Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23792

150 (2019) 157–165
May

Relationship between Si/Al ratio and the sorption of Cd(II) by natural and modified clinoptilolite-rich tuff with sulfuric acid

Y. Abdellaoui[a], M.T. Olguin[b], M. Abatal[c,*], A. Bassam[a], G. Giácoman-Vallejo[a]

[a]*Facultad de Ingeniería, Universidad Autónoma de Yucatán, Av. Industrias no Contaminantes por Periférico Norte, Cordemex, 150 Mérida, YUC, México*
[b]*Departamento de Química, Instituto Nacional de Investigaciones Nucleares, A.P. 18–1027, C.P. 11801, Ciudad de México, México*
[c]*Facultad de Ingeniería, Universidad Autónoma del Carmen, C.P. 24180, Ciudad del Carmen, Campeche, México, email: mabatal@pampano.unacar.mx*

Received 30 September 2018; Accepted 10 January 2019

ABSTRACT

In this paper, the differences in the adsorption mechanisms and adsorption capacities of clinoptilolite materials with different Si/Al ratio (SAR) for Cd^{2+} ions from aqueous solutions are discussed. The adsorbents were characterized with respect to their phase composition, morphology, specific surface area, cation exchange capacity and point of zero charge. Batch adsorption experiments were performed considering the Cd initial ion concentration, contact time, adsorbent dose, SAR, and pH. The regression coefficient value revealed that the experimental data best fit to Pseudo-second-order model, whilst the kinetic rate constant k_2 (g/mg min^{-1}) showed an exponential behavior as a function of adsorbent mass for all clinoptilolite materials. The equilibrium adsorption data were best described by the Langmuir adsorption isotherms with highest q_m = 5.974 mg/g for Nat-CLI, whereas K_L parameter was found increased with increasing SAR. The adsorption capacities of the acid-modified clinoptilolite (high SAR) were lower than that of natural zeolite because of the dealumination of the zeolitic material and consequently the loss of the ion exchange sites.

Keywords: Cadmium; Sorption; Clinoptilolite; Sulfuric acid

---

1. Introduction

Cadmium is among the most toxic heavy metals to plants, animals, and human beings in the environment, even at very low concentrations [1]. In fact, it is classified by the International Agency for Research on Cancer (IARC) and the Environmental Protection Agency (EPA) as a priority pollutant due to the high degree of toxicity and as a "known" or "probable" human carcinogen [2]. While, the World Health Organization (WHO) established a limit value of 3 µg/L for Cd in drinking water [3]. This stringent limit of cadmium in potable water is due to its severe toxicity to the human body, and indeed, the accumulation of this metal in organisms tends to cause numerous health diseases and disorders [4–6]. The wastewaters of heavy metals including cadmium are generated by different activities, among them batteries manufacturing, painting, and mining. Therefore, a necessary treatment is required before the disposal of polluted effluent into the ecosystem. Thus various techniques have been used for the removal of heavy metals which include chemical precipitation [7], chemical coagulation [8], electro-coagulation treatment [9], bioflocculation [10], membrane technologies (reverse osmoses) [11], emulsion liquid membrane [12], nanofiltration membranes [13], complexation-assisted ultrafiltration [14], photocatalysis [15], and ion exchangers as nylon 6,6 Zr(IV) phosphate, Ti(IV) iodovanadate and acetonitrile stannic(IV) selenite composite [16–18]. In general, these methods are expensive and insufficient particularly

---

* Corresponding author.

1944-3994/1944-3986

when the toxic metals are present in the wastewater at low concentrations.

Many investigations suggest that zeolites are among the best adsorbents and ion-exchanger for the removal of cadmium according to their microporous structures made from the interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4) moieties [19].

Clinoptilolite is the most abundant; it is commonly used in environmental applications by its high affinity for some heavy metals, especially for cadmium and lead elements [20]. Thermal treatment, inorganic salts treatment, and acid leaching are the most common modification methods of natural zeolites, which have a great influence on their practical applications [21–23]. The treatment of natural clinoptilolite with mineral acids, such as HCl and H_2SO_4, causes a destruction of impurities that block the pores and then creates an extra-porosity modifying their morphology and chemical compositions [24,25]. However, the effectiveness of acid treatment depends on several factors including the chemical composition, mineral purity and treatment condition [26].

The SiO_2/Al_2O_3 ratio (SAR) is one of the important factors that influence on the performance of the zeolites. The SAR indicates the amount of aluminum present in the zeolite framework which introduces the creation of negative charges in the zeolite structure. Thereunto, a low SAR zeolite provides more binding sites and extra framework cations in its structure. Theoretically, low SAR of the zeolite has a high sorption capacity of heavy metals compared with the high SAR ones. Leinonen and Lehto studied the removal of Ni, Zn, Cd, Cu, Cr, and Co from wastewater using some types of zeolite with different SAR value [27]. The results showed that the best uptake of heavy metals was achieved with the low SAR zeolite. Furthermore, a previous study [28] reported that Cd(II) adsorption capacity is highly dependent on the mineral characteristic. However, to the best of our knowledge an integrated research about the removal of Cd ions from aqueous solution with different Si/Al ratio of clinoptilolite modified by sulfuric acid has not been published elsewhere. Therefore, the aim of this work was to describe the removal behavior of Cd(II) from aqueous media by natural and acid-modified clinoptilolite considering different parameters among them Cd initial ion concentration, contact time, adsorbent dose and pH. It is important to mention that the novelty of this paper was to know about the influence of Si/Al ratio, on the sorption properties of the acid-modified zeolitic materials for the sorption of Cd^{2+} from aqueous solutions.

