

**CADMIUM REMOVAL USING CLINOPTILOLITE: INFLUENCE OF
CONDITIONING AND REGENERATION**

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ABSTRACT

CADMIUM REMOVAL USING CLINOPTILOLITE: INFLUENCE OF CONDITIONING AND REGENERATION

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Clinoptilolite samples obtained from two deposits in Turkey were tested for their potential in removing cadmium from aqueous solutions. Preliminary experiments in batch mode revealed inferior cadmium uptake at low pH. Particle size was found to have no effect on cadmium removal efficiency suggesting the use of exchangeable cations found in the internal/available sites. Increasing temperature yielded positive, whereas prewashing had no effect on cadmium removal using both clinoptilolite samples.

The Langmuir model fitted the equilibrium data for both samples better than the Freundlich model. The capacity reached after conditioning represents about 4 and 3 fold increase for Gördes and Bigadiç samples, respectively. The relatively poor performance of Bigadiç clinoptilolite was due to low

clinoptilolite/high impurity contents. Further studies were carried out only with Gördes clinoptilolite.

The performance of the Gördes samples conditioned with various chemicals were NaCl>KCl>As-received>CaCl₂>HCl. 20BV of NaCl solution was found to be sufficient with no pH adjustment or water quality requirement during column conditioning.

In column experiments, among the tested flowrates 5, 10 and 15 BV/hr, highest flowrate indicated inferior utilization of the removal capacity. No significant difference by decreasing particle size indicated pore diffusion resistance not to be a limiting factor. In five conditioning and regeneration cycles, clinoptilolite exhibited 36% increase in operating capacity. Cadmium removed by clinoptilolite in progressing cycles was concentrated by about 7 times.

Overall, this study shows that Manisa-Gördes clinoptilolite is advantageous for the removal of cadmium ions from aqueous solutions and hold great potential to be used in practical applications.

Keywords: Clinoptilolite; cadmium; conditioning; regeneration; ion exchange

ÖZ

KLİNOPTİLOLİT KULLANILARAK KADMIYUM GİDERİMİ: ŞARTLANDIRMA VE REJENERASYONUN ETKİSİ

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Bu çalışmada, Türkiye'nin iki rezervinden alınan klinoptilolit örnekleri sulu çözeltilerden kadmiyum giderme potansiyelleri açısından test edilmiştir. Kesikli test reaktörlerinde yapılan öncü deneyler düşük pH'ta kadmiyum gideriminin etkilendiğini göstermiştir. Parçacık boyutunun kadmiyum giderim verimine etkisi olmaması gideriminin başlıca iç/ulaşılabilir yerlerdeki değişebilir katyonlarla olduğuna işaret etmektedir. Artan sıcaklıkla kadmiyum giderimi pozitif etkilenirken ön yıkamanın giderime bir etkisi olmadığı her iki örnek için de bulunmuştur.

Langmuir modeli her iki klinoptilolit örneğine ait denge deneyleri sonuçlarına Freundlich modelinden daha iyi uymuştur. Şartlandırma işlemi sonucunda kapasitenin, Gördes ve Balıkesir klinoptiloliti için sırasıyla yaklaşık 4 ve 3 kat arttığı belirlenmiştir. Bigadiç klinoptilolitinin doğal ve şartlandırılmış formları

için elde edilen düşük metal giderim verimi, içerdiği safsızlık oranının yüksekliği/düşük klinoptilolit içeriğiyle açıklanmıştır. Çalışmanın devamı sadece Gördes klinoptiloliti kullanılarak yapılmıştır.

Çeşitli kimyasallarla şartlandırılan Gördes örneklerinin performansları sırasıyla NaCl>KCl>Doğal>CaCl₂>HCl olarak bulunmuştur. Kolonda şartlandırma için 20 Yatak Hacmi NaCl çözeltisi yeterli görülürken başlangıç pH ayarlamasına ve farklı kalitede su kullanımına gerek olmadığı saptanmıştır.

Kolon çalışmalarında, test edilen 5, 10 ve 15 YH/saat akış debileri arasında en yüksek akış debisinde kolonun varolan kadmiyum giderim kapasitesi kullanımını azalttığı bulunmuştur. Parçacık boyutunun düşürülmesi metal giderim kapasitesini önemli ölçüde etkilememiştir. Bu durum test edilen parçacık boyutları arasında kanal difüzyon direncinin metal gideriminde sınırlayıcı faktör olmadığını göstermektedir. Yapılan beş şartlandırma ve geri kazanma döngüsü sonucunda işletme kapasitesinde %36 artış kaydedilmiştir. İlerleyen döngülerde giderilen kadmiyum yaklaşık 7 kat konsantre edilmiştir.

Çalışma neticesinde, Manisa-Gördes klinoptilolitinin sulu çözeltilerden kadmiyum gideriminde avantajlı olduğu ve pratik uygulamalar için yüksek potansiyele sahip olduğu belirlenmiştir.

Anahtar kelimeler: Klinoptilolit; kadmiyum; şartlandırma; geri kazanma; iyon değişimi

To my grandfather and grandmother,

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CHAPTER 1

INTRODUCTION

Natural concentrations of heavy metals in the aquatic environment have been disturbed after considerable industrialization all over the world. It is known that metals may be concentrated to dangerous levels by microorganisms, fish, and plants in the food chain. Thus, the removal of heavy metal containing wastewaters is required prior to discharge into receiving environment when their well known toxicity is taken into consideration.

Several processes can be used for removing heavy metals such as chemical precipitation, oxidation, membrane processes (e.g. ultrafiltration, reverse osmosis), ion exchange or adsorption (Peric et al., 2004). But many of them have disadvantages including production of significant amounts of sludge, disposal of the concentrates and mainly cost. In particular, applicability of treatment methods becomes costly at lower metal concentrations. Therefore, requirements during the determination of a treatment strategy involve the use of simple and effective technologies utilizing local resources. Low-cost technologies that enable recovery, hence that result in no further waste production, are becoming popular for metal-contaminated wastewaters.

Ion exchange is one of the common methods used for the removal of toxic substances from wastewater. Natural zeolites, meanwhile, are widely used in ion exchange studies as sorbents for pollution control applications, owing to their high reserves, advantageous ion exchange capacities, and low cost combined with a recovery potential for both metals and the material (Curkovic et al., 1997; Ouki & Kavannagh, 1999; Langella et al., 2000). While as-received forms of natural zeolites are being used in studies successfully,

conditioning favors their ability to remove metal cations by increasing the content of a single exchangeable cation in the structure (Curkovic et al., 1997; Ouki et al., 1993; Panayotova & Velikov, 2003; Semmens & Martin, 1988; Englert & Rubio, 2005).

Clinoptilolite is regarded as the most abundant natural zeolite found in nature. It is also among the most widely studied natural zeolites and, was shown to have high selectivity for most heavy metals (Malliou et al., 1994). Clinoptilolite is a hydrated aluminosilicate belonging to the family of the heulandite group, where the spatial net structure is made from $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedrons joined by common oxygen atoms. Structurally, isomorphous replacement of some aluminum atoms with silicon atoms results in a negatively charged structure. This negative charge is balanced by alkali (sodium, potassium, lithium, and cesium) and/or alkaline earth (calcium, strontium, barium, and magnesium) cations, thus, enabling ion exchange (Tsitsishvili et al., 1992).

In this study, clinoptilolite samples from two important reserves in Turkey, namely Manisa-Gördes and Balıkesir-Bigadiç were tested for their potential in removing cadmium ions from aqueous solutions. More specifically, the objectives of the study were:

- To investigate main parameters affecting cadmium removal and the maximum cadmium uptake capacities of both as-received and conditioned forms of clinoptilolite samples obtained from Gördes and Bigadiç reserves in batch mode,
- To determine the conditioning/regeneration parameters in order to obtain favorable cadmium removal and regeneration conditions with the clinoptilolite sample that performed the best,

- To investigate the performance of clinoptilolite packed beds for cadmium removal/clinoptilolite recovery in successive metal removal/sorbent regeneration cycles,

- To examine exchangeable ions in the aqueous phase in order to develop an understanding about prevailing cadmium removal mechanisms

CHAPTER 2

THEORETICAL BACKGROUND

2.1. CADMIUM

Industrialization has led to a substantial increase, especially in natural concentrations of the heavy metals in the environment all over the world. Since heavy metals cannot be biodegradable and tend to accumulate in living organisms, their removal from wastewaters is required prior to discharge.

The statistics has shown that the primary production of cadmium has increased by a factor of 14 in the last decade (Ahmed et al., 1998). Being a toxic substance, cadmium is one of the five (Cr^{3+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+}) most toxic metals, and has a biological half-life of 10-30 years (Lee et al., 2001). In this regard, its removal from wastewaters is of important concern.

Many industries discharge cadmium in their wastewaters (Table 2.1). Knowing the extent of pollution, the necessity of treatment of metal containing wastewaters before discharging into the receiving environment have particular importance while concerning the toxic effects of these metals (Fergusson, 1990). There are several methods to remove heavy metals from wastewater. However, approaches must be intended to reduce the accessibility of polluting heavy metals (Wingenfelder et al., 2005b), cost effective, simple, and locally addressed. Ion exchange is one of the methods used for the removal of toxic substances from wastewater. This method is practicable in wastewaters having low concentration of competing

Table 2.1. Cadmium concentrations reported for some industrial wastewaters (Fergusson, 1990).

Process	Cadmium (mg/L)
Plating rinsewaters	
Automobile heating control manufacturing	14-22
Automatic barrel Cd and Zn plant	10-15
Large installations	15-50
Recirculating rinse	1000-3330
Rinse dragout	0.1-6
Metal finishing plant	2-8
Bright dip and passivation plating baths	2000-5000
Acid mine drainage	400-1000
Nonferrous metals manufacture	
Zinc smelting and refining	0.02-33
Copper smelting	0.09-1.08
Iron foundry wastewater	0.16-0.95
Porcelain enameling	0-9.6

ions (Ouki and Kavannagh, 1999), and has an advantage of recovery of both exchanger material and heavy metals treated. Several sorbents can be used as an exchange material. However, the cost is the primary property of ion exchange material to be used. Although the comparison is difficult among the sorbents, several materials used as sorbents are given in Table 2.2 to give an idea about the reported capacities for cadmium.

Assessment of Table 2.2 reveals a competition of low cost sorbents, especially zeolites with oxides and activated carbon in cadmium removal capacities. Therefore, use of natural zeolites as an exchanger may offer an economical way of removing heavy metals.

Table 2.2. Reported adsorption capacities for cadmium with various sorbents

Material	Cadmium (meq/g)	Source
Chitosan	9.93	Masri et al., 1974
Clay	0.29	Pradas et al., 1994
Dead biomass	0.50	Matis and Zouboulis, 1994
Modified wool	1.55	Masri and Friedman, 1974
Moss	0.83	Low and Lee, 1991
Seaweed	3.83	Holan et al., 1993
Aluminum oxide	0.55	Srivastava et al., 1988
Ferric oxide	1.28	Srivastava et al., 1988
Waste slurry	0.28	Lee and Davis, 2001
As-received fibrous activated carbon	2.60	Mendez and Streat, 2002
Natural zeolite	1.50	Leppert, 1990

2.2. NATURAL ZEOLITES

Zeolites can be categorized as either synthetic or naturally occurring aluminosilicates minerals. Natural ones are preferred over the synthetic ones, owing to economic concerns. However, they have attracted great attention after the discovery of their structural properties and large minable deposits over the world in addition to their low costs. This study concerns the use of a natural zeolite, clinoptilolite, for cadmium removal. Therefore, hereafter, the term “zeolite” will be used as a substitute for “natural zeolite” throughout the chapters.

Zeolites are hydrated aluminosilicates belonging to the family of the tectosilicates, where spatial net structure is made from $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedrons joined by common oxygen atoms. Structurally, isomorphous replacement of some Al^{3+} atoms with Si^{4+} atoms results in a negatively charged structure (Fig. 2.1). This negative charge is balanced by alkali (sodium, potassium, lithium, and cesium) and/or alkaline earth (calcium,

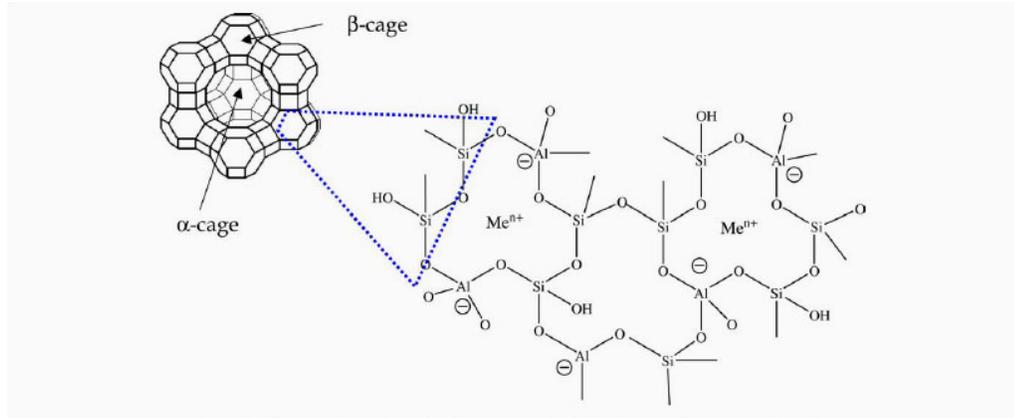
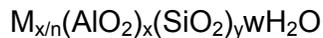


Figure 2.1. The framework structure of zeolites (Valdes et al., 2006)

strontium, barium, and magnesium) cations, thus, providing zeolites with the property of ion exchange (Tsitsishvili et al., 1992).

The generalized chemical formula of the zeolites is



where “M” is (Na^+ , K^+ , Li^+) and/or (Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+}), “n” is the cation charge, “w” is the number of water molecules, and “y/x” is the ratio lying within the limits of 1 to 6.

The crystalline framework may be formed by a three-dimensional arrangement of TO_4 ($T = Si, Al, B, Ga, Ge, Fe, P$ and Co) tetrahedra bonded by oxygen atoms. The $T-O-Si$ links result in rings of great range that is responsible for the formation of cages, cavities, and channels in the zeolite structure (Valdes et al., 2006). This internal space is one of the most important properties of zeolites for the molecular sieve actions.

The cavities and channels in zeolite structure are occupied by water molecules and cations under normal conditions. The alkali and/or alkaline

earth cations are coordinated with water molecules, and located on specific sites in framework channels of the zeolite structure (Peric et al., 2004). As an example, magnesium ions are coordinated only by water molecules, while potassium and barium ions are surrounded preferentially by oxygen atoms of the lattice. On the other hand, the coordination of calcium and sodium ions depends on the geometry of the cavity (Tsitsishvili et al., 1992).

2.2.1. Clinoptilolite

The zeolite group contains more than 40 naturally occurring species (Tsitsishvili et al., 1992). But only those containing chabazite, clinoptilolite, erionite, ferrierite, phillipsite, mordenite and analcime are available in sufficient quantity and purity to be considered as utilizable natural resources (Zamzow et al., 1990; Cincotti et al., 2001). Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature. It is very stable towards dehydration, and thermally stable up to 700 °C in air (Çulfaz & Yağız, 2004). This amount is considerably greater than the stability of other natural zeolites with a similar structure, such as heulandite. The chemical composition of clinoptilolite is characterized by significant variations in the Si/Al ratio as well as in the composition of the exchangeable cations. The Si/Al (y/x ratio) ratio changes between 4 and 5.5, and low-silica members are enriched with calcium, whereas high-silica clinoptilolites are enriched with potassium, sodium, and magnesium (Tsitsishvili et al., 1992).

The framework of clinoptilolite points out that the hydrated mineral has four cation sites, two in the main 10-ring channels and two in the 8-ring ones (Trgo & Peric, 2003). In general, clinoptilolite is stable in acidic environment (Malliou et al., 1992) while unstable in alkali media. Regarding the porosity, clinoptilolite can be characterized by two types: The microporosity is caused by the specific crystal building of zeolite mineral grains. But the secondary

one, meso- and macropores, is related to the size of zeolite, and other mineral grains in the rock as well as by structural features of the rock proper (Kowalczyk et al., 2006).

2.2.2. Applications of Zeolites

Structural properties and large natural deposits make the potential use of clinoptilolite attractive due to being a low cost material or more of the following properties (Mumpton, 1999):

- Cation exchange
- Adsorption and related molecular sieving
- Catalytic
- Dehydration and rehydration
- Biological reactivity

Zeolites have been utilized for many applications in numerous fields such as construction, agriculture, medical applications, consumer products, etc., and recently in the field of environmental applications owing to clearly stated unique characteristics. The potential use of zeolite in pollution control areas can be given as:

- Ammonia removal (Baykal, 1998; Cincotti et al., 2001; Langella et al., 2000; Sarioğlu, 2005; Rozic et al., 2005; Watanabe et al., 2003)
- Heavy metal removal (Panayotova, 2001; Mier et al., 2001; Semmens & Seyfarth, 1978; Curkovic et al., 1997; Inglezakis et al., 2003; Blanchard et al., 1984)
- Organic compound removal (Garcia et al., 1993; Li et al., 2000)
- Air pollution control (Ackley et al., 2003; Khulbe et al., 1994)
- Radioactivity removal (Abusafa & Yücel, 2002; Dyer & Zubair, 1998; Um & Papelis, 2004; Faghihian et al., 1999)

2.2.3. Zeolites in Turkey

The majority of the investigated zeolite occurrences are located in Japan, USA, Russia, Eastern and Southern Europe. On the other hand, Turkey has also large occurrences of sedimentary zeolite, especially in central and western Anatolia regions. The zeolitic tuffs are associated with clay minerals, borates, carbonates, and soda minerals akin to many other parts of the world. They are also found in close association with lignite-bearing lacustrine rocks (Ören & Kaya, 2006).

Western Anatolia is rich in clinoptilolite deposits. Manisa-Gördes and Balıkesir-Bigadiç basins are two of the most important clinoptilolite reserves in Turkey, with estimated reserves of 20 million tons and 500 million tons, respectively (DPT, 1996). The total estimated amount of zeolite occurrences (Table 2.3) is about 50 billion tons, even though there is no comprehensive investigation on zeolite deposits for the other regions of Turkey (DPT, 1996).

Table 2.3. Zeolite deposits and types detected so far in Turkey (DPT, 1996)

Categorization	Deposits
Analcime	Bahçelik, Gölpazarı, Göynük, Ankara-Polatlı, Mülk, Oğlakçı, Ayaş, Nallıhan, Çayırhan, Beypazarı, Mihaliççik, Kalecik, Çandır, Sabanözü, Hasayaz
Clinoptilolite	Balıkesir-Bigadiç, Manisa-Gördes, Emet-Yoncağağaç, Kütahya-Saphane, Gediz-Hisarcık, İzmir-Urla, Amasya-Doğantepe
Chabazite and Erionite	Kayseri-Tuzköy

Researchers in Turkey investigated the chemical compositions of some of the clinoptilolite rich rocks, and reported large discrepancies among them.

The major difference in chemical composition has been attributed to the different original cation content of mined clinoptilolite bearing samples. The purity and mineralogical characteristics were seen to be different for clinoptilolites with different origins and even the same origin (Çulfaz et al., 1995; Cerri et al., 2002; Abusafa & Yücel, 2002). In Table 2.4, some examples for the chemical composition of clinoptilolite samples of different regions are compared.

Table 2.4. The examples of chemical composition of different clinoptilolite samples from Turkey given in the literature.

Oxides	Clinoptilolite origin						
	Bigadiç ^a			Gördes ^b		Doğantepe ^c	
	1	2	3	4	5	6	7
SiO₂	65.85	63.98	65.17	68.83	70.00	74.7	70.27
Al₂O₃	11.22	12.84	12.40	11.62	14.00	13.7	12.90
Fe₂O₃	1.09	0.62	1.00	0.53	0.75	1.45	1.38
MgO	1.07	1.17	0.78	0.77	1.15	0.69	1.71
CaO	2.94	3.46	2.58	2.37	2.50	2.76	2.05
Na₂O	0.49	0.45	0.75	0.11	0.20	1.07	3.21
K₂O	3.05	2.90	3.41	3.17	2.30	5.25	1.49
MnO	-	-	0.02	-	-	-	0.02
TiO₂	-	-	0.19	0.10	0.05	0.15	0.19
P₂O₅	-	-	-	-	0.02	-	0.04
H₂O	-	15.37	12.34	12.46	9.02	-	6.57
Si/Al	4.98	4.23	4.46	5.03	4.24	4.63	4.62
TCEC (meq/g)	2.39	2.58	2.27	1.94	2.02	2.79	2.29

(a)1. Ören & Kaya, 2006; 2. Abusafa & Yücel, 2002; 3. Çulfaz & Yağız, 2004; (b)4. Esenli & Sirkecioğlu, 2005; 5. Turan et al., 2005; 6. Kurtoğlu & Atun, 2006; (c)7. Sarioğlu, 2004.

2.3. HEAVY METAL REMOVAL BY ZEOLITES

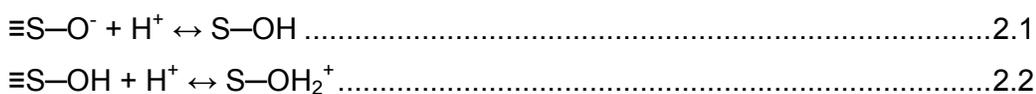
2.3.1. Factors Affecting Heavy Metal Removal

In general, the dynamics of the metal uptake is affected by several factors grouped mainly as solution and solid specific factors (Morali, 2006). Solution specific factors include pH, temperature, presence of other ions, pretreatment solutions, and characteristics of the heavy metals studied. On the other hand, surface dust, particle size, impurities found in the zeolite sample, and pretreatment type applied to zeolite can be grouped under solid specific factors. Each factor is explained in the following sub-sections.

Effect of pH

The pH of the solution has a remarkable effect on the removal efficiency of the compounds. This is mostly due to the fact that pH influences both the surface charges of an adsorbent (Martinez et al., 2004) and the character of the metal specie. The speciation of any metal in solution, i.e. whether as complex or a free ion, has significant impact on sorption and selectivity behavior of zeolites.

