Adsorption Kinetics and Isotherms for the Removal of Zinc Ions from Aqueous Solutions by an Ion-Exchange Resin

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Summary: The capacity of ion exchange resins, Dowex HCR-S, for removal of Zinc from aqueous solution was investigated under different conditions such as initial solution pHs, stirring speeds, temperatures, initial concentrations and resin dosages. Adsorption equilibrium isotherms were analyzed by Langmuir, Freundlich, Temkin, Elovich, Khan, Sips, Toth, Radke-Praunstrzki, Koble-Corrigan, models. Khan model was found to show the best fit for experimental data. The experimental kinetic data were analyzed using the first-order, second-order, Elovich and intra-particle kinetic models and the second-order kinetic model described the ion exchange kinetics accurately for Zn (II) ions. Thermodynamic activation parameters such as ΔG*, ΔS* and ΔH* were also calculated.

Keywords: Zinc, ion exchange, Dowex HCR-S, kinetics, isotherm.

Introduction

High concentrations of heavy metals in the environment are mostly due to uncontrolled wastewater discharge. It is often the discharge of industrial wastewaters from plating, metal finishing and rinsing manufacturing processes. Some industries of organic compounds such as pesticides, pigments metal additives; petroleum refining and pulp industries produce large amounts of solid and liquid waste that contains different types and quantities of heavy metals [1, 2].

There are various methods for the removal of heavy metals in the literature. Some of them are chemical precipitation [3], ion exchange [4], adsorption [5], biosorption [6] and electrocoagulation [7] such methods can be sorted.

Ion-exchange method is one of the most effective methods used in removing heavy metals from waste water. This method is used in the ion exchange resins can be used again due to chemical or physical, this method has not changed and is very economical compared to other methods. The stabilization treatment of this waste always includes the operation of their removal and possible recycling in the process using ion exchangers. The synthetic resins [4, 8, 9] have recently become recognized as an improved material for removal of heavy metals from wastewaters, contaminated surface and groundwater using ion exchange process.

The aim of our study, strongly acidic cation exchange resin DOWEX HCR-S using a batch system, aqueous solutions of different initial conditions for the equilibrium curves of Zn^{+2} to achieve metal removal and the maximum adsorption capacity is to find experimentally.

Results and Discussion

Effect of pH

Fig. 1 represented the effect of initial pH on the removal of the Zn (II) by Dowex HCR-S. In order to find the optimum pH for maximum removal efficiency, experiments were carried out in the pH range 3-6. Because of precipitation of the Zn (II) ion, higher pH values were not preferable. The effect of pH on Zn (II) sorption was determined as batch experiments and the results were given in Fig. 1. The sorption of Zn (II) with Dowex HCR-S increased slightly with the increase in pH from 3 to 6. Therefore, the optimum pH which is maximum removal was chosen as 6.0 [10].

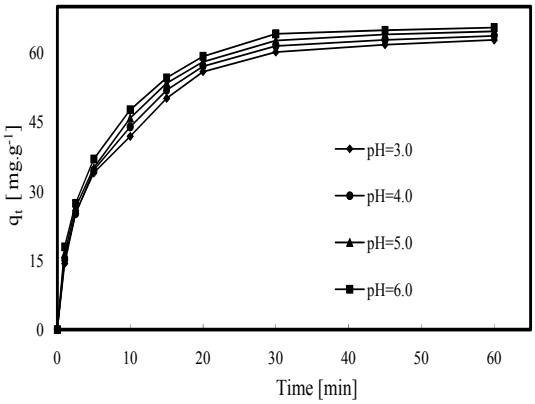

Fig. 1: The effect of initial pH on adsorption capacity (250 mg L^{-1} initial Zn^{+2} concentration, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage).

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Effect of Stirring Time and Initial Metal Concentration

A series of agitation time studies for zinc ions have been carried out with the initial metal concentration from 25 to 1000 mg/L at 293 K. Fig. 2 showed that the amount of the sorbed Zn (II) ions onto strongly acidic cation-exchanger increased with time. The agitation time necessary to reach equilibrium was 15 min. The sorption capacities (q_t) increased from 11.712 to 124.232 mg/g with the increase in initial concentration from 25 to 1000 mg/L. The equilibrium uptake in the case of Dowex HCR-S occurred after 60 min. The sorption capacities of the resin were equal to 11.712, 22.205, 42.888, 65.457, 85.764, and 124.232 mg/g for the zinc solutions having initial concentration of 25, 50, 100, 250, 500 and 1000 mg/L, respectively [11, 12].