2. Materials and methods

2.1. Materials

The natural zeolite used in the present work was collected from "Villa de los Reyes" deposit located in the San Luis Potosí State, Mexico. The samples were sieved to obtain a grain size of 40 mesh, and washed with deionized water several times to remove water-soluble impurities. The clinoptilolite samples were then dried for the overnight at 80°C (labeled as Nat-CLI) and used to prepare the acid-form of natural clinoptilolite with sulfuric acid. This modification was carried on using 0.1, 0.2 ,0.5 ,and 1.0 M H_2SO_4 solutions in contact with the zeolitic material at the ratio of 1:20 W/V under reflux condition by 4 h. The samples were washed with excess deionized water until the pH of the washing solution reached approximately 6, and then dried overnight at 80°C. The samples were labeled as follows: HCLI-0.1M, HCLI-0.2M, HCLI-0.5M, and HCLI-1M.

2.2. Characterization methods

The clinoptilolite samples were characterized using XRD APD 2000 PRO X-Ray diffractometer (35 Kv and 25 mA; angular scanning range 2°–60°, and angular speed 0.025 deg/s; step time = 10 s). The obtained crystalline phases of the samples were identified by comparison with JCPDS cards. The morphology and elemental composition were examined on a SEM HITACHI S-3400N fitted with an electron dispersive X100 ray (10 Kv and 30 pA; image magnification 1,500X and the work distance of 10.5 mm). Infrared absorption measurements were carried out using a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 670 FT-IR) within a range from 4,000 to 400 cm^{-1} with a resolution of 4 cm^{-1} in a KBr water.

The pH of the point of zero charge (pH_{PZC}) of natural and modified clinoptilolite was determined by introducing 0.10 g of each adsorbent with 50 mL of 0.01 M NaCl adjusted to different initial pH values (pH = 2, 4, 5, 6, 8, 10, and 12). The suspensions were allowed to equilibrate for 24 h under agitation at 25°C, decanted and the final pH values of each remaining solution were measured using the pH-meter Thermo Scientific (ORNION 3star pH Benchtop). The plot of $pH_{initial}$ vs. pH_{final} was constructed which the intersection of these curves determines the pH_{pzc}.

2.3. Sorption

The experiment was performed using batch the technique to determine the kinetics of the sorption of Cd(II) by Nat-CLI, HCLI-0.1M, HCLI-0.2M, HCLI-0.5M, and HCLI-1M zeolitic samples. For this purpose, 0.10 g of each adsorbent was added to 10 mL of 10–100 mg L^{-1} of Cd(II) solutions at pH = 2. The mixtures were placed in centrifuge tubes and shaken for 15, 30, 60, 120, 180, 240, 300, 360, 720, and 1,440 min. At the end of the given contact time, the tubes were centrifuged at 4,500 rpm for 2 min, and adsorbent was removed by filtration, while the final Cd(II) concentration was determined by atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series) at λ of 213.9 nm. The amount of Cd(II) sorbed on natural and modified clinoptilolite was calculated using the mass balance expression:

$$q = \frac{\left(C_0 - C_t\right)V}{W} \quad (1)$$

where q is the amount of Cd(II) sorbed in the natural and modified zeolites (mg/g), V is the solution volume (mL), W is the amount of sorbent (g), C_o and C_t are the initial and final metal concentration (mg L^{-1}), at time t (min).

The effects of (i) Cd(II) initial concentration, (ii), initial pH, (iii) adsorbent dosage and (iv) time, on the sorption by clinoptilolite samples were also performed by a similar procedure described above considering the experimental conditions presented in Table 1. All the experiments were conducted in duplicate to ensure reproducibility of the collected data and the results are expressed as average values.

3. Results and discussions

3.1. Materials characterization

3.1.1. X-ray diffraction

The X-ray diffraction (XRD) results of natural and acid treated clinoptilolite showed the presence of the crystalline structure reported in the literature by main characteristic peaks at 2θ = 9.85°, 11.19, 22.21°; 22.34°; 25.96°, and 28.09° in accordance with the JCPDS card 25–1,349 [29]. Moreover, slight decrease was observed in the relative intensity of the diffractions peaks of modified clinoptilolite with the increase of the concentration of sulfuric acid in the solution from 0.1 to 1 M. These results suggest the successful replacing of the exchangeable cations by H^+ ions with the treatment by H_2SO_4 causing a decrease in the crystallinity and an increase of the porosity. It is important to mention that the structural changes could be associated also to the dealumination of the natural zeolite after the acid treatment as will be discussed later.

3.1.2. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

SEM images indicate that the surface of the natural and acid-treated clinoptilolite shows a similar morphology and typical tabular and coffin shapes of heulandite/clinoptilolite crystals [30]. This result was also confirmed by XRD analysis.

The surface of natural and acid-modified clinoptilolite was analyzed by Energy Dispersive Spectroscopy technique. Chemical composition obtained by EDS indicated that the treatment of the Nat-CLI with sulfuric acid promotes the total elimination of Na^+ and Mg^{2+} and notably decreases the percentage of K^+ and Ca^{2+} ions. The decrease of aluminum cations in the zeolite framework leads a decrease of exchangeable cations (K^+ and Ca^{2+}) percentage and a total elimination of Na+ and Mg^{2+} when acid concentration is 0.1 and 0.2M, respectively.

3.1.3. Infrared spectroscopy

The FTIR spectra of clinoptilolite samples showed a broader band corresponding to symmetric and asymmetric stretching vibration of O–H at 3,446 cm^{-1}. This band became more intensive and is broadened as the acid concentration increased from 0.1 to 1.0 M. The bands related to the Si–O and O–Si–O vibrations respectively at 1,079 and 790 cm^{-1} appeared more intensive after acid modification. The data obtained shows a progressive extraction of aluminum atoms from zeolite framework and consequently the formation of silanol nests.

