KINETICS AND ISOTHERM ANALYSIS OF Cd^{2+} REMOVAL FROM AQUEOUS SOLUTIONS BY ION EXCHANGE PROCESS

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Abstract

In the present study, Dowex HCR-S/H, cationic resin was used as a resin for the removal of cadmium from aqueous solutions. The experiments were carried out in a batch vessel. Subsequent experiments were performed as a function of initial solution pH, resin dosage, agitation time, initial Cd^{2+} concentration, solution temperature and agitation speed. Ion exchange rate increased with the increase in initial cadmium concentration, stirring speed and temperature. The Langmuir, Freundlich, Elovich, Temkin, Khan, Sips, Toth, Koble-Corrigan and the Radke-Prausnitz isotherm models were tested for their applicability. It was found that the Sips equation appears to fit the equilibrium data. The ion exchange data obtained at various temperatures were applied to pseudo first-order, pseudo second-order, intra-particle diffusion and Elovich models. Pseudo-second-order rate equation was able to provide realistic description of ion exchange kinetics. Intra-particle diffusion process was identified as the main mechanism controlling the rate of the metal exchange. Thermodynamic activation parameters such as ΔG^*, ΔS^* and ΔH^* of the ion exchange of Cd^{2+} on Dowex HCR-S/H cationic resin were also calculated.

Key words: cadmium, dowex HCR-S/H, ion exchange, isotherm, removal

1. Introduction

Cadmium is a toxic transition metal of continuing occupational and environmental concern. Cadmium exposure leads to a variety of adverse effects (Huang et al., 2016; Waalkes, 2000). The extremely long biological half-life of cadmium essentially makes it a cumulative toxin, so long past exposures could still result in direct toxic effects of the residual metal. Unfortunately, there are no proven effective treatments for chronic cadmium intoxication (Goering et al., 1994). The long residence time of cadmium is in part attributable to metallothionein (MT), a metal-binding protein that is induced at the transcriptional level by cadmium and tightly binds the metal (Waalkes, 2000). Cadmium accumulates primarily in the liver and kidney where

it is bound to MT, and it is felt that cadmium bound to MT is essentially detoxicated, at least temporarily, through this high affinity sequestration (Klaassen et al., 1999). The body has limited capacity to respond to cadmium exposure, as the metal cannot undergo metabolic degradation to less toxic species and is only poorly excreted, making long-term storage a viable option for dealing with this toxic element (Waalkes, 2003).

The accumulation of heavy metals in the environment has received increased attention because of the threat to public health. The most commonly used procedures for heavy metal removal include chemical precipitation, ion exchange, reverse osmosis, and solvent extraction (Sternberg and Dorn, 2002). Ion-exchange technology offers a viable alternative for treating such waste streams. By using

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an ion exchange resin, either all metal-ions can be removed from a solution, or one specific metal ion can be selectively removed, thus, achieving their separation. By carefully choosing the type of ion-exchange resin, the heavy metal ions can be completely separated and removed from the waste solutions to meet stringent environmental regulations.

Several researchers studied ion exchange as a means to remove cadmium from aqueous solutions (Wang and Fthenakis, 2005). The tested adsorbents included activated carbon, bone char, peat, lignite, vermiculite, chitin, zeolite, and treated pinus pinaster bark. These studies focused on the ion exchange of cadmium from low concentration aqueous solutions. Ion exchange process has been widely used to remove heavy metals from aquatic medium using ion exchange resins such as clinoptilolite (Çoruh, 2008), Lewatit FO36 (Ahmadi et al., 2011), Dowex HCR-S/H (Fil et al., 2012c), Heterocycle-containing polystyrene chelating resin (Xiong et al., 2012c), Amberlite XAD7 (Ciopec et al., 2011), Purolite S930 (Bulai et al., 2009), synthetic Dowex 50W (Pehlivan and Altun, 2006), ethylenediamine functionalized chelating resin (ED resin) (Xiong et al., 2012a), zeolite tuff (Ali and El-Bishtawi, 1997), Amberlite IRA 400 (Chabani et al., 2006), titanosilicate ETS-10 (Camarinha et al., 2009), alkali metal zirconium silicates (Bortun et al., 1997) and fibrous ion exchanger FIBAN X-1 (Soldatov et al., 2011).

In the present work, the removal of Cd^{2+} ions from aqueous solutions using an ion-exchange resin (Dowex HCR-S/H) was investigated.

The main objectives of the study include two consecutive steps: (1) to study the sorption characteristics of Cd^{2+} ions on the resin under equilibrium conditions, (2) to understand the kinetics mechanism. For these aims, various affecting factors on the sorption process, such as initial pH of the solution, contact time, ion exchanger dosage, stirring speed, solution temperature and initial metal ion concentration were investigated. The experimental information was also fitted to The Langmuir, Freundlich, Elovich, Temkin, Khan, Sips, Toth, Koble-Corrigan and The Radke-Prausnitz isotherm models. The results were analyzed on the basis of Elovich, first-order Lagergren, and pseudo second-order models.

