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Adsorption behavior of cadmium onto natural chabazite: batch and column investigations

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ABSTRACT

The objective of the proposed work focused to provide promising solid-phase materials that combine relatively inexpensive and high removal capacity of cadmium ion from aqueous solutions. Four various zeolite minerals including natural clinoptilolite, natural chabazite, natural mordenite, and synthetic mordenite were investigated. The obtained results revealed that natural chabazite has the highest surface area and mesopore volume and appears to be the best adsorbent towards cadmium ion rather than the other investigated zeolite materials. The effective key parameters on the sorption behavior of cadmium on natural chabazite were investigated using batch equilibrium and flow through technique with respect to solution pH, contacting time, adsorbent weight, adsorption isotherm, bed depth, and flow rate. Kinetic curves rather showed a fast adsorption for cadmium, as equilibrium reached within 60 min. The affinity and adsorption capacity of natural chabazite with good fits being obtained using Dubinin–Radushkevich adsorption isotherm giving a maximum capacity of 120 mg/g. Cd^{+2} and adsorption found to be pH dependent over 2.5–8.5 range; this reveals that the adsorption mechanism may be controlled by chemisorption with the experimental conditions used. The results indicated the feasibility and spontaneous nature of adsorption process at high temperature. Thermodynamic parameter was determined. Column studies showed that cadmium ion removal was a strong function of initial flow rate and bed height. Natural chabazite recommended to be used as reactive barrier for hazardous heavy metals control.

Keywords: Cadmium; Natural zeolite; Adsorption; Treatment

1. Introduction

Among the various environmental pollutants, exposure to heavy metals, such as cadmium, chromium, mercury, and lead metals contribute as serious health problems worldwide. The heavy use and application of toxic heavy metals in the last few decades has resulted in excessive release of metallic species into various environments with a strong impact on aquatic and soil systems [1]. Cadmium is considered as one of the most toxic heavy metals [2,3]. Cd is frequently used in electroplating, pigments, paints (as a stabilizer), welding, and rechargeable Ni–Cd batteries. Cadmium is not regarded as essential to human life and accumulates in humans, mainly in the kidneys,

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for a relatively long time, leads to severe kidneys dysfunction [4]. Cadmium is also known to produce health effects on the respiratory system and bone disease [5]. More recently, the possible role of cadmium in human carcinogenesis has been also studied. In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment [2]. Chemical reduction and oxidation, precipitation, adsorption, electrolytic removal, and reverse osmosis are some of the methods widely practiced to remove or sequester cadmium from polluted water. The materials used are costly and the methods which treat metal ions as a waste rather than a material may be recycled [6]. As alternative for these methods, researchers have been worked on low-cost adsorbents having good adsorption capacities and are locally available.

Cost-effective materials have been investigated for their potential use as adsorbents for cadmium. Semerjian [7] studied the removal of Cd^{2+} from aqueous solution using untreated *Pinus halepensis* sawdust [7]. The maximum capacity of sawdust was found to be 5.36 mg/g at pH 9.0 for the investigated cadmium concentration range 1–50 mg/L. Huang [8] studied the thermodynamics and kinetics of cadmium adsorption onto nitric acid which oxidized activated carbon under various conditions. Adsorption isotherms correlated well with the Langmuir isotherm model and the adorption capacity of oxidized activated carbon was 5.73 mg/g [8]. The application of orange wastes, generated in the orange juice industry, for cadmium treatment was evaluated. Strong positive correlation of the metal ions uptake with pH was observed. The maximum adsorption capacity of orange waste for cadmium was found to be 44.96, 46.08, and 48.33 mg/g at pH 4–6, respectively [9].

Recently, different environmentally friendly biosorbents were used for biosorptive removal of Cd^{2+} ions from aqueous solution. Farooq et al. [6] investigated the use of wheat straw (WS) powder from Triticum aestivum in cadmium treatment [6]. The behavior of untreated WS was found to follow Freundlich model, while the modified microwave urea modified wheat straw followed Langmuir model with maximum biosorption capacity ($q_{\max}$) of 39.22 mg/g at pH 6.

Clay is another potential alternative adsorbent for the removal cadmium from different waste streams. Clay minerals are important inorganic components in soil and their sorption capabilities come from their high surface area and exchange capacities of surface negative charge… Bentonite is a common mineral mainly consists of clay, silt, and sand. Pradas et al. [10] used this mineral to adsorb Cd^{2+} and Zn^{2+} from aqueous solution. It was reported that Cd^{2+} with maximum capacity 11.41 mg/g is adsorbed two times more than Zn^{2+} (4.54 mg/g) due to the fact that Cd^{2+} have less polarizing effects to the surface charge of bentonite than zinc ions [10].

Natural zeolite is another important inorganic adsorbent and has been widely used in separation and purification processes in the past decades. Natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis, and sorption. Extensive research has been done on the use of activated and non-activated clinoptilolite (the most abundant natural zeolite) for removing cadmium from different aqueous solutions [11–15]. The results revealed a wide range of adsorption capacity for Cd^{2+} starting from 0.0053 to 0.19 meq/g for Bigadic, Turkey, and Sardinian clinoptilolite, respectively.