In acidic solutions, H_3O^+ ions may compete with heavy metal cations for the exchange sites in the zeolite surface (Englert and Rubio, 2005; Inglezakis et al., 2001). Thus, the metal uptake decreases with decreasing pH due to less availability of accessible sites as the aluminol and silanol groups are more protonated. The protonation of neutral and negative surface hydroxyl groups can be given by the following reactions (Doula and Ioannou, 2003):



In addition to the role played by the concentration of protons in changing the state of active metal ion binding sites, there are also two other ways in which the pH influences sorption:

Firstly, zeolite surfaces become negatively charged as the solution pH increases (Benhammou et al., 2005), which can be given by equation 2.3. The adsorption of metal cations and their hydroxides is favored by increasing numbers of negative sites, due to the formation of surface metal complexes (Doula et al., 2002). Secondly, surface functional groups may dissociate at higher pH values leaving anionic surface sites that may make a significant contribution to the metal removal (Ouki and Kavannagh, 1999).



According to Abollino et al. (2003), Cd^{2+} , Pb^{2+} , and Cu^{2+} capacities are reduced under low pH owing to the loss of electrostatic attraction between the surface charge and the dissolved cations and hydroxocomplexes. This is due to the fact that Cd^{2+} and Pb^{2+} have relatively large ionic radius, hence lower charge densities and, so, protonation has a more pronounced effect on the removal capacity of these metals. On the contrary to given information, Martinez et al. (2004) stated no significant variations on cadmium uptake at pH values of 3, 5, and 7 with Na-modified zeolite. Such findings show that there may be numerous possible mechanisms acting during zeolite-metal interactions.

In addition to all above features, clinoptilolite also have an ability to neutralize the aqueous medium acting as proton acceptor or as a proton donor, which reveals its amphoteric character (Rivera et al., 2000). This feature further complicates the chemistry of heavy metal-clinoptilolite systems.

Effect of temperature

Metal uptake by zeolites is generally increased by increasing temperature. Malliou et al. (1992) revealed that cadmium removal increases with temperature in 25-50°C range. In general, the endothermic nature of adsorption processes in zeolites enhances the sorption processes by increasing temperature due to activation of the adsorption sites (Payne & Abdel-Fattah, 2004). The higher diffusion coefficients resulting in a fast movement of cations increase the metal uptake at higher temperatures. This may be explained by the weakness of electrostatic interactions and smaller hydrated radii of the ions with increasing temperature (Inglezakis et al., 2004).

Effect of inorganics and organics

In general, anions and neutral solutes are not readily taken up by the zeolite (Martinez et al., 2004). However, the removal of heavy metals in the presence of inorganic and organic ligands can be affected by direct or indirect mechanisms. The ligands present in the solution may influence the metal ion behavior and the surface properties of the sorbents (Doula and Ioannou, 2003). Formation of surface complexes with ligands may decrease the ion exchange reactions compared to a ligand-free system. The ligands may favor the metal removal by changing the surface electrical properties or by adsorbing strongly to the zeolite surface, compared to the case where either one is present alone (Doula and Ioannou, 2003).

Mier et al., (2001) found that the presence of phenol can hinder the cadmium uptake capacity by the formation of organometallic complexes that cannot penetrate the clinoptilolite channels. Wingenfelder et al., (2005b) examined the adsorption of Cd^{2+} and Pb^{2+} by amine modified clinoptilolite, and showed the decrease of metal removal with increasing amounts of amines sorbed.

This reduction was attributed to blockage of clinoptilolite channels by amine molecules. On the other hand, Ahmed et al. (1998) stated the degree of cadmium and lead exchange to be independent of the chloride and nitrate concentrations in the aqueous phase. The presence of calcium and magnesium ions was also shown to influence the cadmium (Panayotova and Velikov, 2003) and lead uptake (Petruzzelli et al., 1999) negatively.

Effect of Conditioning

The theoretical cation exchange capacity (TCEC) of zeolite is mainly a function of the amount of extra-framework cations to balance the negative charge due to aluminum substitution. So, one can easily state that TCEC cannot be altered under ordinary conditions. In other words, this capacity is independent of any pretreatment or modification applied. The effective ion exchange capacity, on the other hand, refers to the amount of cations, which can be exchanged, and contained in a specific quantity of the material under specific experimental conditions (Hellferich, 1995). The differentiation between the two capacity definitions is due to the fact that some of the zeolite cations cannot be removed easily due to low mobility and strong bonding forces within the structure of the material (Gradev et al., 1988).

Zeolites normally provide a number of different specific sites for calcium, sodium, magnesium, and potassium in the framework. These cations have also different exchange properties for every environment. Therefore, main aim can be to increase this theoretical value to optimum practical or effective levels. In this sense, pretreatment which is interchangeably used instead of conditioning in the literature, aims to remove certain cations from the structure of the zeolite, and locates more easily removable ones. To sum up, the reason of why pretreatment is recommended can be explained as the aim of reaching a near homoionic state of the zeolites, and hence to improve their effective exchange capacities in ion exchange applications. The improvement

in effective exchange capacity after pretreatment is verified by several researchers (Curkovic et al., 1997; Ouki et al., 1993; Panayotova & Velikov, 2003; Semmens & Martin, 1988; Englert & Rubio, 2005).

The ion exchange capacity of clinoptilolite depends considerably on the way in which it is pretreated. Below is a list of the different chemicals used for conditioning;

- NaCl seems to be the most widely used and most effective conditioning solution cited in the literature (Mier et al., 2001; Çulfaz & Yağız, 2004; Milan et al., 1997; Trgo & Peric, 2003; Panayotova, 2001; Bektaş & Kara, 2004; Semmens & Seyfarth, 1988),
- NaOH (Panayotova, 2001; Ouki et al., 1993),
- HCl (Sprynskyy et al., 2005; Panayotova, 2001; Kurama et al., 2002; Vasylechko et al., 2003),
- CaCl₂ (Milan et al., 1997; Jama & Yücel, 1990; Abusafa & Yücel, 2002),
- KCl (Abusafa & Yücel, 2002; Milan et al., 1997),
- HNO₃, H₂SO₄, NH₄Cl, MgCl₂, and CH₃COONa can also be used as conditioning agents (Vasylechko et al., 2003; Abusafa & Yücel, 2002; Milan et al., 1997; Panayotova, 2001).

The reason for the most frequent use of NaCl for conditioning purposes is related to the characteristics of sodium (Na⁺) ion in the zeolite. Na⁺ ions are the weakest bound ions; hence, they are most easily exchanged with various cations from solutions (Zamzow et al., 1990; Rozic et al., 2005). Jama and Yücel (1990) have stated that sodium bonds to two framework oxygen atoms and five water molecules. Calcium coordinated with three framework oxygen atoms and five water molecules; hence, it has more tightly bonds to the framework. Potassium has very low mobility because of the location occupied, where it is coordinated with six framework oxygen atoms and three

molecules of water. In the case of magnesium, this cation is located in a site coordinated by six water molecules, which theoretically gives this cation a great facility for exchange.

As stated before, NaCl solution treatment seems to be the best method of clinoptilolite conditioning. Batch mode and ion exchange packed beds can be used to treat the zeolite. Nava et al., (2005) found out an increase of sodium of about a hundred percent compared to as-received zeolitic rock in a 0.1 M NaCl reflux solution, but, this sodium increase was not observed when the samples were placed in a 5 M NaCl solution at room temperature. Inglezakis et al., (2001) revealed that raising the NaCl concentration above 0.4 M has practically no effect on the effective capacity in packed bed applications. Therefore, temperature and concentration play an important role in cation exchange processes of zeolites regardless of the conditioning mode.

Down-flow operation may decrease the conditioning efficiency compared to up-flow mode due to channeling in packed beds especially at high flowrates. But, Inglezakis and Grigoropoulou (2004) showed that both high and low flowrates should be avoided in packed bed applications. A wide range of volume of conditioning solution is used: 20-30 BV (Semmens & Martin, 1988), but, no significant difference is detected by increasing the volume. In addition to this, the effect of water quality and initial pH adjustment was investigated and found not to be important factors in conditioning (Inglezakis et al., 2001).

Characteristics of the heavy metal

The hydration free energy is one of the important factors for preference of the exchanger for one cation over another. As is evident from Table 2.5, ionic radius is inversely related with hydrated radius except for Na^+ and Pb^{2+} . This shows the great preference of lead by clinoptilolite (Petrus & Warchol, 2003;

Semmens & Seyfarth, 1978; Inglezakis et al., 2004). Dimensions of channels in clinoptilolite framework should be large enough to allow the passage of hydrated ions (Castaldi et al., 2005). Therefore, the examination of Table 2.5 may provide a rough estimate for the selectivity series of clinoptilolite towards heavy metals.

Table 2.5. Properties of certain cations relevant to the study, from Woods and Gunter (2001)^a and Semmens and Seyfarth (1978)^b

Cation	Ionic radius (Å)	Hydrated ionic radius (Å)	Hydration free energy (kcal/mol)
^a Mg ²⁺	0.7	4.3	-450
^b Cu ²⁺	0.82	4.19	-498.7
^b Zn ²⁺	0.83	4.30	-484.6
^b Na ⁺	0.98	3.58	-98.2
^a Ca ²⁺	1.0	4.1	-373
^b Cd ²⁺	1.03	4.26	-430.5
^a K ⁺	1.3	3.3	-79
^b Pb ²⁺	1.32	4.01	-357.8

Effect of prewashing zeolite

Surface dusts that occur during the grinding processes may hinder the metal uptake capacity of zeolites by clogging the pores and causing structural damages in small particles (Zorpas et al., 2002). The reduced metal removal efficiency may be attributed to the fact that metal uptake not only takes place on the external surface, but also in the internal sites of the zeolites. Therefore, rinsing the sorbent material prior to metal removal studies is recommended by some researchers to enhance the removal efficiency. For example, Englert and Rubio (2005) found that ammonia uptake was increased by 14% after washing Chilean natural zeolite with deionised water. In addition, Athanasiadis and Helmreich (2005) found out that dust particles produced during the grinding process makes up 8% of clinoptilolite, and they

recommended removal of fine fraction prior to any application. Moreover, Abadzic and Ryan (2001) showed that prewashing of the clinoptilolite grains resulted in a decrease in distribution coefficients by a factor of 1.8 for both the fine and coarse particles.

Effect of particle size

In spite of being a common fact that decreasing the particle size causes higher metal uptake capacity, this increase can mainly be related to the contact time and the structural properties of the material used. The effect of particle size can be explained depending on the experimental type used either batch or continuous mode. This is due to the short contact times needed for continuous mode compared to batch applications.

When the literature is sought, it is noteworthy to mention here that there is an inconsistency regarding the particle size effect. The finding of Wingenfelder et al., (2005a) is in agreement with Malliou et al., (1992) which suggest that the Cd^{2+} and Pb^{2+} uptake is greatly affected by grain size only at shorter contact times (e.g. 6 hrs for cadmium) in batch mode experiments. On the contrary Panayotova (2001), Um and Papelis (2004), and Ouki et al. (1993) showed by batch experiments that particle size has no significant effect on the zeolites exchange capability. This is probably due to the high specific surface area of zeolites, which becomes a weak function of particle size, suggesting that the majority of the surface area is internal and accessible. In other words, ion exchange mechanism takes place within the zeolite cavities rather than at their surfaces.

The dynamic conditions of continuous mode applications restrain the use of fractions finer than 0.35 mm according to Sprynskyy et al. (2005) or 0.80 mm according to Inglezakis and Grigoropoulou (2004) due to operational problems. Fine particles have an advantage to overcome the diffusional

resistance which is usually the controlling resistance for most zeolite particle-cation systems (Sarioğlu, 2004). For example, Inglezakis and Grigoropoulou (2004) found an increase by a factor near two of Pb^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} removal capacities in clinoptilolite packed bed by decreasing particles size from 1.4-1.7 mm to 0.8-1 mm. On the other hand, improved adsorption and ion exchange performance by fine particles further may result in high flow resistance of the column, and therefore, should be avoided.

Effect of impurities

Impurities such as quartz, feldspar, clays, etc. can be found in the zeolite occurrences, and decrease percent zeolite content of the material. Therefore, this non-zeolitic mineral affects the utilization of material indirectly and negatively as a sorbent. Feldspars are anhydrous aluminosilicates of potassium, sodium, and calcium. These cations may participate in ion exchange reactions with heavy metal cations (Inglezakis, 2005). Clays also play an important role in metal removal applications due to their high cation exchange capacities. Quartz is a neutrally charged inert mineral that has a three-dimensional rigid framework but does not have a capacity for cation exchange, since there are no aluminum atoms present (Inglezakis, 2005). On the contrary, Sarioğlu (2004) stated that quartz and feldspar do not influence the results because of their absence of adsorption abilities. Nevertheless, natural materials such as clinoptilolite have an inherent disadvantage due to the presence of an unknown proportion of impurities, even from the same deposit, resulting in an unpredictable exchange capacity.

2.3.2. Packed-bed Column Studies

Column operation is different from that of batch operation due to the continuity of flow through packed particles. The dynamics of ion exchange

has an advantage over static mode by means of capacity in column application due to higher concentration gradients and constant removal of exchange products under dynamic conditions (Sprynskyy et al., 2005). However, the properties of ion exchanger (ionic form, capacity, degree of crosslinking), the composition of the feed, and the operating conditions (flowrate, temperature) may influence this capacity (Helfferich, 1995).

Inglezakis (2005) discusses that the operating capacity, defined as the amount of cations exchanged during fixed bed operation (Inglezakis & Grigoropoulou, 2003) in the case of infinite contact time and ideal flow in column operation, is independent of the flowrate according to Helfferich (1995). He continues to discuss that the operating capacity may be dependent on flowrate due to non-idealities of flow such as channeling or insufficient wetting of the material in column methods. The rate of ion exchange also influences the capacity. Ion exchange is usually not fast enough to allow the exchange reactions while the ion exchange zone moves in the flow direction in a limited time. Therefore, time to reach attaining local equilibrium for ion exchange should be well specified. Small particles can be used to achieve high rates of ion exchange if particle diffusion is the rate controlling step (Helfferich, 1995). But, fine particles may also result in high flow resistances (Inglezakis & Grigoropoulou, 2004). Column size and shape can also affect the degree of utilization capacity. An increase in column height up to certain level (high flow resistances at long columns) increases the overall metal uptake capacity (Helfferich, 1995; Inglezakis, 2005).

2.3.3. Regeneration of Metal-Loaded Zeolites

The degree of the reversibility is of major importance when concerned with the release of sorbed metals into solution during regeneration studies. The metal release, on the other hand, is greatly related to the elution of industrial

based valuable metals, and thus in the use of adsorbent material in further cycles. Therefore, one can say that this synergy is crucial, especially when low cost materials are used as a sorbent reasoning the economy.

A series of studies was performed in the literature to determine if elution is possible, and if the concentration of metal ions could be increased in the eluate. The binding forces between the cations and the zeolite matrix are relatively weak when ion exchange is considered as the main removal mechanism. Hence, the cations resident on a specific site could then be replaced in progressing cycles by other cations (Inglezakis et al., 2003). As a result, the capacity of clinoptilolite increases with the number of regeneration cycles (Semmens & Seyfarth, 1978). Turan et al. (2005) investigated the desorption of lead from clinoptilolite particles, and found that optimum regeneration of clinoptilolite is obtained with 30 g/L NaCl solution at pH 11.5. Zamzow et al., (1990) revealed the complete elution of cadmium from zeolite packed column using 3% NaCl solution, and concluded that the possibility of cadmium that did not come off during one elution could possibly come off during a later one. Carland and Aplan (1995), studying on elution of copper from clinoptilolite, concluded that the use of NaCl concentrations greater than 0.5 M has no additional effect on the elution process. So as to recover the adsorbed cadmium from the zeolite bed, Vasylechko et al. (2003) passed 15 ml of an eluent at a flow rate of 1 ml/min through the sorption cartridge, and extracted cadmium up to 92% by KCl. However, Gunneriusson (1994) found slower desorption or lower recovery of cadmium ions due to occlusion in the goethite structure after considerable extended adsorption reaction times.

2.3.4. Metal-Clinoptilolite Interaction Mechanisms

In the light of given information affecting the heavy metal removal by zeolites, one can easily state that various metal removal mechanisms and reactions

prevail in metal-clinoptilolite interaction. The sorption processes on zeolitic particles is a complex process owing to 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). While this is the sorbent based approach, metal characteristics i.e. hydration free energy, valence and characteristics of the aqueous solution i.e. formation of metal complexes are also of importance during metal removal.

For the uptake of heavy metals from aqueous solutions by clinoptilolite, ion exchange and adsorption can be regarded as the main removal mechanism whereas surface precipitation and dissolution is the co-mechanism. Ion exchange involves replacement of ions present in zeolite crystalline structure by metal ions from the solution (Mozgawa & Bajda, 2005), and stands for the prevailing metal removal mechanism. Reaction 2.4 summarizes the ion exchange reaction between zeolite and cadmium.



where *m* is the valence of exchangeable cations M (Na⁺, K⁺, Ca²⁺, Mg²⁺), and the subscripts (*aq*) and (*z*) refer to solution and zeolite phases, respectively.

During ion exchange, heavy metal cation diffuses into and extra-framework cations diffuse out from the solid structure as a result of concentration gradient between the solid and liquid phase. In zeolites, the framework charge (negative) is balanced by exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺), and is not localized but is more or less uniformly distributed in the framework. It can be concluded that the net negative charge forming a nonlocalized electric field affects the exchange process regardless of the complete or partial exchange of its balancing cations in the diffusion process (Inglezakis et al., 2005). Ion exchange is also named as outer sphere complexation in the literature (Doula & Ioannou, 2003; Mozgawa & Bajda, 2005). Outer

sphere complexes are less stable due to electrostatic bonding mechanisms and intermolecular forces between metal ions (Mozgawa & Bajda, 2005) and surface counterbalance cations (Doula & Ioannou, 2003). Cation diffusion within the crystal structure is regarded as the rate controlling step, but also the external solution can be of great influence (Malliou et al., 1992). In addition, the ion exchange rate is controlled by surface charge at low metal concentrations and the concentration of the counter ion in the bulk solution at high metal concentration (Athanasiadis and Helmreich, 2005).

Adsorption is another important removal mechanism that affects the transport of heavy metals in zeolites. The forces involved in adsorption can be listed as weak, physical, Van der Waals and electrostatic outer sphere complexes to chemical interactions, i.e. covalent bonding, hydrogen bridges, and steric or orientation effects (Doula and Ioannou, 2003). Adsorption is also referred as chemisorption or inner sphere complexation in the literature (Mozgawa and Bajda, 2005; Doula and Ioannou, 2003). In addition to inner sphere complexation, Trgo and Peric (2003) stated that the oxygen atom in the Si-O-Al species bears a negative charge of the lattice and acts as a potential adsorption location as well as arising negative charge from isomorphous Si/Al substitution.

Ion exchange is the provoking mechanism for the adsorption. Outer sphere complexes are formed on external surface sites at initial state of the adsorption process. As metal concentration increases, metal ions are forced into internal surface sites and form more stable inner sphere complexes due to formation of covalent bonds. Hydrogen ions are released as products, so decrease the solution pH. Outer sphere complexation is usually rapid and reversible, whereas inner sphere complexation is slower and irreversible (Doula and Ioannou, 2003). The heavy metal ion also determines the availability and the accessibility of an exchange site. Mozgawa and Bajda (2005) stated that the participation of ion exchange and chemisorption in the

case of cadmium and nickel removal seems to be equal; however, adsorption predominates for the removal of lead and chromium. Martinez et al. (2004) confirmed the same behavior of cadmium on natural zeolites which have undoubtedly a heterogeneous surface and, therefore, exhibit different activation energies for chemisorption.

Surface precipitation can form when the amounts of sorbed metal ions on a surface cover the whole surface. As surface coverage increases, new solid phases (distinct entities or aggregates) are formed on the surface, hence, surface precipitation becomes the main removal mechanism (Doula and Ioannou, 2003). However, surface precipitation may probably reduce the zeolite ion exchange ability due to the blockage of the micropores by the precipitated phase (Inglezakis et al., 2005).

Dissolution can be defined as destruction of zeolite framework by detachment of central metal ions (Si^{4+} or Al^{3+}). Presence of anions (Cl^-), surface protonation and formation of inner sphere complexes may influence the dissolution of zeolite by facilitating detachment of the central metal ions (Doula et al., 2002). According to Rozic et al. (2005) and Wingenfelder et al. (2005a) at low pH values ($\text{pH} < 2$), dissolution of aluminum is increased markedly whereas silica dissolution may appear under both acidic and basic conditions (Doula and Ioannou, 2003). Dissolution of zeolitic material leads to an increased number of potential sorption sites (Trgo and Peric, 2003) and participate in the removal mechanism indirectly. In addition to examined removal mechanisms, ion pairing can also be listed as indirect removal mechanism. Ion pairing is defined as by which the presence of one ion can possibly facilitate adsorption of the other. For instance, extensive ion pairing of SO_4^{2-} with multivalent cations, but this is questionable whether ion pairs facilitate or inhibit cation adsorption (Doula and Ioannou, 2003).

2.4. MODELING OF HEAVY METAL REMOVAL

The adsorption isotherms exemplify the equilibrium of an ion in solid phase with the concentration of the ion in solution. The theoretical adsorption capacity of an adsorbent can be calculated with an appropriate isotherm. The Langmuir and Freundlich models are the most commonly used ones for aqueous solutions and porous material interactions (Altin et al., 1998; Balci, 2004; Payne & Abdel-Fattah, 2004; Peric et al., 2004; Petrus & Warchol, 2003).

Natural sorbents have nonhomogenous surfaces or heterogeneity of adsorption sites. For this reason, different isotherms are needed to explain the equilibrium phenomena. As an example, Langmuir-Freundlich, Toth, Redlich Peterson, Dubinin-Radushkevich, and Lineweaver-Burk can be given (Balci, 2004; Altin et al., 1998; Peric et al., 2004; Petrus & Warchol, 2005). These isotherms are principally derived from Langmuir and Freundlich models, and need nonlinear regression analysis to handle the experimental data (Balci, 2004).

Langmuir isotherm defines the equilibrium parameters of homogenous surfaces, monolayer adsorption and distribution of adsorption sites. On the other hand, adsorption on nonuniform sites, either preexisting in the different adsorption sites or caused by repulsive forces between adsorbed atoms or molecules, is the basis of the Freundlich model (Payne & Abdel-Fattah, 2004). Langmuir and Freundlich isotherms can be given as follows:

$$q_e = \frac{q_{\max} K C_e}{1 + K C_e} \dots\dots\dots 2.5$$

$$q_e = K_F C_e^{1/n} \dots\dots\dots 2.6$$

Where;

q_e : equilibrium metal concentration in the clinoptilolite phase (meq/g)

q_{max} : maximum achievable capacity (meq/g)

K : equilibrium Langmuir constant (L/mg)

C_e : equilibrium metal concentration in the aqueous phase (mg/L)

$1/n$: Freundlich intensity parameter

K_F : Freundlich capacity factor (L/mg)

CHAPTER 3

MATERIALS AND METHODS

3.1. REAGENTS

All chemicals used in the experiments were analytical grade reagents. The aqueous solutions of related metals were prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka), NaCl, KCl, CaCl_2 , and HCl (Merck) in high purity deionised water (average conductivity of $0.92 \mu\text{S}/\text{cm}$). HNO_3 and NaOH were used to adjust the initial pH of metal solutions.

