

Removal of cadmium from aqueous solutions using clinoptilolite: Influence of pretreatment and regeneration

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Abstract

In this study, Cd removal from aqueous solutions via clinoptilolite was investigated in terms of the effect of pretreatment and regeneration. Four different chemicals (NaCl, KCl, CaCl₂ and HCl) were tested for this purpose. Samples treated by a total of 20 bed volume (BV) of 1 M NaCl solution prepared in tap water with no pH adjustment were found to perform satisfactorily. Five exhaustion and regeneration cycles were then carried out, revealing an increasing Cd removal capacity, coupled with constant Cd elution efficiency in progressing cycles. Furthermore, the change of pH and the presence of exchangeable (Na, K, Ca and Mg) and framework cations (Si and Al) in the aqueous phase were investigated. Subsequently, these were discussed in terms of progressive conversion of clinoptilolite to its homoionic Na-form, and the presence of different Cd removal mechanisms in the system. This study emphasizes the potential of clinoptilolite to be a part of sustainable wastewater treatment technologies, enabling the recovery of both the sorbent and the metal, via demonstration of effective Cd removal and clinoptilolite recovery, besides successful concentration of metal in the regenerant solution.

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1. Introduction

Natural concentrations of heavy metals in the aquatic environment have been disturbed after considerable industrialization all over the world. Therefore, metal containing wastewaters are subjected to treatment before discharging into the receiving environment, concerning the toxic effects of these metals. An additional advantage for such systems is the potential for recovery of resources (sorbent and metal) following wastewater treatment. Such systems are becoming popular especially for metal-contaminated wastewaters. Use of relatively simple yet effective technologies utilizing local resources would be advantageous for the establishment of sustainable treatment strategies. Natural zeolites, especially clinoptilolite, are effectively used in ion exchange processes as sorbent materials for heavy metal removal applications, owing to their high reserves, advantageous ion exchange capacities, and low cost [1–4]. Clinoptilolite is abundant in nature, hence a low cost mineral, therefore its recycle

may not seem profitable at first glance. However, development of sustainable treatment technologies oblige no further waste production in addition to conservation of resources. Subsequently, regeneration of clinoptilolite would enable the recovery of both the sorbent and metal from the resulting concentrated regenerant solution. Such studies are therefore important for future practical use of this natural material in wastewater treatment.

Clinoptilolite can be used both in its natural/as-received as well as in its chemically modified/pretreated forms for heavy metal removal [5,6]. Pretreatment aims to replace exchangeable cations (Na, K, Ca and Mg) on clinoptilolite with a cation that is more willing to undergo ion exchange, thus helps to increase metal removal capacity [7–9]. NaCl seems to be the most widely used chemical for pretreatment [5,6,8,10,11], yet chemicals such as HCl [12], CaCl₂, KCl [13] or NaOH [8] have been used among others.

Several aspects of Cd removal via clinoptilolite, such as determination of removal capacity, effect of particle size, temperature, other cations or pretreatment have been investigated by a number of researchers in the last decades [3,9,14–16]. On the other hand, a relatively smaller number of studies were performed on the regeneration of clinoptilolite after Cd removal. Blanchard et al.

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[17] investigated the optimum regeneration conditions for good reproducibility in removing NH_4 and mixed metals including Cd from solution using clinoptilolite packed beds. Zamzow et al. [10] demonstrated effective removal and complete elution of Cd for 27–37 removal/regeneration cycles from a clinoptilolite packed column, aiming water treatment to meet US EPA drinking water standards. While Zamzow et al. [10] used NaCl for regeneration, Vasylechko et al. [12] used HCl-modified clinoptilolite during Cd removal and salts of potassium for successful regeneration of the packed bed.

When utilizing natural materials for the purpose of future practical applications, it is important to characterize the materials well and carry out studies on a reserve-specific basis, since due to the nature of the material, a wide variation in capacity and other aspects is expected [3]. Few studies exist on the use of clinoptilolite from the extensive reserve in Manisa–Gördes region of Western Anatolia for its use potential in heavy metal removal [18–23].

This study aims to investigate the influence of pretreatment and regeneration on Cd removal via Western Anatolian clinoptilolite. For this purpose, firstly, four different chemicals were tested for the pretreatment and regeneration of clinoptilolite. The one that performed the best was used in further optimization of pretreatment conditions (total volume, pH, water quality) in a fixed bed column arrangement. The effect of regeneration was then tested via operation of successive Cd removal/c clinoptilolite regeneration cycles. The change of pH and the concentration of exchangeable and framework cations in the aqueous phase was monitored in order to obtain information regarding cadmium removal mechanisms.

2. Materials and methods

2.1. Source and characterization of clinoptilolite

The sorbent material was taken from a sedimentary deposit in Gördes region, Western Anatolia, Turkey. Samples were ground and sieved to 0.83–1.18 mm size fraction and washed with distilled water to remove surface dust that may cause operational problems. Clinoptilolite samples were then let to dry for 24 h at 105 °C in an oven, and finally stored in a desiccator until use. Minimum processing of clinoptilolite was aimed, considering possible future practical applications.

