

Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A

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Abstract

The sorptive removal of zinc and cadmium ions from aqueous solutions using synthetic zeolite A was investigated. Experiments were carried out as a function of solute concentration and temperature (298–333 K). Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the sorption process. Various parameters such as effective diffusion coefficient, activation energy and entropy of activation were evaluated. Equilibrium sorption data were analyzed using Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Of the model tested, both Freundlich and D–R isotherm expressions were found to give better fit to the experimental equilibrium data compared to Langmuir model. The mean free energy is in all cases in the range corresponding to the ion exchange type of sorption. The results indicated that synthetic zeolite A can be used as an efficient ion exchange material for the removal of zinc and cadmium ions from industrial and radioactive wastewaters.

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1. Introduction

The presence of heavy metals in the aquatic ecosystem has been of increasing concern because of their toxic properties and other adverse effects on natural waters quality [1]. Elevated environmental levels of zinc and cadmium ions come from a variety of sources. Cadmium finds its way to water bodies through wastewater from metal plating industries, cadmium–nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [2]. On the other hand, waste containing zinc and its compounds arise from many industrial processes, such as acrylic fiber, rayon, cellophane, and special synthetic rubber [3]. Moreover, the national cyclotron at Inshas site produces ⁶⁷Ga and ¹¹¹In isotopes from irradiation of metallic zinc and cadmium by accelerated protons [4]. The waste arising during the production process contains considerable amounts of zinc

and cadmium and it was of interest to investigate an efficient removal technique for these ions from produced waste.

Various treatment technologies have been developed for the purification of water and wastewater contaminated by heavy metals. The most commonly used methods for the removal of metal ions from industrial effluents include: chemical precipitation, solvent extraction, reverse osmosis, ultra filtration, adsorption and ion exchange [5]. Heavy metals ion exchange is certainly an attractive option because of the basic simplicity of the application. Synthetic aluminosilicate zeolites act as efficient porous exchange media and its cation exchange is widely used in nuclear industry, agriculture, laundry detergent industry, and environmental protection [6–13]. The potential applications of zeolites and other selective ion exchangers have been well documented by Dyer [14]. The objective of this study is to investigate the applicability of synthetic zeolite A as an adsorbent material for the removal of zinc and cadmium ions from aqueous solutions and to examine the kinetics of sorption and other parameters involved.

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2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were of AR grade. Silica (Aerosil 200, Degussa), sodium aluminate (Riedel-De Haen AG), and sodium hydroxide (Merck) were used as silicon, aluminium and sodium sources in zeolite A synthesis mixture, respectively. Both of zinc chloride and cadmium chloride were BDH products.

2.2. Zeolite A preparation and characterization

Zeolite A was synthesized in its sodium form from mixture consisting of sodium aluminosilicate substrate contacted with sodium hydroxide. In 1 L polypropylene bottle supplied with a magnetic stirrer, 7.88 g SiO₂ and 104.63 g H₂O was mixed. Then, 10.5 g NaOH was added and exactly 22.8 g NaAlO₂ was also added drop wise for about 2 h. The resultant product was aged over night at 353 K for completion of the reaction. The inorganic amorphous product was collected on Buchner funnel, washed with 3 L of distilled water for removal of unreacted species and partially dried.

The crystallinity, morphology as well as chemical composition of the prepared material were measured using X-ray diffraction (XRD), X-ray fluorescence (XRF), differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and scanning microscope. The results have been presented elsewhere [15]. Based on these results, the oxide chemical composition of the synthetic zeolite A can be expressed via the formula: Na₂O·Al₂O₃·1.85SiO₂·5.1H₂O. The theoretical cation exchange capacity (CEC) of synthetic zeolite A in Na⁺ form equals 5.45 meq/g as calculated from the chemical formula. The quantitative elemental analysis indicated that the Si/Al ratio was about 0.82, which is in the characteristic range of zeolite A [13]. The BET surface area of the solid powder, measured after the thermal treatment for 2 h at 473 K, was 634.52 m²/g.

2.3. Kinetic measurements

Kinetic studies were investigated by taking 100 mg of synthetic zeolite A in 100 ml of aqueous solution containing known concentration of metal ion (500 mg/l for each metal ion). The solution in the beaker was kept stirred in a thermostat shaker adjusted at the desired temperature. A fixed volume (2 ml) of the aliquot was withdrawn as a function of time while the solution was being continuously stirred. Thus, the ratio of the volume of solution to the weight of adsorbent in the beaker does not change from the original ratio. The withdrawn solution was centrifuged to separate the adsorbent and a fixed volume (1 ml) of the clear solution was pipetted out for the determination of the amount of unadsorbed metal ion still present in solution. The measurements were carried out using atomic absorption spectrophotometer (Buck scientific

model VGP 210). Temperature was adjusted over the range 298–333 K.