3.2. PREPARATION AND CHARACTERIZATION OF CLINOPTILOLITE SAMPLES

3.2.1. Clinoptilolite Samples

The sorbent materials were taken from two different sedimentary deposits located in Western Anatolia, namely Gördes (Manisa) and Bigadiç (Balıkesir). Gördes clinoptilolite was obtained from the Civil Engineering Department of METU, and Bigadiç clinoptilolite from Etibank A.Ş. Both samples were crushed and sieved to 0.17-0.83 mm (20/80 mesh), 0.35-0.50 mm (35/45 mesh), 0.83-1.18 mm (16/20 mesh), and 1.18-1.14 mm (14/16 mesh) fractions. Samples were, then, dried at 105°C for 24 hrs and stored in a

desiccator until use. Minimum prior handling, processing of clinoptilolite was aimed, considering possible future practical applications. No extensive drying was performed on clinoptilolite samples, therefore stated capacity values in further sections can be considered on a wet basis.

3.2.2. Mineral Characterization

Identification of mineral phases in the clinoptilolite samples was performed using X-ray diffraction analysis (XRD, Rigaku X-Ray Diffractometer Ultima Model:D/MAX 2200/PC) on raw samples in the Department of Metallurgical and Materials Engineering at METU.

Microscopic examination method was used to identify the purity and other existing phases in the samples in the Department of Geological Engineering at METU.

Determination of the major and trace elemental composition of both clinoptilolite samples was performed by X-ray fluorescence (XRF, Rigaku X-Ray Spectrometer RIX 3000) technique in General Directorate of Mineral Research and Exploration laboratories. Scanning electron microscopy (SEM, JEOL JSM-6400 Scanning Microscope) was used for photomicrographs as well as to analyze the chemical composition (EDS, Energy Dispersive Spectroscopy) of clinoptilolite samples in the Department of Metallurgical and Materials Engineering at METU.

The specific surface area of the clinoptilolite samples was measured by BET method using N₂ as adsorbate by Quantochrome Autosorb Automated Gas Sorption System, pore size distribution was determined by using Quantochrome Autosorb Automated Gas Sorption System and density in Helium pycnometer in the Central Laboratory at METU.

3.3. CONDITIONING IN BATCH MODE EXPERIMENTS

In order to improve their effective capacity, as-received clinoptilolite samples were converted into near homoionic form. For this purpose, clinoptilolite samples of 10 g were treated with 250 mL in 2M NaCl solution at 30 °C for 1 day at 150 rpm. At the end of the conditioning period, samples were washed with deionised water until no Cl^- was detected in the wash water. The suspensions were left to settle, and the solid was extracted from the liquid by centrifugation. Afterwards, the conditioned samples were dried at 105 °C for 24 hours, and stored in a desiccator until use.

3.4. EXPERIMENTS IN BATCH MODE

Batch type experiments were conducted at constant conditions of 1g clinoptilolite/100mL metal solution ratio in flasks for all tested parameters. Initial pH adjustment was done in metal solutions using 0.1N HNO_3 and 0.1N NaOH solutions. Flasks were sealed and shaken at 125 rpm using an Edmund Buhler KS-15 type orbital shaker in ambient temperature for 48 hours. Samples were taken from the suspensions at selected time intervals and at equilibrium. Immediately after withdrawal, mixtures were centrifuged at 3800 rpm for 5 minutes to ensure solid-liquid separation. After centrifugation, samples were acidified with HNO_3 to keep all ions in their free forms, and then stored in a refrigerator until the time of analysis. In analyses, aside from Cd^{2+} , exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and silicon were also analyzed for specified experimental conditions in the liquid phase. All experiments were carried out in duplicates with appropriate blanks, and mean values were used in the analysis of data.

3.4.1. Preliminary Experiments

The response of two clinoptilolite sample under various initial conditions is so significant to scrutinize the possible removal mechanisms. The samples having 0.17-0.83 mm diameter were equilibrated with solutions containing 40 mg/L cadmium with pH values of 3, 4, and 5 for the determination of optimum initial pH. Studies for the effect of particle size on cadmium uptake were conducted in solutions containing 40 mg/L cadmium using 0.17- 0.83 mm, 0.83-1.18 mm, 1.18-1.40 mm fractions of clinoptilolite samples at pH 4.

The effect of solution temperature on metal uptake capacity of both as-received and conditioned clinoptilolite samples was determined using solutions having 3000 mg/L initial cadmium concentration, at 25 and 50°C, for 6 hrs and 24 hrs for Gördes and Bigadiç samples, respectively.

A given amount of as-received Gördes and Bigadiç samples were washed with distilled water several times to remove dust which aimed to find out the effects of prewashing on metal uptake capacity. Washed samples were dried for 24 hrs at 105°C in an oven, and stored in desiccators, then were mixed with solutions containing 750 mg/L initial cadmium concentration for 6 hrs and 24 hrs for Gördes and Bigadiç samples, respectively.

3.4.2. Equilibrium Experiments

A wide range of cadmium concentrations (5-10000 mg/L) were tested to find out the maximum capacity for both as-received and conditioned clinoptilolite samples at initial pH of 4 and particle size of 0.83-1.18 mm. Preliminary experiments yielded equilibration time of 6 hrs for Gördes and 24 hrs for Bigadiç samples. Therefore, equilibrium studies at various initial cadmium concentrations were ended at these time periods.

3.4.4. Deionised Water-Clinoptilolite Interaction

The behavior of clinoptilolite samples in cadmium-free solution was investigated at pH of 4, and the time period of 6 and 24 hrs for both as-received and conditioned forms of Gördes and Bigadiç samples, respectively.

3.5. SELECTION OF THE CONDITIONING/REGENERATION CHEMICAL

The determination of best conditioning/regeneration conditions formed the basis of column experiments. As stated in the theoretical background section, it is well known that NaCl pretreatment seems to be the best method of clinoptilolite for improving its metal uptake capacity. However, regeneration is also an important parameter for the reuse of clinoptilolite in further cycles and recovery of metal ions as well as conditioning. Due to this fact, four different chemicals (NaCl, KCl, CaCl₂, HCl) were tested for conditioning and regeneration of Gördes samples in batch mode. A simple flowchart summarizing the process is given in Fig. 3.1.

Gördes clinoptilolite samples of 10 g were treated with 500 mL of 1M NaCl, KCl, CaCl₂, and HCl at 25°C for 1 day at 150 rpm. At the end of the conditioning period, samples were washed with deionised water until no Cl⁻ was detected in washing water. Subsequently, the conditioned samples were dried at 105°C for 24 hours, and stored in a desiccator until further use. Metal removal was, then, conducted these samples at 125 rpm, 1g/100mL solid to liquid ratio, 200 mg/L initial cadmium concentration, and pH of 4 at 25°C for 6 hours. After metal removal, cadmium-loaded samples were dried and stored in a desiccator. 3 g of it were, then, transferred to flasks and regenerated with 150mL of 1M NaCl, KCl, CaCl₂, and HCl solutions under same

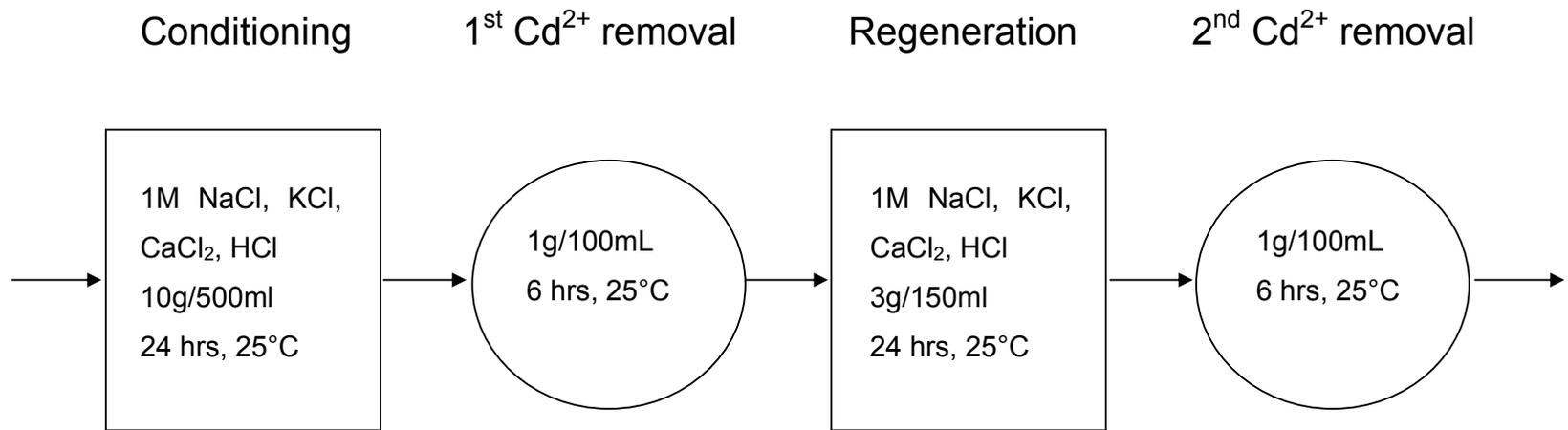


Figure 3.1. Flow chart describing conditioning/regeneration experiments in batch mode

experimental procedures as in the conditioning step. The regenerated forms also were then used for cadmium removal in same experimental procedure as in the first metal removal step in an orbital shaker. In analyses, aside from Cd^{2+} , exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were also analyzed in the liquid phase. All experiments were carried out in duplicates with appropriate blanks, and mean values were used in the analysis of data.

3.6. DETERMINATION OF CONDITIONING PARAMETERS IN CONTINUOUS MODE

Column experiments were conducted in glass columns of 26.5 cm height, 2.5 cm internal diameter. In order to guarantee the complete wetting of the clinoptilolite particles, solutions were pumped into columns in upflow mode using a peristaltic pump. In column pretreatment experiments, firstly, the determination of operational and chemical conditions for conditioning in continuous mode were aimed. For this purpose, following parameters were tested:

- total volume of conditioning solution (10, 20, 30 BV),
- initial pH of conditioning solution (5.5, 7),
- water quality used for the preparation of conditioning solution (deionised and tap water).

For all column experiments, Gördes samples were washed using distilled water in order to remove the surface dust, then, let to dry for 24 hrs at 105°C in an oven, and finally stored in a desiccator. Clinoptilolite samples of about 110 g are loaded into the column, which occupied 0.13 L of bed volume, and then treated with 1M NaCl at 2 BV/h flowrate for 10 hours. After conditioning process, samples were washed to remove excess Cl^- at 10 BV/h flowrate for 90 minutes. The efficiency of column conditioning was tested by cadmium

removal experiments in batch mode. They were conducted using column conditioned samples at 125 rpm, 1g/100mL solid to liquid ratio, 200 mg/L initial cadmium concentration, pH of 4, and 25°C. Samples were taken from the suspensions at the end of 6 hrs. Immediately after withdrawal, samples were centrifuged at 3800 rpm for 5 minutes to ensure solid liquid separation. After centrifugation, samples were acidified with concentrated HNO₃ to keep all ions in their free forms, and then stored in a refrigerator until the time of analysis. In analyses, aside from Cd²⁺, exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) were also analyzed in the liquid phase. All experiments were carried out in duplicates with appropriate blanks, and mean values were used in the analysis of data.

3.7. EXPERIMENTS IN CONTINUOUS MODE

The effect of volumetric flowrate (5, 10, 15 BV/h), particle size (0.35-0.50, 0.83-1.18 mm) and also the regeneration of metal loaded clinoptilolite samples were investigated using initially specified cadmium concentration, pH and temperature as 200 mg/L, 4, and 25°C, respectively. The corresponding values for volumetric flowrates are given in Table 3.1.

Table 3.1. Experimental range of conditions used in column operation

Flowrate (BV/hr)	Loading rate		Empty bed contact time (min)
	m/s	mL/min	
5	9.21*10 ⁻⁵	10.8	12
10	1.84*10 ⁻⁴	21.7	6
15	2.76*10 ⁻⁴	32.5	4

The initial concentration, 200 mg/L, was selected because it was high enough to investigate the removal capacity of the column in a reasonable time frame, and low enough to justify the use of the amount of metal salt during the preparation of large volumes of metal solutions for the continuous mode applications.

In order to obtain unified capacity terminology in continuous mode experiments due to encountered confusion in capacity explanation in the field of zeolite science, two types of capacity were used in this study;

- Total capacity: defines the capacity utilized until exhaustion, that is, when $C/C_0=1$ is observed on the breakthrough curve. Total (exhaustion) capacity term is used in experiments where the effect of flowrate and particle size on cadmium removal was investigated.
- Breakthrough capacity: defines the loading of the clinoptilolite in a column when the incoming cadmium ion is first detected in the effluent or when the concentration in the effluent reaches some arbitrarily defined value (e.g. $C/C_0=0.01$). Breakthrough capacity is used during the discussion of regeneration experiments.

In regeneration experiments, the column operation was stopped when the cadmium concentration of the effluent reached to about 10% in the first and about 1% of the influent for the rest of the cycles. Cadmium-loaded clinoptilolite bed was subsequently regenerated (or clinoptilolite bed reconditioned) with 1M NaCl at 2 BV/h flowrate for 10 hours. After regeneration, clinoptilolite bed was washed to remove excess Cl^- at 10 BV/h flowrate for 90 minutes. During column operation, samples were collected from the exit of the column at designated time intervals, then acidified with HNO_3 and kept at 4°C prior to analysis. In analyses, aside from Cd^{2+} , silicon, aluminum and exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were also analyzed for specified experiments in the liquid phase. All experiments were carried out in duplicates and mean values were used in the analysis of data.

3.8. ANALYSES OF SAMPLES

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

- Na^+ and K^+ ions by Jenway PFP7 Model Flame Photometer,
- Cd^{2+} , Ca^{2+} , and Mg^{2+} ions by ATI Unicam 929 Atomic Absorption Spectrometer,
- Silica by Hach DR 2400 Spectrophotometer (as SiO_2),
- Alumina by Leeman Labs Inc. Direct Reading Echelle Inductively Coupled Plasma-Optic Emission Spectrometer (ICP-OES),
- Cl^- ions by Argentometric Method (Standard Methods, 1998),
- pH and temperature by CyberScan 500 pH Meter.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. CHARACTERIZATION OF CLINOPTILOLITE SAMPLES

4.1.1. Mineral Characterization

X-ray diffraction analysis was used to determine the mineralogical composition of the Gördes (GC) and Bigadiç (BC) clinoptilolite samples. Diffractometer traces of clinoptilolite samples are matched with data given by ICDD (International Center for Diffraction Data) using Qualitative Analysis software and the clinoptilolite peaks obtained are pointed out in Figure 4.1.

Microscopic analysis has revealed that the GC sample contains coarse grained clinoptilolite (approximately 80%) particles, whereas BC sample has fine grained clinoptilolite (approximately 50%) particles. In addition to quartz as the main impurity for GC sample, BC sample contained biotite and illite as impurities.

The chemical compositions of the as-received clinoptilolite samples are presented in Table 4.1. Both samples have poor sodium content, as it is the case in the other zeolite occurrences of Western Anatolia (Çulfaz et al., 1995; Çulfaz and Yağız, 2004) and, are high in calcium and potassium content. A comparison of the two samples regarding their chemical composition is given

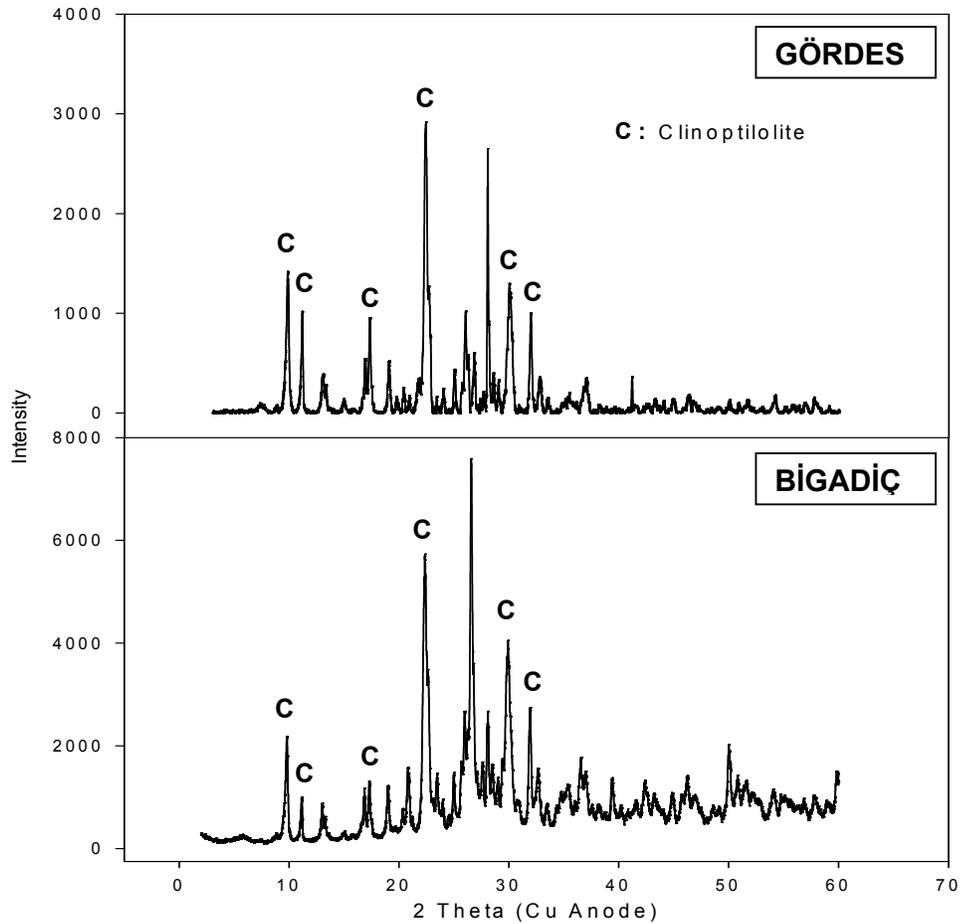


Figure 4.1. Diffractometer patterns of the two clinoptilolite samples used in this study

in Table 4.2. The Si/Al ratio for both samples is in typical ranges of 4 to 5.5 given for clinoptilolite (Tsitsishvili et al., 1992). The obvious difference of distribution of exchangeable cations in both samples is mainly related to their clinoptilolite and impurity content. This fact is also proven by the calculation of theoretical cation exchange capacities (TCEC). As stated in the theoretical background section, the unique ion exchange characteristics of zeolites result from the Al^{3+} substitution with Si^{4+} in the framework. Therefore, TCECs calculated from the number of equivalent of exchangeable cations and

Table 4.1. Chemical analysis of clinoptilolite samples used in this study

Oxides	Gördes (% w/w)	Bigadiç (% w/w)
SiO ₂	74.36	72.76
Al ₂ O ₃	11.87	11.93
Fe ₂ O ₃	1.03	1.26
MgO	0.85	1.26
CaO	1.95	4.16
Na ₂ O	0.59	0.10
K ₂ O	4.07	3.13
MnO	0.02	0.03
TiO ₂	0.07	0.09
P ₂ O ₅	0.01	0.01
H ₂ O	6.50	1.40

aluminum content should be equal for pure clinoptilolite. The total sum equivalent cation content of BC sample (2.81) exceeded the number of aluminum atoms (2.31) which provided additional evidence of the presence of exchangeable cations in impurities. The variation in Gördes sample is much smaller, and hence may arise from the experimental errors or sensitivity of the equipment.

The physical properties of as-received and conditioned clinoptilolite samples are given in Table 4.3. The most significant finding is the considerable difference between the surface areas determined for the Gördes clinoptilolite samples when compared to those for Bigadiç. The former is about three folds of the latter. The surface areas of Gördes and Bigadiç as-received samples increased slightly after being treated with NaCl solution, but their pore sizes remained similar. However, the same detection technique of specific surface area and pore size was not applicable for clinoptilolite samples used in

Table 4.2. Comparison of clinoptilolite samples regarding their characteristics

Cations	Gördes		Bigadiç	
	meq/g	% eq./eq.	meq/g	% eq./eq.
Ca ²⁺	0.70	32	1.48	53
Na ⁺	0.19	9	0.03	1
K ⁺	0.86	40	0.66	24
Mg ²⁺	0.42	19	0.63	22
Si/Al		5.32		5.17
TCEC _{Ex} (meq/g)		2.17		2.81
TCEC _{Al} (meq/g)		2.30		2.31

Ex: Exchangeable based, Al: Aluminum based theoretical cation exchange capacity

Table 4.3. Physical properties of as-received and conditioned clinoptilolite samples

Clinoptilolite samples	Specific surface area (m ² /g)	Average pore diameter (Å)	Density (g/L)
Gördes as-received	36.95	17.5	2.27
Gördes batch conditioned	37.40	17.9	-
Bigadiç as-received	11.77	17.0	2.24
Bigadiç batch conditioned	12.92	17.0	-
Gördes column conditioned	40.40	17.5	2.23
Gördes exhausted/regenerated	N. D. *	N. D. *	2.22

* N. D.; could not be detected

repetitive cadmium exhaustion/NaCl regeneration cycles, due to significant alterations on their surface properties.

SEM examination of the clinoptilolite samples reveals important information on the surface structure and the presence of amorphous material (Figure 4.2). The surface property of the two as-received clinoptilolite samples, being initially amorphous (not crystalline), turns to well formed plate crystals for GC and flat crystals for BC after conditioning (i.e. crystals become visible after conditioning). Thus, this improvement in apparent crystallinity may ease the

cation diffusion to pores and proves the benefits of conditioning as a visual image.

