Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Affinity of Clinoptilolite-based Zeolites towards Removal of Cd from Aqueous Solutions

K. Gedik[a]; I. Imamoglu[a]
[a] Department of Environmental Engineering, Middle East Technical University, Ankara, Turkey

To cite this Article Gedik, K. and Imamoglu, I.(2008) 'Affinity of Clinoptilolite-based Zeolites towards Removal of Cd from Aqueous Solutions', Separation Science and Technology, 43: 5, 1191 — 1207
To link to this Article: DOI: 10.1080/01496390801888060
URL: http://dx.doi.org/10.1080/01496390801888060

Separation Science and Technology, 43: 1191–1207, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390801888060

Affinity of Clinoptilolite-based Zeolites towards Removal of Cd from Aqueous Solutions

K. Gedik and I. Imamoglu

Department of Environmental Engineering, Middle East Technical
University, Ankara Turkey

Abstract: Cd removal from aqueous solutions using as-received and pretreated forms of two different clinoptilolite samples (denoted GC and BC) was investigated and dissimilar sorption affinities were revealed. Equilibrium behavior of systems were modeled using six different adsorption isotherms. The maximum sorption capacities, as obtained from the solubility-normalized Dubinin-Astakhov model for as-received samples, were determined as 0.18 meq/g and 0.12 meq/g for GC and BC, whereas 0.72 meq/g and 0.41 meq Cd/g was determined for their pretreated forms, respectively. Examination of the release of exchangeable cations into the solution at equilibrium and the change of pH were discussed in terms of varying prevalence of ion exchange, dissolution of the sorbent and adsorption.

Keywords: Pretreatment, isotherm modeling, ion exchange, adsorption, exchangeable cations

INTRODUCTION

Industrialization has led to a substantial increase of the natural concentrations of heavy metals in the aquatic environment all over the world. Toxicity and carcinogenicity of heavy metals necessitate the treatment of metal-laden wastewaters for environmental quality. Cost-effective, simple to operate treatment technologies that use natural materials are becoming popular for

Received 20 July 2007, Accepted 25 November 2007

Address correspondence to I. Imamoglu, Department of Environmental Engineering, Middle East Technical University, 06531 Ankara, Turkey. Tel.: +90 312 2105861; Fax: +90 312 2102646; E-mail: ipeki@metu.edu.tr

the establishment of sustainable treatment strategies. Natural zeolites are widely used in pollution control applications as sorbents owing to their high reserves, advantageous removal capacities, and low cost combined with a recovery potential for both metal and the material (1, 2).

Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature (2) and cadmium is considered to be one of the prevalent toxic metals found in industrial wastewaters. Consequently, several aspects of Cd removal via clinoptilolite have been investigated by a number of researchers, especially in the last two decades (2, 3). Depending on experimental conditions and sample origin, the results reveal a cadmium removal capacity in a range of 0.05–0.78 meq/g for as-received forms (4–10). It is well known that the ability of clinoptilolite to remove heavy metals is favored by pretreatment with a cation that is more willing to undergo ion exchange and correspondingly, a Cd removal capacity in the range of 0.25–1.24 meq/g for pretreated forms of clinoptilolite were observed (8–14).

Modeling of sorption equilibria present a rapid estimate for the applicability of metal-sorbent interaction processes in a wide range of concentrations. Langmuir and Freundlich isotherm models are the most commonly used ones to describe equilibrium phenomena for various metal-sorbent interactions (15). However, the complexity of sorption processes when heterogeneous materials used such as natural zeolites limit the use of these simple models concerning the explanation of sorption equilibria. The heterogeneity in surface and active sites, isomorphic substitutions, broken bonds, lattice imperfections, porous structure, impurities, the pretreatment conditions among other factors influence the sorption phenomena in zeolite studies. Hence, various researchers have illustrated the advantage of using different isotherms such as Toth, Dubinin-Radushkevich (DR) as well as others to better explain the equilibrium phenomena (16, 17). For example, a recent publication by Inglezakis (18) recommend the use of Dubinin-Astakhov (DA) isotherm instead of the DR isotherm for porous materials since the former takes into account the pore structure of the material. Moreover, use of the DA isotherm with a solubility-normalized (SN) adsorption potential, as opposed to the solubility non-normalized (SNN) form is recommended (18).

There are large occurrences of clinoptilolite-rich zeolite in Turkey, especially in central and western Anatolia regions. Manisa-Gördes and Balikesir-Bigadiç basins are two of the most important clinoptilolite reserves, with estimated reserves of 20 million tons and 500 million tons, respectively (19). In this study, clinoptilolite samples from these two deposits were tested for their potential in Cd uptake from aqueous solutions by as-received and pretreated forms. Eight isotherm models (including SN and SNN forms of DA and DR isotherms) were tested for explaining the sorption of Cd via clinoptilolite. Moreover, cation diversity in the aqueous phase was investigated in order to explain prevailing metal removal mechanisms.

MATERIALS AND METHODS

Source, Characterization, and Pretreatment of Clinoptilolite

Zeolite samples from Gördes and Bigadiç deposits were crushed and sieved to different fractions of which 0.83–1.18 mm particle size was used after the preliminary experiments (20). Prior to all experiments, samples were dried at 105°C for 24 hrs and stored in a desiccator until use. Minimum processing of clinoptilolite was aimed, considering possible future practical applications.

The characterization of as-received samples was performed by X-ray fluorescence (Rigaku X-Ray Spectrometer RIX 3000) and X-ray diffraction analysis (Rigaku X-Ray Diffractometer Ultima Model:D/MAX), and photographed using scanning electron microscopy (JEOL JSM-6400 Scanning Microscope). Specific surface area and average pore diameter were determined by N_2-BET method using Quantochrome Autosorb Automated Gas Sorption System and density of the samples was determined using a Helium pycnometer.

Pretreatment was carried out by contacting 10 g of clinoptilolite samples with 250 mL of 2M NaCl solution at 30°C for 24 hours at 150 rpm. Samples were then washed with deionised water until no Cl^- was detected in washing water. Finally, pretreated samples were dried at 105°C for 24 hours, and stored in a desiccator until use.

