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Adsorption and Kinetic Study of Ni(II) Ions from Aqueous Solution using Natural Syrian Zeolite

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Adsorption and Kinetic Study of Ni(II) Ions from Aqueous Solution using Natural Syrian Zeolite

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Abstract- Adsorption of Ni(II) ions from aqueous solution using natural Syrian zeolite has been studied. Batch shaking adsorption experiments were performed in order to determined the effects of contact time, pH and initial concentration on removal process. The experimental equilibrium data were tested for the Langmuir and Freundlish isotherms. It was determined that removal of Ni(II) ions was well fitted by pseudo-first order kinetic model. The adsorption involves a film diffusion, an intra-particle diffusion and a chemical ion-exchange between Na^+ ions of adsorbent and the Ni^{2+} ions. The adsorption is endothermic and spontaneous process under studied conditions.

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I. Introduction

Environmental preservation is nowadays mater of deep concern. Heavy metals release in wastewaters is on of most worrying pollution causes, as it effects on life may be particularly serious, either referring to plants and animals, or to man, reached indirectly by the toxic through food chain. Heavy metals are well-known toxic substances and therefore their removal from wastewater is require prior to discharge into receiving water[1,2].

Ions of heavy metals like copper, nickel, zinc, cadmium, lead, chromium and mercury as a significant impact on the environment since they are often detected in industrial wastewaters. Many techniques are using to removal of heavy ions. Conventional methods involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction biosorption, adsorption, etc [3-6].

Adsorption and ion-exchange methods are widely using for removal of the heavy ions from aqueous solutions because of simple and low coast of these methods.

Natural zeolite is generally regarded as the suitable material for using as a adsorbent and exchanger for wastewater treatment. Zeolites are widely used in ion-exchange applications, where they exchange cations from there structure with dissolved ones. The most important property of zeolite is the ion-exchange capacity expressing the ability of the material to take up cations. It also important that Zeolites are environmentally friendly materials[3,7,8].

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The present study discusses the possibility of the Syrian natural zeolite for removing nickel ions from aqueous solution. Also, the effect of different parameters on ion-exchange process were investigated. Some kinetic parameters were calculated for determination of adsorption mechanism. It is thought that results of this study can be useful for treatment processes of sectors containing heavy metal in their wastewaters.

II. Eperimental

a) *Materials*

All chemicals used in this study were analytical grade reagents. The natural zeolite ore using in this work collected from Omm'Ozen region in Syria. It was crushed and then sieved to different fractions, of which 100-200μ, was used in this study. This adsorbent is containing different zeolite phases (analcim, philipsite and shabazite) [9]. A certain amount of natural zeolite washed with distilled water tree times to avoid any effects from dissolved salts in the equilibrium solution. The adsorbent was then dried at 120°C for 24h and named Z. Modified zeolite with Na ions was prepared as following: 20g of Z sample was added to 500ml of NaCl(1M) solution, agitated at room temperature for 24h filtrated and washed by distilled water and then dried at 120°C for 24h.and named Z-Na sample. The stock solution of Ni(II)(1000mg/l) was prepared by dissolving a weighed quantity of $NiCl_2.6H_2O$ salt in bi-distilled water. The stock solution was used to prepare different solutions with Ni(II) concentration ranging (100, 200, 400, 700, 1000mg/l). Before adding the adsorbent, the pH of each solution adjusted to the required value by adding (0.1 M NaOH or 0.1 M HNO_3).

b) *Equilibrium Studies*

The batch ion-exchange experiments performed in a wide variety of conditions including contact time, pH, temperature and initial concentration. Effects of each factor were determined keeping other variables constant. In the experiments 0.3g of adsorbent was added to 50ml of Ni(II) solutions. Solutions were shacked for predetermined period. At the end of the experiment, solution filtered and the metal contents in solution determined by Atomic Absorption Spectroscopy method. In these experiments, the averages of three tested samples reported.

c) Isotherm Studies

The adsorption capacity was calculated using following formula:

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

Where q_e(mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration(mg/L), respectively, V(L) is the volume and m(g) is the amount of the adsorbent.