2. Material and methods

Synthetic Dowex HCR-S/H proton form was obtained from Fluka Co. The properties of Dowex HCR-S/H the parameters chosen in the experiments such as initial pH of the solution, contact time, ion exchanger dosage, stirring speed, solution temperature and initial metal ion concentration, whose ranges were reported on other studies (Fil et al., 2012b; http://www.dowwaterandprocess.com/products/ix/dx_hcrs.htm). Both acidic and salt forms of the resin are stable at temperatures up to 100∘C. Stock solutions of

Cadmium(II) chloride (Analytical grade from Sigma Co) were prepared in double-distilled water.

A batch system was used for removing by the exchange process of cadmium from wastewater. A Heidolph RZR 2021 mechanic stirrer at continuously stirring the mixture was used. The temperature of the vessel was controlled with a HAAKE D8 thermostat connected to vessel. The pH measurements were made using a pH meter (WTW 340i). Experimental set up was seen in Fig. 1.

Fig. 1. Experimental set up (1. pH meter, 2. Speed controller, 3. Stirrer, 4. Reactor, 5. Circulator)

The amount of metal adsorbed (mg g⁻¹), (q_e), onto Dowex HCR-S/H was calculated from the mass balance equation as Eq. (1):

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

where: C_o and C_e are the initial and equilibrium liquid phase concentrations of metal solution (mg L⁻¹), respectively; V the volume of metal solution (L), and m the mass of resin amount used (g).

Kinetic experiments were made by using 500 mL of cadmium solutions of various concentrations. Samples were taken at different time intervals and remaining metal concentrations were analyzed with a Shimadzu AA-6800 atomic absorption spectrophotometer according to Standard Methods (APHA, 1985). The rate constants were calculated using conventional rate expressions. Following formula was used to determine adsorbed metal concentration q_t (Eq. 2):

$$q_t = \frac{(C_0 - C_t).V}{m} \qquad (2)$$

where q_t (mg g⁻¹) is the ion exchange capacity at time t, C_o (mg L⁻¹) is the initial metal concentration, C_t (mg L⁻¹) is the concentration of metal ions in solution at time t, V (L) is the volume, and m (g) is the amount of the resin.

3. Results and discussion

3.1. Effect of pH on removal by ion exchange

Hydronium ion concentration is an important parameter affecting the ion-exchange process. This is

partly because hydrogen ions themselves are strongly competing sorbed and the solution pH influences the ionization of surface functional groups. Ion exchange of cadmium onto Dowex HCR-S/H was carried out for the examination of the effect of pH at a range of 3.0-7.0. High pH values were not investigated due to formation of $Cd(OH)_2$ during process of Cd^{2+} ions with OH^-. Constant resin amount (1 g) was added to all vessel and solutions were agitated for 1 h at 400 rpm speed. It was found that the ion exchange capacity increased with a changed in pH; as it could be seen from Fig. 2. Fig. 2 showed that the amount of cadmium sorbed increased from 95 to 123 mg g⁻¹ when the pH was increased from 3 to 7. The variation in the removal of cadmium by the resin with respect to pH can be explained by considering the surface charge of the sorbent materials and the speciation of Cd^{2+} (Fil et al., 2012a).
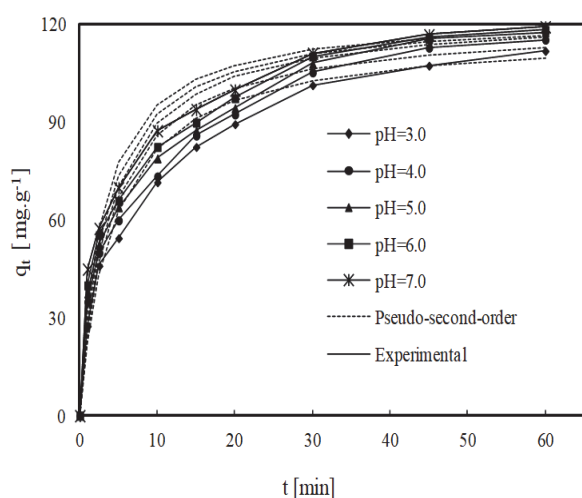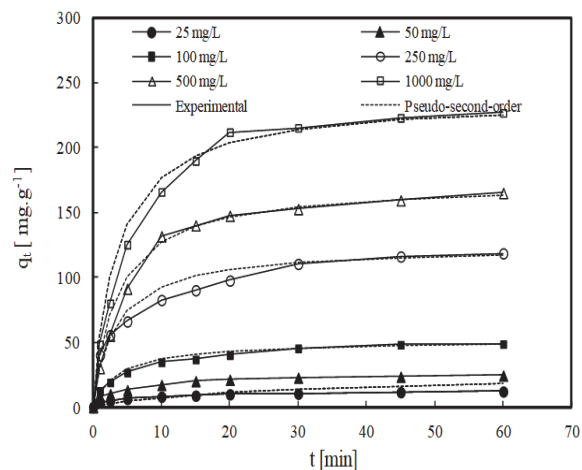

