activated carbons. Rarely, they are also used for the adsorption of organic solutes and ion exchange/adsorption of metal ions from aqueous solutions on porous sorbents (Inglezakis, 2007).

DR isotherm is a special case of DA isotherm, where the heterogeneity parameter, n is set equal to 2 in the equation. The value of n is mainly related with the adsorbate microporous structure and 2 is suitable for the adsorption of vapors on activated carbons. However, Inglezakis (2007) proposes that it does not comply with zeolites which are more homogeneous than activated carbons, hence values greater than 3-4 may be used for them. For that reason, DA isotherm is more appropriate for zeolite systems with its adjustable heterogeneity parameter. There are two forms of the equations; solubility-normalized (SN) and solubility non-normalized (SNN) but SN form is recommended by Inglezakis (2007).

Table 2. 2. Equation of adsorption isotherms from adsorption relations and Dubinin-Polanyi theory

Isotherm	**Equation**	**Parameters**
Langmuir (L)	$q=\frac{KCM}{1+KC}$	q : Amount adsorbed per gram of clinoptilolite (meq/g) M : Maximum amount adsorbed per gram of clinoptilolite (meq/g) C : Equilibrium solute concentration (mg/L) C_S : Solubility of cadmium (mg/L) K : Surface adsorption equilibrium constant (L/mg) β : Surface heterogeneity factor R : The universal gas constant (kJ/mol . K) T : The absolute temperature (K) E : Adsorption energy (kJ/mol) n : Heterogeneity parameter for pore structure
Freundlich (F)	$q=(KC)^{\beta}$	
Redlich-Peterson (RP)	$q=\frac{KCM}{1+(KC)^{\beta}}$	
Toth (T)	$q=\frac{KCM}{(1+(KC)^{\beta})^{1/\beta}}$	
Dubinin-Astakov (DA$_{SN}$)	$q=M\exp\left[-\left(\frac{RT}{\sqrt{2}E}\right)^{n}\left(\ln\left(\frac{C_S}{C}\right)\right)^{n}\right]$	

2.5.3. Mass action Law

Although ion exchange is often treated as a simple adsorption process and the data is fitted to sorption isotherms, actually it is different from adsorption such that it can be expressed as a reversible, stoichiometric chemical reaction as below (Seader and Henley, 1998):

$$z_A B_Z^{Z_B^+} + z_B A_S^{Z_A^+} \leftrightarrow z_A B_S^{Z_B^+} + z_B A_Z^{Z_A^+} \tag{2.8}$$

where A is a cation of valance z_A and B is a cation of valance z_B. The subscript z is used for zeolite and s for solution phases (Culfaz and Yagiz, 2004). Ion exchange isotherms are used to describe the exchange equilibrium in which the equivalent cation fraction of the ion in solution is plotted against the fraction in the adsorbent (Pabalan and Bertetti, 2001).

For ion exchange systems, Helfferich (1995) states that thermodynamic treatment is superior to any other approach since it is exact and requires no assumptions and models. It is applicable to all ion exchangers of any structure. Yet, for practical applications, its usage is limited because of the difficulty and accuracy in the calculations of the activity coefficients in both phases.

Thermodynamic treatment deals with the changes in macroscopic physical properties thus, it is not possible to infer the mechanisms taking place only from thermodynamic data. However, it can provide a tool for understanding ion-exchange behavior and for predicting ion exchange equilibria (Pabalan and Bertetti, 2001).

Thermodynamic equilibrium constant is an integral quantity characteristic of the whole isotherm surface and depends on temperature only (Helfferich, 1995). It is defined by (Culfaz and Yagiz, 2004):

$$K_a = \frac{A_z^{z_B} B_s^{z_A}}{B_z^{z_B} A_s^{z_A}} \frac{(N/z_B)^{z_A}}{(N/z_A)^{z_B}} \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} \frac{f_A^{z_B}}{f_B^{z_A}} \tag{2.9}$$

where;

K_a: Thermodynamic equilibrium constant

A_z and A_s: The equivalent fraction of cation A in the zeolite and in the solution phase

B_z and B_s: The equivalent fraction of cation B in the zeolite and in the solution phase

N: Normality of the solution (N)

z: valency of the charges

γ: activity coefficient in the solution

f: activity coefficient in the exchanger

Once the equilibrium constant is found, the standard free energy of exchange per equivalent, ΔG° (kJ/eq) can be calculated from the equation (Culfaz and Yagiz, 2004):

$$\Delta G^\circ = -\frac{RT}{z_A z_B}\ln K_A \qquad (2.10)$$

where;

R: Universal gas constant (8.31×10^{-3} kJ/K mol)
T: Temperature (K)

2.6. INDICATORS OF REMOVAL MECHANISMS

2.6.1. Exchangeable Cations

Monitoring of exchangeable cations is important for ion exchange systems for inferring removal mechanisms. That is because ion exchange is a stoichiometric process, i.e. the amount of sorbed cations must be equal to the amount of released cations in equivalent basis. Whereas in adsorption, cations are taken up without being replaced by other cations. Accordingly, comparison of the total amount of sorbed cations with the total amount of released cations can be helpful in the interpretation of the prevailing removal mechanisms. There are several studies revealing removal mechanisms by monitoring exchangeable cations (Doula and Ioannou, 2003; Llanes-Monter et al., 2007; Peric et al., 2004; Wen et al., 2006).

2.6.2. Conductivity

Specific conductivity, κ is the conductivity of an electrolyte solution at 25°C for electrolytes and it depends greatly on the concentration of the ions present in the solution. Comparison of the electrical conductivities of different electrolytes is more appropriate when the values of κ are converted to a concentration basis e.g., moles/L or equivalents/L. In this way, molar conductivity term is defined as;

$$Molar\,conductivity = \Lambda_{m,c} = \frac{Specific\,conductivity\,at\,concentration\,c}{moles/L\,of\,electrolyte} \tag{2.11}$$

The corresponding equation becomes;

$$Molar\,conductivity = \Lambda_{m,c} = \frac{1000\kappa_c}{c} \tag{2.12}$$

if units of S/cm for κ_c (specific conductivity at concentration c), and moles/L for c (electrolyte concentration) is used where the units of molar conductivity ($\Lambda_{m,c}$) is s.cm^2/mol.

For strong electrolytes, molar conductivity decreases only slightly as the concentration increases so for rough calculations it is permissible to assume Λ_c is constant and independent of concentration. For this purpose, the *limiting molar conductivity*, $\Lambda_{m,0}$, values of different electrolytes are used which is a finite value found by the extrapolation of $\Lambda_{m,c}$ to zero concentration, i.e., complete dissociation (Figure 2.3) (Atkins and Paula, 2002).

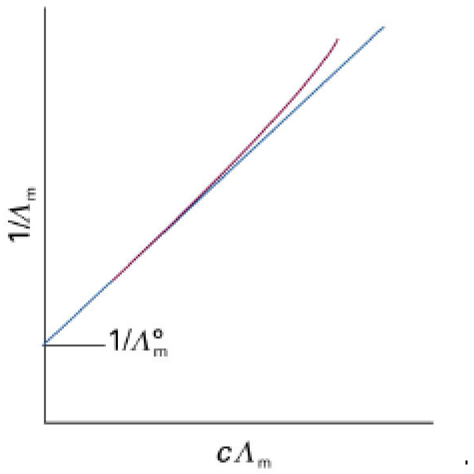

Figure 2. 3. Extrapolation to zero concentration to find the limiting molar conductivity of a solution

Kohlrausch (1899) deduced the *law of independent ionic mobilities* by extensive measurements of electrolytic conductance. The law states that; each type of ion in an electrolyte contributes a characteristic amount to the total conductance. Thus, as an example, the molar conductivity Λ_0 for potassium chloride consists of two parts – a quantity due to potassium cations $(\lambda_0)_{K^+}$ and the other due to chloride anions $(\lambda_0)_{Cl^-}$ – where λ_0 is the *limiting ionic conductivities.* The following equation illustrates the application of the law (on the equivalent basis),

$$(\Lambda_0)_{KCl} = (\lambda_0)_{K^+} + (\lambda_0)_{Cl^-} \qquad (2.13)$$

This equation is only valid for zero concentration and Λ_0 values of different electrolytes can be calculated in this way (Potter, 1956).

Table 2.3 gives values of limiting ionic conductivities, λ_0 on equivalent basis for the cations that take part in this study (i.e. Cd^{2+}, Ca^{2+}, Mg^{2+}, Na^+, K^+ and H^+) (Milazzo, 1963). From that Table it can be seen that, except from hydrogen, cations possess λ_0 values that are close to each other (between 50 and 75 s.cm^2/equivalent). Based on this, it can be deduced that the conductivity of the solution should remain constant if the prevailing mechanism is ion exchange. Accordingly, if the main mechanism is adsorption, a decrease is expected in the solution conductivity. Hydrogen ion (H^+) is an exception and not included in this rule with its very high ionic conductivity. Thus, if the exchange occurs between Cd^{2+} and H^+ ions, H^+ ions being replaced by Cd^{2+} ions will increase the conductivity of the solution.

Table 2. 3. Limiting equivalent ionic conductivities, λ_0 (s.cm^2/eq) in aqueous solutions at 25°C

Cations	**λ_0**
½ Cd^{2+}	54.00
½ Ca^{2+}	59.50
½ Mg^{2+}	53.06
Na^+	50.11
K^+	73.50
H^+	349.80

Eventually, monitoring of conductivity change can be a supplementary tool in the investigation of the removal mechanisms. A heavy metal removal study by clinoptilolite of Stylianou et al. (2007) involves such an investigation of removal mechanisms based on conductivity changes.

2.6.3. pH

pH of the solution has many remarkable effects in the removal of compounds so its monitoring during equilibrium experiments is necessary. First of all, for ion exchange systems, H^+ ions compete with heavy metal cations that affects their removal from solution (Englert and Rubio, 2005). Furthermore, pH of the solution may have an indirect effect by changing surface functional groups, altering the structure of the sorbent, forming metal-hydroxyl species, etc. (Benhammou et al., 2005; Doula and Ioannou, 2003; Tsitsishvili et al., 1992). Moreover, at high pH values, hydrolysis of heavy metal ions can take place. In case of cadmium, hydrolysis occurs above a pH of 8 (Berber-Mendoza et al., 2006b).

2.6.3. Aluminum and Silicon

Aluminum and Silicon are the framework cations of clinoptilolite structure. Dissolution of the clinoptilolite structure causes aluminum and silicon atoms to migrate into solution. Detection of these atoms in the solution is an indication of dissolution taking place, monitoring of these cations can provide help in understanding the overall mechanisms involved in the removal of heavy metals by clinoptilolite. Studies are present in literature that monitor Al and Si to determine the dissolution of the framework structure (Dimirkou, 2007; Doula et al., 2002).

CHAPTER 3

MATERIALS AND METHODS

3.1. CHEMICALS

All the chemicals used were analytical grade reagents. Cd^{2+} stock solutions and NaCl solutions were prepared by dissolving $Cd(NO_3)_2.4H_2O$ (Fluka) and NaCl (Merck Grade) salts respectively in high purity deionized water. HNO_3 and NaOH were used for adjusting initial pH of Cd^{2+} stock solutions. Standard solutions which were used in the calibration of Atomic Absorption Spectrometry and Flame Photometry were prepared from 1000 mg/L certified reference solutions (Merck Grade) of related cations. pH meter was calibrated with buffer solutions of pH 4, 7 and 10 (YSI Incorporated) and conductivity meter calibration was done by preparing stock solutions from 1000 μS/cm certified reference solution of potassium chloride (YSI Incorporated).

3.2. SORBENTS

3.2.1. As-received Clinoptilolite Samples (AsC)

Clinoptilolite samples obtained from Rota Madencilik were taken from Gördes (Manisa) deposits. Samples were crushed and sieved to 0.425-0.85 mm (20-40 mesh) size then washed with high purity deionized water and dried at 105°C for 24 hrs and stored in a desiccator until used.

Properties of the as-received clinoptilolite which is taken from Rota Madencilik is given Tables 3.1 and 3.2.

Table 3. 1. General information and mineral composition of AsC samples

General Information	
Chemical Name	Calcium, Potassium, Sodium Aluminosilicate
Chemical Family	Natural Zeolites
Chemical Formula	$(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96}.24H_2O$
Mineral Composition	**% by weight**
Clinoptilolite	88 – 95
Feldspar	3 – 5
Montmorillonite	2 – 5
Cristobalite	0 – 2
Muscovite	0 – 3

Table 3. 2. Chemical composition of AsC samples

Chemical Composition	% by weight
SiO_2	65 – 72
Al_2O_3	10 – 12
CaO	2.5 – 3.7
K_2O	2.3 – 3.5
Fe_2O_3	0.8 – 1.9
MgO	0.9 – 1.2
Na_2O	0.3 – 0.65
TiO_2	0 – 0.1
MnO	0 – 0.08
Loss of Ignition (LOI)	9 – 12
SiO_2 / Al_2O_3	5.4 – 6.0
Total Cation Exchange Capacity (TCEC)	1.5 – 1.9 meq/g

3.2.2. Conditioned Clinoptilolite Samples (CnC)

In order to prepare conditioned clinoptilolite samples, AsC samples were put in a series of batches of 2M NaCl solutions (10 g/100 mL zeolite to solution ratio) over a period of 7 days with 24 h renewal of the solution, with constant shaking at 200 rpm and at a constant temperature of 60°C. Samples were then washed with high purity deionized water until no Cl^- was detected in washing water. Finally, conditioned samples were dried at 65°C for 24 hours, and stored in a desiccator over saturated NaCl solutions for about 10 days until constant mass is attained.

3.3.3. Ion Exchange Resin (IR)

Commercial gel-type Amberlite IR 120 (Merck) Na-form was used in the experiments as an ion exchanger which had a 0.3-1.18 mm (16-50 mesh) particle size. No pretreatment was performed on the IR samples prior to the experiments.

3.3.4. Granulated Activated Carbon (GAC)

Granular activated carbon (Sigma-Aldrich, Darco) 0.42-0.85 mm (20-40 mesh) particle size was used. Activated carbon samples were washed with high purity deionized water in order to remove surface dust and impurities, then dried at 105°C for 24 hours, and stored in a desiccator until used.

3.3. EXPERIMENTAL

All experiments were conducted in batch mode in duplicate together with a sorbent-free blank. The average value of the duplicates was always used during the presentation and analysis of data. Experiments were conducted in an orbital type shaker (Edmund Buhler KS-15) at 150 rpm at a constant temperature of 25°C ± 1°C. Initial pH of all Cd^{2+} solutions were adjusted to 4 using 0.1 N HNO_3 and 0.1 N NaOH solutions. Depending on the experiment, at equilibrium or at selected time intervals sorbents were separated from the supernatant by filtration using a 0.45 μm filter paper. After filtration, samples were acidified with HNO_3 to keep all ions in their free forms, and then stored in a refrigerator until analysis. pH and conductivity change were monitored during the experiments. Analysis of Cd^{2+} and exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were performed on all samples. Framework cations of clinoptilolite (Al^{3+} and Si^{4+}) were analyzed in selected samples. During the analysis of exchangeable cations K^+, Ca^{2+} and Mg^{2+} were not detected for IR and Na^+, K^+, Ca^{2+}, Mg^{2+} were not detected for GAC so they are not given in the results.

3.3.1. Preliminary Experiments

In preliminary experiments, equilibration times of all sorbent-Cd^{2+} pairs were determined. For this purpose, 2g sorbent/200 mL Cd^{2+} solution ratio was used for all sorbents. Concentrations used for this purpose were 50 mg/L, 200 mg/L, 1000 mg/L and 50 mg/L for clinoptilolite, conditioned clinoptilolite, ion exchange resin and activated carbon, respectively. Solutions were analyzed at specified time intervals until no further uptake of Cd^{2+} was detected. Total sampling volume was approximately 12 % of the total solution volume for each sorbent and volume correction is done in the analysis.

3.3.2. Equilibrium Experiments

100 mL solution volume was used during equilibrium experiments. Two different experimental procedures (P1 and P2) were performed in equilibrium experiments for all sorbents. In the first procedure, solid-to-liquid ratio was held constant and solution concentration was varied. In the

second procedure, solution concentration was held constant and solid-to-liquid ratio was varied. S/L ratio and normality used in each procedure and for each sorbent are given in Table 3.3.

Table 3. 3. S/L ratio and normality used in two different procedures for each sorbent

Procedure / **Sorbent**	**P1**		**P2**	
	Normality (N)	**S/L ratio (g/mL)**	**Normality (N)**	**S/L ratio (g/mL)**
AsC	0,001 – 0,1	1/100	0,01	0,05/100 – 20/100
CnC	0,001 – 0,2	1/100	0,01	0,01/100 – 4/100
IR	0,001 – 0,5	1/100	0,3	0,05/100 – 40/100
GAC	0,0004 – 0,02	1/100	0,001	0,05/100 – 30/100

3.3.3. Deionized Water-Clinoptilolite Interaction

In order to investigate sorbent-deionized water interactions, equilibrium experiments were carried out with all sorbents in Cd^{2+}-free deionized water at an initial pH of 4. pH and conductivity change were monitored during the experiments. Analysis of Cd^{2+} and exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were performed on all samples. Framework cations of clinoptilolite (Al^{3+} and Si^{4+}) were analyzed in selected samples.

3.3.4. Maximum Exchange Level (MEL)

Maximum exchange level of the sorbents were determined by the repeated equilibrations method. 1 g of each sorbent was added to a flask containing a 100 mL volume of Cd^{2+} solution. Initial concentrations were set equal to the concentrations that were used in equilibrium experiments, Procedure 2 for each sorbent. The solutions were replaced with a fresh solution (of the same cation and the same concentration) at the end of specified time intervals, which were the equilibration times that were determined in preliminary experiments for each sorbent. The solutions that were drawn were analyzed for cadmium uptake and that procedure continued until no further uptake was detected.

3.4. ANALYTICAL TECHNIQES

Analysis and measurement of various parameters was carried out by the following methods/instruments;

- Cd^{2+}, Ca^{2+}, and Mg^{2+} ions by Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer
- Na^{+} and K^{+} ions by Jenway PFP7 Model Flame Photometer
- Aluminum and Silicon by Perkin Elmer Optima 4300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Central Laboratory, METU)
- pH, conductivity and temperature by CyberScan PC Meter
- Cl^{-} ions by Argentometric Method, Standard methods (APHA, 2005)

3.5. CALCULATION OF PARAMETERS FOR EQUILIBRIUM EXPERIMENTS

The amount of cadmium sorbed per gram of clinoptilolite (q_e) is calculated according to the equation:

$$q_e = \frac{(C_i - C_e) \times V}{m \times Eq.Wt.} \tag{3.1}$$

where;

q_e: amount adsorbed per gram of clinoptilolite (meq/g)
C_i: initial metal concentration in solution (mg/L)
C_e: equilibrium metal concentration in solution (mg/L)
V: volume of solution (L)
m: amount of sorbent added (g)
Eq.Wt.: equivalent weight of the metal added (g/eq)

The isotherm parameters (K, β, M, E, and n) and the correlation coefficient (R^2) were calculated from experimental data by using MATLAB software with their 95 % confidence bounds. Two error functions; sum of squares of errors (SSE) and hybrid fractional error function (HYBRID) given below are calculated in addition to the correlation coefficient (R^2).

$$SSE = \sum_{i=1}^{p} (q_{\exp} - q_{calc})_i^2 \tag{3.2}$$

$$HYBRID = \frac{100}{p-n} \sum_{i=1}^{p} \left[\frac{(q_{\exp} - q_{calc})^2}{q_{\exp}} \right]_i \tag{3.3}$$

$$R^2 = 1 - \frac{SSE}{\sum_{i=1}^{p} \left(q_{\exp} - \bar{q}_{calc} \right)_i^2} \tag{3.4}$$

where;

q_{exp}: the experimental data

q_{calc}: the modeled data

$\bar{q}_{calc}$: mean of the modeled data

p: the number of data points

n: the number of model parameters

In the fitting of the results, Maximum Exchange Levels (MEL) are substituted for M in order to obtain more reliable results. For the isotherms that are not compatible with the estimated MEL, Langmuir isotherm is allowed to give a capacity value which is an alternative to the repeated equilibration method to determine MEL (Inglezakis, 2005).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. PRELIMINARY EXPERIMENTS

Preliminary experiments were performed in order to determine the equilibration times of each sorbent. The results for each sorbent are given in Figures 4.1A, B, C and D. These results show that the equilibrium times for each sorbent are different from each other (Table 4.1). While the as-received clinoptilolite reached equilibrium at 96 hrs (4 days), when the clinoptilolite is converted to its homoionic form, it takes much shorter, that is 6 hrs to reach equilibrium.

Table 4. 1. Equilibration times determined for each sorbent for Cd^{2+} removal

Sorbent	AsC	CnC	IR	GAC
Equilibration Time (hr)	96	6	24	24

This big difference between the equilibration times of AsC and CnC shows that there are interfering effects arising from the impurities of AsC which extend the time needed to reach equilibrium. That is, the resulting “homogeneity” of the sorbent, CnC, enable much shorter equilibration times. The other sorbents, IR and GAC, reach equilibrium considerably shorter than AsC, yet somewhat longer than CnC.

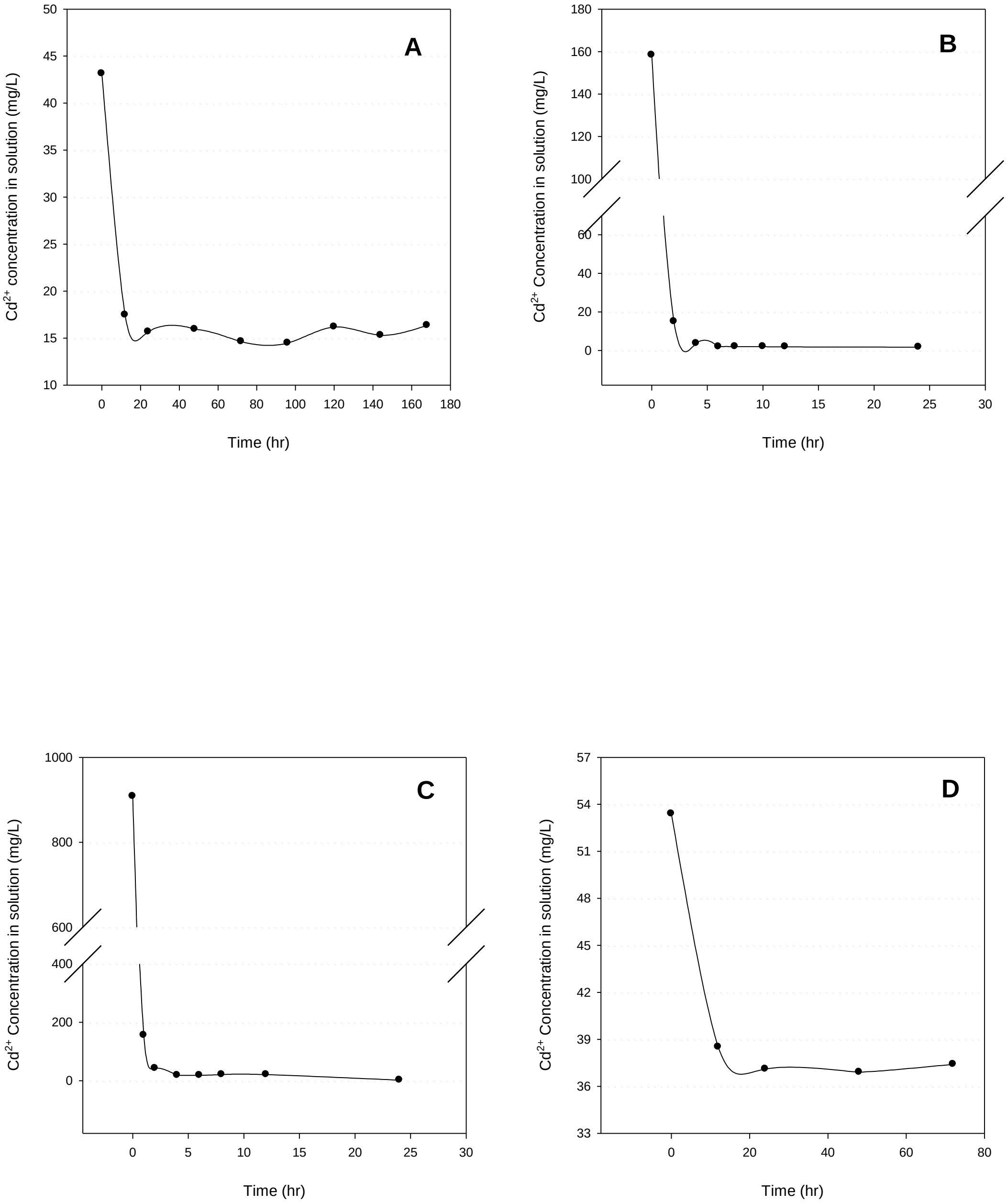

Figure 4. 1. Equilibration time graph of A. AsC, B. CnC, C. IR and D. GAC

4.2. EQUILIBRIUM EXPERIMENTS

4.2.1. Experiments with As-received Clinoptilolite (AsC)

a. Cadmium Removal

Removal of cadmium for AsC-P1 and P2 can be seen in Figures 4.2A and 4.3A. The marked estimation that can be made from these figures is the different capacity values obtained from each procedure. In P1, an approximate capacity of 0.60 meq/g is attained, whereas in P2 the maximum amount of sorbed Cd^{2+} does not reach a plateau. The maximum Cd^{2+} sorbed is when 0.05 g clinoptilolite is used for 0.01 N, resulting in 0.42 meq/g Cd^{2+} sorption.