The cadmium exchange on chabazite has been the subject of very few works. In one of those works, the research focused mainly on performing detailed characterization of natural chabazite and clinoptilolite from the USA and comparing their capacity for Cd(II) adsorption [16,17]. In this paper, cadmium removal from the aqueous solution using batch and column adsorption methods was investigated by a low-cost available adsorbent (natural chabazite). Factors affecting sorption, such as pH, agitation time, temperature, and adsorbent dosage were investigated. Kinetic and isotherm studies were under taken in order to illustrate the adsorption mechanism of cadmium on this zeolite material. Thermodynamic parameters were calculated. Additionally, the removal of cadmium by natural chabazite in the column mode is systematically investigated, which can provide a practical application of this adsorbent in water/wastewater treatment in the future.

2. Experimental

2.1. Materials and instrumentation

Natural clinoptilolite and mordenite originated from Japan, Futatsui (Akita prefecture), and Kawarago (Miyagi prefecture), respectively. Synthetic mordenite (Zeolon 900 H) with the size 10–14 mesh was from Norton Company, USA. Chabazite sample used for these investigations was marketed as AW-500 (Linde Corporation, USA), which was the forerunner of lonsiv IE-96 (presently supplied by UOP). All chemicals and reagents used for experiments and analyses were of analytical grade and were used without further purification. Stock solution of 1,000 mg/L Cd(II), was prepared from $CdSO_4$ salt in bidistilled water with 1% HNO_3. Potassium oxalate was supplied from Carlo Erba, Italy. Potassium chloride from BDH, England, while 4-(2-pyridylazo) resorcinol produced by Alfa Aesar, USA.

2.2. Samples preparation

Zeolite samples were prepared according to the procedures described by one of the co-author [18]. Briefly, the as-received zeolites were air dried, lightly ground, and sieved. Fine particles with a diameter of < 150 μm were used in subsequent experiments. A pre-exchange process with 1 M KCl solutions was used to remove deleterious exchangeable cations from the natural chabazite and mordenite that can significantly improve their cation exchange capacity. About 5 g of each material was suspended in 100 mL of 1 M KCl at room temperature. The mixture was maintained for 24 h on end-over-end stirrer. The resulting mixture was filtered, washed thrice by bidistilled water, and finally twice by ethanol then air-dried [19].

2.3. Adsorbents characterization

Crystal structures of the zeolite samples were identified from X-ray diffraction (XRD) patterns recorded with analytical X'pert Pro MPD XRD system using X'pert High Score Plus software. Coarse elemental analyses were carried out from energy-dispersive X-ray spectroscopy (EDX) spectra recorded by Oxford INCA 350 micro-analysis system connected to a Hitachi S-4800 field emission scanning electron microscope and using INCA suite version 4.05 software. Nitrogen gas adsorption isotherms, volumetrically obtained from relative pressures 10^{-6}–1 at 77 K using a Quantochrome NOVA 1000e were used to determine the surface area and pore size distribution of the zeolites samples. At the beginning, the sample was degassed under vacuum at 150°C for > 12 h to drive off moisture and any other volatile material that could interfere with the adsorption experiment. Surface area of the samples was calculated from Brunauer-Emmett-Teller (BET) equation. The relative pressure range used for the BET calculation was 0.01–0.1. Micromerities Density Functional Theory (DFT) software was used to determine the pore size distribution of zeolites samples.

2.4. Batch adsorption studies

To select the best zeolite among four different types (natural clinoptilolite, natural mordenite, synthetic mordenite, and chabazite), a preliminary test was carried out using 10 mL of 50 mg/L Cd (II) solution and 0.1 g from each adsorbent sample. The equilibrium sorption experiments of cadmium on natural chabazites were carried out at pH = 5.5, constant temperature (25 ± 2°C), and ionic strength (0.01 M) by $NaNO_3$ in 50 mL polypropylene centrifuge tube with screw cap. The solutions were shaken and mixed for 24 h, to ensure equilibration. The samples were removed from the shaker, and the solution was centrifuged using Hettich Centrifuge, model Rotofix 32, and then zeolites were isolated by filtration. The amount of cadmium ions remaining in the supernatant was taken and analyzed by UV spectrophotometer at 409 nm using 0.4 mM 4-(2-pyridylazo) resorcinol (PAR) as complexing agent. After choosing chabazite as the best adsorbent, the same conditions and solid/liquid ratio were applied to study the effect of contact time on cadmium adsorption by shaking of cadmium/chabazite mixture for different time intervals ranging from 5 to 120 min and to study the effect of cadmium initial concentration ranging from 10 to 50 mg/L.

To study the effect of pH on the adsorption behavior of cadmium, the suspension pH from 2.5 to 8.5 was adjusted by HNO_3 or NaOH, before adding metal ions mixture. All pH experiments were performed with the solid/liquid ratio 0.1 g chabazite/10 mL solution of initial concentrations 50 mg/L of Cd^{2+}. The pH values at the beginning and the end of experiments were measured using HANNA instruments pH meter.