Cadmium Removal Experiments

All experiments were conducted in batch mode with a 1 g clinoptilolite/100 mL solution ratio using sealed flasks shaken at 125 rpm with an Edmund Buhler KS-15 type orbital shaker at 25 ± 1°C temperature. Preliminary studies revealed 6 hrs and 24 hrs to be adequate to reach equilibrium for Gördes and Bigadiç samples, respectively (20). Initial pH adjustment was done using 0.1N HNO_3 and 0.1N NaOH solutions. $Cd(NO_3)_2 \cdot 4H_2O$ salt with a solubility of 2150 g/L (corresponding Cd solubility = 873.5 mg/mL) was dissolved in high purity deionised water. Cadmium solution concentrations ranged from 5 to 10000 mg/L in equilibrium experiments. Samples taken at equilibrium were immediately centrifuged at 3800 rpm for 5 minutes to ensure solid-liquid separation. Samples were then acidified with concentrated HNO_3 and stored in a refrigerator until analysis.

Analytical Techniques

All chemicals used were analytical grade reagents, and all solutions were prepared in high purity deionized water. Aside from Cd, exchangeable cations (Na, K, Ca, Mg) expected to be released from the clinoptilolite structure were also analyzed in the liquid phase. Cd, Ca, and Mg measurements were carried out by ATI Unicam 929 Atomic Absorption Spectrometer; Na and K by Jenway PFP7 Flame Photometer. Si was measured in the aqueous phase by Hach DR 2400 Spectrophotometer (as SiO_2). Cl^- ions in washing water (after pretreatment) were measured by Argentometric Method (21). pH measurements were carried out using a digital pH meter (CyberScan 500). All experiments were carried out in duplicates and mean values are presented.

RESULTS AND DISCUSSION

Mineral Characterization

The chemical composition of the as-received Gördes (GC) sample is as follows (in %wt): SiO_2: 74.36, Al_2O_3: 11.87, Fe_2O_3: 1.03, MgO: 0.85, CaO: 1.95, Na_2O: 0.59, K_2O: 4.07, MnO: 0.02, TiO_2: 0.07, P_2O_5: 0.01, H_2O: 6.50 and that of Bigadiç (BC) sample is as follows (in %wt): SiO_2: 72.76, Al_2O_3: 11.93, Fe_2O_3: 1.26, MgO: 1.26, CaO: 4.16, Na_2O: 0.10, K_2O: 3.13, MnO: 0.03, TiO_2: 0.09, P_2O_5: 0.01, H_2O: 1.40. Both samples have poor sodium content, and high calcium and potassium content. Diffractometer traces of as-received samples revealed approximately 80% clinoptilolite with quartz as minor impurity for GC, whereas approximately 50% clinoptilolite with quartz, biotite and illite as impurities for the BC sample.

A comparison of the two samples regarding their physical and chemical characteristics is given in Table 1. The Si/Al ratios of both samples are typical for clinoptilolite (1). The theoretical cation exchange capacity of BC sample based on exchangeable cations (2.81 meq/g) exceeded the capacity based on aluminum atoms (2.31 meq/g) indicating the presence of

Table 1. Comparison of clinoptilolite samples regarding their characteristics

	Gördes		Bigadiç	
Characteristic	As-received	Pretreated	As-received	Pretreated
Specific surface area (m^2/g)	37.0	37.4	11.8	12.9
Average pore diameter (Å)	17.5	17.9	17.0	17.0
Density (g/L)	2.27	—	2.24	—
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.

exchangeable cations in impurities. Specific surface area (SSA) measurements reveal that the GC samples have about three times the SSA of the BC samples. SEM examination of the clinoptilolite samples (Fig. 1) reveals that the surface properties of the samples, being initially amorphous, turns to visible plate crystals for GC and flat crystals for BC after pretreatment.

Analysis of Equilibrium Plots with Isotherm Models

The equilibrium behavior of Cd-clinoptilolite interaction is modeled using Langmuir (L), Freundlich (F), Toth (T), Redlich-Petersen (RP), and solubility-normalized (SN) and non-normalized (SNN) forms of Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) isotherms. Isotherm parameters (K, β, M,

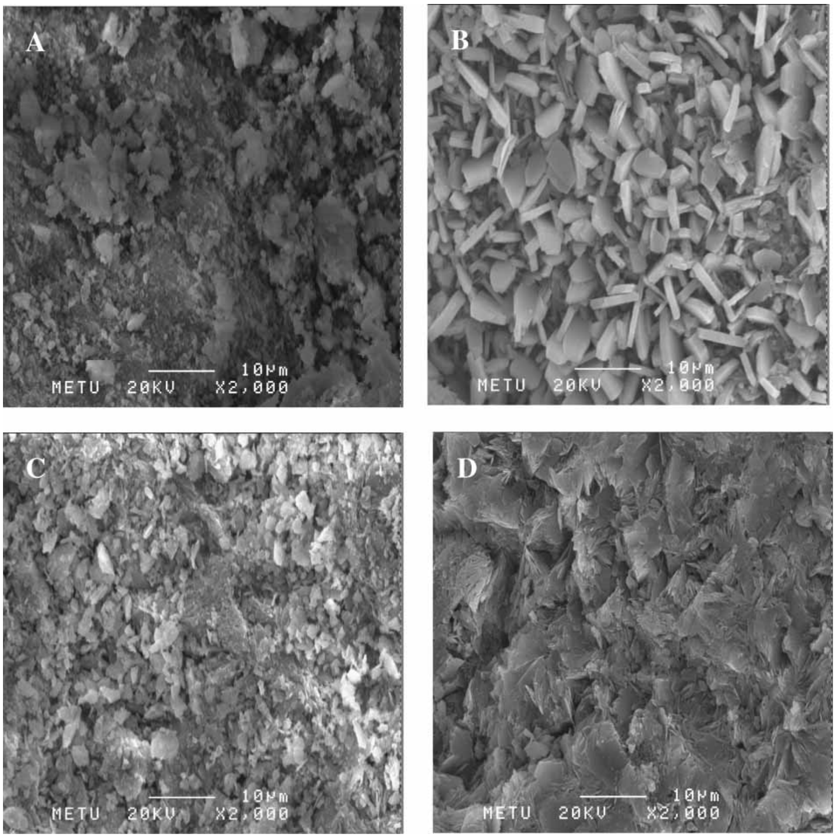

Figure 1. SEM photographs of Gördes clinoptilolite samples in their (A) as-received and (B) pretreated forms; and Bigadiç clinoptilolite samples in their (C) as-received and (D) pretreated forms.

