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Evaluation of Natural and Surfactant-Modified Zeolites in the Removal of Cadmium from Aqueous Solutions

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ABSTRACT

The present study involves an investigation on the comparison of a Mexican clinoptilolite-heulandite zeolitic mineral and the modified zeolitic material with the surfactant hexadecyltrimethylammonium bromide (HDTMA) for the removal of cadmium from aqueous solutions. The effects of pH and contact time on the adsorption process were examined. The optimum pH for adsorption was found to be 7. Cadmium retention

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reached equilibrium in 32 h and the rate of cadmium adsorption by the zeolites was rapid in the first 10 h. Elovich's model best described the reaction rate. Batch adsorption experiments conducted at room temperature showed that the adsorption pattern followed the Langmuir–Freundlich isotherm model. The cadmium retention capacity decreased very slightly when the zeolite surface was modified with the surfactant HDTMA, and this material has advantages for its use in the removal of some other contaminants, such as anions and nonpolar organic compounds, like phenols. The results showed that natural zeolite and the surfactant modified zeolite could be considered as potential adsorbents for cadmium removal from aqueous solutions.

Key Words: Clinoptilolite; Ion exchange; Cadmium; Adsorption, HDTMA.

INTRODUCTION

The contamination by heavy metals occurs in aqueous waste streams of several industries, such as metal finishing, mining and mineral processing, coal mining, oil refining and tanneries, among others. Some metals associated with these activities are the following: cadmium, cooper, chromium, iron, mercury, nickel, lead, and zinc.[1]

In particular, cadmium is found in surface waters as a free ion; its solubility is affected by the hardness, the pH, the soluble complexes, and the colloidal sulfides of the aqueous stream. Cadmium is a dangerous heavy metal that causes severe problems due to its high toxicity.[2]

There are several processes to remove heavy metals from wastewater. However, many of them can be very expensive or difficult to implement in developing countries. Therefore, it is necessary to find treatment processes that will be simple and will involve local resources.[3,4] Natural zeolites provide an economic and effective mechanism to remove heavy metals dissolved in a waste stream. Clinoptilolite, in particular, shows great affinity for lead and partially for cadmium, but not so great an affinity for zinc and other heavy metals.[5–7]

Clinoptilolite is a natural zeolite of the heulandite group. The structure of a zeolite consists of a three-dimensional framework of $SiO_4{}^{4-}$ and $AlO_4{}^{5-}$ tetrahedra. The aluminum ion is small enough to occupy the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Al^{3+} for Si^{4+} atoms raises negative charges in the lattice. The net negative charges are balanced by exchangeable cations (sodium, potassium, and calcium, among others). These cations are exchangeable with those from the solution such as lead, cadmium, zinc, manganese, etc.[7,8] Due to their

unique cage-like structure with channel openings of the order of a few angstroms, zeolites have found wide use as molecular sieves, because small organic or inorganic
molecules may be trapped within these channels. Molecules and ions too large to fit into the zeolite's channels are excluded from the internal surfaces and interact only with the external surfaces of zeolite crystals. Furthermore, in general, anions and neutral solutes are not readily taken up by the zeolite. Anions, in fact, are repelled by the negatively charged zeolite. Raw zeolites are useful for water treatment to remove cations, particularly relatively small cations such as ammonium and metal ions.[9]

The negatively charged surfaces of natural zeolites can be modified by cationic surfactants, like hexadecyltrimetylammonium bromide (HDTMA). Charge-balancing cations present on the surfaces of the zeolite can be replaced by this kind of compounds by exchanging quantitatively, and essentially irreversibly, with inorganic cations on the external surface of the mineral, but they are too large to enter the internal pore structure of the zeolite. The internal or zeolitic exchange sites potentially remain available for smaller inorganic cations. This modification produces a surfactant-modified zeolite (SMZ), which can sorb nonpolar organic compounds, inorganic cations, and inorganic anions. Recently, great interest has been shown for this kind of material due to its great ability to adsorb different types of pollutants and for its relative low cost.[9–11]

The purpose of this study was to evaluate the retention of cadmium from an aqueous solution by using both a Mexican clinoptilolite and the modified zeolite with HDTMA. Although different studies on the retention of cadmium on different types of materials have been reported, the study of the retention of cadmium by the modified Mexican clinoptilolite is important since this material may be used in the removal of cations, anions, and nonpolar organic compounds simultaneously. It also was important to fit the experimental results to kinetics and isotherms models to analyze the sorption process of cadmium(II) onto both types of materials.

EXPERIMENTAL

Materials

Reagents-grade chemicals were used as received, without further purification, except when it is specified.

The zeolite used in this study was obtained from a deposit located in the state of Sonora, in northwest Mexico. The zeolitic mineral was ground and sieved; a grain size fraction between 1.7 and 1.18 mm was selected to carry out the experiments. This selected fraction was washed with distilled water and converted to its homoionic sodium form. To achieve this form of the zeolite mineral, it was put in reflux with a 1 M sodium chloride solution during 36 h, after this time, the zeolite was washed with distilled water to eliminate any excess of chloride ions from the material.