2.4. Sorption isotherms

Batch sorption studies of zinc and cadmium ions were performed at different temperatures (298, 313 and 333 K) to obtain the equilibrium isotherms. For isotherm studies, a series of 50 ml test tubes were employed. Each test tube was filled with 25 ml of each metal ion solution of varying concentrations (100–2000 mg/l) and a known amount of prepared zeolite A (25 mg) was added into each test tube and agitated for a sufficiently long time (~3 h) required to reach equilibrium. The amount of metal ion retained in the zeolite phase, q_e (mmol/g), was calculated using:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mmol/l) of metal ion in solution, V is the volume (l) and m the weight (g) of the adsorbent.

3. Results and discussion

3.1. Kinetic studies

Preliminary investigations on the rate of uptake of both zinc and cadmium ions onto prepared zeolite A indicated that the processes are quite rapid and typically 60–70% of the ultimate sorption of each ion occurs within the first 20 min of contact. The initial rapid sorption subsequently gives way to a slow approach to equilibrium, and saturation is reached in about 45 min. The amounts of both zinc and cadmium ions sorbed after each interval time, for a fixed concentration of 500 mg/l and at different studied temperatures, are plotted in Fig. 1. The data showed that the amount of Zn²⁺ and Cd²⁺ sorbed at equilibrium increase with increase in temperature indicating an endothermic nature of the process and the time required to reach saturation remained practically unaffected.

It is well recognized that the characteristic of sorbent surface is a critical factor that affects the sorption rate parameters and that diffusion resistance plays an important role in the over all transport of the solute. To describe the changes in the sorption of studied ions with time, several kinetic models were tested. The rate constant of each metal ion removal from the solution by zeolite A was determined using pseudo-first-order and pseudo-second-order rate models. The Lagergren first-order rate expression [16] is written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e and q_t are the amounts of metal ion sorbed onto zeolite A at equilibrium and at time t (mmol/g), respectively, and k_1 is the rate constant of first-order adsorption (min⁻¹). The slopes and intercept of the linear plots of $\log(q_e - q_t)$

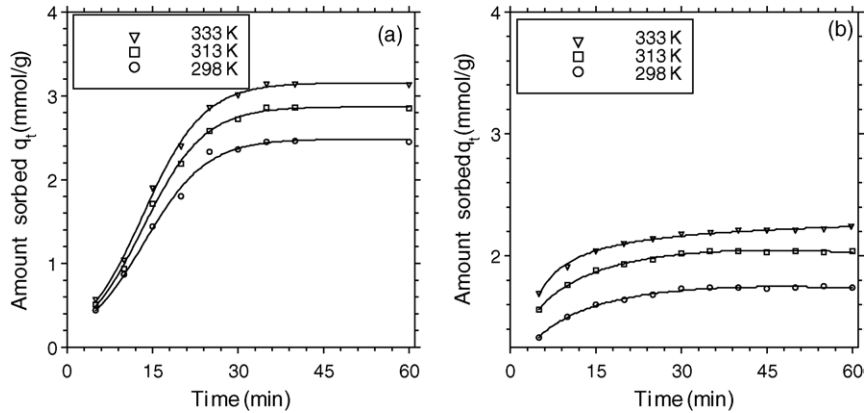


Fig. 1. Effect of contact time on the amount sorbed of (a) Zn²⁺ and (b) Cd²⁺ from aqueous solutions onto zeolite A.

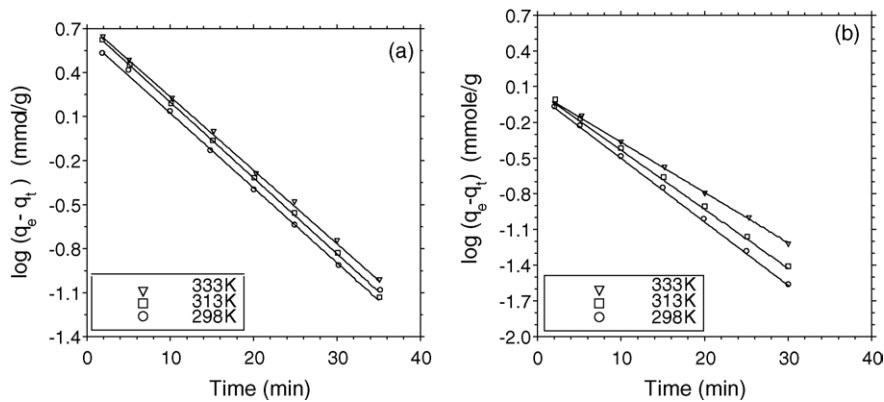


Fig. 2. Lagergren plots for the sorption of (a) Zn²⁺ and (b) Cd²⁺ ions from aqueous solutions onto zeolite A.

versus *t*, as shown in Fig. 2, were used to determine the first-order rate constant *k*₁. It was observed that the sorption of both ions followed the Lagergren equation over the entire range of shaking time explored and the values of the first order rate constants did not change with temperature as reported in Table 1. In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the sorption processes [17].

The pseudo-second-order rate model [18] is expressed as:

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

where *k*₂ (g/mmol min) is the rate constant of second-order kinetic model.