To achieve the optimized amount of adsorbent in batch experiment, different amounts of chabazite (10–200 mg) were added in 10 mL of 50 mg/L cadmium solutions at room temperature and stirred for 1 h. Finally, the adsorption behavior of cadmium at different initial concentrations was studied as a function of three different temperatures including 25, 45, and 55°C.

2.5. Flow-through investigations

Column experiments were conducted for determining adsorption characteristic of cadmium ions. The experiments were carried out in glass columns, 25 mm i.d. filled with 10 g (5 cm height) of chabazite. Breakthrough experiments were performed by preparing input solution with Cd^{2+} concentration 50 mg/L after adjusting the pH to the desired value (5.5). The input solution was pumped through the column at different three flow rates including 1.3, 2, and 3 mL min^{-1}. The effluents were collected every 25 mL and analyzed as described in the previous case of batch experiments by UV-spectrophotometer (see paragraph 2.4). To study the effect of bed length, the same experiments were repeated for three different column's height 3, 5, and 10 cm using 4 mL min^{-1} as flow rate.

3. Results and discussion

3.1. Adsorbents characterization and zeolite selection

3.1.1. Characterization

The XRD analysis of the investigated zeolites was done by one of the co-author and diffractograms showed that the zeolite materials were structurally pure mordenite, clinoptilolite, and chabazite. Also, traces (<1%) of Cl, Fe, Mg, Ca, and K were found in most samples using EDX method [18,19]. The value of CEC was found to be 149.22 meq/100 g for chabazite.

Surface areas and pore size structure of natural and synthetic zeolites samples were measured and calculated using nitrogen adsorption method at 77 K. The nitrogen sorption isotherms and pore size distributions of N. chabazite, N. clinoptilolite, N. mordenite, and S. mordenite were shown in Figs. 1 and 2 and the textural properties obtained are summarized in Table 1. The nitrogen adsorption/desorption isotherms for the four zeolites samples almost show a typical type I isotherm which is indicative of porous materials with different values. The surface area and pore size distributions for the zeolites samples in this study were determined by the application of the BET and DFT; DFT equation, respectively, to the experimental nitrogen adsorption isotherm. As seen from the data, the surface area of chabazite is 73.61 m^2/g. This value is significantly higher than that reported for other samples with surface area range 16.06–21.45 m^2/g. The total surface area of N. chabazite, N. clinoptilolite, and N. mordenite is mainly due to mesopore, while the micropore surface area contributes about 67% of the total value for S. mordenite. The mesopore volume found to be higher than micropore volume for all the samples. Moreover, the distributions of the sizes of heterogeneities (volume vs. diameter) for zeolites samples were calculated using the DFT equation are presented in Fig. 2. It is shown that the local maximum of size distribution curves of N. chabazite and S. mordenite occurs at nearly same diameter (about 1.07 nm), whereas that of N. clinoptilolite and N. mordenite occurs at the diameter of around ~1.40 nm. The characterization of different zeolites samples concludes that N. chabazite is expecpted to be a promising inorganic adsorbent relative to other natural and synthetic investigated samples.

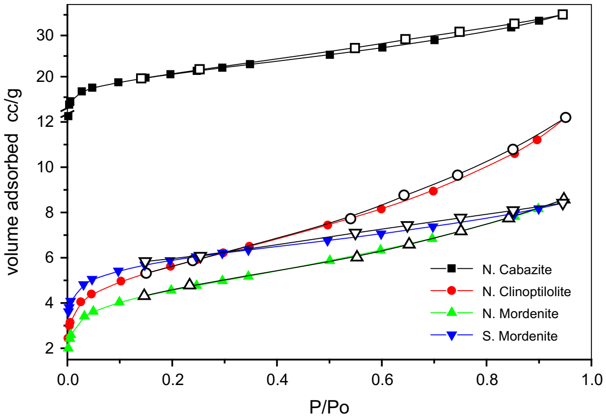

Fig. 1. N_2 adsorption/desorption isotherm at 77 K for different zeolites samples. Solid symbols: adsorption; open symbols: desorption.

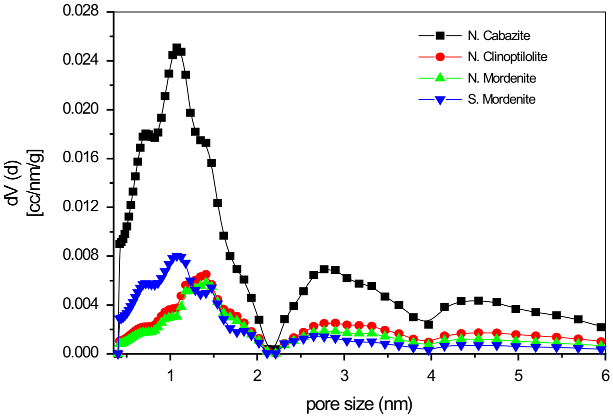

Fig. 2. Pore size distributions for zeolites samples calculated using DFT method.