Cation Exchange Capacity

The cation exchange capacity (CEC) was determined by saturating the mineral with ammonium according to the method reported elsewhere.[12] The natural zeolite in its Na^+ form (NaZ) was mixed with dry sand previously washed with HNO_3 and distilled water. A 1 N ammonium acetate solution was added to the mixture, and it was left for 48 h, then the mixture was centrifuged and the phases separated; the solid was washed with 100 mL of ethylic alcohol. The ammonium ions in the zeolitic mineral were exchanged with a 1 N KCl solution for 48 h. After the mixture was centrifuged and the phases separated, the NH_4^+ ions were distilled from the supernatant, and they were measured by titration with a 0.01 N HCl solution.

Electron Microscopy

For scanning electron microscopy (SEM) observations, the samples were mounted directly on the holders and were covered with sputtered gold, and then observed at 10, 20, and 25 kV in a Philips, XL 30 electron microscope (Philips Electron Optic, Netherlands Eidhoven).

Modification of the Zeolitic Mineral with HDTMA

The SMZ was prepared by treating the mineral with an aqueous solution of HDTMA. A total of 32 g of NaZ were mixed with 57.6 mL of a 1.816 mM HDTMA solution in a sealed flask, and it was gently shaken for 24 h at 30°C. Then, the zeolite was centrifuged and separated from the solution, and it was air-dried at room temperature. The SMZ was washed several times with distilled water at 30°C until HDTMA was not detected in the washing solutions, HDTMA was determined by using an ultraviolet-visible spectrophotometer analyzer at $\lambda = 194.15$ nm.

Kinetics Experiments

Batch-type experiments were performed to determine the kinetics removal of cadmium. Aliquots of 20 mL of a 0.005 N $Cd(NO_3)_2$ solution and 200 mg of each type of zeolite samples (this ratio was selected on the basis of previous experiments reported elsewhere[13,14]) were placed in centrifuge tubes and shaken for different times (5, 15, and 30 min, and 1, 3, 7, 24, 32, and 48 h) at room temperature; later, the samples were centrifuged, decanted, and washed. The cadmium concentrations were determined by using a GBC-932plus atomic absorption spectrometer at wavelength 326.1 nm.

Influence of pH

Batch experiments were conducted at different pH values. These experiments were carried out by putting in contact 200 mg of both zeolite types samples, separately, in flasks with 20 mL aliquots of a 0.01 N cadmium nitrate solution, the pH of the solutions was previously adjusted to 3, 5, 7, and 9. The solutions were shaken during 48 h at room temperature and then centrifuged and decanted to determine the remaining cadmium in the liquid phases by atomic absorption spectroscopy.

Isotherms

A total of 200 mg samples of each kind of zeolite, separately, and 20 mL aliquots of different concentrations of cadmium nitrate solutions (0.001, 0.003, 0.005, 0.01, 0.03, 0.05, 0.1, 0.2, 0.3, and 0.5 N) were used. The mixtures were shaken for 48 h at room temperature. The samples were centrifuged and decanted; cadmium was analyzed in the liquid phases as described above.

RESULTS AND DISCUSSION

Materials

The SEM image of a natural zeolite sample (Fig. 1) clearly reveals the presence of the characteristic crystals of natural clinoptilolite; the morphology coincides with the one reported by Mumpton and Ormsby,[15] most of the crystals present monocyclic symmetry. The cavities that confer the porosity to the material, are important in the sorption processes, also can be appreciated. The components of the zeolitic mineral determined by x-ray diffraction have been reported elsewhere;[16] they are estilbite, cristobalite, clinoptilolite, modernite, analcime, quartz, calcite, and heulandite.

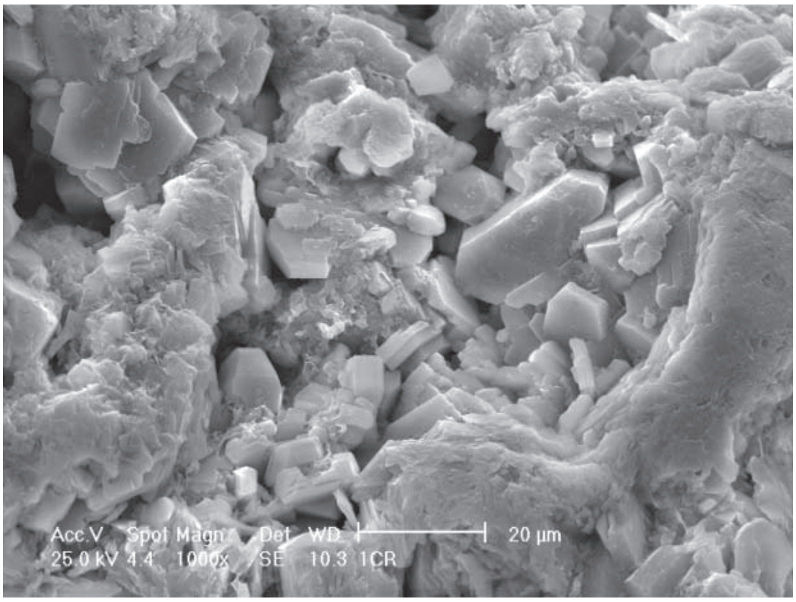

Figure 1. SEM image of a natural zeolite sample. 1000×.

