Sorption of Cadmium from Aqueous Solutions at Different Temperatures by Mexican HEU-type Zeolite Rich Tuff

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Abstract

Many factors may affect the heavy metals sorption on natural zeolites among them the temperature, for this reason in this paper the cadmium retention behavior on Mexican zeolitic rich tuff as a function of temperature is considered. The kinetic and the isotherms were determined at 303, 318, and 333 K, the remaining cadmium in the solution samples was analyzed by atomic absorption spectrometry. The pseudo-second order rate constant, k, as well as the apparent diffusion coefficients were calculated from the cadmium uptake by the zeolitic rock as a function of the contact time and temperature, the highest amounts were found for the experiments done at 333 K. The maximum cadmium adsorption capacity by the zeolitic material was 12.2 mg Cd^{2+}/g at 318 K corresponding to 20% of the effective ion exchange capacity of the Chihuahua zeolitic rock. In order to explain the cadmium sorption behavior different kinetics and isotherm models were considered.

Introduction

Cadmium occurs naturally in the environment at low levels usually with zinc, lead and copper ore deposits. High cadmium concentrations are often associated with industrial emission sources, e.g., mining and smelting operations. A primary use for cadmium metal is as an anticorrosive, electroplated onto steel. Although cadmium is easily complexed with some organic compounds (e.g., thiocarbamates), organometallic compounds have been synthesized, they have not been found in the general environment since they are rapidly decomposed [1–4].

In fresh surface waters and most ground waters, cadmium levels are generally less than 1 μg/l. The use of galvanized pipes in water distribution systems can result in a 5- to 10-fold increase in cadmium levels in drinking water (i.e. up to 10 μg/l) [1, 2].

Cadmium is a contaminant which may enter the food chain from a number of natural and industrial sources. A vast amount of literature exists which document the adverse health effects from acute and chronic exposure to cadmium in both humans and animals. The primary adverse health effects which have been observed are lung cancer and kidney damage [1, 3, 5, 6].

Between two thirds and three quarters of all the cadmium, in the superficial and subterranean water, is adsorbed to particles in suspension. This metal can be removed of sediments through complexes' maker agents.

In Mexico, the maximum permissible level for cadmium is 0.2 mg/l and 0.1 mg/l in water used to irrigation and drinking water, respectively [7].

There are different technologies to separate toxic metals residues, some of them are: precipitation, ultra-filtering, nano-filtering, reverse osmosis, electro-dialysis and electrolysis. Some of these technologies can remove 99% of those metals even though they are low concentrations. Unfortunately, these methods are expensive [8]. Different materials have been considered for the removal of cadmium from waste water [9–11].

Natural zeolites are important aluminosilicates in sorption processes [12–15] because of its low cost and selectivity which depends on some factors such as: cations nature, temperature, cations concentration, associated anions and zeolites structure. In the zeolite structure three relatively independent components are found: the aluminosilicate framework, exchangeable cations, and zeolitic water. The aluminosilicate framework is the most conserved and stable component and defines the crystalline structure type, for instance the crystalline structure of clinoptilolite is monoclinic with a symmetry C2/m) [16]. A most remarkable feature of

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zeolites, and one which practically defines the specific properties of these minerals, is the presence of a system of voids and channels, in their structures. For sorption and catalysis, the dimensions and locations of these channels, through which the molecules diffuse into the intercrystalline free volume, are of great importance. One of the most recognized heterogeneous catalysts are zeolites-type catalysts which are ideal catalytic materials for many processes because of their well-defined nanostructure with pore sizes in the molecular scale. Clinoptilolite with its catalytic [17–19] and ion exchange properties is widely used for protection of the environment [20]. In this paper we investigated the ion exchange properties of a Mexican clinoptilolite. In Mexico there are many places where this aluminosilicate is located [21, 22].

Adsorption of cadmium on natural clinoptilolites in different conditions has been reported. Babel and Kurniawan [23] evaluated the adsorption capacities of various low-cost adsorbents for heavy metal removal from contaminated water among them natural zeolites. In this particular case they reported that zeolitic materials removed 175 and 137 mg/g of Pb^{2+} and Cd^{2+}, respectively. In this context, Langella et al. [24], evaluated the cation exchange properties of natural zeolite from deposits in northern Sardinia in view of a possible future utilization of the parent rock. They found that the cation selectivity sequence for this zeolitic material was $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} \cong Zn^{2+}$.