Fig. 2. The effect of initial pH on solid loading (250 mg L⁻¹ initial Cd^{2+} concentration, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage)

3.2. Effect of initial cadmium concentration on removal by ion exchange

To observe the effect of concentration of the cadmium, the concentration range of 25-1000 mg L⁻¹ was taken for the cadmium at 293 K, pH 6.0, 400 rpm of stirring speed and contact time 60 min for Dowex HCR-S/H. The results were illustrated in Fig. 3. The figure showed that ion exchange capacity increased at higher initial cadmium concentrations for a particular time of ion exchange. It is obvious that the removals of the heavy metal by various ion exchangers were dependent on the concentration of the heavy metal. The higher initial cadmium concentration increased the amount of the cadmium adsorbed on the ion exchangers. The obtained results agreed with literature (Yasmine et al., 2012).
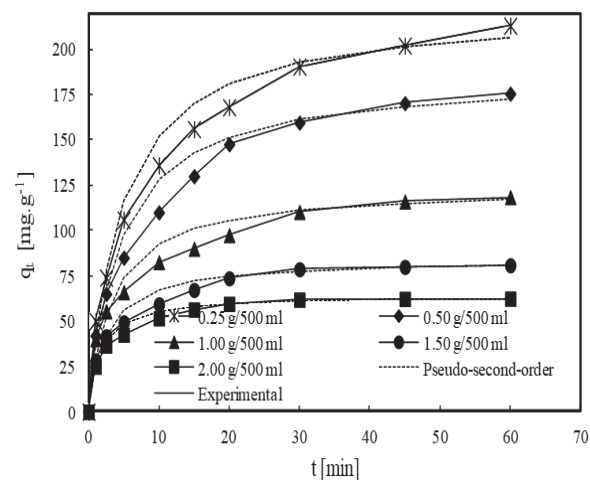
3.3. Effect of resin dosage on removal by ion exchange

Ion exchanger dosage is an important parameter because it determines the capacity of the ion exchanger for a given initial concentration of the solute.

Fig. 3. The effect of initial cadmium concentration on solid loading (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage)

The effect of resin dosage on the ion exchange rate of the cadmium was studied, while other experimental conditions were kept constant as the resin dosage was varied from 0.25 to 2.0 g/500 mL. The equilibrium sorption capacities of cadmium using various dosages from the different prepared ion exchangers were given in Fig. 4.

Fig. 4. The effect of resin dosage on solid loading (pH 6.0, 293 K solution temperature, 400 rpm stirring speed and 250 mg L⁻¹ initial Cd^{2+} concentrations)

It was observed from this figure that the amount of cadmium ions removed per gram of ion exchanger tends to decrease with the increasing of its amount. As was expected, increasing the ion exchanger dosage at the fixed cadmium ion concentration provided more available area for exchanging cadmium and thus the extent of cadmium removal was increased. However the decrease in the amount of cadmium ions removed per gram of ion exchanger is basically due to the ion exchange sites that remained unreached during the ion exchange process. The obtained results agreed with literature (Fil et al., 2012b).

3.4. Effect of solution temperature on removal by ion exchange:

To determine the effect of temperature on the ion exchange of cadmium, experiments were also conducted at 293, 313, 333 and 353 K. The data was obtained by contacting 1.00 g resin with 500 mL solution containing 250 mg L^{-1} initial cadmium concentration, at initial pH 6.0 and 400 rpm stirrer speed. Results obtained were shown in Fig. 5.
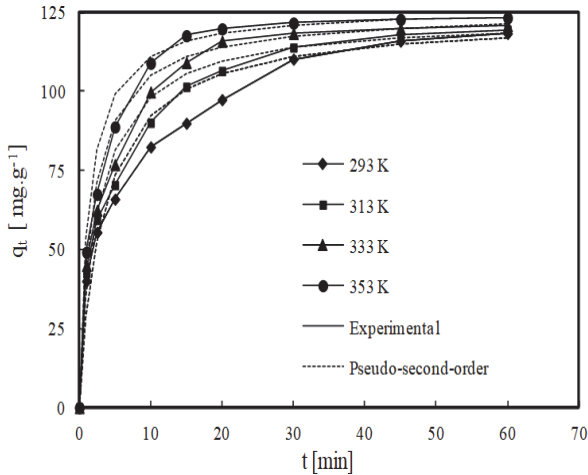