CEC

The CEC determined in the zeolitic mineral NaZ was 0.8576 ± 0.0464 meq/g, Breck[8] reported a higher CEC for a clinoptilolite, the difference could be attributed to the composition of the zeolitic mineral.

Kinetics Experiments

Figures 2 and 3 show the results obtained from kinetics experiments with the zeolitic mineral treated with sodium and with modified zeolite, respectively. According to these figures, the cadmium removal by NaZ and SMZ curves present a shape characterized by a fast increase of removal in the first minutes of contact, followed by a slow increase until equilibrium is reached. It can be observed that the quantity of cadmium removed in the experiments with NaZ is slightly higher (16.37 ± 0.24 mg/g) than those obtained with SMZ (15.86 ± 0.26 mg/g). Besides, it can be observed that after 24 h of contact with NaZ, a higher removal of this metal is obtained, which represents a better efficiency in the exchange compared with the

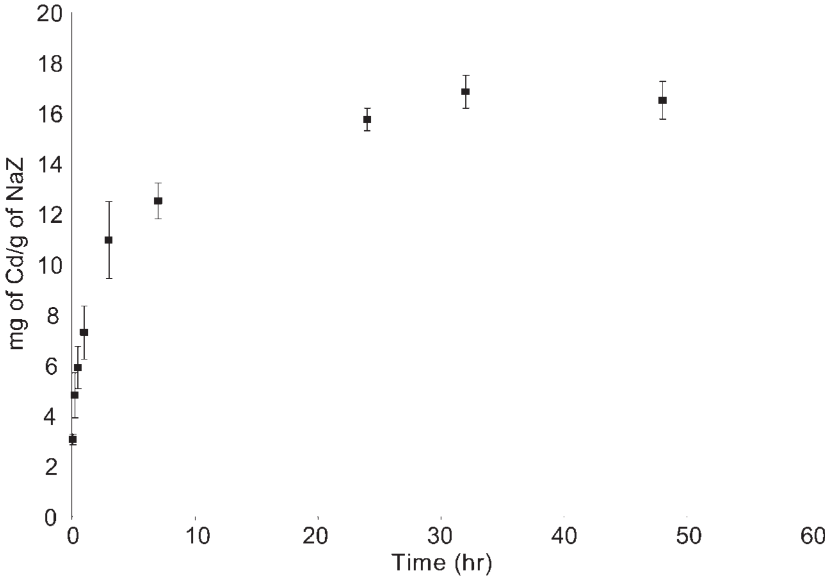

Figure 2. Removal of cadmium ions by NaZ (■) at different contact times.

modified zeolite. After 32 h of contact, changes are no longer observed in the cadmium concentration. These results suggest that the modification does not affect the retention of cadmium by the zeolitic mineral, as expected. Therefore, the modified material can be used to retain anions, nonpolar organic compounds, and cations.

Data Treatment

The data obtained from the kinetics tests were adjusted to the following models that have been used for this type of system:

1. The Lagergren first-order model is represented by the following equation:[17]

$$q_t = q_e[1 - \exp(-K_L t)] \tag{1}$$

where K_L is the Lagergren rate constant (h^{-1}), q_t is the amount of metal ion adsorbed at any given time t(mg/g), and q_e is the amount of metal ion adsorbed at equilibrium (mg/g).

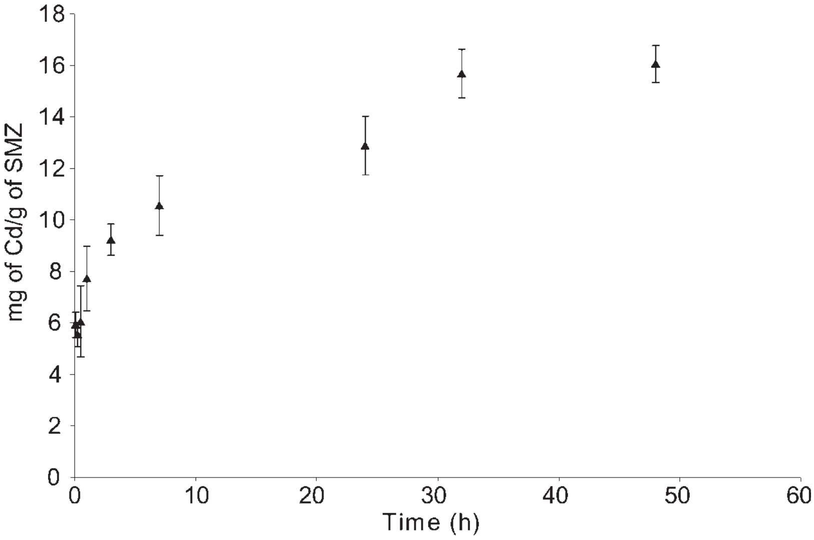

Figure 3. Removal of cadmium ions by SMZ (▲) at different contact times.