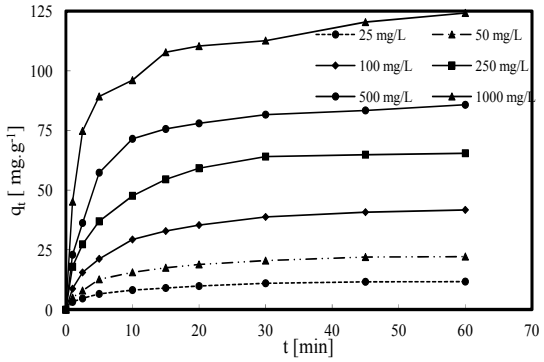

Fig. 2: The effect of initial zinc concentration on adsorption capacity (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage)

Effect of Temperature

A plot of the zinc exchange as a function of temperature (293, 313, 333 and 353 K) was shown in Fig. 3. The results revealed that the metals exchange slightly increased with increasing temperature at 293 K 65.457 mg/g; 313 K 68.225 mg/g; 333 K 70.662 mg/g and 353 K 74.100 mg/g). The exchange of metal at higher temperatures was found to be greater than that at a lower temperature. Therefore, the exchange capacity should largely depend on the chemical interaction between the functional groups on the resin surface and the adsorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the adsorbate into the active sites. At higher temperatures the resin might contribute to the exchange of Zn (II) as diffusion is an endothermic process [13].

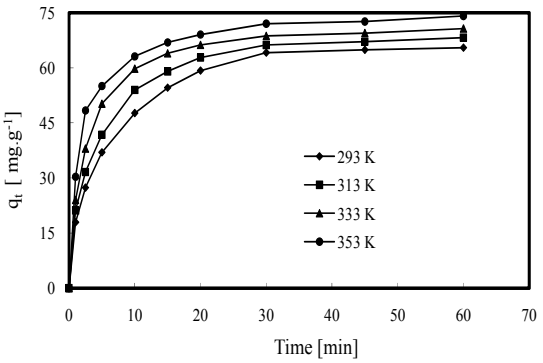

Fig. 3: The effect of solution temperature on adsorption capacity (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Zn^{+2} concentrations).

Effect of Resin Dosage

The effect of the amount of resin on sorption of Zn (II) ions was investigated. For this purpose, the resin amounts were taken between 0.25 and 2.00 g/500 ml. The results in Fig. 4 showed that the retention of Zn (II) ions increased with increasing of resin amount but sorption density decreased and then attained equilibrium. It is readily understood that the number of available sorption sites increases by increasing the resin amount, therefore results in the increase of removal efficiency for Zn (II) ion. The decrease in sorption density can be attributed to the fact that some of the sorption sites remain unsaturated during the sorption process; whereas the number of available sorption sites increases by an increase in resin amount and this results in an increase in removal efficiency [14, 15].

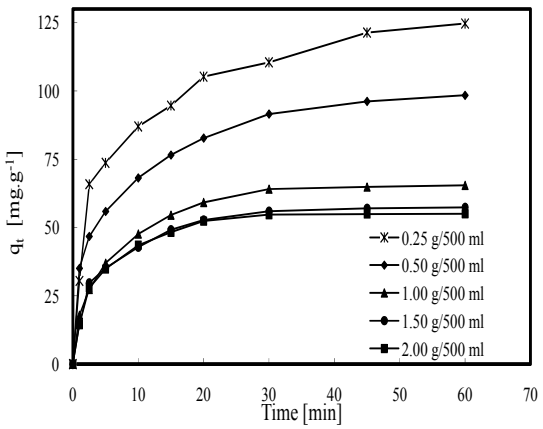

Fig. 4: The effect of resin dosage on adsorption capacity (pH 6.0, 293 K solution temperature, 400 rpm stirring speed and 250 mgL^{-1} initial Zn^{+2} concentrations).