On the other hand Vasylechko et al. [25] reported the adsorption of cadmium on acid-modified clinoptilolite under dynamic conditions. The authors concluded that the adsorption capacity of the H-form for clinoptilolite depends on the nature, concentration and contact time with acid in the modification process. They also found that the extraction of cadmium reached 88–92%. In general, it has been reported that treatment of natural materials with sodium chloride, converted them to the near homoionic state in Na-form, improves both the exchange capacity and the removal efficiency of cadmium and it has been concluded that sodium clinoptilolites are the most suitable exchanger for the removal of cadmium from solution [15, 26–29]. Although Faghihian et al. [30] investigated three different samples of Iranian clinoptilolites and its sodium exchange forms for the uptake of cadmium and other cations. They found the Na-exchanged clinoptilolite nearly followed the same pattern of exchange, although the cations were better retained by the untreated clinoptilolites.

Some other parameters such as temperature and zeolite particle size have been considered in studies on metal ion exchange in zeolites. Curkovic et al. [15] found that the metal uptake increased with increasing temperature during the ion-exchange process and Malliou et al. [27] reported, the exchange of cadmium occurs only by sodium ions, irrespective of the temperature of the solution and metal uptake increases with decreasing particle size. It has been reported that the removal of heavy metals from aqueous solutions using zeolites and

the effect of pH over sorption of cadmium, lead, and chromium were studied [31].

Binary [32] and multi-component [31] ion exchange equilibriums has been studied by the batch technique to determine the interactions and competition for ion-exchange sites in naturally occurring clinoptilolite, particularly in a ternary and quaternary ion-exchange equilibria between heavy metal solution (Pb^{2+}, Cd^{2+}, Cu^{2+}) and Na-form of clinoptilolite, Petrus and Warchol [33] found that the exchange capacity of clinoptilolite for a given M^{2+} is not constant and differs in one- or multi-component systems.

In general, the ability of zeolites to retain metal ions has been demonstrated. The influence of the pH, concentration, origin of the zeolitic rock, or temperature on the heavy metal sorption processes are important parameters to be considered. This led to the conclusion that any practical utilization of a clinoptilolite-rich rock as cation exchanger should be preceded by basic studies on representative samples from the deposit under examination. For these reasons the purpose of this work was to evaluate the kinetics and isotherms of the Cd^{2+} ions sorption process in a zeolitic rock from a recently discovered deposit of Chihuahua (Mexico), at different temperatures.

Experimental

Material

A zeolitic rock from a new discovery deposit place "Arroyo de la Cantera", Chihuahua, Mexico was milled and sieved. The characterization of the zeolite has been reported elsewhere [34]. The main components reported were clinoptilolite, helandite and quartz. 66.9%, 10.5%, 1.0%, 0.1% and 1.0% as SiO_2, Al_2O_3, MgO, CaO and Fe_2O_3 respectively were found for the composition of the material. The effective ion exchange capacity for the sodium material was reported to be 1.09 ± 0.08 meq/g. The grains size used in this work were between 20 and 40 mesh. The height and width of various zeolitic particles in the samples were measured by electron microscopy. In order to standardize the measurements, the particles were considered as spheres and the average diameter was found to be 0.95 mm.

The zeolitic rock was treated with a 5 M NaCl solution for 8 days and it was washed with deionized water until no presence of chloride ions were observed, using the $AgNO_3$ test. The Na-treated zeolitic rock was then dried at 373 K for 5 h and finally the sample was left in a humid medium to equilibrate with water.

Characterization of the Mexican HEU-type zeolite rich tuff

Powder diffractograms of the samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms

were used to identify the mineral compounds and to verify crystalline structure.

The natural zeolitic samples were mounted directly onto the holders and then observed at 10 and 20 kV in a Philips XL 30 electron microscope for scanning electron micrographs. The microanalysis was done with an EDS system.