Fig. 5. The effect of solution temperature on solid loading (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Cd^{2+} concentrations)

Comparing the ion exchange values at different temperatures, it was seen that the ion exchange capacity at higher temperature was higher than that of lower temperature at the beginning of process time. This might be a result of increase in the mobility of cadmium ions with increasing temperature (Xiong et al., 2012b). The second-order rate constants listed in Table 6 have been used to estimate the activation energy of Cadmium ion exchange on Dowex HCR-S/H using Arrhenius equation Eq. (3) (Dogan et al., 2007):

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \tag{3}$$

where E_a is activation energy (kJ mol^{-1}); k_2 is the rate constant of pseudo-second-order model (g $mol^{-1}min^{-1}$); k_0 is Arrhenius factor, which is the temperature independent factor (g $mol^{-1}min^{-1}$); R_g is the gas constant (J $K^{-1}mol^{-1}$); and T is the solution temperature (K). The slope of plot of $\ln k_2$ versus $1/T$ is used to evaluate E_a, which was found to be 12.419 kJ mol^{-1} for Cadmium exchange, respectively (Fig. 6). Activation energy was calculated from Arrhenius plot (Fig. 6).

The value of activation energy indicates the type of sorption (physical, 5-40 kJ mol^{-1}) or chemical (40-800 kJ mol^{-1}) (Nollet et al., 2003). The activation energy obtained (12.419 kJ mol^{-1}) for sorption of cadmium by Dowex HCR-S/H indicates that the sorption faced a potential barrier (Krobba et al.,
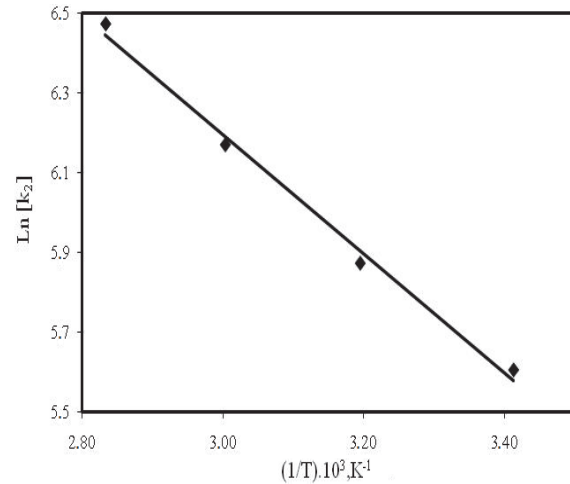
2012).

Fig. 6. Arrhenius plots for ion exchange Cd^{2+} onto Dowex HCR-S/H (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Cd^{2+} concentrations)

3.5. Effect of stirring speed on removal by ion exchange:

The effects of stirring speed on removal rate of cadmium with Dowex HCR-S/H at different stirring speeds was shown in Fig. 7, using different stirring speeds in the range of 200-600 rpm at 250 mg L^{-1} initial cadmium concentration, 293 K solution temperature, 1.00 g/500 mL resin dosage and solution pH 6.0.
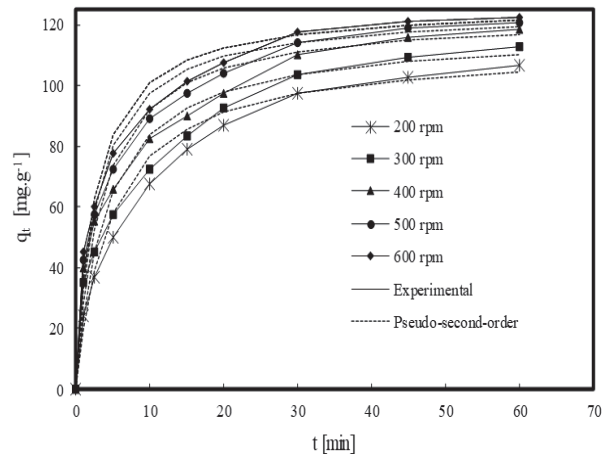
Fig. 7. The effect of stirring speed on solid loading (pH 6.0, 1 g/500 mL resin dosage, 293 K solution temperature and 250 mg L^{-1} initial Cd^{2+} concentration)

As seen Fig. 7, when stirring speed was increased from 200 to 400 rpm, solid loading increased. It was observed that above 400 rpm, the rate of sorption increased marginally which indicated that 400 rpm was sufficient to minimize the mass transfer coefficient in the film (Rao et al., 2010).