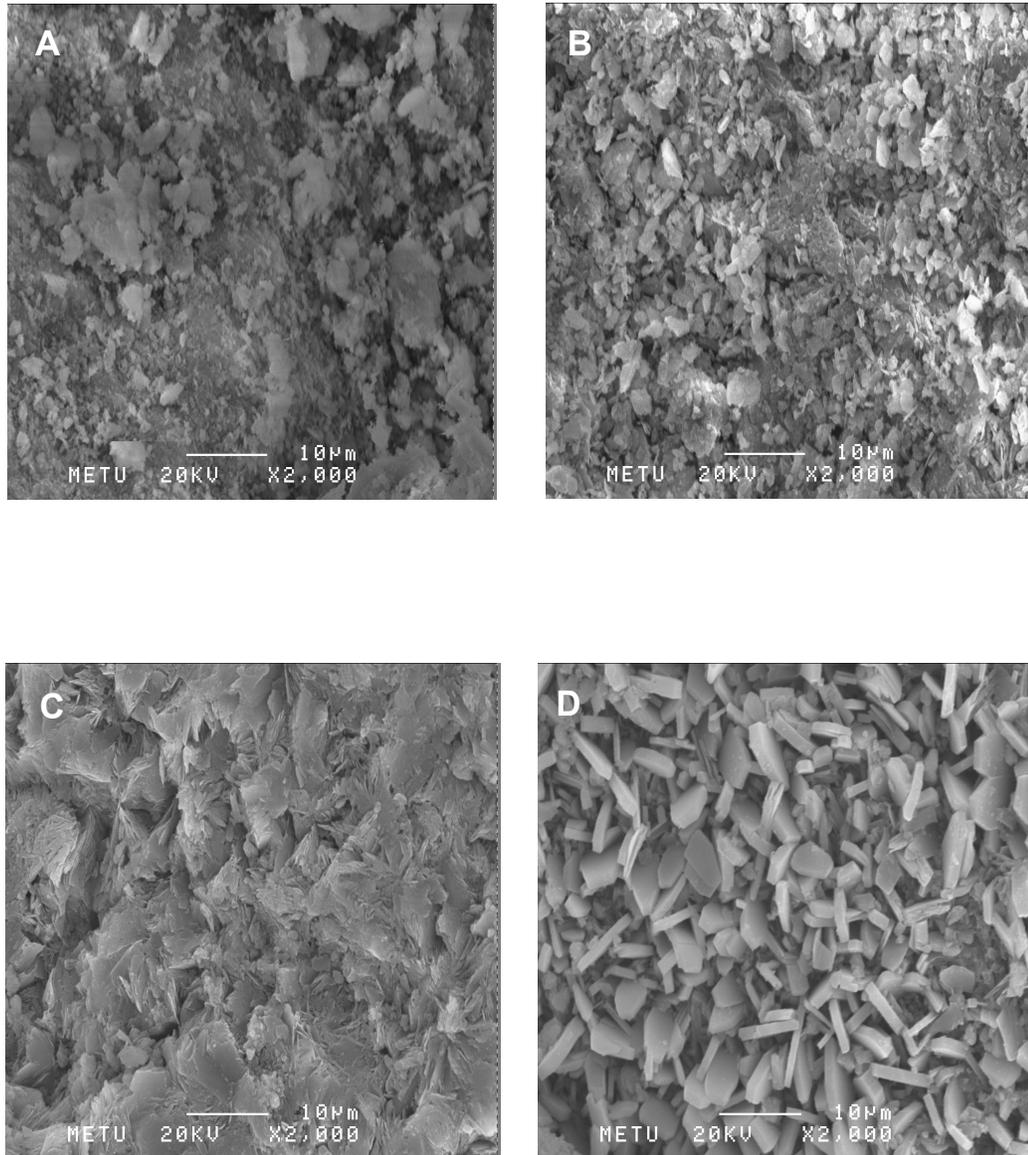


Figure 4.2. SEM photographs of clinoptilolite samples, A. Gördes as-received; B. Bigadiç as-received; C. Gördes conditioned; D. Bigadiç conditioned

4.2. STUDIES IN BATCH MODE

4.2.1. Preliminary Studies

Effect of pH

The results of the influence of pH on cadmium removal via both clinoptilolite samples are presented in Figure 4.3. As expected, cadmium removal efficiency was observed to decrease with decreasing pH for both samples. The lowest cadmium uptake obtained at pH 3 may be attributed to the increase in the competition for active adsorption sites by hydrogen ions. A positive charge develops on the surface of the clinoptilolite samples in highly acidic medium (protonation) and increase the electrostatic repulsion between cadmium ions and the surface (Cabrera et al., 2005), thus, lowering the metal uptake. As a preliminary finding, Figure 4.3 also shows that Gördes sample is better at removing cadmium from aqueous solutions when compared to Bigadiç clinoptilolite.

In addition, Figure 4.3 represents change of cadmium removal as a function of time for both clinoptilolite samples. The concentration of cadmium did not change appreciably after 6 hrs for GC and 24 hrs for BC, suggesting the end of equilibrium period. This may be interpreted as the effect of diverse removal mechanisms of cadmium removal in the two clinoptilolite samples. At the end of equilibration period, for pH 4 and/or 5, approximately 87 % and 61 % of cadmium was removed from the solution by GC and BC samples, respectively.

On the contrary to cadmium removal efficiencies at different pH values, samples represented similar pH change profiles during the metal removal studies for tested pH values as shown in Figure 4.4. The pH of the solutions

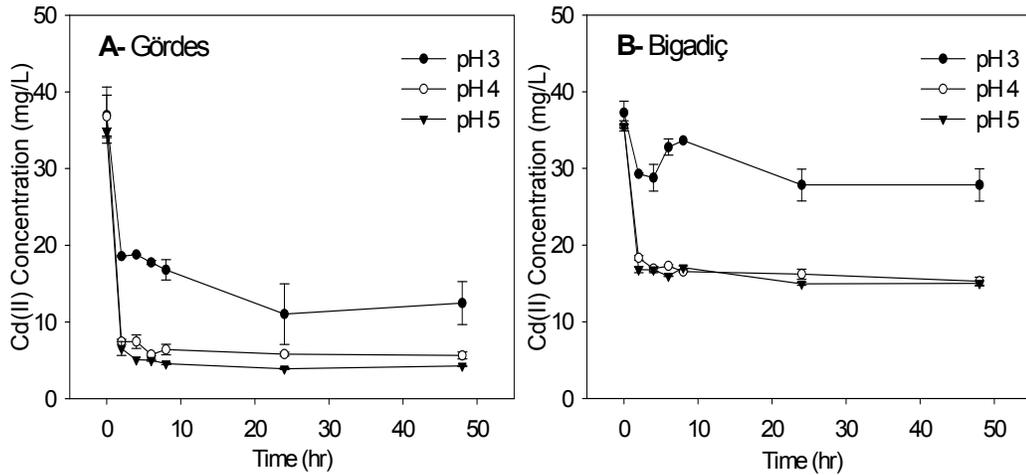


Figure 4.3. Effect of the initial pH on cadmium removal by as-received A. Gördes, and B. Bigadiç clinoptilolite samples.

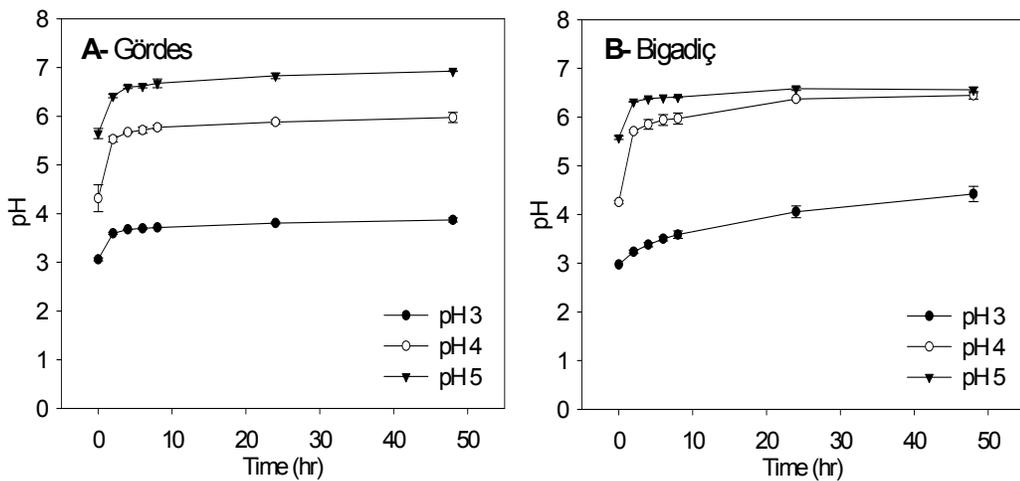


Figure 4.4. The change of pH with respect to time for A. Gördes, and B. Bigadiç clinoptilolite samples.

increased during the exchange of the heavy metal ion for both samples. Additionally, higher hydrogen ion uptake by BC sample at pH 3 favors surface protonation, thus, affects the cadmium uptake negatively and more when compared to the GC sample. As a result of these findings, pH 4 was selected as the optimum initial pH for both clinoptilolite samples, also considering the acidic character of metal bearing wastewaters.

Effect of particle size

Grain size was found to have no effect on metal removal efficiency for the particle sizes tested in this study. In porous materials, the involvement of the external surface area in the exchange process is limited, and therefore, size reduction has a negligible effect on increasing the total surface area (Ören & Kaya, 2006). It is evident from Figure 4.5 that an increase in external surface area has little effect on cadmium removal for any of the clinoptilolite samples. This indicates that cadmium removal occurs mainly via exchangeable cations found in the internal/available sites rather than on the surfaces of the particles.

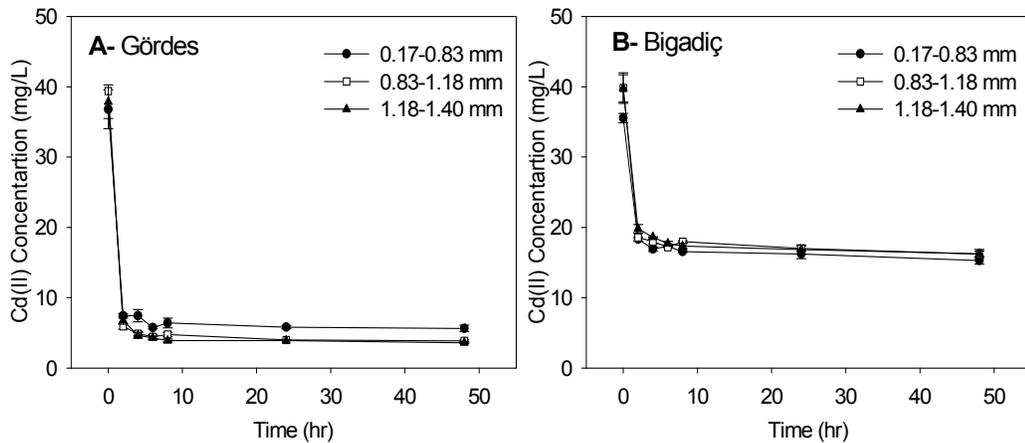


Figure 4.5. Effect of particle size on cadmium removal by as-received A. Gördes, and B. Bigadiç clinoptilolite samples.

The findings of this study, however, are not unique in this sense. There are studies reporting that the high surface area is a weak function of particle size (Ouki et al., 1993; Um and Papelis, 2004; Wingenfelder et al., 2005a).

The removal efficiency of GC and BC remained around 85% and 60%, respectively for all three particle sizes tested. The results also revealed that decreasing particle size would not yield an increase in the hydrogen ion uptake by clinoptilolite samples as shown in Figure 4.6. Consequently, the median particle size, namely, 0.83-1.18 mm was selected and used for both clinoptilolite samples in further experiments.

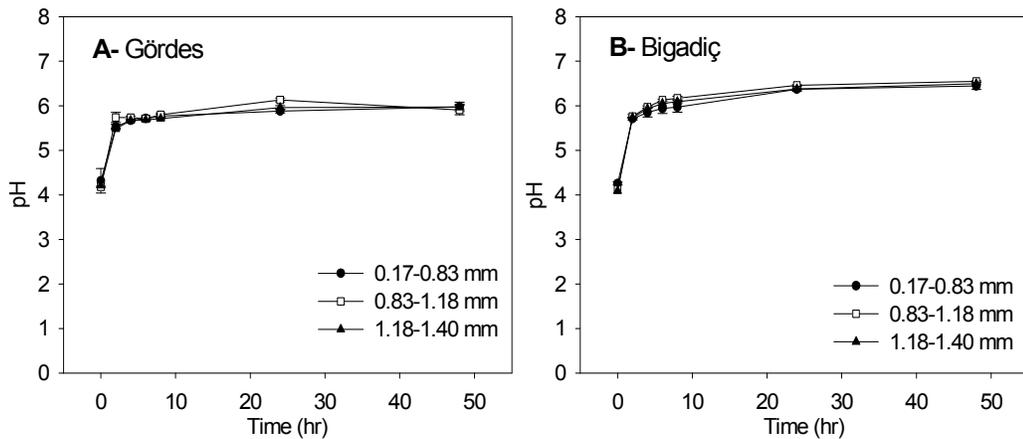


Figure 4.6. pH changes during particle size experiments using A. Gördes, and B. Bigadiç clinoptilolite samples.

Effect of temperature

Experimental studies performed to find out the influence of temperature and prewashing on cadmium removal capacity of both clinoptilolite samples were conducted parallel to equilibrium experiments. Therefore, initial cadmium

concentrations tested in these experiments were determined using information from equilibrium studies.

The cadmium uptake capacity is increased slightly by increasing temperature (Fig. 4.7). The capacity reached at 50°C from 0.17 meq/g to 0.25 meq/g for as-received and from 0.67 meq/g to 0.77 meq/g for conditioned GC samples, respectively. For Bigadiç samples, the uptake of cadmium ions was increased from 0.11 meq/g and 0.38 meq/g to 0.14 meq/g and 0.45 meq/g for as-received and conditioned forms, respectively. At higher temperature, cations are moving faster to the activated sites during the exchange process, due to the endothermic characteristics of sorption processes in the zeolites (Payne and Abdel-Fattah, 2004). A small decline in the increase of uptake with increasing temperature was observed for both conditioned forms. Panayotova (2001) also found similar results for copper removal with NaCl conditioned Bulgarian zeolite and concluded the possibility of increased desorption of copper with increasing temperature.

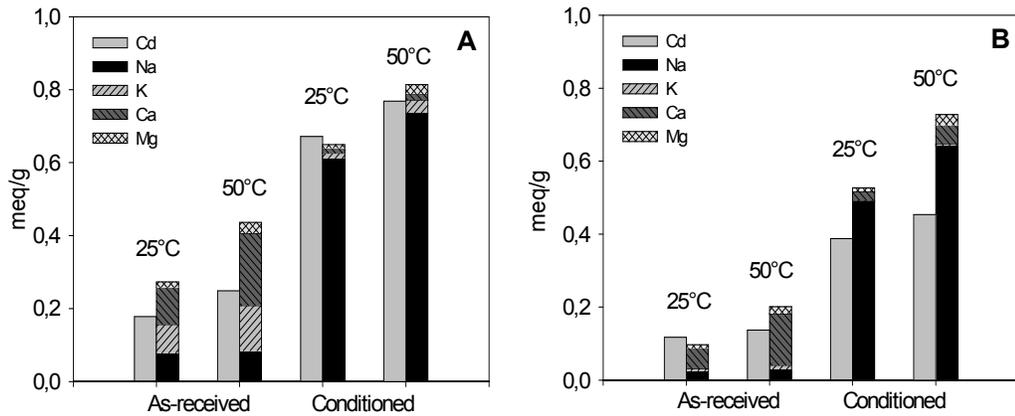


Figure 4.7. Effect of temperature on cadmium uptake capacity and release of exchangeable cations for A. Gordes, and B. Bigadiç clinoptilolite samples

Investigation of exchangeable cations, except the sodium ions, points to the exchange of cadmium ions with especially calcium ions in GC in BC structure. This indicates the participation of calcium ions into the exchange processes for cadmium under high temperatures. In general, the increase in temperature lead to a greater release of exchangeable cations, not in accordance with cadmium removed from solution. This could be explained by further dissolution of impurities with temperature. Overall, the slight increase of cadmium removal capacity does not justify the doubling of ambient temperature, which would mean an immense energy requirement when practical applications are considered. Therefore, further studies will be conducted at 25°C.

Effect of prewashing

Many studies in the literature state that the clinoptilolite surface and pore openings are partially covered by dust (Zorpas et al. 2002; Athanasiadis and Helmreich, 2005). This was also seen from the amorphous materials on zeolite surfaces of micrographs of both as-received samples, resulting in pore clogging leading to smaller ion exchange capacity and slower ion exchange rates. Therefore, as-received samples were washed prior to their use in cadmium removal experiments in order to find out if the same is applicable for our clinoptilolite samples. However, in this study, prewashing of as-received clinoptilolite samples showed that surface dust makes no changes on the effective capacity (Fig. 4.8). Additionally, apart from a slight relative increase of magnesium release from both samples, no major changes were observed regarding exchangeable cations in the aqueous phase. Therefore, prewashing of crushed and sieved as-received samples is not necessary, and was not performed in the rest of the study.

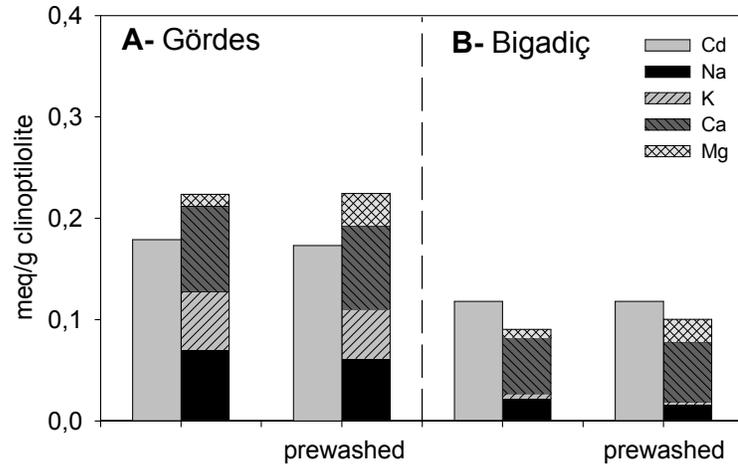


Figure 4.8. Effect of prewashing on cadmium uptake capacity and release of exchangeable cations for A. Gördes, B. Bigadiç as-received clinoptilolite samples.

4.2.2. Equilibrium Studies

In order to calculate the maximum metal uptake capacities, different cadmium concentrations were brought into contact with the same quantity of as-received and conditioned forms of Gördes and Bigadiç clinoptilolites until equilibrium was reached. The amount of cadmium ion removed onto clinoptilolite samples is calculated by:

$$q_e = \frac{C_i - C_e}{S} \dots\dots\dots 4.1$$

where q_e is the cadmium ion sorbed on clinoptilolite (mg/g or meq/g), C_i is the initial metal ion concentration (mg/L), C_e is the final metal ion concentration in the solution (mg/L), and S is the clinoptilolite amount (g/L).

The experimental results of the removal of cadmium ions on both clinoptilolite samples indicate a high degree of ion removal at lower initial metal

concentrations. However, the amount of cadmium uptake decreased as initial concentrations reached to 300 mg/L and 1000 mg/L for as-received (GC) and conditioned (GCC) Gördes, 300 mg/L and 500 mg/L for as-received (BC) and conditioned (BCC) Bigadiç clinoptilolite samples, respectively (Figure 4.9). Equilibrium cadmium removal experiments carried out with both samples were fitted to well known Langmuir and Freundlich adsorption isotherm models (Table 4.4) using non-linear regression analysis. Use of linear parabolic equation on fitting the experimental data was shown to result in inconsistencies in a wide range of concentrations (Peric et al., 2004).

Table 4.4. The parameters for Langmuir and Freundlich isotherms

Isotherm parameters	Gördes		Bigadiç	
	As-received	Conditioned	As-received	Conditioned
Langmuir				
q_{max}	0.18	0.65	0.11	0.37
K	0.051	0.054	0.027	0.725
r^2	0.97	0.92	0.99	0.90
Freundlich				
$1/n$	0.120	0.139	0.151	0.103
K_F	0.071	0.221	0.038	0.185
r^2	0.74	0.88	0.81	0.87

The Langmuir isotherm has shown good fit for both forms and origins of examined clinoptilolite samples as given in Table 4.4 and Figure 4.9, when compared to the fit of Freundlich isotherm. Maximum cadmium removal capacities obtained were 0.18 meq/g and 0.11 meq/g for as-received, and 0.65 meq/g and 0.37 meq/g for conditioned Gördes and Bigadiç samples, respectively. The capacity reached after conditioning shows a 261% and 236% increase of the cadmium uptake capacities for Gördes and Bigadiç samples when compared to their natural forms, respectively.

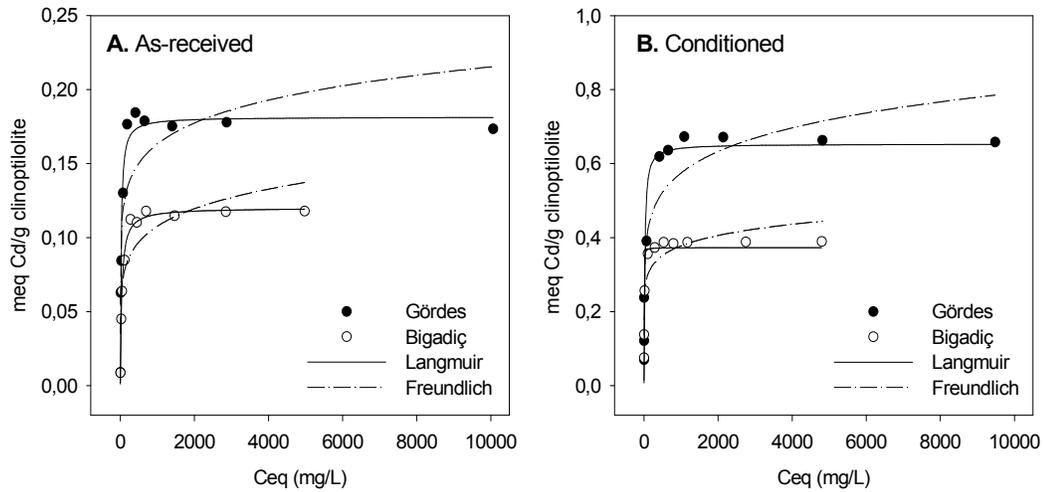


Figure 4.9. Isotherm plots of cadmium uptake by as-received and conditioned forms of Gördes and Bigadiç clinoptilolite samples

The results reveal a significant difference between the cadmium uptake capacities of Gördes and Bigadiç samples. The purity of clinoptilolite, identity of impurities, accessibility of exchangeable cations all contribute to this observed difference. The results of this study compares well with findings obtained for cadmium removal with clinoptilolite-rich natural materials in the literature (Table 4.5). However, caution should be taken while comparing the cadmium removal capacities since the presence of impurities, clinoptilolite content, heterogeneity of active sites, rearrangement of location and type of active sites and exchangeable ions after conditioning process, as well as experimental conditions used are not the same. Even though the cadmium removal capacities are similar for as-received forms in literature, conditioned forms of different zeolite deposits showed superior capacity. Conditioned samples from Bigadiç reserve, for example, was shown to remove cadmium much better in Çulfaz and Yağız's (2004) study. The main reason can be attributed to the higher purity of clinoptilolite (>80%) and different Si/Al ratio (4.46), a parameter that may substantially affect the cation selectivity, when compared to Bigadiç sample used in this study (50% clinoptilolite content and Si/Al ratio of 5.17).