Table 1
Pseudo-first-order rate constants of Lagergren plots for Zn²⁺ and Cd²⁺ ions sorbed onto zeolite A

Temperature (K)	<i>k</i> ₁ (min ⁻¹)		<i>R</i> ²	
	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺
298	0.115	0.097	0.947	0.942
313	0.118	0.114	0.927	0.946
333	0.119	0.123	0.941	0.936

The kinetic plots of *t/q_t* versus *t* for Zn²⁺ and Cd²⁺ removal at different temperatures are presented in Fig. 3. The relationship is linear, and the correlation coefficient (*R*²), suggests a strong relationship between the parameters and also explains that the process of sorption of each ion follows pseudo-second-order kinetics. The product *k*₂*q_e*² is the initial sorption rate represented as *h* = *k*₂*q_e*². From Table 2, it can be shown that the values of the initial sorption rate ‘*h*’ and rate constant ‘*k*₂’ were increased with increase in temperature. The correlation coefficient *R*² has an extremely high value (>0.99), and its calculated equilibrium sorption capacity ‘*q_e*’ is consistent with the experimental data. These results suggest that the pseudo second order sorption mechanism is predominant and that the over all rate constant of each ion appears to be controlled by the chemisorption process [17,18].

Other simplified models are also tested because of the above two equations cannot give definite mechanism. It is also known that at an intensive stirring of the sorptive system, the intraparticle diffusion of the solute sorbed from the solution into the sorbent pores could be a limiting step. In this study, two models namely those of Weber and Morris model [19] and that suggested by Helfferich [20] were also used. The Morris–Weber equation is written as:

$$q_t = K_{ad} t^{1/2} \tag{4}$$

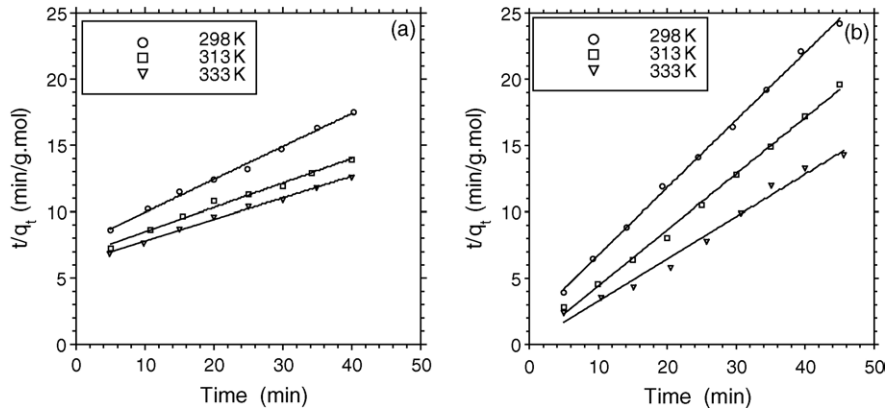


Fig. 3. Pseudo-second-order kinetic plots for the sorption of (a) Zn^{2+} and (b) Cd^{2+} ions from aqueous solutions onto zeolite A.

Table 2

The calculated parameters of the pseudo-second-order kinetic models

Temperature (K)	q_e (mmol/g)		h (mmol/g min)		k_2 (g/mmol min)		R^2	
	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}
298	4.027	1.965	0.134	0.603	0.0083	0.156	0.993	0.998
313	5.440	2.367	0.275	5.210	0.0093	0.931	0.991	0.996
333	6.157	3.142	0.397	10.930	0.0105	1.107	0.995	0.993

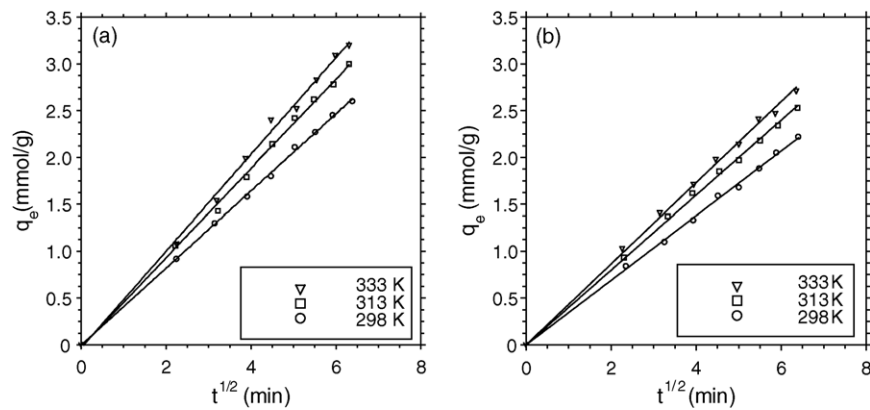


Fig. 4. Morris–Weber kinetic plots for the sorption of (a) Zn^{2+} and (b) Cd^{2+} ions from aqueous solutions onto zeolite A.

where K_{ad} is the rate constant of intraparticle transport ($\text{mmol/g min}^{1/2}$).