The nickel removal percentage was calculated using the formula:

$$\text{Re}\,moval(\%) = \frac{C_0 - C_e}{C_0}.100 \quad (2)$$

The data obtained were applied to Langmuir isotherm using the following liner expression of this model [10]:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}.K_L}.\frac{1}{C_e} \quad (3)$$

Where q_{max}(mg/g) and K_L(L/mg) the Langmuir constants related to the ion-exchange capacity and energy of ion-exchange, respectively. Another isotherm, the Freundlish isotherm also used, which expressed as follows [10]:

$$Log\ q_e = Log\ K_f + \frac{1}{n} Log\ C_e \quad (4)$$

Where K_f and n are the Freundlish constants.

d) Kinetic and Thermodynamic studies

Kinetic experiments were performed by using 50ml of nickel solution of various concentrations (100, 200, 400mg/L). To these solutions, we added 0.3g of modified zeolite Z-Na and shacked. Samples were taken at different time intervals (0-480 min) and different temperatures (298,313, 333 K) and remaining metal concentrations were determined. The rate constants were calculated using tow reaction-based kinetic models, the pseudo-first rate equation whose integrated form is given by formula [11].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

Where q_e and q_t are the amount of Ni(II) adsorbed(mg/g) at equilibrium and at the time t, respectively, and k_1(min^{-1}) is the rate constant. The integrated form of the pseudo-second order rate reaction also was used [11].

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where k_2($g.mg^{-1}.min^{-1}$) is the rate constant of the pseudo-second order adsorption.

The effect of the temperature on the removal of Ni(II) by Z-Na adsorbent was studied and the activated energy was calculated using Arrhenius equation:

$$Ln\ k = Ln\ A - \frac{E_a}{R}.\frac{1}{T} \quad (7)$$

Thermodynamic parameters such as enthalpy ΔH^0, entropy change ΔS^0 and Gibbs free energy ΔG^0 for the adsorption of Ni(II) were calculated using the equations[12]:

$$Ln\ K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

$$\Delta G^0 = -RT\ LnK_d \quad (9)$$

Where R is the general gas constant, 8.314 J/mol.K and T is the adsorption absolute temperature, K_d(ml/g) is the distribution coefficient which is obtained by the following equation:

$$K_d = \frac{q_e}{C_e} = \frac{C_0 - C_e}{C_e}.\frac{V}{m} \quad (10)$$

III. Results and Discussion

a) Effect of contact time

Due to equilibrium nature of the removal process of Ni(II) by the modified zeolite Z-Na, it seen that the contact time affect the removal efficiency of the used adsorbent. Hence, the effect of contact time on the removal of Ni(II) by the Z-Na was studied in the batch experiment. The corresponding results are given in Fig.1. It cam be seen that the removal of Ni(II) ions from aqueous solution using The Z-Na increased during time and reached to nearly constant amount at equilibrium conditions after 360min. This obtained time was selected for the next adsorption experiments. The variation in the time of adsorption may also be due to the fact that initially all sites on the surface of Z-Na were vacant and the Ni(II) ion concentration gradient was relatively high. After 360min the adsorbent surface becomes saturated with respective metal and the removal efficiency becomes almost constant.

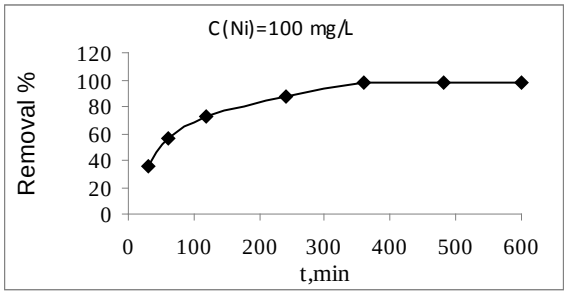


Fig.1 : Effect of contact tine on Ni(II) removal by Z-Na

$C_{Ni(II)}$=100mg/L, V=50mL, m=0.3g, T=298K, pH=6

b) Effect of pH solution

The effect of pH on the ion-exchange of Ni(II) by the Z-Na is presented in Fig.2. The pH of aqueous solution was an important parameter that controlled the ion-exchange process.

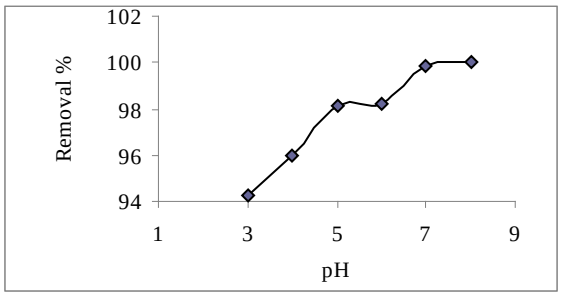


Fig.2 : Effect of pH on the removal of Ni(II)