Table 4.5. Summary of literature on cadmium exchange capacity

<i>Zeolite origin</i>	<i>Cd (meq/g)</i>		<i>Reference</i>
	<i>As-received</i>	<i>conditioned</i>	
Croatia	0.24	0.42	Curkovic et al., 1997
Iran	0.25-0.45	0.57-0.68	Faghihian et al., 1999
Sardinia, Italy	0.06-0.17	0.25	Cincotti et al., 2001
Sardinia, Italy	-	0.83	Langella et al., 2000
Sardinia, Italy	0.05-0.19	-	Cincotti et al., 2006
Sonora, Mexico	0.18	-	Martinez et al., 2004
California, USA	-	0.84-1.24	Semmens and Martin, 1988
USA	-	1.07-1.24	Ouki et al., 1993
USA	0.78	-	Zamzow et al., 1990
Bigadiç, Türkiye	-	0.94	Çulfaz and Yağız, 2004
Bigadiç, Türkiye	0.7	-	Kurama and Kaya, 1995
Bigadiç, Türkiye	0.11	0.37	This study
Gördes, Türkiye	0.18	0.65	This study

pH change in equilibrium experiments

Since the surface charge of the zeolites can be modified by changing the pH of the solution, the pH is one of the most crucial controlling parameters influencing the uptake of metal ions (Martinez et al., 2004). As shown in Figure 4.10, the equilibrium pH values decreased with increasing initial metal concentrations for both clinoptilolite samples when compared to the initially adjusted pH of 4. However, the difference in hydrogen ion uptake capacities (Figure 4.10A and 4.10B) showed the higher affinity of BC and BCC samples for hydrogen ions over both forms of Gördes samples. This may be explained by the adsorptive characteristics of the impurities found in Bigadiç clinoptilolite. However, no significant difference of hydrogen ion uptake behavior was observed between as-received and conditioned forms of both samples during equilibrium experiments. It is generally observed that better cadmium removal capacity is coupled with low affinity for hydrogen ions, as is

the case for Gördes samples. This reveals the competition between metal ions and H^+ for possibly the same sites on clinoptilolite.

In addition to the role of hydrogen ions in increasing the pH values by exchanging with framework exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) of clinoptilolite throughout the equilibrium experiments, there are also other mechanisms affecting pH:

- Protonation of aluminol and silanol groups (Abollino et al., 2003; Doula and Ioannou, 2003; Ersoy and Çelik, 2002)
- Hydrolysis of metal cations especially at higher metal concentrations (Schnoor, 1996)

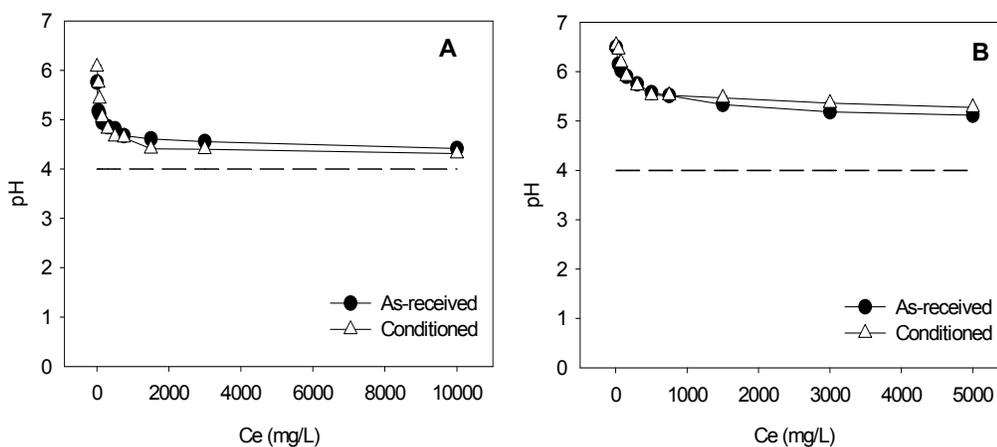
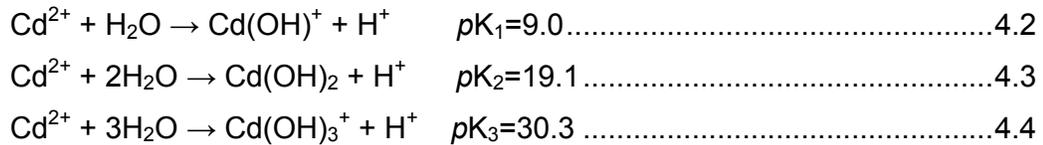


Figure 4.10. pH changes during equilibrium experiments for A. Gördes, B. Bigadiç clinoptilolite samples, regarding adjusted initial pH (dashed line).

Formation of metal complexes may also influence the equilibrium pHs of heavy metal-clinoptilolite interaction. For instance, Mendoza et al. (2006) offered the speciation diagram (Fig. 4.11) of cadmium using the following chemical reactions and equilibrium constants:



It can be observed that cadmium is mainly present in free ion form at pH ≤ 8; the Cd(OH)⁺ ion is formed at pH > 8; most of the cadmium is present as Cd(OH)₂ with the remainder Cd(OH)⁺ at pH > 9 and finally Cd(OH)₃⁻ is the predominant species at pH > 13 (Fig. 4.11). The findings of this study showed equilibrium pH values smaller than 7 for all tested conditions. Therefore, it can be theoretically said that cadmium exists predominantly as free ion when anions and cations resulted from chemicals used is assumed as negligible.

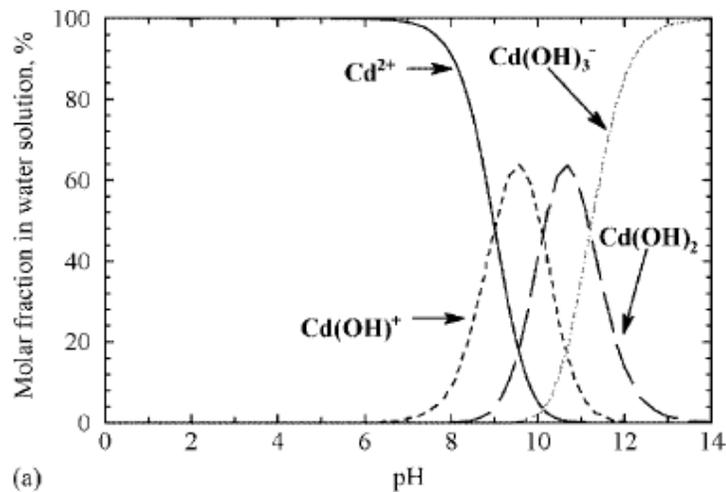


Figure 4.11. Speciation diagram of cadmium in water solution at 25°C (Mendoza et al., 2006).

Exchangeable ions in equilibrium experiments

Investigation of exchangeable cations released out from the framework of the clinoptilolite samples is of particular importance when determining the

prevailing removal mechanisms in cadmium-clinoptilolite interaction. The balance of ions leaving the clinoptilolite structure ($2\text{Na}^+ + 2\text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) and the incoming ion (Cd^{2+}) are presented in Figure 4.12 and 4.13 for as-received and conditioned clinoptilolite samples, respectively. Exchangeable cations were analyzed for three concentrations only. These were selected to represent concentrations where cadmium removal capacity is not reached (~40 mg/L), around the lowest concentration where maximum capacity is reached (~750 mg/L) and a concentration where much more cadmium ions are present when compared to the amount that can be removed (~3000 mg/L).

In cadmium-GC interaction, mostly sodium and potassium ions are exchanged with cadmium ions followed by calcium ions (Fig. 4.12A). As the amount of cadmium retained in GC increases, the ions released from clinoptilolite structure increases too and this increase is noticeable especially for calcium ions. Therefore, this increase can also affect the maximum exchange capacity of GC sample. However, cadmium is generally replaced mostly by calcium and then sodium in BC containing solutions over the whole concentration ranges (Fig. 4.12B). This is not surprising because Bigadiç clinoptilolite is rich in calcium content as chemical composition data also indicates (Table 4.1 and 4.2). The lack of exchange of magnesium ions with cadmium for both as-received samples may come from its presence in partially unavailable sites and/or low selectivity of cadmium ions for magnesium when compared to the other exchangeable cations.

A better correlation between incoming and outgoing ions is observable in cadmium-GCC and -BCC systems (Fig. 4.13). In general, the release trends of exchangeable cations from both clinoptilolite structures showed sodium as the predominant outgoing cation during metal exchange process as expected due to NaCl conditioning. Other than sodium, to a lesser extent, potassium and calcium present on clinoptilolite exchange sites are exchanged with the ingoing cadmium ions at high concentrations for both clinoptilolite samples.

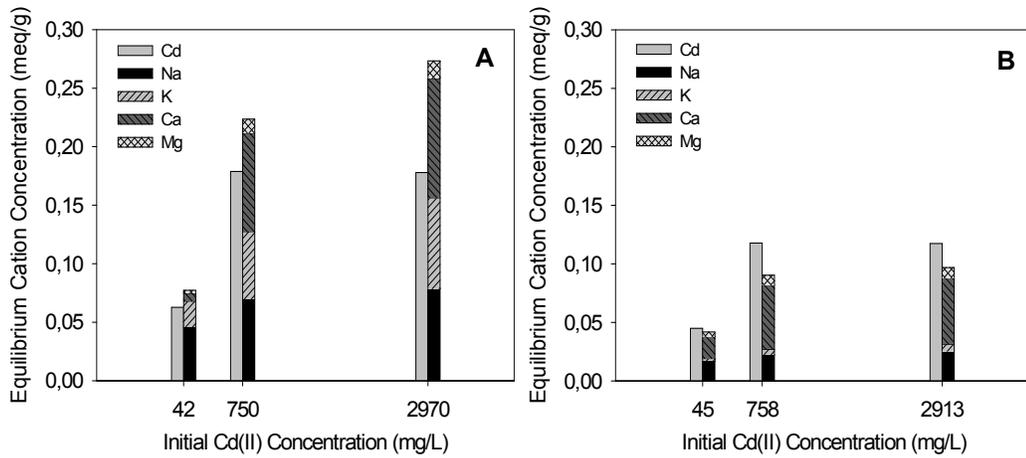


Figure 4.12. Incoming and outgoing ions of as-received clinoptililite samples of A. Gördes and B. Bigadiç

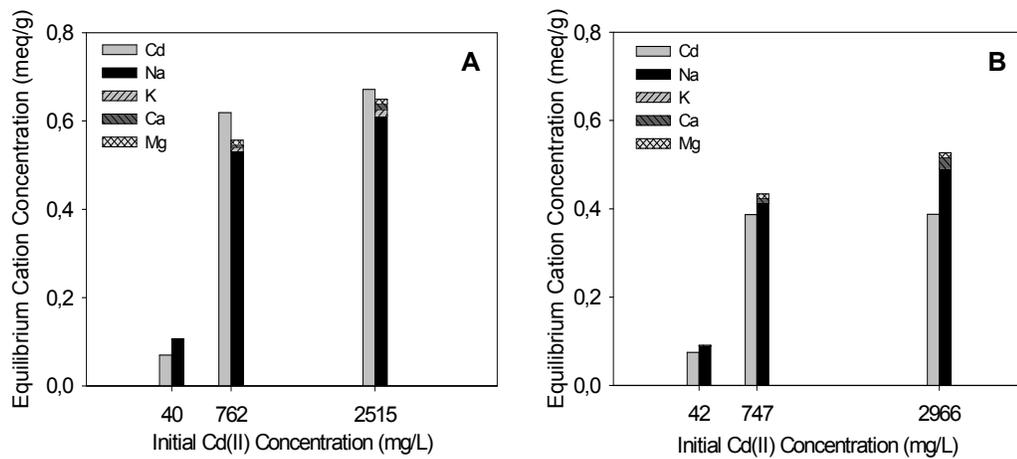


Figure 4.13. Incoming and outgoing ions of conditioned clinoptililite samples of A. Gördes, B. Bigadiç

In the original GC and BC samples, only about 9% and 1% of the total exchangeable cations was sodium, respectively, while a major increase of these initial percentages can be proved by the amount of released sodium ions from the structure for both samples after conditioning. However, examination of the detected outgoing potassium, calcium, and magnesium

ions in the solution during metal exchange for conditioned samples indicates that some of the cations are not exchangeable after exposure to NaCl solution for 24 hours. This finding is also consistent with similar results given in the literature about partial exchange of framework cations with sodium (Semmens and Martin, 1988; Dyer and White, 1999; Çulfaz and Yağız, 2004; Abusafa and Yücel, 2002).

Generally, the quantity of cadmium ion exchanged into the as-received and conditioned form of both clinoptilolite samples agrees well with the outgoing cations found in solution. However, a greater amount of released cations for GC sample may be attributed to the presence of ions arising from the dissolution of impurities or possibly of clinoptilolite itself (Doula et al., 2002; Trgo and Peric, 2003). The same is not observed for BC as is evident from Fig 4.12B and 4.13B, even though a greater percentage of impurities is present (about 50%). This may be due to the different nature of impurities in the two clinoptilolite samples tested in this study. It must also be stated that as the zeolites were not composed of clinoptilolite alone, but contained quartz, biotite and illite; it is not possible to specify which of the phases dissolved to what extent. Based on the findings, it can be argued that the dominating mechanism of sorption is ion exchange and adsorption also plays a significant role as a co-removal mechanism.

4.2.3. Deionised Water-clinoptilolite Interaction

The behavior of both clinoptilolite samples was examined in cadmium-free solutions to shed light into their tendency for protonation and dissolution, as well as release of exchangeable cations under the same conditions in equilibrium cadmium removal experiments. The results are given in Table 4.6 and Figure 4.14. The equilibrium pH increased from the initially adjusted pH in deionised water for all systems (Table 4.6). The pH increase is due to

exchange of hydrogen ions from the solution with the exchangeable cations in the zeolite matrix. The substantial increase in pH for both Bigadiç forms showed its affinity to hydrogen ions. Furthermore, silicon ions were detected in considerable concentrations in cadmium-free solutions, which indicate the dissolution of either clinoptilolite or possibly impurities in Bigadiç samples at experimental pH values. On the other hand, Gördes samples did not show such behavior.

Table 4.6. pH changes and silicon release from clinoptilolite samples

Clinoptilolite		pH _{initial}	pH _{equilibrium}	Si (meq/g)
Gördes	As-received	4.37	6.41	0.03
	Conditioned	4.16	6.86	0.02
Bigadiç	As-received	4.22	8.64	0.09
	Conditioned	4.15	9.31	0.07

The total amount of exchanged cations was around 0.01 meq/g for both Gördes clinoptilolite forms (Fig. 4.14). For the Bigadiç conditioned clinoptilolite, sodium ions were predominantly released into the solution and increased to approximately 0.05 meq/g at the end of the equilibration period. This considerable increase may be explained by the release of excess sodium ions that were sorbed on the surfaces of impurities during interaction with water. For each type of clinoptilolite, sodium was observed to be more easily exchanged than the other cations in the clinoptilolite structure and thus has the largest effect on total amount of released cations. Overall, Bigadiç clinoptilolite, in both of its forms, was seen to release considerably more exchangeable cations into the solution. This may be due to the presence of a higher proportion of impurities when compared to Gördes samples.

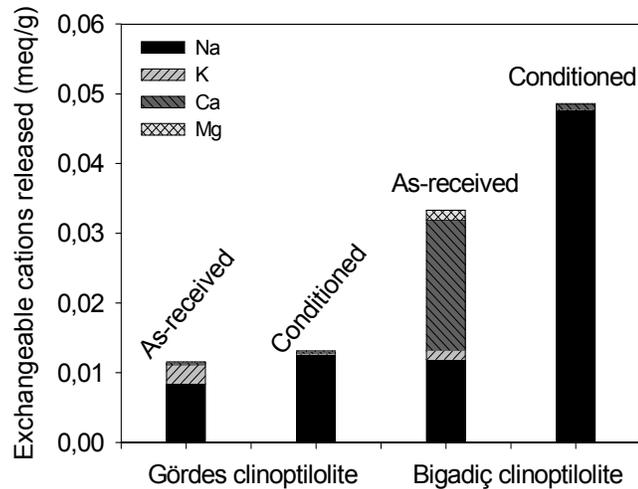


Figure 4.14. Behavior of clinoptilolite samples in cadmium-free solution

4.2.4. Selection of the Clinoptilolite Sample to be used in Further Studies

- Both preliminary and equilibrium experiments showed better performance of Gördes clinoptilolite for cadmium removal,
- Conditioning with NaCl seem to improve cadmium removal considerably,
- Presence of greater proportion of impurities results in a greater uncertainty (and hence difficulty) concerning discussing about exchangeable cations and relevant metal removal mechanisms,
- It is possible to obtain purer clinoptilolite from Bigadiç reserve, however our sample had 50% clinoptilolite and hence possibly not a very good choice for sorbent material in metal removal,
- Overall, Gördes clinoptilolite was chosen for further detailed studies. Even though conditioning was performed with NaCl, before commencement of cadmium removal studies in continuous mode,

other chemicals that may be used for conditioning/regeneration were also tested. The results of these experiments are given in the next section.

4.3. SELECTION OF THE CONDITIONING/REGENERATION CHEMICAL

The effectiveness of clinoptilolite conditioning on cadmium uptake when different chemicals are used is of particular importance for the rest of the study, especially in column regeneration part. The aim of this study is to show the reuse capability of clinoptilolite after exposing it to cadmium several times. Therefore, regeneration of metal loaded clinoptilolite has also considerable importance on reuse potential of the material by means of sustainable removal technologies. For this fact, the performances of various near homoionic Gördes clinoptilolite samples were compared to determine the form with the best efficiency in batch mode experiments. Four different chemicals, namely, NaCl, KCl, CaCl₂ and HCl were tested. As-received Gördes clinoptilolite were initially conditioned with each for 24 hours. Then, metal removal studies in batch mode were conducted. Afterward, these clinoptilolite samples were regenerated with the corresponding chemical by shaking for 24 hours in batch mode. The regenerated clinoptilolite samples (RNaCl, RKCl, RCaCl₂ and RHCl) were then used for cadmium removal again. By this way, both the conditioning and regeneration abilities of the chemicals/c clinoptilolite forms were tested and compared with the performance of as-received Gördes clinoptilolite sample (GC).

In Fig. 4.15, the cadmium uptake capacities of conditioned GC samples are given with their exchangeable cations released into the solution during the experiments. As is evident from the figure, the capacity of the NaCl

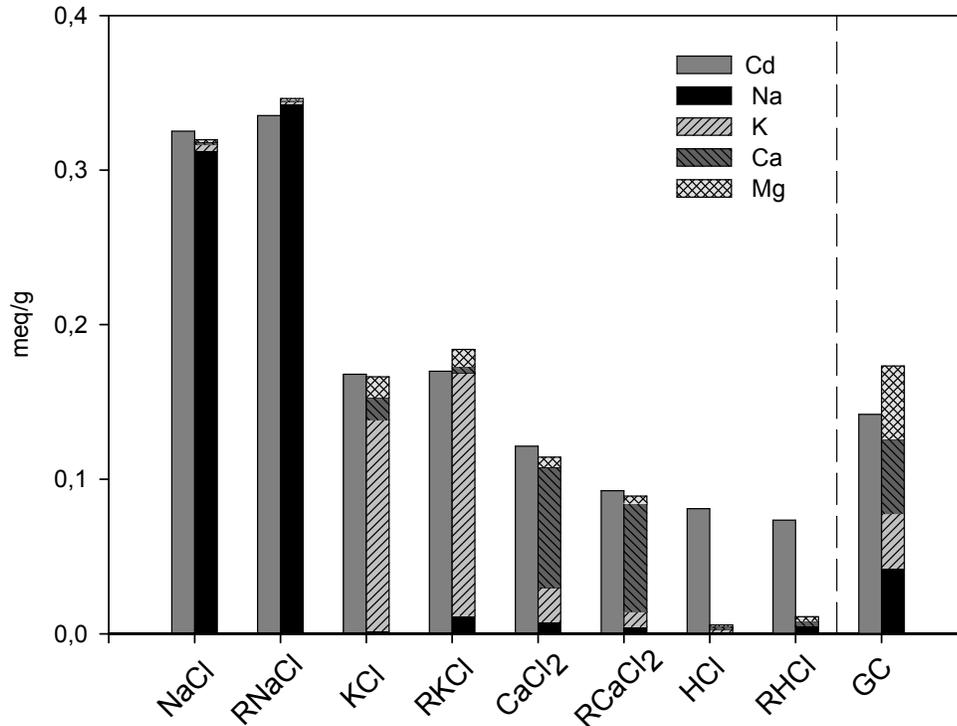


Figure 4.15. Chemical conditioning effect on cadmium removal by Gördes clinoptilolite

conditioned/regenerated form is higher than those of the KCl, CaCl₂ and HCl conditioned/regenerated and as-received clinoptilolite samples. On the other hand, cadmium uptake capacity is decreased considerably when GC sample is treated with CaCl₂ and HCl compared to as-received sample.