According to this model, plotting a graphic of q_t versus $t^{1/2}$, if a straight line passing through the origin is obtained, it can be assumed that the involved mechanism is a diffusion of the species. In this case the slope of the linear plot is the rate constant of intraparticle transport. As can be seen in Fig. 4, for times up to 30 min, the Morris–Weber relationship holds good and the values of K_{ad} were calculated, from the slope of the linear plots obtained, and presented in Table 3.

Kinetic data were also analyzed by the procedure given by Helfferich [20]. Various parameters were calculated using the following equations as given by Boyd et al. [21].

$$F = 1 - \left(\frac{6}{\pi^2} \right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp \left[\frac{-D_i t \pi^2 n^2}{r_0^2} \right] \quad (5)$$

$$F = 1 - \left(\frac{6}{\pi^2} \right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp [-n^2 B t] \quad (6)$$

$$B = \frac{\pi^2 D_i}{r_0^2} \quad (7)$$

Table 3

Intraparticle diffusion rate constant for the sorption of Zn^{2+} and Cd^{2+} onto zeolite A

Temperature (K)	K_{ad} (mmol/g $\text{min}^{1/2}$)		R^2	
	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}
298	0.406	0.344	0.999	0.979
313	0.471	0.400	0.993	0.987
333	0.510	0.433	0.998	0.969

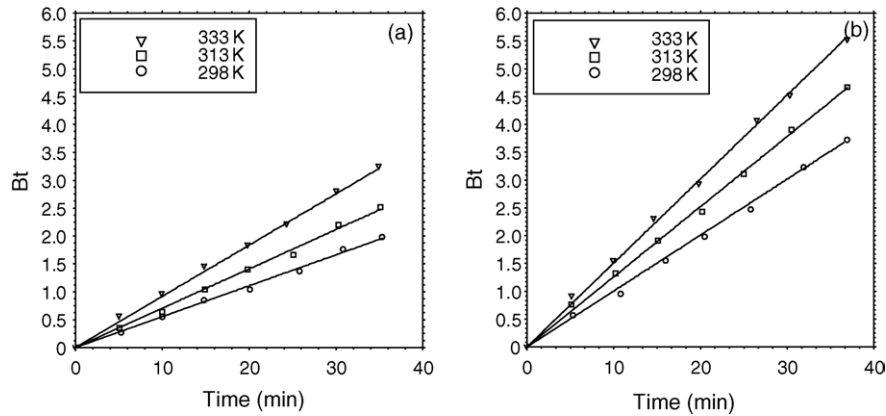


Fig. 5. Plots of Bt as a function of time for the diffusion of (a) Zn^{2+} and (b) Cd^{2+} ions from aqueous solutions onto zeolite A.

Table 4
Diffusion and thermodynamic parameters for the sorption of Zn^{2+} and Cd^{2+} onto zeolite A

Metal ion	$D_i \times 10^{12} \text{ (m}^2\text{/s}^{-1}\text{)}$			$D_0 \times 10^7 \text{ (m}^2\text{/s)}$	$E_a \text{ (kJ/mol)}$	$\Delta S^\ddagger \text{ (J/mol K)}$	$\Delta H^\ddagger \text{ (kJ/mol)}$	$\Delta G^\ddagger \text{ (kJ/mol)}$
	298 K	313 K	333 K					
Zn^{2+}	1.83	2.34	3.05	1.06	9.97	-107.21	7.50	39.45
Cd^{2+}	3.35	4.18	5.00	0.67	8.85	-111.06	6.37	39.46

where F is the fractional attainment of equilibrium at time t ($F = q_t/q_e$), B the time constant, D_i the effective diffusion coefficient of metal ion, r_0 the radius of the solid particle, and n integers 1, 2, 3, ...

Bt values as derived from Eq. (6) for the observed values of F were obtained from Reichenberg's table [22]. The linearity test of Bt versus time plots is employed to distinguish the film and particle diffusion-controlled rates of sorption process. If the plot is a straight line passing through the origin, then the sorption rate is governed by particle diffusion mechanism otherwise it is governed by film diffusion. Fig. 5 depicts the Bt versus time plots for Zn^{2+} and Cd^{2+} at different temperatures. The plots are linear and pass through the origin for both metal ions, indicating the sorption process to be particle diffusion at all studied temperatures. The values of D_i calculated at different studied temperatures for both ions are presented in Table 4.

Plotting of $\ln D_i$ versus $1/T$ gave a straight line, as shown in Fig. 6, proves the validity of the linear form of Arrhenius equation:

$$\ln D_i = \ln D_0 - \frac{E_a}{RT} \quad (8)$$

where D_0 is a pre-exponential constant analogous to Arrhenius frequency factor.