$C_{Ni(II)}$=100mg/L, V=50mL, m=0.3g, T=298K, t=360min

Adsorption of Ni(II) increased with increasing pH to a pH in range 5-6, then increased up to pH 7-8 where beginning the precipitation process. Under acidic conditions the Z-Na surface will be completely covered with H^+ ions and the Ni(II) ions cannot compete with them. However, with increasing pH, the competition from the $H^=$ ions decreases and the positively charged Ni(II) ions can be exchanged and be also adsorbed at the negatively charged sites on the Z-Na. At pH higher 8 the precipitation process $Ni(OH)_2$ will accurse[13]. Based on these results, Z-Na exhibited a good capacity for removing Ni(II) from solution at a range of pH values from 5-8. The maximum removal about 98% was at pH=5.

c) Adsorption isotherm

Adsorption equilibrium measurements were used to determine the maximum adsorption capacity and the obtained data were formulated into the most commonly models include Langmuir and Freundlish isotherms[14].

The adsorption capacity was calculated using formula (1). Fig.3 shows the adsorption isotherm for Ni(II) on adsorbent Z and Z-Na zeolite.

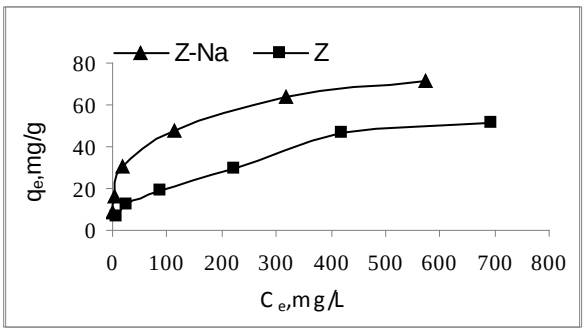


Fig.3 : The adsorption isotherm for Ni(II) on Z and Z-Na zeolite

V=50mL, m=0.3g, T=298K, t=360min

It is seen from Fig.3 that the adsorption capacity of both Z and Z-Na zeolite increases with the Ni(II) solution concentration. The equilibrium data from Fig.3 have been analyzed according to equation (3) and (4).

The Langmuir isotherm is a commonly applied model for adsorption on a completely homogeneous surface. The model assumes uniform adsorption energies onto the surface. The Freundlish model is shown to be consistent with exponential distribution of active sites, characteristic of heterogeneous surfaces. The values of the Langmuir constants K_L and q_{max} and Freundlish constants K_f and n were determined from the slope, intercept in Fig.4(a) and Fig.4(b) respectively and the results presented in table (1).

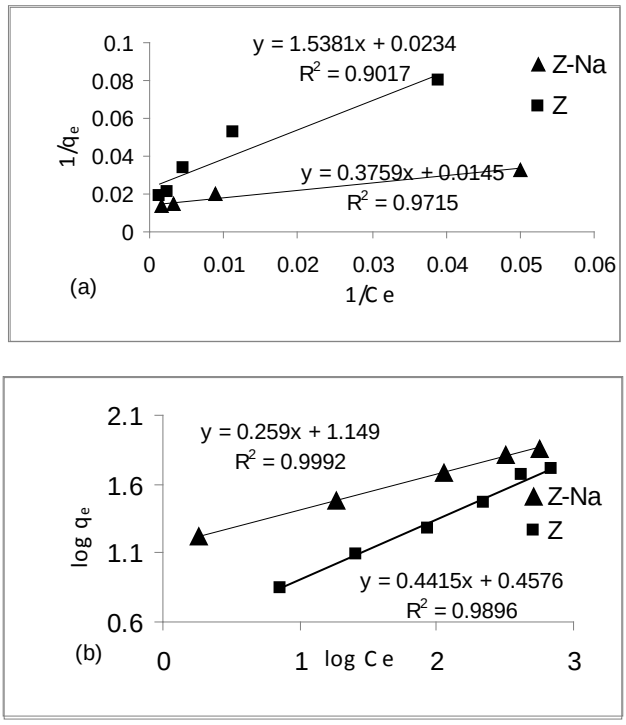


Fig.4 : Langmuir (a) and Freundlish (b) adsorption isotherms of Ni(II)