In nature, the cations present on clinoptilolite are calcium, sodium, magnesium and potassium. However, the cationic form can be changed by conditioning, and it is well known that the cation on the zeolite has an effect on the metal uptake properties of the zeolite (White and Bussey, 1997). The results of the study are in agreement with this fact by means of attainment of different capacities with different forms. The ion exchange capacity of clinoptilolite depends significantly according to the chemical with which it is pretreated. This can be explained as follows:

Clinoptilolite pretreated with NaCl has an improved uptake of cadmium ions, considerably in agreement with literature findings. Curkovic et al. (1997), Faghihian et al. (1999), and Cincotti et al. (2001) found out the enhancement in the removal efficiency of cadmium ions after conditioning with NaCl. The exchange of sodium with cadmium in the clinoptilolite structure is the easiest and thus has the largest effect on capacity. This is due to the fact that sodium ions are the weakest bound ions or the selectivity of clinoptilolite for sodium is the lowest (Semmens and Martin, 1988); hence, they are most easily exchanged with cations from solutions (Zamzow et al., 1990; Rozic et al., 2005). This fact can also be proven by the correlation found between the amounts of sodium released into the solution and amount of immobilized cadmium ions in Figure 4.15.

In the case of KCl modified forms, a slight increase in the removal of cadmium ions was observed when compared to the as-received sample. This poor exchange capacity can be explained by the location of potassium ions in the framework of zeolites. It is proposed that potassium is located at a specific site in the crystal which is coordinated with six framework oxygens and three water molecules (Abusafa and Yücel, 2002). Therefore, strong bonding at specific sites and low mobility of potassium affects the exchange with cadmium ions.

The underlying reason behind the negative cadmium uptake capacity of CaCl₂ and HCl forms compared to as-received forms is different in nature. In the literature, it is stated that the calcium ions interfere with the uptake of metal ions greatly, and hence increases the amount of zeolite needed to treat a given volume of wastewater (Zamzow et al., 1990); calcium form of the clinoptilolite has high water sorption capacity (White and Bussey, 1997); and the presence of calcium as a competing cation affects the cadmium adsorption negatively (Yuan et al., 1999). In addition to these, the selectivity series given by Semmens and Martin (1988)

$Pb^{2+} > K^+ > Ba^{2+} > NH_4^+ > Ca^{2+} > Cd^{2+} > Cu^{2+} > Na^+$ indicates the low selectivity of clinoptilolite for cadmium when compared to calcium.

The findings in the literature related to zeolites pretreated with HCl have different arguments on metal removal process. Vasylechko et al. (2003) demonstrated that the adsorption capacity of the H-form of clinoptilolite depends on the nature and concentration of acid as well as the duration of contact of clinoptilolite with acid in the process of modification. The most effective adsorption of cadmium was demonstrated by clinoptilolite pretreated with 1M HCl during 24 hrs with capacity of 0.13 meq Cd/g clinoptilolite and was immobilized without considerable dealumination. However, Panayotova (2001) revealed the decrease in exchange capacity of zeolite for Cu^{2+} after HCl conditioning and explained this fact as the increase to some extent in Si/Al ratio (aluminum dissolution) after treatment with HCl. Sprynskyy et al. (2005) also indicated the destruction of the clinoptilolite aluminosilicate structure by HCl.

Among the four solutions used for the desorption of cadmium ions or regeneration of cadmium-loaded clinoptilolites, NaCl removed the maximum amount of cadmium, followed by KCl. According to experimental results obtained, sodium homoionic clinoptilolite, followed by potassium homoionic clinoptilolite gave the best results for the removal of cadmium in this study. However, findings in the literature showed a metal specific removal efficiency of different homoionic clinoptilolites. For example, Milan et al. (1997) found Na-Zeo > Ca-Zeo > K-Zeo > Mg-Zeo exchange capacity order for ammonia removal from anaerobically pretreated piggery manure. Abusafa and Yücel (2002) used natural and cation-enriched (Na^+ , K^+ , NH_4^+ and Ca^{2+}) forms of clinoptilolite for cesium removal and found satisfactory breakthrough capacities (Na-CLI > NH_4 -CLI > K-CLI > As-received-CLI > Ca-CLI) except calcium enriched form. This poor performance of calcium form is referred to be due both to low distribution coefficient and unfavorable exchange kinetics.

Overall, comparison of the exchangeable cations released into the solution during cadmium uptake revealed efficacy of both conditioning and regeneration (i.e. reconditioning) with NaCl and KCl, but the ineffectiveness of CaCl₂ and HCl treatment options. In the light of these findings, it can easily be stated that NaCl is the best conditioning/regeneration agent among the chemicals tested; hence, it will be used throughout further studies.

4.4. STUDIES IN CONTINUOUS MODE

4.4.1. Optimization of Column Conditioning

Determination of the effective cation exchange capacity of clinoptilolite depends significantly on what it is conditioned with and how. The optimization of the conditions of conditioning for effective cadmium removal necessitates understanding the factors affecting the conditioning process to lower the costs and process time. Hence, this part of the study is primarily aimed to find out the optimum conditions of conditioning. For this purpose, the effect of total volume (10, 20, 30 BV), initial pH (5.5, 7), and the water quality (deionised and tap water) used for the preparation of the NaCl solution were investigated in columns packed with Gördes clinoptilolite (Fig. 4.16).

The effect of total conditioning solution volume on cadmium removal efficiency was not found to be considerable. A slight enhancement in cadmium uptake capacity by increasing solution volume from 10 BV to 40 BV was noticed (%5) and this is also in agreement with the finding of Inglezakis et al. (2001) which is 5-10 % increase in effective capacity among the tested solution volumes (10-50 BV). Knowing the competitive sorption of hydrogen ions with other heavy metals at low pHs by zeolites, it is expected to observe higher capacity for high values of pH according to Inglezakis et al. (2001).

However, an increase in the pH of the NaCl solution from 5.5 to 7 was observed to have no effect on cadmium removal capacity. Likewise, water quality was also found not to be an important factor in conditioning despite the diverse ion content of tap water (Table 4.7) when compared to deionised water for the preparation of the NaCl solution. Since the use tap water is cost effective and also gives the same quality for conditioning as deionised water, this result is of particular importance when practical applications are considered. Consequently, the following pretreatment conditions were adopted: the median volume of 20 BV, pH of 5.5 (no pH adjustment), and deionised water. Deionised water was selected to be used in the preparation of NaCl solutions in further studies since the use of tap water would interfere during analysis of exchangeable cations in further stages of the study.

Table 4.7. Chemical analysis of tap water^a

Ions	mg/L^b
Na ⁺	72 ±0.6
K ⁺	4
Ca ²⁺	74 ±0.5
Mg ²⁺	22 ±0.4
NO ₃ ⁻	6 ±0.2
SO ₄ ²⁻	20 ±2
Cl ⁻	120 ±2

a. $\lambda = 960 \pm 9 \mu\text{S/cm}$ (24°C)

b. Conc. presented as mean and standard deviation of three replicates

4.4.2. Effect of Volumetric Flowrate and Particle Size

Following the determination of optimum conditioning conditions, the influence of volumetric flowrate on cadmium uptake for conditioned GC samples was

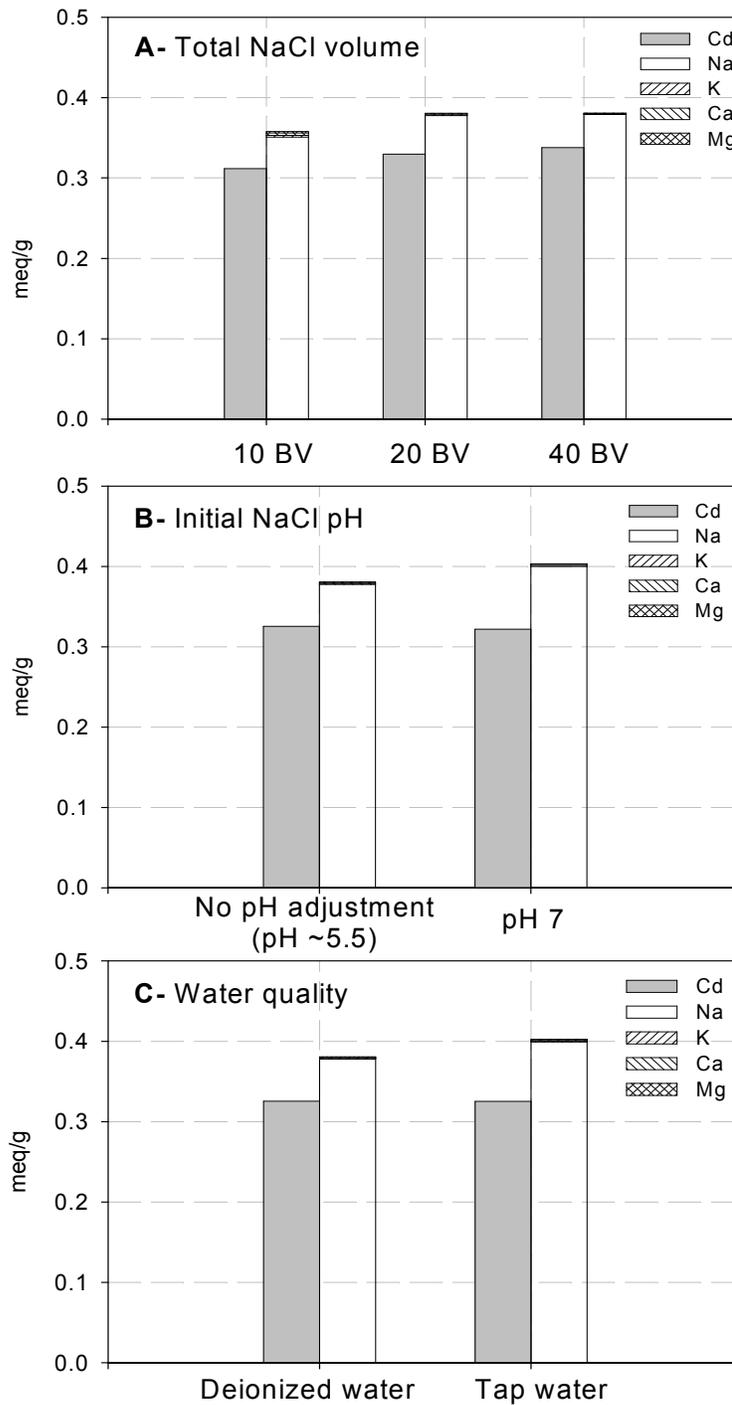


Figure 4.16. The impact of operational and chemical conditions of conditioning on cadmium removal in columns packed with G6rdes clinoptilolite

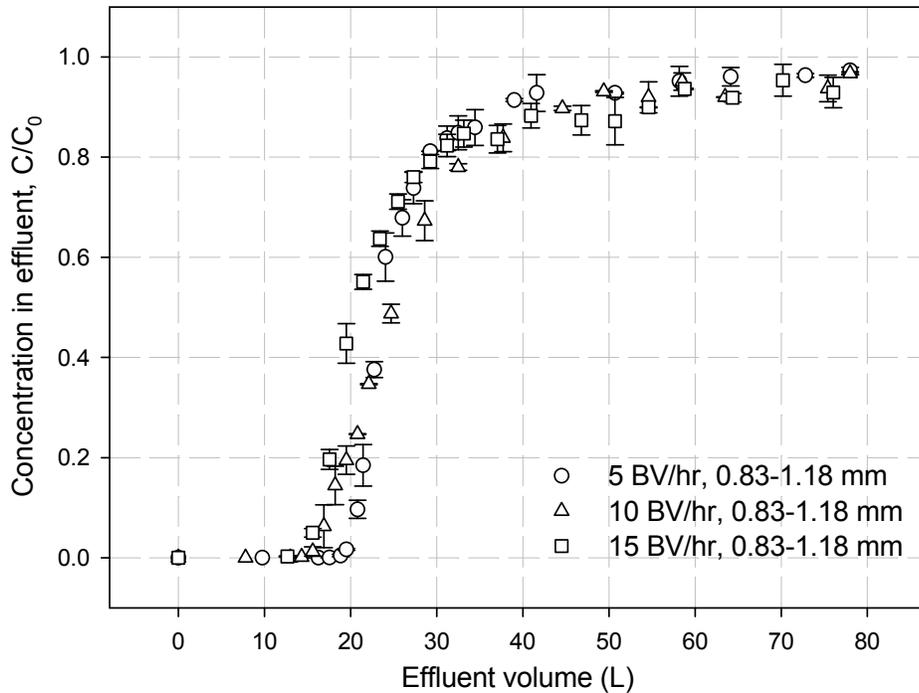


Figure 4.17. Effect of volumetric flowrate on cadmium breakthrough curves

investigated. The typical breakthrough curves for the three flowrates tested are given in Figure 4.17. As can be seen from Fig. 4.17, breakthrough was achieved around 19 L, 16 L, 13 L for 5, 10 and 15 BV/hr, respectively. Approximately 60 L of metal solutions was used to exhaust the beds for all tested flowrates. The metal removal capacity utilized at exhaustion is calculated approximately as 0.82 meq/g and 0.84 meq/g by lower volumetric flowrates 5 and 10 BV/h, respectively, while this is 0.64 meq/g for 15 BV/h. In theory, the operating capacity is independent of the flowrate (Inglezakis, 2005). However, findings of the study showed flowrate-dependent cadmium removal capacity, particularly at a higher flowrate. The disproportional distribution of metal uptake capacity found may be attributed to the lower residence times and the corresponding failure of attaining local equilibrium (Inglezakis and Grigoropoulou, 2004). In other words, ion exchange is usually

not fast enough to allow the exchange reactions while the ion exchange zone moves in the flow direction in a limited time (Helfferich, 1995).

Consequently, flowrates higher than 15 BV/h should be avoided since the degree of column utilization is unfavorable and breakthrough occur much faster for cadmium removal. On the other hand, flowrates lower than 5 BV/h are supposed to be favorable on metal removal efficiency; however it results in loss of time in practice. In addition, no comparable data were presented in the literature for the examined flowrates for cadmium removal via packed bed columns. As a result, 10 BV/h was selected to be a reasonable flowrate to be used during further studies.

The effect of two particle sizes on cadmium removal by GC in packed beds is shown in Figure 4.18. Decreasing the particle size from 0.83-1.18 mm to 0.35-0.50 mm did not enhance the metal removal capacity detectably in column mode. The cadmium removal capacity utilized at exhaustion (i.e. total capacity) is calculated roughly as 0.84 meq/g and 0.90 meq/g for 0.83-1.18 mm and 0.35-0.50 mm particle sizes, respectively, at 10 BV/h flowrate. The significant reduction in particle size does not lead to a major increase in cadmium uptake capacity. It is generally accepted that by decreasing the particle size, the performance of adsorption and ion exchange processes are improved due to accessibility of active sites located in the channels of the clinoptilolite structure and low pore diffusion resistance in small sizes (Inglezakis and Grigoropoulou, 2004; Sarioglu, 2005). However, results indicated that among the two ranges of particle sizes tested, this is not the case. This may be attributed to the bypassing of the pore clogging effect which influences the diffusion phenomena via washing of clinoptilolite samples before use in column application.

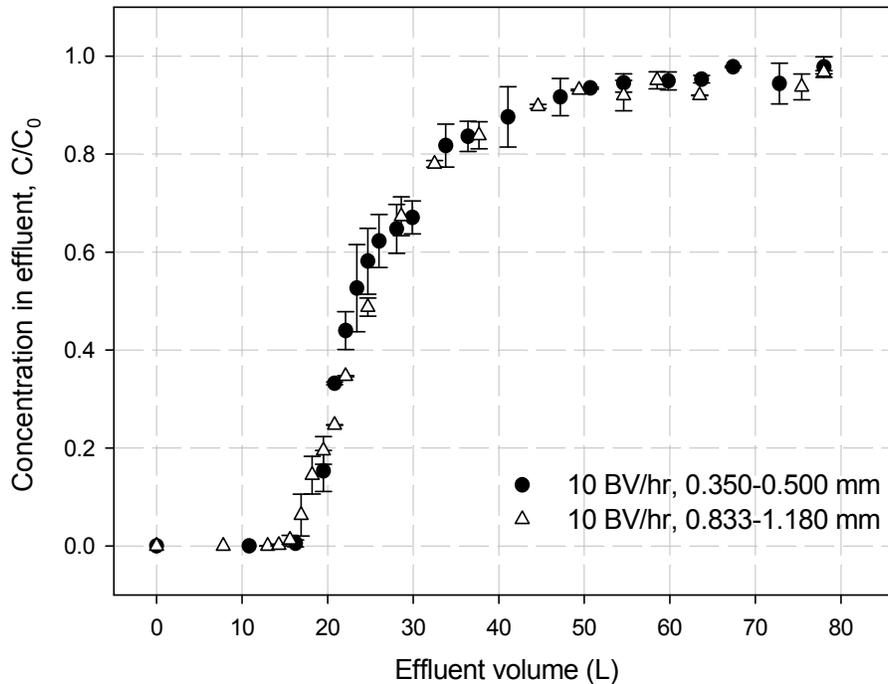


Figure 4.18. Effect of particle size on cadmium breakthrough curves

Moreover, the maximum uptake capacity determined to be 0.65 meq/g during batch mode studies is seen to be exceeded significantly even at an initial concentration of 200 mg/L which is much lower than the minimum concentration (750 mg/L) determined from isotherm studies to give the maximum capacity. Consequently, 0.83-1.18 mm size was chosen for the investigation of the reuse potential of exhausted clinoptilolite samples.

pH changes during volumetric flowrate and particle size experiments

Hydrogen ion uptake shows distinct variations with tested flowrates and particle sizes unlike that of cadmium (Fig. 4.19). During the metal removal process pH values changed, following the opposite shape of the breakthrough curves. The initially adjusted pH value of 4 was raised to about 6 at the earlier stages of the runs due to protonation of clinoptilolite and amounted to around 4-4.5, which is the pH of influent cadmium solution,

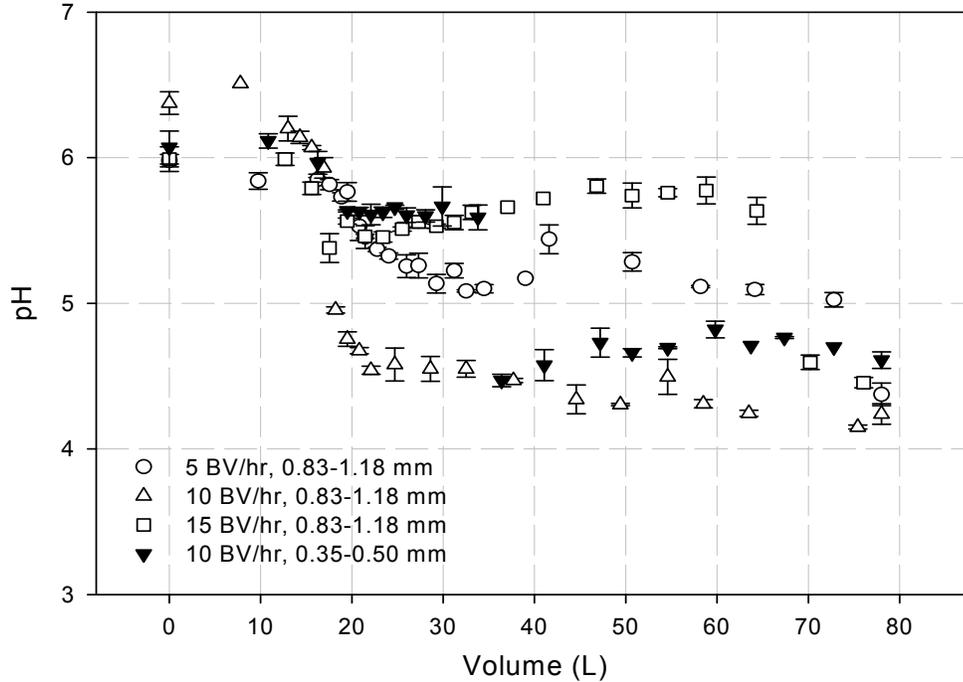


Figure 4.19. pH change with percolated volume in all runs

close to exhaustion, at later stages for all tested volumetric flowrates and particle sizes.

There are two significant points about the results presented in Figure 4.19. For the 15 BV/hr run, relatively lower cadmium removal is seen which is coupled with considerably higher effluent pH values throughout the run. On the other hand, for the 10 BV/hr run, after breakthrough (>20 L), pH is seen to decrease to about 4.5. For 15BV/hr, where possibly protonation is fast enough to take place and cadmium removal is not, pH remains considerably high (~5.5-6.0) until exhaustion.

Secondly, when the different particle sizes with same flowrate (10 BV/hr) are compared both are shown to yield significant pH drops yet at different points on the breakthrough curve. For the larger particle size, this occurs between

10-20L, however for the smaller particle size, it is between 30-40L (Fig. 4.19). For the latter, this somehow corresponds to a region where a slight jump in cadmium removal is observed (Fig. 4.18). Considering that parallel columns were operated and the standard deviations are quite low, the pH drops are real. The difference in pH profile between two particle size profiles is quite evident, even though no major difference was observed for cadmium removal.

Exchangeable ions

The profile of outgoing ions versus volume for each tested experimental parameters are given in Fig. 4.20. When the cadmium solution is first fed to the column, it exchanges cadmium ions with exchangeable cations in the structure of clinoptilolite of different ion exchange zones in the flow direction. As the feed is continued, the top layers of the clinoptilolite bed are constantly exposed to fresh cadmium solution. Eventually, the clinoptilolite bed loses its capacity for removing cadmium ions and becomes exhausted. In the light of this brief introduction, the amount of the release of exchangeable cations and the uptake of cadmium ions by clinoptilolite was investigated to enlighten the mechanisms involved in cadmium removal with clinoptilolite. As evidence for the purpose of conditioning, sodium ions were the primarily released into the solution, followed by little amounts of potassium and calcium, respectively, in all runs. Sodium ions, as expected, began to descend at breakthrough point as the exchange sites becomes fully exhausted with cadmium ions and leveled off at exhaustion point.