E, and n) and information on the goodness of fit (r^2) were calculated from experimental data by nonlinear regression using MATLAB software with the confidence level set at 95% according to equations presented in Table 2. In addition, two error functions, namely sum of squares of errors (Eq. (1)) and hybrid functional error function (Eq. (2)), equations of which are given below, were applied as additional criteria to evaluate the quality of fit of isotherm equations to experimental data.

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

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

Table 2. Adsorption isotherm equations used in this study

Isotherm	Equation	Reference
Langmuir (L)	$q = \frac{KCM}{1+KC}$	(15)
Freundlich (F)	$q = (KC)^{\beta}$	(15)
Redlich-Petersen (RP)	$q = \frac{KCM}{1+(KC)^{\beta}}$	(15)
Toth (T)	$q = \frac{KCM}{(1+(KC)^{\beta})^{1/\beta}}$	(15)
Dubinin-Radushkevich (DR_{SNN})	$q = M \exp\left[-\left(\frac{RT}{\sqrt{2}E}\right)^2 \left(\ln\left(1+\frac{1}{C}\right)\right)^2\right]$	(18)
Dubinin-Radushkevich (DR_{SN})	$q = M \exp\left[-\left(\frac{RT}{\sqrt{2}E}\right)^2 \left(\ln\left(\frac{C_S}{C}\right)\right)^2\right]$	(18)
Dubinin-Astakov (DA_{SNN})	$q = M \exp\left[-\left(\frac{RT}{\sqrt{2}E}\right)^n \left(\ln\left(1+\frac{1}{C}\right)\right)^n\right]$	(18)
Dubinin-Astakov (DA_{SN})	$q = M \exp\left[-\left(\frac{RT}{\sqrt{2}E}\right)^n \left(\ln\left(\frac{C_S}{C}\right)\right)^n\right]$	(18)

Explanation of parameters: q = Amount adsorbed per gram of clinoptilolite (meq/g); M = Maximum amount adsorbed per gram of clinoptilolite (meq/g); C = Equilibrium solute concentration (g/g or mg/L); C_S = Solubility of cadmium (mg/L); K = Surface adsorption equilibrium constant (L/mg); β = Surface heterogeneity factor; R = The universal gas constant (kJ/mol · K); T = The absolute temperature (K); E = Adsorption energy (kJ/mol); n = Heterogeneity parameter for pore structure

Note: "SNN" denotes solubility non-normalized, and "SN" denotes solubility normalized forms of the isotherms.

where $q_{\exp}$ is the experimental data, q_{calc} is the modeled data, p is the number of data points, and n is the number of model parameters. SSE is a very common error function and HYBRID was developed to compensate for the tendency of SSE to favor numbers of larger value over numbers of smaller value (22).

Isotherm model fit information presented in Table 3 suggest Cd removal trends associated with the presence or absence of pretreatment, i.e., as-received vs. pretreated Gördes clinoptilolite (GC vs. pGC), rather than the origin of clinoptilolite samples, Gördes clinoptilolite vs. Bigadiç clinoptilolite (i.e., GC vs. BC). The presence of significantly different ratio of impurities among clinoptilolite samples does not seem to have a major impact on their Cd removal behavior. Plots corresponding to the information in Table 3 are presented for as-received samples (GC and BC) in Fig. 2 and pretreated samples (pGC and pBC) in Fig. 3.

All models, reasonably estimate the equilibrium data for as-received clinoptilolite samples, with the possible exception of the F and to some extent DR isotherms, as given by the high correlation coefficients that are almost equal to each other (Table 3). Moreover, the two other goodness of fit criteria indicates similarly well fit (the smaller the error value, the better the fit) for these models for both GC and BC. L and T models seem to give slightly better fit results compared to others. As can be seen from the isotherm equations (Table 2), RP and T models reduce to the L model when the β parameter approaches unity (indicating energetically uniform surface (23) or homogeneous sorbent surface). From Table 3, it follows that for as received clinoptilolite samples, L, RP, and T models act as a similar type of isotherm by also yielding very similar K and M values, indicating monolayer adsorption of Cd on as-received clinoptilolite.

Isotherm data of pretreated samples are better represented by especially the DA isotherm (with almost identical results for DA_{SN} and DA_{SNN}) and to some extent T model among others, as can be seen in Fig. 3 and indicated by all goodness of fit criteria (r^2, SSE, and HYBRID, Table 3). L and RP models underestimate the experimental points for low concentrations in both pBC and pGC containing reactors. F, and to a lesser extent, DR_{SN} and DR_{SNN} models are generally not successful at representing the equilibrium data when compared to the other tested models. Additionally, during model fitting, it was observed that isotherms other than L are sensitive to the maximum adsorption (M) values. That is, a small change in the M value causes a notable deviation in the r^2 calculation. On the other hand, changes up to 10% in M values have a relatively small effect on the value of E and n parameters of the DA and DR models, as was also noted by Campos (24).