Capacity values of as-received clinoptilolite obtained in some studies for Cd^{2+} removal are given in Table 4.2. It can be seen that the clinoptilolite used in this study have a superior capacity among others.

Table 4. 2. Capacities of as-received clinoptilolite for Cd^{2+} in literature

Reference	Capacity (meq/g)
Curkovic et al. (1997)	0.24
Cincotti et al. (2001)	0.06
Arambula et al. (2006)	0.22
Gedik and Imamoglu (2008)	0.18
Minceva et al. (2008)	0.09
This study	0.65

AsC-Procedure 1 (AsC-P1)

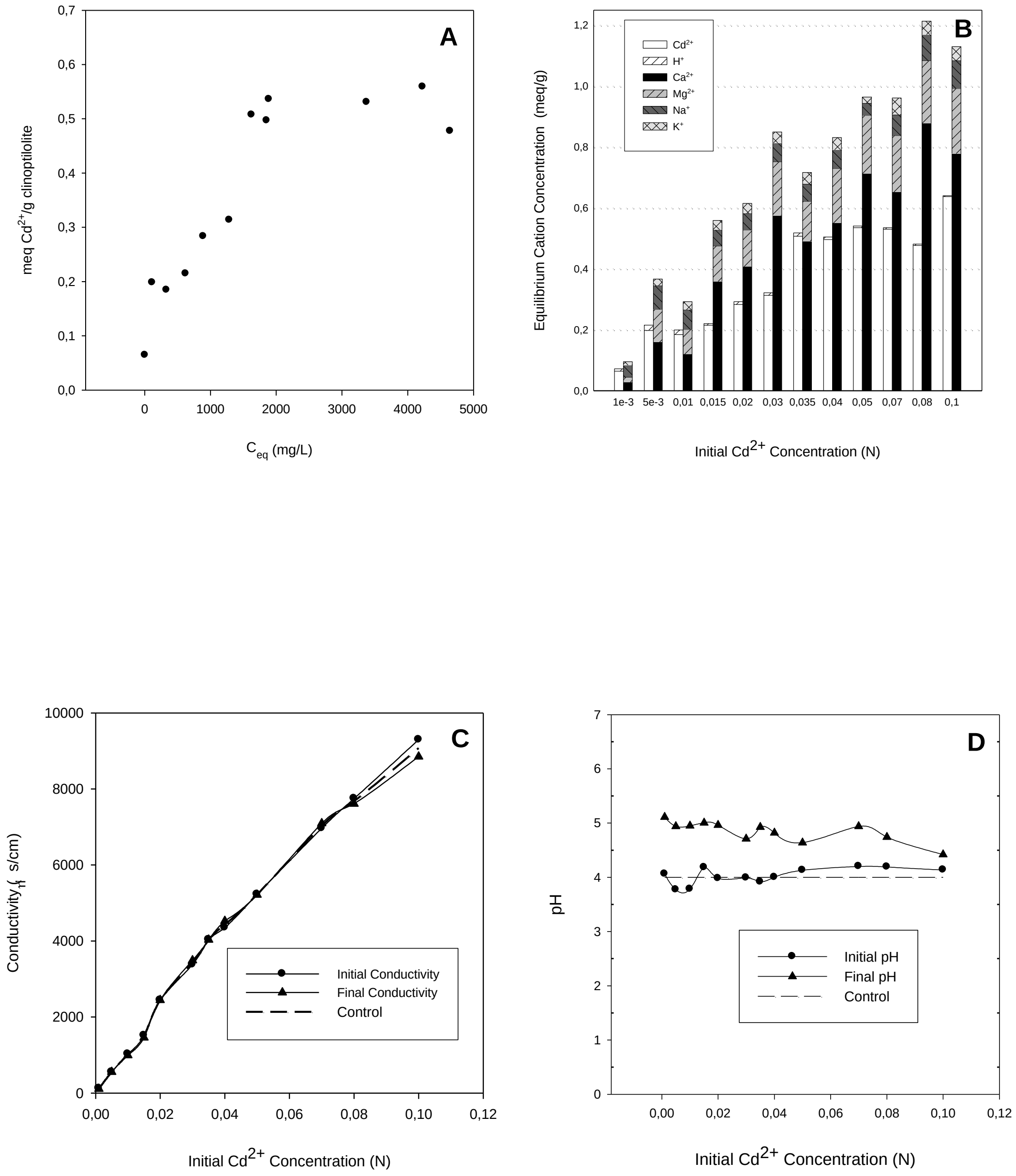

Figure 4. 2. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of AsC-P1

AsC-Procedure 2 (AsC-P2)

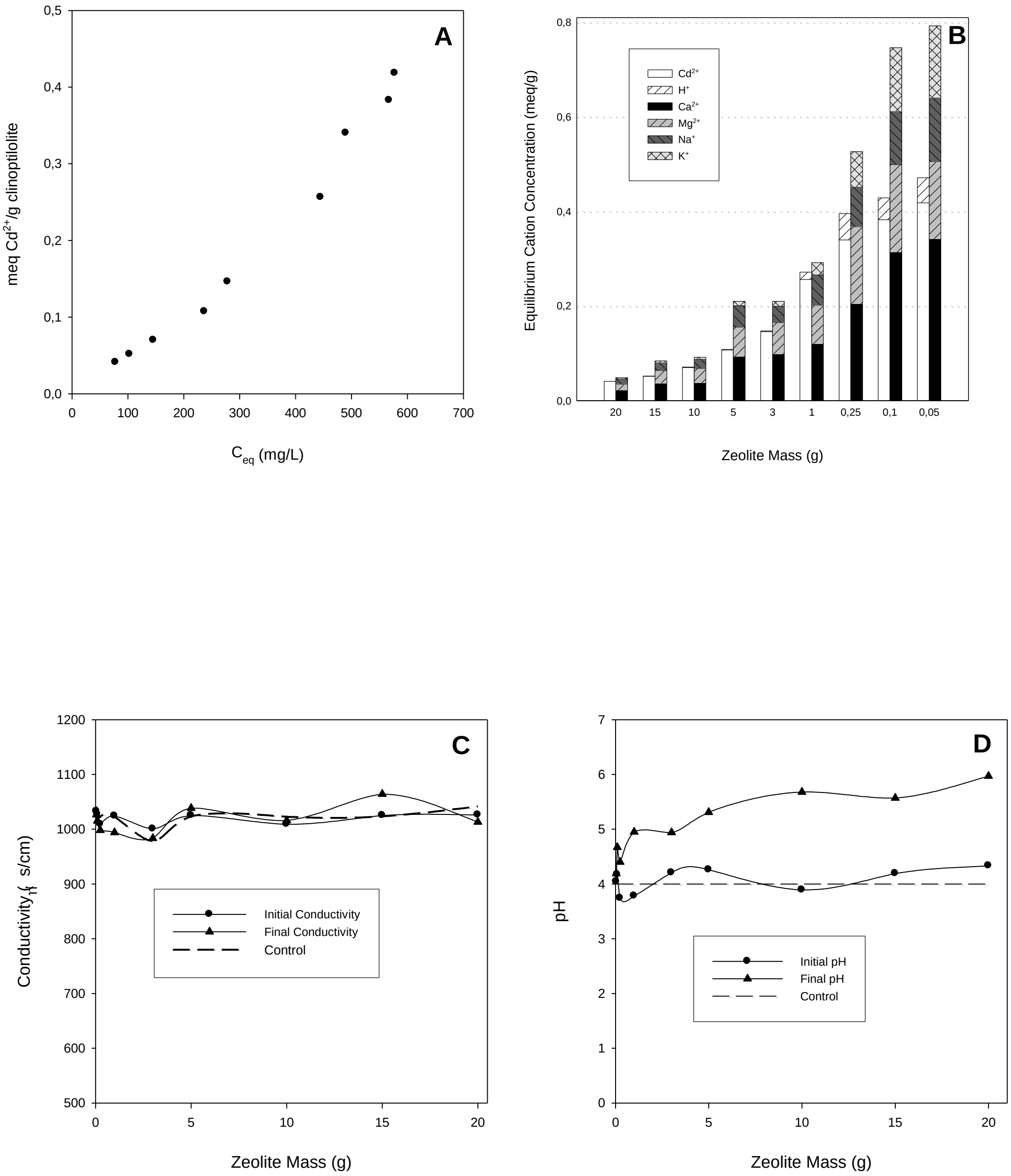

Figure 4. 3. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of AsC-P2

The result of the Maximum Exchange Level (MEL) experiment for AsC is shown in Figure 4.4. The MEL for AsC is estimated as 0.65 meq/g. In both procedures (P1 and P2) maximum sorbed amounts do not reach that level, however come close. The MEL experiments are exhaustive Cd^{2+} exchange experiments when the sorbent interacts with Cd^{2+} for several days with refreshment of the solution until no uptake is observed. Therefore batch equilibrium experiments are not expected to reach this level, typically. There are examples in the literature that MEL is not attained during equilibrium studies (Langella et al., 2000; Townsend and Loizidou, 1984).

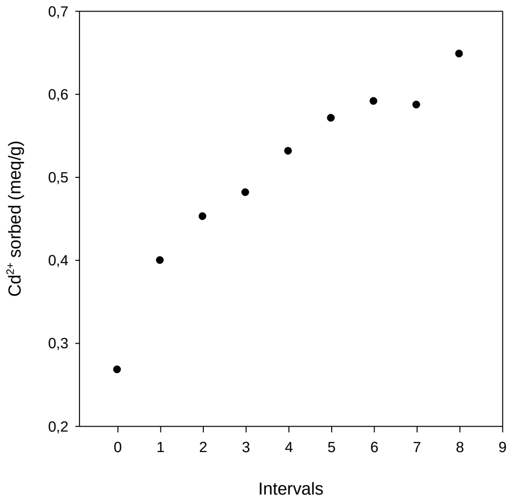

Figure 4. 4. Maximum Exchange Level of AsC

b. Exchangeable Cations

Exchangeable cations of AsC P1 and P2 are given in Figures 4.2B and 4.3B, respectively. The high Ca^{2+} release can be explained by the structure of the clinoptilolite, as given in the chemical composition in Table 3.2. According to this, although K^+ ions are much more than Mg^{2+} and Na^+ ions in the clinoptilolite's structure, fewer K^+ ions are detected in the solutions at equilibrium. This can be attributed to the preference of K^+ ions over Mg^{2+} and Na^+ by clinoptilolite. As a consequence; mostly Mg^{2+} and Na^+ exchange their sites with Cd^{2+} instead of K^+.

Total exchangeable cations released are more than Cd^{2+} amount sorbed for both in P1 and P2, for all concentrations and masses. Peric et al. (2004) observed the same behavior for clinoptilolite used in their study, for each of the three metals; Zn^{2+}, Cu^{2+} and Pb^{2+}. They explained this behavior by higher hydration radius of the heavy metal ions as well as by adsorption of their positive monovalent hydroxy-species on the inner surface. It is concluded that these effects may block the diffusion of heavy metal ions to the exchangeable sites in the channels of the porous structure. Another explanation made by Doula (2006) for that nonstoichiometry is the dissolution of impurities of the clinoptilolite which are dissolved and enrich the solution with exchangeable cations.

However the gap between the released and sorbed amounts is lower in P2 except for small masses. The average values of the fraction of sorbed over released cations in P1 and in P2 can be seen in Table 4.3 with their standard deviations. The values indicate that ion exchange is proceeding more in P2.

Table 4. 3. Average values of Sorbed/Released amounts for AsC-P1 and P2

Parameter Procedure	Sorbed/Released Cations	Standard Deviation
P1	0.56	0.13
P2	0.70	0.14

In order to have an idea about the dissolution tendency of clinoptilolite or the impurities in the natural material, deionized water-clinoptilolite experiments are conducted, and results are given in Figure 4.5. In general, the amounts of released cations are scarce, compared to the values obtained in equilibrium experiments. It is interesting that maximum released cation is Na^+ although in equilibrium experiments it was the Ca^{2+} ion. Studies that attained similar results are present in literature which came up with a conclusion that most of the Na^+ ions released from the dissolution of the impurities in the clinoptilolite structure (Doula and Dimirkou, 2008; Rivera et al., 2000; Semmens and Seyfarth, 1978). Moreover, Ca^{2+} ions being the least released cations among others show that they are released in equilibrium experiments mostly due to ion exchange.

The only sorbed ion in this case is H^+ and it can be seen that total amount of released cations are higher than the amount of sorbed H^+ ions. This difference can be attributed to the dissolution process and it can be deduced that only small portion of exchangeable cations exchanged their sites with H^+ ions.

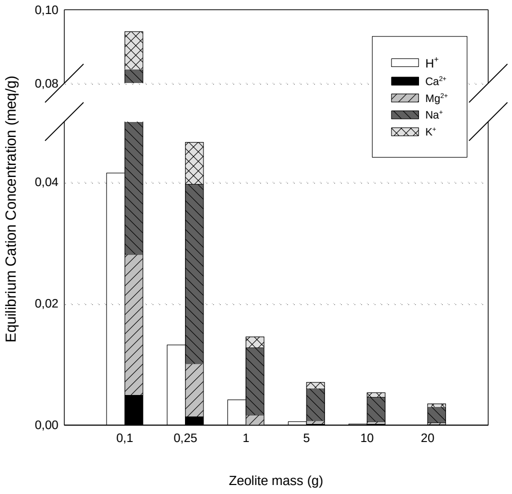

Figure 4. 5. Deionized water-AsC interaction

c. Conductivity Change

Conductivity change of the solution can give an idea about the removal mechanisms involved. A clinoptilolite-heavy metal removal study of Stylianou et al. (2007) provides an example for that. Conductivity changes were detected in that study during removal of three different metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) by clinoptilolite. In this study, it was observed that conductivity values remain constant for Pb^{2+}, but decrease for Cu^{2+} and Zn^{2+}. Then it was concluded that Pb^{2+} was removed by ion exchange mechanism, and for Cu^{2+} and Zn^{2+} adsorption took place in addition to ion exchange. This provides an example of how conductivity change of a solution can give an idea about the mechanism. This also shows that it is not just the sorbent that determines the removal mechanism, sorbate has a part as well.

Figures of conductivity change for AsC-P1 and P2 are given in Figures 4.2C and 4.3C, respectively. A slight change is observed between the initial and final conductivity both for P1 and P2. Accordingly, the conductivity profiles for both P1 and P2 shows an overall good agreement between initial and final conductivities indicating Cd^{2+} removal mechanism to be dominantly ion exchange.

The change in conductivity of AsC in deionized water is given in Figure 4.6A. As expected, conductivity increases as the mass of the clinoptilolite increases since the amount of the released cations increases with the increase of mass.

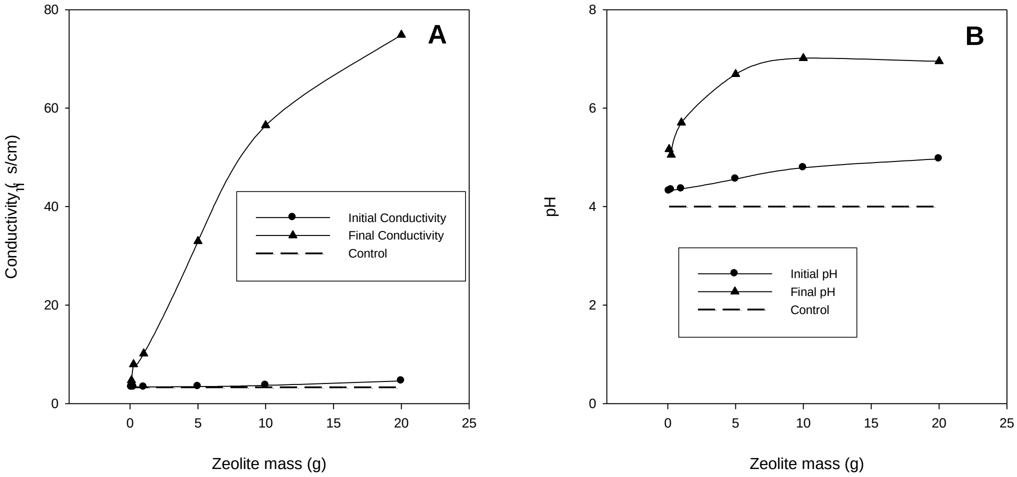

Figure 4. 6. A. Conductivity B. pH change of AsC in deionized water

d. pH Change

Changes of pH for AsC-P1 and P2 are shown in Figures 4.2D and 4.3D. pH increases from an initial value of 4 to an approximate value of 5 in P1 and to 5-6 in P2, depending on the mass used.

The increase of pH in P1 and P2 is attributed to the amphoteric characteristic of clinoptilolite for which tends to neutralize water acting either as a proton acceptor or a donor (Filippidis et al., 1996). The uptake of H^+ ions takes place by ion exchange and/or by surface protonation. As the mass increases, pH increases accordingly.

For deionized water pH change shows a similar trend as in the equilibrium experiments with a single difference; it reaches up to values above 6, as the mass increases (Figure 4.6B). pH cannot rise up to higher values in equilibrium experiments because H^+ ions are in competition with Cd^{2+} ions.

4.2.1. Experiments with Conditioned Clinoptilolite (CnC)

a. Cadmium Removal

Removal of cadmium for CnC P1 and P2 can be seen in Figures 4.7A and 4.8A. A plateau in Cd^{2+} removal is reached in both isotherms but the ultimate capacities are different from each other. The maximum sorbed Cd^{2+} is about 27 % higher in P2 when compared to P1. This result is interesting since the sorbent and the sorbate are the same for P1 and P2, yet it seems that the method of metal-clinoptilolite interaction has an effect on the maximum amount of Cd^{2+} sorbed.

CnC-Procedure 1 (CnC-P1)

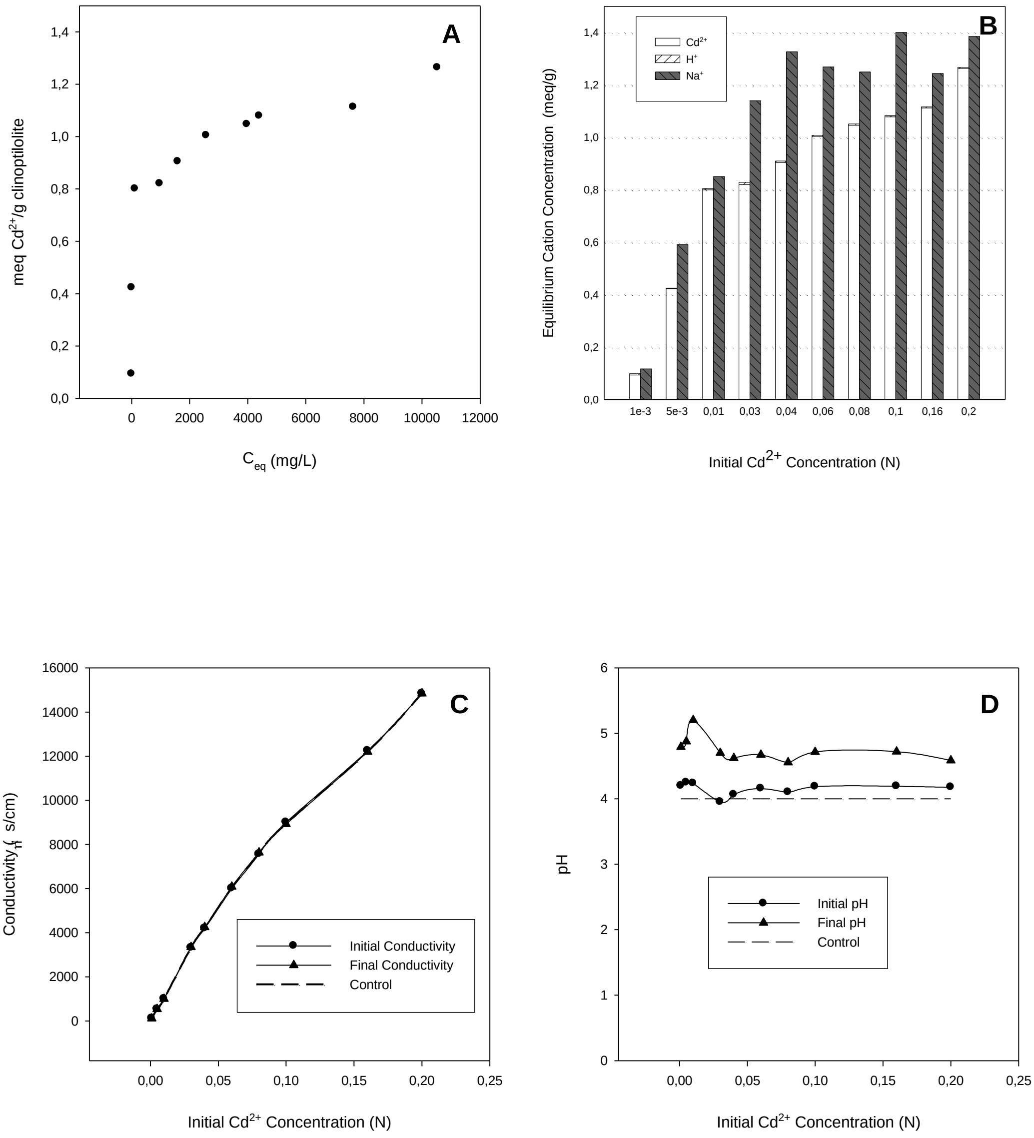

Figure 4. 7. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of CnC-P1

CnC-Procedure 2 (CnC-P2)