The energies of activation for both ions, E_a , were calculated from the slope of the straight lines in Fig. 6 and the obtained values were presented in Table 4. Such a low value of the activation energy for the sorption of each metal ion indicates a chemical sorption process involving weak interaction between sorbent (zeolite A) and sorbate (Zn^{2+} and/or Cd^{2+}) and suggest that each sorption process has a low potential energy.

The Arrhenius equation would be also used to calculate D_0 , which in turn is used for the calculation of entropy of activation, ΔS^\ddagger , of the sorption process using [23]:

$$D_0 = \frac{2.72d^2KT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (9)$$

where K is the Boltzmann constant, h the Plank constant, d the distance between two adjacent active sites in the solid matrix, R the gas constant, and T the absolute temperature. Assuming that the value of d is equal to 5×10^{-8} cm [23], the values of ΔS^\ddagger for both ions were calculated and presented in Table 4. The negative values of entropy of activation obtained for the sorption of both metal ions normally reflect that no significant

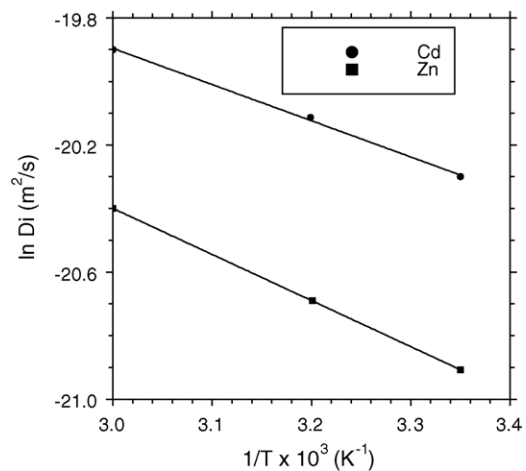


Fig. 6. Arrhenius plot for the sorption of Zn^{2+} and Cd^{2+} ions from aqueous solutions onto zeolite A.

Table 5
Kinetic parameters and normalized standard deviations for the sorption of Zn²⁺ and Cd²⁺ onto zeolite A

Kinetic constants	Zn ²⁺			Cd ²⁺		
	298 K	313 K	333 K	298 K	313 K	333 K
Pseudo-first-order rate model						
K_1 (min ⁻¹)	0.115	0.118	0.119	0.097	0.114	0.123
R^2	0.947	0.927	0.941	0.942	0.946	0.936
Δq (%)	20.4	29.6	23.1	18.1	16.4	16.8
Pseudo-second-order model						
k_2 (g/gmmol min)	0.0083	0.0093	0.0105	0.156	0.931	1.107
R^2	0.993	0.991	0.995	0.998	0.996	0.993
Δq (%)	14.9	11.5	9.4	12.19	10.87	9.88
Helfferich model						
$D_i \times 10^{12}$ (m ² /s)	1.83	2.34	3.05	3.35	4.18	5.00
R^2	0.993	0.995	0.987	0.962	0.993	0.991
Δq (%)	7.9	5.4	2.5	2.3	1.6	4.2
Morris–Weber rate model						
K_d (mmol/g min ^{1/2})	0.406	0.471	0.510	0.344	0.400	0.433
R^2	0.999	0.993	0.998	0.979	0.987	0.969
Δq (%)	9.32	7.81	5.61	4.69	6.44	7.53

change occurs in the internal structure of the zeolite solid matrix during the sorption of ions [23].

The Gibbs free energy of activation, ΔG^\ddagger , was calculated from the well-known equation [24]:

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger = E_a - RT - T \Delta S^\ddagger \quad (10)$$

where ΔH^\ddagger is the enthalpy of activation.

The estimated values of ΔH^\ddagger and ΔG^\ddagger were presented in Table 4. The positive ΔG^\ddagger values suggest the existence of an energy barrier and that the reaction is non-spontaneous process [24]. The positive values of ΔH^\ddagger indicate the endothermic nature for the diffusion process.

In order to compare the validity of each model more efficiently, a normalized standard deviation, Δq is calculated using the following equation [25]:

$$\Delta q (\%) = 100 \times \sqrt{\frac{\sum [(q_t^{\text{exp}} - q_t^{\text{calc}})/q_t^{\text{exp}}]^2}{n - 1}} \quad (11)$$

where the superscripts ‘exp’ and ‘calc’ are the experimental and calculated values and n is the number of measurements. Based on the Δq values, as given in Table 5, the removal of both Zn²⁺ and Cd²⁺ from aqueous solutions using zeolite A can be best described by the intraparticle diffusion model given by Helfferich. A good correlation of the rate data in this model can justify the mechanism. Previous workers [26–28] in this direction reported diffusion coefficient ‘ D_i ’ values in the range of 10⁻¹² to 10⁻¹³ m²/s for intraparticle diffusion to be the rate limiting step for the sorption of metal ions. As per this, the rate-limiting step appears to be particle diffusion since the D_i values are in the order of 10⁻¹² m²/s. The increase in values of the kinetic parameters with increasing temperature is mainly due to (i) the increase of the mobility of the ion and a decrease in retarding forces acting on the diffusing ion; and (ii) a consequence of the effective size of ion caused both by a decrease of the ion hydration shell and a reduction of the limitation for diffusion in the inner part of the