Abusafa and Yucel (25) point out that a good fit of data to a given isotherm model should not be taken as a sufficient test for its validity considering the relative difficulty of interpreting isotherm models for liquid-solid systems when compared to those of gas-solid systems. Especially, when a number of isotherms with different theoretical assumptions and approach to equilibrium data modeling show reasonable fit for the same data set, careful

Table 3. Adjustable parameters and goodness of fit information for adsorption isotherms applied on Cd-clinoptilolite interaction

	As-received (GC)						Pretreated (pGC)					
Isotherms	K or E^*	β or n^*	M	r^2	SSE	HYBRID	K or E^*	β or n^*	M	r^2	SSE	HYBRID
Gördes clinoptilolite												
L	0.051	—	0.181	0.971	0.00099	0.200	0.057	—	0.652	0.924	0.04142	2.851
F	0.071	0.12	—	0.74	0.00904	3.595	0.22	0.139	—	0.875	0.06826	3.682
RP	0.051	1	0.181	0.971	0.00099	0.228	0.325	0.933	0.419	0.95	0.02706	1.533
T	0.06	0.901	0.183	0.972	0.00097	0.209	1.66	0.347	0.774	0.977	0.01259	0.463
$\mathrm{DR}_{\mathrm{SN}}$	19.83*	2*	0.241	0.847	0.00530	1.364	18.92*	2*	0.885	0.947	0.02879	1.126
$\mathrm{DR}_{\mathrm{SNN}}$	20.12*	2*	0.244	0.845	0.00537	1.397	19.20*	2*	0.898	0.946	0.0295	1.170
$\mathrm{DA}_{\mathrm{SN}}$	19.75*	6.79*	0.183	0.969	0.00107	0.246	20.60*	3.52*	0.721	0.98	0.01094	0.381
$\mathrm{DA}_{\mathrm{SNN}}$	20.17*	6.90*	0.184	0.969	0.00108	0.246	21.02*	3.58*	0.722	0.98	0.01102	0.384
	As-received (BC)						Pretreated (pBC)					
	K or E^*	β or n^*	M	r^2	SSE	HYBRID	K or E^*	β or n^*	M	r^2	SSE	HYBRID
Bigadiç clinoptilolite												
L	0.027	—	0.12	0.987	0.00017	0.083	0.727	—	0.373	0.905	0.01176	1.011
F	0.038	0.151	—	0.812	0.00247	1.238	0.185	0.103	—	0.871	0.01592	1.137
RP	0.027	1	0.12	0.987	0.00017	0.095	2.37	0.948	0.253	0.957	0.00537	0.559
T	0.029	0.944	0.121	0.987	0.00017	0.090	25.1	0.322	0.432	0.988	0.00143	0.105
$\mathrm{DR}_{\mathrm{SN}}$	17.73*	2*	0.171	0.891	0.00144	0.520	23.25*	2*	0.495	0.947	0.00656	0.379
$\mathrm{DR}_{\mathrm{SNN}}$	18.02*	2*	0.174	0.889	0.00146	0.536	23.56*	2*	0.501	0.946	0.00673	0.392
$\mathrm{DA}_{\mathrm{SN}}$	18.44*	7.14*	0.12	0.984	0.00021	0.144	24.47*	3.84*	0.409	0.991	0.00108	0.076
$\mathrm{DA}_{\mathrm{SNN}}$	18.86*	7.32*	0.12	0.984	0.00021	0.144	24.90*	3.91*	0.409	0.991	0.00109	0.076

*E and n, instead of K and O, are valid for SN and SNN forms of DR and DA isotherms.

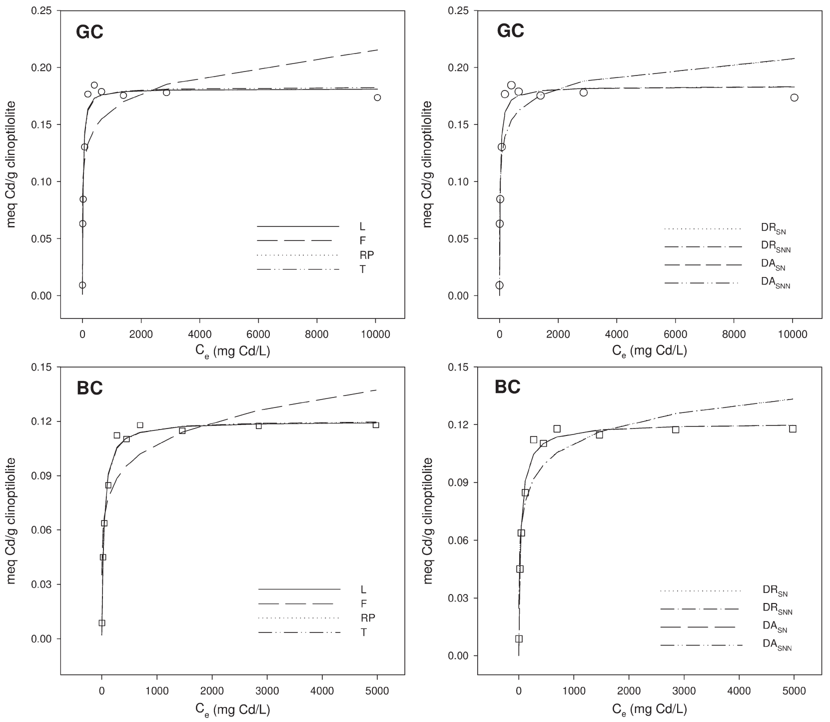

Figure 2. Cadmium uptake and comparison of adsorption isotherms for reactors containing as-received Gördes clinoptilolite (GC) samples and as-received Bigadiç clinoptilolite (BC) samples.

examination may be necessary. Robinson (26) argues that choice of the most representative isotherm model for an experimental system should depend mainly on the adsorbent (i.e., incorporating heterogeneous nature of zeolites) and adsorbate characteristics. For example, the constants in L, F, RP, and T models do not give any idea about the physical or chemical nature of sorption process. On the other hand, the Polanyi potential theory based DA model and its special form of DR ($n = 2$) compensate this deficiency in estimating the equilibrium behavior of porous materials (26). These models suggest the adsorption process via micropore volume filling rather than layer-by-layer adsorption on pore walls (23) and hence are more applicable and meaningful when porous sorbents are concerned (18). The characteristic of the sorption process (physical or chemical) and heterogeneity in pore structure are incorporated in the DA model by E (adsorption energy) and *n* parameters, respectively, when compared to other listed models.