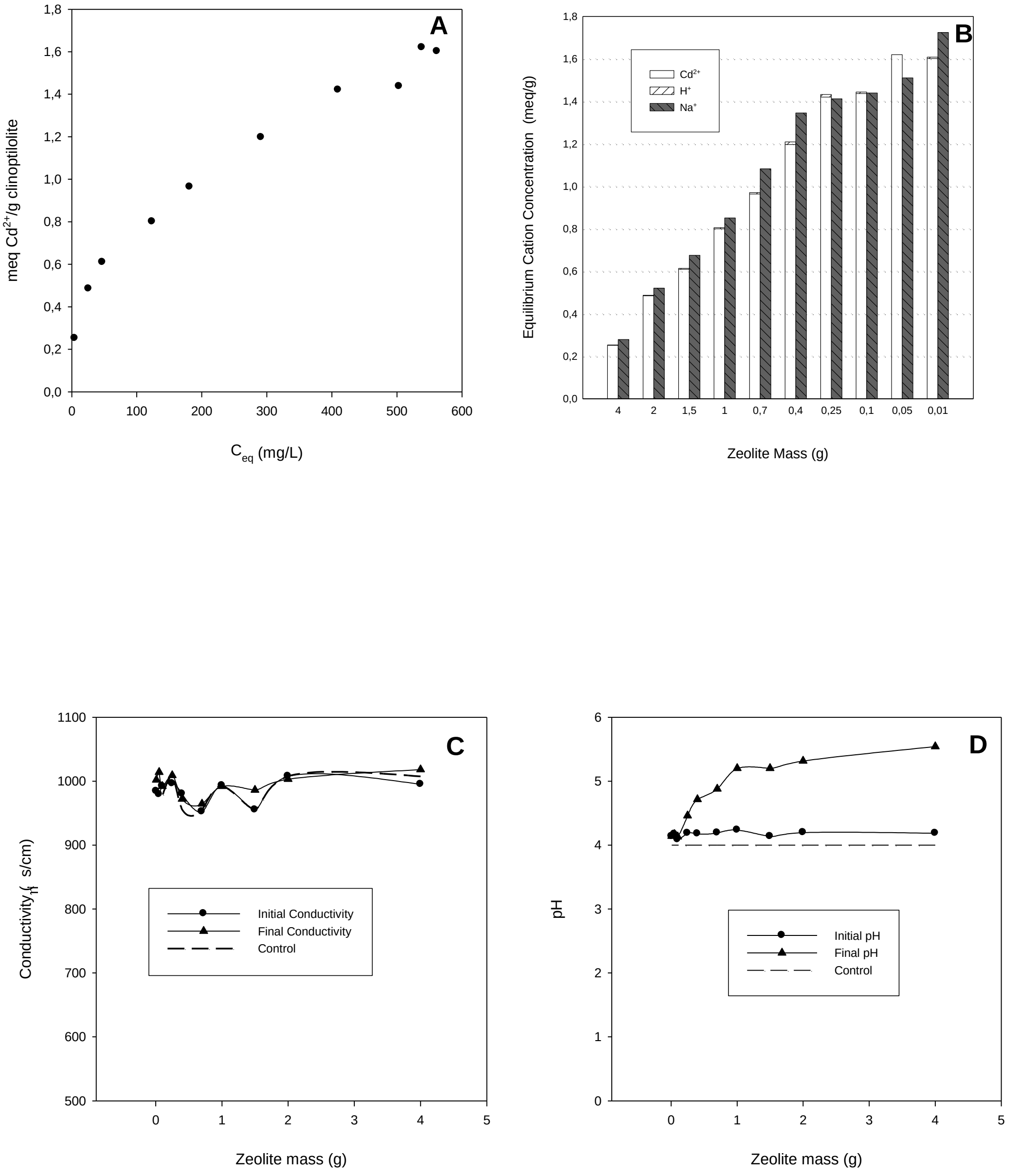

Figure 4. 8. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of CnC-P2

Maximum Exchange Level (MEL) of CnC is determined as 1.46 meq/g, which is shown in Figure 4.9. Sorbed amounts do not reach to that level in P1 whereas interestingly it exceeds in P2. This is due to the usage of smaller masses in P2. Use of much smaller mass of sorbent (e.g. 0.001 g, 0.05 g) than the one used in the MEL experiments (1 g) may have caused this. That is, even a small error in the mass of sorbent used would lead to a significant difference when used in the denominator for the calculation of the amount of metal sorbed in terms of meq/g. Hence, such an outcome is expected to be due to errors in measurement and its reflection on calculations.

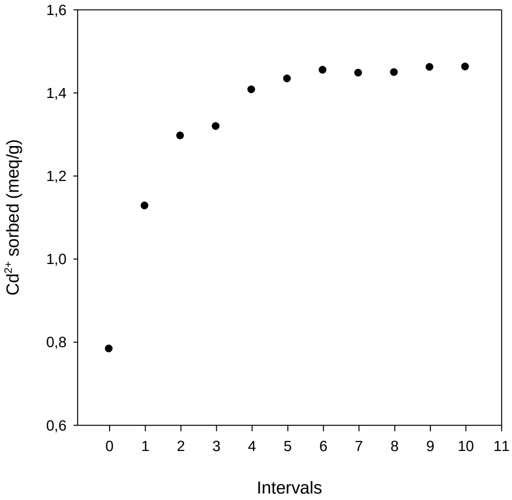

Figure 4. 9. Maximum Exchange Level of CnC

Capacity values of conditioned clinoptilolite for Cd^{2+} found in literature are given in Table 4.4. The clinoptilolite used in this study have a superior capacity among others, as it was also the case for AsC. This can be attributed to the physical properties of the clinoptilolite as well as its high purity.

Table 4. 4. Capacities of conditioned clinoptilolite for Cd^{2+} in literature

Reference	Capacity (meq/g)
Ouki et al. (1993)	1.25
Curkovic et al. (1997)	0.42
Langella et al. (2000)	0.83
Cincotti et al. (2001)	0.25
Çulfaz and Yağız (2004)	0.94
Gedik and Imamoglu (2008)	0.72
This study	1.46

b. Exchangeable Cations

Figure 4.7B and 4.8B show the exchangeable cations released for CnC-P1 and P2, which is only Na^+ in this case. Analysis of other exchangeable cations (Ca^{2+}, Mg^{2+} and K^+) was also performed but they were all below the detection limit.

Na^+ ions released are more than Cd^{2+} sorbed amounts for all concentrations in P1 whereas a much better balance is observed in P2 for all masses used. This means that the total amount of sorbed cations is equal to the total amount of released cations, indicating an ion exchange mechanism is dominant.

Cadmium sorbed amounts increases together with released Na^+ amounts in P1, as the initial concentration increases. However, no correlation can be made for the discrepancy between them. At normalities 0.01 and 0.001, sorbed and released ions are very close to each other but this is not the case for other concentrations. This may designate that mechanisms besides ion exchange may be involved for any other concentrations.

Table showing the average values of the ratio of sorbed over released cations for each procedure is given below with standard deviations (Table 4.5). The average value of the proportions of sorbed and released cations in P2 are closer to 1, indicating a dominating ion exchange removal mechanism. Besides, this proportion is kept for all masses, as can also be understood from the low standard deviation. From that result, it can be deduced that same mechanism is taking place at a particular concentration and that different mechanisms may be prevailing for different concentrations.

Table 4. 5. Average values of Sorbed/Released amounts for CnC-P1 and P2

Parameter / **Procedure**	**Sorbed/Released Cations**	**Standard Deviation**
P1	0.81	0.09
P2	0.95	0.06

Sorbed and released cations of the CnC in Cd^{2+} free deionized water can be seen in Figure 4.10. Amounts of released Na^+ cations are low relative to the amounts released during equilibrium experiments. Some part of the released amounts is due to ion exchange with H^+ ions. Most of the impurities of CnC are expected to have dissolved during conditioning. Because of that, the remaining amounts of Na⁺ are likely to arise from the dissolution of the clinoptilolite.

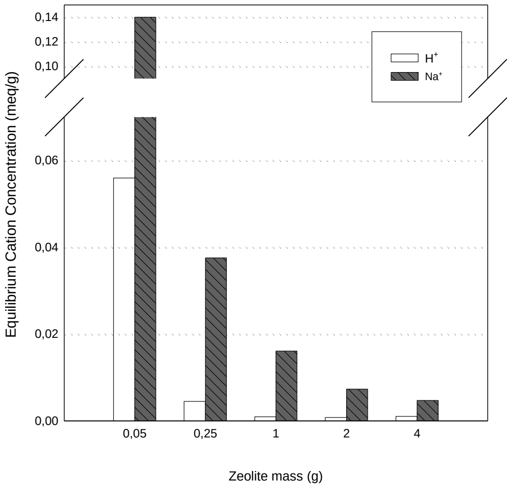

Figure 4. 10. Deionized water-CnC interaction

c. Conductivity Change

The change of conductivity in CnC is very small for both P1 and P2 (Figures 4.7C and 4.8C). For P1 especially, initial and final conductivities cannot be distinguished from each other indicating ion exchange to be the removal mechanism.

Conductivity change of CnC in deionized water can be seen in Figure 4.11A. More Na⁺ ions are released as the mass increases, and the conductivity increases accordingly.

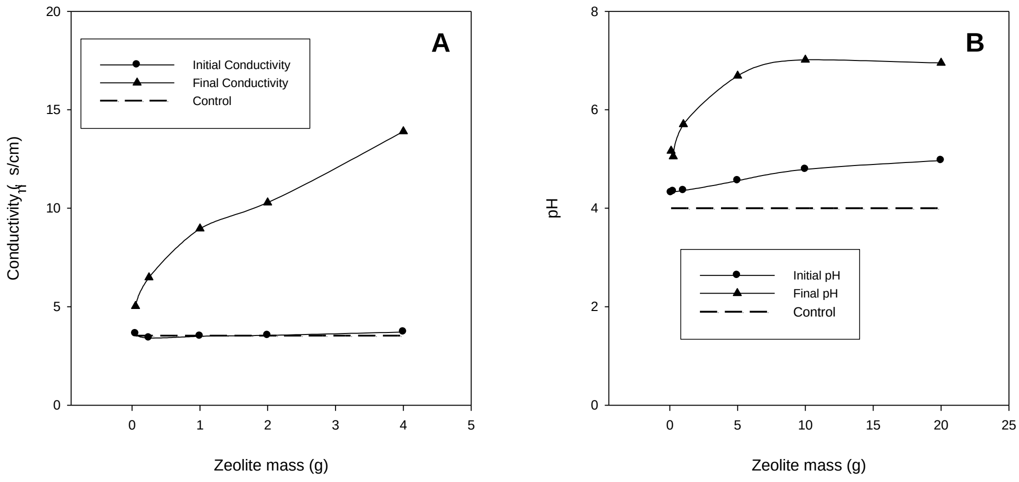

Figure 4. 11. A. Conductivity B. pH change of CnC with deionized water

d. pH Change

pH changes of CnC-P1 and P2 are shown in Figures 4.7D and 4.8D, respectively. The pH eventually stabilizes from an initial value of 4 to values close to 5 in P1, while in P2, it approaches up to 6 as the mass increases. The reasons of the pH increase are the same as in AsC; the uptake of H^+ ions of clinoptilolite by ion exchange and/or surface protonation. There is a differentiation between the equalization of pH for P1 and P2 reactors. The almost 1 pH unit difference between the two can be explained by the difference of clinoptilolite amount in each reactor. Due to the amphoteric character of clinoptilolite, the higher the amount of clinoptilolite used in reactors, the more close to neutral the final pH gets.

In deionized water-clinoptilolite interaction pH increases beyond the limits of 6 and stabilizes around 7 proportional to the mass used (Figure 4.11B).

This is an expected result, same as happened in AsC since there is no competition for exchangeable sites between H^+ and Cd^{2+} ions, all H^+ is taken up by clinoptilolite and the solution is neutralized.

4.2.3. Experiments with Amberlite IR 120

a. Cadmium Removal

Cd removal of IR-P1 and P2 can be seen in Figures 4.12A and 4.13A. The capacities reached are the same for both procedures. The resin showed a high selectivity for Cd^{2+} and the capacities attained (about 2.85 meq/g) are higher than in both forms of clinoptilolite. A capacity of about 1.64 meq/g for Cd^{2+} is reported for Amberlite IR 120 in the studies of Demirbas et al. (2005) and Kocaoba (2007) which is a lower value compared to this study. The difference may be due to many reasons like; different conditions, different forms (i.e. H^+ form) of the resin, and the errors occurred during the experiment and/or analysis.

IR-Procedure 1 (IR-P1)

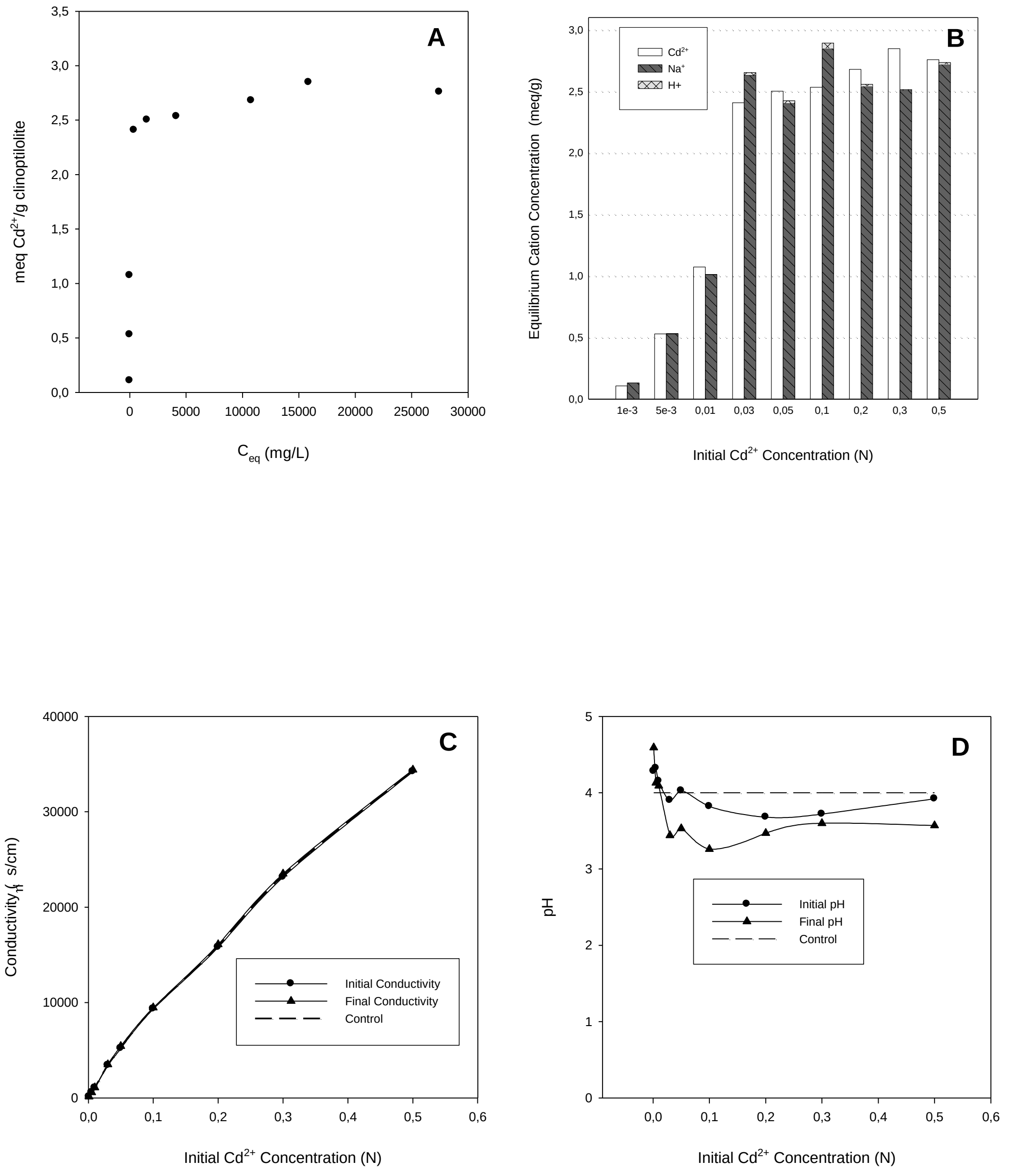

Figure 4. 12. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of IR-P1

IR-Procedure 2 (IR-P2)

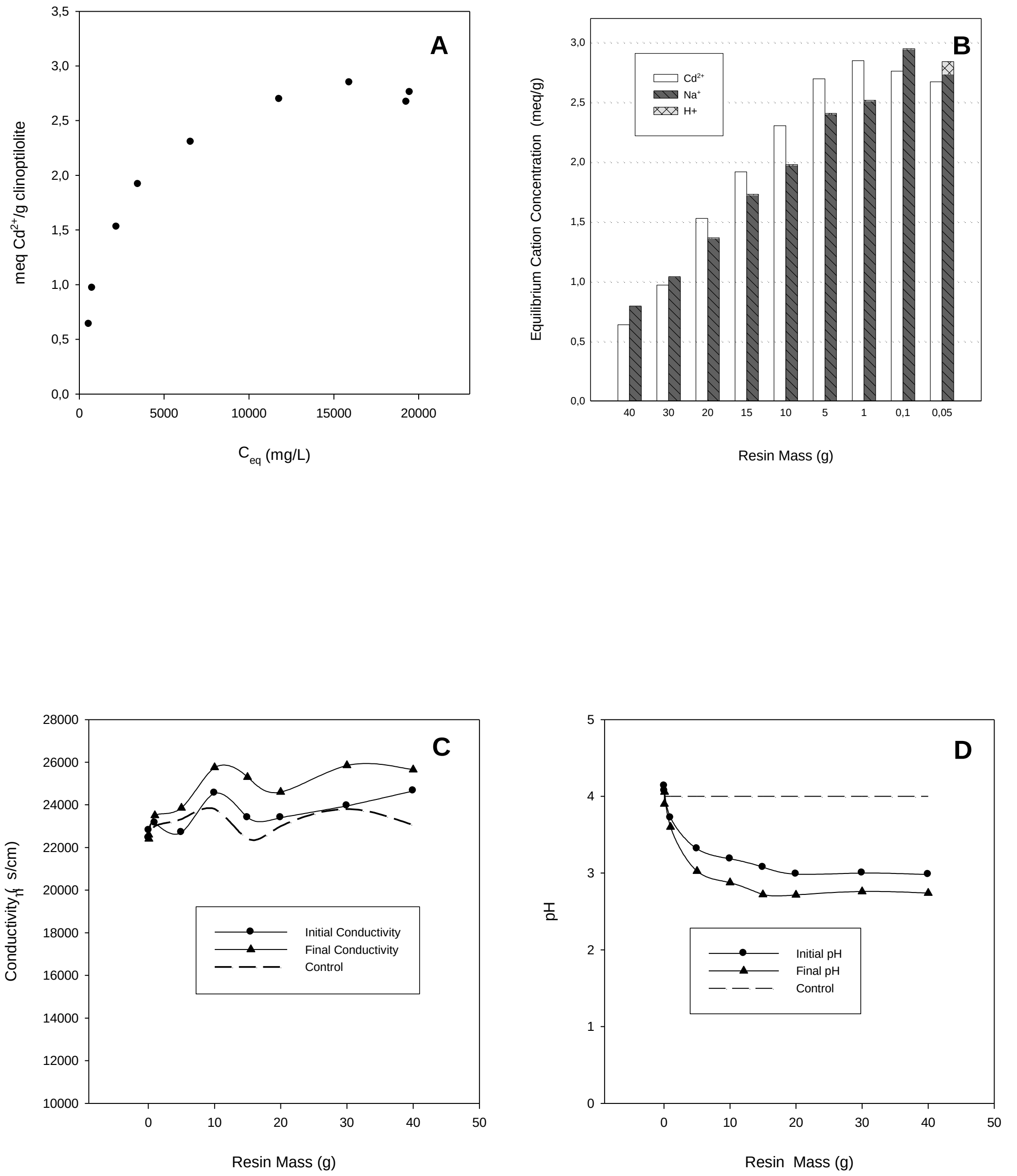

Figure 4. 13. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of IR-P2

Maximum Exchange Level (MEL) of IR is found to be as 2.70 meq/g (Figure 4.14), which is close to the amount observed in both procedures.

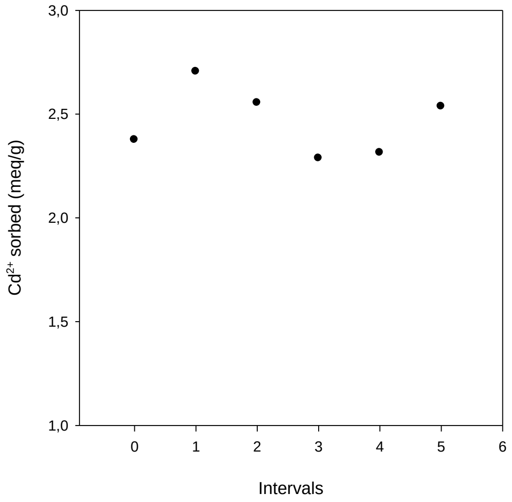

Figure 4. 14. Maximum Exchange Level of IR

b. Exchangeable Cations

Exchangeable cations (Na^+) for IR are given in Figures 4.12B and 4.13B for P1 and P2, respectively. The most prominent result evident from both of the figures is that Cd^{2+} sorbed and Na^+ released amounts are very close to each other, independent of the concentrations or the masses used. As an ideal exchanger, manufactured solely for this purpose, the favorable stoichiometry between sorbed and released ions is an expected consequence for which only ion exchange is considered to be taking place. By this way, IR constitutes a model and a guide for inferring ion exchange mechanism.

In Table 4.6 the average values of the ratio of the sorbed over released amounts are given with their standard deviations. The ideal behavior of the resin can be seen clearly that the average value of sorbed over released cations are both close to 1 in P1 and P2. This shows that ion exchange is the prevailing mechanism for all concentrations and masses.

Table 4. 6. Average values of Sorbed/Released amounts for IR-P1 and P2

Parameter / Procedure	Sorbed/Released Cations	Standard Deviation
P1	0.99	0.11
P2	1.04	0.13

In order to understand the behavior of the resin (purchased in Na-form) in aqueous solution, the amount of Na^+ released is monitored for the resin-deionized water system. In deionized water the amount of released Na^+ amounts are very low compared to the amounts exchanged in equilibrium experiments (Figure 4.15). Interesting trend is observed that Na^+ amounts released per mass of clinoptilolite are equal for every mass except in the mass 0.05 g. However, in 0.05 g, the situation is different; such that the mass of the ion exchange resin is so small that ion exchange occurring between H^+ and Na^+ ions becomes the primary mechanism. This is because water having an initial pH of 4 have sufficient H^+ ions to provide exchange for 0.05 g resin. Taking 0.05 g as an exception, the amounts of released Na^+ ions per gram of resin are equal for every mass. This finding shows that the ion exchange resin has a homogeneous structure and it behaves ideally.

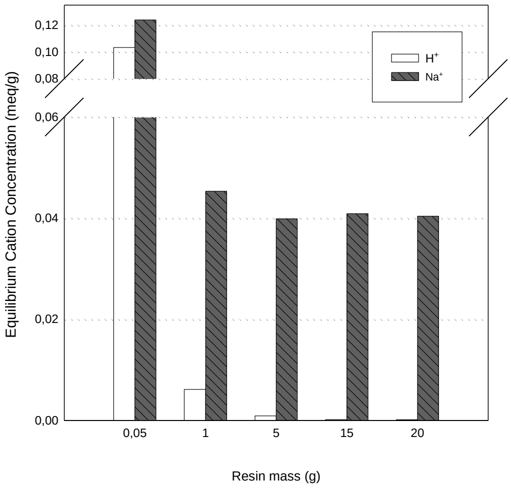

Figure 4. 15. Deionized water-IR interaction

c. Conductivity Change

Conductivity of IR both for P1 and P2 is shown in Figures 4.12C and 4.13C. The graph for P1 is smooth but a slight increase can be observed that the initial and final conductivity do not exactly equal to each other. This distinction is more obvious in the graph for P2; conductivity increases as the mass increases. A change in conductivity values for ion exchange resin is not expected since ideal ion exchange is considered to be happening. The reason for that increase is supposed to be due to the release of H^+ ions to the solution from the resin structure. H^+ ions increase the conductivity of the solutions much more than metal ions because they have much higher equivalent ionic conductances in aqueous solutions as briefly explained in Section 2.6.2

(Milazzo, 1963). A study of Karagunduz and Unal (2006) is related to that issue. In this study, the authors managed to determine H^+ ion concentration in solution by the change in conductivity of the solution.