Magnesium ions, on the other hand, show an interesting series of profiles. For 5 BV/hr run, a significant peak is observed around breakthrough point,

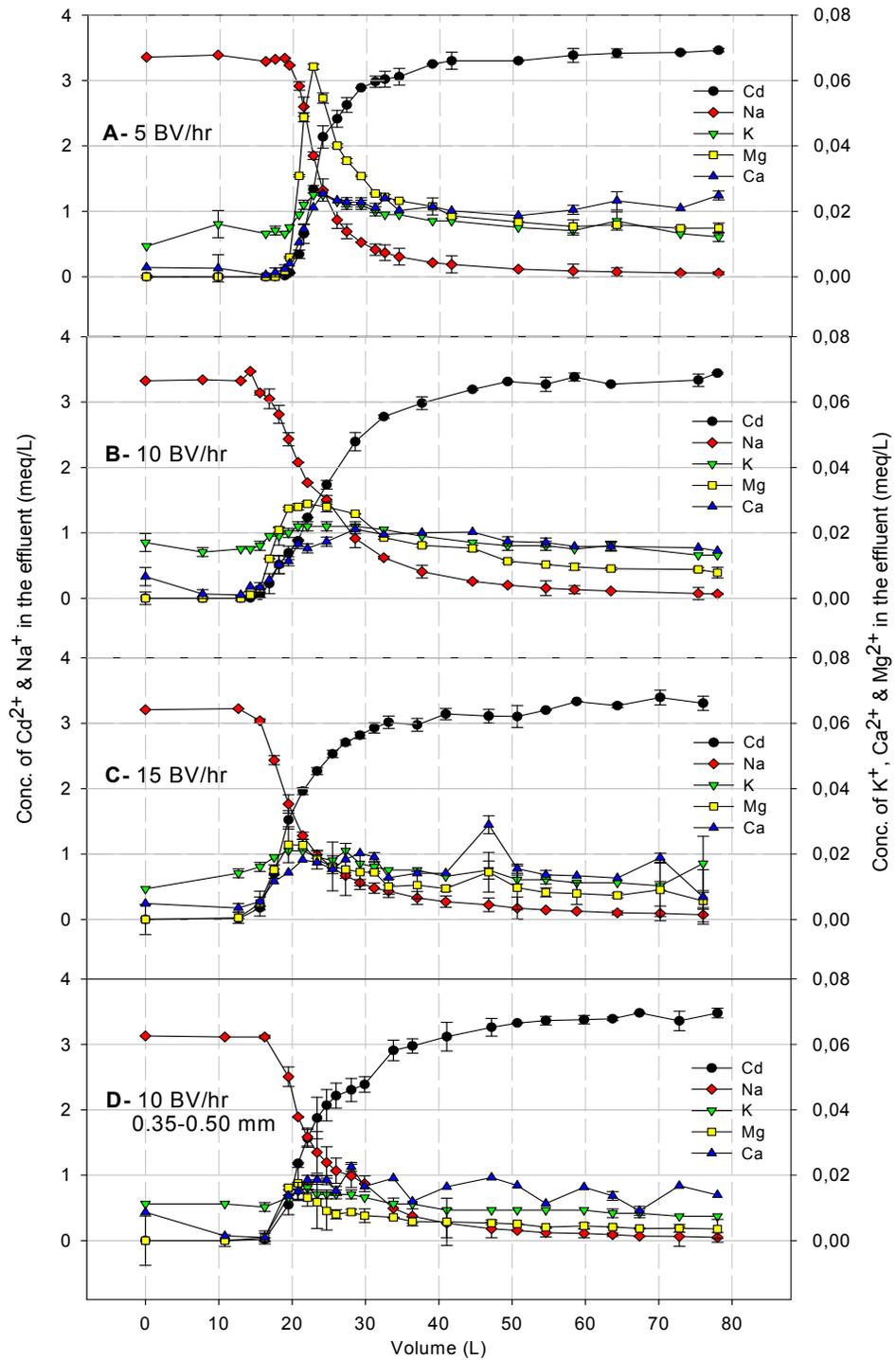


Figure 4.20. Relationship between cadmium and the concentration of exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in the effluent. A. 5 BV/h & 0.83-1.18 mm, B. 10 BV/h & 0.83-1.18 mm, C. 15 BV/h & 0.83-1.18 mm, D. 10 BV/h & 0.35-0.50 mm.

however, progressively smaller peaks are observed for 10 BV/hr, 15 BV/hr and 10 BV/hr smaller particle size runs. This finding indicates the presence of a different condition enabling magnesium exchange at 5 BV/hr. Compared to the other flowrates, 5 BV/hr enable the largest retention time in the column and hence may provide enough time for cadmium to move inside the channels of clinoptilolite to reach the magnesium-occupied sites which are too difficult to reach otherwise. Smaller particle size, however, at 10 BV/hr, does not enable the right conditions for such cadmium-magnesium ion exchange.

A comparison between the cadmium uptake and the total amount of exchangeable cations released from clinoptilolite is given for all runs in Fig. 4.21. The generally good agreement between the two indicates ion exchange as the dominant removal mechanism. However, the difference in coincided plots also point to the presence of adsorption as another prevailing mechanism for the removal of cadmium ions in clinoptilolite packed bed columns.

4.4.3. Regeneration of Metal-loaded Clinoptilolites

Clinoptilolite beds should be regenerated so that the clinoptilolite can be economically reused in further cycles several times and that the metal removed can be eluted once the beds have been exhausted with wastewater. This further enables metal recovery from the eluate. For this purpose, a series of exhaustion (cadmium removal) and regeneration cycles were performed to determine if elution of clinoptilolite bed was possible, and if cadmium can be concentrated in the eluate. In order to recover the adsorbed cadmium from the clinoptilolite bed and restore the clinoptilolite for the next cycles, 1M NaCl solution at a flowrate of 2 BV/h was passed through the column after each exhaustion cycle. The results obtained in the

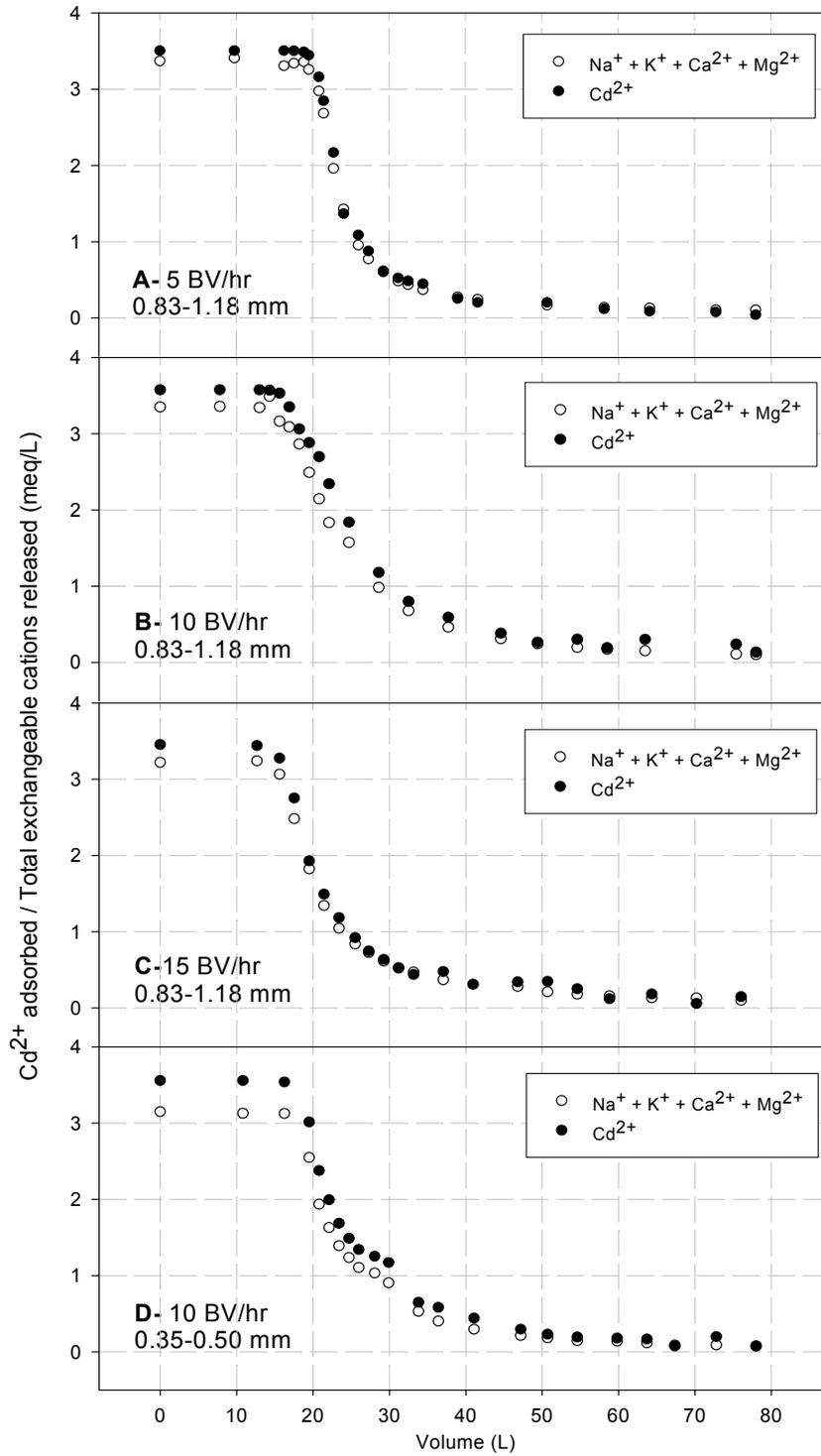


Figure 4.21. Comparison between cadmium uptake and total amount of exchangeable cations. A. 5 BV/h & 0.83-1.18 mm, B. 10 BV/h & 0.83-1.18 mm, C. 15 BV/h & 0.83-1.18 mm, D. 10 BV/h & 0.35-0.50 mm.

exhaustion/regeneration studies are represented in Fig. 4.22. The columns were operated at breakthrough point set at about 10% for the first cycle and about 1% due to increasing cadmium uptake capacity utilized at breakthrough for the rest of the cycles in exhaustion studies. Metal removal capacities attained at breakthrough were determined as approximately 0.62 meq/g and 0.66 meq/g for the first and second exhaustion cycles, respectively, and 0.84 meq Cd/g clinoptilolite for the last three cycles. At the fifth exhaustion cycle, clinoptilolite exhibited an operating capacity that was 36 % higher than that obtained in the first cycle. Cadmium ions on exhausted clinoptilolite bed were eluted effectively as also seen from the increasing metal uptake capacity in progressing exhaustion cycles with 1M NaCl solution in regeneration cycles. However, the elution of cadmium ions remained around 0.60 meq Cd/g clinoptilolite for all regeneration cycles. This showed the constant cadmium recovery efficiency in spite of increasing metal uptake capacity in exhaustion cycles. Cadmium removed by clinoptilolite is concentrated in the eluates by about 7 times.

Since the material in the column was not changed, the increase in the metal removal efficiency may be attributed to several possible mechanisms. Ion exchange is a dynamic process, where the binding forces between the cations and the zeolite matrix are relatively weak (Inglezakis et al., 2003). Therefore, clinoptilolite gets closer to the homoionic Na-form as strongly bonding cations resident on a specific site exchange with sodium with the effect of concentrated NaCl in progressing regeneration cycles. This can be explained by the examination of released ions from structure to solution during each exhaustion cycles (Fig. 4.23).

It can be seen from Fig. 4.23 that cadmium is replaced primarily with sodium ions as expected and potassium also participates ion exchange in small amounts in progressing exhaustion cycles. The detection of potassium ions is

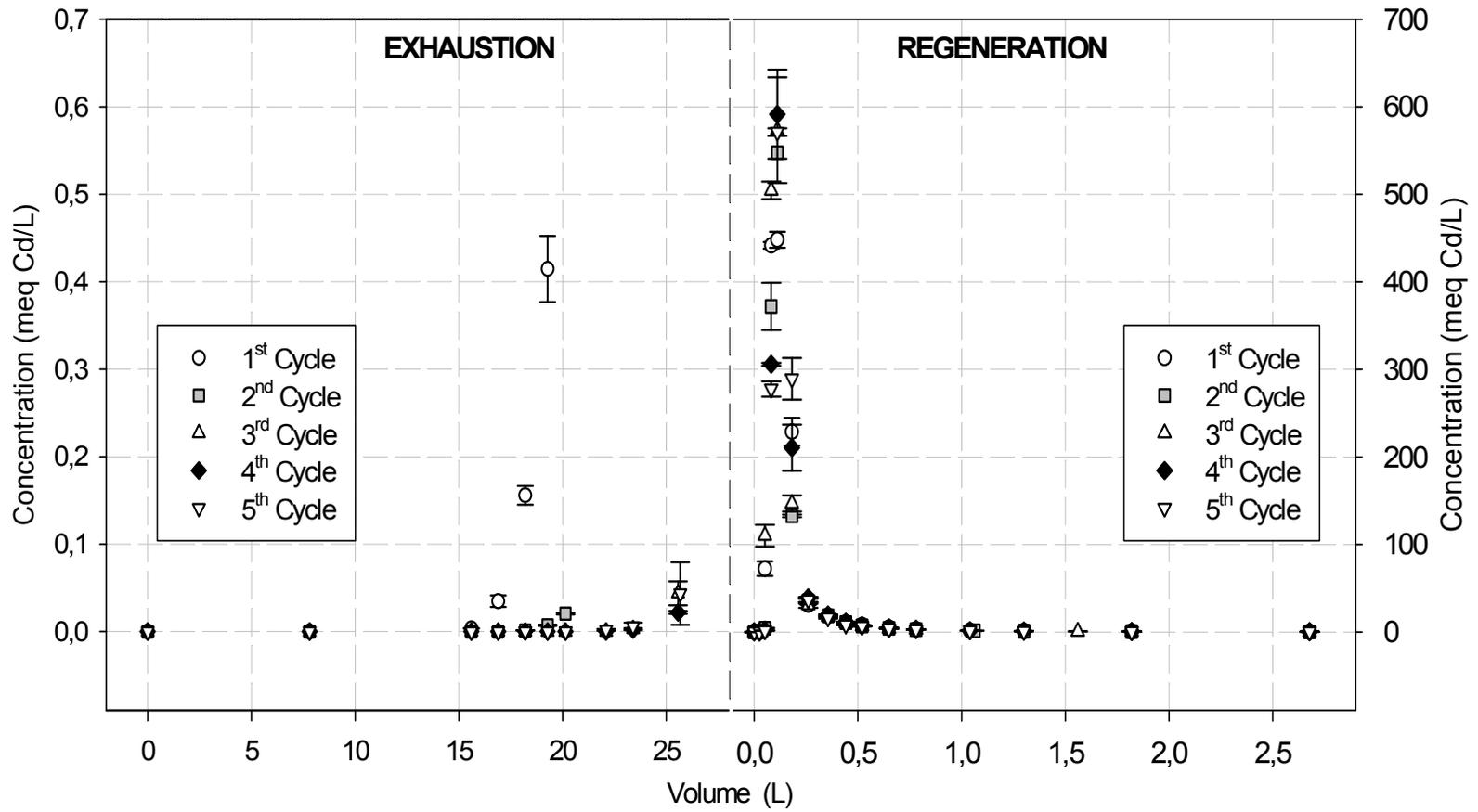


Figure 4.22. The exhaustion of clinoptilolite bed and elution of cadmium during regeneration in progressing cycles

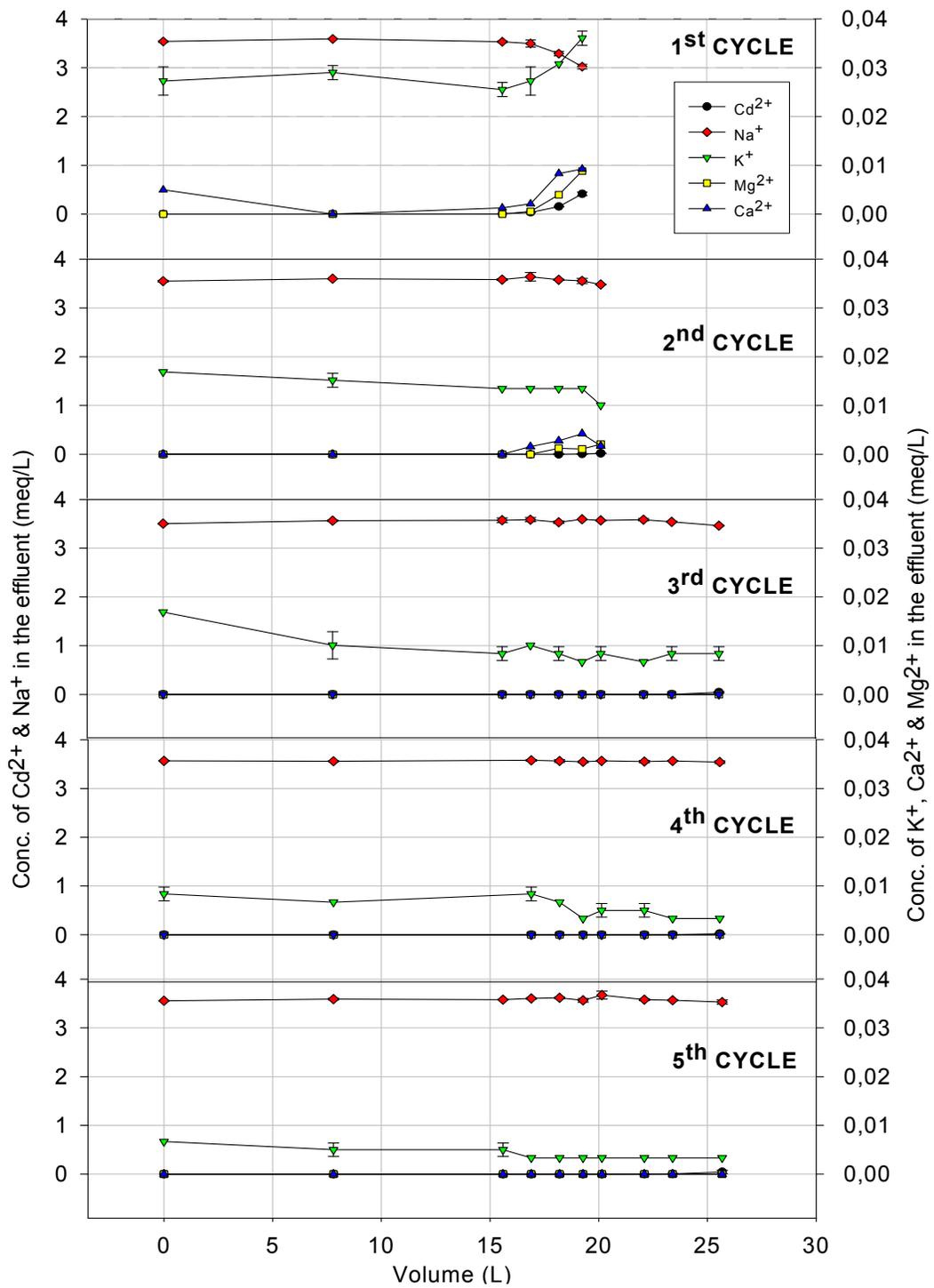


Figure 4.23. Release of exchangeable cations during progressing exhaustion cycles

not surprising in all cycles since Gördes clinoptilolite is potassium rich in its nature (Table 4.1 and 4.2). However, from the second exhaustion cycle forward, magnesium and calcium were diminished in exchange process. This provides evidence for homoionic Na-clinoptilolite to be created after exposing concentrated NaCl solution in progressing cycles to explain the increasing cadmium uptake capacity.

Cadmium replacement, especially with low mobility and strongly bonded cations in exhaustion cycles, may make replacement of sodium with cadmium in regeneration steps easier compared to other structural cations. Thus, this mechanism may indirectly improve the conditioning efficacy and metal uptake capacity as well.

It was also possible that the cadmium ions that were not eluted during the first regeneration could come off during later cycles (Zamzow et al., 1990), and may interfere with the calculation of the amount of metal sorbed.

The entrapped Cl⁻ ions in the channels or cavities of clinoptilolite after regeneration with NaCl may stabilize the surface groups by the formation of outersphere complexes with surface central metals and enhance the adsorption of cadmium indirectly in exhaustion steps (Doula and Ioannou, 2003).

Regeneration experiments showed how strongly cadmium ions were immobilized by clinoptilolite. The cadmium recovery efficiency was about 97 % and 91 % in the first and second regeneration cycles, respectively, but decreased to about 72 % for the last three cycles. The lack of elution of all sorbed cadmium at the end of regeneration experiment might be attributed to the formation of inner-sphere complexes and surface precipitates. According to Doula and Ioannou (2003), as metal concentration increases, metal ions are forced into internal sites and also form inner-sphere complexes which are

more stable due to the formation of covalent bonds. Therefore, the type of complexation can affect the rate and reversibility of sorption reactions where inner-sphere complexation appears to be irreversible. Gunneriusson (1994) also stated slower desorption or lower recovery of cadmium due to occlusion in the goethite structure. Nevertheless, this should not pose a problem during practical applications, since bound cadmium is unlikely to be released if the spent clinoptilolite is to be sent to a landfill, etc.

The specific surface area of all forms of Gördes clinoptilolite samples was determined by BET method using N₂ as adsorbate in Quantochrome Autosorb Automated Gas Sorption System. However, this technique could not be applied because N₂ could not be adsorbed on the clinoptilolite samples that were used in five exhaustion/regeneration cycles. This could indicate some form of modification of the surface properties of clinoptilolite. Further studies are required to understand this phenomenon and whether this is an indication of complex formation on the outer or inner surfaces of the clinoptilolite sample and clogging of its pores, hence, disabling N₂ entry.

As mentioned earlier, pH is a very important parameter affecting efficient removal of heavy metals by ion exchange. As shown in Fig. 4.24, the initially adjusted pH value of 4 changed during cadmium removal cycles and reached around 5 in the effluent at breakthrough point. In the successive regeneration steps, the pH values decreased suddenly from 5 to minimum values of approximately 3.9, 3.8, 3.5, 3.2, and 2.8 for progressing cycles, respectively. They were equilibrated at approximately 4.5 for all cycles when the regeneration was stopped.

Analysis of silicon and aluminum in the aqueous phase was also done and the results are presented in Fig. 4.25. Aluminum was not detected in exhaustion cycles and exhibits a small peak in the early phase of regeneration for all cycles. However, silica yields a much different pattern,

and is released mostly at the initial exposure of cadmium and NaCl solution in progressing cycles.