Although no significant difference in terms of goodness of fit was observed between its SN and SNN forms, use of the DA_{SN} isotherm is supported for all Cd-clinoptilolite systems considering its theoretical

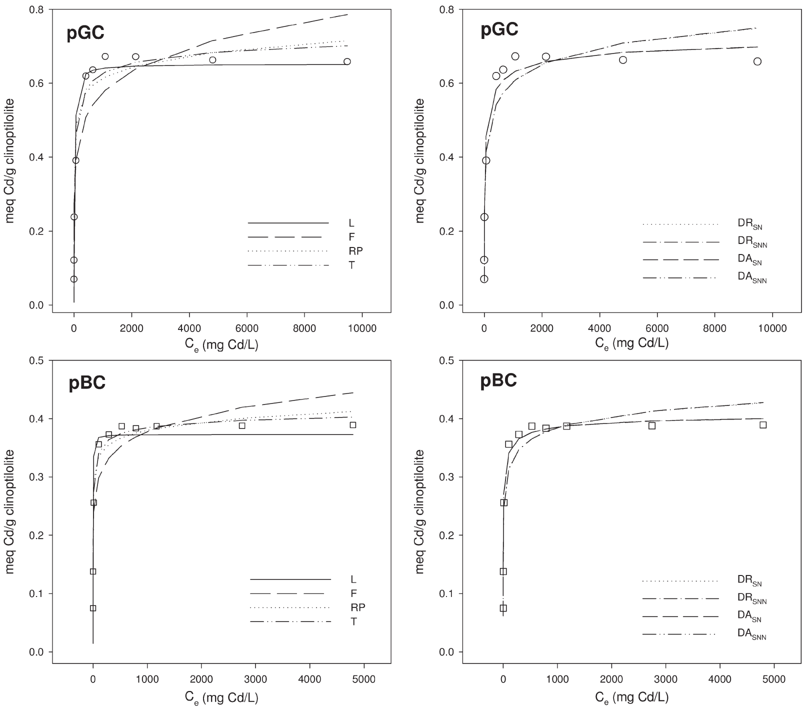

Figure 3. Cadmium uptake and comparison of adsorption isotherms for reactors containing pretreated Gördes clinoptilolite (pGC) samples and pretreated Bigadiç clinoptilolite (pBC) samples.

background and applicability for zeolite systems that are described with a heterogeneity factor other than 2. The maximum capacity values obtained from the DA_{SN} agree well with experimental findings. The value of the adsorption energies obtained from the DA model (18–25 kJ/mol, Table 3) are compared with the ranges reported by Helfferich (27) for ion exchange (8–16 kJ/mol). These suggest an ion exchange mechanism with presence of other interactions such as surface precipitation and/or co-precipitation (18, 28). Similar to Inglezakis's (18) findings, the adsorption energies were also observed to show an increase after pretreatment for both sorbents in this study. This increase was more prominent between BC and pBC, than for GC and pGC. Furthermore, the heterogeneity parameters for the pore structure were found to be 6.8 and 7.1 for as-received clinoptilolite systems, whereas 3.5 and 3.8 were obtained for pretreated clinoptilolite systems. This significant decrease in the value of n after pretreatment indicates an increase of pore heterogeneity as a result of pretreatment. It should be noted here that a similar trend is also observable for the surface heterogeneity factor (β) obtained from the Toth isotherm, pointing to the increase in surface heterogeneity after pretreatment. This may be attributed to the formation of new inner/outer active sites, and an increase in the difference between the affinity of non-participating sites with the affinity of those that are actively involved with Cd removal (via ion exchange or adsorption).

Overall, the maximum capacity values obtained from modeling studies (M), which correlate well with experimental findings, show that the GC sample yielded a higher Cd sorption capacity (0.18 meq/g) than that of the BC sample (0.12 meq/g). Treatment of clinoptilolite samples by sodium chloride increased their sorption ability effectively in comparison to their as-received forms. As seen from Fig. 2 and Fig. 3, pretreatment caused a more than three fold increase in Cd uptake for pGC and pBC samples (0.72 meq/g and 0.41 meq/g), respectively. These results are comparable with findings obtained for Cd removal with clinoptilolite-rich natural and modified materials in the literature (4–14). The observed Cd removal capacities are promising, however, they are still significantly lower than the theoretical cation exchange capacities (TCEC) calculated from the chemical composition of clinoptilolite samples.

pH Profiles in Equilibrium Experiments

The change in the equilibrium pH values for the reactors in isotherm studies can be seen in Fig. 4. Even though all reactors have an adjusted initial pH of 4.0 (which was previously selected after preliminary experiments (20)), different behaviors in terms of pH were observed. For example, overall, in reactors containing BC and pBC, pH stabilized at values almost one unit higher than those of GC and pGC. A major factor affecting system pH is the hydrolysis of metal ions in the aqueous medium. Cd concentrations used in GC and pGC containing reactors are about twice those containing BC and pBC. This is expected to have an effect on the stabilization of pH at a lower value in GC and pGC containing reactors when compared to the others. However, when Cd-free reactors are considered, a difference of two units is evident between GC and BC containing reactors, pointing out the greater affinity of Bigadiç clinoptilolite for H^+ ions. This would lead to greater surface protonation which in turn is expected to affect metal removal negatively (29). Meanwhile, no significant difference in pH trend was observable between as-received and pretreated clinoptilolite sample pairs (Fig. 4).