Effect of Stirring Speed

Stirring is an important parameter in adsorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of external boundary film. Fig. 5 showed the adsorption rate of Zn (II) using resin at different stirring speed (200, 300, 400, 500 and 600 rpm) within contact time of 60 min. From the figure it is clear that with increasing stirring speed from 200 to 600 rpm, the maximum adsorption capacity of Zn (II) increases 50.267 mg/g to 70.778 mg/g at the end of 60 min of operation. The increasing in ion exchange capacity can be explained by the fact that increasing stirring speed reduced the film boundary layer surrounding ions, thus increasing the external film transfer coefficient, and hence the adsorption capacity, similar result is also reported in the literature [16].

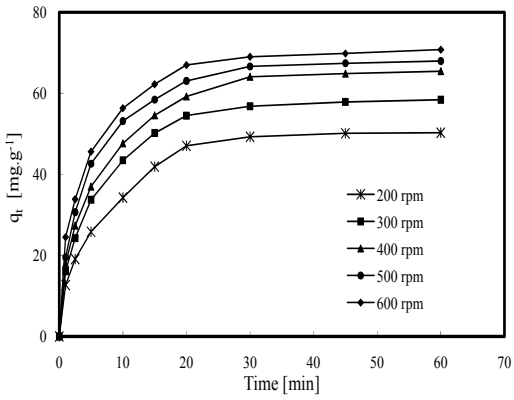

Fig. 5: The effect of stirring speed on adsorption capacity (pH 6.0, 1 g/500 mL resin dosage, 293 K solution temperature and 250 mgL^{-1} initial Zn^{+2} concentration)

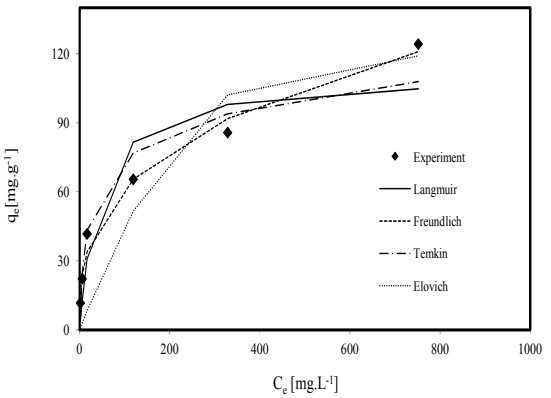

Fig. 6: The comparison between experimental data and isotherm data for two parameter models (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage)

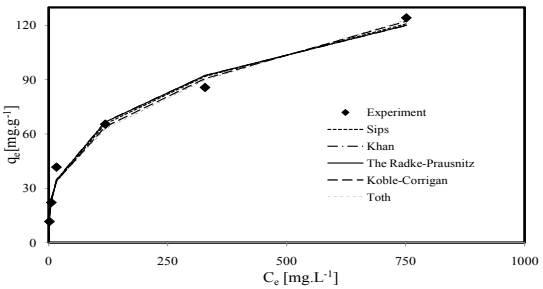

Fig. 7: The comparison between experimental data and isotherm data for three parameter models (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage).

Adsorption Isotherm, *Kinetics*, *Activation Parameters*

Adsorption Isotherms

The capacity of Dowex HCR-S for heavy metal can be determined by measuring equilibrium isotherms. Basically, adsorption isotherm is important to describe how adsorbate interacts with adsorbents. The relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at the equilibrium can be given by the adsorption isotherms. These equations which are often used to describe the experimental isotherms were developed isotherm models in Table-1 [17-25]. In order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained, equations of Langmuir, Freundlich, Elovich, Temkin, Sips, Khan, Toth, Koble–Corrigan and Temkin have been considered.

Table-1: Isotherm models equations.