The chemical composition of sample was determined by X-ray fluorescence (Rigaku X-Ray Spectrometer RIX 3000) technique, and the results are as follows (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. The Si/Al ratio of the sample as calculated from this composition is 5.32, which is within the typical range of 4–5.5 given for clinoptilolite [1]. The theoretical cation exchange capacity (TCEC), calculated by taking into account all the exchangeable cations (Na, K, Ca and Mg) in the structure, is 2.17 mequiv. g^{-1} . Identification of mineral phases performed by X-ray diffraction analysis (Rigaku X-Ray Diffractometer Ultima Model: D/MAX) on as-received sample demonstrated the presence of clinoptilolite as the major component (approximately 80%), with main impurity

Table 1
Physical properties of different forms of clinoptilolite sample

Parameters	Clinoptilolite sample		
	As-received	Pretreated	Regenerated
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	36.7	40.4	ND
Average pore diameter (Å)	17.5	17.5	ND
Density (g l^{-1})	2.27	2.23	2.22

ND could not be detected.

identified as quartz. The diffractometer pattern of the clinoptilolite used in this study is given in [Supplementary Data, Fig. A](#).

Specific surface area and average pore diameter of the sorbent were determined by BET method using N_2 as adsorbate by Quantochrome Autosorb Automated Gas Sorption System and the density of samples was determined using a helium pycnometer (Table 1). As seen from Table 1, pretreatment resulted in a slight increase of the surface area of clinoptilolite. Specific surface area and average pore diameter could not be detected on the five-time regenerated samples using the same measurement techniques mentioned above.

2.2. Selection of the pretreatment and regeneration chemical

Four different chemicals (NaCl, KCl, CaCl_2 and HCl) were tested for their performance in both pretreating clinoptilolite for higher Cd removal capacity, and regenerating it to sustain or improve Cd removal capacity. These studies were carried out in batch mode using an orbital shaker (Edmund Buhler KS-15). Pretreatment was performed as follows: 1 g 50 ml^{-1} solid to liquid ratio, 1 M NaCl, KCl, CaCl_2 , or HCl, at 25 ± 1 °C, for 24 h, at 150 rpm. Clinoptilolite samples were then washed with deionized water until no Cl^- was detected in washing water. The pretreated samples were dried at 105 °C for 24 h, and stored in a desiccator until further use. Metal removal was performed as follows: 1 g 100 ml^{-1} solid to liquid ratio, 200 mg l^{-1} initial Cd concentration at a pH of 4, at 25 ± 1 °C, 125 rpm, until equilibrium is reached (6 h). The Cd-loaded clinoptilolite was then dried and stored in a desiccator. The regeneration step was performed under the same experimental procedures as the pretreatment step. Finally, the regenerated clinoptilolite samples were used for Cd removal following the previously mentioned metal removal procedure.

2.3. Optimization of pretreatment conditions

After selection of the appropriate pretreatment chemical, studies were performed in continuous mode for the determination of optimum pretreatment conditions. The concentration and flowrate of NaCl solution was selected as 1 M and 2 bed volume (BV) h^{-1} (where 1 BV refers to the empty column volume of 130 mL occupied by clinoptilolite) in upflow mode. The following conditions were tested under the mentioned conditions: total volume of pretreatment solution (10,

20, 40 BV), initial pH of pretreatment solution (no adjustment (pH 5.5), 7), and water quality used for the preparation of pretreatment solution (deionized and tap water). After unloading the column, clinoptilolite was thoroughly mixed and duplicate samples were taken to determine the efficiency of pretreatment in terms of its effect on Cd removal. After all tested pretreatment alternatives, the following conditions were used during Cd removal: batch mode of operation using an orbital shaker, 1 g 100 ml⁻¹ solid to liquid ratio, 200 mg l⁻¹ initial Cd concentration, pH of 4, 25 ± 1 °C, 125 rpm, until equilibrium is reached (6 h). Samples were then immediately centrifuged at 3800 rpm for 5 min to ensure solid–liquid separation and acidified using concentrated HNO₃ and kept at 4 °C until analysis.

2.4. Cd removal/clinoptilolite regeneration experiments

Successive Cd removal and regeneration cycles were conducted in continuous mode using duplicate glass columns of 26.5 cm height and 2.5 cm internal diameter, packed with clinoptilolite (approximately 110 g). Metal solutions were pumped into columns in upflow mode using a peristaltic pump, following pretreatment of column with 1 M NaCl (prepared with deionized water) at 2 BV h⁻¹ for 10 h. Cd removal experiments were performed using 200 mg l⁻¹ initial metal concentration in deionized water, at pH 4, 10 BV h⁻¹ flowrate at 25 ± 1 °C. During column operation, water samples were collected from the exit of the column at designated time intervals, and after pH measurement, they were acidified with HNO₃ and kept at 4 °C prior to analysis. Column operation was terminated at breakthrough (BT) point which was defined as 1% of the influent Cd concentration. After regeneration, clinoptilolite bed was washed with deionized water to remove excess Cl⁻ at 10 BV h⁻¹ flowrate for 90 min. Successive metal removal/clinoptilolite regeneration cycles were conducted in the same manner. BT capacity and the total amount of Cd eluted were calculated using MATLAB 6.5 Curve Fitting Toolbox.