2. Ho et al.[18] used a pseudo-second-order equation on the kinetics removal of heavy metals on peat; this equation is represented on its linear form as follows:

$$\frac{t}{q_t} = \frac{1}{(Kq_e^2)} + \frac{t}{q_e} \tag{2}$$

Rearranging:

$$q_t = \frac{Kq_e^2 t}{1 + 2Kq_e t} \tag{3}$$

where K is the pseudo-second-order rate constant for adsorption (g/mg h), q_t is the amount of metal ion adsorbed at any given time t (mg/g), and q_e is the amount of metal ion adsorbed at equilibrium (mg/g). The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate.[19]

3. The last model used in this study was the Elovich rate equation, which has been commonly used in the kinetics of chemisorption of gases on solids. However, some researchers have applied this model to solid–liquid sorption systems, especially on the sorption

of heavy metals.[20,21] This model is represented by the following equation:

$$q_t = \frac{1}{b}\ln(1 + abt) \tag{4}$$

The linear form of this equation is:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0) \tag{5}$$

where a and b are the parameters of the equation and $t_0 = 1/ab$.

The experimental data were fitted to these equations by nonlinear regression analysis, using the software Statistica 6.0 for Windows. Tables 1 and 2 show the results of the analysis, describing the equations that correspond to the model used in each case, as well as their correlation coefficient values for each type of zeolite. Figures 4 and 5 show the pseudo-second-order model plots for the removal of cadmium by NaZ and SMZ, respectively. Figures 6 and 7 present the Elovich model plots for both types of zeolites. According to these plots, the experimental data are best described by the Elovich equation for NaZ and SMZ. Ho and McKay[22] have reported that the experimental results may be described by the Elovich model when the chemisorption is the process involved in the retention.

The value of constant a for the sorption of cadmium(II) onto NaZ is 72.359 mg g^{-1}, the constant b is 0.427 mg^{-1} g, and the parameter t_0 is 0.03 h. In the case of cadmium uptake onto SMZ, the value of constant a is 195.358 mg g^{-1}, the value of constant b is 0.575 mg^{-1} g, and the parameter t_0 is 0.008 h. It has been proposed that the constant a is related to the initial rate of chemisorption and the constant b is related to the surface coverage.[20] Therefore, increasing the concentration of solution will increase the rate of chemisorption. If the constant b is related to the surface coverage, then the increase of concentration of solution will decrease the available sorption surface of the sorbates.

An acceptable adjustment of data also was obtained by using the pseudo-second-order equation only for NaZ (Fig. 4); in the case of the SMZ, these

Table 1. Rate equations for cadmium removal by NaZ.

Model type	Model equation	R
Lagergren	$q_t = 16.6(1 - e^{-0.5123t})$	0.9155
Ho et al.	$t/q_t = 1/[(0.0541)(16.6)^2] + t/16.6$	0.9711
Elovich	$q_t = 1/(0.4269)\ln[1 + (72.3595)(0.4269)t]$	0.9947

Table 2. Rate equations for cadmium removal by SMZ.

Model type	Model equation	R
Lagergren	$q_t = 15.7(1 - e^{-0.5405t})$	0.5831
Ho et al.	$t/q_t = 1/[(0.0632)(15.7)^2] + t/15.7$	0.7900
Elovich	$q_t = 1/(0.5754)\ln[1 + (195.3586)(0.5754)t]$	0.9582

models presented slight deviations, and, therefore, lower correlation coefficient values were obtained than those obtained when using the Elovich equation. The Lagergren first-order model did not show a good correlation in comparison to the other two models. Cheung et al.[20] found, as well, that the latter model was not very suitable for use on the sorption of cadmium onto bone char. Furthermore, it has been reported that applying simple kinetic models is often incorrect, such as first- or second-order rate equations, to a sorption with solid surfaces that are rarely homogeneous and because the effects of transport phenomena and chemical reactions often are experimentally inseparable.[19]

The general explanation for the Elovich equation kinetic law involves a variation of the energetics of chemisorption with the extent of surface

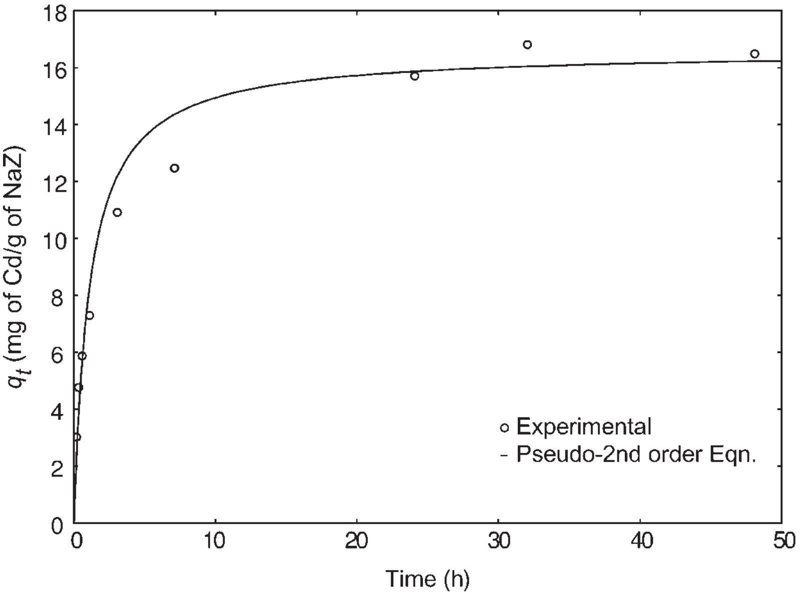

Figure 4. Pseudo-second-order model plot for removal of Cd^{2+} ions by NaZ.