Cadmium sorption

The kinetic experiments were done as follows: aliquots of 10 ml 0.002 M cadmium nitrate solution were put in contact with 100 mg of zeolitic rock samples for 0.08, 0.25, 0.5 1, 3, 5, 24 and 48 h, under occasional stirring at 303, 318, and 333 K for each series of experiments. The liquid phases were separated from the solids by centrifugation after the period of time was concluded; finally the zeolitic rock samples were washed and dried. The experimental uptake data were fitted using the first [35], pseudo second order [36], and the Elovich [37] kinetic models. The diffusion coefficients [38, 39] were also calculated.

In order to determine the isotherms, cadmium nitrate solutions (0.002, 0.005, 0.020, 0.050, 0.100, 0.200, 0.360, 0.520, 0.700, 0.840, and 1.000 M) were put in contact during 48 h with Na-treated zeolitic rock samples at temperatures of 303, 318, and 333 K. The experiments were performed as described above. The pH of the solutions was measured before and after treatments. Cadmium was determined using a GBC 932 plus atomic absorption spectrometer, at wavelength of 326.1 nm.

The experimental data were fitted by the Langmuir and Freundlich [40] adsorption equations.

Results and discussion

Characterization

Electron microscopy

The SEM images of the new discovered zeolitic rock and the materials treated with sodium showed morphologies characteristic of clinoptilolite which occurred as euhedral plates and laths, crystals display characteristic monoclinic symmetry, and many are coffin-shaped, and cubic-like crystals [41].

Table 1 shows the chemical composition of the crystals before and after the preparation of the sodium form determined by EDS analysis. As it is observed sodium was not found in the unconditioned zeolitic rock, potassium and calcium increased in the conditioned material perhaps by the ionic exchange with sodium. It was found as well that in the unconditioned zeolitic rock the cations followed the order:

$$K > Ca > Fe.$$

The zeolitic samples treated with cadmium nitrate (0.002 M) did not show any morphological differences with respect to the sodium material (Figure 1).

Table 1. Elemental composition of the unmodified and modified zeolitic samples with NaCl determined by EDS analysis

Element weight %	Zeolitic material	
	Unmodified	Modified with NaCl
O	43.95 ± 2.36	43.11 ± 0.85
Na	–	1.81 ± 0.63
Mg	1.29 ± 0.23	1.23 ± 0.35
Al	7.75 ± 0.30	8.22 ± 0.23
Si	38.71 ± 1.17	40.71 ± 1.19
K	3.74 ± 0.25	1.96 ± 0.90
Ca	2.33 ± 0.56	2.34 ± 0.99
Fe	2.20 ± 1.01	0.60 ± 0.54

According to the EDS results (Tables 1 and 2) and the equilibrium pH where only Cd^{2+} species is present, it can be suggested that cadmium was exchanged with cations from the zeolite network.

Table 2 shows the EDS analysis of the zeolitic material treated with 0.002 M $Cd(NO_3)_2$, it can be observed that cadmium was exchanged by sodium and magnesium, however, it is not clear whether calcium or potassium play a role in the ionic exchange process. It is important to note, that considering the experimental errors and the shortcomings of the technique, the content of cadmium in the material is similar in all cases, EDS gives more a surface analysis than a bulk analysis of the zeolite.

X-ray diffraction

Figure 2 shows the powder diffraction patterns of the zeolitic rock treated with sodium chloride. Clinoptilolite (JCPDS 25-1349) and quartz (JCPDS 33-1161) were the components found and there was not observed any clay minerals; the results confirm that reported elsewhere [34]. Natural and conditioned samples of clinoptilolite showed no significant changes in the position of the most intense diffraction peaks. These results suggest that sodium chloride conditioning has no effects on the structure of the zeolitic material. The diffractogram of the conditioned zeolitic rock was also compared with that of the halite (JCPDS 5-0628) and it indicated that it was NaCl free.

Cadmium speciation

According to the chemical equilibrium diagram for cadmium in aqueous solution obtained by the MEDUSA program, the species $Cd(OH)_2$ precipitates at pH higher than 8 and the concentration of Cd^{2+} ions in solution decreases [42]. Under the experimental conditions of the present paper, Cd^{2+} was the only species present in solution, since the initial and equilibrium pH values were between 5 and 6 (Figure 3). The pH effect on sorption of cadmium by this kind of zeolitic rocks (clinoptilolite rich-tuffs) has shown that the sorption of this element is the same in the pH range between 3 and 7

Figure 1. SEM image of zeolitic rock treated with 0.002 M Cd(NO$_3$)$_2$ solution for 48 h at 303 K.