Isotherm	Mathematical equations	References
Langmuir	$q_e = (q_m K_L C_e)/(1+K_L C_e)$	**[17]**
Freundlich	$q_e = K_F C_e^{1/n}$	**[18]**
Elovich	$q_e/q_m = K_E C_e \exp(-q_e/q_m)$	**[19]**
Temkin	$q_e = (RT/b)\ln(K_T C_e)$	**[20]**
Sips	$q_e = (q_m a_S C_e^{1/n})/(1+a_S C_e^{1/n})$	**[21]**
Khan	$q_e = (q_m b_K C_e)/(1+b_K C_e)^{a_K}$	**[22]**
Radke-Prausnitz	$q_e = (ARC_e^{p})/(A+RC_e^{p-1})$	**[23]**
Koble–Corrigan	$q_e = (AC_e^{n})/(1+BC_e^{n})$	**[24]**
Toth	$q_e = (q_m C_e)/(K_{To}+C_e^{n})^{1/n}$	**[25]**

Correlation coefficients and constants of the isotherm models were given in the Table-2 (two parameters) and Table-3 (three parameters). As can be seen from tables and figures (Fig 6-7), experimental results with the best fit Khan Isotherm. The capacity of the adsorption isotherm is

fundamental, and plays an important role in the determination of the maximum capacity of adsorption.

Table-2: The data for two parameter isotherms.

Langmuir Isotherm		Freundlich Isotherm	
K_L	0.023567	K_F	13.35417
q_m	110.6965	1/n	0.332789
R^2	0.93905	R^2	0.99291
Temkin Isotherm		**Elovich Isotherm**	
K_T	0.794756	q_m	628.0824
b	144.2953	K_E	0.000835
R^2	0.96940	R^2	0.87515

Table-3: The data for three parameter isotherms

Sips Isotherm		Koble-Corrigan Isotherm		The Radke-Prausnitz Isotherm	
q_m	8208.831	A	14.07774	A	44.88950
a_S	0.001621	B	0.285073	R	14.99659
n	2.981729	n	0.036349	p	0.314727
R^2	0.99291	R^2	0.99335	R^2	0.99329
Khan Isotherm		**Toth Isotherm**			
q_m	13.62126	q_m	2.160679		
b_K	1.308449	K_{To}	0.284907		
a_K	0.684104	n	-0.122691		
R^2	0.99362	R^2	0.99202		

Adsorption Kinetics

The kinetics of ion-exchange for the treatment of heavy metal containing industrial effluents has already been operated. Numerous kinetic models explaining the mechanism by which pollutants are adsorbed have been suggested in Table-4 [26-29]. The kinetics of adsorption is important because this is what controls the efficiency of the process. Various kinetic models have been used and different systems use different models.

The feasibility of the pseudo-second-order models can be examined by the linear plot of *t*/*qt* versus *t* respectively, as were shown in Fig. 8-12. The correlation coefficient R^2 showed that the pseudo-second-order model is indicative of a chemisorptions mechanism, which fit the experimental data slightly better than Elovich and the pseudo-first order models. In other words the ion exchange of Zinc can be approximated more favorably by the pseudo-second-order model. This model has been successfully applied to describe the kinetics of many adsorption systems. The calculated correlations were closer to unity for the second order kinetics model; therefore, the heavy metals adsorption kinetics could well be more favorably when approximated by a second-order kinetic model. The calculated k_2 (g/mg min) R^2 values were listed in Table-5. The results also defined that an intra-particle diffusion mechanism played a significant role in the adsorption process, while the adsorption rate was controlled by a film-diffusion step.

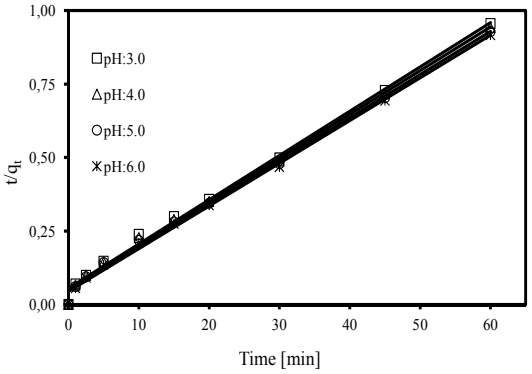

Fig. 8: Second-order kinetic equation for ion exchange Zn(II) onto Dowex HCR S/H at different pHs (250 mg L^{-1} initial Zn^{+2} concentration, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage).