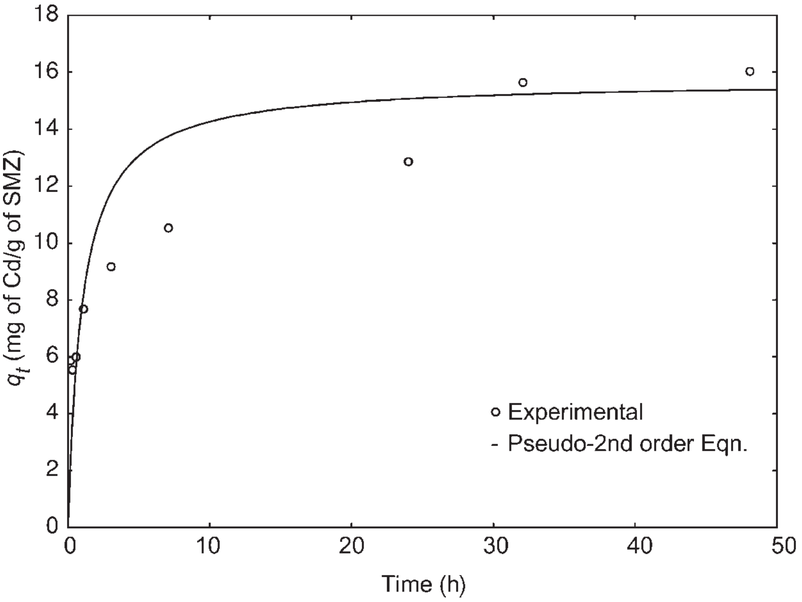

Figure 5. Pseudo-second-order model plot for removal of Cd^{2+} ions by SMZ.

coverage. It has proved suitable for highly heterogeneous systems.[22] The adsorption of cadmium(II) on natural zeolites is undoubtedly such a case, since they are composed by different minerals and, therefore, exhibit different activation energies for chemisorption. If the sorption of cadmium ions onto the zeolitic mineral is predominantly chemisorption, the Elovich equation describes the sorption system as mentioned above. This equation has a general application on chemisorption kinetics and will cover a large range of the course of slow adsorption, failing only toward the end of the reaction where the process becomes excessively slow.[18,23] In chemisorption, the mechanism consists of a quasi-explosive production of active sites upon contact with the adsorbate. This is offset by a first-order spontaneous decay of sites, resulting in an initial steady-state site concentration and, at that stage, it is marked by an amount of adsorbate that is instantaneously adsorbed. From that point on, slow adsorption occurs, with bimolecular disappearance of sites and the corresponding exponential decline in the rate of adsorption.[23] In this way, the behavior observed on the sorption of cadmium ions onto NaZ and SMZ (Figs. 6 and 7) can be explained, where it can be observed, as an initial rapid uptake and subsequent slow uptake rate.

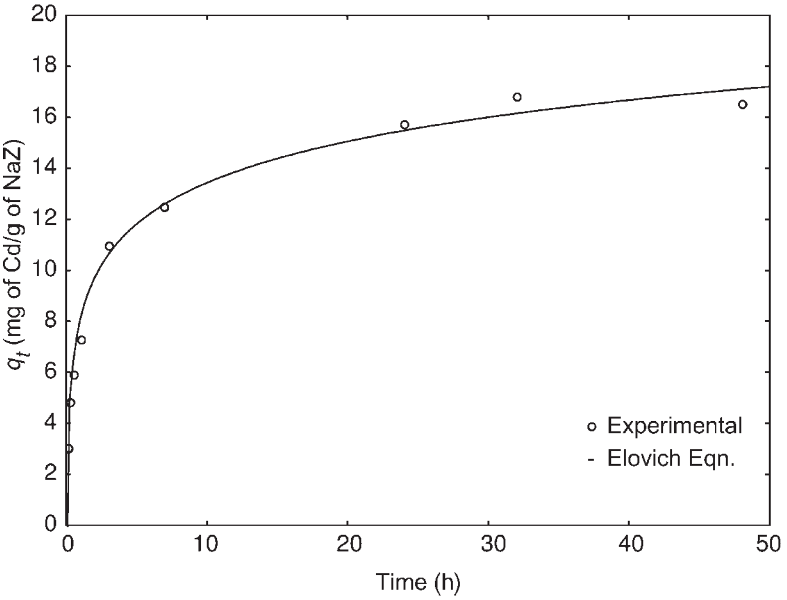

Figure 6. Elovich equation model plot for the removal of Cd^{2+} by NaZ.

Influence of pH

Since the surface charge of an adsorbent can be modified by changing the pH of the solution, the pH is one of the most important parameters affecting the adsorption process of metal ions. Figure 8 shows the retention of cadmium by NaZ and SMZ at different pH values. The quantity of cadmium removed is very similar at pH values of 3, 5, and 7. It is also clear that the removal by NaZ is higher than the removal by SMZ in every case. The increase of cadmium retention observed in the materials at pH 9 can be explained by the cadmium precipitation on the zeolitic minerals as $Cd(OH)_2$. The chemical equilibrium diagram for cadmium on aqueous solution shows the formation of a precipitate of $Cd(OH)_2$, (Fig. 9) as the pH increases, the concentration of Cd^{2+} ions decreases. The chemical diagram was obtained by using the MEDUSA (make equilibrium diagrams using sophisticated algorithms)[24] program.