Similar calculations are performed in order to provide clarification, however it was found that the released amounts of H^+ ions were inadequate to explain the increase. Then it is concluded that there are other impurities responsible from that increase which are arising during the preparation of the resin. Helfferich (1995) states that materials that are shipped by the manufacturer tend to give irreproducible results and he recommends thoroughly conditioning of the resin before use. Kocaoba and Akcin (2005) used Amberlite IR 120 in their study and conditioned it before use in case of the solvents and functionalizing agents trapped in the matrix of the resins during their preparation.

In deionized water, conductivity of IR is showing an increase with the mass (Figure 4.16A). The growth is in an increase since more amounts of Na^+ ions together with the impurities are released as more masses of the resin is used.

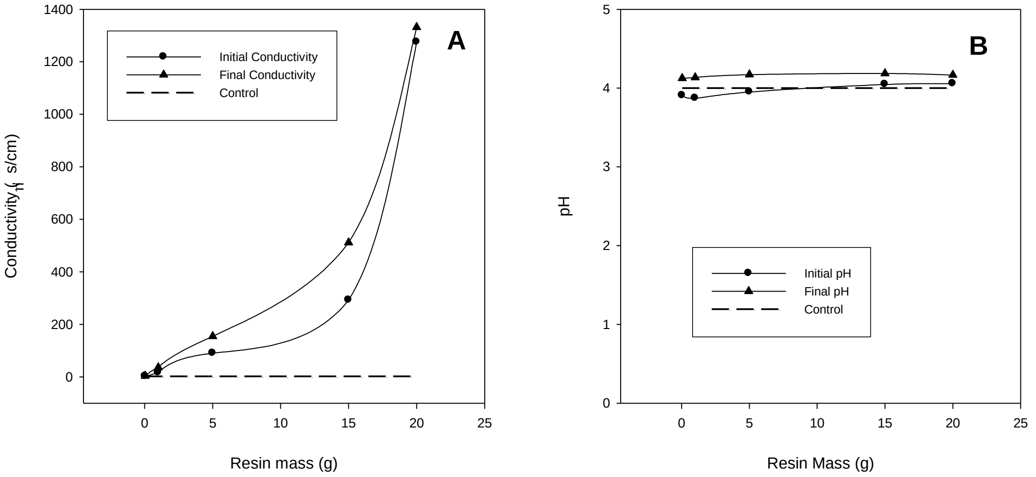

Figure 4. 16. A Conductivity. B. pH change of IR with deionized water

d. pH Change

The results of pH change for IR-P1 and P2 are given in Figures 4.12D and 4.13D. pH decreases from an initial value of 4 to approximately value of 3,5 in P1 and to below 2,5 for P2. This means H^+ ions exists in the structure of the resin and the release of the H^+ ions are responsible for that decrease.

In deionized water, different from the equilibrium experiments, the pH increases slightly (Figure 4.16B). Since no Cd^{2+} ions are present in the solution, there is no release of hydrogen ions from the resin structure, besides uptake of them from solution takes place which causes an increase in the solution pH.

4.2.4. Experiments with Granulated Activated Carbon

a. Cadmium Removal

Cadmium removal results of GAC-P1 and P2 are presented in Figures 4.17A and 4.18A. The unusual shape of the isotherm in P2 might be an indication that the procedure is inconvenient for adsorption dominant systems. The capacity of GAC for Cd^{2+} is low, which was reported in a study of Gabaldon (2000) as well, in which the same type of GAC (Darco) is used. There are so many types of activated carbons depending on their starting materials and many examples are present in the literature. However, in general, the reported capacities for cadmium are low (0.05 – 0.60 meq/g) (Demirbaş et al., 2006; Kobya et al., 2005; Minceva et al., 2007).

GAC-Procedure 1 (GAC-P1)

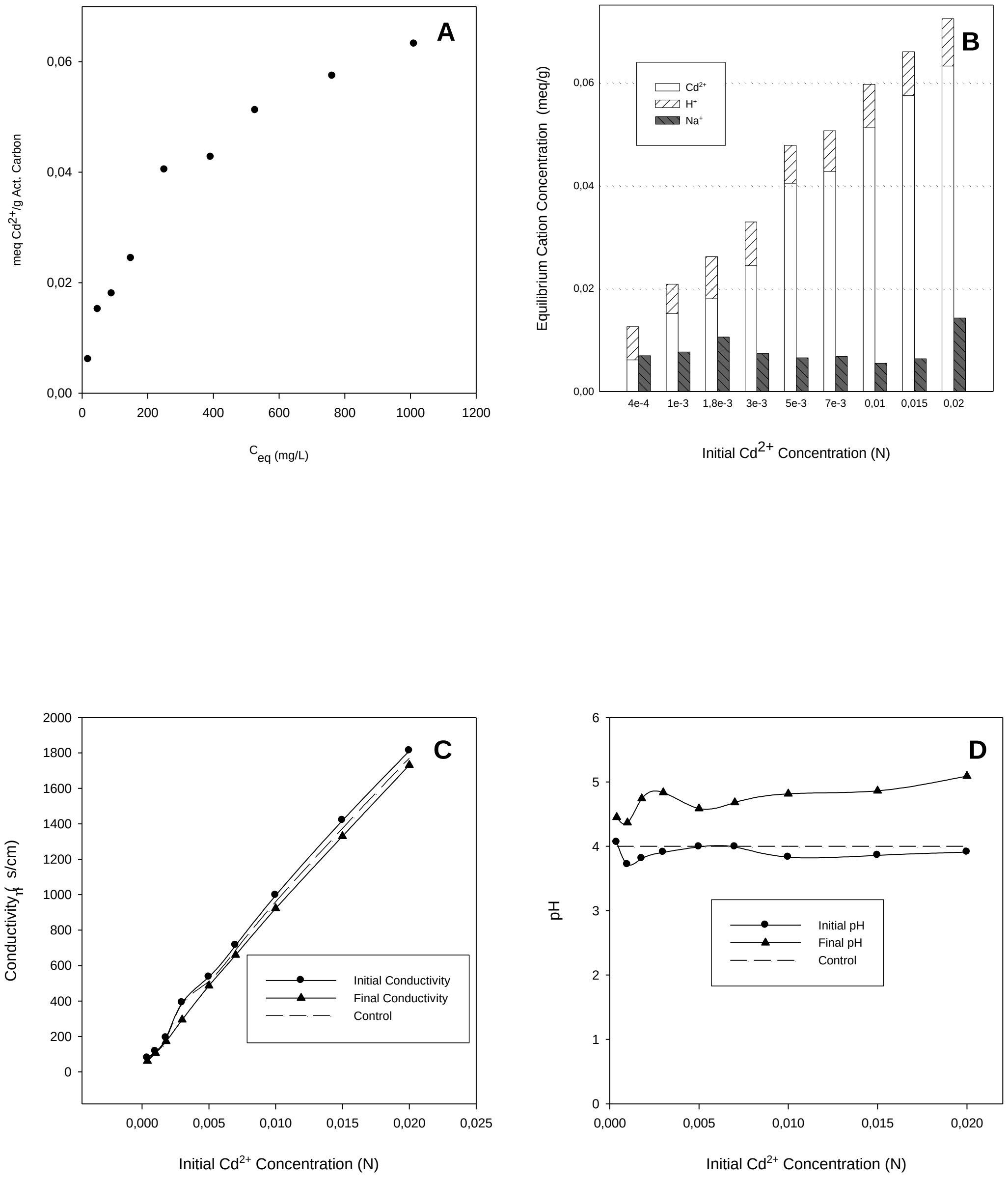

Figure 4. 17. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of GAC-P1

GAC-Procedure 2 (GAC-P2)

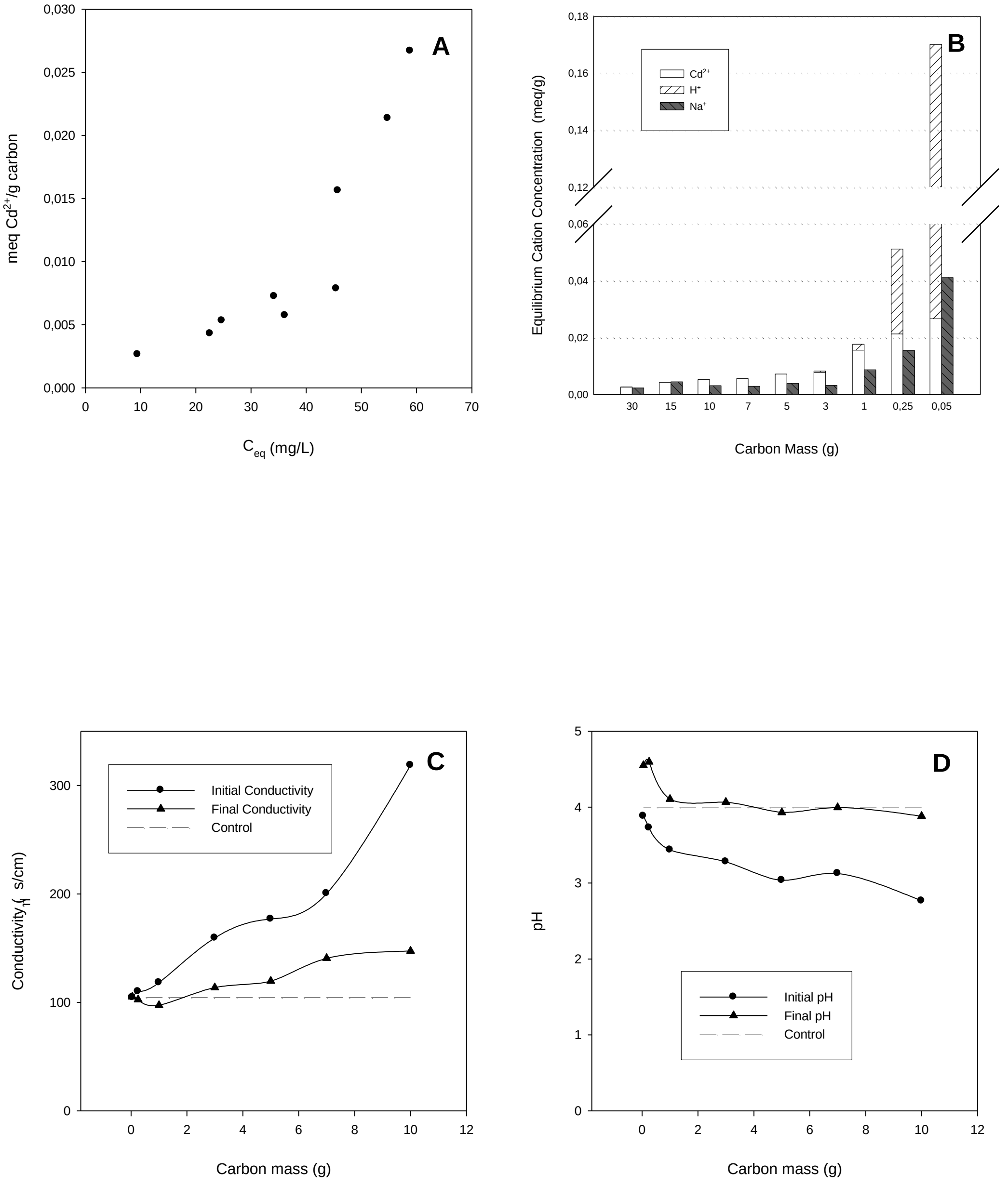

Figure 4. 18. A. Experimental data points B. Sorbed and released cations C. Conductivity change D. pH change of AsC-P2

Maximum Exchange Level (MEL) of GAC is estimated as 0.03 meq/g (Figure 4.19). In P2, maximum amount of sorbed Cd^{2+} is in accordance with the MEL, however a capacity can not be attained since the isotherm does not reach a plateau. On the other hand, in P1 a capacity is attained but it is two times higher than the MEL. This shows that the conditions in the batch reactors of Figure 4.17 are significantly different from that in MEL experiments, enabling twice as much Cd^{2+} to be sorbed. It seems that even though GAC is not selective for heavy metals, when it is subjected to much higher Cd^{2+} concentrations, i.e. 0.02 N, when compared to the 0.001 N used in MEL study, higher Cd^{2+} removal can take place. Besides, there is a practical problem associated with using large amounts of GAC (i.e. greater than 10 g in 100 mL solution) in P2. The density of GAC is much smaller than that of AsC or CnC of the same particle size (Bulk Density; GAC: 0.336 kg/L Clinoptilolite: 0.85 kg/L). Therefore the amounts associated with GAC are much more than the amounts used for clinoptilolite for the same masses. Due to this, reactors containing higher solid-to-liquid ratio could not be efficiently operated.

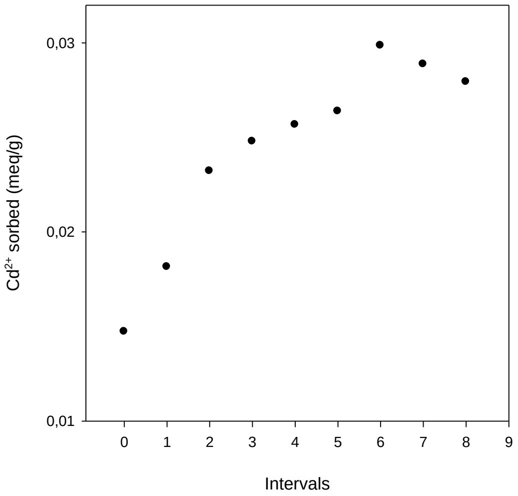

Figure 4. 19. Maximum Exchange Level of GAC

b. Sorbed and Released Cations

Sorbed and released cations of GAC-P1 and P2 are given in Figures 4.17B and 4.18B. These cations can not be regarded as exchangeable cations since they are not sorbed or released by ion exchange. Na^+ and H^+ ions are released from its structure arising from the ashes (Suzuki, 1990). The amounts of Na^+ released per gram of carbon are the same for all concentrations and is proportional to masses used. In P2, for small masses it seems released Na^+ ions are higher, however they are not very significant since the absolute values of Na^+ in reactors is rather small. Adsorbed H^+ ions comprise a significant proportion since the amounts of Cd^{2+} sorbed are low.

The amounts of Na^+ released in deionized water are similar as in equilibrium experiments (Figure 4.20). Though it seems more Na^{2+} is being released for small masses of carbon (i.e. smaller than 1 g), it is only a misperception resulting from the division by an extremely small number. These show that Na^+ ions are released not as a result of exchange with Cd^{2+}, but rather due to the ashes in GAC.

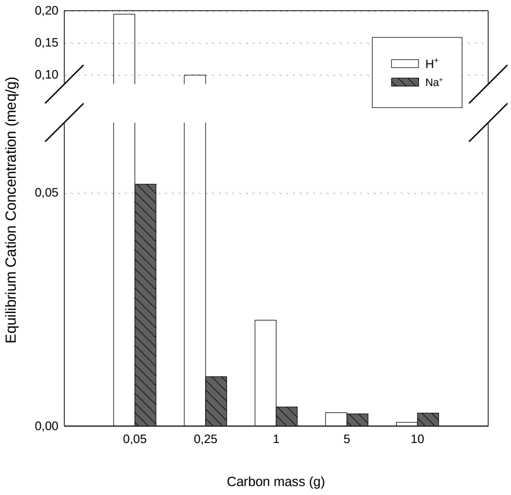

Figure 4. 20. Deionized water-GAC interaction

c. Conductivity Change

Conductivity change of GAC-P1 and P2 are shown in Figures 4.17C and 4.18C. In P1 there is a prominent decrease in the conductivity values. From that, it can be deduced that adsorption is taking place and activated carbon removes H^+, Na^+ and Cd^{2+} ions by adsorption resulting a decrease in the total conductivity of the solution. The reason for the slight increase observed in the initial conductivity values is the release of cations from the ashes that GAC contains.

In P2 there is an increase in the initial conductivity values as the mass increases due to the increase in the concentrations of the cations from the ashes. (Reliable measurements can not be performed for 15 g and 30 g due to excessive masses, so could not be given in the results). The decrease in the final conductivity shows that adsorption is taking place, however the values remain higher than those in the control values because of the ashes released to the solution.

In deionized water conductivity follows the same trend as in equilibrium experiments, with an initial increase and then a final decrease owing to the aforementioned reasons (Figure 4.21A).

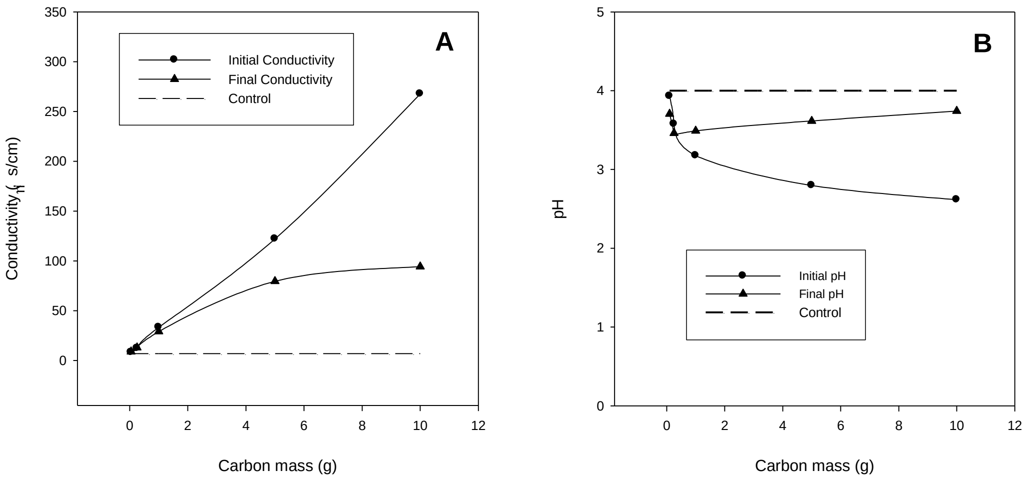

Figure 4. 21. A. Conductivity B. pH change of GAC with deionized water

d. pH Change

The pH change of GAC-P1 and P2 are given in Figures 4.17D and 4.18D. In P1, the initial pH values are lower than 4, however final pH values reach an approximate value of 5. An initial decrease is due to the H^+ release and this decrease is more clear in P2 together with increasing sorbent mass. As the mass increases more H^+ ions are released to the solution, and adsorption of them causes pH to increase.

pH change in deionized water is similar to that in equilibrium experiments owing to the same reasons, related to the sorbent mass (Figure 4.21B).

4.3. ALUMINUM and SILICON (Al and Si) MONITORING

The main factor that causes the dissolution of the framework is surface protonation since it creates highly polarized bonds close to the central metal ions (Al and Si) resulting of the detachment of them (Doula et al., 2002). Initial concentrations of the solutions have an indirect effect on dissolution. That is; high solution concentration results in a high ionic strength of solution. At high ionic strengths, the reactions of H^+ ions with the surface (i.e. surface protonation) decreases which causes a decrease in dissolution (Doula et al., 2002).

Although the main reason for framework dissolution is surface protonation, there are some special conditions that trigger particularly Al or Si dissolution.

Dissolution of Al occurs by the reactions (Doula et al., 2002):

$$\equiv Al - OH + H^{+} \leftrightarrow \equiv Al - OH_2^{+} \leftrightarrow Al^{3+} + H_2O \tag{4.1}$$

It can be seen that Al dissolution proceeds by surface protonation, i.e. taking up H^+ ions from solution. Due to that, it generally occurs in acidic conditions. The lower is the initial pH of the solution, the more Al dissolution takes place.

Si dissolution is expressed by the qualitative reaction (Doula et al., 2002):

$$-\overset{|}{\underset{/}{Si}}- \xrightarrow{H_2O} H_4SiO_{4(aq)} \tag{4.2}$$

Though the reaction does not contain H^+ or OH^- species, surface protonation is responsible from that. In general, Si dissolution occurs at a higher pH (mainly in basic pH) because ≡Si–OH groups do not tend to protonate at low pH values. As a consequence of this, the dissolution of Si increases as the pH increases.

4.3.1 As-received Clinoptilolite (AsC)

Results of the framework cations (Al and Si) of selected samples in P1 and P2 for AsC are given in Figures 4.22A and B, respectively. The result of the 5 g clinoptilolite sample in deionized water is also inserted in Figure 4.22B for comparison purposes. The pH of all the reactors in P1 and P2 are increasing, consistently, aluminum is detected in low quantities but silicon is detected in considerable amounts. Detection of Si shows that dissolution is taking place. In P1, it can be seen that the amounts of silicon shows no variation with concentration. This means that; concentration of Cd^{2+} has no effect on the dissolution of AsC. The amounts of silicon for the same masses in P2 and in deionized water are very close to each other, indicating that the dissolution is independent of solution concentration or the Cd^{2+} amount sorbed on AsC. Those results may indicate that dissolution in AsC originates mainly from the minerals that clinoptilolite contains (i.e. feldspar, montmorillonite, cristobalite and muscovite) which were given in Table 3.1. In P2, silicon detected per gram of clinoptilolite is decreasing implying that the dissolution taking place per gram of clinoptilolite is in a decreasing trend as the mass increases.

Al is only detected in the reactors with the lowest or zero Cd^{2+} concentration. The reason for that is the enhancement of surface protonation at low Cd^{2+} concentrations, which is mentioned above.

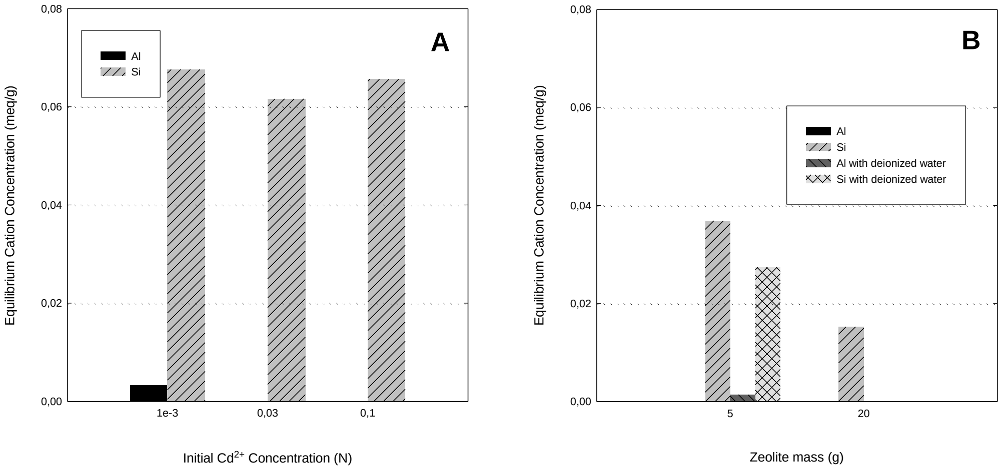

Figure 4. 22. Framework cation concentrations in selected samples for A. AsC-P1 and B. AsC-P2

4.3.2. Conditioned Clinoptilolite (CnC)

Results of the framework cations (Al and Si) of selected samples in P1 and P2 for CnC are given in Figures 4.23A and B, respectively. The result of a 1 g CnC sample in deionized water is also inserted in Figure 4.23B. Silicon is the predominating cation that is detected in solutions, whereas aluminum is detected in relatively trace amounts, which is due to the increase in the solutions pH. For P1, Si concentrations are decreasing as the Cd concentrations increase, as expected. Al concentrations also follow nearly this trend in P1; no Al is detected for the highest Cd^{2+} concentration. The highest Al release however is observed in the reactor with 0.03 N initial Cd^{2+} concentration. The reason for this is; that reactor has the lowest initial pH when compared to other reactors in CnC-P1 (Figure 4.7D), which, therefore triggers Al release from clinoptilolite structure.