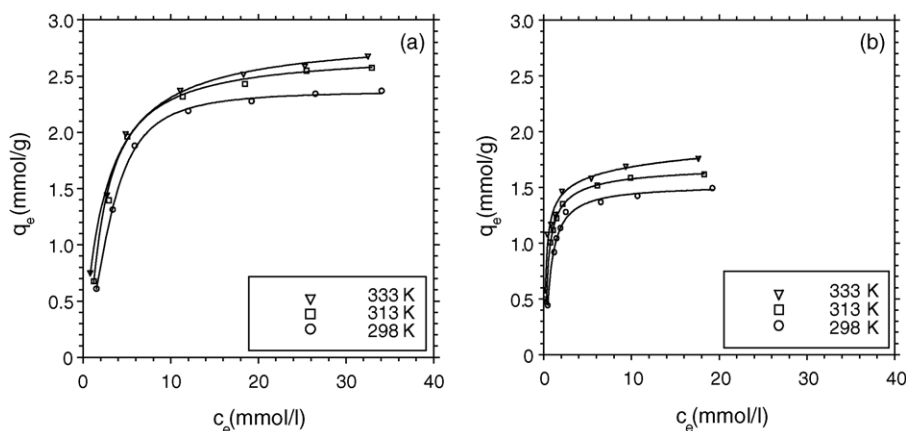


Fig. 7. Effect of temperature on the sorption isotherm of (a) Zn²⁺ and (b) Cd²⁺ onto zeolite A.

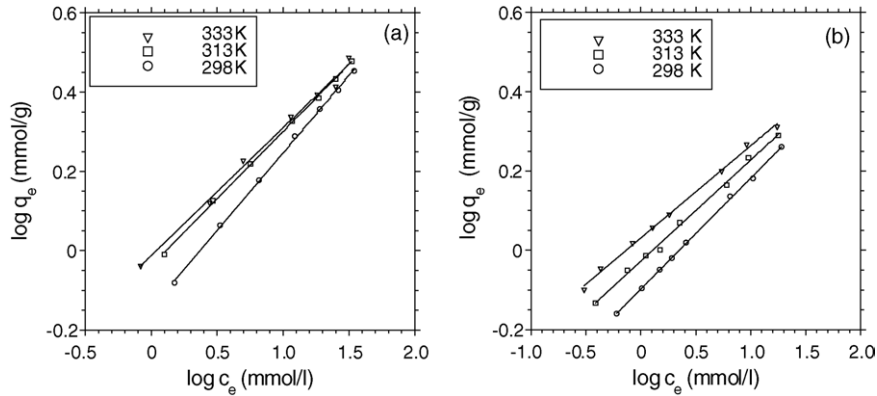


Fig. 8. Freundlich isotherm plots for the sorption of (a) Zn^{2+} and (b) Cd^{2+} ions from aqueous solutions onto zeolite A.

pore system arising from a decrease in the effective radius [29].

3.2. Sorption isotherms

The sorption isotherms for the removal of Zn^{2+} and Cd^{2+} from aqueous solutions onto zeolite A at three different temperatures are shown in Fig. 7. The isotherms are regular, positive, and concave to the concentration axis. The initial rapid sorption gives way to a slow approach to equilibrium at higher ion concentrations. These results reflect the efficiency of synthetic zeolite A for the removal of both ions from aqueous solution in a wide range of concentrations. The uptake of ions increased with the increase in temperature thereby indicating the process to be endothermic.

The sorption studies were carried out at 298, 313 and 333 K to determine the sorption isotherms. The isotherm parameters were evaluated using Langmuir and Freundlich isotherm models. The Langmuir isotherm equation could be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (12)$$

where q_e is the amount of solute sorbed per unit weight of adsorbent (mmol/g), C_e the equilibrium concentration of the

solute in the equilibrium solution (mmol/l), Q^0 the monolayer adsorption capacity (mmol/g) and b the constant related to the free energy of adsorption ($b \propto e^{-\Delta G/RT}$). Also, the logarithmic form of Freundlich equation may be written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (13)$$

where K_f is a constant indicative of the relative adsorption capacity of the adsorbent (mmol/g) and $1/n$ the constant indicative of the intensity of the sorption process. The Langmuir and Freundlich isotherms for the sorption of the two metal ions on the prepared zeolite material are presented in Figs. 8 and 9, respectively. The straight lines obtained for the two-sorption isotherms indicate that the sorption of both ions fit with the two investigated isotherm models. The corresponding Langmuir and Freundlich parameters along with correlation coefficients are given in Tables 6 and 7, respectively. The slope of the Freundlich isotherm for all cases is less than one, indicating a concentration-dependent sorption for both studied ions onto zeolite A. Also, The monolayer sorption capacity (Q^0) for zinc ion was found to be relatively higher than that of cadmium ion. The Langmuir constants Q^0 and b increased with temperature showing that the sorption capacity and intensity of sorption are enhanced at higher temperatures. This increase in sorption capacity with temperature