Exchangeable Cations in Equilibrium Experiments

Recently, a number of researchers have investigated exchangeable cations (ex-c) released from the clinoptilolite framework to explain the prevailing metal removal mechanisms (17, 30–32). Ion exchange is a stoichiometric process in which metal ion removed from the solution is replaced by an

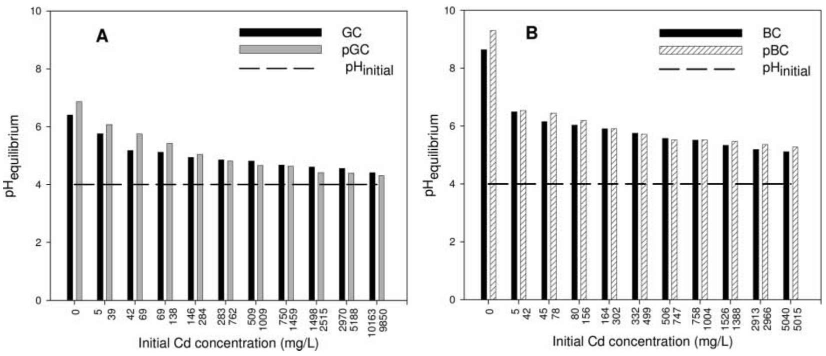

Figure 4. Change in equilibrium pH values with respect to initial metal concentrations for as-received and pretreated clinoptilolite samples of (A) Gördes and (B) Bigadiç.

equivalent amount of ex-c (27). Accordingly, it is expected that if ion exchange were the prevailing removal mechanism, the amount of metal sorbed and ex-c released would agree well with each other, hence, have a good stoichiometry. However, ex-c detected in solution are not only due to the exchange process but may also be as a result of dissolution of impurities and/or clinoptilolite with increasing ionic strength of the aqueous solution and/or surface protonation (30, 31). The balance of ions leaving the clinoptilolite structure ($2Na + 2K + Ca + Mg$) when compared to the amount of Cd removed is presented in Fig. 5. This comparison is made for four representative cases where,

i. no Cd ions are present (to detect initial release of ex-c),
ii. Cd removal capacity of clinoptilolite is not reached,
iii. around the lowest concentration where maximum capacity is reached and
iv. a concentration where much more Cd ions are present when compared to the amount that can be sorbed.

The variety of ex-c release increase with an increase in the amount of Cd retained on as-received samples, GC and BC (Fig. 5a–c). In Cd-GC interaction (Fig. 5a), while very small amount of ex-c are released in Cd free reactors, both the diversity and the amount of ex-c released are significantly different for Cd-BC interaction (Fig. 5c). For the Cd-GC system, as the initial metal concentration increase, greater proportions of Ca and K are released into the solution, with Na and very small contribution of Mg ions in parallel to the increase in Cd removal. Yet in BC containing test reactors, for low Cd concentration, almost the same amount of $Na + Ca$ is observed in the aqueous phase as that of the Cd-free solution. This suggests that the release of these ions is independent of the amount of Cd removed. For higher Cd concentrations, the amount of ex-c double (especially Ca),

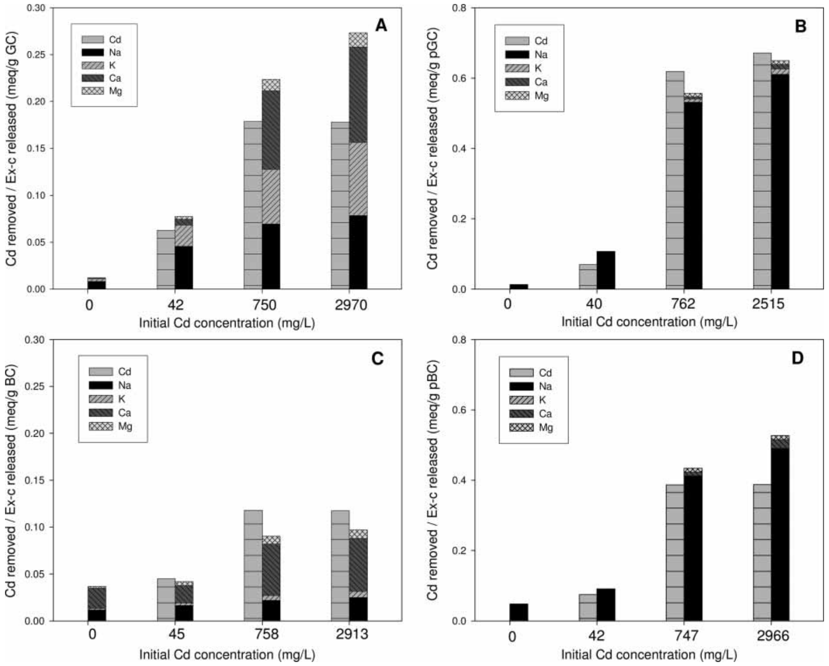

Figure 5. Comparison of equilibrium Cd and exchangeable cations (ex-c) in solid phase and in aqueous phase, respectively, with respect to initial Cd concentrations for Cd removal using Gördes clinoptilolite in (A) as-received (GC) and (B) pretreated forms (pGC), and using Bigadiç clinoptilolite in (C) as-received (BC) and (D) pretreated (pBC) forms.

coupled with a more than doubling of the amount of Cd removed for Cd-BC system. This indicates that the abundance of Ca when compared to the other ex-c in the aqueous phase is related to Cd removal. On the other hand, although, both GC and BC samples are rich in terms of K and Ca, according to their chemical composition, GC releases K as well as Ca in great amounts during increasing Cd removal, whereas BC releases only Ca for the same cases.

Cation diversity after Cd removal is minimized in Cd-pGC and Cd-pBC interaction (Fig. 5b–d), when compared to that of Cd-GC and Cd-BC interactions. This is expected due to pretreatment of GC and BC with concentrated NaCl solution. Almost no ex-c other than Na are detected in the Cd-free pGC reactors, and the amount of Na released increases parallel to the increase in Cd removal. In the Cd-pBC interaction, a similar picture to Cd-pGC is observed, except a relatively higher amount of Na is released in Cd-free test reactors. Related with the impurity content of the Bigadiç samples (~50%); excess Na ions may be attributed to the release following their sorption on the surfaces of impurities during interaction with the NaCl solution. For both Cd-pGC and Cd-pBC, at high Cd concentrations, ex-c other than Na are also detected to a small extent, which indicate that some of the cations are still present in clinoptilolite after pretreatment. Other researchers have pointed out similar findings regarding the partial exchange of framework cations with Na during pretreatment (11, 14, 25).