In P2, silicon detected per gram of clinoptilolite is decreasing as the mass increases. The amounts of Al and Si detected in deionized water are very low, indicating that dissolution takes place in minor quantities. This is because the uptake of H^+ in deionized water is mainly by ion exchange rather than by surface protonation, which is due to the lack of competition between Cd^{2+} ions.

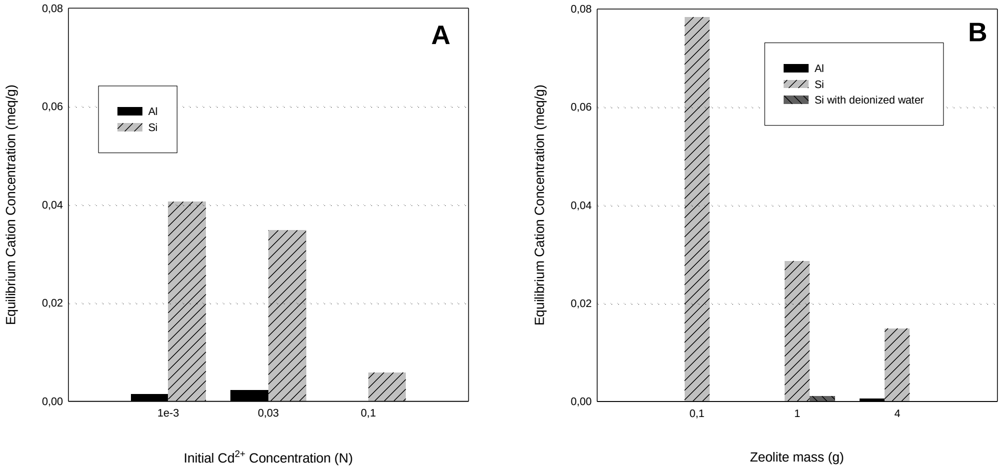

Figure 4. 23. Framework cation concentrations in selected samples for A. CnC-P1 and B. CnC-P2

When the results presented for CnC-P1 and in Figure 4.23A is compared with those in Figure 4.22A for AsC-P1, a number of notable differences is observed: (i) the amount of Si released in CnC-P1 is much less (about half amount) of that released in AsC-P1, (ii) Si concentration is observed to change somewhat with initial Cd^{2+} concentration in CnC-P1 while this was not the case for AsC-P1.

The relatively lower Si release from CnC is expected as this sorbent has undergone an extensive conditioning stage during which some amount of Si release would have taken place. When 1 g of CnC is contacted with deionized water, very low amount of Si is observed, indicating that Si release is associated with Cd^{2+} sorption on clinoptilolite rather than just “unforced” dissolution of the framework.

The trend of Al and Si release for P2 is similar to AsC-P2, where progressively less Si is released per gram of CnC with increasing sorbent mass.

4.3.3. Amberlite IR 120 (IR)

Al and Si are not expected in the reactors with the resin. A sample was tested having 0.3 N initial Cd^{2+} concentration with 5 g sorbent and no Al or Si is detected.

4.3.4. Granulated Activated Carbon (GAC)

Al and Si are not the framework cations of GAC, so the release of them to solution is not expected. A sample was tested having 0.01 N initial Cd^{2+} concentration with 5 g sorbent. Al is not detected, however Si is detected in considerable amounts (about 0.04 meq/g). Si content of GAC is originating from the ashes which was stated by Suzuki (1990). The same amount of sorbent mass (5 g) in deionized water is also tested for comparison purposes. The detected amounts are very close to those in equilibrium experiments (about 0.035 meq/g) indicating that Si release from GAC is not related with Cd^{2+} sorption.

4.4. MODELING HEAVY METAL SORPTION

The equilibrium experimental results are fitted to Langmuir (L), Freundlich (F), Redlich-Peterson (RP), Toth (T), and solubility-normalized Dubinin-Astakhov (DA_{SN}) adsorption isotherms using nonlinear regression analysis (Figures 4.24-4.31). The isotherm parameters (K, β, M, E, and n) and the correlation coefficient (R^2) are given in Tables.4.7 and 4.8 for P1 and P2, respectively.

In the fitting of the results, maximum exchange levels (MEL) that are determined before are used in the place of M in order to obtain more reliable results. L isotherm is allowed to give a capacity value for the isotherms that are not compatible with the estimated MEL. The value which provides the best fitting is used for other isotherms.

4.4.1. Models with Clinoptilolite as Sorbent

a. AsC-Procedure 1 (AsC-P1)

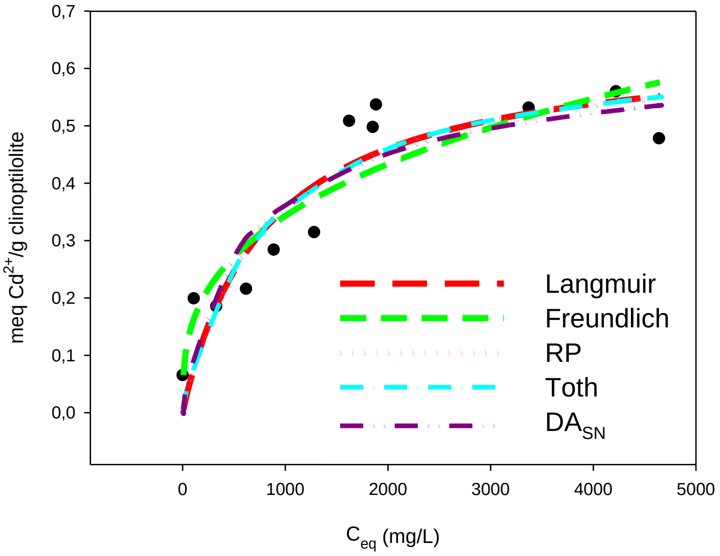

Figure 4. 24. Modeling of the experimental data for AsC-P1

b. AsC-Procedure 2 (AsC-P2)

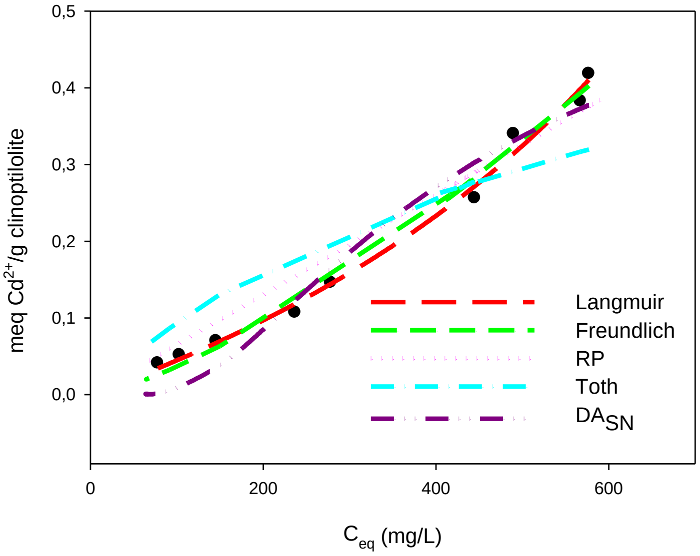

Figure 4. 25. Modeling of the experimental data for AsC-P2

c. CnC-Procedure1 (CnC-P1)

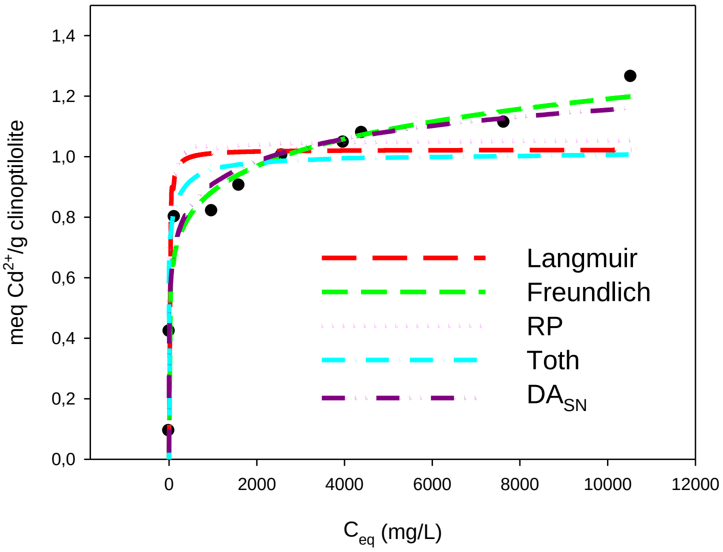

Figure 4. 26. Modeling of the experimental data for CnC-P1

d. CnC-Procedure 2 (CnC-P2)

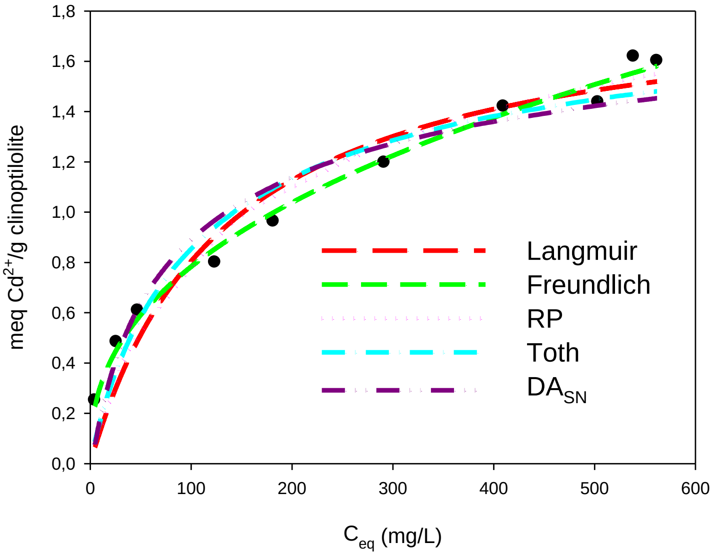

Figure 4. 27. Modeling of the experimental data for CnC-P2

4.4.2. Models with Amberlite IR 120 as Sorbent

a. IR-Procedure 1 (IR-P1)

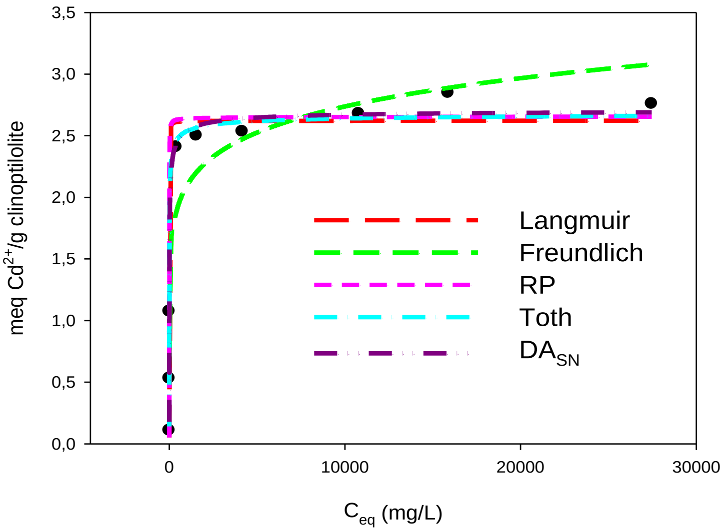

Figure 4. 28. Modeling of the experimental data for IR-P1

b. IR-Procedure 2 (IR-P2)

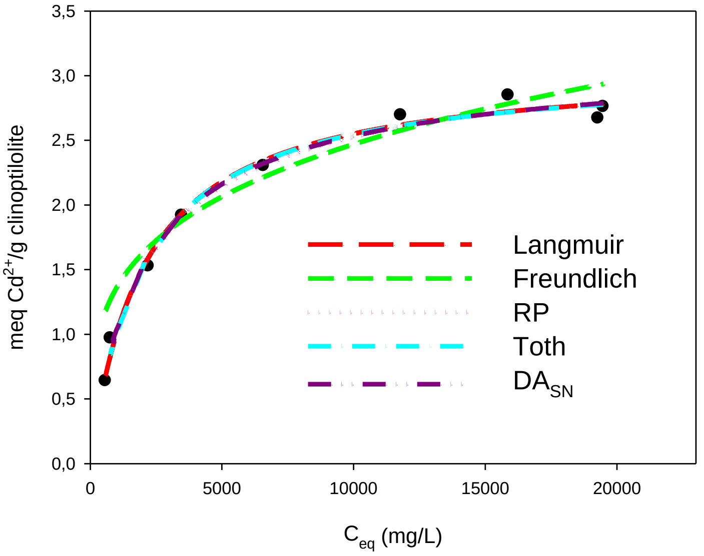

Figure 4. 29. Modeling of the experimental data for IR-P2

4.4.3. Models with Granulated Activated Carbon as Sorbent

a. GAC-Procedure 1 (GAC-P1)

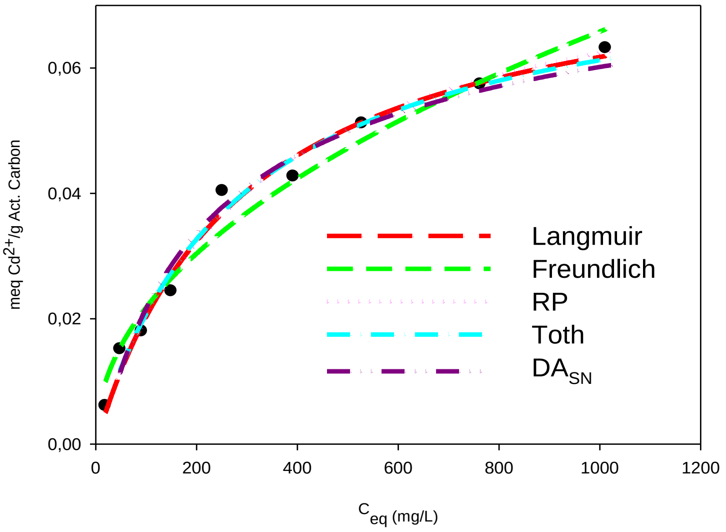

Figure 4. 30. Modeling of the experimental data for GAC-P1

b. GAC-Procedure 2 (GAC-P2)

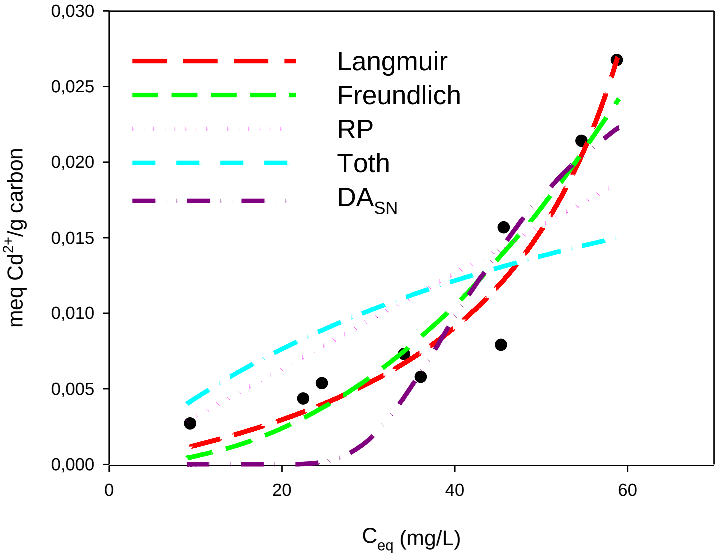

Figure 4. 31. Modeling of the experimental data for GAC-P2

Table 4. 7. Isotherm model parameters and goodness of fit information for all sorbents with P1

Sorbent	Isotherms	P1							
		K	**E**	**β**	**n**	**M***	**R^2**	**SSE**	**HYBRID**
AsC	**L**	0.0012	-	-	-	0.65	0.841	0.052	1.971
	F	$4.2*10^{-5}$	-	0.337	-	-	0.835	0.054	1.442
	RP	0.0012	-	1.006	-	0.65	0.841	0.052	2.170
	T	0.0013	-	0.983	-	0.65	0.841	0.052	2.160
	DA$_{SN}$	-	13.3	-	4.20	0.65	0.828	0.056	2.317
CnC	**L**	0.0845	-	-	-	1.02$^{□}$	0.866	0.150	2.988
	F	0.0004	-	0.128	-	-	0.967	0.037	1.591
	RP	0.0797	-	0.996	-	1.02$^{△}$	0.870	0.145	3.038
	T	17.660	-	0.229	-	1.46	0.952	0.054	1.736
	DA$_{SN}$	-	18.4	-	1.65	1.46	0.962	0.042	1.618
IR	**L**	0.5966	-	-	-	2.62$^{□}$	0.982	0.165	1.809
	F	0.5802	-	0.116	-	-	0.906	0.851	41.840
	RP	0.5955	-	0.999	-	2.62$^{△}$	0.982	0.161	1.805
	T	3.2430	-	0.443	-	2.70	0.993	0.064	0.506
	DA$_{SN}$	-	23.3	-	4.07	2.70	0.993	0.064	1.075
GAC	**L**	0.0034	-	-	-	0.08$^{□}$	0.986	$4.6*10^{-5}$	0.029
	F	$3.5*10^{-6}$	-	0.480	-	-	0.974	$8.6*10^{-5}$	0.062
	RP	0.0034	-	0.987	-	0.08$^{△}$	0.986	$4.6*10^{-5}$	0.030
	T	0.0036	-	0.958	-	0.08$^{△}$	0.986	$4.6*10^{-5}$	0.027
	DA$_{SN}$	-	14.9	-	5.15	0.08$^{△}$	0.980	$6.7*10^{-5}$	0.049

* No initial value is substituted for M for the ones marked with ($^{□}$) and values that is found by the Langmuir isotherm is substituted for the ones marked with ($^{△}$)

Table 4. 8. Isotherm model parameters and goodness of fit information for all sorbents with P2

Sorbent	**Isotherms**	**P2**							
		K	**E**	**β**	**n**	**M***	**R^2**	**SSE**	**HYBRID**
AsC	**L**	0.0017	-	-	-	0.65	0.817	0.033	2.996
	F	0.0009	-	1.375	-	-	0.989	0.002	0.230
	RP	0.0020	-	2.14*10^{-10}	-	0.65	0.956	0.008	0.801
	T	0.0017	-	1.000	-	0.65	0.817	0.033	3.424
	DA$_{SN}$	-	13.5	-	9.64	0.65	0.950	0.009	1.525
CnC	**L**	0.0075	-	-	-	1.88$^{\square}$	0.937	0.136	3.447
	F	0.0055	-	0.407	-	-	0.992	0.018	0.233
	RP	0.0118	-	0.876	-	1.46	0.953	0.102	2.772
	T	0.0109	-	0.834	-	1.88$^{\triangle}$	0.942	0.124	2.610
	DA$_{SN}$	-	16.7	-	4.99	1.88$^{\triangle}$	0.933	0.145	2.842
IR	**L**	0.0005	-	-	-	3.08$^{\square}$	0.989	0.058	0.509
	F	0.0016	-	0.311	-	-	0.935	0.355	4.119
	RP	0.0006	-	0.950	-	2.70	0.989	0.062	0.526
	T	0.0005	-	0.988	-	3.08$^{\triangle}$	0.989	0.058	0.502
	DA$_{SN}$	-	11.4	-	4.07	3.08$^{\triangle}$	0.989	0.058	0.480
GAC	**L**	0.0170	-	-	-	0.03	0.484	3.0*10^{-4}	0.325
	F	0.0746	-	2.145	-	-	0.892	6.2*10^{-5}	0.127
	RP	0.0211	-	0.805	-	0.03	0.676	1.8*10^{-4}	0.276
	T	0.0171	-	0.994	-	0.03	0.483	3.0*10^{-4}	0.373
	DA$_{SN}$	-	17.3	-	33.3	0.03	0.783	1.3*10^{-4}	0.277

* No initial value is substituted for M for the ones marked with ($^{\square}$) and values that is found by the Langmuir isotherm is substituted for the ones marked with ($^{\triangle}$)

4.4.5. Interpretation of Isotherm Models

DA isotherm, different than other isotherm models, can give information about the adsorption process by its parameters. The adsorption energy, E, lies in the ranges of 8-16 kJ/mol if the system is an ion exchange (Inglezakis, 2007). Lower than 8 kJ/mol indicates an adsorption process and higher than 16 kJ/mol shows that there are other interactions such as surface precipitation and co-precipitation besides ion exchange. Another parameter is related to the characteristic of the adsorbent, n, which is called the heterogeneity parameter. The value of n gives an idea of the measure of porousness of the adsorbent; the greater its value the more homogeneous and the less porous is the adsorbent (Inglezakis, 2007). Therefore, a separate interpretation of DA isotherm is necessary to get an idea of the mechanisms.

For AsC-P1 the correlation coefficients (R^2) of all isotherms are close to each other and neither of them are high enough to show well fitting. So it is hard to deduce which one of the isotherms best fits to the results. In AsC-P2, the correlation coefficients seem good enough to show a well fitting however this is not observed in the figure. The isotherms fitted are all Type I isotherms but this is not reflected in the figure. Therefore those isotherms can not be a representation of that adsorption data. F isotherm is the best fitting isotherm with its higher correlation coefficient (R^2) and lower SSE and HYBRID values. Main reason for that is; the isotherm increases exponentially and does not reach to a capacity value, which are the main characteristics of the Freundlich isotherm.

In the figure of CnC-P1, F and DA isotherms seem to be better fitted to the results. This is also supported by their good correlation coefficients. From the two, F isotherm is the best fitted isotherm. In CnC-P2, all the isotherms seem to show a satisfactory fit, and this can be deduced from their goodness of fit values as well. However, F is again the best in describing the adsorption process.

In IR-P1 adsorption does not follow a F type isotherm model as it can also be confirmed from the high value of the HYBRID. T isotherm best fits to results, and DA also shows a well fitting as much as T. In IR-P2 goodness of fit of all models are lower than in P1, except the F isotherm. In addition, all the isotherms show a similar goodness of fit value.

In GAC-P1 all isotherms show good fitting except the F isotherm. L, RP and T are the most well fitted isotherms, having similar goodness of fit parameters. In the figure of GAC-P2 no isotherms seem to show proper fittings. This can also be observed from the low correlation coefficients. F isotherm best fits to results, still not giving a satisfactory fit.

For AsC-P1 E and n values given by DA isotherm are 13.3 kJ/mol and 4.20, respectively. In this respect, the value of E shows an ion exchange system for which it lies in the range of 8-16 kJ/mol. Value of n is an acceptable value for clinoptilolite for which values greater than 3-4 are expected for zeolite systems (Inglezakis, 2007). In AsC-P2 the value of E is 13.5 kJ/mol, showing an ion exchange mechanism. This time n is found to be 9.64 which is a high but an observable value for clinoptilolite systems. Inglezakis (2007) obtained such high values for n in his study while applying the DA model to several different clinoptilolite-metal systems in literature.

Values obtained from DA in CnC-P1 are; 18.4 kJ/mol for E and 1.65 for n. The value of E is close to the findings of Inglezakis (2007) and Gedik et al. (2008) indicating other mechanisms occurring besides ion exchange, i.e. surface precipitation and/or coprecipitation. Values for CnC-P2 are; 16.7 kJ/mol for E and 4.99 for n. The adsorption energies of CnC for both P1 and P2 are higher than of the AsC. The same finding is expressed in the studies of Inglezakis (2007) and Gedik et al. (2008) when the clinoptilolite converted to its homoionic form. Besides, the value of n is lower for CnC than for AsC again for both P1 and P2 which is the case in the study of Gedik et al. (2008). This is explained by the opening of the pores and channels of the clinoptilolite samples during conditioning process.