Table 1
Parameters considered on the adsorption processes of Cd by clinoptilolite samples

Parameters	Time (min)	C_i (mg/L)	pH_i	Adsorbent dosage (g)
Cd(II) initial concentration (C_i)	1,440	10–500	2	0.1
Initial pH (pH_i)	1,440	100	2–10	0.1
Adsorbent dosage	15–360	100	2	0.1–1.0
Time	15–1,440	100	2	0.1

3.1.4. pH of the point of zero charge

The pH_{pzc} for Nat-CLI was found at Ph = 6.00 ± 0.01, while it was 3.00 ± 0.01 for HCLI-0.1M, HCLI-0.2M, HCLI-0.5M, and HCLI-1M. These results can be explained by the dealumination of the zeolitic material, which promotes the decrease of negative charges, the increase of SAR, and consequently diminishes the number of cations and the average electrostatic field generating very strong Lewis acid site in the surface.

3.2. Sorption process

3.2.1. Kinetics

The sorption equilibrium for Cd(II) at pH = 2 by clinoptilolite materials was studied with different SARs at a variable concentration from 10–100 mg/L. Fig. 1 shows the results of sorption capacity of Nat-CLI as a function of the time and the initial concentration Cd(II).

It can be observed that the amount of Cd(II) uptake by Nat-CLI increases with increasing of metal initial concentration (10–100 mg/L). In addition, it can be noted that the adsorption process consisted of two main reaction; initial fast adsorption process within 180 min followed by a slow continuous sorption reaction.

The rapid process can be explained by the presence of large number of vacant active binding sites, and as time increased, the accumulation of Cd(II) on the vacant sites become limited and the access to vacant surface sites by metal ions would be difficult due to repulsive effects.

Pseudo-first-order and Pseudo-second-order models were applied to check the adsorption kinetics for Cd(II) on

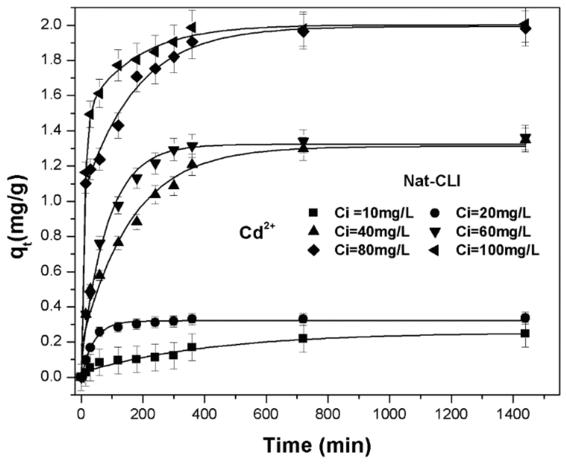

Fig. 1. Cd(II) sorption capacities (q_e) by Nat-CLI as a function of time (C_i = 10–100 mgCd/L).

natural and modified clinoptilolites. The linear forms of the Pseudo-first-order and Pseudo-second-order equations are respectively expressed by Eqs. (2) and (3),

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t (mg/g) are respectively the amounts of Cd(II) adsorbed at the equilibrium and at a time t. k_1 (min^{-1}) and k_2 (mg^{-1} g min^{-1}) are respectively the rate constants of the pseudo-first and the Pseudo-second-order sorption.

The kinetic models mentioned earlier have been considered by other researchers where they described the sorption of heavy metals by synthetic ion exchangers [31–33].

The slopes and intercepts of these curves were used to determine the values of k_1 and k_2, as well as the equilibrium capacity (q_e). The plot of the experimental data according Eqs. (2) and (3) showed that the pseudo second-order kinetics models gave considerably good fit to the data. The calculated values of $q_{e,\text{cal}}$ from the pseudo-second-order kinetics model first-order kinetics model was very close to the experimental values ($q_{,\text{exp}}$) (Table 2). The linearized pseudo-second-order kinetics model, model provided much better R^2 values (0.994–0.999) than those for the first-order model (0.686–0.901).

Fig. 2 shows the effect of the acid modification of natural clinoptilolite on the sorption capacity (q_e). It can be observed that the adsorption efficiency of the sorbents decrease with the increase of the SAR. This can be attributed to low accessibility of the adsorbent active site on the surface, which could be attributed to the following reasons: (a) The high competition between Cd^{2+} ions and H^+ ions at low pH (pH = 2), (b) the high hydration of Cd^{2+} ions, that makes more difficult entering the clinoptilolite channels than the small hydrogen ions (H^+). An explanation on the basis of surface charge could be added regarding the low pH of zero charge recorded for the acid-modified materials with pH value of 3, therein the surface is positively charged and then decrease the electrostatic interaction between the zeolite and cadmium ions; however, this point will be widely discussed in upcoming part of the pH effect and principally, the effect of the dealumination of each acid-modified natural zeolites on the ion exchange capacity for Cd^{2+}.

Furthermore, from the results obtained by the pseudo-second-order kinetic model, it can be noted that the rate constant (k_2) decreases with the increase of Si/Al ratio and this behavior is similar at Cd concentration from 10 to 100 mg/g (Fig. 3). This could be explained considering that at

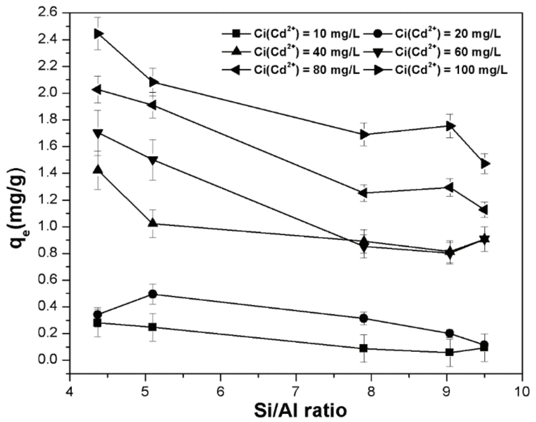

Fig. 2. Cd(II) sorption capacities (q_e) by non- and acid-modified natural zeolites with different SAR (C_i=10–100 mgCd/L).