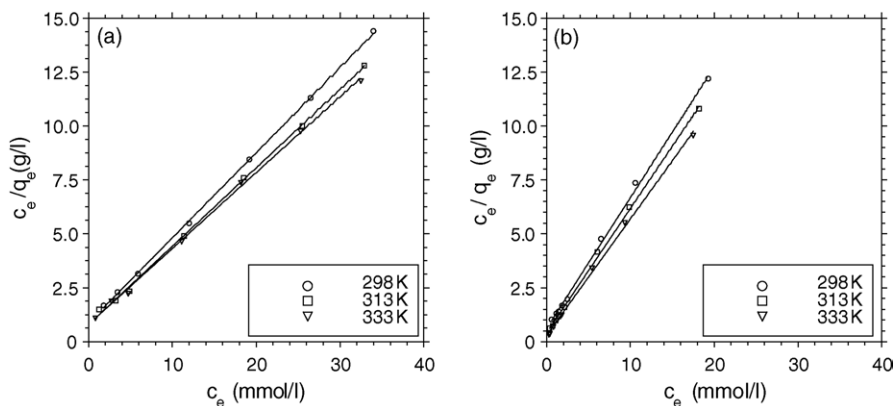


Fig. 9. Langmuir isotherm plots for the sorption of (a) Zn^{2+} and (b) Cd^{2+} ions from aqueous solutions onto zeolite A.

Table 6
Langmuir isotherm parameters of Zn²⁺ and Cd²⁺ sorbed onto zeolite A

Temperature (K)	Q ₀ (mmol/g)		B × 10 ⁻³ l/mol		R ²		Δq (%)	
	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺
298	2.53	1.65	0.455	0.991	0.999	0.996	12.1	15.7
313	2.75	1.73	0.462	1.442	0.998	0.998	24.1	20.7
333	2.84	1.85	0.471	1.873	0.999	0.998	22.4	21.2

Table 7
Freundlich isotherm parameters of Zn²⁺ and Cd²⁺ sorbed onto zeolite A

Temperature (K)	1/n		K _F (mmol/g)		R ²		Δq (%)	
	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺	Zn ²⁺	Cd ²⁺
298	0.391	0.280	0.717	0.810	0.999	0.999	2.6	1.1
313	0.338	0.255	0.916	0.990	0.989	0.996	0.5	1.6
333	0.322	0.233	0.972	1.080	0.999	0.997	0.7	0.7

suggested that the active surfaces available for sorption have increased with temperature. Another reason may be due to the change in pore size and enhanced rate of intraparticle diffusion of solute, as diffusion is an endothermic process [23].

Although the Freundlich and Langmuir constants K_F and Q^0 have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and Q^0 is that Langmuir isotherm assumes sorption free energy independent of both the surface coverage and the formation of monolayer, whereas the solid surface reaches saturation while the Freundlich isotherm does not predict saturation of the solid surface by the sorbate, and therefore, the surface coverage being mathematically unlimited. In conclusion, Q^0 is the monolayer sorption capacity while K_F is the relative sorption capacity or sorption power [23].

The sorption equilibrium data were also tested for another isotherm model, Dubinin–Radushkevich (D–R). The D–R equation has the following linear form [30]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (14)$$

where q_m is the maximum amount of ion that can be sorbed onto unit weight of zeolite A, i.e., sorption capacity (mmol/g),

β the constant related to the sorption energy (mol²/kJ²); and ε the Polanyi potential = $RT \ln(1 + 1/C_e)$, where R the gas constant (kJ/mol K), and T the absolute temperature (K).

The mean free energy of sorption is the free energy change when one mole of ion is transferred to the surface of the solid from infinity in the solution, and it is calculated from:

$$E = (-2\beta)^{-1/2} \quad (15)$$

The magnitude of E can be related to the reaction mechanism. If E is in the range of 8–16 kJ/mol, sorption is governed by ion exchange [20]. In the case of $E < 8$ kJ/mol, physical forces may affect the sorption mechanism.

The D–R plots of $\ln q_e$ versus ε^2 for both ions at different temperatures are given in Fig. 10. These linear plots indicate that the D–R isotherm expression is followed for each metal ion. Linear regression analysis using paired of $\ln q_e$ and ε^2 resulted in the derivation of q_m , β , E and the correlation factor (R^2). The correlation factor is a statistical measure of how well the data points fit the regression line. These D–R parameters, evaluated for sorption of both ions at different temperatures, are presented in Table 8. The values of E obtained through regression and from the slopes of the D–R plots are approximately similar. The maximum