3.1.2. Zeolite selection

After characterization, another experiment was conducted as an attempt to select a suitable zeolite sample from three different types as a low-cost adsorbing material for the removal of Cd^{2+} from aqueous phase. The removal efficiency of 0.1 g of each zeolite sample from 10 mL of 50 mg/L Cd(II) solution was calculated and presented for N. clinoptilolite, N. mordenite, S. mordenite, and N. chabazite in Fig. 3. From the data obtained, it was found that N. chabazite could remove 43.16% of Cd^{2+} followed by N. mordenite with uptake percent 26.32%. The removal of cadmium by N. clinoptilolite and S. mordenite was found to be very close with 22.90 and 21.05%, respectively. Among the four investigated zeolites, N. chabazite was the best in terms of removal efficiency. Based on this fact, further investigations were

Table 1
Textural parameters of natural chabazite derived from nitrogen adsorption isotherms at 77 K

	N. chabazite	N. clinoptilolite	N. mordenite	S. mordenite
BET (m^2/g)	73.61	19.63	16.06	21.45
Micropore surface area (m^2/g)	34.70	2.90	5.18	14.30
Mesopore surface area (m^2/g)	38.91	16.73	10.88	7.15
Vp (cc/g)	0.05421	0.01884	0.01327	0.01302
Micropore volume (cc/g)	0.015	0.001	0.002	0.006
Mesopore volume (cc/g)	0.03921	0.01784	0.01127	0.00702
r (nm)	1.47287	1.91973	1.65255	1.21368

Note: BET: specific surface area, *V*p: total pore volume.

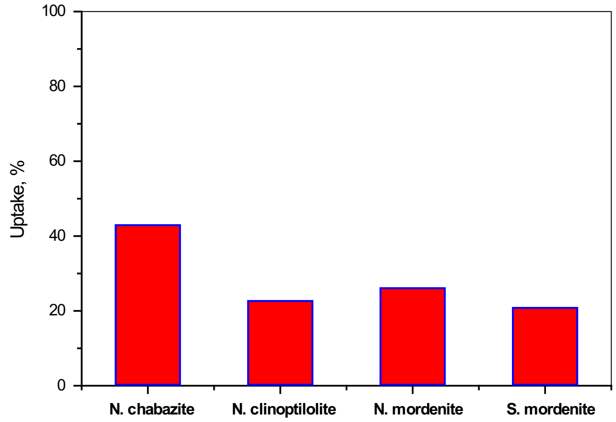

Fig. 3. The uptake of 50 mg/L Cd^{2+} by different zeolites samples using V:S ratio 1:100.

performed for N. chabazite to configure its adsorption behavior towards Cd^{2+} at different conditions. This difference can be explained considering the nature of the adsorbent.

3.2. Adsorption kinetic studies

The effects of contact time on sorption of cadmium onto chabazite are shown in Fig. 4. The amount of adsorption of Cd^{2+} rapidly increased in the early stages and increased more slowly with time, gradually approaching the equilibrium state. A contact time of 1 h is sufficient to reach equilibrium. In order to thoroughly understand the adsorption kinetics, two rate equations were applied to evaluate the adsorption of Cd^{2+} on chabazite. Pseudo-first-order and pseudo-second-order kinetic models were tested. The pseudo-first-order kinetic model is expressed as follows [20,21]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

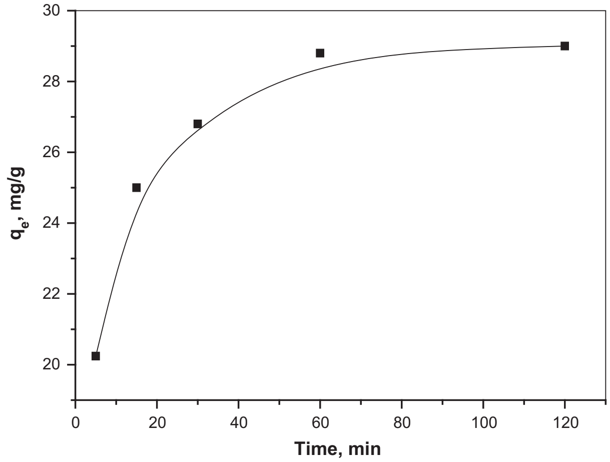

Fig. 4. Influence of the equilibrium time on the Cd(II) adsorption by chabazite.

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t, respectively. k_1 is the rate constant ($L\,min^{-1}$) of the pseudo-first-order kinetic model.