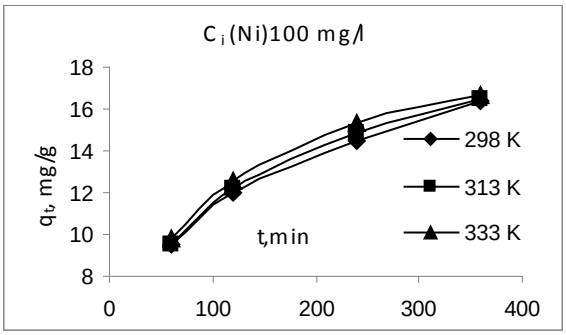
Table(1) : Isotherm Parameters Calculated for Ni(II) Removal on Adsorbent Z and Z-Na

	Langmuir model			Freundlish model		
	q_{max}	K_L	R^2	K_f	n	R^2
Z	43.48	0.0149	0.901	2.86	2.27	0.989
Z-Na	71.43	0.0373	0.971	14.1	3.86	0.999

Comparing of R^2 values of tow isotherm models, confirms that the Freundlish model is the best to describe the adsorption data. On the other hand, a competitive adsorption of Ni(II) accurse on the surface because the value of n>1. From the Langmuir isotherm, the maximum ion-exchange capacity q_{max} was 43.48 and 71.43 mg/g for Z and Z-Na adsorbents, respectively. It was seen the important of the modification process of zeolite for the removal of heavy metals ions from the aqueous solutions.

d) kinetic studies

In order to determined the ion-exchange kinetics of Ni(II) on the modified Z-Na, the pseudo-first order and pseudo-second order kinetics models were examined. On the other hand some of the thermodynamic parameters were determined. The Ni(II) adsorption dependence on time was studied at 298, 313, 333K for solutions with C_0=100,200 and 400mg/L. The uptake values for removal of Ni(II) from solution are shown in Fig.5.



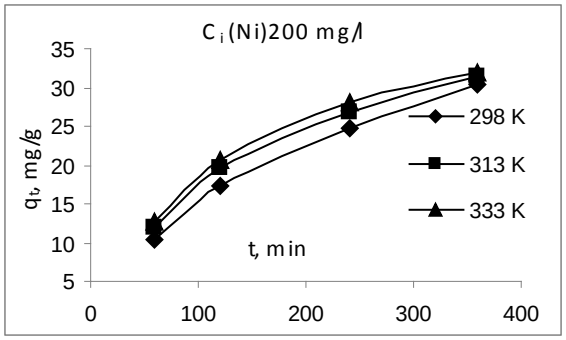
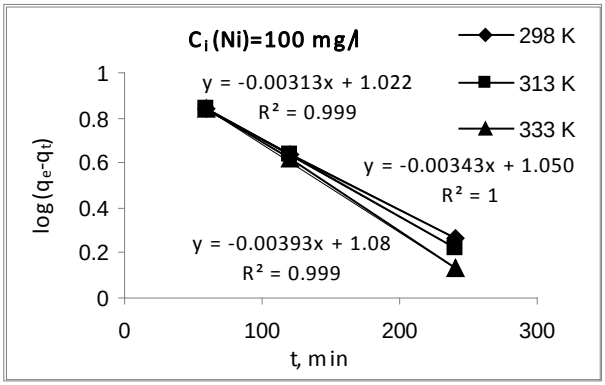
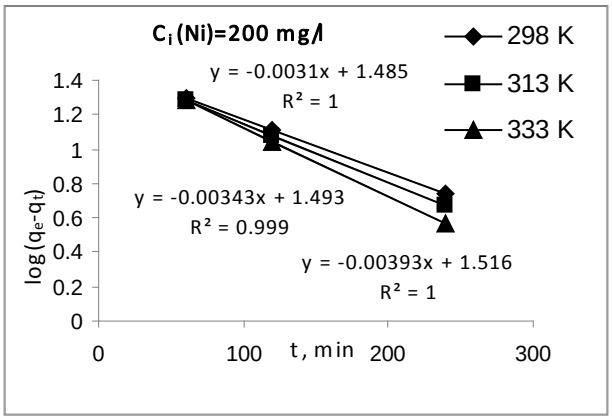


Fig. 5 : Adsorption kinetics for Ni(II) on Z-Na for different initial Ni(II) concentrations

It is seen from the Fig.5 that the adsorption takes place in tow steps. The first step accurse at the beginning stages(i.e. apporx. in the first 50-250 min), when the Ni(II) uptake increases. After these periods adsorption process exhibit slower rate and reach equilibrium after 360min. Similar behavior was found in other systems[15]. The data from Fig.5 were analyzed using (5,6) equations and presented in Fig. 6 and 7. Calculated rate constants k_1, k_2 and correlation coefficients R^2 were summarized in table 2.