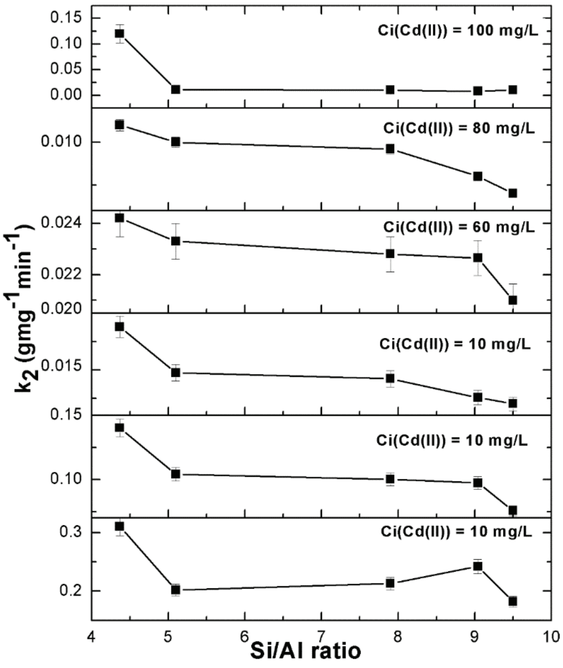

Fig. 3. Second order rate constant (k_2) as a function of SAR of non- and acid-modified natural zeolite (C_i = 10–100 mgCd/L).

Table 2
Kinetic parameters for the sorption of Cd(II) on the Nat-CLI, CLI-0.1M, CLI-0.2M, CLI-0.5M, and CLI-1.0

Zeolitic material	Pseudo-second-order				Pseudo-first-order		
	$q_{e,\text{cal}}$ (mg/g)	$q_{e,\text{exp}}$ (mg/g)	k_2 (*10^{-2})	R^2	$q_{e,\text{cal}}$ (mg/g)	k_1 (*10^{-2})	R^2
Nat-CLI	2.412	2.396	1.262	0.995	0.582	0.21	0.889
CLI-0.1M	2.083	2.025	1.174	0.999	0.723	0.22	0.735
CLI-0.2M	1.691	1.633	0.996	0.994	0.722	0.21	0.852
CLI-0.5M	1.675	1.591	0.962	0.998	0.728	0.20	0.686
CLI-1.0M	1.472	1.419	1.021	0.996	0.707	0.20	0.901

lower concentration, we have lower competition in the sorption surface sites. Whereas, at higher concentration, the competition for the surface active sites is high and consequently lower sorption rates are observed.

3.2.2. Mass effect

The adsorbent dosage is another important parameter, which influences on the metal uptake from the solution. The effect of sorbent dosages on the percentage removal of Cd(II) is shown in Fig. 4. It can be clearly seen that the percent removal of metal ions increases with increasing the amount of clinoptilolite adsorbents from 0.1 to 1.0 g. This increment in adsorption capacity is attributed to the availability of larger surface area and larger number of adsorption sites. As shown in Fig. 4, it can be noted that for Cd(II) (C_i = 100 mg/L) ions, the removal uptake increased approximately from 15% with 0.1 g up to 52% with 1.0 g of the non-modfied and acid-modified zeolitic materials, respectively. On the other hand, the increase of SAR affected the removal efficiency of Cd (II) ions; however, this effect could be clearly seen for the high dosage of the adsorbent materials.

The results calculated by the pseudo-second-order model shows that the variation of kinetic rate constant k_2 (g/mg min) as a function of the adsorbent mass presents an exponential behavior for each SAR clinoptilolite materials. Furthermore, strong dependence on SAR and the kinetic rate constant of the removed metal ions are viewed. Thus, as shown in Fig. 5, k_2 of the sorbent with high SAR has shown the highest value.

3.2.3. pH Effect

The adsorption of metal ions from effluent as a function of the initial pH of the solution is illustrated in Fig. 6. At pH values greater than the pH_{pzc}, the surface of the adsorbent is negatively charged, favoring the adsorption of positively charged metal ions, while at lower pH the surface is positively charged specially for the acidified clinoptilolite, their surface area contain almost positive charge H^+ which affects the exchange ions capacity of the adsorbent in this case.

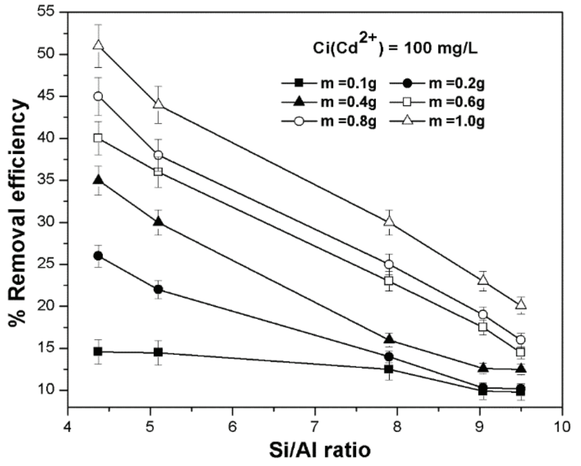

Fig. 4. Cd(II) removal from solutions as a function of SAR of non- and acid-modified natural zeolites (dosage between 0.1 and 1.0 g).