The plot of $\log(q_e - q_t)$ as a function of t provides the k_1 and q_e values (Fig. 5). As shown in Table 2, the calculated value of q_e is far lower than the experimental q_e. This discrepancy shows that the adsorption of Cd^{2+} on chabazite does not fit the pseudo-first-order kinetic model. The pseudo-second-order kinetic model can be expressed as follows [20,21]:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) \times t \tag{2}$$

where k_2 ($g\,mg^{-1}\,min^{-1}$) is the rate constant for pseudo-second-order kinetic model. The q_e and k^2 values were estimated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of the linear plot of t/q_t vs. t at different metal concentrations (Fig. 5). From the data

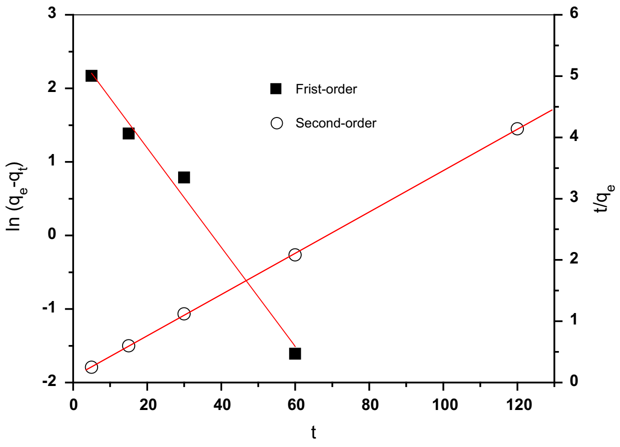

Fig. 5. Pseudo first- and second-order sorption kinetics of Cd^{2+} on natural chabazite. Conditions: initial concentration = 50 mg/L, mass = 100 mg, volume = 10 mL, pH = 5.5, Temp = 25°C.

in Table 2 the pseudo-second-order model provided high correlation coefficients of more than 0.999. Moreover, the calculated value of q_e is very close to the experimental q_e, with deviations of less than 3%. Therefore, the adsorption process is best described by a pseudo-second-order kinetic model. The overall rate of the adsorption process is most likely to be controlled by the chemisorption process [22].

3.3. Effect of pH

The pH of the solution is one of the most important parameter as it controls the sorption at the solid–solution interface. It not only influences the charges on the sorption sites of biomass type but also the speciation of metal ions [23]. So, it is very important to consider the ionic states of the functional groups of the sorbent as well as the metal solution chemistry at different pH values. A decrease in pH means there are more H^+ ions in the solution and the biomass is thus protonated. Thus, the sorption sites are occupied by H^+ ions, before metal ions can attack them. Adsorption of cadmium (II) was measured at 1 h as contact time for five different pH solutions (pH 2.5, 4.5, 5.5, 7.5, and 8.5) is shown in Fig. 6. The Cd(II) adsorption maxed at basic pH values and was negligible at acid pH values. At higher pH value (higher than pH 7), cadmium precipitated from the solutions because of the high concentrations of $(OH)^{-1}$ in the medium. At low pH values; low Cd (II) adsorption of cabazite can be explained by the fact that hydrogen ions compete effectively with metal cations for binding sites at lower pH values. At very low pH values, proton concentration in the aqueous solution increases, and consequently hinder the adsorption of metal cations. From the experimental results, it is observed that at pH 5.5 the maximum sorption capacity (38.2 mg/g) is obtained for 50 mg/L initial metal concentration 0.1 g of adsorbent (Fig. 6).

Table 2
Comparison of the pseudo first- and second-order adsorption rate constants and the calculated and experimental q_e values for Cd^{2+} on chabazite

Model	Parameter	
First-order model	$q_{e,exp}$ (mg/g)	29
	K_1 (min^{-1})	0.07
	$q_{e,cal}$ (mg/g)	12.7
	R^2	0.993
Second-order model	K_2 (g/mg min)	13×10^{-3}
	h (mg/g min)	
	$q_{e,cal}$ (mg/g)	29.8
	R^2	0.9999

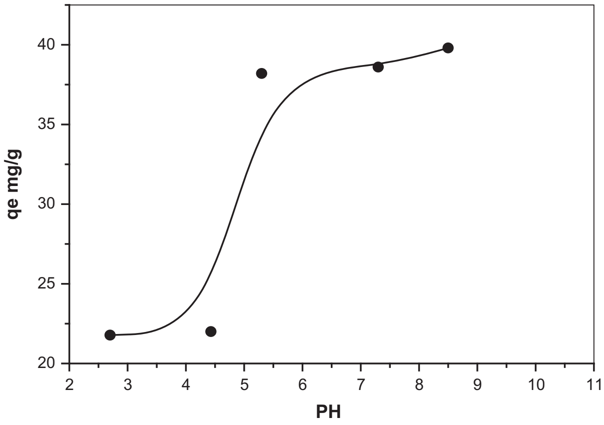

Fig. 6. Influence of the equilibrium pH on the Cd(II) adsorption by chabazite.

3.4. Adsorption isotherms

The adsorption equilibrium data were also obtained and evaluated by Langmuir and Dubinin–Radushkevich models. These isotherm equations have been used extensively to evaluate the equilibrium characteristics of adsorption processes. In the Langmuir model, a basic assumption is that the sorption occurs at specific homogeneous sites within the adsorbent, the Dubinin–Radushkevich isotherm is reported to be more general than the Langmuir isotherm. It helps to determine the apparent energy of adsorption. The characteristic porosity of adsorbent toward the adsorbate does not assume a homogenous surface or constant sorption potential [24].