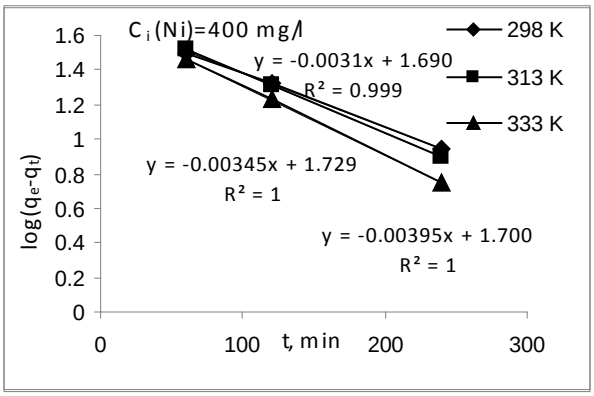
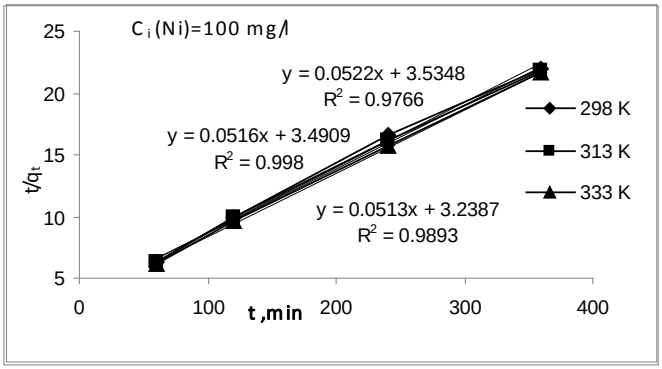
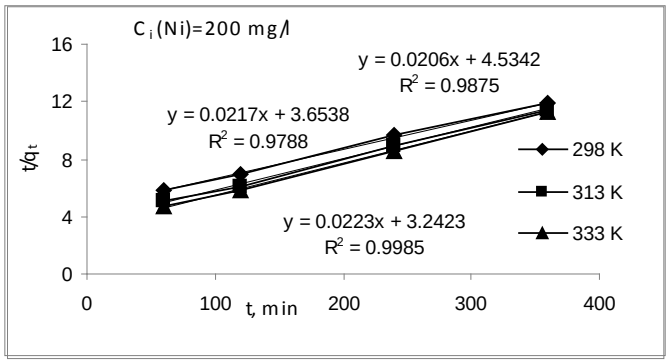


Fig.6 : Pseudo-first order reaction kinetics for the adsorption of Ni(II) onto Z-Na





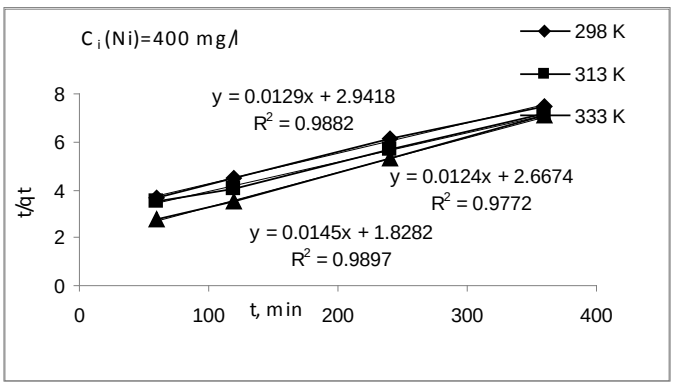


Fig.7 : Pseudo-second order reaction kinetics for the adsorption of Ni(II) onto Z-Na

Table 2 : Rate constants and R^2 values for the pseudo first-and second order reaction kinetics and activation energy of the removal of Ni(II) onto Z-Na

C_0,mg/L	T,K	$k_1.10^3$ min^{-1}	R^2	$k_2.10^3$ g/mg/min	R^2	E_a kJ/mol
100	298	7.2	0.999	0.765	0.976	5.32
	313	7.8	1	0.745	0.998	
	333	9	0.999	0.803	0.989	
200	298	7.1	1	0.088	0.987	5.64
	313	7.8	0.999	0.120	0.978	
	333	9	1	0.149	0.998	
400	298	7.1	0.999	0.049	0.988	5.62
	313	7.9	1	0.054	0.977	
	333	9	1	0.107	0.989	

As seen from table 3 the values of correlation coefficients for pseudo-first order are higher than R^2 for pseudo-second order and the k_1 rate constant increases quite slightly with temperature. The k_2 rate constant variables when initial concentration is increasing. The studied adsorption is better described by the pseudo-first order model. From the results in table 3 we can say, that the process accurse according to the film diffusion and interaction particles diffusion mechanisms[16].