2.5. Analytical techniques

All chemicals used were analytical grade reagents. Metal solutions were prepared by dissolving Cd(NO₃)₂·4H₂O in high purity deionized water. Aside from Cd, exchangeable cations (Na, K, Ca and Mg) expected to be released from 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. For successive Cd removal/clinoptilolite regeneration cycles, Si and Al were also measured in the aqueous phase by Hach DR 2400 Spectrophotometer (as SiO₂) and by Leeman Labs Inc. Direct Reading Echelle Inductively Coupled Plasma-Optic Emission Spectrometer, respectively. Cl⁻ ions in washing water (after regeneration) were measured by Argentometric Method [24]. pH measurements were carried out using a digital pH meter (CyberScan 500). All experiments were carried out in duplicates and mean values are presented.

3. Results and discussion

3.1. Selection of the pretreatment and regeneration chemical

The performance of the four different chemicals, namely, NaCl, KCl, CaCl₂ and HCl during pretreatment and subsequent regeneration of clinoptilolite after Cd removal are presented in Fig. 1, as compared to the performance of the as-received sorbent. Also given in the figure is the corresponding release of exchangeable cations into the aqueous phase, which provide information regarding the effectiveness of pretreatment, such that the higher the ratio of the cation of concern (e.g. Na/(Na + K + Ca + Mg) for P–NaCl), the closer the clinoptilolite is to homoionic form. All exchangeable cations can be observed in significant amounts in the aqueous phase after Cd removal using the as-received clinoptilolite, which is expected since all four cations are present to some extent in the structure.

It is evident from Fig. 1 that NaCl enable the closest achievement of the homoionic form, coupled with the best Cd removal efficiency, both after pretreatment, and after regeneration. Pretreatment is feasible only if it significantly increases the Cd removal capacity of the sorbent. These results indicate that only NaCl succeeds in significantly increasing (more than doubling) the metal removal capacity as compared to that of the as-received form. This is in agreement with a majority of the relevant literature on Cd removal [9,25,26]. Additionally, Zamzow et al. [10] and, Abusafa and Yucel [13] reported comparable increase in loading capacities using Na and K, yet much lower capacities using Ca-pretreated clinoptilolite samples, for lead and cesium removal, respectively. HCl pretreatment was found to be unfavorable for metal removal capacity according to this study as well as others [11,27]. On the other hand, Vasylechko et al. [12] observed favorable Cd removal after pretreatment with HCl.

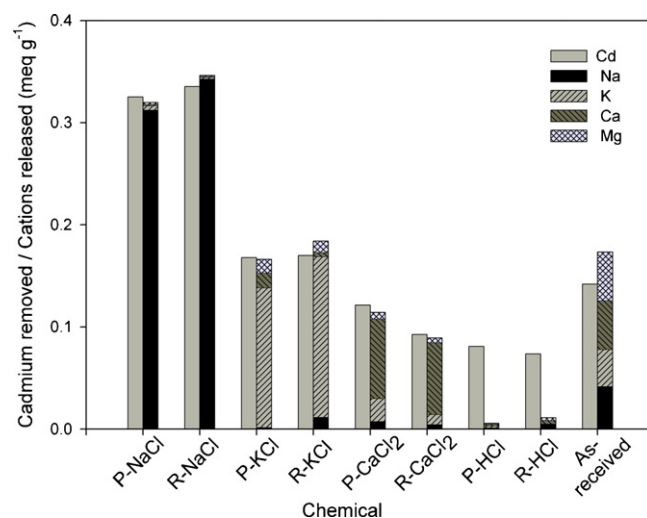


Fig. 1. Performance of clinoptilolite samples pretreated and regenerated using four different chemicals as compared to the as-received form of the sorbent. Bars labeled “P-chemical name” designate the results for pretreated sorbents, whereas those labeled “R-chemical name” designate the results using regenerated clinoptilolite.

Table 2
Effect of pretreatment conditions on Cd removal

Parameters	Condition	Time (h)	Capacity (mequiv. g ⁻¹)
Q_{total}	10 BV	5	0.31
	20 BV	10	0.33
	40 BV	20	0.34
pH	No adjustment (5.5)	10	0.33
	7	10	0.32
Water	Deionized	10	0.33
	Tap	10	0.33

The results of the present study suggest acid-instability of the clinoptilolite used.