Table 2. Elemental composition of the modified zeolitic samples with 0.002 M Cd(NO$_3$)$_2$ at 303, 318 and 333 K

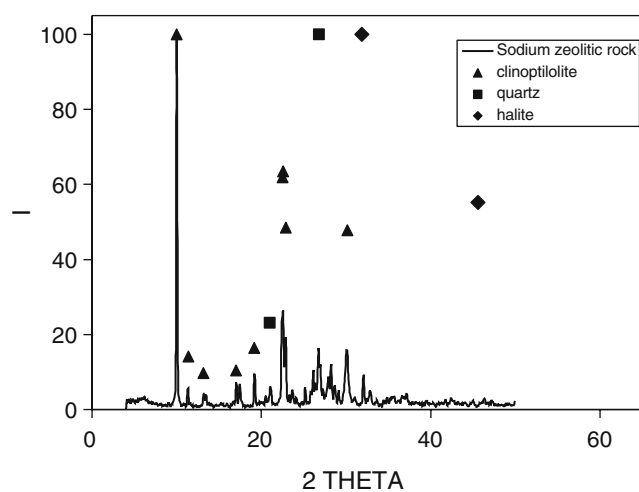| Element weight %	Sample		
	CliNa-Cd 303 K	CliNa-Cd 318 K	CliNa-Cd 333 K
O	40.16 ± 1.74	41.64 ± 1.29	37.95 ± 2.27
Na	1.47 ± 0.35	1.31 ± 0.04	1.18 ± 0.40
Mg	1.04 ± 0.07	1.02 ± 0.03	0.77 ± 0.06
Al	8.64 ± 0.42	8.54 ± 0.64	7.76 ± 0.30
Si	41.56 ± 0.47	41.00 ± 1.09	42.13 ± 0.98
Cd	1.52 ± 0.24	1.16 ± 0.42	2.49 ± 1.63
K	2.56 ± 2.69	1.91 ± 0.97	4.63 ± 1.84
Ca	2.11 ± 0.88	2.54 ± 0.78	1.57 ± 0.41
Fe	1.36 ± 0.62	0.86 ± 0.29	1.51 ± 0.25

Figure 2. Powder diffraction pattern of the zeolitic rock treated with sodium chloride solution.

[43, 44], this behavior is expected since at lower pH the material may suffer some changes in their structure and as the concentration of hydrogen ions increases, the competition with cadmium ions for the sites in the zeolite network increases as well. The sorption increases when the pH is 8 or higher depending on the concentration of cadmium in solution, this increment has been attributed to the precipitation of cadmium as Cd(OH)$_2$ as discussed above.

Cadmium kinetics

Figure 4 shows sorption behavior of Cd^{2+} vs. time (h) at different temperatures. It is observed that the sorption rate is rapid at the beginning and then becomes slower as equilibrium is approached. The time required to reach the equilibrium was higher than 10 h for the experiments performed at 303 and 318 K and less than 1 h when the experiments were performed at 333 K. It is known that increasing the temperature, the chemisorption and diffusion processes rates increase as well.
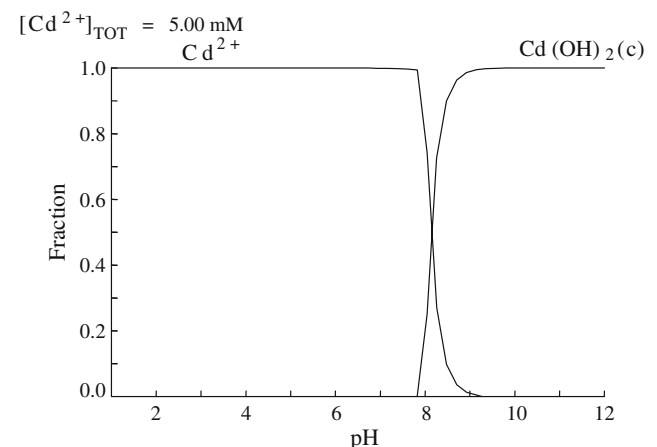