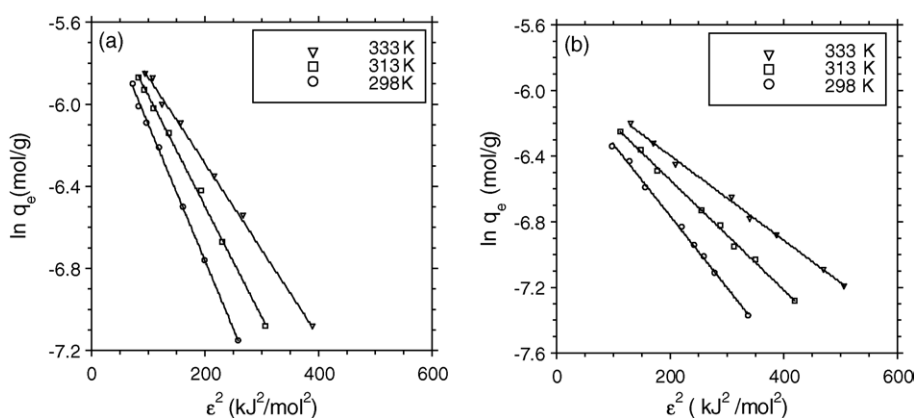


Fig. 10. D–R isotherm plots for the sorption of (a) Zn²⁺ and (b) Cd²⁺ ions from aqueous solutions onto zeolite A.

Table 8
D–R isotherm parameters of Zn²⁺ and Cd²⁺ sorbed onto zeolite A

Metal ion	Temperature (K)	B (mol ² /kJ ²)	$[q_e]_m$ (mmol/g)	(r)	E (kJ/mol)		Δq (%)
					Regression	Graphical	
Zn ²⁺	298	−0.00683	4.306	0.985	9.15	8.55	1.35
	313	−0.00541	4.445	0.997	10.05	9.62	4.14
	333	−0.00421	4.484	0.995	11.25	10.41	3.98
Cd ²⁺	298	−0.00436	2.761	0.997	10.95	10.71	2.84
	313	−0.00334	2.795	0.997	12.35	12.22	2.92
	333	−0.00258	2.805	0.998	13.95	13.91	2.31

Table 9
Isotherm constants and normalized standard deviation for the sorption of Zn²⁺ and Cd²⁺ onto zeolite A

Isotherm constant	Zn ²⁺			Cd ²⁺		
	298 K	313 K	333 K	298 K	313 K	333 K
Langmuir						
Q^0 (mmol/g)	2.53	2.75	2.84	1.65	1.73	1.85
$b \times 10^{-3}$ (l/mol)	0.455	0.462	0.471	0.991	0.144	0.187
R^2	0.999	0.998	0.999	0.996	0.998	0.998
Δq (%)	12.1	24.1	22.4	15.7	20.7	21.2
Freundlich						
K_f (mmol/g)	0.717	0.916	0.972	0.810	0.990	1.080
$1/n$	0.391	0.338	0.322	0.280	0.255	0.233
R^2	0.999	0.989	0.999	0.999	0.996	0.997
Δq (%)	2.6	0.5	0.7	1.1	1.6	0.7
D–R						
q_m (mmol/g)	4.306	4.445	4.484	2.761	2.795	2.805
$\beta \times 10^3$ (mol ² /kJ ²)	−6.83	−5.41	−4.21	−4.36	−3.34	−2.58
R^2	0.985	0.997	0.995	0.997	0.997	0.998
Δq (%)	1.35	4.14	3.98	2.84	2.92	2.31

sorption capacities (q_m) are in that ranges of 2.15–2.24 and 1.38–1.4 meq/g zeolite A for Zn²⁺ and Cd²⁺, respectively. These values are considerably less than the theoretical exchange capacity (CEC) calculated from the chemical formula of zeolite A (5.45 meq/g). This could be due to the size window of the zeolite A and to the radius of Zn²⁺ and/or Cd²⁺ ions, which make difficult the ion exchange and therefore the values determined experimentally were lower. On the other hand, the value of q_m for Cd²⁺ is in a reasonable agreement with the value quoted by Biskup and Subotic [2] for Cd²⁺ removal with zeolite A at 298 K (1.25 meq/g). The values of the mean free energy, E , of sorption in all cases were found to be in the range of 8–16 kJ/mol, which are within the energy ranges of ion exchange reaction.

Among with the isotherm models tested and based on the normalized standard deviation Δq values, as listed in Table 9, both Freundlich and D–R approaches provided a best fit over the entire range of concentration for all systems. This suggests that some heterogeneity in the surface or pores of zeolite A will play a role in the metal ion sorption.

4. Conclusion

The results, of Zn²⁺ and Cd²⁺ ions sorption reported, showed that synthetic zeolite A is an efficient sorbent media

for the removal of zinc and cadmium ions from aqueous solutions and wastewater. The removal of these two metal ions by the sorbent material takes place via a particle diffusion mechanism, and the thermodynamic parameters reflect the feasibility of the process. Freundlich and D–R isotherm models are the best choice to describe the observed equilibrium data. The sorption of both metal ions is an endothermic process and the results show that zeolite A can be fruitfully employed for the removal of these metal ions in a wide range of concentrations.

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