Values obtained from DA isotherm for IR-P1 are 23.3 kJ/mol for E and 4.07 for n. The value of adsorption energy is interesting since energies higher than 16 kJ/mol shows that there are other mechanisms interacting such as surface precipitation and/or co-precipitation. In the IR-P2 adsorption energy is 11.4 kJ/mol indicating, this time, ion exchange. Value of n is 4.07 which is similar to the value obtained from IR-P1 showing that the resin has a porous structure.

For GAC-P1, DA isotherm gives 14.9 kJ/mol for E and 5.15 for n. These are not expected values for an activated carbon system. Adsorption energy value is expected to be less than 8 kJ/mol, in order to indicate an adsorption mechanism. And secondly; the value of n is expected to be lower which is in the case for highly porous structures, hence for activated carbons. In GAC-P2, DA isotherm does not show a proper fit so the values given for the parameters do not present much explanation (e.g. n having 33).

4.5. OVERALL DISCUSSION

Maximum sorbed amounts differ from each other in P1 and P2 both for AsC and CnC, while it is the same for IR. This indicates that there are other mechanisms interfering both in AsC and CnC. However the values are not so divergent from each other, as is in the case for GAC, hence not simulating an adsorption dominant system.

For AsC, the amount of released cations are higher than the sorbed cations. Possible reasons for that are: (i) dissolution of the impurities, (ii) dissolution of the framework and (iii) blokage of the pores. First of all, in deionized water studies, Na^+ is detected and the quantities are much higher than those detected for CnC-deionized water. These show that dissolution is taking place in AsC and it is much higher than in CnC. Considering that most of the impurities have disappeared in CnC, dissolution in AsC is more likely to be due to impurities present. Secondly, in Al and Si monitoring for equilibrium experiments, detected Si amounts are higher than in CnC, besides same amounts are observed for different concentrations. Moreover, Si is detected in the same amounts in equilibrium and in deionized water studies for the same mass. All of those indicate that dissolution in AsC is primarily due to impurities. Blokage of the pores may be another reason, however no verification can be made regarding this.

The slight variation of the conductivity values show that ion exchange is the dominating mechanism. However, when compared to the conductivity graph of CnC, it can be said that other mechanisms other than ion exchange are interfering, one of them being the dissolution of the impurities. On the other hand, the average value of the proportions of sorbed over released cations in P2 being higher and more regular than in P1 indicates that ion exchange is more prominent in P2.

For CnC, the amount of released cations are higher than the sorbed cations in P1, but they are equal in P2. This shows that the mechanisms prevailing show discrepancy. However, the average value of the ratio of sorbed over released amounts are higher than in AsC for each procedure. This shows that the system for clinoptilolite has become more ion exchange dominating by means of conditioning. On the other hand, the cumulation of errors that arise during the analysis of the exchangeable cations of AsC might be another potential reason for that difference. The ratios in CnC are not as high as in IR which may indicate interfering mechanisms are present also in CnC.

Possible reasons that released amounts being higher than sorbed amounts for P1 are: (i) dissolution of the framework and (ii) blokage of the pores. The studies in deionized water show that small amounts of Na^+ is observed and that demonstrates no impurities are present in CnC. Thus Na^+ amounts detected should be due to the dissolution of the framework, and presence of Si in deionized water verifies this. Al and Si monitoring in equilibrium experiments also showed that considerable amounts of dissolution is taking place. All of these may indicate that it is the dissolution of the framework which is responsible for that nonstoichiometry. However, the released Na^+ ions in excess are not in correlation with the detected Si amounts, i.e. they are not decreasing as the dissolution (Si) is decreasing as the concentration of Cd^{2+} increases. That can show that blokage of the channel pores may still be another valid reason for that.

Smooth conductivity graphs for CnC are indicating that ion exchange is the dominating mechanism. The average value of the fraction of sorbed over released amounts being closer to 1 also supports this.

pH increase of the both forms of clinoptilolite agrees well with each other and reflects the characteristic property of clinoptilolite as expected. Moreover, the maximum observed pH values are lower than 8, indicating no hydrolysis of metal ions occur.

Regarding modeling studies, F model is the best in describing clinoptilolite systems, whereas it is the poorest for the IR system. This result may reveal that differences exist in the mechanisms between clinoptilolite and IR. This is mainly because, clinoptilolite shows an increase while reaching a capacity value, whereas IR stabilizes at that value. This indicates that other mechanisms like adsorption and surface precipitation may be present in clinoptilolite accompanying ion exchange.

However, there are similarities as well especially between CnC and IR. There are isotherms in common which fits well to both for P1 and P2 (eg. RP, T and DA). This may be an implication of similar mechanisms existing in both sorbents, which means that CnC is close to an ion exchange system.

The disordered trends in AsC-P2 and GAC-P2 may indicate that impurities are inhibiting the isotherm from having a characteristic shape.

Values of adsorption energies given by DA isotherm shows that ion exchange mechanism is dominating for AsC and CnC. The value that it gives for IR implies an ion exchange mechanism only for P2. This may show that P2 may be a more appropriate methodology for ion exchange systems.

CHAPTER 5

CONCLUSION

Two procedures (i.e. by keeping the sorbent mass constant vs. by keeping the metal concentration constant) namely Procedure 1 (P1) and Procedure 2 (P2) are applied to four sorbents; as-received Clinoptilolite (AsC), Conditioned clinoptilolite (CnC), ion exchange resin (IR) and granulated activated carbon (GAC) in order to investigate the prevailing mechanisms of both forms of clinoptilolite for Cd^{2+} removal and the impact of the methodology on investigating such systems.

Differences are observed between the two procedures which was observed as well in the study of Robinson et al. (1993). The difference is observed due to the concentration valence effect, occuring in ion exchange dominating systems in the exchange of ions of different valences.

The overall results of the study (monitoring of exchangeable cations, pH, conductivity, framework cations and modeling studies) reveal that ion exchange system is the prevailing mechanism both for AsC and CnC. However in CnC, ion exchange is more dominating due to the lack of interfering effects, mainly coming from impurities.

Although the difference in both procedures is clear, it is still hard to decide on a procedure that is more proper since there are some drawbacks in P2 as well. There are many physicochemical changes occuring in the solution by using P2 as more masses are used. For example, clinoptilolite is affecting the pH of solution more, more Si and exchangeable cations are being released from clinoptilolite structure, IR is releasing more impurities to solution, etc. Those are interfering effects and may complicate the sorption process. They even can change the system and/or trigger some other co-mechanisms taking place.

As mentioned before, clinoptilolite-metal interaction is a complex process in which many mechanisms take place. Moreover, different mechanisms and/or factors like, solution pH, ionic strength, presence of anions, temperature, etc. can affect and trigger each other. For example the pH of the solution affects Cd^{2+} removal, framework dissolution, surface complexation and surface precipitation. In turn, Cd^{2+} removal, framework dissolution and surface complexation have an effect on the pH of the solution. Cd^{2+} removal triggers the exchangeable and framework cation release. The release of cations affect Cd^{2+} removal and the ionic strength of the solution. Ionic strength of the solution have control over Cd^{2+} removal, framework dissolution, pH, surface complexation and surface precipitation. Concentration of the solution has also effect on Cd^{2+} removal, exchangeable and framework cation release and ionic strength. It can be seen that mechanisms prevailing are very complex and interrelated with each other. Under that circumstances, minumum change of interfering factors is preferable in order to study the equilibria.

It is true that normalities have an effect on the ion exchange isotherm. However other unfavorable effects arising from P2 should be considered as well. It is important to study the effects of the physicochemical changes on the removal mechanism.

Further investigations on this subject can be beneficial as most of the studies in literature uses P1 in their studies. Another alternative method to P2 is to introduce another cation, which helps to compose different proportions while the normality remains constant. This alternative procedure may be examined as well, with its advantages and disadvantages in order to come to a resolution.

CHAPTER 6

RECOMMENDATIONS

Further recommendations for future can be listed as:

- Studying of the effects caused during the evaluation of Procedure 2 (P2), on Cd^{2+} removal
- Investigation of mechanism and P2 for different metal ions
- Comparison of P2 with the alternative procedure (i.e. keeping the normality constant by different proportion of ions)
- Developing new tecniques in order to discover the clinoptilolite-metal interaction mechanisms

In addition to those, extensive conditioning before use is recommended for heavy metal removal studies by clinoptilolite in order to get rid of the dust and impurities within the structure and to have a more efficient removal. Lastly, the clinoptilolite used in this study is recommended with its superior capacity among the others reported in literature.

REFERENCES

Abusafa, A. and Yucel, H. (2002) Removal of Cs-137 from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite. Separation and Purification Technology 28(2), 103-116.

Ackley, M.W. and Yang, R.T. (1991) Diffusion in Ion-Exchanged Clinoptilolites. Aiche Journal 37(11), 1645-1656.

Ahmad, A., Rafatullah, M. and Danish, M. (2007) Sorption studies of Zn(II)- and Cd(II)ions from aqueous solution on treated sawdust of sissoowood. Holz Roh Werkst 65, 429–436.

Akgul, M., Karabakan, A., Acar, O. and Yurum, Y. (2006) Removal of silver (I) from aqueous solutions with clinoptilolite. Microporous and Mesoporous Materials 94(1-3), 99-104.

Al-Anber, M. and Al-Anber, Z.A. (2008) Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. Desalination 225, 70-81.

Altın, O., Özbelge, Ö. and Doğu, T. (1998) Use of general purpose isotherms for heavy metal-clay mineral interactions. Journal of Colloid and Interface Science 198, 130-140.

APHA (2005) Standard Methods for the Examination of Water & Wastewater, APHA, AWWA, WEF Joint Publication, Washington, DC.

Arambula-Villazana, V., Solache-Rios, M. and Olguin, M.T. (2006) Sorption of cadmium from aqueous solutions at different temperatures by Mexican HEU-type zeolite rich tuff. Journal of Inclusion Phenomena and Macrocyclic Chemistry 55(3-4), 229-236.

Athanasiadis, K. and Helmreich, B. (2005) Influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite. Water Research 39(8), 1527-1532.

Atkins, P. and Paula, J.d. (2002) Atkins' Physical chemistry, Oxford University Press, Oxford, New York.

Auerbach, S.M., Carrado, K.A. and Dutta, P.K. (2003) Handbook of Zeolite Science and Technology, Marcel Dekker, New York.

Balci, S. (2004) Nature of ammonium ion adsorption by sepiolite:analysis of equilibrium data with several isotherms. Water Research 38, 1129–1138.

Balkaya, N. and Cesur, H. (2008) Adsorption of cadmium from aqueous solution by phosphogypsum. Chemical Engineering Journal 140, 247–254.

Barrer, R.M. (1982) Hydrothermal chemistry of zeolites, Academic Press, London New York.

Barrer, R.M. and Klinowski, J. (1974) Ion exchange selectivity and electrolyte concentration. J. Chem. Soc. Faraday Trans. 1 70.

Barri, S.A.I. and Rees, L.V.C. (1980) Binary and ternary cation exchange in zeolites. Journal of Chromatography 201(21), 21-34.

Bektas, N. and Kara, S. (2004) Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies. Separation and Purification Technology 39(3), 189-200.

Benhammou, A., Yaacoubi, A., Niboub, L. and Tanout, B. (2005) Adsorption of metal ions onto Moroccan stevensite:kinetic and isotherm studies. Journal of Colloid and Interface Science 282, 320–326.

Berber-Mendoza, M.S., Leyva-Ramos, R., Alonso-Davila, P., Fuentes-Rubio, L. and Guerrero-Coronado, R.M. (2006a) Comparison of isotherms for the ion exchange of Pb(II) from aqueous solution onto homoionic clinoptilolite. Journal of Colloid and Interface Science 301(1), 40-45.

Berber-Mendoza, M.S., Leyva-Ramos, R., Alonso-Davila, P., Mendoza-Barron, J. and Diaz-Flores, P.E. (2006b) Effect of pH and temperature on the ion-exchange isotherm of Cd(II) on Pb(II) on clinoptilolite. Journal of Chemical Technology and Biotechnology 81(6), 966-973.

Blanchard, G., Maunaye, M. and Martin, G. (1984) Removal of heavy metals from waters by means of natural zeolites. Water Research 18(12), 1501-1507.

Breck, D.W. (1974) Zeolite Molecular Sieves, Wiley-Interscience, New York.

Brunauer, S. (1943) The Adsorption of Gases and Vapors Vol I - Physical Adsorption, Princeton University Press, USA.

Castaldi, P., Santona, L., Enzo, S. and Melis, P. (2008) Sorption processes and XRD analysis of a natural zeolite exchanged with Pb^{2+}, Cd^{2+} and Zn^{2+} cations. Journal of Hazardous Materials 156, 428–434.

Cincotti, A., Lai, N., Orru, R. and Cao, G. (2001) Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling. Chemical Engineering Journal 84(3), 275-282.

Cincotti, A., Mameli, A., Locci, A.M., Orru, R. and Cao, G. (2006) Heavy metals uptake by Sardinian natural zeolites: Experiment and modeling. Industrial & Engineering Chemistry Research 45(3), 1074-1084.

Colella, C. (2005) Zeolites and ordered mesoporous materials: progress and prospects. Cejka, J. and Bekkum, H.v. (eds).

Cremers, A. (1977) Ion exchange in zeolites. Katzer, J.R. (ed), pp. 179-193, Washington, DC.

Culfaz, M. and Yagiz, M. (2004) Ion exchange properties of natural clinoptilolite: lead-sodium and cadmium-sodium equilibria. Separation and Purification Technology 37(2), 93-105.

Curkovic, L., CerjanStefanovic, S. and Filipan, T. (1997) Metal ion exchange by natural and modified zeolites. Water Research 31(6), 1379-1382.

Çoruh, S. (2008) The removal of zinc ions by natural and conditioned clinoptilolites. Desalination 225, 41-57.

Demirbas, A., Pehlivan, E., Gode, F., Altun, T. and Arslan, G. (2005) Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. Journal of Colloid and Interface Science 282, 20–25.

Demirbaş, A., Arslan, G. and Pehlivan, E. (2006) Recent Studies on Activated Carbons and Fly Ashes from Turkish Resources. Energy Sources 28, 627–638.

Deng, X., Yi, X.E. and Liua, G. (2007) Cadmium removal from aqueous solution by gene-modified Escherichia coli JM109. Journal of Hazardous Materials 139(2), 340-344.

Dimirkou, A. (2007) Uptake of Zn2+ ions by a fully iron-exchanged clinoptilolite. Case study of heavily contaminated drinking water samples. Water Research 41, 2763 – 2773.

Doula, M., Ioannou, A. and Dimirkou, A. (2002) Copper adsorption and Si, Al, Ca, Mg, and Na release from clinoptilolite. Journal of Colloid and Interface Science 245(2), 237-250.

Doula, M.K. (2006) Removal of Mn2+ ions from drinking water by using Clinoptilolite and a Clinoptilolite-Fe oxide system. Water Research 40(17), 3167-3176.

Doula, M.K. and Dimirkou, A. (2008) Use of an iron-overexchanged clinoptilolite for the removal of Cu^{2+} ions from heavily contaminated drinking water samples. Journal of Hazardous Materials 151, 738–745.

Doula, M.K. and Ioannou, A. (2003) The effect of electrolyte anion on Cu adsorption-desorption by clinoptilolite. Microporous and Mesoporous Materials 58(2), 115-130.

DPT (1996) Devlet Planlama Teşkilatı, Madencilik Özel İhtisas Komisyonu Endüstriyel Hammaddeler Alt Komisyonu-Diğer Endüstri Mineralleri Çalışma

Grubu Raporu. http://ekutup.dpt.gov.tr/madencil/sanayiha/oik480c1.pdf Retrieved: November, 2009.

Dyer, A. and Enamy, H. (1981) The Plotting and Interpretation of Ion-Exchange Isotherms in Zeolite Systems. Separation Science and Technology 16(2), 173-183.
Englert, A.H. and Rubio, J. (2005) Characterization and environmental application of a Chilean natural zeolite. International Journal of Mineral Processing 75(1-2), 21-29.

Ennigrou, D.J., Gzara, L., Romdhane, M.R.B. and Dhahbi, M. (2009) Cadmium removal from aqueous solutions by polyelectrolyte enhanced ultrafiltration. Desalination 246, 363–369.

Ersoy, B. and Celik, M.S. (2002) Electrokinetic properties of clinoptilolite with mono- and multivalent electrolytes. Microporous and Mesoporous Materials 55(3), 305-312.

Filippidis, A., Godelitsas, A., Charistos, D., Misaelides, P. and Kassoli-Fournaraki, A. (1996) The chemical behavior of natural zeolites in aqueous environments: Interactions between low-silica zeolites and 1 M NaCl solutions of different initial pH-values Applied Clay Science 11, 199-209.

Foo, K.Y. and Hameed, B.H. (2009) Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal; doi: 10.1016/j.cej.2009.09.013.

Gabaldón, C., Marzal, P., Seco, A. and Gonzalez, J.A. (2000) Cadmium and Copper Removal by a Granular Activated Carbon in Laboratory Column Systems. Separation Science and Technology 35(7), 1039–1053.

Gedik, K. and Imamoglu, I. (2008) Affinity of clinoptilolite-based zeolites towards removal of Cd from aqueous solutions. Separation Science and Technology 43(5), 1191-1207.

Genc-Fuhrman, H., Mikkelsen, P.S. and Ledin, A. (2007) Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. Water Research 41, 591 – 602.

Helfferich, F. (1995) Ion Exchange, Dover Publications, New York.

Hizal, J. and Apak, R. (2006) Modeling of cadmium(II) adsorption on kaolinite-based clays in the absence and presence of humic acid. Applied Clay Science 32, 232–244.

Ho, Y.S., Porter, J.F. and Mckay, G. (2001) Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. Water Air Soil Pollution 141, 1-33.

Inglezakis, V.J. (2005) The concept of "capacity" in zeolite ion-exchange systems. Journal of Colloid and Interface Science 281(1), 68-79.

Inglezakis, V.J. (2007) Solubility-normalized Dubinin-Astakhov adsorption isotherm for ion-exchange systems. Microporous and Mesoporous Materials 103, 72-81.

Inglezakis, V.J., Loizidou, M.D. and Grigoropoulou, H.P. (2002) Equilibrium and kinetic ion exchange studies of Pb2+, Cr3+, Fe3+ and Cu2+ on natural clinoptilolite. Water Research 36(11), 2784-2792.

Inglezakis, V.J., Loizidou, M.M. and Grigoropoulou, H.P. (2004) Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility. Journal of Colloid and Interface Science 275(2), 570-576.

Inglezakis, V.J. and Poulopoulos, S. (2006) Adsorption, ion exchange, and catalysis : design of operations and environmental applications Elsevier, Boston.

Inglezakis, V.J., Zorpas, A.A., Loizidou, M.D. and Grigoropoulou, H.P. (2005) The effect of competitive cations and anions on ion exchange of heavy metals. Separation and Purification Technology 46(3), 202-207.

IUPAC (1997) Compendium of Chemical Terminology-The Gold Book.

Karagunduz, A. and Unal, D. (2006) New method for evaluation of heavy metal binding to alginate beads using pH and conductivity data. Adsorption 12, 175-184.

Kesraouiouki, S., Cheeseman, C.R. and Perry, R. (1994) Natural Zeolite Utilization in Pollution-Control - a Review of Applications to Metals Effluents. Journal of Chemical Technology and Biotechnology 59(2), 121-126.

Kesraoulouki, S., Cheeseman, C. and Perry, R. (1993) Effects of Conditioning and Treatment of Chabazite and Clinoptilolite Prior to Lead and Cadmium Removal. Environmental Science & Technology 27(6), 1108-1116.

Kinniburgh, D.G. (1986) General Purpose Adsorption Isotherms. Environmental Science and Technology 20, 895-904.

Kobya, M., Demirbas, E., Senturk, E. and Ince, M. (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource Technology 96, 1518–1521.

Kocaoba, S. (2007) Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals. Journal of Hazardous Materials 147, 488–496.

Kocaoba, S. and Akcin, G. (2005) Removal of chromium (III) and cadmium (II) from aqueous solutions. Desalination 180, 151-156.

Kocaoba, S., Orhan, Y. and Akyüz, T. (2007) Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. Desalination 214, 1–10.

Kohlrausch, F. (1899) The Fundamental Laws of Electrolytic Conduction. Goodwin, H.M. (ed), Harper and Brothers Publishers, New York and London.

Langella, A., Pansini, M., Cappelletti, P., de Gennaro, B., de' Gennaro, M. and Colella, C. (2000) NH4+, Cu2+, Zn2+, Cd2+ and Pb2+ exchange for Na+ in a sedimentary clinoptilolite, North Sardinia, Italy. Microporous and Mesoporous Materials 37(3), 337-343.

Langwaldt, J. (2008) Ammonium Removal From Water by Eight Natural Zeolites: A Comparative Study. Separation Science and Technology 43(2166–2182).

Lee, D.H. and Moon, H. (2001) Adsorption equilibrium of heavy metals on natural zeolites. Korean Journal of Chemical Engineering 18(2), 247-256.

Llanes-Monter, M.M., Olguín, M.T. and Solache-Ríos, M.J. (2007) Lead Sorption by a Mexican, Clinoptilolite-Rich Tuff. Env. Sci. Pollut. Res. 14(6), 397–403.

Loizidou, M. and Townsend, R.P. (1987) Ion-Exchange Properties of Natural Clinoptilolite, Ferrierite and Mordenite .2. Lead Sodium and Lead Ammonium Equilibria. Zeolites 7(2), 153-159.

Milazzo, G. (1963) Electrochemistry; theoretical principles and practical applications, Elsevier Pub. Co., Amsterdam, New York.

Minceva, M., Fajgar, R., Markovska, L. and Meshko, V. (2008) Comparative Study of Zn^{2+}, Cd^{2+}, and Pb^{2+} Removal From Water Solution Using Natural Clinoptilolitic Zeolite and Commercial Granulated Activated Carbon. Equilibrium of Adsorption. Separation Science and Technology 43, 2117–2143.

Minceva, M., Markovska, L. and Meshko, V. (2007) Removal of Zn2+, Cd2+ and Pb2+ from binary aqueous solution by natural zeolite and granulated activated carbon. Macedonian Journal of Chemistry and Chemical Engineering 26(2), 125–134.

Mumford, K.A., Shallcross, D.C., Snape, I. and Stevens, G.W. (2008) Industrial & Engineering Chemistry Research. Application of a Temperature-Dependent Semiempirical Thermodynamic Ion-Exchange Model to a Multicomponent Natural Zeolite System 47(21), 8347-8354.

Ouki, S.K. and Kavannagh, M. (1999) Treatment of metals-contaminated wastewaters by use of natural zeolites. Water Science and Technology 39(10-11), 115-122.

Pabalan, R.T. and Bertetti, F.P. (2001) Cation-exchange properties of natural zeolites. Natural Zeolites: Occurrence, Properties, Applications 45, 453-518.

Peric, J., Trgo, M. and Medvidovic, N.V. (2004) Removal of zinc, copper and lead by natural zeolite - a comparison of adsorption isotherms. Water Research 38(7), 1893-1899.

Petrus, R. and Warchol, J. (2003) Ion exchange equilibria between clinoptilolite and aqueous solutions of Na+/Cu2+, Na+/Cd2+ and Na+/Pb2+. Microporous and Mesoporous Materials 61(1-3), 137-146.

Petrus, R. and Warchol, J.K. (2005) Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems. Water Research 39(5), 819-830.

Potter, E.C. (1956) Electrochemistry, principles & applications, Cleaver-Hume Press, London.

Redlich and Peterson, D.L. (1959) A Useful Adsorption Isotherm. Journal of Physical Chemistry 63.

Rivera, A., Rodriguez-Fuentes, G. and Altshuler, E. (2000) Time evolution of a natural clinoptilolite in aqueous medium: conductivity and pH experiments. Microporous and Mesoporous Materials 40(1-3), 173-179.

Robinson, S.M., Arnold, J.W.D. and Byers, C.W. (1993) Multicomponent liquid ion exchange with chabazite zeolites, Engineering Development Section, Chemical Technology Division, Oak Ridge National Laboratory.