3.2. Optimization of pretreatment conditions in continuous mode

In order to optimize pretreatment of clinoptilolite bed to achieve the most favorable Cd removal capacity, the effect of total volume, pH and water quality of pretreatment solution (1 M NaCl) was investigated (Table 2). A very small improvement is observable in Cd uptake capacity by increasing the total volume of NaCl solution from 10 to 40 BV. Hence, 20 BV was selected for pretreatment, which is 10 h of pretreatment at 2 BV h⁻¹ flowrate. Likewise, no significant change in Cd removal capacity was observed between the bed that was pretreated with NaCl having pH 5.5 (unadjusted) and that pretreated with NaCl having a pH of 7.0. This is possibly due to the superior concentration gradient between Na and H ions in 1 M NaCl solution. Similarly,

water quality was also found not to be an important factor despite the diverse ion content of tap water (in mg l⁻¹: Na⁺: 72; K⁺: 4; Ca²⁺: 74; Mg²⁺: 22; NO₃⁻: 6; SO₄²⁻: 20; Cl⁻: 120; conductivity = 960 $\mu\text{S cm}^{-1}$ at 24 °C) when compared to deionized water (conductivity = 0.920 $\mu\text{S cm}^{-1}$ at 24 °C) used in the preparation of the NaCl solution. The latter result is in fact quite significant since the use of tap water would be highly favorable in terms of cost when future practical applications are considered.

The findings regarding total volume and water quality of pretreatment solution are in complete agreement with those of Inglezakis et al. [5], who used Greek clinoptilolite and examined the same parameters among others on their influence on the effective capacity, using lead. In their study, however, a dependence of pH was noted (pH 7.5 to be more favorable when compared to acidic or basic pHs) whereas the results of this study indicates no notable difference. Consequently, 1 M NaCl solutions prepared with deionized water and no pH adjustment were used for pretreatment and regeneration throughout the rest of the study. Detection of exchangeable cations in the aqueous phase in further studies necessitated the preference for the use of deionized water over tap water in pretreatment solution preparation.

3.3. Cd removal/c clinoptilolite regeneration experiments

Five cycles of Cd removal/c clinoptilolite regeneration were performed and the results are presented in Fig. 2. Metal removal capacity of the bed at breakthrough (BT) was observed to increase until the third cycle, from approximately 0.62 mequiv. Cd g⁻¹ and 0.66 mequiv. Cd g⁻¹ in the first and

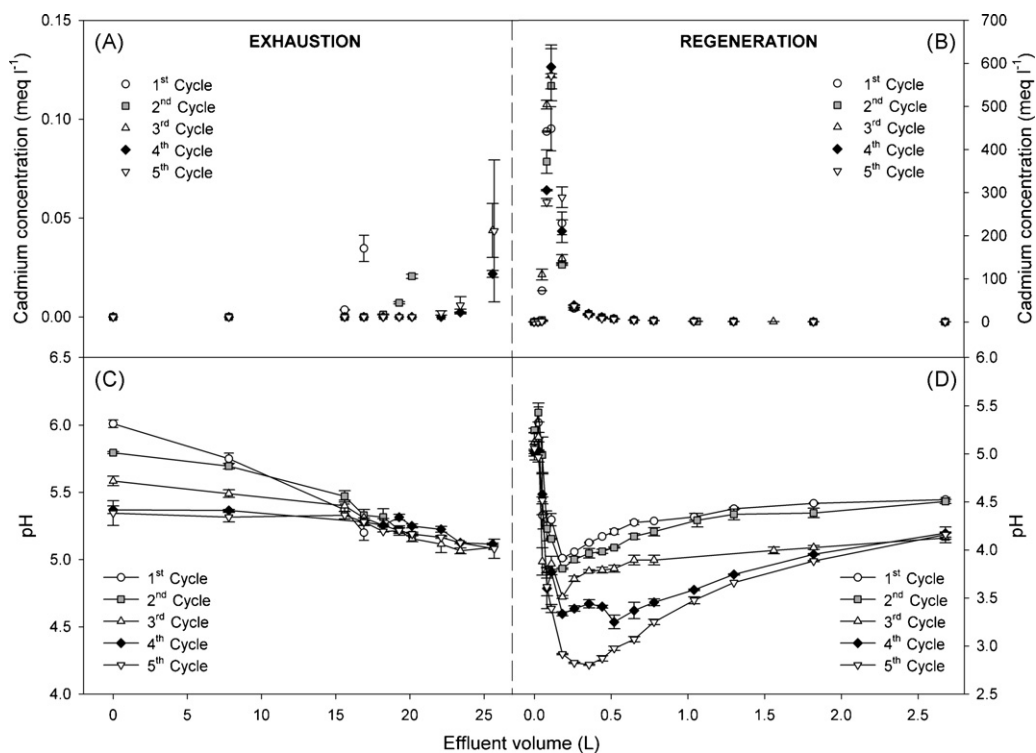


Fig. 2. The change in Cd concentration (A and B), and pH (C and D) during Cd removal and clinoptilolite regeneration cycles.

second cycles, respectively, to a steady $0.84 \text{ mequiv. Cd g}^{-1}$ for the last three cycles (Fig. 2A). Although these results would suggest complete elution of Cd from the bed, calculations indicate an almost constant elution of Cd for all cycles ($0.60 \pm 0.04 \text{ mequiv. g}^{-1}$), yielding 97%, 91% and 72% elution efficiencies for the first, second and rest of the cycles, respectively (Fig. 2B). A fixed residual Cd capacity of $0.005 \text{ mequiv. g}^{-1}$ was observed at the end of all regeneration cycles. The steady Cd removal capacity obtained in continuous mode experiments represents about 30% increase from the maximum capacity observed in batch equilibrium studies ($0.65 \text{ mequiv. Cd g}^{-1}$) [19]. Other researchers have noted either unchanging or decreasing metal removal capacity of the clinoptilolite columns in progressing cycles, with almost complete elution of the sorbed metal [10,12,22,28,29].