Langmuir and D–R equation is given as:

$$\text{Langmuir equation: } \frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} k_l}\right)\frac{1}{C_e} \tag{3}$$

$$D\text{–}R \quad \text{equation:} \quad \ln q_e = \ln q_m - B\varepsilon^2 \tag{4}$$

where $q_{\max}$, the monolayer capacity of the adsorbent (mg/g); K_L, the Langmuir constant (L/mg) and related to the free energy of adsorption; q_m, the theoretical saturation capacity (mg/g); and ε, the Polanyi potential, which is equal to RT $\ln(1 + (1/C_e))$, where R (J/mol K) is the gas constant and T (K) is the absolute temperature; β, a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2). $q_{\max}$ and K_L, of Langmuir equation can be determined from the linear plot of $1/C_e$ vs. $1/q_e$ q_m and β of D–R equation can be determined by plotting ln q_e vs. ε^2.

The Langmuir, and D–R parameters for the adsorption of cadmium adsorption onto natural chabazite is being listed in Table 3. As it is obvious from a comparison of the correlation coefficients, R^2, the data fit well with D–R model than Langmuir model. The constant β in D–R isotherm gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [25]:

$$E = \frac{1}{\sqrt{2B}} \tag{5}$$

The sorption energy, $E = 7.5 \pm 0.12\,\text{kJ mol}^{-1}$ for cadmium ions onto natural chabazite. This value is close to the range of 8–16 kJ mol^{-1} designated for chemical adsorption mechanism [26].

Table 3
Isotherm constants for the adsorption of cadmium onto natural chabazite

Langmuir	
$q_{\max}$ (mg/g)	50
K_L (L/mg)	0.03
R^2	0.9
D–R	
q_m (mg/g)	120
β (mol^2/kJ^2)	0.009
R^2	0.98
E (kJ/mol)	7.5

3.5. Influence of adsorbent dose

Sorbent dose is an important factor which affects the sorption process. Generally, as the sorbent dose increases the sorption also increases due to availability of the sorption sites for metal ions binding. Therefore, the effect of sorbent dose on sorption of Cd^{2+} was studied and the amount of chabazite was varied from 0.03 to 0.15 g. For all these runs, initial concentration of cadmium was fixed as 100 or 50 mg/L. Fig. 7 shows that increasing the sorbent amount decrease the adsorption capacity (q_e). There are many factors, which can contribute to this adsorbent concentration effect, the *first* and most important factor is that as the dosage of adsorbent is increased, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity (q_e). The *second* cause may be the aggregation/agglomeration of sorbent particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusional path length. As a result, the removal of a given amount of solute can be accomplished with greater economy of adsorbent if the solution is treated with separate small batches of adsorbent rather than in a single batch, with filtration between each stage.

3.6. Influence of solution temperature

The reaction rate, the amount of adsorbed ion on the adsorbent and the diffusion of ions into the pores of the adsorbent are mainly controlled by the temperature [27]. As a result temperature has a direct influence on the amount of sorbed substance. Therefore, our aim was to investigate the effect of temperature on the uptake of cadmium at 25–55°C. The experimental results given in Fig. 8 indicate that the magnitude of

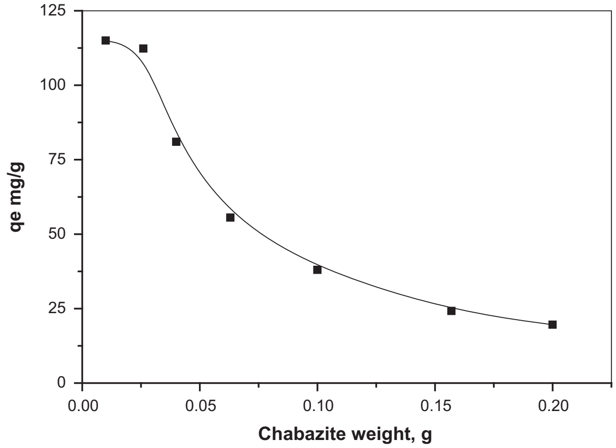

Fig. 7. Effect of chabazite adsorbent dose on cadmium ions adsorption.

adsorption is proportional to the solution temperature in adsorption of cadmium. It was found that, according to the adsorption isotherm, the amount of cadmium adsorbed on to chabazite increases with the solution temperature. The increase of cadmium capacity with respect to temperature is a direct consequence of:

1. Enlargement of pore size of the adsorbent surface or creation of some new active sites on the adsorbent surface [28,29].
2. Rapid kinetics at higher temperature due to enhanced mobility of cadmium ions from the bulk solution towards the adsorbent surface and extent of penetration within the chabazite structure [28,30].
3. Overcoming the activation energy barrier and acceleration the rate of intra-particle diffusion given the short time span of the kinetic experiments [30].

Thus, cadmium may be good adsorbed on chabazite from very weakly acid solutions(at pH $\approx$ 6) or from warmed solutions.