An examination of pH changes in Cd-free reactors help in understanding the tendency towards surface protonation and subsequent dissolution under the same conditions as other reactors used in equilibrium experiments. As mentioned before, Fig. 5 shows differences in chemical behavior to metal removal for Gördes and Bigadiç clinoptilolite samples. Si measurements in the aqueous phase correlate well with the observed affinity of BC for surface protonation. Large amounts (~0.10 meq/g when compared to ~0.04 meq/g for BC and GC, respectively) of Si was released into Cd-free solutions in BC containing reactors, pointing to the presence of dissolution (of clinoptilolite and/or impurities). Surface protonation may cause ex-c to be released into the solution (33) unrelated to the amount of Cd removed, which is the case observed during Cd removal with BC (Fig. 5c). However, it is interesting that although the dissolution of Si is higher for both forms of Bigadiç samples compared to those obtained from Gördes, overall release of ex-c, when compared to the total amount of Cd removed are lower. For Cd-GC interaction especially (Fig. 5a), this is the opposite, where much higher amounts of ex-c are released when compared to the total amount of Cd removed. This was observed by others (30, 31) and explained by dissolution of clinoptilolite this time due to the effect of increasing ionic strength. A similar effect, however, is not observable on BC (Fig. 5c).

The findings of this study together with previous studies (31, 34) suggest that it is clinoptilolite in GC, rather than impurities, that is especially sensitive to dissolution due to increasing ionic strength. Cagin et al. (31) and Morali (34) utilized a higher purity of Bigadiç clinoptilolite (~80%) and similar increasing dissolution in relation to increasing ionic strength were observed using as-received samples during Cu, Ni, Zn, and Pb removal. Subsequently, in this study, the release of ex-c from BC (~50% purity) is interpreted as partly from dissolution of clinoptilolite as a result of ion exchange and partly from dissolution of impurities. The comparison of $TCEC_{Ex}$ with $TCEC_{Al}$ values presented in Table 1 also support this, by indicating the presence of ex-c in the impurities of BC. In pretreated samples, the Si release is observed to be slightly less than (~0.08 meq/g and ~0.03 meq/g for pBC and pGC, respectively) those of GC and BC containing Cd-free reactors. This may be interpreted by the increasing surface stability as well as formation of a homogenized chemical structure after pretreatment.

Overall, a discrepancy exists between the quantity of Cd removed and ex-c released for Gördes and Bigadiç samples. While modeling results of the DA_{SN} isotherm indicate similar removal mechanisms for the systems studied, investigation of cation release following Cd removal provides some insight for differentiation between ion exchange and adsorption among the two clinoptilolite samples. A general overview of the results suggests that the dominant mechanisms of Cd removal may not be the same for the two samples and point to a correlation between increasing clinoptilolite content of zeolite and increasing contribution of ion exchange. Since ion exchange is affected by the normality of the solution and adsorption is not (18, 35), studies may be conducted by taking advantage of this difference to further understand the metal-clinoptilolite interaction.

CONCLUSIONS

A comparative study of Cd removal from aqueous solutions using both as-received and pretreated forms of Gördes and Bigadiç clinoptilolite was studied. Sorption affinities for Cd interaction with both forms of Gördes samples are higher in all metal concentrations tested, indicating that Gördes clinoptilolite has a larger number of available sorption sites when compared to both forms of Bigadiç clinoptilolite samples.

Langmuir, Freundlich, Toth, Redlich-Petersen, Dubinin-Radushkevich and Dubinin-Astakhov isotherm models (both solubility-normalized and solubility non-normalized forms of the last two isotherms) were tested and Cd sorption equilibria via both as-received and pretreated samples was best modeled by the DA isotherm with high r^2 and good quality of fit (low SSE and HYBRID values). Furthermore, the GC sample yielded a higher Cd sorption capacity (0.18 meq/g) than did BC sample (0.12 meq/g). Treatment of clinoptilolite samples by concentrated NaCl solution increased their sorption ability effectively in comparison with as-received forms yielding more than three fold increase in Cd uptake for pGC (0.72 meq/g) and pBC samples (0.41 meq/g).

An examination of exchangeable cations revealed a discrepancy between the quantity of Cd removed and exchangeable cations released for Gördes and Bigadiç samples. A general overview of the results suggests that the dominant removal mechanisms of Cd removal are not the same for the two samples, and involve varying contributions of ion exchange and adsorption.

ACKNOWLEDGMENTS

This research was funded by the Turkish Prime Ministry-State Planning Organization and Middle East Technical University Research Fund (BAP-DPT 2002K120510).