3.6. Isotherm models

This part of investigation was experimented Cd^{2+} ion exchange onto Dowex HCR-S/H. In this

experiment was added 1 g synthetic resin to 100 mL different initial metal concentration solutions at 293K temperature and after ion exchange calculate the solution new metal concentration C_e (mg L^{-1}) according to equilibrium time heavy metal concentration adsorption q_e (mg g^{-1}) were calculated using Eq. (1). It was seen from Fig. 3 that 20 minutes was enough for ion exchange equilibrium. The results obtained on the ion exchange of Cd^{2+} ion were analyzed by the well-known models given by Langmuir, Freundlich, Elovich, Temkin, Sips, Khan, Radke-Prausnitz, Koble-Corrigan and Toth model. The mathematical equations for these models were given in Table 1). The data related isotherms defined above were shown in Table 2. The fittingness between experimental data and isotherm data were shown in Fig. 8. When listing in order as error values for two-parameter isotherm was made, it was seen that arrangement was **Langmuir > Temkin > Elovich > Freundlich.** Three parameters isotherm models resulted better performance than two parameter model and order of fitting degree of isotherm models were obtained as **Sips > the Koble-Corrigan > the Radke-Prausnitz > Khan > Toth.** Consideration of all error values reveals that fitting degree of isotherm models were classified as **Sips > the Koble-Corrigan > the Radke-Prausnitz > Khan > Langmuir > Toth > Temkin > Elovich > Freundlich**. Evaluating all models indicated that Sips model has better performance for fitting with experimental data.
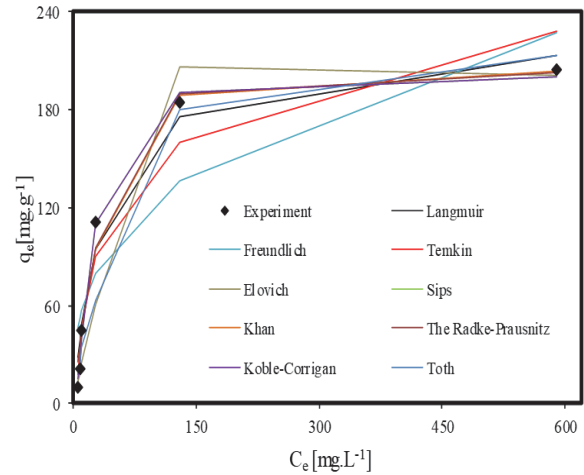

Fig. 8. The comparison between experimental data and isotherm data for two and three parameter models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Foo and Hameed, 2010; Limousina et al., 2007). Upon contacting an amount of adsorbent with in aqueous solution an adsorbable substance (adsorbate) adsorption will take place. Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state.

Table 1. Isotherm models equations

Isotherm	Mathematical equations	References
Langmuir	$q_e = (q_m K_L C_e)/(1 + K_L C_e)$	Langmuir (1918)
Freundlich	$q_e = K_F C_e^{1/n}$	Freundlich (1906)
Elovich	$q_e/q_m = K_E C_e \exp(-q_e/q_m)$	Elovich and Larionov (1962)
Temkin	$q_e = (RT/b)\ln(K_T C_e)$	Temkin (1941)
Sips	$q_e = (q_m a_S C_e^{1/n})/(1 + a_S C_e^{1/n})$	Sips (1948)
Khan	$q_e = (q_m b_K C_e)/(1 + b_K C_e)^{a_K}$	Khan et al. (1997)
Radke-Prausnitz	$q_e = (A R C_e^p)/(A + R C_e^{p-1})$	Radke and Prausnitz (1972)
Koble–Corrigan	$q_e = (A C_e^n)/(1 + B C_e^n)$	Koble and Corrigan (1952)
Toth	$q_e = (q_m C_e)/(K_{To} + C_e^n)^{1/n}$	Toth (1971)

Table 2. The data for all isotherm models

Langmuir Isotherm		Freundlich Isotherm		Temkin Isotherm	
K_L	0.026533	K_F	26.01693	K_T	0.276922
q_m	226.8440	$1/n$	0.339851	b	54.50999
R^2	0.98414	R^2	0.90632	R^2	0.97356
Elovich Isotherm		Khan Isotherm		Toth Isotherm	
q_m	298.9665	q_m	355.4983	q_m	216.0679
K_E	0.008195	b_K	0.014726	K_{To}	0.284907
R^2	0.94922	a_K	1.196689	n	-0.122691
		R^2	0.98892	R^2	0.98195
Sips Isotherm		Koble-Corrigan Isotherm		The Radke-Prausnitz Isotherm	
q_m	201.279	A	0.939905	A	4.955332
a_S	0.004619	B	1.688409	R	531.0145
n	0.590957	n	0.004669	p	-0.139286
R^2	0.99798	R^2	0.99596	R^2	0.98977

At equilibrium a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent). At first, adsorption of heavy metal onto same quantitative resin particles rapidly increases, while increasing initial metal concentration. But, after a certain period, comes equilibrium. This is the maximum adsorption capacity (q_{max}) of resin material to the surface is known as. Maximum adsorption capacity of Cd^{2+} onto resin was calculated as 204.885 mg g^{-1} at 293 K, 400 rpm stirring speed, pH: 6.0 and 1 g resin dosage end of ion exchange time of 60 min. Comparison of the adsorption capacity of Cd^{2+} onto resins were shown Table 3.