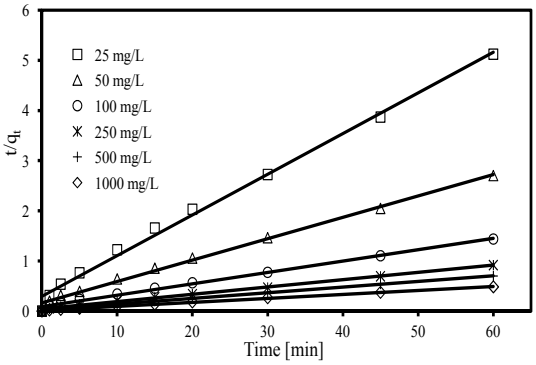

Fig. 9: Second-order kinetic equation for ion exchange Zn (II) onto Dowex HCR S/H at different initial metal concentrations (pH 6.0, 293 K solution temperature, 400 rpm stirring speed, 1 g/500 mL resin dosage)

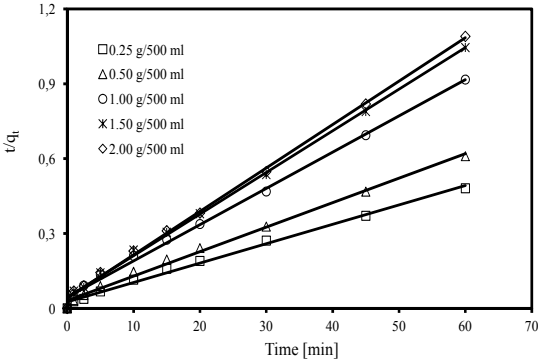

Fig. 10: Second-order kinetic equation for ion exchange Zn (II) onto Dowex HCR S/H at different resin dosages (pH 6.0, 293 K solution temperature, 400 rpm stirring speed and 250 mgL^{-1} initial Zn^{+2} concentrations).

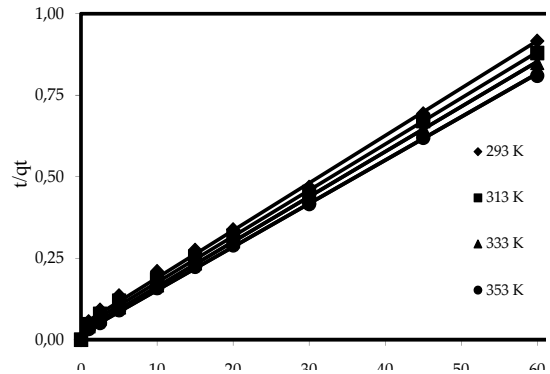

Fig. 11: Second-order kinetic equation for ion exchange Zn (II) onto Dowex HCR S/H at different temperatures (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Zn^{+2} concentrations).

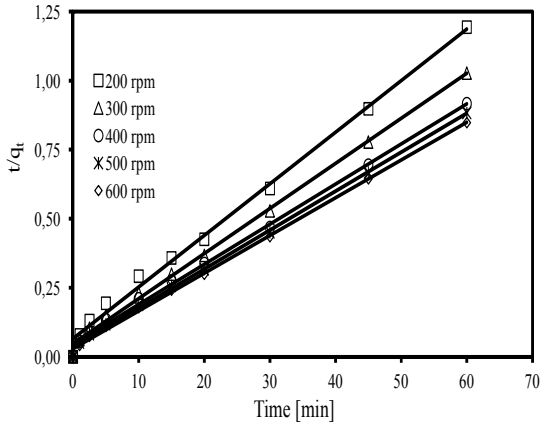

Fig. 12: Second-order kinetic equation for ion exchange Zn (II) onto Dowex HCR S/H at stirring speeds (pH 6.0, 1 g/500 mL resin dosage, 293 K solution temperature and 250 mgL^{-1} initial Zn^{+2} concentration).

Activation Parameters

The activation energy was calculated from the linearized Arrhenius Eq (3).

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \qquad (3)$$

where E_a is activation energy (kJ/mol); k_2 is the rate constant of sorption (g/mol s); k_0 is Arrhenius factor, which is the temperature independent factor (g/mol s); R_g is the gas constant (J/K mol); and T is the solution temperature (K). The slope of plot of ln k_2 versus 1/T was used to evaluate E_a, which was found to be 10.091 kJ/mol for Zinc exchange, respectively (Fig 13).