Seader, J.D. and Henley, E.J. (1998) Separation process principles, Wiley, New York.

Semmens, M. and Seyfarth, M. (1978) Natural zeolites: occurrence, properties, use. Sand, L.B. and Mumpton, F.A. (eds), pp. 517-526, Pergamon Press.

Semmens, M.J. and Martin, W.P. (1988) The Influence of Pretreatment on the Capacity and Selectivity of Clinoptilolite for Metal-Ions. Water Research 22(5), 537-542.

Sheta, A.S., Falatah, A.M., Al-Sewailem, M.S., Khaled, E.M. and Sallam, A.S.H. (2003) Sorption characteristics of zinc and iron by natural zeolite and bentonite. Microporous and Mesoporous Materials 61(1-3), 127-136.

Stylianou, M.A., Hadjiconstantinou, M.P., Inglezakis, V.J., Moustakas, K.G. and Loizidou, M.D. (2007) Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column. Journal of Hazardous Materials 143, 575-581.

Subba Rao, H.C. and David, M.M. (1957) Equilibrium in the system Cu^{++}-Na^{+}-Dowex 50. A.I.Ch.E Journal 3, 187-190.

Suzuki, M. (1990) Adsorption Engineering, Elsevier, Tokyo.

Townsend, R.P. and Loizidou, M. (1984) Ion-Exchange Properties of Natural Clinoptilolite, Ferrierite and Mordenite .1. Sodium Ammonium Equilibria. Zeolites 4(2), 191-195.

Trgo, M. and Peric, J. (2003) Interaction of the zeolitic tuff with Zn-containing simulated pollutant solutions. Journal of Colloid and Interface Science 260(1), 166-175.

Tsitsishvili, G.V., Andronikashvili, T.G., Kirov, G.M. and Filizova, L.D. (1992) Natural Zeolites, E.Horwood, New York.

Vaughan, D.E.W. (1978) Natural zeolites: occurrence, properties, use. Sand, L.B. and Mumpton, F.A. (eds), pp. 353-371, Pergamon Press.

Walter J. Weber, J. (1972) Physicochemical processes for water quality control Wiley-Interscience, New York.

Wang, Y., Tang, X., Chen, Y., Zhan, L., Li, Z. and Tang, Q. (2009) Adsorption behavior and mechanism of Cd(II) on loess soil from China. Journal of Hazardous Materials 172, 30–37.

Weatherley, L.R. and Miladinovic, N.D. (2004) Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. Water Research 38(20), 4305-4312.

Wen, D.H., Ho, Y.S., Xie, S.G. and Tang, X.Y. (2006) Mechanism of the adsorption of ammonium ions from aqueous solution by a chinese natural zeolite. Separation Science and Technology 41(15), 3485-3498.

APPENDIX A

CALIBRATION CURVES

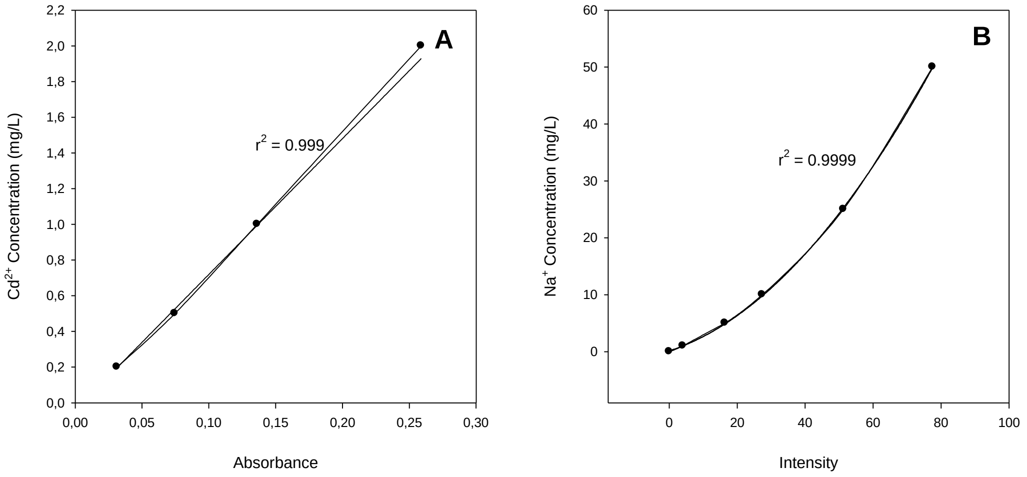

Figure A. 1. Calibration Curves of A. Cd^{2+} B. Na$^+$

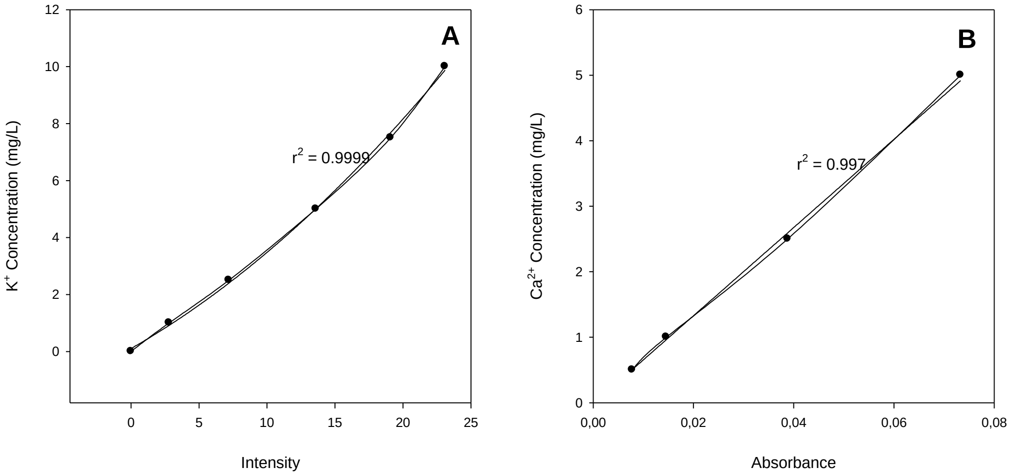

Figure A. 2. Calibration Curves of A. K$^+$ B. Ca^{2+}

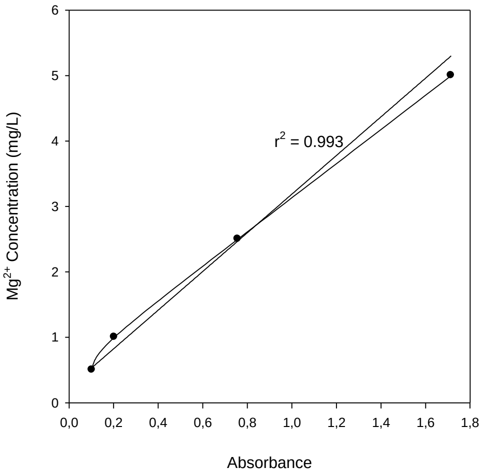

Figure A. 3. Calibration Curve of Mg^{2+}

Table B. 1. Equilibration Time data of AsC

Time (hr)	Beaker	Cd^{2+} in solution (mg/L)	Cd^{2+} in solution (mg/L) with volume correction
0	A	41,25	41,25
	B	45,00	45,00
	A-B Average	43,13	43,13
	C	42,95	-
12	A	17,66	18,21
	B	16,19	16,69
	A-B Average	16,93	17,45
	C	-	-
24	A	14,30	15,21
	B	15,15	16,12
	A-B Average	14,73	15,66
	C	-	-
48	A	14,02	15,41
	B	14,99	16,47
	A-B Average	14,51	15,94
	C	-	-

Table B. 1. Cont’d

Time (hr)	Beaker	$^{+}$ in solution (mg/L)	Cd^{2+} in solution (mg/L) with volume correction
72	A	14,10	16,02
	B	11,64	13,23
	A-B Average	12,87	14,63
	C	-	-
96	A	12,64	14,87
	B	11,95	14,06
	A-B Average	12,30	14,46
	C	-	-
120	A	13,57	16,55
	B	12,97	15,82
	A-B Average	13,27	16,18
	C	-	-
144	A	12,34	15,62
	B	11,82	14,96
	A-B Average	12,08	15,29
	C	-	-
168	A	12,83	16,88
	B	12,00	15,79
	A-B Average	12,42	16,34
	C	48,20	-

Table B. 2. Equilibration Time data of CnC

Time (hr)	Beaker	Cd^{2+} in solution (mg/L)	Cd^{2+} in solution (mg/L) with volume correction
0	A	160,4	160,4
	B	156,2	156,2
	A-B Average	158,3	158,3
	C	167,6	-
2	A	14,48	14,93
	B	14,48	14,93
	A-B Average	14,48	14,93
	C	-	-
4	A	3,38	3,60
	B	3,38	3,60
	A-B Average	3,38	3,60
	C	-	-
6	A	1,68	1,85
	B	1,80	1,98
	A-B Average	1,74	1,91
	C	-	-
7,5	A	1,64	1,86
	B	1,77	2,01
	A-B Average	1,71	1,94
	C	-	-

Table B. 2. Cont'd

Time (hr)	Beaker	Cd^{2+} in solution (mg/L)	Cd^{2+} in solution (mg/L) with volume correction
10	A	1,61	1,89
	B	1,74	2,05
	A-B Average	1,67	1,97
	C	-	-
12	A	1,44	1,75
	B	1,61	1,96
	A-B Average	1,52	1,86
	C	-	-
24	A	1,35	1,70
	B	1,35	1,70
	A-B Average	1,35	1,70
	C	175,4	-

Table B. 3. Equilibration Time data of IR

Time (hr)	**Beaker**	**Cd^{2+} in solution (mg/L)**	**Cd^{2+} in solution (mg/L) with volume correction**
0	A	926,0	926,0
	B	890,0	890,0
	A-B Average	908,0	908,0
	C	825,0	-
1	A	164,5	169,6
	B	135,5	139,7
	A-B Average	150,0	154,6
	C	-	-
2	A	43,20	45,96
	B	36,20	38,51
	A-B Average	39,70	42,23
	C	-	-
4	A	16,40	18,02
	B	15,70	17,25
	A-B Average	16,05	17,64
	C	-	-
6	A	15,20	17,27
	B	16,50	18,75
	A-B Average	15,85	18,01
	C	-	-

Table B. 3. Cont'd

Time (hr)	Beaker	Cd^{2+} in solution (mg/L)	Cd^{2+} in solution (mg/L) with volume correction
8	A	16,70	19,65
	B	17,90	21,06
	A-B Average	17,30	20,35
	C	-	-
12	A	17,40	21,22
	B	17,40	21,22
	A-B Average	17,40	21,22
	C	-	-
24	A	1,60	2,03
	B	1,70	2,15
	A-B Average	1,65	2,09
	C	747,0	-

Table B. 4. Equilibration Time data of GAC

Time (hr)	**Beaker**	**Cd^{2+} in solution (mg/L)**	**Cd^{2+} in solution (mg/L) with volume correction**
0	A	53,00	53,00
	B	53,70	53,70
	A-B Average	53,35	53,35
	C	54,70	-
12	A	39,90	41,13
	B	37,00	38,14
	A-B Average	38,45	39,64
	C	-	-
24	A	37,50	39,89
	B	36,60	38,94
	A-B Average	37,05	39,41
	C	-	-
48	A	37,45	41,15
	B	36,25	39,84
	A-B Average	36,85	40,49
	C	-	-
72	A	37,05	42,10
	B	37,65	42,78
	A-B Average	37,35	42,44
	C	55,70	-

APPENDIX C
EQUILIBRIUM DATA

The amount of cadmium sorbed per gram of clinoptilolite (q_e) is calculated as has been given by the Equation 3.1:

$$q_e = \frac{(C_i - C_e) \times V}{m \times Eq.Wt.}$$

where;

q_e: amount adsorbed per gram of clinoptilolite (meq/g)

C_i: initial metal concentration in solution (mg/L)

C_e: equilibrium metal concentration in solution (mg/L)

V: volume of solution (L)

m: amount of sorbent added (g)

Eq.Wt.: equivalent weight of the metal added (g/eq)

A sample calculation is provided below:

$$q_e = \frac{(43{,}45 - 7{,}43) \times 0{,}1}{1 \times \frac{112.411 g/mol}{2 eq/mol}} \cong 0{,}064 meq/g$$

Table C. 1. Initial and equilibrium concentrations of equilibrium data for AsC

Equilibrium Data Beaker	P1		P2	
	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)
A	43,25	7,33	581,5	577,0
B	43,25	7,53	589,0	577,5
A-B Average	43,45	7,43	585,3	577,3
A	234,2	117,5	581,5	565,5
B	221,0	115,4	589,0	569,5
A-B Average	227,6	116,5	585,3	567,5
A	432,0	335,5	516,5	495,0
B	444,5	333,5	559,0	485,0
A-B Average	438,3	334,5	537,8	490,0
A	742,0	623,0	581,5	445,0
B	749,5	627,5	589,0	445,0
A-B Average	745,8	625,3	585,3	445,0
A	1073	883,0	524,4	277,6
B	1034	906,0	524,6	279,2
A-B Average	1053,5	894,5	524,5	278,4
A	1467	1292	516,5	231,4
B	1464	1287	559,0	242,6
A-B Average	1465,5	1289,5	537,8	237,0
A	1902	1634	516,5	144,7
B	1926	1624	559,0	146,8
A-B Average	1914	1629	537,8	145,8
A	2134	1850	516,5	102,0
B	2142	1868	559,0	104,5
A-B Average	2138	1859	537,8	103,3
A	3130	2854	516,5	77,40
B	3144	2818	559,0	78,90
A-B Average	3137	2836	537,8	78,20
A	3672	3372		
B	3680	3384		
A-B Average	3676	3378		
A	4912	4656		
B	4920	4640		
A-B Average	4916	4648		
A	4728	4408		
B	4724	4728		
A-B Average	4726	4412		

Table C. 2. Initial and equilibrium concentrations of equilibrium data for CnC

Equilibrium Data / Beaker	P1		P2	
	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)
A	52,60	0,00	569,0	4,81
B	51,90	0,00	570,5	4,69
A-B Average	52,30	0,00	569,8	4,75
A	245,2	6,40	569,0	24,95
B	242,6	6,74	570,5	27,15
A-B Average	243,9	6,57	569,8	26,05
A	569,0	123,9	562,0	47,65
B	577,5	123,5	559,0	46,75
A-B Average	573,3	123,7	560,5	47,20
A	1421	963,0	569,0	123,9
B	1450	987,0	577,5	123,5
A-B Average	1435,5	975,0	573,3	123,7
A	2104	1624	562,0	182,2
B	2108	1572	559,0	181,1
A-B Average	2106	1598	560,5	181,7
A	3136	2564	562,0	288,0
B	3140	2584	559,0	295,0
A-B Average	3138	2574	560,5	291,5
A	4616	3992	569,0	365,5
B	4516	3964	570,5	375,0
A-B Average	4566	3978	569,8	370,3
A	5092	4372	581,5	494,0
B	4912	4420	580,0	513,0
A-B Average	5002	4396	580,8	503,5
A	8010	7760	581,5	537,5
B	8520	7520	580,0	540,0
A-B Average	8265	7640	580,8	538,8
A	11290	10410	581,5	576,0
B	11200	10660	580,0	574,5
A-B Average	11245	10535	580,8	575,3

Table C. 3. Initial and equilibrium concentrations of equilibrium data for IR

Equilibrium Data / Beaker	P1		P2	
	Initial Concentration (mg/L)	**Equilibrium Concentration (mg/L)**	**Initial Concentration (mg/L)**	**Equilibrium Concentration (mg/L)**
A	60,20	0,00	19730	19300
B	60,10	0,00	19000	19280
A-B Average	60,10	0,00	19365	19290
A	304,2	0,30	19690	19480
B	292,2	0,30	19590	19490
A-B Average	298,2	0,30	19640	19485
A	595,5	1,32	17050	16020
B	614,0	1,30	18000	15830
A-B Average	604,8	1,31	17525	15925
A	1715	382,2	19730	11850
B	1769	395,8	19000	11740
A-B Average	1742	389,0	19365	11795
A	2948	1536	17140	4000
B	2960	1561	17040	4300
A-B Average	2954	1548,5	17090	4150
A	5512	4200	19690	3572
B	5656	4120	19590	3392
A-B Average	5584	4160	19640	3482
A	12280	10610	19730	2222
B	12210	10870	19000	2200
A-B Average	12245	10740	19365	2211
A	17050	16020	17140	784,0
B	18000	15830	17040	761,0
A-B Average	17525	15925	17090	772,5
A	32175	29750	15210	585,0
B	31175	30500	14620	578,5
A-B Average	31675	30125	14915	581,8

Table C. 4. Initial and equilibrium concentrations of equilibrium data for GAC

Equilibrium Data / Beaker	P1		P2	
	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)
A	23,26	19,36	59,60	59,00
B	22,42	19,48	59,60	58,70
A-B Average	22,84	19,42	59,60	58,85
A	55,30	48,60	57,55	55,10
B	58,90	48,60	58,00	54,45
A-B Average	57,10	48,60	57,78	54,78
A	102,0	92,80	53,85	44,50
B	102,0	91,00	55,25	47,10
A-B Average	102,0	91,90	54,55	45,80
A	163,8	149,0	59,20	44,25
B	163,6	151,0	58,15	46,65
A-B Average	163,7	150,0	58,68	45,45
A	273,8	251,6	53,85	34,40
B	274,8	251,6	55,25	34,05
A-B Average	274,3	251,6	54,55	34,23
A	420,0	390,0	59,20	36,30
B	412,5	394,5	58,15	36,05
A-B Average	416,3	392,3	58,68	36,18
A	576,0	530,0	53,85	24,35
B	578,5	526,0	55,25	25,10
A-B Average	577,3	528,0	54,55	24,73
A	777,0	766,0	59,20	21,80
B	813,5	760,0	58,15	23,35
A-B Average	795,3	763,0	58,68	22,58
A	1037	1014	53,70	9,82
B	1057	1009	54,05	9,12
A-B Average	1047	1011,5	53,88	9,47

Table C. 5. Equilibrium data of AsC-P1

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
							t_0	t_{eq}	t_0	t_{eq}
0,001	A	0,064	0,03	0,02	0,04	0,01	119,0	112,2	4,05	5,04
	B	0,064	0,03	0,02	0,04	0,01	120,1	110,2	4,07	5,17
	A-B Average	0,064	0,03	0,02	0,04	0,01	119,6	111,2	4,06	5,11
	C	-	-	-	-	-	124,9	115,2	4,07	4,34
0,005	A	0,20	0,15	0,11	0,09	0,02	548,0	553,0	3,97	4,90
	B	0,20	0,17	0,11	0,08	0,02	548,0	557,0	3,57	4,97
	A-B Average	0,20	0,16	0,11	0,08	0,02	548,0	555,0	3,77	4,94
	C	-	-	-	-	-	557,0	552,0	3,57	4,01
0,01	A	0,18	0,12	0,08	0,06	0,03	1020	998,0	3,74	4,89
	B	0,19	0,12	0,09	0,07	0,03	1027	990,0	3,82	5,00
	A-B Average	0,18	0,12	0,08	0,07	0,03	1023,5	994,0	3,78	4,95
	C	-	-	-	-	-	1024	985,0	3,83	3,84
0,015	A	0,22	0,36	0,12	0,05	0,03	1501	1463	4,14	4,82
	B	0,21	0,35	0,12	0,05	0,03	1519	1457	4,22	5,19
	A-B Average	0,21	0,36	0,12	0,05	0,03	1510	1460	4,18	5,01
	C	-	-	-	-	-	1474	1508	4,19	4,33

Table C. 5. Cont'd

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
							t_0	t_{eq}	t_0	t_{eq}
0,02	A	0,30	0,42	0,12	0,06	0,03	2400	2470	4,01	5,00
	B	0,26	0,40	0,12	0,05	0,03	2480	2420	3,95	4,93
	A-B Average	0,28	0,41	0,12	0,05	0,03	2440	2445	3,98	4,97
	C	-	-	-	-	-	2470	2500	3,91	3,92
0,03	A	0,31	0,83	0,18	0,07	0,04	3390	3490	3,97	4,65
	B	0,32	0,35	0,17	0,06	0,04	3370	3490	4,01	4,77
	A-B Average	0,31	0,59	0,18	0,06	0,04	3380	3490	3,99	4,71
	C	-	-	-	-	-	3400	3510	3,95	3,96
0,035	A	0,50	0,50	0,13	0,06	0,04	4040	4030	3,86	4,92
	B	0,52	0,48	0,13	0,06	0,04	4030	4040	3,97	4,93
	A-B Average	0,51	0,49	0,13	0,06	0,04	4035	4035	3,92	4,93
	C	-	-	-	-	-	4010	4050	3,95	4,03
0,04	A	0,51	0,55	0,18	0,06	0,04	4340	4500	4,00	4,82
	B	0,48	0,55	0,18	0,06	0,04	4360	4550	4,00	4,81
	A-B Average	0,50	0,55	0,18	0,06	0,04	4350	4525	4,00	4,82
	C	-	-	-	-	-	4510	4500	3,98	3,99

Table C. 5. Cont'd

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
							t_0	t_{eq}	t_0	t_{eq}
0,05	A	0,50	0,72	0,21	0,09	0,04	5230	5260	4,17	4,62
	B	0,58	0,71	0,17	0,06	0,04	5220	5170	4,09	4,66
	A-B Average	0,54	0,71	0,19	0,08	0,04	5225	5215	4,13	4,64
	C	-	-	-	-	-	5320	5240	4,22	4,12
0,07	A	0,54	0,68	0,17	0,06	0,05	6980	7120	4,23	4,93
	B	0,52	0,63	0,21	0,07	0,06	6950	7070	4,17	4,94
	A-B Average	0,53	0,65	0,19	0,07	0,06	6965	7095	4,20	4,94
	C	-	-	-	-	-	6980	7230	4,24	4,47
0,08	A	0,46	0,87	0,20	0,08	0,04	7720	7600	4,16	4,68
	B	0,49	0,88	0,22	0,09	0,04	7770	7620	4,22	4,79
	A-B Average	0,48	0,88	0,21	0,09	0,04	7745	7610	4,19	4,74
	C	-	-	-	-	-	7900	7630	4,33	4,31
0,1	A	0,55	0,78	0,22	0,09	0,05	9290	8850	4,14	4,33
	B	0,57	0,78	0,21	0,09	0,05	9300	8850	4,13	4,51
	A-B Average	0,56	0,78	0,21	0,09	0,05	9295	8850	4,14	4,42
	C	-	-	-	-	-	9470	8880	4,19	3,94

Table C. 6. Equilibrium data of AsC-P2

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
							t$_0$	t$_{eq}$	t$_0$	t$_{eq}$
0,05	A	0,43	0,35	0,17	0,13	0,16	1027	1021	4,06	4,23
	B	0,41	0,33	0,16	0,14	0,15	1038	1032	4,02	4,15
	A-B Average	0,42	0,34	0,16	0,14	0,15	1032,5	1026,5	4,04	4,19
0,1	A	0,42	0,34	0,20	0,12	0,14	1028	1017	4,20	4,62
	B	0,35	0,29	0,17	0,11	0,13	1025	1013	4,14	4,72
	A-B Average	0,38	0,32	0,19	0,11	0,14	1026,5	1015	4,17	4,67
0,25	A	0,30	0,22	0,15	0,09	0,08	1014	1007	3,74	4,32
	B	0,38	0,20	0,18	0,08	0,07	1003	989,0	3,74	4,43
	A-B Average	0,34	0,21	0,16	0,08	0,07			3,74	4,38
1,0	A	0,26	0,12	0,08	0,06	0,03	1020	998,0	3,74	4,89
	B	0,26	0,12	0,08	0,07	0,03	1027	990,0	3,82	5,00
	A-B Average	0,26	0,12	0,08	0,06	0,03	1023,5	994,0	3,78	4,95
3,0	A	0,15	0,09	0,06	0,03	0,01	1004	978,0	4,16	4,88
	B	0,15	0,10	0,07	0,03	0,01	997,0	989,0	4,25	5,00
	A-B Average	0,15	0,10	0,07	0,03	0,01	1000,5	983,5	4,21	4,94
5,0	A	0,11	0,11	0,07	0,06	0,009	1022	1038	4,29	5,27
	B	0,11	0,09	0,05	0,03	0,009	1028	1039	4,22	5,34
	A-B Average	0,11	0,09	0,06	0,05	0,009	1025	1038,5	4,26	5,31