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called adsorption isotherm. Equilibrium isotherm equations are used to describe the experimental sorption data and the parameters obtained from the different models (Foo and Hameed, 2010; Vasanth Kumar and Sivanesan, 2007). Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration (Foo and Hameed, 2010; Ncibi, 2008). Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Bulut et al., 2008; Foo and Hameed, 2010).

3.7. Kinetic study

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 overall 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 cadmium ion removal from the solution by Dowex HCR-S/H was determined using pseudo-first order, pseudo-second-order rate models, Elovich model and intra particle model. The mathematical equations for these models were given Table 4 (Furusawa and Smith, 1974; Ho and Mckay, 1998; Ho et al., 1996; Mckay et al., 1999). The results of the kinetic parameters and coefficients (R^2) were shown in Table 5. The highest correlation coefficients were obtained with the pseudo – second – order kinetic model (Caliskan et al., 2011).

As seen in Table 5, the correlation coefficients for the Elovich equation have changed in the range of 0.939 - 0.996. This result has shown that the experimental data did not fit the Elovich equation when compared with the pseudo second-order kinetic model. If the intraparticle diffusion is involved in the ion exchange process, then the plot of the square root of time versus the uptake (q_t) would result in a linear relationship, and the intraparticle diffusion would be the controlling step if this line passed through the origin. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of ion exchange.

3.8. Half-exchange time and diffusion coefficient

The half-exchange time of the heavy metal ions, $t_{1/2}$, i.e. the time required for the resin to uptake half of the amount exchanged at equilibrium, is often considered as a measure of the rate of exchange and for the second-order process is given by the Eq. (4) (Weber and Morris, 1963):

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{4}$$

Table 3. Comparison of maximum adsorption capacity of cadmium

Resin Name	Max. Adsorption Capacity (mg g^{-1})	Reference
Gel-type weak acid resin (GTWAR)	282	Xiong et al. (2009a)
D152 resin	378	Xiong and Yao (2009b)
Chitosan-phenylthiourea (CSTU) resin	120	Monier and Abdel-Latif (2012)
Amberjet 1200H resin	168.615	Bai and Bartkiewicz (2009)
001×7 strong-acid cation exchange resin	355	Wang et al. (2009)
Dowex HCR-S/H	204.885	This study

Table 4. Kinetic models equations

Kinetic model	Mathematical equations	References
Pseudo-first order rate model	$\ln(q_e - q_t) = \ln q_e - k_1 t$	Ho and Mckay (1998)
Pseudo-second-order rate model	$t/q_t = \left[1/k_2 q_e^2\right] + (1/q_e)t$	Ho et al. (1996)
Elovich model	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	Mckay et al. (1999)
Intra Particle model	$q_t = k_{dif} t^{1/2} + C$	Furusawa and Smith (1974)