The pH of the effluent was also continuously monitored during exhaustion and regeneration cycles (Fig. 2C and D). The effluent pH value was recorded to be two units above the influent (pH of 4) immediately after the solution was introduced to the column. This can be explained by sorption of hydrogen ions during exhaustion cycles. The difference between the effluent and influent pH values becomes less prominent, however, in progressing cycles when the pH value is gradually reduced in the first three cycles and seems to be stable for the last two cycles. This may be an indication of a change in Cd removal mechanism in progressing cycles. Later on in each cycle, a decrease in the effluent pH is evident as BT approaches, owing to the release of H^+ ions from clinoptilolite structure with increasing Cd concentration, as well as the increase in the effect of hydrolysis of Cd due to its increasing concentration.

During regeneration, a significant drop of pH followed by its relatively mild increasing trend accompanies a sharp peak in Cd concentration (Fig. 2B and D). The effluent pH value of the regenerant solution does not reach the influent for the regenerant volume used in the study, however, a slowly increasing trend of pH is apparent. Similar trends of metal concentration and pH were observed by Medvidovic et al. [29] where the pH and lead concentration trends from one regeneration cycle was presented for a clinoptilolite bed completely exhausted with lead. Interestingly in the present study, the pH trends of successive cycles given in Fig. 2D do not overlap, but are characterized by a consistently greater pH drop with each progressing cycle. This results in highly acidic conditions in solution especially in the last two regeneration cycles. Furthermore, the first and second regeneration runs which result in significantly greater Cd elution efficiencies, stabilize at a higher pH value (4.5), when compared to the rest of the regeneration runs, where the pH stabilizes consistently at a value about 0.5 units less than this.

The sorbent in the column was not changed, therefore the increase in the metal removal efficiency may be interpreted as a change in the dominance of different Cd removal mechanisms. The increase in Cd removal in further cycles may be attributed to a couple of mechanisms:

- (1) Ion exchange of Cd with Na and other exchangeable cations on clinoptilolite structure is expected to be the dominant removal mechanism [6,30]. As ion exchange is a dynamic

process, the binding forces between the cations and clinoptilolite can be considered to be relatively weak [31]. This would allow clinoptilolite to get closer to its homoionic Na-form with each progressing regeneration cycle as it is repetitively exposed to concentrated NaCl solution. Cd replacement, especially with low mobility and strongly bonded cations (K, Ca) in exhaustion cycles, may make replacement of Na with Cd in regeneration steps easier when compared to other structural cations. Examination of exchangeable cations (Na, K, Ca and Mg) in the effluent of Cd removal runs reveals this progressive conversion of clinoptilolite into its homoionic form (Fig. 3). As can be seen from Fig. 3A, in the effluent of the first Cd removal run, apart from the expected high concentrations of Na, appreciable concentrations of K throughout the run, and detectable