Table C. 6. Cont'd

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
							t_0	t_{eq}	t_0	t_{eq}
10,0	A	0,07	0,04	0,03	0,02	0,004	1018	1015	3,86	5,63
	B	0,07	0,04	0,04	0,02	0,004	1000	1017	3,91	5,73
	A-B Average	0,07	0,04	0,03	0,02	0,004	1009	1016	3,89	5,68
15,0	A	0,05	0,04	0,02	0,01	0,003	1021	1073	4,04	5,56
	B	0,05	0,04	0,03	0,02	0,003	1028	1055	4,33	5,57
	A-B Average	0,05	0,04	0,03	0,02	0,003	1024,5	1064	4,19	5,57
20,0	A	0,04	0,02	0,01	0,01	0,002	1023	1000	4,38	5,97
	B	0,04	0,02	0,01	0,01	0,002	1029	1026	4,28	5,97
	A-B Average	0,04	0,02	0,01	0,01	0,002	1026	1013	4,33	5,97
-	C1	-	-	-	-	-	1033	1050	4,07	4,05
	C2	-	-	-	-	-	1033	1014	4,17	4,14
	C3	-	-	-	-	-	1036	1009	3,79	3,96

Table C. 7. Equilibrium data of CnC-P1

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,001	A	0,09	0,12	109,7	113,9	4,16	5,01
	B	0,09	0,11	109,5	109,1	4,23	4,57
	A-B Average	0,09	0,11	109,6	111,5	4,20	4,79
	C	-	-	110,1	110,7	4,07	4,10
0,005	A	0,42	0,59	531,0	530,0	4,18	5,53
	B	0,42	0,59	517,0	538,0	4,31	4,22
	A-B Average	0,42	0,59	524,0	534,0	4,25	4,88
	C	-	-	534,0	530,0	4,31	4,22
0,01	A	0,80	0,85	995,0	1005	4,21	5,40
	B	0,80	0,86	991,0	979,0	4,26	5,00
	A-B Average	0,80	0,85	993,0	992,0	4,24	5,20
	C	-	-	993,0	992,0	4,20	4,40
0,03	A	0,84	1,12	3250	3310	3,94	4,64
	B	0,80	1,16	3370	3370	3,96	4,76
	A-B Average	0,82	1,14	3310	3340	3,95	4,70
	C	-	-	3240	3360	3,95	4,03
0,04	A	0,86	1,32	4170	4300	4,05	4,50
	B	0,95	1,33	4200	4190	4,07	4,74
	A-B Average	0,90	1,33	4185	4245	4,06	4,62
	C	-	-	4310	4180	4,02	4,12

Table C. 7. Cont'd

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,06	A	1,02	1,26	6070	6070	4,16	4,57
	B	0,99	1,28	5930	6100	4,15	4,77
	A-B Average	1,00	1,27	6000	6085	4,16	4,67
	C	-	-	6020	6085	4,11	4,15
0,08	A	1,02	1,25	7400	7640	4,08	4,56
	B	1,07	1,25	7700	7620	4,12	4,55
	A-B Average	1,05	1,25	7550	7630	4,10	4,56
	C	-	-	7690	7380	4,16	4,23
0,1	A	1,12	1,39	8820	8760	4,15	4,73
	B	1,04	1,41	9180	9070	4,22	4,70
	A-B Average	1,08	1,40	9000	8915	4,19	4,72
	C	-	-	8910	8810	4,25	4,32
0,16	A	0,90	1,27	12240	12200	4,16	4,65
	B	1,33	1,22	12240	12200	4,22	4,79
	A-B Average	1,11	1,24	12240	12200	4,19	4,72
	C	-	-	12300	12100	4,05	4,16
0,2	A	1,49	1,35	14860	14920	4,13	4,55
	B	1,04	1,42	14800	14750	4,22	4,62
	A-B Average	1,26	1,39	14830	14835	4,18	4,59
	C	-	-	14714	14950	4,30	4,35

Table C. 8. Equilibrium data of CnC-P2

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,01	A	1,66	1,74	983,0	985,0	4,14	4,17
	B	1,58	1,71	985,0	1019	4,13	4,11
	A-B Average	1,62	1,72	984,0	1002	4,14	4,14
0,05	A	1,66	1,56	979,0	1015	4,22	4,13
	B	1,58	1,46	979,0	1013	4,12	4,21
	A-B Average	1,62	1,51	979,0	1014	4,17	4,17
0,1	A	1,61	1,45	975,0	975,0	4,07	4,04
	B	1,27	1,43	1009	1009	4,10	4,22
	A-B Average	1,44	1,44	992,0	992,0	4,09	4,13
0,25	A	1,45	1,40	1007	1007	4,21	4,47
	B	1,39	1,43	985,0	1011	4,16	4,45
	A-B Average	1,42	1,41	996,0	1009	4,19	4,46
0,4	A	1,21	1,35	977,0	986,0	4,19	4,65
	B	1,18	1,34	983,0	958,0	4,16	4,78
	A-B Average	1,20	1,35	980,0	972,0	4,18	4,72
0,7	A	0,96	1,06	949,0	964,0	4,19	4,82
	B	0,96	1,10	955,0	965,0	4,19	4,94
	A-B Average	0,96	1,08	952,0	964,5	4,19	4,88
1,0	A	0,80	0,85	995,0	1005	4,21	5,40
	B	0,80	0,86	991,0	979,0	4,26	5,00
	A-B Average	0,80	0,85	993,0	992,0	4,24	5,20

Table C. 8. Cont'd

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
1,5	A	0,61	0,67	958,0	985,0	4,15	5,17
	B	0,61	0,68	952,0	987,0	4,12	5,23
	A-B Average	0,61	0,68	955,0	986,0	4,14	5,20
2,0	A	0,49	0,52	1006	977,0	4,17	5,35
	B	0,48	0,53	1009	1029	4,22	5,28
	A-B Average	0,48	0,52	1007,5	1003	4,20	5,32
4,0	A	0,25	0,28	981,0	1031	4,21	5,52
	B	0,25	0,28	1009	1005	4,16	5,56
	A-B Average	0,25	0,28	995,0	1018	4,19	5,54
-	C1	-	-	978,0	977,0	4,10	4,10
	C2	-	-	1009	1006	4,10	3,95
	C3	-	-	955,0	956,0	4,12	4,08

Table C. 9. Equilibrium data of IR-P1

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,001	A	0,11	0,13	107,5	122,6	4,25	4,58
	B	0,11	0,13	107,8	121,7	4,30	4,59
	A-B Average	0,11	0,13	107,7	122,2	4,28	4,59
	C	-	-	104,0	103,0	4,35	4,34
0,005	A	0,53	0,53	549,0	577,0	4,31	4,12
	B	0,53	0,53	550,0	579,0	4,33	4,14
	A-B Average	0,53	0,53	549,5	578,0	4,32	4,13
	C	-	-	552,0	574,0	4,32	4,18
0,01	A	1,07	1,01	1055	1083	4,19	3,97
	B	1,07	1,01	1040	1092	4,10	4,21
	A-B Average	1,07	1,01	1047,5	1087,5	4,15	4,09
	C	-	-	1047	1036	4,21	3,93
0,03	A	2,42	2,66	3380	3510	3,87	3,39
	B	2,40	2,60	3430	3490	3,92	3,49
	A-B Average	2,41	2,63	3405	3500	3,90	3,44
	C	-	-	3430	3474	3,90	3,44
0,05	A	2,52	2,45	5190	5430	4,01	3,40
	B	2,48	2,36	5180	5430	4,04	3,66
	A-B Average	2,50	2,40	5185	5430	4,03	3,53
	C	-	-	5240	5150	4,26	4,09

Table C. 9. Cont'd

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (μs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,1	A	2,46	2,85	9360	9520	3,85	3,31
	B	2,61	2,86	9300	9400	3,78	3,21
	A-B Average	2,54	2,85	9330	9460	3,82	3,26
	C	-	-	9290	9160	3,98	3,82
0,2	A	2,91	2,57	15760	15990	3,67	3,32
	B	2,45	2,52	15830	16200	3,68	3,62
	A-B Average	2,68	2,54	15795	16095	3,68	3,47
	C	-	-	15830	16060	3,90	4,15
0,3	A	2,68	2,50	23000	23500	3,71	3,56
	B	3,02	2,52	23300	23500	3,72	3,63
	A-B Average	2,85	2,51	23150	23500	3,72	3,60
	C	-	-	23100	23200	4,04	4,12
0,5	A	3,43	2,67	34400	34400	3,87	3,55
	B	2,09	2,77	34000	34400	3,97	3,59
	A-B Average	2,76	2,72	34200	34400	3,92	3,57
	C	-	-	33900	34200	4,24	4,31

Table C. 10. Equilibrium data of IR-P2

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (μs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,05	A	2,31	2,82	22500	22500	4,09	3,84
	B	3,03	2,65	22400	22700	4,18	3,96
	A-B Average	2,67	2,73	22450	22600	4,14	3,90
0,1	A	2,85	2,81	22700	22500	4,02	3,94
	B	2,67	3,07	22900	22300	4,12	4,17
	A-B Average	2,76	2,94	22800	22400	4,07	4,06
1,0	A	2,68	2,50	23000	23500	3,71	3,56
	B	3,02	2,52	23300	23500	3,72	3,63
	A-B Average	2,85	2,51	23150	23500	3,72	3,60
5,0	A	2,67	2,38	22500	24400	3,26	3,02
	B	2,71	2,42	22900	23300	3,37	3,03
	A-B Average	2,69	2,40	22700	23850	3,32	3,03
10,0	A	2,33	1,96	24600	25400	3,14	2,93
	B	2,28	1,97	24500	26100	3,23	2,82
	A-B Average	2,30	1,97	24550	25750	3,19	2,88
15,0	A	1,91	1,72	23400	25300	3,13	2,66
	B	1,93	1,73	23400	25300	3,02	2,78
	A-B Average	1,92	1,72	23400	25300	3,08	2,72

Table C. 10. Cont'd

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (μs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
20,0	A	1,53	1,35	23200	24800	2,99	2,65
	B	1,53	1,37	23600	24400	2,98	2,78
	A-B Average	1,53	1,36	23400	24600	2,99	2,72
30,0	A	0,97	1,03	24100	25800	3,05	2,73
	B	0,97	1,04	23800	25900	2,95	2,79
	A-B Average	0,97	1,04	23950	25850	3,00	2,76
40,0	A	0,64	0,81	24700	25900	2,97	2,72
	B	0,64	0,77	24600	25400	2,99	2,76
	A-B Average	0,64	0,79	24650	25650	2,98	2,74
-	C1	-	-	23000	22400	4,30	4,30
	C2	-	-	22300	23000	4,04	4,03
	C3	-	-	23100	23000	4,11	3,78

Table C. 11. Equilibrium data of GAC-P1

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,0004	A	0,006	0,007	78,90	60,90	4,06	4,45
	B	0,006	0,007	76,60	61,30	4,06	4,45
	A-B Average	0,006	0,007	77,80	61,10	4,06	4,45
	C	-	-	67,30	66,20	4,10	4,07
0,001	A	0,015	0,007	115,8	106,0	3,75	4,40
	B	0,015	0,009	114,2	105,8	3,68	4,33
	A-B Average	0,015	0,008	115,0	105,9	3,72	4,37
	C	-	-	101,7	102,9	3,98	4,43
0,0018	A	0,016	0,011	192,1	172,8	3,83	4,79
	B	0,020	0,010	191,4	172,3	3,79	4,69
	A-B Average	0,018	0,011	191,8	172,6	3,81	4,74
	C	-	-	193,0	210,0	3,96	4,17
0,003	A	0,026	0,010	393,0	295,0	3,94	4,91
	B	0,023	0,005	387,0	293,0	3,87	4,76
	A-B Average	0,024	0,007	390,0	294,0	3,91	4,84
	C	-	-	378,0	391,0	3,78	3,62
0,005	A	0,040	0,007	545,0	479,0	4,02	4,51
	B	0,040	0,006	526,0	493,0	3,96	4,66
	A-B Average	0,040	0,007	535,5	486,0	3,99	4,59
	C	-	-	520,0	542,0	4,15	4,09

Table C. 11. Cont'd

Conc. (N)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,007	A	0,047	0,007	701,0	651,0	4,06	4,63
	B	0,039	0,007	727,0	668,0	3,92	4,73
	A-B Average	0,043	0,007	714,0	659,5	3,99	4,68
	C	-	-	712,0	714,0	4,01	4,15
0,01	A	0,048	0,006	985,0	934,0	3,82	4,76
	B	0,055	0,005	1007	911,0	3,84	4,87
	A-B Average	0,051	0,005	996,0	922,5	3,83	4,82
	C	-	-	972,0	981,0	4,11	4,13
0,015	A	0,052	0,006	1440	1308	3,86	4,74
	B	0,062	0,006	1398	1352	3,86	4,98
	A-B Average	0,057	0,006	1419	1330	3,86	4,86
	C	-	-	1418	1414	3,93	4,00
0,02	A	0,059	0,014	1834	1733	3,91	5,05
	B	0,068	0,014	1789	1730	3,91	5,13
	A-B Average	0,063	0,014	1811,5	1731,5	3,91	5,09
	C	-	-	1854	1789	4,01	4,05

Table C. 12. Equilibrium data of GAC-P2

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
0,05	A	0,021	0,029	104,6	105,0	3,88	4,59
	B	0,032	0,054	104,3	105,1	3,88	4,51
	A-B Average	0,027	0,041	104,5	105,1	3,88	4,55
0,25	A	0,019	0,016	106,9	103,5	3,73	4,57
	B	0,024	0,015	112,8	101,4	3,72	4,62
	A-B Average	0,021	0,016	109,9	102,5	3,73	4,60
1,0	A	0,018	0,009	118,8	95,70	3,47	4,05
	B	0,013	0,008	117,4	98,80	3,40	4,16
	A-B Average	0,016	0,009	118,1	97,30	3,44	4,11
3,0	A	0,009	0,003	156,0	115,2	3,24	4,07
	B	0,007	0,003	162,7	112,2	3,32	4,06
	A-B Average	0,008	0,003	159,4	113,7	3,28	4,07
5,0	A	0,007	0,004	179,2	123,0	2,82	3,88
	B	0,007	0,004	174,3	116,1	3,25	3,98
	A-B Average	0,007	0,004	176,8	119,6	3,04	3,93
7,0	A	0,006	0,003	214,0	151,5	3,19	3,99
	B	0,006	0,003	186,5	129,7	3,06	4,00
	A-B Average	0,006	0,003	200,3	140,6	3,13	4,00

Table C. 12. Cont'd

Mass (g)	Beaker	Cd^{2+}(meq/g) (sorbed)	Na^{+}(meq/g)	Conductivity (µs/cm)		pH	
				t_0	t_{eq}	t_0	t_{eq}
10,0	A	0,005	0,003	309,0	151,7	2,84	3,93
	B	0,005	0,003	328,0	143,0	2,69	3,83
	A-B Average	0,005	0,003	318,5	147,4	2,77	3,88
-	C1	-	-	103,9	106,7	3,80	4,20
	C2	-	-	104,0	107,7	3,64	3,96
	C3	-	-	104,2	108,1	3,96	4,13

Table C. 13. Equilibrium data of AsC in deionized water

Mass (g)	Beaker	Ca^{2+}(meq/g)	Mg^{2+}(meq/g)	Na^{+}(meq/g)	K^{+}(meq/g)	Conductivity (µs/cm)		pH	
						t_0	t_{eq}	t_0	t_{eq}
0,1	A	0,01	0,03	0,06	0,01	3,46	4,62	4,32	5,11
	B	0,0003	0,02	0,05	0,01	3,24	4,76	4,31	5,22
	A-B Average	0,005	0,02	0,06	0,01	3,35	4,69	4,32	5,17
0,25	A	0,00	0,007	0,02	0,05	3,25	5,79	4,34	4,66
	B	0,003	0,01	0,04	0,09	3,42	10,14	4,34	5,44
	A-B Average	0,001	0,009	0,03	0,07	3,34	7,97	4,34	5,05
1,0	A	0,00	0,002	0,01	0,02	3,32	9,97	4,37	5,89
	B	0,00	0,002	0,01	0,02	3,39	10,34	4,35	5,52
	A-B Average	0,00	0,002	0,01	0,02	3,36	10,16	4,36	5,71
5,0	A	$0,8*10^{-4}$	$0,5*10^{-3}$	0,06	0,001	3,43	33,90	4,56	6,75
	B	$0,2*10^{-3}$	$0,6*10^{-3}$	0,05	0,001	3,45	32,00	4,56	6,63
	A-B Average	$0,1*10^{-3}$	$0,6*10^{-3}$	0,05	0,001	3,44	32,95	4,56	6,69
10,0	A	$0,1*10^{-3}$	$0,3*10^{-3}$	0,04	0,001	3,73	46,40	4,84	6,91
	B	$0,2*10^{-3}$	$0,5*10^{-3}$	0,03	0,001	3,65	66,60	4,74	7,12
	A-B Average	$0,2*10^{-3}$	$0,4*10^{-3}$	0,04	0,001	3,69	56,50	4,79	7,02
20,0	A	$0,1*10^{-3}$	$0,3*10^{-3}$	0,03	0,001	4,10	76,90	4,92	6,85
	B	$0,1*10^{-3}$	$0,3*10^{-3}$	0,03	0,001	5,12	72,80	5,02	7,05
	A-B Average	$0,1*10^{-3}$	$0,3*10^{-3}$	0,03	0,001	4,61	74,85	4,97	6,95
-	C	-	-	-	-	3,27	3,34	4,34	4,66

Table C. 14. Equilibrium data of CnC in deionized water

Mass (g)	**Beaker**	**Na^+(meq/g)**	**Conductivity (µs/cm)**		**pH**	
			t_0	**t_{eq}**	**t_0**	**t_{eq}**
0,05	A	0,14	3,64	4,94	4,37	5,08
	B	0,14	3,61	5,11	4,47	4,91
	A-B Average	0,14	3,63	5,03	4,42	5,00
0,25	A	0,04	3,37	6,58	4,65	4,93
	B	0,04	3,45	6,39	4,68	5,03
	A-B Average	0,04	3,41	6,49	4,67	4,98
1,0	A	0,02	3,40	8,99	5,03	5,28
	B	0,01	3,60	8,93	4,81	5,74
	A-B Average	0,02	3,50	8,96	4,92	5,51
2,0	A	0,008	3,61	10,40	4,87	5,87
	B	0,007	3,48	10,17	4,77	6,20
	A-B Average	0,007	3,55	10,29	4,82	6,04
4,0	A	0,005	3,67	14,36	4,30	6,93
	B	0,005	3,76	13,44	4,51	6,95
	A-B Average	0,005	3,72	13,90	4,41	6,94
-	C	-	3,52	3,54	4,39	4,80

Table C. 15. Equilibrium data of IR in deionized water

Mass (g)	**Beaker**	**Na^+(meq/g)**	**Conductivity (µs/cm)**		**pH**	
			t_0	**t_{eq}**	**t_0**	**t_{eq}**
0,05	A	0,13	2,57	3,86	4,00	4,19
	B	0,12	2,41	3,54	3,81	4,06
	A-B Average	0,12	2,49	3,70	3,91	4,13
1,0	A	0,05	17,52	37,30	3,87	4,09
	B	0,05	15,43	35,20	3,87	4,18
	A-B Average	0,05	16,48	36,25	3,87	4,14
5,0	A	0,04	86,20	151,5	3,98	4,14
	B	0,04	93,80	157,2	3,92	4,20
	A-B Average	0,04	90,00	154,4	3,95	4,17
15,0	A	0,04	270,0	540,0	4,04	4,23
	B	0,04	315,0	483,0	4,05	4,14
	A-B Average	0,04	292,5	511,5	4,05	4,19
20,0	A	0,04	1273	1240	4,18	4,19
	B	0,04	1277	1423	3,93	4,14
	A-B Average	0,04	1275	1332	4,06	4,17
-	C	-	1,77	2,03	3,77	3,93

Table C. 16. Equilibrium data of GAC in deionized water

Mass (g)	Beaker	Na$^+$(meq/g)	Conductivity (µs/cm)		pH	
			t_0	t_{eq}	t_0	t_{eq}
0,05	A	0,06	8,16	9,62	4,03	3,71
	B	0,04	8,15	8,20	3,83	3,70
	A-B Average	0,05	8,16	8,91	3,93	3,71
0,25	A	0,01	11,22	12,40	3,64	3,49
	B	0,01	13,20	13,46	3,51	3,43
	A-B Average	0,01	12,21	12,93	3,58	3,46
1,0	A	0,004	32,70	30,10	3,21	3,43
	B	0,005	33,90	28,10	3,14	3,55
	A-B Average	0,004	33,30	29,10	3,18	3,49
5,0	A	0,002	127,9	69,80	2,80	3,60
	B	0,003	116,0	89,50	2,79	3,63
	A-B Average	0,003	122,0	79,65	2,80	3,62
10,0	A	0,003	288,0	94,10	2,67	3,73
	B	0,003	247,0	94,40	2,56	3,75
	A-B Average	0,003	267,5	94,25	2,62	3,74
-	C	-	6,97	7,00	3,98	4,02

APPENDIX D

ALUMINUM AND SILICON

Table D. 1. Aluminum and Silicon data for AsC

Concentration (N)	Mass (g)	Aluminum (meq/g) ± Std. Dev.	Silicon (meq/g) ± Std. Dev.
0,01	20,0	-	$0,021 \pm 0,1*10^{-3}$
0,01	5,0	-	$0,058 \pm 0,6*10^{-3}$
0,001	1,0	$0,003 \pm 0,1*10^{-3}$	$0,175 \pm 0,3*10^{-3}$
0,03	1,0	-	$0,169 \pm 0,6*10^{-3}$
0,1	1,0	-	$0,173 \pm 0,7*10^{-3}$
-	5,0	$0,001 \pm 0,2*10^{-4}$	$0,049 \pm 0,6*10^{-4}$

Table D. 2. Aluminum and Silicon data for CnC

Concentration (N)	Mass (g)	Aluminum (meq/g) ± Std. Dev.	Silicon (meq/g) ± Std. Dev.
0,01	4,0	$0,001 \pm 0,3*10^{-4}$	$0,015 \pm 0,2*10^{-3}$
0,01	1,0	-	$0,029 \pm 0,4*10^{-3}$
0,01	0,1	-	$0,078 \pm 0,1*10^{-2}$
0,001	1,0	$0,001 \pm 0,2*10^{-4}$	$0,041 \pm 0,4*10^{-3}$
0,03	1,0	$0,002 \pm 0,2*10^{-3}$	$0,035 \pm 0,4*10^{-3}$
0,1	1,0	-	$0,006 \pm 0,1*10^{-3}$
-	4,0	$0,001 \pm 0,3*10^{-4}$	$0,001 \pm 0,4*10^{-4}$

Table D. 3. Aluminum and Silicon data for GAC

Concentration (N)	**Mass (g)**	**Aluminum (meq/g) ± Std. Dev.**	**Silicon (meq/g) ± Std. Dev.**
0,01	5,0	-	$0{,}044 \pm 0{,}4*10^{-3}$
-	5,0	-	$0{,}035 \pm 0{,}4*10^{-3}$