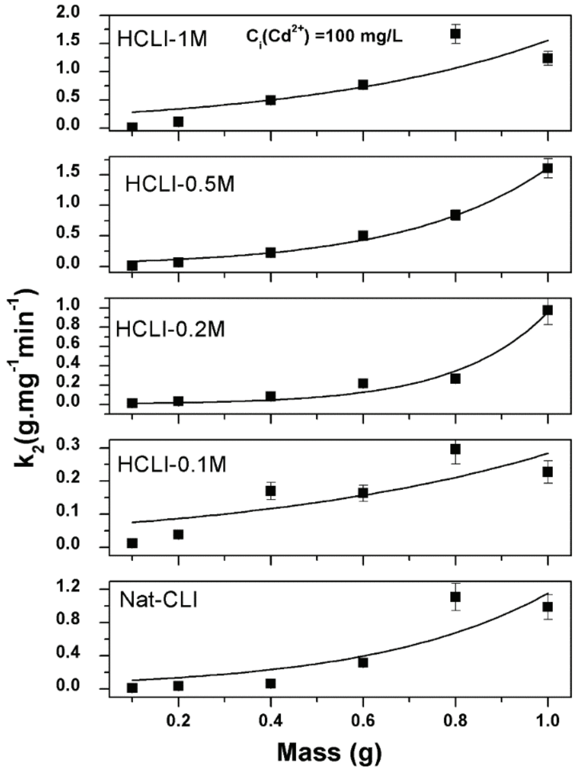

Fig. 5. k_2 as a function of dosage of SAR of non- and acid-modified natural zeolites.

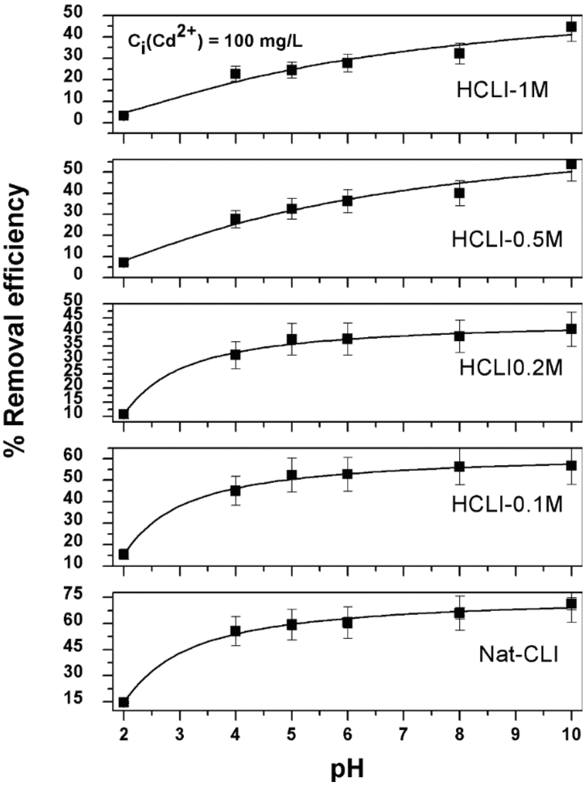

Fig. 6. Cd(II) removal from solutions as a function of initial pH for non- and acid-modified natural zeolites with different SAR.

Insignificant adsorption was therefore recorded at lower pH. Furthermore, at low pH, the excess H^+ ions in solution compete with the metals for the active sites on the clinoptilolite, leading to decreased metal uptake with the increase of acid treatment intensity. As the pH increases, the number of H^+ ions in solution decreases, thereby reducing the competition with metal ions and leading to greater adsorption.

At pH > 4.0, the hydrolysis of hydrated Cd(II) complexes started forming highly charged metal complexes (e.g. $CdOH^+$ and Cd_2OH^{3+} at pH values of 4.2 and 6.5, respectively) which promote the adsorption capacity of clinoptilolite materials because of small radius of Cd(II) in these complexes rather than the hydrated ones [20]; in addition, after the pH reached the value of 8, the metal precipitation started resulting an increment of Cd(II) removal. The behavior of the materials changes with the value of SAR. As a result, the sorption onto clinoptilolite with high SAR increases with increasing pH whereas the low SAR values of the sorption reached a plateau at pH value of 6.

From Fig. 7 it can observed the influence of SAR on the Cd(II) removal efficiency. At pH value lower than 4, the H^+ should be considered as competitive ions in the exchange process. When pH of the Cd solutions increases, the ion-exchange between cation-containing adsorbent materials (Na^+ and Ca^{2+} for Nat-CLI and H^+ for HCLI), and $Cd^{2+}$is favored.

3.3. Isotherm

The equilibrium data can be evaluated using well known adsorption isotherms providing the basis for the design of adsorption systems. Langmuir and Freundlich equations are the most widely used for modeling the experimental data [31–33], which determine whether the sorption is of monolayer or multilayer nature, in order to predict the type of adsorption mechanism involved.

Langmuir isotherm model assumes that the adsorption takes place at specific homogeneous sites of the adsorbent. The results of Cd(II) adsorption on the clinoptilolite materials were analyzed using the Langmuir model represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e q_m} \tag{4}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_L is the Langmuir constant related to the affinity of the binding site (L/mg) and q_m is the maximum amount of solute adsorbed (mg/g).

Freundlich isotherm assumes that the adsorbent is heterogeneous and that the adsorption is multilayered. It can be expressed by the following equation:

$$\ln q_e = \ln q K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F (mg/g)(L/g)$^{1/n}$ is the adsorption coefficient, n an empirical constant, q_e is the amount adsorbed at equilibrium and C_e is the equilibrium concentration (mg/L).

Fig. 8 shows the isotherms of Cd(II) for the zeolitic materials Nat-CLI, HCLI-0.1M, HCLI-0.2M, HCLI-0.5M, and HCLI-1M. It was found that the experimental data were well fitted to Langmuir model to describe the sorption mechanism involved with the highest determination coefficient values (R^2 > 0.992, 0.994 and 0.990).

The theoretical parameters of Langmuir and Freundlich models are listed in Table 3, the highest Cd(II) adsorption capacity was for Nat-CLI (with lowest SAR) where the $q_{m,\text{Nat-CLI}}$ value is 2 and 2.5 times higher than HCLI-0.5M and HCLI-1M values, respectively. The affinity of the binding site constant (K_L) was found lowest for Nat-CLI, whilst it increases with increasing SAR after acid modification, this indicated the higher affinity of cadmium ions toward acid-modified materials.

The maximum cadmium sorption capacity of Nat-CLI is comparable with that observed by banana peels (around 5 mg/g) [34]. However, the synthetic ion exchangers present capacities 50 times higher than that for the natural zeolite considered in the present work, for example the curcumin formaldehyde resin [35].