3.7. Sorption thermodynamics

Thermodynamic parameters are crucial for determining the spontaneity of an adsorption process. Standard Gibbs free energy changes (G°), standard enthalpy changes (H°), and standard entropy changes (S°) are associated with the sorption process.

These parameters can be calculated from the following equations [31]:

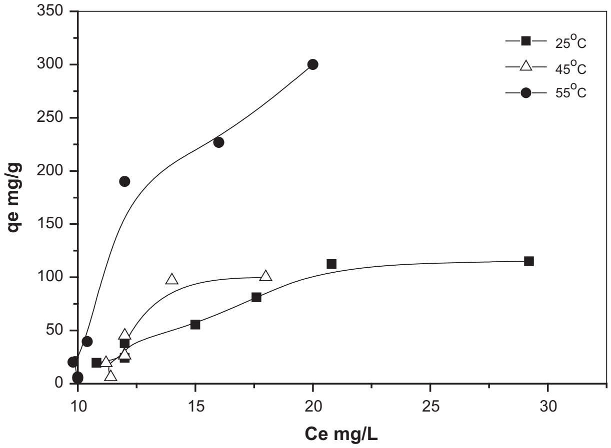

Fig. 8. Influence of solutions temperature on the Cd(II) adsorption by chabazite.

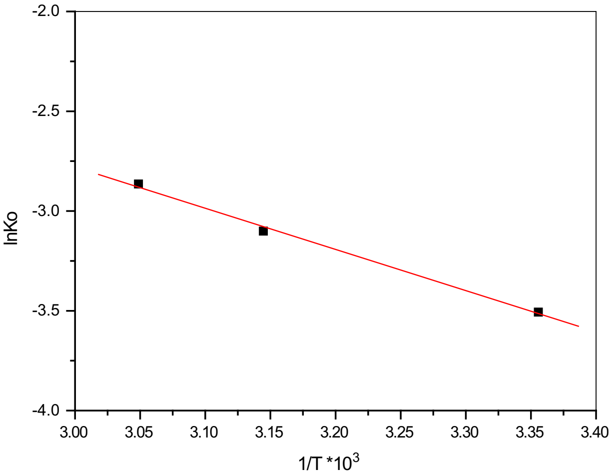

Fig. 9. Plot of ln K vs. $1/T$ for estimation of thermodynamic parameters.

$$\mathrm{In}K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

where k is the equilibrium constant calculated by dividing the equilibrium concentration of metal ion on the adsorbent (C_s) by the equilibrium concentration of metal ion in the solution (C_e). R is the universal gas constant (8.314 J mol−1 K−1), and T is the absolute temperature. The values of S° and H° are obtained from the slope and intercept by plotting ln$k$ vs. $1/T$ (Fig. 9). The thermodynamic parameters are listed in Table 4. The negative G° values suggesting that adsorption of Cd(II) by chabazite is spontaneous. The value G° increases with increasing temperature suggesting the feasibility and the spontaneous nature of adsorption process at high temperature. The positive value of H° reflects that the sorption is endothermic in nature. H° values are greater than 10 kJ/mol. This indicates that sorption of cadmium on chabzite under investigation is chemical in nature. The positive value of entropy changes S° show the increased randomness at the solid/solution interface during the adsorption of cadmium ion onto chabazite which suggests cadmium ions replace some water molecules from the

Table 4
Thermodynamic parameters of Cd(II) adsorption by chabazite

ΔH° (kJ/mol)	ΔS° (J/mol k)	ΔG^o (kJ/mol)		
		298 K	318 K	328 K
17.0	28.3	−8.4	−9.0	−9.3

solution, previously adsorbed on the surface of chabazite. These displaced molecules gain more translation entropy than is lost by the absorbate ions resulted in the creation of steric hindrance, thus allowing the prevalence of randomness in the system. The results indicate that the adsorption capacity increases with increasing temperature; therefore, higher temperature is favorable to the adsorption.

3.8. Column experiment

3.8.1. Effect of bed depth

Fig. 10 shows the cadmium breakthrough plots at different bed depths (*L*) of 3, 5, and 10 cm. Fixed bed column parameters of cadmium adsorption on natural chabazite are given in Table 5. The breakthrough point was taken at $C_t/C_o = 0.05$. As the amount of chabazite (column depth) increases, the service time increases and breakthrough curve becomes gentler (i. e. slope decreases). The breakthrough volume values are $V_b = 100$ mL at $L = 3$ cm, $V_b = 150$ mL at $L = 5$ cm, and $V_b = 430$ mL at $L = 10$ cm and consequently the breakthrough time increase with bed depth. This can be explained by the fact that when the bed depth is increased, the number of sorption sites is also increased. Thus, a larger bed depth will take a longer time to become saturated with a similar amount of cadmium ions at constant flow and concentration conditions [32]. In other words, as the bed depth increases, the residence time of the fluid inside the column increases, allowing the adsorbate molecules to diffuse deeper inside the adsorbent [33]. This effect of column depth on breakthrough curve indicate that intra-particle diffusion may be considered as a rate-limiting step in the sorption process of cadmium on chabazite [34].