Since the pH of natural water is, in general, between 5 and 7, the pH selected to carry out the experiments in this work was 6. Mathialagan and Viraraghavan found that the kinetics of cadmium adsorption on vermiculite behaved similarly between pH 5 and 7.[17]

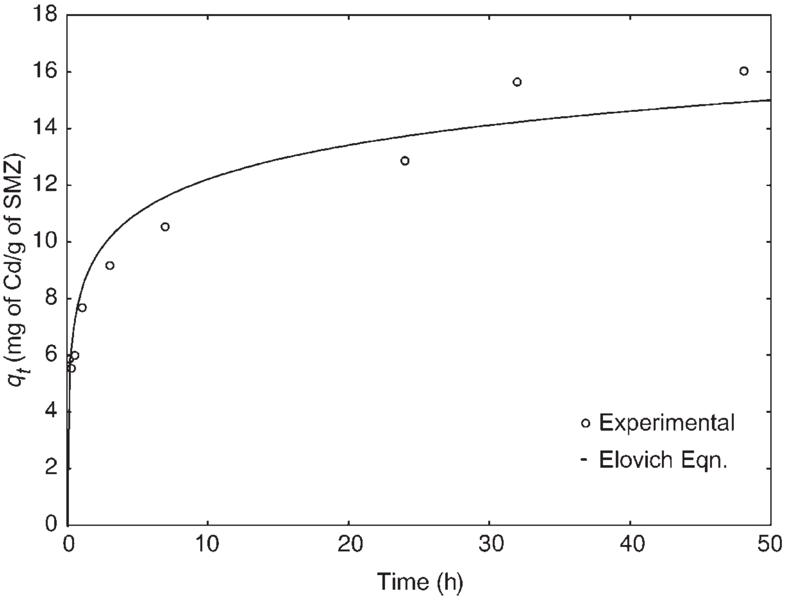

Figure 7. Elovich equation model plot for the removal of Cd^{2+} by SMZ.

Isotherms

The ion exchange isotherms for cadmium uptake are represented in Figs. 10 and 11 for NaZ and SMZ, respectively. These isotherms are presented as a plot of raw data obtained from batch experiments. Afterward, the data were fitted to the well-known Freundlich, Langmuir, and Langmuir–Freundlich isotherm models by a nonlinear regression analysis by using the software Statistica 6.0, these models are represented by the following equations:

1. Freundlich:

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

where q_e is the amount of cadmium per unit weight of zeolite (meq Cd/g zeolite), C_e is the equilibrium concentration of cadmium in solution (meq Cd/L), K_f is the equilibrium constant indicative of adsorption capacity, and n is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity.

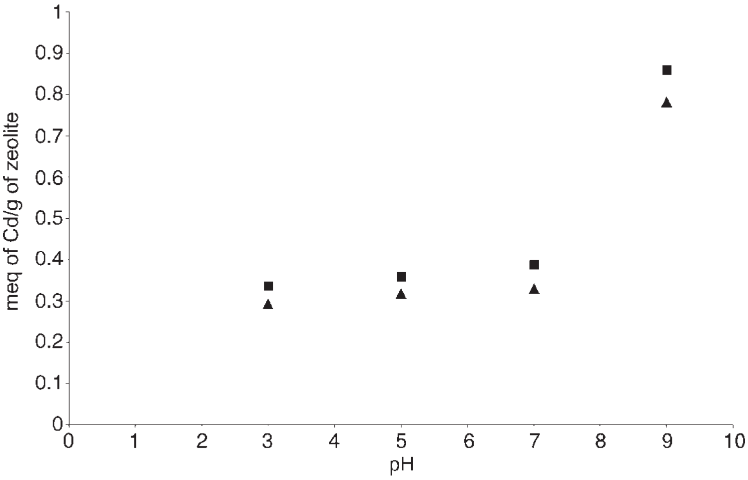

Figure 8. Influence of pH on the sorption of cadmium by NaZ (■) and SMZ (▲).

2. Langmuir:

$$q_e = \frac{q_0 b C_e}{1 + bC_e}$$

where q_e is the amount of cadmium per unit weight of zeolite (meq Cd/g zeolite), C_e is the equilibrium concentration of cadmium

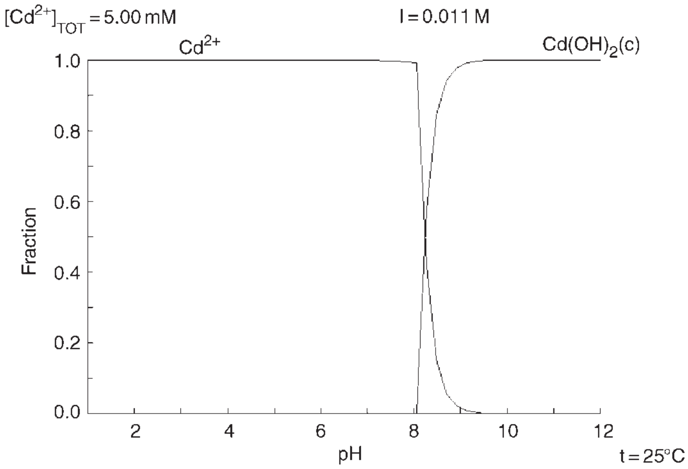

Figure 9. Chemical equilibrium diagram for cadmium in aqueous solution.