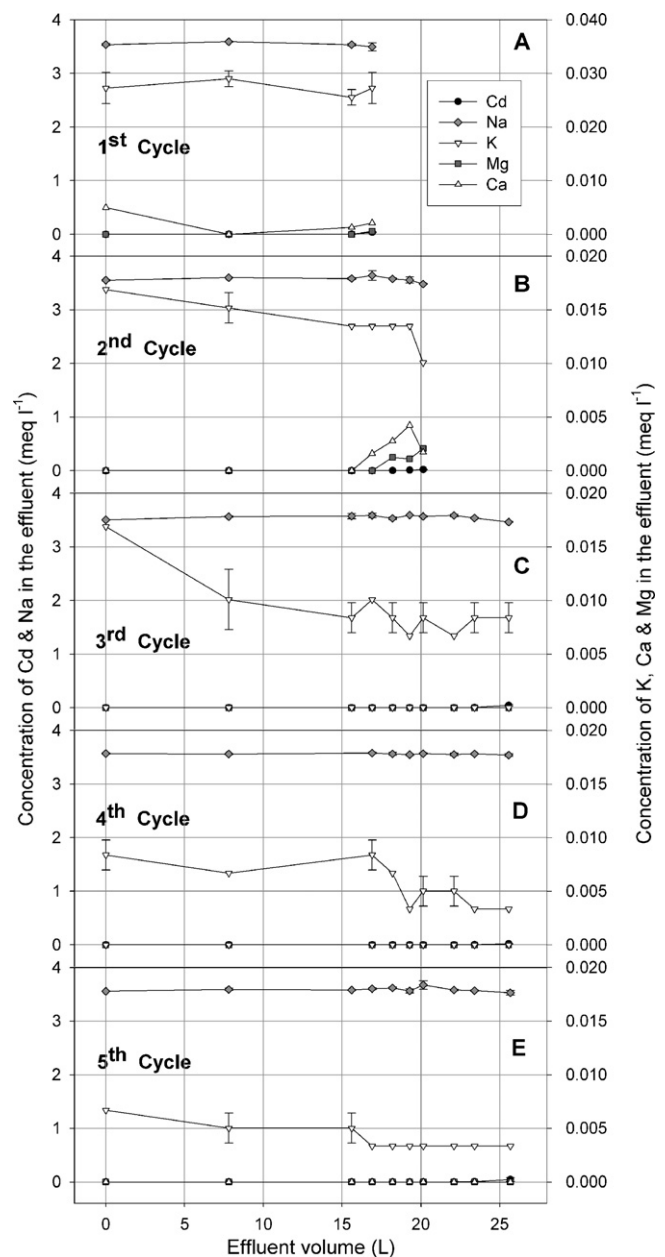


Fig. 3. Release of exchangeable cations during progressing Cd removal cycles.

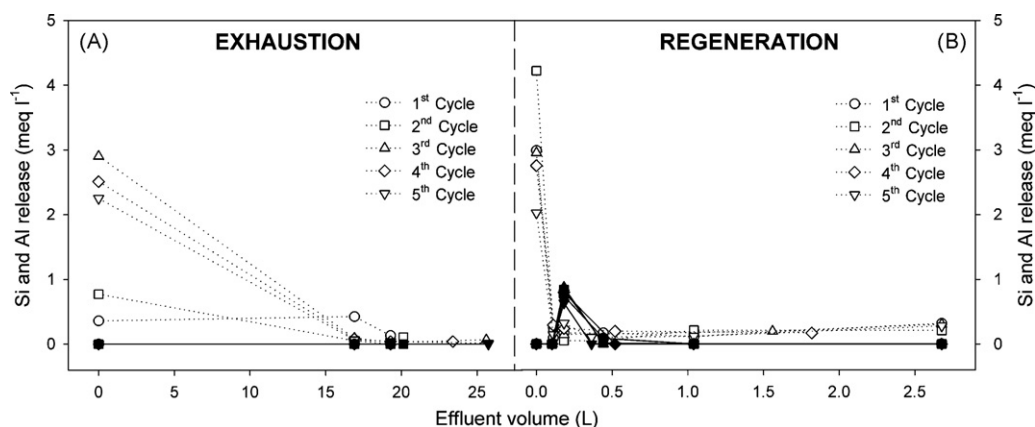


Fig. 4. Release of Si (open symbols) and Al (filled symbols) during progressing A. Cd removal and B. Clinoptilolite regeneration cycles.

amounts of Ca and Mg near the BT point, were measured. This shows the participation of cations other than Na during Cd removal in the first run. The presence of K may be explained by the K-rich nature of the clinoptilolite used in this study, however, much less K is observable in the effluent of the last Cd removal run (Fig. 3E). A similar trend is observed for Ca and Mg ions. This suggests that sites initially occupied by these exchangeable ions which were not replaced by Na during pretreatment, are being replaced by this ion (reaching homoionic Na-form) in progressing regeneration runs. Quantitatively, however, the amount of K or other ions replaced by Na is too small to fully explain the increase in Cd removal capacity.

- (2) As metal concentration increases, the metal ions which can no longer form outer-sphere complexes (e.g. ion exchange), are forced into internal sites and start forming inner-sphere complexes [32]. It may be possible that during regeneration with NaCl, Cl^- ions may be entrapped in the channels or cavities of clinoptilolite and remain even after washing of the bed following regeneration. These may in turn form

inner-sphere complexes with Cd ions during removal runs, and account for the increasing Cd removal capacity. The results of Doula and Ioannou [32] reveal inner-sphere complex formation of Cu in the presence of KCl. The type of complexation is stated to affect the reversibility of sorption reactions where inner-sphere complexation appears to be irreversible due to the formation of covalent bonds [30,32]. The results of the present study are in line with these discussions, such that lower desorption efficiencies were obtained for the third and later regeneration runs accompanied with higher metal removal capacities when compared to the initial runs. Furthermore, an inner-sphere complex with Cl^- is expected to facilitate dissolution of clinoptilolite [32]. In order to investigate this, framework cations (Si and Al) of clinoptilolite were measured in the aqueous phase (Fig. 4). Results show a significantly greater amount of Si release in the third Cd removal run onwards (Fig. 4A), pointing to the presence of dissolution and supporting this explanation for the enhanced Cd removal in further cycles. A part of the Si release may be due to dis-

Table 3
Comparison of heavy metal removal studies using fixed bed columns packed with clinoptilolite