Table 5
Parameters in fixed-bed column for cadmium adsorption by natural chabazite

Flow rate (mL/min)	Bed depths (cm)	Breakthrough volume (mL)
4	10	430
4	5	150
4	3	100
3	5	40
2	5	130
1.3	5	170

3.8.2. Effect of flow rate

Fig. 11 shows the cadmium column removal with chabazite bead depth 5.0 cm, at different flow rates (*Q*) of 1.3, 2, and 4 mL/min at 50 mg/L influent cadmium concentration. As indicated, at he lowest flow rate of 1.3 mL/min, the highest treated cadmium solution volume was observed. Much sharper breakthrough curves were obtained by chabazite at higher flow rates (3 mL/min). The breakpoint volume decreased with increasing flow rate ($v_b = 40$ mL at flow rate 3 mL/min and $v_b = 130$ mL at flow rate 2 mL/min). This behavior can be explained on the basis that cadmium sorption by chabazite is affected by (i) insufficient residence time of solute in the column, (ii) the diffusion of the solute into the pores of sorbent, (iii) limited number of active sites and (iv)

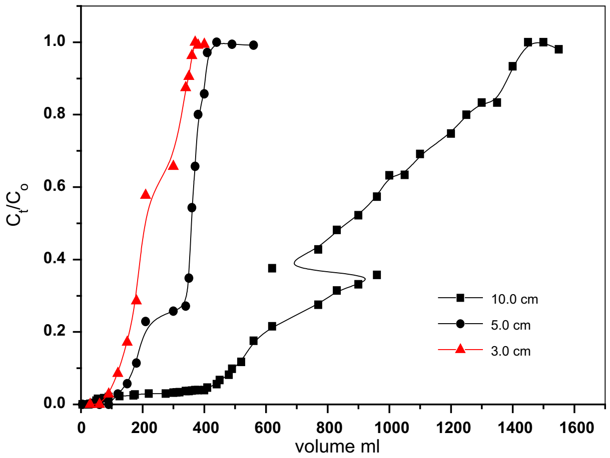

Fig. 10. Experimental breakthrough curves of cadmium at different bed depths, *L* (3, 5, 10 cm) with respect to volume treated (mL). Conditions: $C_o = 50$ mg/L and $Q = 4$ mL/min.

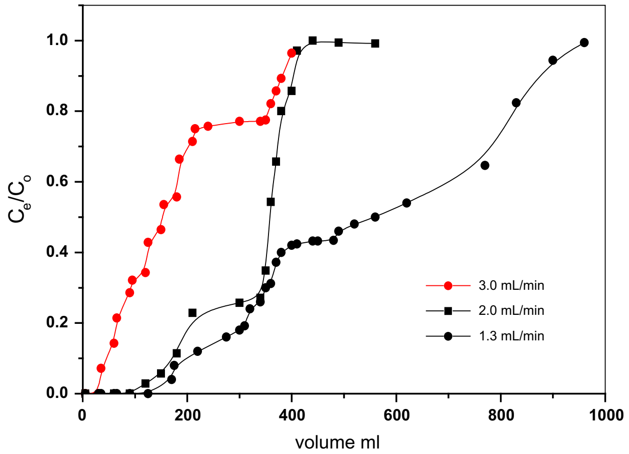

Fig. 11. Experimental breakthrough curves of cadmium at different flow rates, *Q* (1.3, 2, 4 mL/min) with respect to volume (mL). Conditions: Co = 50 mg/L mg/L and *L* = 5 cm.

ionic groups of biomass for sorption in the matrix [35]. If the residence time of the solute in the column is not long enough for adsorption equlibrium to be reached at that flow rate, the cadmium ion solution leaves the column before equilibrium occurs. Thus, at higher flow rate the contact time of cadmium with chabazite is very short, and adsorption equilibrium is not reached, so cadmium ions leave the column before equilibrium occurs causing a reduction in its removal efficiency [36].

4. Conclusion

This study provided valuable information about the sorption behaviour of chabazite, and their efficiency to reduce cadmium mobility and availability. N. chabazite shows high surface area and mesopore volume. As a result, sorption performance of N. chabazite for cadmium ions was generally superior to that of other natural and synthetic investigated zeolites. Adsorption of Cd is found to be effective in the higher pH range and higher temperatures. In addition, the fast Cd adsorption onto chabazite makes this material suitable for continuous flow water treatment systems. Pseudo-second-order adsorption mechanism is predominant which suggest the chemisorption to control the adsorption process. The equilibrium data were satisfied by Dubinin–Radushkevich isotherm and the related parameters were indicated for ion exchange mechanism. The results show a feasible, spontaneous, and exothermic adsorption process. Fixed bed column sorption studies have shown that cadmium ion removal was a strong function of initial flow rate and bed height. Increase in bed height and decreased flow rate lead to higher contact time, thus higher effluent volume. These reported results showed that chabazite is an efficient ion exchange material for the removal of cadmium ions from aqueous and wastewater solutions.

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