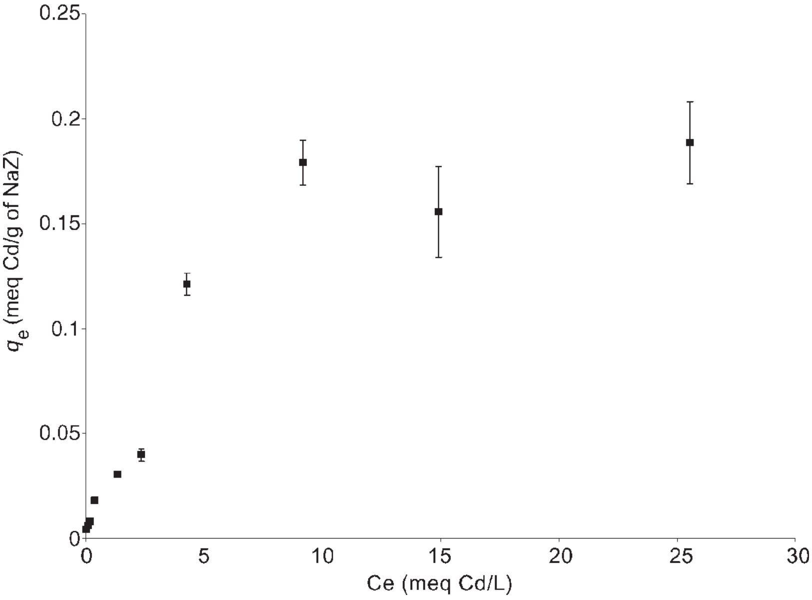

Figure 10. Sorption isotherm of cadmium on NaZ (■).

in solution (meq Cd/L), q_0 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.

3. The Langmuir–Freundlich isotherm model, which has been used elsewhere,[20] also was applied. The equation that represents this model is:

$$q_e = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}}$$

where q_e is the amount of cadmium per unit weight of zeolite (meq Cd/g zeolite), and C_e is the equilibrium concentration of cadmium in solution (meq Cd/L), and K_{LF} and a_{LF} are the empirical constants.

Tables 3 and 4 show the results of the nonlinear regression analysis of experimental data, for NaZ and SMZ, respectively, describing the equations corresponding to the model used in each case, as well as their correlation coefficient values for each type of zeolite. The Langmuir–Freundlich model isotherm (Figs. 12 and 13) gave the best correlation in both types of zeolites used.

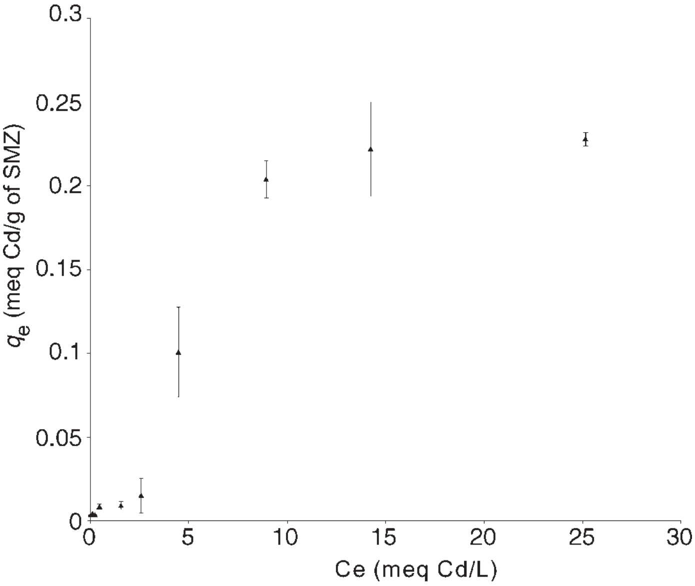

Figure 11. Sorption isotherm of cadmium on SMZ (▲).

It is important to mention that the model calculations in this case were done in meq/L units instead of the mg/L that were used for the kinetics models, because the results obtained when the data were used in mg/L were not completely reliable, since they were not statistically significant at a confidence level of 95%, according to the *p*-levels delivered from the software.

Theoretically, the equilibrium isotherms, the capacity, and the diffusion coefficient for a specific ion exchange or adsorption system are independent of the experimental method used for their determination. The theoretical adsorption capacity of the zeolitic mineral for cadmium can be calculated from the Langmuir–Freundlich model. Values of 0.183 and 0.224 meq Cd^{2+}/g were

Table 3. Isotherm equations for the removal of cadmium by NaZ.

Model type	Model equation	*R*
Freundlich	$q_e = (0.0445)Ce^{(1/2.1213)}$	0.9411
Langmuir	$q_e = (0.2309{*}0.1808{*}Ce)/1 + (0.1808{*}Ce)$	0.9665
Langmuir–Freundlich	$q_e = (0.0074{*}Ce^{(1/0.3733)})/(1 + (0.0423{*}Ce^{(1/0.3733)}))$	0.9871

Table 4. Isotherm equations for the removal of cadmium by SMZ.