Free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation can be calculated by Eyring equation[30]:

$$\ln\left(\frac{k_2}{T}\right) = \left[\left(\frac{k_b}{h}\right) + \frac{\Delta S^*}{R_g}\right] - \frac{\Delta H^*}{R_g}\frac{1}{T} \qquad (4)$$

where k_b and h are Boltzmann's and Planck's constants, respectively. According to Eq. (4), 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 (Fig. 14). Gibbs energy of activation may be written in terms of entropy and enthalpy of activation:

$$\Delta G^* = \Delta H^* - T.\Delta S^* \qquad (5)$$

It was calculated at 313 K from Eq. (5). It was found that the values of the free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation for Zinc were 57.782 kJ/mol, 7.423 kJ/mol and −0.1719 kJ/mol K, respectively. The results were shown in Table-6.

Table-4: Kinetic models equations.

Kinetic model	Mathematical equations	References
pseudo-first order rate model	$\ln(q_e - q_t) = \ln q_e - k_1 t$	[26]
pseudo-second-order rate model	$t/q_t = \left[1/k_2 q_e^2\right] + (1/q_e)t$	[27]
Elovich model	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	[28]
Intra Particle model	$q_t = k_{dif} t^{1/2} + C$	[29]

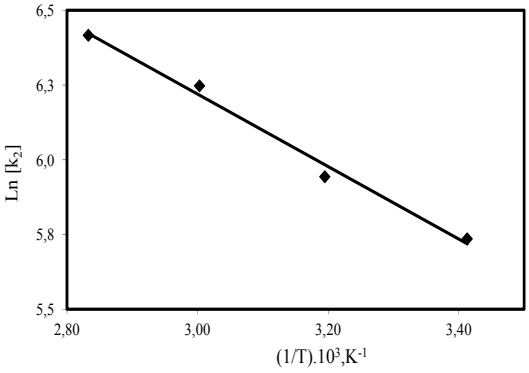

Fig. 13: Arrhenius plots for ion exchange Zn (II) onto Dowex HCR S/H (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Zn^{+2} concentrations).

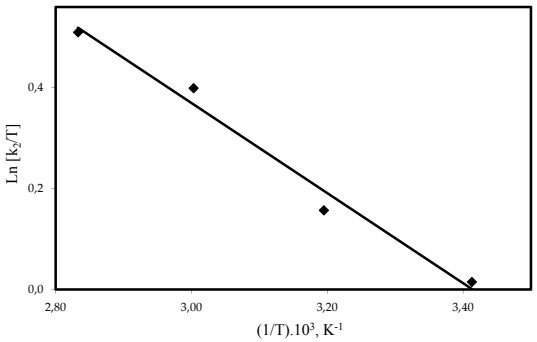

Fig. 14: Plots of $ln(k_2/T)$ versus $1/T$ for ion exchange Zn (II) onto Dowex HCR S/H (pH 6.0, 1 g/500 mL resin dosage, 400 rpm stirring speed and 250 mg L^{-1} initial Zn^{+2} concentrations).

Experimental

Ion exchange experiments were carried out in a batch process by using synthetic aqueous metal solution. The heavy metal solutions of Zn (II) chloride (Analytical grade from Sigma Co) were prepared in double-distilled water. Synthetic Dowex HCR S/H in hydrogen form was obtained from Fluka Co. The properties of Dowex HCR S/H were given in Table-7.

Table-7: Properties of Dowex HCR-S resin.

Parameters	Value
Type	Strong acid cation
Change capacity	1.8 meq/ml
Particul size	300 µm - 1200 µm
pH	0 - 14
Max. oper. temperature	100 ºC
Ionic form	H^+
Ionic density	1.22 g/cm^3
Physical form	Uniform particle size spherical beads

The parameters chosen in the experiments were initial pH of the solution, contact time, adsorbent dosage, stirring speed, solution temperature and initial metal ion concentration, whose ranges were given in Table-8.