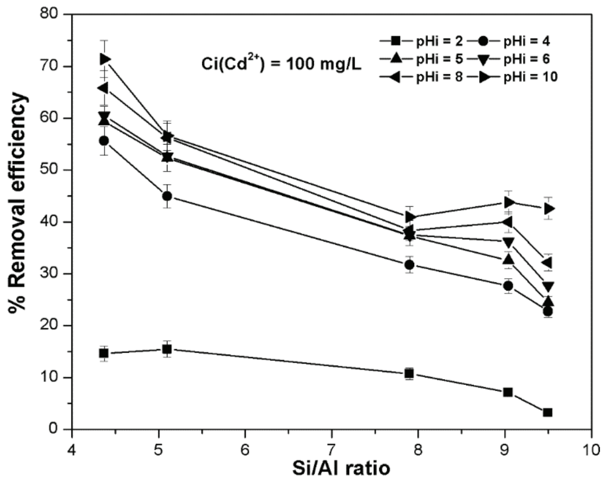

Fig. 7. Cd(II) removal as a function of SAR of non- and acid-modified natural zeolites.

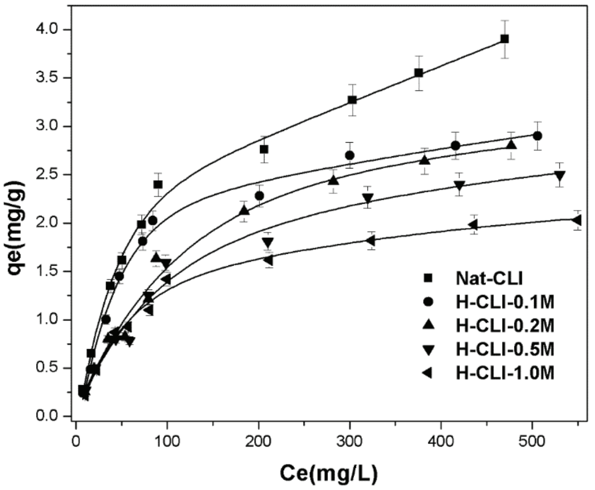

Fig. 8. Cd(II)sorption isotherms for non- and acid-modified zeolitic materials.

Table 3
Parameters obtained from Langmuir and Freundlich models that describe the Cd(II) sorption by non- and acid-modified natural zeolites

Adsorbents	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	1/*n*	R^2
Nat-CLI	5.974	0.66×10^{-2}	0.996	0.129	1.710	0.923
HCLI-0.1M	4.907	0.68×10^{-2}	0.995	0.122	1.802	0.884
HCLI-0.2M	3.128	0.93×10^{-2}	0.992	0.082	1.662	0.961
HCLI-0.5M	2.590	1.11×10^{-2}	0.988	0.090	1.791	0.953
HCLI-1M	2.391	1.16×10^{-2}	0.997	0.100	1.948	0.908

4. Proposal mechanism for cadmium sorption

The clinoptilolite framework has two-dimensional system formed by 10-ring and 8-ring channels parallel to [001] (called channels A and B, respectively) which are interconnected to 8-ring channels parallel to [100] (channel C) [36,37]. The Ca^{2+} and Na^+ occupy two sites in the framework, M1 and M2 in channels A and B, respectively. There are two sites, M3 occupied by K^+ in channel C, and M4 in channel A occupied by Mg^{2+} [38]. M3 is in a more confined position within clinoptilolite structure. Therefore, K^+ is less probable to be exchanged [37]. According to the zeolite framework characteristics and the previously performed elemental composition (Table 2), a decrement of the Na^+, Mg^{2+}, K^+ and Ca^{2+} content from clinoptilolite after the modification with sulfuric acid is observed and consequently the zeolite partially collapsed diminishing the ion exchange sites, into the clinoptilolite structure. Furthermore, the maximum capacity of the acid modified zeolitic materials for Cd^{2+} diminished as well with base on these results. It is reasonable to propose that the M1 and M2 sites are the most probable positions for Cd^{2+} in clinoptilolite. Garcia-Basabe et al. [39] pointed that the extra-framework cations in channels A and B are the most exchangeable species for this zeolite type.

5. Sensitivity analysis

A sensitivity analysis was conducted in order to quantify the relative influence of each parameter studied on the behavior of removal efficiency. In the current work, the ReliefF [40] method was used to carry out the analysis; it detects the conditional dependencies between attributes and provides a unified view of the relevancy based on probability and information theories [41]. This method assigned an importance weight value to each parameter, where the parameter with higher weight indicates a greater influence. In order to adequately represent all possible interactions that affect the removal efficiency, the analysis considered all the experimental results reported in the previous sections.

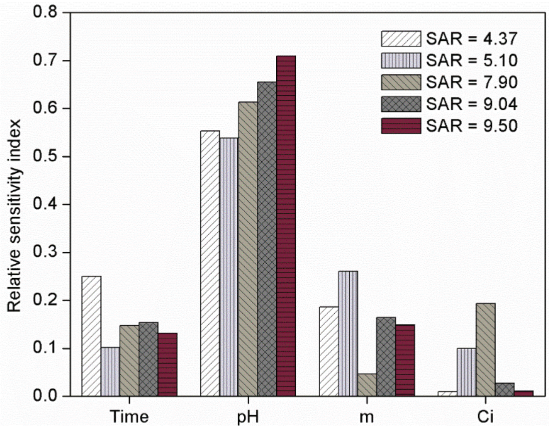

Fig. 9. Sensitivity analysis results for each of the SAR evaluated.