REFERENCES

1. Tsitsishvili, G.V., Andronikashvili, T.G., Kirov, G.M., and Filizova, L.D. (1992) *Natural Zeolites*; Ellis Horwood: Chichester, U.K.
2. Kesraoui-Ouki, S., Cheeseman, C.R., and Perry, R. (1994) Natural zeolite utilization in pollution control: A review of applications to metals' effluents. *J. Chem. Technol. Biotechnol.*, 59 (2): 121.
3. Kallo, D. (2001) Applications of natural zeolites in water and wastewater treatment. In *Natural Zeolites: Occurrence, Properties, Application*; Bish, D.L. and Ming, D.W. (eds.); Mineralogical Society of America: Washington, DC.
4. Zamzow, M.J., Eichbaum, B.R., Sandgren, K.R., and Shanks, D.E. (1990) Removal of heavy metals and other cations from wastewater using zeolites. *Sep. Sci. Technol.*, 25 (13–15): 1555.
5. Kurama, H. and Kaya, M. (1995) Removal of heavy metals from wastewater with Bigadic (Turkiye) Clinoptilolite. In *Treatment and Minimization Heavy Metal Containing Wastes*; Hager, P., Mishra, B., Davidson, C.F., and Litz, J.L. (eds.); Pennsylvania..
6. Cortes-Martinez, R., Martinez-Miranda, V., Solache-Rios, M., and Garcia-Sosa, I. (2004) Evaluation of natural and surfactant-modified zeolites in the removal of cadmium from aqueous solutions. *Sep. Sci. Technol.*, 39 (11): 2711.
7. Cincotti, A., Mameli, A., Locci, A.M., Orru, R., and Cao, G. (2006) Heavy metals uptake by Sardinian natural zeolites: Experiment and modeling. *Ind. Eng. Chem. Res.*, 45 (3): 1074.
8. Curkovic, L., Stefanovic, S.C., and Filipan, T. (1997) Metal ion exchange by natural and modified zeolites. *Water Res.*, 31 (6): 1379.
9. Faghihian, H., Marageh, M., and Kazemian, G.H. (1999) The use of clinoptilolite and its sodium form for removal of radioactive cesium, and strontium from nuclear wastewater and Pb^{2+}, Ni^{2+}, Cd^{2+}, Ba^{2+} from municipal wastewater. *Appl. Radiat. Isotopes*, 50 (4): 655.
10. Cincotti, A., Lai, N., Orru, R., and Cao, G. (2001) Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling. *Chem. Eng. J.*, 84 (3): 275.
11. Semmens, M.J. and Martin, W.P. (1988) The influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions. *Water Res.*, 22 (5): 537.
12. Kesraoui-Ouki, S., Cheeseman, C., and Perry, R. (1993) Effects of pretreatment of chabazite and clinoptilolite prior to lead and cadmium removal. *Environ. Sci. Technol.*, 27 (6): 1108.
13. Langella, A., Pansini, M., Cappelletti, P., de Gennaro, B., de' Gennaro, M., and Colella, C. (2000) NH_4^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} exchange for Na^+ in a sedimentary clinoptilolite, North Sardinia, Italy. *Micropor. Mesopor. Mat.*, 37 (3): 337.
14. Culfaz, M. and Yagiz, M. (2004) Ion exchange properties of natural clinoptilolite: lead-sodium and cadmium-sodium equilibria. *Sep. Purif. Technol.*, 37 (2): 93.
15. Kinniburgh, D.G. (1986) eneral purpose adsorption isotherms. *Environ. Sci. Technol.*, 20 (9): 895.
16. Balci, S. (2004) Nature of ammonium ion adsorption by sepiolite: analysis of equilibrium data with several isotherms. *Water Res.*, 38 (5): 1129.
17. Peric, J., Trgo, M., and Medvidovic, N.V. (2004) Removal of zinc, copper and lead by natural zeolites-a comparison of adsorption isotherms. *Water Res.*, 38 (7): 1893.
18. Inglezakis, V.J. (2007) Solubility-normalized Dubinin-Astakhov adsorption isotherm for ion-exchange systems. Macropor. *Mesopor. Mat.*, 103 (1–3): 72.

19. Report of Industrial Minerals Working Group (1996) DPT:2421-OIK:480C1; State Planning Organization: Prime Ministry, Turkey.
20. Gedik, K. and Imamoglu, I. (2006) A comparative study of Cd^{2+} removal from aqueous solutions using two different Turkish clinoptilolite samples. In *Proceedings of the 7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites*; Bowman, R.S. and Delap, S.E. (eds.); Socorro: New Mexico, U.S.A., p. 115.
21. Clesceri, L.S., Greenberg, A.E., and Eaton, A.D. (eds.) (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th edn.; American Public Health Association: Washington, DC.
22. Porter, J.F., Mckay, G., and Choy, K.H. (1999) The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory. *Chem. Eng. Sci.*, 54 (24): 5863.
23. Suzuki, M. (1990) *Adsorption Engineering*; Elsevier: Kodansha, Tokyo.
24. Campos, A. (2004) Adsorption of MTBE on high-silica zeolites: Effects of adsorbent characteristics and natural organic matter on adsorption isothermsM.Sc. Thesis, North Carolina State University: Raleigh, NC..
25. Abusafa, A. and Yucel, H. (2002) Removal of ^{137}Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite. *Sep. Purif. Technol.*, 28 (2): 103.
26. Robinson, S.M., Arnold, W.D., Jr., and Byers, C.W. (1993) Multicomponent liquid ion exchange with chabazite zeolites. ORNL/TM-12403; US Department of Energy.
27. Helfferich, F. (1995) *Ion exchange*; Dover Publications Inc.: New York.
28. Wang, X.S., Huang, J., Hu, H.Q., Wang, J., and Qin, Y. (2007) Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite. *J. Hazard. Mat.*, 142 (1–2): 468.
29. Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., and Mentasti, E. (2003) Adsorption of heavy metals on Na-montmorillonite: Effect of pH and organic substances. *Water Res.*, 37 (7): 1619.
30. Doula, M.K. (2006) Removal of Mn^{2+} ions from drinking water by using clinoptilolite and clinoptilolite-Fe oxide system. *Water Res.*, 40 (17): 3167.
31. Cagin, V., Morali, N., and Imamoglu, I. (2007) Use of a natural mineral for the removal of copper and nickel from aqueous solutions to reduce heavy metal content of precipitation sludges. *J. Residuals Sci. Technol.*, 4 (1): 45.
32. Sprynskyy, M., Buszewski, B., Terzyk, A.P., and Namiesnik, J. (2006) Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. *J. Colloid Interf. Sci.*, 304 (1): 21.
33. Doula, M., Ioannou, A., and Dimirkou, A. (2002) Copper adsorption and Si, Al, Ca, Mg, and Na release from clinoptilolite. *J. Colloid Interf. Sci.*, 245 (2): 237.
34. Morali, N. (2006) Investigation of zinc and lead removal from aqueous solutions using clinoptilolite M.Sc. Thesis, Middle East Technical University: Ankara, Turkey.
35. Inglezakis, V.J. and Poulopoulos, S.G. (2006) *Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications*; Elsevier: The Netherlands.