Model type	Model equation	*R*
Freundlich	$q_e = (0.0353)\mathrm{Ce}^{(1/1.5862)}$	0.9367
Langmuir	$q_e = (0.3854{*}0.0777{*}\mathrm{Ce})/1 + (0.00777{*}\mathrm{Ce})$	0.9617
Langmuir–Freundlich	$q_e = (0.611 \times 10^{-3}{*}\mathrm{Ce}^{(1/0.2652)})/$ $(1 + (0.0027{*}\mathrm{Ce}^{(1/0.2652)}))$	0.9989

obtained as the adsorption capacities for NaZ and SMZ, respectively, from batch studies under the present experimental conditions.

CONCLUSIONS

The NaZ and SMZ showed a good capacity for the removal of cadmium from aqueous solutions. This capacity decreased very slightly when the zeolite surface was modified with the surfactant HDTMA.

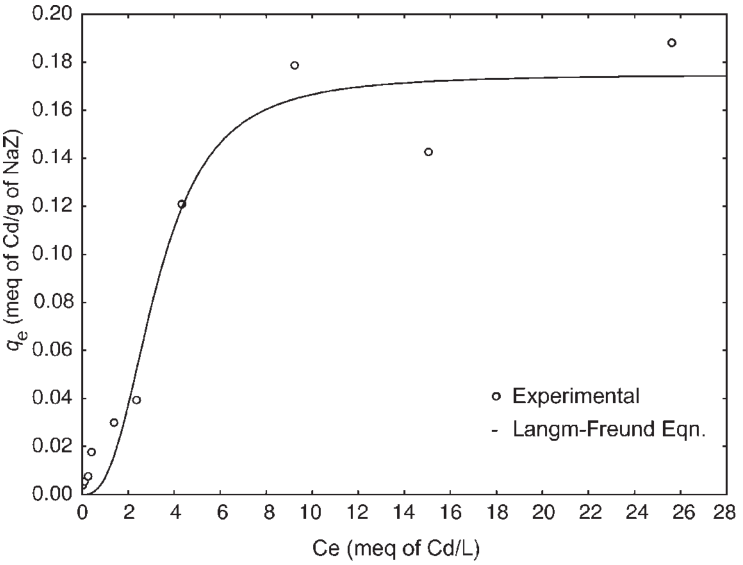

Figure 12. Langmuir–Freundlich isotherm model plot for the removal of cadmium by NaZ.

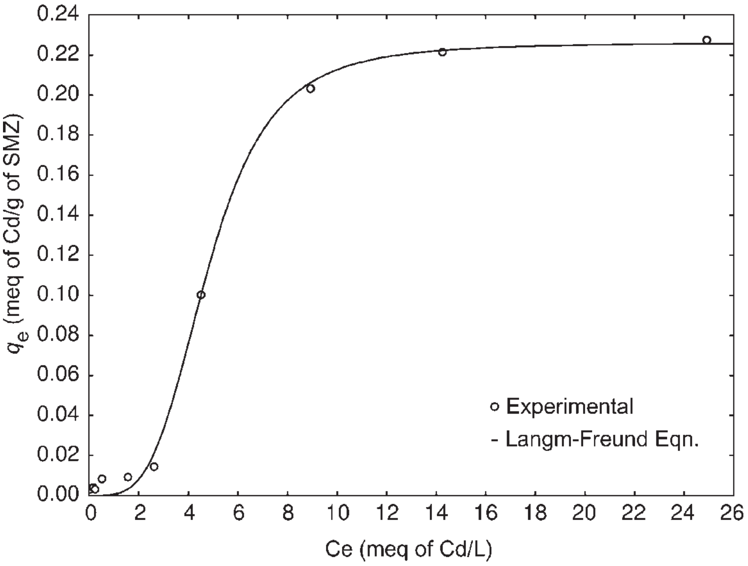

Figure 13. Langmuir–Freundlich isotherm model plot for the removal of cadmium by SMZ.

According to the results from the kinetics experiments, the time in which equilibrium is attained was about 32 h for NaZ and SMZ. The experimental data could be fitted well to the mathematical kinetic models such as pseudo-second-order model and Elovich's equation, both based on the assumption of chemisorption as rate-limiting step. The Elovich model showed higher correlation compared with the other two models used to describe the sorption of cadmium ions onto the zeolitic mineral, since this kind of material contains various types of binding sites, and, therefore, they have heterogeneous surfaces. The correlation coefficient obtained for the experiments done with SMZ are lower than those obtained with NaZ.

Although kinetics models were well adjusted to the experimental data, one of the main selection criteria is whether to apply a kinetic or diffusion-controlled model. Because the sorption of metal onto zeolitic mineral was completed within several hours, it would be interesting in the future to consider long-time diffusional controlled processes.

The pH did not cause significant variations on cadmium uptake in the range from 3 to 8; but, at pH 9, a precipitation of $Cd(OH)_2$ was observed and it interfered directly in the removal processes.

The isotherm pattern that best describes the behavior of the data obtained experimentally is the Langmuir–Freundlich isotherm. In the experiments done with SMZ, a higher correlation was obtained in comparison with those carried out with NaZ.

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