Cation	Solution characteristics	Pretreatment chemical	Regeneration chemical	Cycle	Regeneration performance	Reference
Pb, Cd, Cs, Cu, Co, Cr, Zn, Ni, Hg	Mixed metal solution	–	NaCl	27–37	Influent 30 times concentrated, regeneration efficiency for Cd = 100%	[10]
Cd	Single metal	HCl, HNO ₃ , H ₂ SO ₄ , NH ₄ Cl	NaCl, HNO ₃ , HCl + HNO ₃ , KNO ₃ , KClO ₃	1	Regeneration efficiency = 55–92%	[12]
NH ₄ ⁺ , Pb, Zn, Cu, Cd	Mixed metal solution	NaCl	NaCl	3	Breakthrough for Cd occurs at 175 BV, whereas 40 BV found adequate for regeneration	[17]
Pb	Single metal	–	NaCl, NaOH	1	Regeneration efficiency = 95% (for clinoptilolite)	[22]
Pb and other cations	Synthetic battery wastewater	NaCl	NaCl	>30	4–5 mg/L influent Pb concentrated to 270 mg/L in regenerant solution	[28]
Pb	Single metal	–	NaNO ₃	8	Volume of regenerant used is three to four times smaller than the metal solution volume per cycle	[29]
Cd	Single metal	NaCl	NaCl	5	Influent seven times concentrated, regeneration efficiency = 72–97%	This study

solution of the main impurity, quartz, however, a greater release of Si in the last three cycles suggests its association with Cd removal. Al, on the other hand, was only observed during regeneration at the point of highest ionic strength and lowest pH (Fig. 2B and D), which is in agreement with Doula et al.'s [33] observations. Moreover, the BET technique using N₂ as adsorbate, which was applied successfully for the determination of specific surface area of as-received and pretreated samples, could not be applied for the five-time regenerated clinoptilolite samples. This suggests some form of modification of clinoptilolite, possibly due to formation of Cd complexes on the outer or inner surfaces, resulting in clogging of the pores and preventing N₂ entry.

By using 20 BV of the regenerant solution, Cd could be concentrated by about seven times in each cycle, when compared to the influent Cd concentration. A brief summary of relevant work on heavy metal removal using clinoptilolite in packed bed column arrangement incorporating regeneration is presented in Table 3. The performance criteria presented by researchers in these studies differ from one another significantly; therefore general information regarding performance was presented in the sixth column of the table. As can be seen in Table 3, researchers noted concentration of the influent metal by 4–5 times to 30 times, achieving regeneration efficiencies of up to 100% and reaching concentrations in the order of thousands of ppm, depending on the influent metal concentration, identity of the metal, etc. In general, these results are very promising when the application of metal recovery is considered from these regenerant solutions, because metal recovery systems such as electrolysis works more efficiently for solutions containing relatively high metal concentrations [34].

4. Conclusions

Clinoptilolite from the Manisa–Gördes deposit in Turkey was modified to investigate its Cd removal potential from aqueous solutions considering the effect of pretreatment conditions and regeneration. The conclusions are as follows:

- Clinoptilolite sample treated by a total of 20 BV of 1M NaCl solution prepared in tap water with no pH adjustment was found to be satisfactory for efficient Cd removal after pretreatment.
- Five exhaustion and regeneration cycles were conducted and clinoptilolite exhibited a 36% higher removal capacity in the last three runs (0.84 mequiv. g⁻¹) when compared to the first two runs (0.62 and 0.66 mequiv. g⁻¹). Cd desorption results indicate an almost constant elution of Cd for all cycles (0.60 ± 0.04 mequiv. g⁻¹), yielding 97%, 91% and 72% elution efficiencies for the first, second and rest of the cycles, respectively. A fixed residual Cd capacity of 0.005 mequiv. g⁻¹ was observed at the end of all regeneration cycles.
- The increase in Cd removal capacity was discussed in terms of the progressive conversion of clinoptilolite to its homoionic

Na-form, as well as the presence of other removal mechanisms accompanying ion exchange.

- Promising results in terms of the potential for metal recovery were obtained during regeneration cycles with the concentration of the influent Cd by about seven times.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.12.101.