Figure 3. Species-distribution diagram obtained by the program ME-DUSA (5×10^{-3} M cadmium nitrate solution).
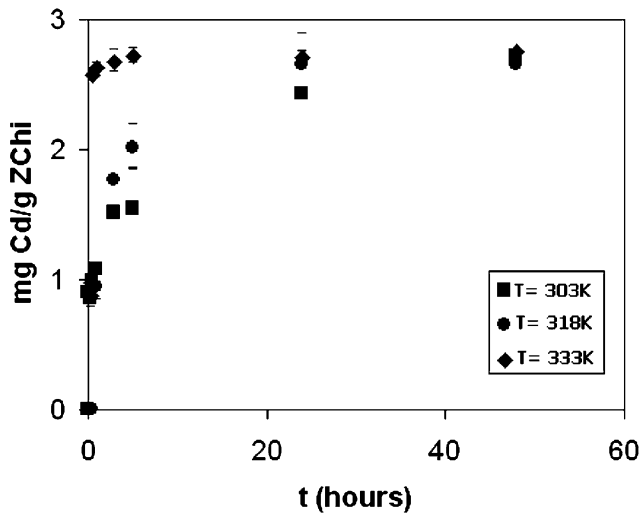
Figure 4. Sorption behavior of Cd^{2+} vs. time (h) at different temperatures.

The kinetics of adsorption by aluminosilicates has been described previously by the first order expression given by Lagergren [35, 43]:

$$\ln(q_e - q_t) = \ln(q_e) - kt$$

where q_e = mass of metal adsorbed at equilibrium (mg g^{-1}); q_t = mass of metal adsorbed at time, t (mg g^{-1}); k = rate constant (s^{-1}).

It was found that, this equation provided a good description of the current data. Table 3 shows the first-order kinetics equations and r^2 corresponding to cadmium sorption on the zeolitic rock from Chihuahua at different temperatures.

The sorption kinetics may be described as well by the pseudo-second order model [36] which is shown in the following equation:

$$1/(q_e - q_t) = 1/q_e + kt$$

rearranging this equation to a lineal form:

$$t/q_t = (1/kq_e^2) + t/q_e$$

The data in straight-line plots of t/q_t against t were tested to obtain rate parameters. The pseudo-second order rate constant, k, initial sorption rate, kq_e^2, equilibrium sorption capacity, q_e, and correlation coefficients, r^2, for Cd^{2+} under different temperatures were calculated. Table 4 shows the pseudo-second order kinetics equations, the pseudo-second order rate constant, k, and correlation coefficients, r^2 corresponding to

Table 3. First order kinetics equations corresponding to cadmium sorption on zeolitic rock from Chihuahua at different temperatures

T (K)	First-order model equations	r^2
303	$\ln(q_e-q_t) = 0.5696-2 \times 10^{-5}t$	0.9881
318	$\ln(q_e-q_t) = 0.931-9 \times 10^{-5}t$	0.9984
333	$\ln(q_e-q_t) = 0.5761-9 \times 10^{-4}t$	0.8775

Table 4. Pseudo-second order kinetics equations corresponding to cadmium sorption on zeolitic rock from Chihuahua at different temperatures

T (K)	Pseudo-second order model equations	k (g mg^{-1} s^{-1})	r^2
303	$t/q_t = 2190.2 + 0.3613t$	5.9601×10^{-5}	0.9936
318	$t/q_t = 876.46 + 0.3703t$	1.5645×10^{-4}	0.9971
333	$t/q_t = 230.95 + 0.362t$	5.6741×10^{-4}	0.9999

cadmium sorption on the zeolitic rock from Chihuahua at different temperatures. The values of k were found to increase from 5.9601×10^{-5} to 5.6741×10^{-4} g mg^{-1} s^{-1} as the temperature increased from 303 to 333 K. There is a linear relationship between the natural logarithm of the pseudo rate-constants and the reciprocal of the temperature (Figure 5, $r^2 = 0.988$). Ho *et al.* [36, 45, 46], have observed the same behavior working with lead and dye removal using different sorbents. The sorption rate constant may be expressed as a function of temperature by the following relationship:

$$k = k_0 \exp(-E/RT)$$

The relationship between k and T can be represented in an Arrhenius form as

$$k = 37.678 \times 10^5 \exp(-62.8229 \times 10^3/8.314T)$$

In the equation, the rate constant of sorption k_0 is 37.678×10^5 g mg^{-1} s^{-1}. Furthermore, the activation energy of sorption, E, is 62.8229 kJ/mole for the sorption system of Cd^{2+} on sodium zeolitic rock from Chihuahua, this value is out of the range of physisorption processes from 5 to 20 kJ/mole [36], Ho *et al.* [46] reported an activation energy value of this last order of magnitude for the sorption of dye by an activated clay. The activation energy for the sorption of Cd^{2+} ions by the zeolitic rock from Chihuahua is between the values obtained by Ho *et al.*, using tree fern and peat for lead removal, they proposed that the mechanism involved was a chemical sorption [36, 45]. Therefore, the activation energy depends on the properties of the sorbents and on the pollutants involved in the sorption processes.
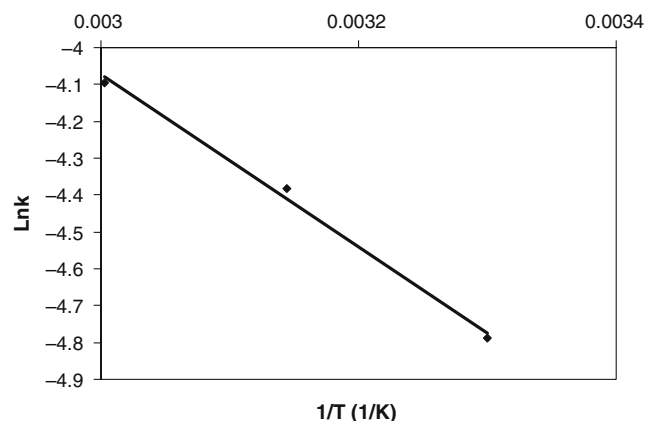

Figure 5. Behavior of ln k of pseudo rate constant as a function of $1/T$.

Although, the experimental points could be adjusted to the first- and pseudo-second order kinetics equations, in general the best adjustments were observed with the pseudo-second order kinetics equation.

The kinetic behavior found at different temperatures show that the pseudo-second order rate constant k, in relation with the cadmium ions to reach the ion exchangeable sites of the clinoptilolite, increases as the temperature increases in the experimental conditions of this work.

It is important to mention that the Elovich model [37] was also considered in this work, however the correlations obtained from the fitting of the experimental results were 0.95 at 303 and 318 K, and 0.7 at 333 K.

According with the experimental conditions, the results obtained in this work and literature, ion exchange is the mechanism involved in the sorption of cadmium by clinoptilolite rich-tuffs.

Diffusivity

The diffusivity was calculated considering r as 0.473 mm. Q_t/Q_0 was plotted against $t^{1/2}$ and the apparent diffusion coefficients (Di) for the different temperatures were obtained from the slopes of the curves. The diffusion coefficients for each temperature were 2.55×10^{-9}, 24.74×10^{-9} and 462×10^{-9} cm^2 s^{-1} for 303, 318 and 333 K, respectively. In order to know the correlation between the apparent diffusion coefficient (Di) of the Cd^{2+} ions into the pores of the irregular zeolitic rock grains and the pseudo-second order rate constant k, it was plotted Di vs. $T*k$ for each studied temperature and it was found an exponential relationship described by the following equation: $Di = 2 \times 10^{-5} Tk^{2.2145}$ with $r^2 = 1$ (Figure 6).

Isotherms

The data were fitted to the well-known Langmuir and Freundlich isotherm models, these models are represented by the following equations:
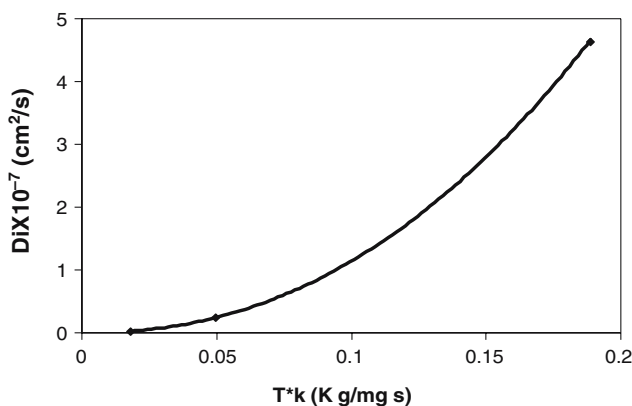
(a) Langmuir

$$q_e = q_o b C_e / (1 + b C_e)$$

where q_e is the amount of cadmium per unit weight of zeolite (mg g^{-1}), C_e is the equilibrium concentration of cadmium in solution (mg l^{-1}), q_o is the amount of solute retained per unit weight of adsorbent in forming a complete monolayer on the surface, and b is the constant related to the energy or net enthalpy of adsorption.