Fig. 9 illustrates the results in percentage form of this analysis for the different SAR values. According to this figure, the pH, adsorbent dosage, and contact time are the parameters with the greatest influence in most cases (SAR of 4.37, 5.10, 9.04, and 9.50). The pH is the parameter with the greatest impact on the removal efficiency for the four values of SAR evaluated. It can be appreciated that as SAR increases the influence of pH on the removal capacity acquires greater relevance (55.34%, 53.76%, 61.33%, 65.45%, and 70.95% at SAR of 4.37, 5.10, 7.90, 9.04, and 9.50, respectively) until reaching 70.95% at a SAR value of 9.5. The results also indicate that the contact time is the second parameter with the greatest influence to a SAR of 4.37 (25.02%), followed by the adsorbent dosage (18.65%). Nevertheless, for SAR of 5.10 (*t* = 10.16% and *m* = 26.03%), 9.04 (*t* = 15.35% and *m* = 16.43%), and 9.5 (*t* = 13.15% and *m* = 14.84%) the relevance impact of sorbent dosage on the adsorption capacity of Cd increases with respect to contact time, reaching similar and almost stable relevance in the highest SAR. Finally, the initial concentration was the least relevant parameter for SAR of 4.37, 5.1, 9.04, and 9.5 with values of 1%, 10%, 2.7%, and 1.05%, respectively; where according to Fig. 9 as the SAR approaches to 7.09, the influence of the initial concentration increases.

6. Conclusions

The acid treatment of the natural zeolite (clinoptilolite-rich tuff) causes structural changes of the natural clinoptilolite, whereas, promotes the release of the aluminum from the zeolitic network increasing the SAR. The pH_{PZC} is similar for all the acid-modified materials ($pH_{PZC} = 3$), while the pH_{PZC} of the Nat-CLI has a value slightly acid.

The pseudo-second-order kinetic model best describes the sorption behavior and the k_2 values depend on the initial concentration of the Cd(II) and SAR of the clinoptilolite materials.

The experimental data of the Cd(II) sorption isotherms well fit to the Langmuir model, the maximum adsorption capacity (q_m) for the Nat-CLI is higher 2 and 2.5 times than

HCLI-0.5M and HCLI-1M. The K_L parameter increases with increasing SAR after acid modification.

The increase of adsorbent dosage increases the Cd(II) uptake from 15% with 0.1 g up to 52% with 1.0 g for Nat-CLI. However, these adsorption values decrease significantly after acid modification from 10% with 0.1 g up to 21% with 1.0 g for HCLI-1.0M.

The sorption of Cd(II) by non- and acid-modified natural zeolites is carried out preferentially by ion exchange mechanism. The natural clinoptilolite shows the highest adsorption capacity owing to the high mobility of exchangeable cations (Na^+, Ca^{2+}) presents in its framework.

Acknowledgment

The authors gratefully acknowledge the financial support of the National Council of Science and Technology of Mexico (Projects 254665).