References

- [1] G.V. Tsitsishvili, T.G. Andronikashvili, G.M. Kirov, L.D. Filizova, *Natural Zeolites*, Ellis Horwood, Chichester, 1992.
- [2] S. Kesraoui-Ouki, C.R. Cheeseman, R. Perry, *Natural zeolite utilization in pollution control: a review of applications to metals' effluents*, *J. Chem. Technol. Biotechnol.* 59 (2) (1994) 121–126.
- [3] A. Langella, M. Pansini, P. Cappelletti, B. de Gennaro, M. de' Gennaro, C. Colella, NH₄⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ exchange for Na⁺ in a sedimentary clinoptilolite, North Sardinia, Italy, *Micropor. Mesopor. Mater.* 37 (3) (2000) 337–343.
- [4] V.J. Inglezakis, M.M. Loizidou, H.P. Grigoropoulou, *Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility*, *J. Colloid Interface Sci.* 275 (2) (2004) 570–576.
- [5] V.J. Inglezakis, K.J. Hadjiandreou, M.D. Loizidou, H.P. Grigoropoulou, *Pretreatment of natural clinoptilolite in a laboratory-scale ion exchange packed bed*, *Water Res.* 35 (9) (2001) 2161–2166.
- [6] V. Cagin, N. Morali, I. Imamoglu, *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) (2007) 45–54.
- [7] M.J. Semmens, W.P. Martin, *The influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions*, *Water Res.* 22 (5) (1988) 537–542.
- [8] S. Kesraoui-Ouki, C. Cheeseman, R. Perry, *Effects of conditioning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal*, *Environ. Sci. Technol.* 27 (6) (1993) 1108–1116.
- [9] L. Curkovic, S. Cerjan-Stefanovic, T. Filipan, *Metal ion exchange by natural and modified zeolites*, *Water Res.* 31 (6) (1997) 1379–1382.
- [10] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, *Removal of heavy metals and other cations from wastewater using zeolites*, *Sep. Sci. Technol.* 25 (13–15) (1990) 1555–1569.
- [11] D.H. Lee, S.J. Kim, H. Moon, *Preparation of a clinoptilolite-type Korean natural zeolite*, *Kor. J. Chem. Eng.* 16 (4) (1999) 525–531.
- [12] V.O. Vasylychko, G.V. Gryshchouk, Y.B. Kuz'ma, V.P. Zakordonskiy, L.O. Vasylychko, L.O. Lebedynets, M.B. Kalytov's'ka, *Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite*, *Micropor. Mesopor. Mater.* 60 (1–3) (2003) 183–196.
- [13] A. Abusafa, H. Yucel, *Removal of ¹³⁷Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite*, *Sep. Purif. Technol.* 28 (2) (2002) 103–116.
- [14] E. Maliou, M. Malamis, P.O. Sakellarides, *Lead and cadmium removal by ion exchange*, *Water Sci. Technol.* 25 (1) (1992) 133–138.
- [15] G. Yuan, H. Seyama, M. Soma, B.K.G. Theng, A. Tanaka, *Adsorption of some heavy metals by natural zeolites: XPS and batch studies*, *J. Environ. Sci. Health A* 34 (3) (1999) 625–648.

- [16] A. Cincotti, A. Mameli, A.M. Locci, R. Orru, G. Cao, Heavy metals uptake by Sardinian natural zeolites: experiment and modeling, *Ind. Eng. Chem. Res.* 45 (3) (2006) 1074–1084.
- [17] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, *Water Res.* 18 (12) (1984) 1501–1507.
- [18] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.* 280 (2) (2004) 309–314.
- [19] K. Gedik, I. Imamoglu, in: R.S. Bowman, S.E. Delap (Eds.), *Zeolite'06—7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites*, Socorro, New Mexico, USA, 2006, pp. 115–116.
- [20] K. Gedik, I. Imamoglu, in: R.S. Bowman, S.E. Delap (Eds.), *Zeolite'06—7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites*, Socorro, New Mexico, USA, 2006, pp. 117–118.
- [21] A. Top, S. Ulku, Silver, zinc and copper exchange in a Na-clinoptilolite and resulting effect on antibacterial activity, *Appl. Clay Sci.* 27 (1/2) (2004) 13–19.
- [22] M. Turan, U. Mart, B. Yuksel, M.S. Celik, Lead removal in fixed-bed columns by zeolite and sepiolite, *Chemosphere* 60 (10) (2005) 1487–1492.
- [23] A.E. Turkman, S. Aslan, I. Ege, Treatment of metal containing wastewaters by natural zeolites, *Fres. Environ. Bull.* 13 (6) (2004) 574–580.
- [24] L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, Washington, USA, 1998.
- [25] H. Faghihian, M.G. Marageh, H. Kazemian, 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) (1999) 655–660.
- [26] A. Cincotti, N. Lai, R. Orru, G. Cao, Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling, *Chem. Eng. J.* 84 (3) (2001) 275–282.
- [27] M.I. Panayotova, Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite, *Waste Manage.* 21 (7) (2001) 671–676.
- [28] D. Petruzzelli, M. Pagano, G. Tiravanti, R. Passino, Lead removal and recovery from battery wastewaters by natural zeolite clinoptilolite, *Solvent Extr. Ion Exc.* 17 (3) (1999) 677–694.
- [29] N.V. Medvidovic, J. Peric, M. Trgo, Column performance in lead removal from aqueous solutions by fixed bed of natural zeolite-clinoptilolite, *Sep. Purif. Technol.* 49 (3) (2006) 237–244.
- [30] M.K. Doula, Removal of Mn^{2+} ions from drinking water by using clinoptilolite and clinoptilolite-Fe oxide system, *Water Res.* 40 (17) (2006) 3167–3176.
- [31] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange of Pb^{2+} , Cu^{2+} , Fe^{3+} , and Cr^{3+} on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake, *J. Colloid Interface Sci.* 261 (1) (2003) 49–54.
- [32] M.K. Doula, A. Ioannou, The effect of electrolyte anion on Cu adsorption-desorption by clinoptilolite, *Micropor. Mesopor. Mater.* 58 (2) (2003) 115–130.
- [33] M. Doula, A. Ioannou, A. Dimirkou, Copper adsorption and Si, Al, Ca, Mg, and Na release from clinoptilolite, *J. Colloid Interface Sci.* 245 (2) (2002) 237–250.
- [34] C.S. Brooks, *Metal Recovery from Industrial Waste*, Lewis Publishers, Chelsea, MI, 1991.