Table 5. Kinetics data calculated for ion exchange of Cd^{2+} onto Dowex HCR-S/H

Resin dosage (g/500 mL)	Temperature (K)	Initial metal concentration (mg L⁻¹)	pH	Stirring speed (rpm)	Elovich α (x10⁻⁵) mg g⁻¹ min⁻¹	Elovich β (g mg⁻¹)	Elovich R²	Pseudo–first–order k₁ (min⁻¹)	Pseudo–first–order R²	Pseudo–second–order h=k₂qe² (mg g⁻¹ min⁻¹)	Pseudo–second–order k₂(x10³) (g mol⁻¹ min⁻¹)	Pseudo–second–order R²	D(x10⁹) cm² s⁻¹	Intra-particle k₁ (mg g⁻¹ min⁻¹/²)	Intra-particle R₁²	Intra-particle k₂ (mg g⁻¹ min⁻¹/²)	Intra-particle R²
1	293	250	6	200	5.389	0.0462	0.989	0.0713	0.99	24.09	1.897	0.991	150.791	19.121	0.997	6.891	0.933
1	293	250	6	300	8.371	0.0483	0.983	0.0728	0.991	29.216	2.091	0.991	174.753	16.952	0.999	7.419	0.927
1	293	250	6	400	12.682	0.0494	0.992	0.0794	0.987	36.59	2.417	0.993	208.62	19.155	0.984	7.385	0.913
1	293	250	6	500	15.49	0.0491	0.993	0.0896	0.988	44.571	2.858	0.996	251.116	21.414	0.993	5.958	0.907
1	293	250	6	600	18.43	0.0494	0.99	0.0917	0.987	50.057	3.119	0.997	277.734	21.898	0.983	5.396	0.887
1	293	25	6	400	0.973	0.4744	0.992	0.0625	0.97	3.148	20.726	0.99	179.771	1.99	0.999	0.787	0.967
1	293	50	6	400	2.209	0.2287	0.979	0.0712	0.96	7.79	12.313	0.995	217.947	4.215	0.999	1.079	0.96
1	293	100	6	400	3.308	0.1068	0.993	0.0929	0.981	14.299	5.79	0.995	184.983	10.218	0.995	3.687	0.929
1	293	250	6	400	12.682	0.0494	0.992	0.0794	0.987	36.59	2.417	0.993	208.62	19.155	0.984	7.385	0.913
1	293	500	6	400	9.307	0.0286	0.956	0.074	0.92	48.168	1.605	0.995	196.064	47.662	0.998	6.126	0.983
1	293	1000	6	400	13.441	0.021	0.968	0.0907	0.961	68.829	1.199	0.995	203.664	55.25	0.991	5.429	0.966
1	293	250	3	400	6.881	0.0467	0.992	0.0679	0.987	27.057	1.968	0.99	161.529	18.402	0.982	7.565	0.948
1	293	250	4	400	9.106	0.0481	0.986	0.078	0.987	30.205	2.069	0.99	176.312	17.008	0.99	7.824	0.936
1	293	250	5	400	10.659	0.0484	0.99	0.0806	0.982	32.936	2.183	0.991	187.346	18.829	0.988	8.037	0.926
1	293	250	6	400	12.682	0.0494	0.992	0.0794	0.987	36.59	2.417	0.993	208.62	19.155	0.984	7.385	0.913
1	293	250	7	400	16.943	0.0516	0.993	0.0787	0.983	41.896	2.756	0.995	238.298	19.548	0.999	6.655	0.929
1	293	250	6	400	12.682	0.0494	0.992	0.0794	0.987	36.59	2.417	0.993	208.62	19.155	0.984	7.385	0.913
1	313	250	6	400	16.263	0.0494	0.984	0.0902	0.986	48.404	3.158	0.997	275.136	20.245	0.992	4.665	0.923
1	333	250	6	400	21.133	0.0495	0.955	0.1074	0.958	66.188	4.25	0.998	372.517	25.023	0.997	2.585	0.879
1	353	250	6	400	33.505	0.0515	0.923	0.1201	0.944	92.11	5.754	0.999	509.604	27.833	0.99	1.383	0.897
0.25	293	250	6	400	11.519	0.0238	0.994	0.0632	0.982	48.483	0.974	0.99	153.595	40.254	0.993	14.625	0.965
0.5	293	250	6	400	9.682	0.0259	0.988	0.0745	0.992	41.581	1.209	0.991	158.203	30.002	0.995	11.072	0.918
1	293	250	6	400	12.682	0.0494	0.992	0.0794	0.987	36.59	2.417	0.993	208.62	19.155	0.984	7.385	0.913
1.5	293	250	6	400	11.346	0.0731	0.983	0.0975	0.98	33.442	4.752	0.997	279.839	12.882	0.975	3.192	0.8
2	293	250	6	400	16.624	0.1037	0.962	0.1422	0.994	38.917	9.443	0.999	426.8	10.522	0.965	1.394	0.74

The determined values of $t_{1/2}$ for the tested parameters are given in Table 5. The values of diffusion coefficient largely depend on the surface properties of resins. The diffusion coefficients for the intra-particle transport of cadmium ions within the active sites of resin particles have been calculated at different temperatures, stirring speed, resin dosage, initial metal concentrations and pH by employing the Eq. (5) (Yadava et al., 1987):

$$t_{1/2}= \frac{0.030\, r_0^2}{D} \qquad (5)$$

where: D is the diffusion coefficient with the unit $cm^2 s^{-1}$; $t_{1/2}$ is the time, min, for half exchange of cadmium and r_0 is the radius of the resin particle in cm.

The value of r_0 was calculated as 3.75×10^{-2} cm for Dowex HCR-S/H sample. For the present study, the pore diffusion coefficient values obtained from Eq. (5) were given in Table 5. The values of diffusion coefficient for exchange of cadmium were found to vary between 150.791×10^{-9} cm^2 s^{-1} to 509.604×10^{-9} cm^2 s^{-1}. Diffusion coefficient values are affected by many factors such as heavy metal molecular weight, structure; functional groups have in the type and amount of resin materials used electrokinetic surface properties. On increasing the initial metal concentration from 25 to 1000 mg L^{-1} and the resin dose from 0.25 to 2.00 g/500 mL, the value of D increased from 179.771×10^{-9} to 203.664×10^{-9} cm^2 s^{-1} and from 153.595×10^{-9} to 426.800×10^{-8} cm^2 s^{-1} respectively. The values of the internal diffusion coefficient, announce the chemisorption nature of cadmium adsorption. This is in agreement with pseudo-second-order kinetic model.