References

[1] S. Lin, Y. Yang, G. Chen, C. Xin, Z. Wei, X. Meng, L. LIili, L. Kualngfei, Study on the influence of thiolation on the adsorption and magnetic recovery of superparamagnetic nanoadsorbents for Cd^{2+} removal, Appl. Surf. Sci., 425 (2017) 141–147.
[2] WHO Guidelines for Drinking-water Quality, 4th ed., 2017.
[3] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Heavy metal toxicity and the environment, Molecular, Clinical and Environmental Toxicology, 2012, pp. 133–164.
[4] A. Bernard, Cadmium and its adverse effects on human health, Indian. J. Med. Res., 128, (2008) 557–564.
[5] F.M. Rebelo, E.D. Caldas, Arsenic, lead, mercury and cadmium: toxicity, levels in breast milk and the risks for breastfed infants, Environ. Res., 151 (2016) 671–688.
[6] C.N. Smith, Determining the Protective Effects of Quercetin Against Cadmium Toxicity in Human Embryonic Kidney Cells, 2017.
[7] J.O. Esalah, M.E. Weber, J.H. Vera, Removal of lead from aqueous solutions by precipitation with sodium di-(*n-octyl*) phosphinate, Sep. Purif. Technol., 18 (1999) 25–36.
[8] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, Water. Sci. Technol., 39 (1999) 135–138.
[9] S. Vasudevan, J. Lakshmi, Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water – A novel approach, Sep. Purif. Technol., 80 (2011) 643–651.
[10] H. Chen, C. Zhong, H. Berkhouse, H. Zhang, Y. Lv, W. Lu, Y. Yang, J. Zhou, Removal of cadmium by bioflocculant produced by Stenotrophomonas maltophilia using phenol-containing wastewater, Chemosphere, 155 (2016) 163–169.
[11] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metal, Chem. Eng. J., 118 (2006) 83–98.
[12] H.R. Mortaheb, H. Kosuge, B. Mokhtarani, M.H. Amini, H.R. Banihashemi, Study on removal of cadmium from wastewater by emulsion liquid membrane, J. Hazard. Mater., 165 (2009) 630–636.
[13] E. Saljoughi, S.M. Mousavi, Preparation and characterization of novel polysulfone nanofiltration membranes for removal of cadmium from contaminated water, Sep. Purif. Technol., 90 (2012) 22–30.
[14] K. Trivunac, S. Stevanovic, Removal of heavy metal ions from water by complexation-assisted ultrafiltration, Chemosphere, 64 (2006) 486–491.
[15] T. Mishra, J. Hait, N. Aman, R.K. Jana, S. Chakravarty, Effect of UV and visible light on photocatalytic reduction of lead and cadmium over titania based binary oxide materials, J. Colloid Interface Sci., 316 (2007) 80–84.
[16] Z.A. ALOthman, M. Mezbaul Alam, Mu. Naushad, Heavy toxic metal ion exchange kinetics: validation of ion exchange process on composite cation exchanger nylon 6,6 Zr(IV) phosphate, J. Ind. Eng. Chem., 19 (2013) 956–960.
[17] Mu. Naushad, Z.A. ALOthman, Md. RabiulAwual, M. MezbaulAlam, G.E. Eldesoky, Adsorption kinetics, isotherms, and thermodynamic studies for the adsorption of Pb^{2+} and Hg^{2+} metal ions from aqueous medium using Ti(IV) iodovanadate cation exchanger, Ionics, 21 (2015) 2237–2245.
[18] Mu. Naushad, Alok Mittal, M. Rathore, V. Gupta, Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II), and Pb(II) metal ions over a composite cation exchanger, Desal. Wat. Treat., 54 (2015) 2883–2890.
[19] Renu, M. Agarwal, K. Singh, Heavy metal removal from wastewater using various adsorbents: a review, J. Water. Reuse. Desal., 7 (2017) 387–419.
[20] S. Babel, T.A.Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater., 97 (2003) 219–243.
[21] G.E. Christidis, D. Moraetis, E. Keheyan, L. Akhalbedashvili, N. Kekelidze, R. Gevorkyan, H. Yeritsyan, H. Sargsyane, Chemical and thermal modification of natural HEU-type zeolitic materials from Armenia, Georgia and Greece, Appl. Clay. Sci., 24 (2003) 79–91.
[22] K. Gedik, I. Imamoglu, Removal of cadmium from aqueous solutions using clinoptilolite: influence of pretreatment and regeneration, J. Hazard. Mater.,155 (2008) 385–392.
[23] M. Abatal, M.T. Olguin, Y. Abdellaoui, A. EL Bouari, Sorption of Cd(II), Ni(II) and Zn(II) on natural, sodium-, and acid-modified clinoptilolite-rich tuff, Environ. Prot. Eng., 44 (2018) 42–59.
[24] H.S. Nalwa, Handbook of Surfaces and Interfaces of Materials, 5 vols., Elsevier, San Diego, 2001.
[25] J. Liu, X. Cheng, Y. Zhang, X. Wang, Q. Zou, L. Fou, Zeolite modification for adsorptive removal of nitrite from aqueous solutions, Microporous. Mesoporous. Mater., 252 (2017) 179–187.
[26] V.O. Vasylechko, G.V. Gryshchouk, Y.B. Kuz'ma, V.P. Zakordonskiy, L.O.Vasylechko, L.O. Lebedynets, M.B. Kalytovs´ka, Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite, Microporous. Mesoporous. Mater., 60 (2003) 183–196.
[27] H. Leinonen, J. Lehto, Purification of metal finishing waste waters with zeolites and activated carbons, Waste. Manage. Res., 19 (2001) 45–57.
[28] M.R. Panuccio, A. Sorgonà, M. Rizzo, G. Cacco, Cadmium adsorption on vermiculite, zeolite and pumice: batch experimental studies, J. Environ. Manage., 90 (2009) 364–374.
[29] M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites, 5th ed. Elsevier, 2007.
[30] M.C. Díaz-Nava, M.T. Olguín, M. Solache-Ríos, M.T. Alarcón-Herrera, A. Aguilar-Elguezabel, Characterization and improvement of ion exchange capacities of Mexican clinoptilolite-rich tuffs, J. Inclusion. Phenom. Macrocyclic. Chem., 51 (2005) 231–240.
[31] A.A. Alqadami,M. Naushad, Z. Abdullah Alothman, A.A. Ghfar, Novel metal–organic framework (MOF) based composite material for the sequestration of U(VI) and Th(IV) metal ions from aqueous environment, ACS Appl. Mater. Interfaces, 9 (2017) 36026–36037.
[32] M. Naushad, T. Ahamad, B.M. Al-Maswari, A.A. Alqadami, S.M. Alshehri, Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium, Chem. Eng. J., 330 (2017) 1351–1360.
[33] M. Naushad, Z.A. ALOthman, Inamuddin, H. Javadian, Removal of Pb(II) from aqueous solution using ethylene diamine tetra acetic acid-Zr(IV) iodate composite cation exchanger: kinetics, isotherms and thermodynamic studies, J. Ind. Eng. Chem., 25 (2015) 35–41.
[34] K. Pyrzynska, Removal of cadmium from wastewaters with low-cost adsorbents, J. Environ. Chem. Eng., 7 (2019) 102795.
[35] M. Naushad, T. Ahamad, Z.A. ALOthman, M.A. Shar, N.S. AlHokbany, S.M. Alshehri, Synthesis, characterization and

application of curcumin formaldehyde resin for the removal of Cd^{2+} from wastewater: kinetics, isotherms and thermodynamic studies, J. Ind. Eng. Chem., 29 (2015) 78–86.

[36] C. Baerlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, 6th ed., Elsevier, 2007. Available at:http://www.sciencedirect.com/science/book/9780444507013.

[37] E.L. Uzunova, H. Mikosch, Cation site preference in zeolite clinoptilolite: a density functional study, Microporous. Mesoporous. Mater., 177 (2013) 113–119.

[38] D.A. Kennedy, F.H. Tezel, Cation exchange modification of clinoptilolite-screening analysis for potential equilibrium and kinetic adsorption separations involving methane, nitrogen, and carbon dioxide, Micropor. Mesopor. Mat., 262 (2018) 235–250.

[39] Y. Garcia-Basabe, A.R. Ruiz-Salvador, G. Maurin, L.C. De Menorval, I. Rodriguez-Iznaga, A. Gomez, Location of extra-framework $Co^{2+,}$ Ni^{2+}, Cu^{2+} and Zn^{2+} cations in natural and dealuminated clinoptilolite, Microporous. Mesoporous. Mater., 155 (2012) 233–239.

[40] M. Robnik-Šikonja, I. Kononenko, Theoretical and Empirical Analysis of ReliefF and RReliefF, Mach. Learn., 53. (2003) 23–69.

[41] N.-D. Hoang, C.-T. Chen, K.-W. Liao, Prediction of chloride diffusion in cement mortar using multi-gene genetic programming and multivariate adaptive regression splines, Measurement., 112 (2017) 141–149.