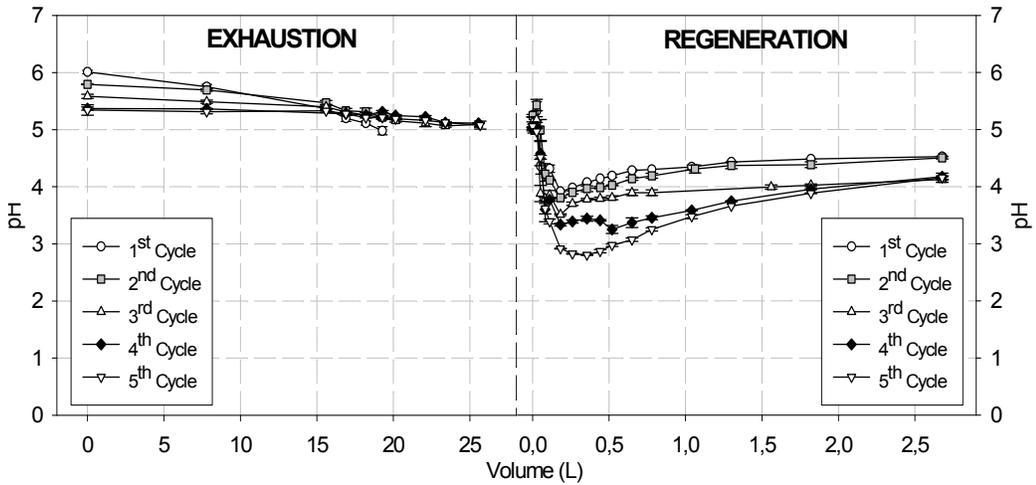


Figure 4.24. pH profiles of exhaustion and regeneration studies in progressing cycles

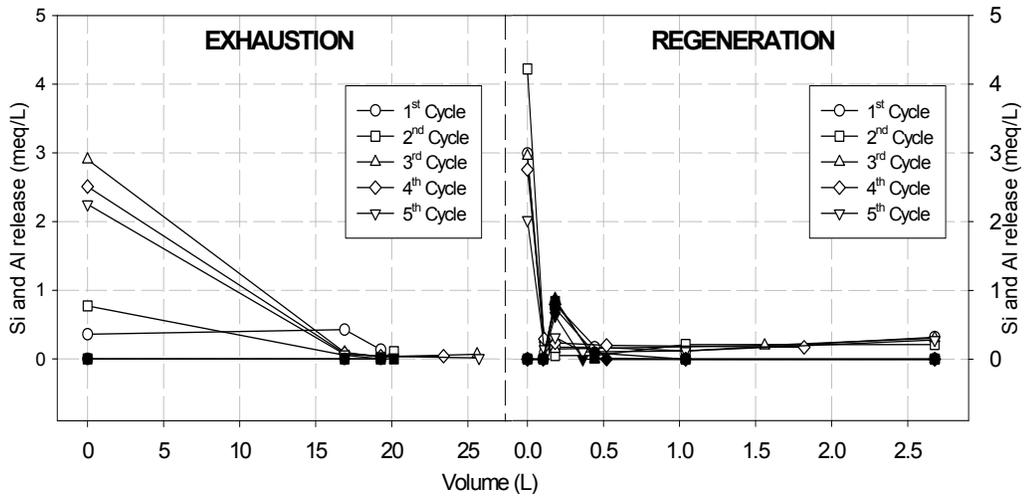


Figure 4.25. Silicon (open symbols) and Aluminum (filled symbols) release during exhaustion and regeneration studies in progressing cycles.

The observed pH profiles during exhaustion and regeneration cycles (Fig. 4.24) may be related to silica and aluminum release from clinoptilolite structure. Silica release into the solution is continuously increased at the initial exposure of cadmium solution with decreasing initial pH values at exhaustion cycles. Doula et al. (2002) discusses that due to inner sphere complexation, as more copper is sorbed, more silicon is released into the solution. Results shown in Figure 4.25 may also support this discussion. During the first and second cycles much less silica release is observed, and less cadmium uptake, when compared to the further cycles where much higher cadmium removal was achieved. On the other hand, silica release during the earliest stage of regeneration can not be explained with the available data.

Aluminum dissolution increased with the increase in ionic strength. The considerable decrease in pH may be attributed to the hydrolysis of cadmium ions with the increased amounts due to pulse release. Also, the dissolution of aluminum ions due to increasing protonation and ionic strength may contribute to decrease in pH during regeneration cycles, parallel to Doula et al's discussion (2002) for copper adsorption by clinoptilolite.

CHAPTER 5

CONCLUSIONS

Clinoptilolite samples from two important reserves in Turkey were compared with respect to their cadmium ion removal from aqueous solutions considering the effect of various parameters in batch mode applications.

Initial results demonstrated that pH 4 was found as the optimum initial pH for both clinoptilolite samples, with 6 hrs and 24 hrs as the equilibration period for Manisa-Gördes and Balıkesir-Bigadiç clinoptilolite samples, respectively. This is interpreted as the effect of diverse removal mechanisms of cadmium removal in the two clinoptilolite samples. Particle size (0.17-0.83 mm, 0.83-1.18 mm, 1.18-1.40 mm) was found to have no significant effect on metal removal efficiency. This indicated that high surface area does not have an effect on the ion exchange mechanism. Cadmium removal occurs mainly via exchangeable cations found in the internal/available sites rather than on the surfaces of clinoptilolite. Cadmium uptake was increased by 47% and 27% for as received, 15% and 18% for conditioned GC and BC samples, respectively by increasing temperature from 25°C to 50°C. Prewashing of the as-received clinoptilolite samples showed that surface dust make no changes on metal removal capacity.

Equilibrium cadmium removal experiments carried out with both samples were fitted to well known Langmuir and Freundlich isotherm models using non-linear regression analysis. Langmuir isotherm model revealed a better correlation with experimental data yielding maximum capacities of 0.18

meq/g for GC and 0.11 meq/g for BC sample. However, metal removal capacities after conditioning were increased to 0.65 meq/g (261% increase) and 0.37 meq/g (236% increase) for GCC and BCC, respectively. Generally, the quantity of cadmium ion exchanged compare closely with the outgoing cations found subsequently in solution. The difference between the adsorption capacity of Gördes and Bigadiç clinoptilolites can be explained as participation of ion exchange accompanied with external or/and internal surface adsorption. The results reveal a significant difference between the cadmium uptake capacities of Gördes and Bigadiç samples. The purity of clinoptilolite, identity of impurities, accessibility of exchangeable cations all contribute to this observed difference.

Overall, results indicate that use of samples from Gördes reserve is more advantageous in terms of both rate and capacity of cadmium ion removal when compared to samples from Bigadiç reserve. These results are valid for the clinoptilolite samples tested in this study, and may not be representative of the entire reserves.

The performances of the different homoionic GC samples were compared to determine the form with the best efficiency by means of conditioning and regeneration, and the order of cadmium exchange was found as; Na-Clinoptilolite>K-Clinoptilolite>As received-Clinoptilolite>Ca-Clinoptilolite>H-Clinoptilolite. Furthermore, none of the parameters tested for the enhancement of pretreatment conditions was found to affect cadmium removal significantly.

In column experiments, the metal removal capacity utilized at exhaustion is calculated approximately as 0.82, 0.84 and 0.64 meq/g for 5, 10 and 15BV/h, respectively. Decreasing the particle size from 0.83-1.18 mm to 0.35-0.50 mm did not enhance the metal removal capacity detectably indicating that pore diffusion resistance is not a major limiting factor in tested particle sizes.

A comparison between the cadmium uptake and the total amount of exchangeable cations released from clinoptilolite clearly revealed the ion exchange as a dominant removal mechanism with some contribution of adsorption.

The cadmium removal capacity of conditioned GC sample increases with the number of regenerations. Five conditioning and regeneration cycle was conducted and at the fifth exhaustion cycle, clinoptilolite exhibited an operating capacity that was 36 % higher than that obtained in the first cycle. After regeneration, cadmium is collected in a small volume (2.6 L), and concentrated by about 7 times enabling its recovery such as by electrolysis.

Overall, according to the samples tested in this study, Gördes clinoptilolite has a great potential for use in industrial applications especially for industries discharging wastewaters containing cadmium, when compared to Bigadiç sample as an alternative low cost material. Further specific investigations are, however, required for a more comprehensive assessment of the clinoptilolite available in the reserves.

CHAPTER 6

RECOMMENDATIONS

A list of suggestions for further studies may be in the order of source (deposit) application, laboratory application and finally industrial application as given;

- A comprehensive mineralogical and chemical characterization of clinoptilolite samples, even for the same origin.
- Use of clinoptilolites in its original as-received forms (i.e. no drying and storing in desiccators) for experimental studies
- Study on the effect of presence of inorganics and organics in the aqueous phase on process efficacy
- Investigation of the effect of multi component (i.e. mixed metal solutions) ion exchange systems
- Optimization of regeneration conditions under different experimental conditions
- Metal removal using industry originated wastewaters

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APPENDIX A

CALIBRATION CURVES

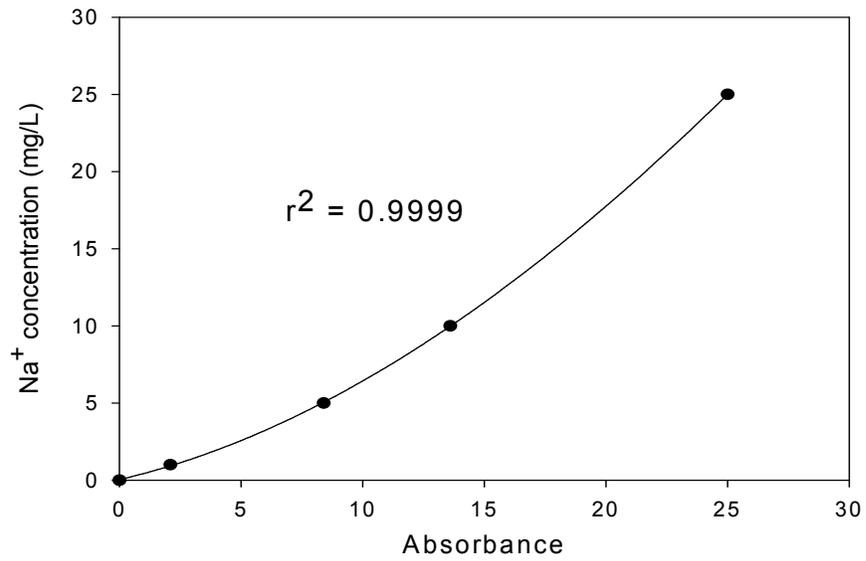
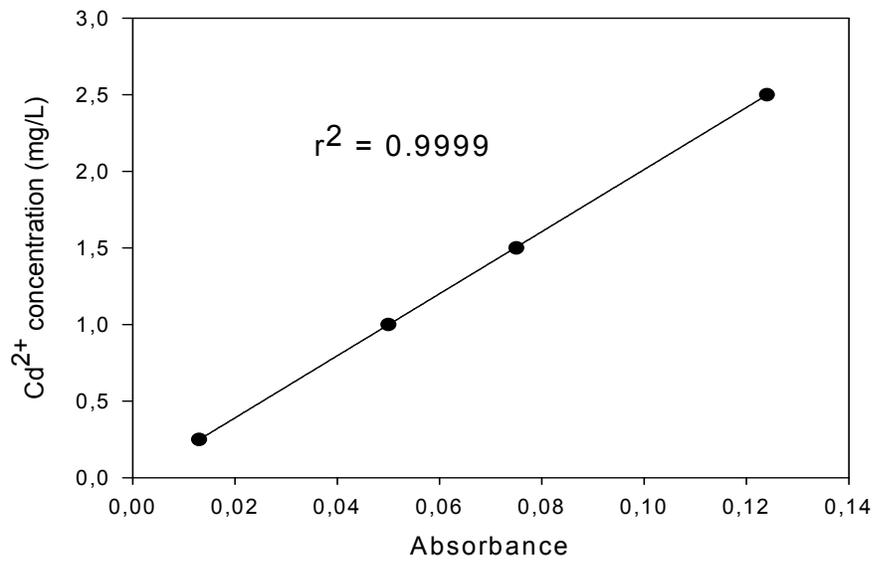


Figure A.1. Calibration curves. Cd²⁺ Calibration, Na⁺ Calibration

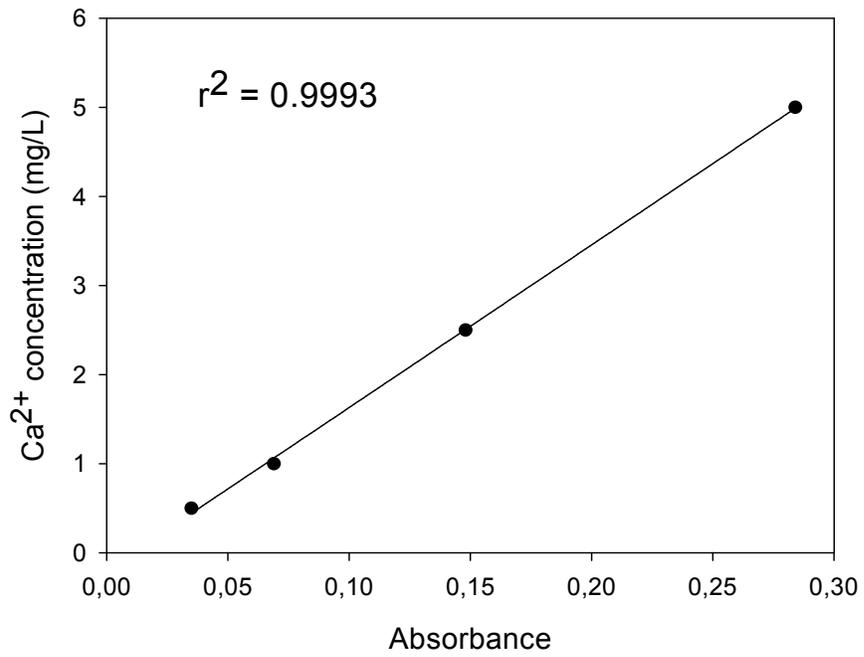
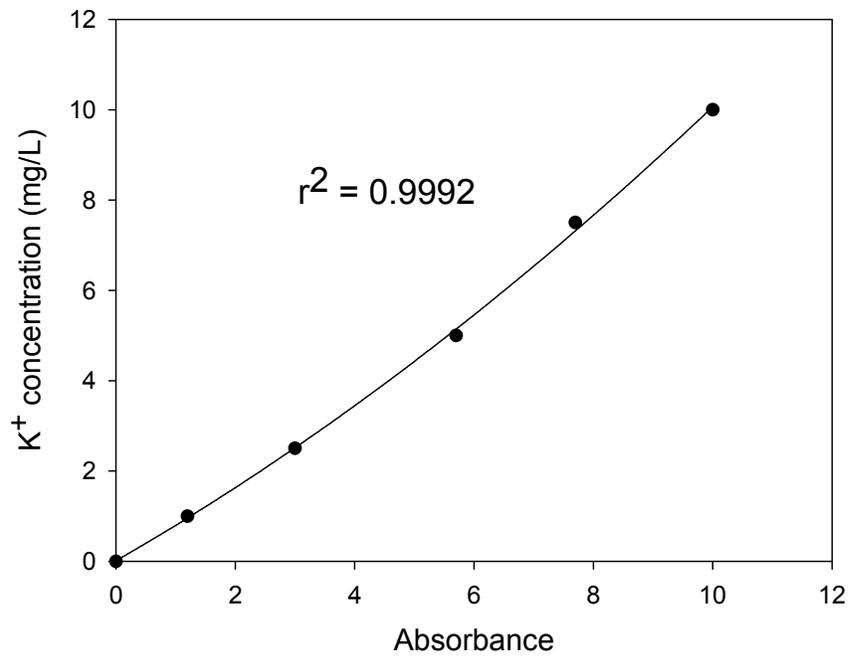


Figure A.2. Calibration curves. K⁺ Calibration, Ca²⁺ Calibration

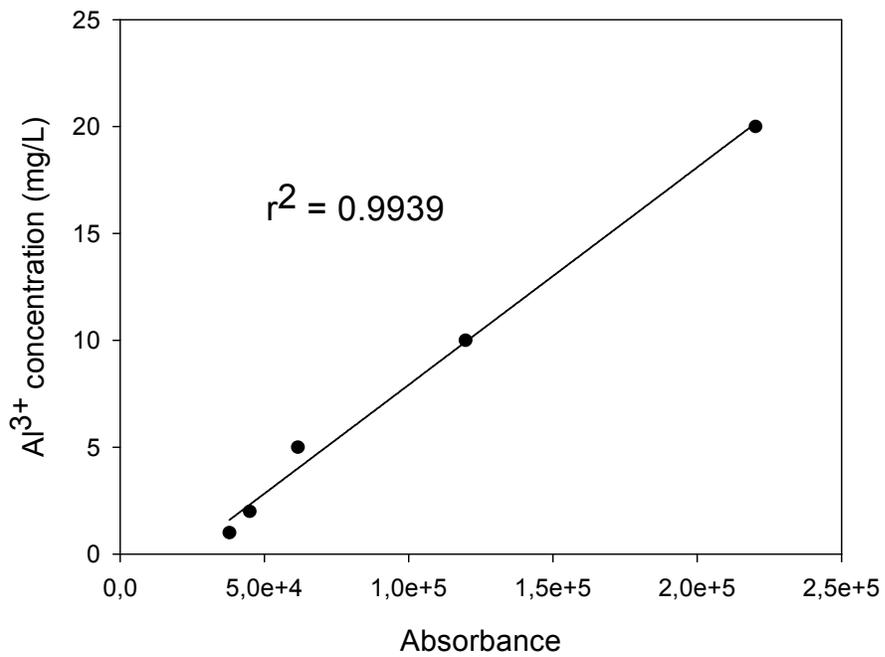
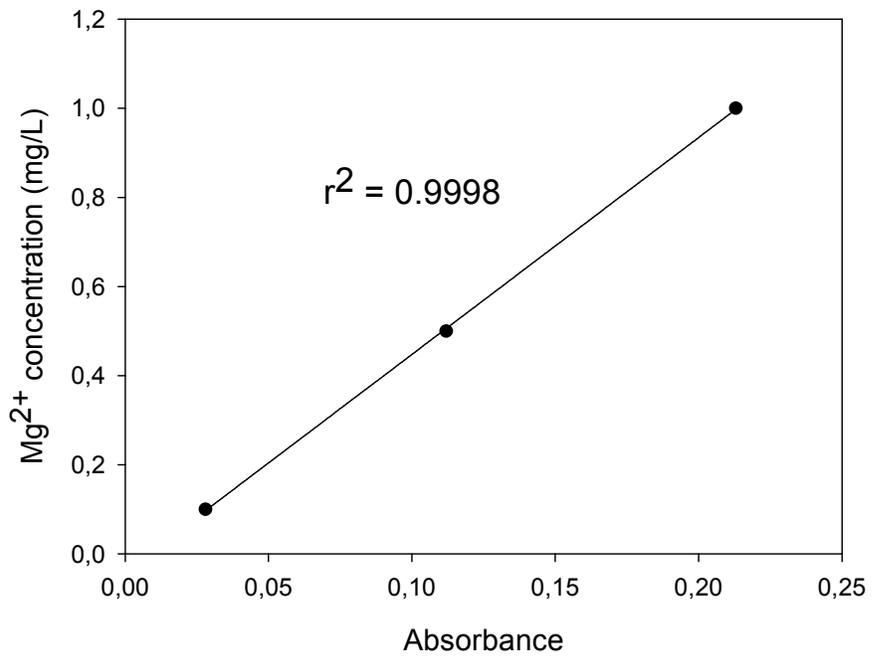


Figure A.3. Calibration curves. Mg²⁺ Calibration, Al³⁺ Calibration

APPENDIX B

EQUILIBRIUM DATA

Table B.1. Equilibrium data for each isotherm

Gördes clinoptilolite			
As-received		Conditioned	
Equilibrium concentration (mg/L)	Capacity (meq/g)	Equilibrium concentration (mg/L)	Capacity (meq/g)
0.119	0.009	0.216	0.070
6.71	0.063	0.445	0.121
21.7	0.084	4.75	0.238
73.0	0.130	64.7	0.391
183	0.177	414	0.619
406	0.184	651	0.636
650	0.179	1081	0.673
1400	0.175	2138	0.672
2870	0.178	4815	0.663
10065	0.173	9480	0.658

Bigadiç clinoptilolite			
As-received		Conditioned	
Equilibrium concentration (mg/L)	Capacity (meq/g)	Equilibrium concentration (mg/L)	Capacity (meq/g)
0.597	0.009	0.055	0.075
19.8	0.045	0.605	0.138
44.3	0.064	12.4	0.256
116	0.085	102	0.356
269	0.112	289	0.373
444	0.110	529	0.387
692	0.118	789	0.383
1462	0.115	1171	0.387
2847	0.117	2748	0.388
4974	0.118	4796	0.389

APPENDIX C

CALCULATION OF EQUILIBRIUM CAPACITY OF CLINOPTILOLITE

The amount of ions removed from the solution by clinoptilolite is calculated as follows:

$$q_e = \frac{(C_i - C_e) \times V}{S} \times \frac{1}{Eq.Wt.} \dots\dots\dots C1$$

Where,

q: cadmium ion sorbed on clinoptilolite (meq/g)

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

C_e: final cadmium concentration in solution (mg/L)

V: volume of solution (L)

S: amount of clinoptilolite added to solution (g)

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

A sample calculation is illustrated as follows:

$$q_e = \frac{(5.11 \text{ mg/L} - 0.119 \text{ mg/L}) \times 0.1 \text{ L}}{1 \text{ g clinoptilolite}} \times \frac{1}{\frac{112.411 \text{ g/mol}}{2 \text{ eq/mol}}} \cong 0.009 \text{ meq/g}$$

APPENDIX D

CALCULATION OF EXHAUSTION AND BREAKTHROUGH CAPACITY OF CLINOPTILOLITE

Exhaustion Capacity

The capacity utilized at exhaustion can be determined graphically from the equation D1 as given;

$$Q_E = \frac{\int_0^{V_E} (C_i - C_e) dV}{S} \dots\dots\dots D1$$

- Where,
- Q_E= exhaustion capacity of clinoptilolite (mg/g or meq/g)
 - C_i= initial cadmium concentration (mg/L)
 - C_e= cadmium concentration in the effluent at exhaustion (mg/L)
 - S = amount of clinoptilolite packed in column (g)
 - V_E= volume of effluent at exhaustion (L)

Breakthrough Capacity

The breakthrough capacity of the clinoptilolite bed can be calculated by the graphical integration of the relationship;

$$Q_B = \frac{\int_0^{V_B} (C_i - C_b) dV}{S} \dots\dots\dots D2$$

Where, Q_B = breakthrough capacity of clinoptilolite (mg/g or meq/g)
 C_b = cadmium concentration at breakthrough (mg/L)
 V_B = volume of effluent at breakthrough (L)

Overall, the utilized capacities were calculated by using a numerical method called the Cubic Spline Interpolation in the Curve Fitting Toolbox of MATLAB version 6.5 software.