(b) Freundlich

$$q_e = K_f C_e^{1/n}$$

and in the linear form

$$\log(q_e) = \log(K_f) + 1/n \log(C_e)$$

where q_e is the amount of cadmium per unit weight of zeolite (mg g^{-1}), C_e is the equilibrium concentration of cadmium in solution (meq l^{-1}), K_f is the equilibrium constant indicative of adsorption capacity, and n is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity.

The experimental data could not be adjusted to the Langmuir model. Figure 7 shows the experimental data, obtained at 303 K, fitted to the Freundlich equation which showed the highest correlation value and Table 5 shows the results of the experimental data treated with the above model for cadmium sorption on zeolitic rock from Chihuahua at different temperatures. This empirical model can be applied to heterogeneous surfaces which is the case of the zeolitic rock of this work.

The equilibrium constant K_f and the adsorption intensity, $1/n$, are highest at 318 K, which indicate that the sorption capacity is the highest in these conditions.

Granular or powdered activated carbon is the most widely used adsorbent because of its excellent adsorption capacity, but their use may be limited due to its high cost [47]. Bone char, traditionally used for color removal in sugar refining, has been studied for the sorption of cadmium ions, the experimental data has been analyzed using different kinetic models-the pseudo-first order, the Ritchie second order, the modified second order, and the Elovich equations. Based on the sum of the errors squared, it was reported that the Elovich equation is the best choice among the four kinetic models to describe
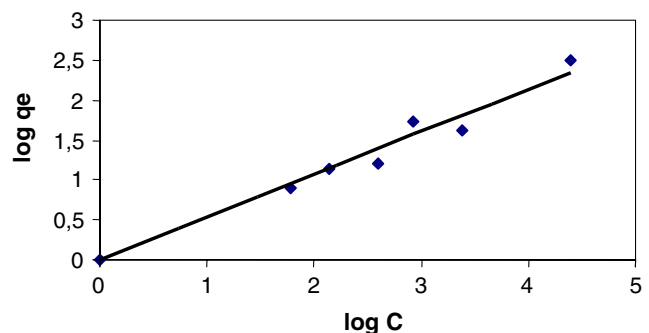
Figure 6. Behavior of the apparent diffusion coefficients (Di) as a function of the product of the temperatures by the pseudo-second order constants.

Figure 7. Isotherm at 303 K fitted to the Freundlich equation.

Table 5. Freundlich isotherm equations, K_f and n^{-1} parameters values for cadmium sorption on zeolitic rock from Chihuahua at different temperatures

T (K)	Equation	K_f (mg/g)	n^{-1}	r^2
303	Log $(q_e) = 0.5871$ log $C_e - 0.1655$	0.6831	1.703	0.9343
318	Log $(q_e) = 0.3963$ log $C_e + 1.0859$	12.187	2.523	0.902
333	Log $(q_e) = 0.466$ log $C_e + 0.8533$	7.1334	2.145	0.877

the sorption of cadmium ions into bone char since the bone char contains various types of binding sites and therefore is a heterogeneous surface. The sorption capacities of bone char and leonardite for cadmium ions were 64.1 mg/g and 50.6 mg/g, respectively [48, 49] which are about five and four times higher than the zeolitic rock used in this work, Pesavento *et al.* [50] reported that activated carbon is not a very strong adsorbing solid for copper (II), and lead (II), and less strongly for Cd (II) up to pH 6. This may have important implications when real water is considered. For instance, relative weak complexing substances can effectively compete with carbon for the combination with metal ions.