Table-8: Experimental parameters

Parameter	Study Ratio
Initial zinc concentration mg/L	25,50, 100, 250, 500 and 1000
Adsorbent dosage (g/500 ml)	0.25, 0.50, 1.00, 1.50 and 2.00
pH	3.0, 4.0, 5.0, and 6. 0
Stirring speed (rpm)	200, 300, 400, 500 and 600
Solution temperature (K)	293, 313, 333 and 353

A batch system was used for removing by the exchange reaction of zinc from wastewater. The temperature of the reactor was controlled with a HAAKE D8 thermostat connected to reactor. Experimental set up was seen Fig. 15. The amount of metal adsorbed (mg g^{-1}), (q_e), onto Dowex HCR S/H was calculated from the mass balance equation as follows:

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

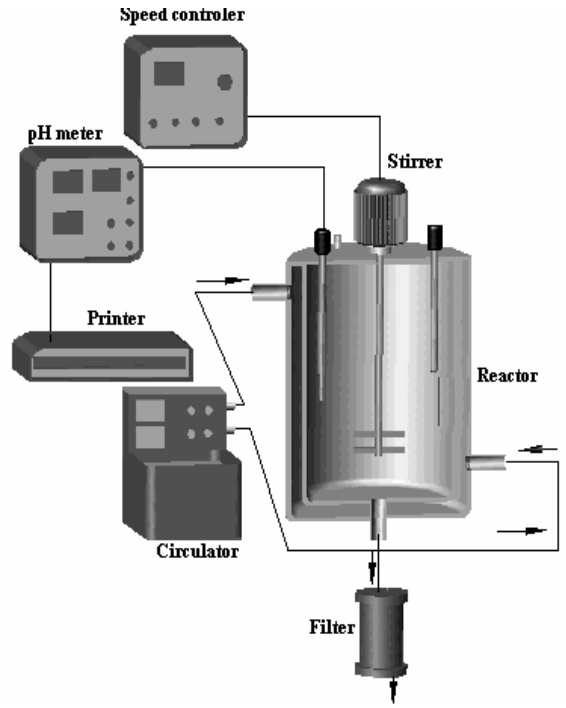

Fig. 15: Experimental set up.

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 zinc solutions of various concentrations. Samples were taken at different time intervals and remaining metal concentrations were analyzed. The rate constants were calculated using conventional rate expressions. Following formula was used to determine adsorbed metal concentration qt:

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

where qt (mg g^{-1}) is the adsorption capacity at time t, Co (mg L^{-1}) is the initial metal concentration, Ct (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.

Table-5**:** Kinetics data calculated for ion exchange of Zn (II) on Dowex HCR-S/H.