3.9. Activation parameters

Free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation can be calculated by Eyring equation Eq. (6) (Laidler and Meiser, 1999):

$$\ln\left(\frac{k_2}{T}\right)=\left[\left(\frac{k_b}{h}\right)+\frac{\Delta S^*}{R_g}\right]-\frac{\Delta H^*}{R_g}\frac{1}{T} \qquad (6)$$

where: k_2, k_b and h are pseudo-second-order rate constant, Boltzmann's and Planck's constants, respectively. According to Eq. (6), a plot of $\ln(k_2/T)$ versus $1/T$ should be a straight line with a slope $-\Delta H^*/R_g$ and intercept $[\ln(k_b/h) + \Delta S^*/R_g]$. ΔH^* and ΔS^* were calculated from slope and intercept of line, respectively.

Gibbs energy of activation may be written in terms of entropy and enthalpy of activation Eq. (7):

$$\Delta G^* = \Delta H^* - T.\Delta S^* \qquad (7)$$

was calculated at 293 K from Eq. (7). It is found that

the values of the free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation for cadmium are 58.125 kJ mol^{-1}, 9.752 kJ mol^{-1} and -0.1651 kJ mol^{-1} K^{-1}, respectively (Fig. 9). The results were shown in Table 6.

It was observed a non-spontaneous process, as all ΔG^* values were found positive. Moreover, an increase in temperature rendered, an increase in ΔG^* values the system gained energy from an external source. Positive value of ΔH^* indicated that the ion exchange of Cd^{2+} is endothermic and higher temperature makes the ion exchange easier. Positive value of ΔH^* reflect the bonding energies of the solvated metal ion in the resin loading. A negative value of ΔS^* showed a lower randomness tendency at the solid/solution interface during the ion exchange of Cd^{2+} on the synthetic resin.

Table 6. Thermodynamic parameters for ion exchange of Cd^{2+} onto Dowex HCR-S/H

	293 K	303 K	313 K	323 K
ΔG* (kJ mol⁻¹)	58.125	61.426	64.728	68.030
ΔH* (kJ mol⁻¹)	9.752			
ΔS* (kJ mol⁻¹ K⁻¹)	-0.1651			
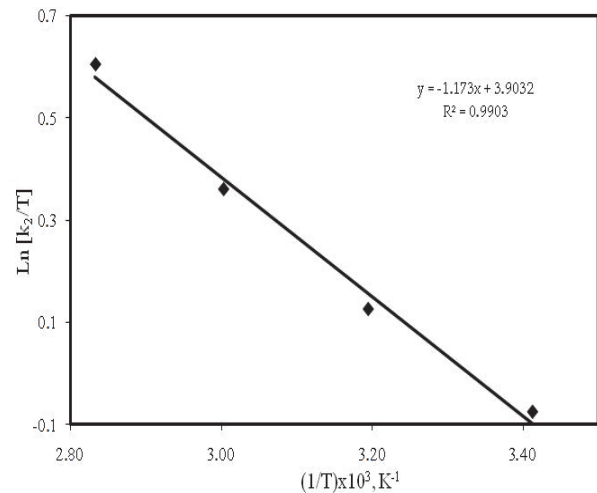
Fig. 9. Plots of $ln(k_2/T)$ versus $1/T$ for ion exchange Cd^{2+} onto Dowex HCR-S/H

4. Conclusions

We investigated the ion exchange kinetics of Cd^{2+} onto Dowex HCR-S/H as a function of stirring speed, initial concentration, pH, resin amount and temperature. The ion exchange equilibrium was best defined by the Sips isotherm model at the same conditions. Close agreement of the values q_e (model) to the same with experimental results suggested that the ion exchange process followed pseudo-second-order kinetics. This indicated that the heterogeneous ion exchange occurred. The maximum capacity of Dowex HCR-S/H for exchange Cd^{2+} ions of the optimum condition in our experiments were obtained as 204.885 mg g^{-1} at 293 K, 400 rpm stirring speed, pH: 6.0 and 1 g resin dosage end of ion exchange

time of 60 min. The positive ΔH^* value revealed the endothermic nature of ion exchange. Ion exchange of Cd^{2+} on resin was favorable influenced by increase in the temperature of the operation. The positive values of ΔG^* indicated that Cd^{2+} exchange by Dowex HCR-S/H was not spontaneous and the negative value of ΔS^* showed the decreasing randomness at the solid/liquid interface during the sorption of Cd^{2+} ions on Dowex HCR-S/H.

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