There are many publications available for cadmium interaction with natural zeolites. The crystals of HEU-type zeolites accommodate two different systems of micropores interconnected within the lattice, the first developed along the c-axis with both eight- and ten-membered rings forming A- and B-type channels (3.3×4.6 and 3.0×7.6 Å, respectively), and the second developed along [102] and the a-axis with eight-membered rings forming c-type channels (2.6×4.7 Å) [51]. Stolz *et al.* [52] found that cadmium preferentially occupies the center of the A channel, where it forms a distorted octahedral $Cd^{2+}(H_2O)_6$ complex, and a central position in the B channel that is sevenfold coordinated by oxygen atoms of the framework and channel H_2O molecules and seven additional low-populated Cd sites were located in the channels. It has been reported as well a detailed crystal-structure for HEU-type crystals completely cation exchanged by Ag^+, Pb^{2+}, Cd^{2+}, Mn^{2+}, and Cd^{2+}, Mn^{2+} and Cu^{2+}, mainly occupy two extra-framework sites: one in the center of the ten-membered ring, octahedrally coordinated by six H_2O molecules, and one in the eight-membered ring, coordinated to framework oxygen and additional H_2O. Fully Cd-exchanged heulandite was used for stepwise dehydration studies, it was confirmed the supposition of a relation between charge, radius, and thus ionic potential of extra-framework cations, and the occurrence of a heat collapsed B-phase in heulandite [53].

The ion exchange reaction is a stoichiometric process for one equivalent of an ion in the solid phase is replaced by equivalent of an ion from solution. For binary ion exchange involving a monovalent cation such as Na^+ and a divalent cation such as Cd^{2+}, the equilibrium reaction may be written as:

$$2Na_z^+ + Cd_s^{2+} \leftrightarrow 2Na_s^+ + Cd_z^{2+}$$
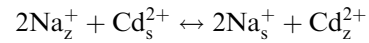
where the subscripts z and s refer to the zeolite and solution phase, respectively.

The effective cation exchange capacity of the zeolitic rock studied in this work is 1.09 meq/g, reported elsewhere [34]. The maximum cadmium exchange capacities obtained were 0.01, 0.22 and 0.13 meq/g at 303, 318 and 333 K respectively, this result show cadmium occupies only from 1 to 20% of the ion exchange sites from the extra-framework cations on the various channel positions of the zeolitic material studied under the experimental conditions.

The octahedral ionic radius for Cd^{2+} is 0.95 Å and the distribution of extra-framework cadmium cations on the various channel positions of HEU-type zeolites, which has a similar structure with clinoptilolite, are 28, 16, 27, and 48% in the channel positions A1, A2, A3, and B, respectively [51].

Ion exchange depends on the temperature, the solution pH, the concentration and on the hydrated ionic radii of the dissolved ions as correlated to the zeolitic channels [51]. The selectivity of clinoptilolite pre-exchanged to the Na-form against for divalent heavy metals cations is predominantly determined by the hydration energies rather than by the cation lattice interactions [32]. The radius of a fully hydrated ion is proportional to the ionic charge but not proportional to the ionic radius without H_2O shell [52]. On the other hand, the pH is also critical (specially in the case of acidic solutions) because the small H^+ cations are very mobile and reactive over any other metallic cations, therefore the pH between 5 and 6 was selected in order to minimize the effect of H^+ cations.

Although a lot of work has been accomplished in the area of low-cost sorbents, much work has to be done for better understanding the low-cost adsorption processes and to demonstrate the technology. In general, inexpensive, effective, readily available materials can be used in place of activated carbon or iron exchange resins for the removal of heavy metals from solution [9].

Conclusions

The crystals morphology does not change after the cadmium sorption process.

The major component of the new deposit of Mexican zeolitic-rich tuff used in this work was clinoptilolite.

The equilibrium sorption of cadmium depends on the solution temperature.

The activation energy of Cd^{2+} removal by the zeolitic rock from Chihuahua indicates a chemical sorption process.

There is an exponential relationship between the diffusion coefficients of Cd^{2+} ions into the pores of the irregular zeolitic rock grains and the pseudo-second order rate constants (k) for the temperature range investigated.

The maximum cadmium capacity of the zeolitic rock from Chihuahua was observed at 318 K, according to the Freundlich model.

Only 20% of the effective exchangeable cations from the natural zeolite from Chihuahua were exchanged by the cadmium ions.

Acknowledgements

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