Resin dosage (g/500 ml)	Temperature (K)	Initial metal concentration (mg L^{-1})	pH	Stirring speed (rpm)	Kinetic Models											
					The Elovich Equation			Pseudo – first – order		Pseudo – second – order			Intra-particle model			
					α mg g^{-1} min^{-1}	β g mg^{-1}	R^2	k_1 min^{-1}	R^2	$h=k_2 x q_e^2$ mg g^{-1} min^{-1}	k_2 x10^3 g mg^{-1} min^{-1}	R^2	k_1 mg g^{-1} $min^{-1/2}$	R_1^2	k_2 mg g^{-1} $min^{-1/2}$	R_2^2
1.00	293	250	6.0	400	51.522	0.079	0.978	0.1061	0.983	22.523	0.0047	0.996	12.690	0.991	2.620	0.800
1.00	303	250	6.0	400	76.657	0.081	0.971	0.0921	0.958	29.326	0.0058	0.998	13.288	0.981	2.181	0.850
1.00	313	250	6.0	400	137.213	0.086	0.945	0.0888	0.917	41.494	0.0079	0.999	13.648	0.941	1.620	0.907
1.00	323	250	6.0	400	353.616	0.097	0.942	0.0826	0.896	52.910	0.0094	0.999	14.248	0.896	1.742	0.910
1.00	293	25	6.0	400	8.545	0.447	0.992	0.1007	0.979	3.397	0.0223	0.994	2.057	0.978	0.693	0.892
1.00	293	50	6.0	400	13.550	0.223	0.989	0.0942	0.979	6.124	0.0112	0.994	4.408	0.966	1.222	0.932
1.00	293	100	6.0	400	23.356	0.117	0.990	0.0807	0.990	10.965	0.0057	0.994	8.430	0.985	2.261	0.933
1.00	293	250	6.0	400	51.522	0.079	0.978	0.1061	0.983	22.523	0.0047	0.996	12.690	0.991	2.620	0.800
1.00	293	500	6.0	400	87.456	0.063	0.943	0.0784	0.906	37.175	0.0047	0.998	18.962	0.945	2.527	0.967
1.00	293	1000	6.0	400	358.180	0.055	0.962	0.0666	0.902	62.500	0.0040	0.997	19.438	0.880	4.337	0.981
0.25	293	250	6.0	400	120.536	0.046	0.981	0.0710	0.963	38.314	0.0023	0.993	19.887	0.858	7.502	0.952
0.50	293	250	6.0	400	118.122	0.061	0.991	0.0778	0.987	32.051	0.0031	0.994	14.150	0.991	5.586	0.924
1.00	293	250	6.0	400	51.522	0.079	0.978	0.1061	0.983	22.523	0.0047	0.996	12.690	0.991	2.620	0.800
1.50	293	250	6.0	400	57.414	0.094	0.970	0.1095	0.992	22.883	0.0064	0.997	11.050	0.933	1.985	0.824
2.00	293	250	6.0	400	58.352	0.097	0.962	0.1448	0.982	24.938	0.0076	0.998	11.202	0.947	1.508	0.678
1.00	293	250	6.0	200	31.373	0.096	0.966	0.1288	0.996	15.221	0.0053	0.994	10.031	0.999	1.862	0.715
1.00	293	250	6.0	300	47.837	0.088	0.970	0.1043	0.984	21.505	0.0057	0.997	11.851	0.992	1.886	0.795
1.00	293	250	6.0	400	51.522	0.079	0.978	0.1061	0.983	22.523	0.0047	0.996	12.690	0.991	2.620	0.800
1.00	293	250	6.0	500	68.467	0.079	0.970	0.1079	0.981	28.409	0.0056	0.998	13.554	0.970	2.225	0.785
1.00	293	250	6.0	600	99.414	0.081	0.964	0.0970	0.949	34.247	0.0064	0.998	13.271	0.981	1.886	0.779
1.00	293	250	3.0	400	66.040	0.061	0.964	0.0801	0.907	17.986	0.0041	0.994	11.926	0.980	2.980	0.831
1.00	293	250	4.0	400	89.345	0.068	0.961	0.1020	0.963	19.120	0.0042	0.995	12.487	0.989	2.803	0.826
1.00	293	250	5.0	400	110.057	0.068	0.970	0.0862	0.964	37.879	0.0050	0.998	12.665	0.992	2.727	0.831
1.00	293	250	6.0	400	53.205	0.058	0.973	0.1043	0.991	26.385	0.0034	0.996	12.690	0.991	2.620	0.800

Conclusion

Dowex HCR S/H resin was a tender of removing zinc from an aqueous solution. It was found that the rate constant of ion exchange increased by increasing initial concentration, stirring speed, pH and temperatures. The adsorption data correlated well with Khan adsorption isotherm model. The results of this research evidence that the second-order kinetic model mechanism played a significant role in the ion exchange of Zn (II) by Dowex HCR S/H resin.

Thermodynamically parameters were evaluated for zinc ions and showed that the ion exchange of the zinc ions is endothermic in nature. The positive value of ΔH^* showed that adsorption was favorable at higher temperature and the presence of possible chemisorptions phenomenon. The positive values of the Gibbs free energy change (ΔG^*) confirm that the ion-exchange process was not spontaneous whereas the negative values of the entropy (ΔS^*) confirm that the decreased randomness at the solid-solute during ion-exchange process.

Table-6: Thermodynamic parameters for ion exchange of Zn (II) on Dowex HCR-S/H

	293 K	303 K	313 K	323 K
ΔG* (kJ mol^{-1})	57.782	61.219	64.657	68.094
ΔH* (kJ mol^{-1})		7.423		
ΔS* (kJ mol^{-1} K^{-1})		-0.1719		

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