The variation of k_1 with temperature in the 298-333K region was used for the calculation of the activation energy(E_a) of the adsorption. The activation energy was calculated using Arrhenius equation(7) as shown in Fig.8.

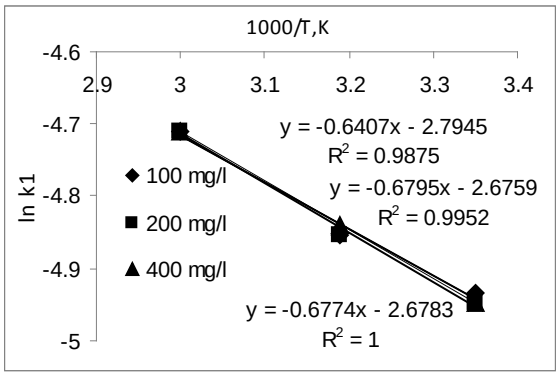


Fig. 8 : The Arrhenius plot using rate constant values from table 3 for the pseudo-first order

The values of the activation energy in table 2 are quite small and change only slightly for different initial concentrations. In general a low E_a value means that the adsorption involved is physisorption[17].

The data obtained from the adsorption experiments at 298, 313 and333K and the initial Ni(II) concentrations of 100, 200 and 400 mg/L, were used for the calculation of thermodynamic properties using (8-10) equations. The plot of ln K_d vs 1/T in Fig.9. gave a strait line, and the values of ΔH^0 and ΔS^0 can obtained from the intercept and slope, respectively. The thermodynamic parameters are presented in table 3.

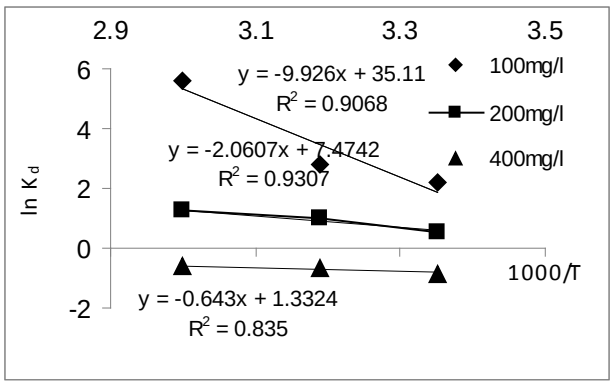


Fig. 9 : The plot of ln K_d vs 1/T for different initial Ni(II) concentrations

Table 3 : Thermodynamic parameters for the Ni(II) adsorption on Z-Na

C_0 mg/L	T,K	LnK_d	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 $J/K.mol$	R^2
100	298	2.207	-5.48	82.4	291.4	0.906
	313	2.803	-7.29			
	333	5.626	-15.50			
200	298	0.509	-1.26	17.12	62.14	0.930
	313	1.014	-2.64			
	333	1.240	-3.43			
400	298	-0.853	2.11	5.34	11.07	0.835
	313	-0.661	1.72			
	333	-0.623	1.72			

The ΔG^0 values in table 4 show that, the adsorption of Ni(II) on Z-Na accurse spontaneously in the 298-333K temperature range and the spontaneity slightly decrease with temperature. The Ni(II) adsorption is endothermic($\Delta H^0 > 0$). It is also evident that the spontaneity as well as the ΔH^0 and ΔS^0 values all decreases as the initial Ni(II) concentration increases. The similar behavior has also been reported for so0me other adsorbents[18]. The positive ΔS^0 values reflect the fact that the adsorption involves the liberation of tow Na^+ when one Ni^{2+} ion is bound to the adsorbent.

IV. Conclusion

The Syrian natural zeolite is effective in removing the nickel(II) ions from aqueous solutions by adsorption.

The Ni(II) ions distributed inside the Z-Na adsorbent indicating that the removal process from water solutions is mainly an ion-exchange. The adsorption kinetics is described by the pseudo-first order model. The activation energy ~ 5kJ/mol. The adsorption involves a combination of the film and interaction particle diffusions, and chemical cation-exchange between Na^+ ions of zeolite and the Ni^{2+} ions. The process is endothermic and spontaneous in the 298-333K temperature range.

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