Thermodynamic Equilibrium and kinetic study of Nickel and Lead sorption by Zeolite 3A

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Abstract

In this study sorption of Ni and Pb ions onto zeolite 3A was investigated at 50 mg/l and different pH to optimize best value for other batch experiments. Therefore, equilibrium isotherms were obtained using batch study by constant pH (6.5 and 5) for Ni and Pb ions respectively, initial concentration 100 mg/l, zeolite dosage and variable temperature and time for thermodynamic and kinetic studies respectively. The results of equilibrium isotherm experiment were analyzed with Langmuir and Freundlich models which show a good fitting with Langmuir model with acceptable regression for Ni and Pb while Freundlich shows good fitting for Pb sorption with a favorable intensity constant (n). Thermodynamic parameters were obtained indicating of endothermic behavior for Ni and exothermic for Pb sorption by Enthalpies values ΔH. Kinetics of the process was studied using Pseudofirst order, Pseudo second order and intra-particle at constant temperature 20C (293 K), at constant condition and variable contact time where the results show smooth increasing of sorption capacity with time until equilibrium and were fitted with pseudo second order model where indicate to chemical sorption for Ni and Pb by zeolite with acceptable Average relative Error ARE values for obtained theoretical sorption compared to experimental one and This makes it noteworthy that sorption does not for the intra particle diffusion process.

Keywords: Ni and Pb , adsorption, zeolite 3A, equilibrium isotherm , kinetic and thermodynamic paramters

Introduction

Water contamination by heavy metals is concerned as a challenge issue in environmental aspects due to their serious harmful effect in ecosystem , Nickel and Lead are toxic heavy metals where their presence in drinking water or untreated waste water out of limitation which cause lung and kidney damages , reproductive system, brain function and dermatitis.[1]

Industrial activities are considered one of biggest sources of heavy metals discharging to the environment especially as illegal waste water effluents or by uncompleted treatment process , so discharged waste water from battery manufacturing , leather products, metals plating etc. are enrich of high (Ni) and (Pb) concentrations.[2] which have ability to accumulate in nature with noneffect by natural biodegradation due to non-biodegradability of heavy metals comparing with organic matters.[3]

The limitation of (Ni) and (Pb) concentrations in Iraq are authorized by ministry of health and environmental according to law number (25) in (1967) which active until now (0.1,0.05)mg/l and (0.2,0.1)mg/l for surface and ground water resource and effluent sources respectively, while the limitation of concentration in drinking water (0.02,0.01) mg/l according to Iraqi specification number (417) in 2009 which authorized by Standardization and Quality control/ Ministry of planning .

Treatment methods selection of waste water polluted by (Ni) and (Pb) depend on theamount of waste water, pollutants concentration, availability of technology, cost, removal efficiency, advantage and disadvantage options [3],there are different methods deal with removal of heavy metals [4] such as separation without chemical reaction like Reverse Osmosis which is characterized as high efficiency with high cost, chemical precipitation/coagulation by neutralization of acidity function pH which is widely useful method for high volume waste water but with disadvantage of sludge product and sorption that selected method as an application technique by accumulation of pollutants by physical / chemical sorption or ion exchange according to characteristics of adsorbent such as surface area , pore volume and size and cationic exchange capacity , well known adsorbents like activated carbon , bentonite, biosorbents and natural/syntheses zeolite.[1]

sorption of (Ni) and (Pb) was found as suitable technique by many researchers in batch an continuous processes under different condition ,flow rate, concentration, contact time,speed of mixing and temperature due to high sorption capacity and reuse after regeneration to improve low operation cost and a good results of removal had been reported[1]

The aim of this study is removal of Ni and Pb from polluted water using zeolite (3A) at selected pH value under variable temperature , adsorbent dosage at equilibrium state to fit with equilibrium isotherm models and determine the thermodynamic values (Gibbs energy , Enthalpy and Entropy), kinetic investigation involves determine the nature of mass transfer of Ni and Pb at different contact time and fixed other variable.

Material and methods

Material

Stock solution of 1000 mg/l of Ni and Pb were prepared by addition of (1 g of Nickel as 4.049 g of $NiCl_2.6H_2O$ and 1 g of Lead as 1.599 Pb(NO3)2 + 0.1 HNO3) which supplied by (Riedel – Dehaen , Fixanal with code numbers 38570 and 38555) respectively.

Ultra pure water was used as solvent with Electrical Conductivity EC 0.05 µs prepared by Water purifier type (EVOQUA , Water Technology)

Ni and Pb solutions were prepared for sorption experiments at 50 mg/l for pH effect experiments and 100 mg/l for equilibrium and kinetics experiments by dilution of stock solution with ultra pure water where pH| adjustment was carried out using acid and base.

Synthesis Zeolite 3A (Ze) (1/8)" pellets and pore diameter 3 Angstrom A supplied by (Union Carbide , Fluka AG , CH- 9490) with chemical formula [K3Na3(ALO2)12(SiO2).27H2O], Ze was treated by thermal activation at 400 C (673 K).

Standard method Analysis of Ni and Pb in their solutions were done according to (ASTM) by using Integrated Coupled Plasma ICP type (Agilant Technology 700 series,ICP-OPS) with auto-sampling SPS3, for accuracy of the prepared solution of 100 mg/l for Ni and Pb the obtained results by ICP show (98.2 and 97.8) mg/l respectively which refers to high detection procedure.

Methods

Effect of pH

Ni and Pb sorption experiments at a variable pH values (3, 4, 5 and 6.5) were studied by preparation of 4 samples of 50 ml solution of 50 mg/l in 100 ml plastic containers for each metals individually and addition 0.2 g of Ze in each solution .Mixing was carried out by shaker type (HT, INFORS, AG, CH-4103 BATTMINGEN) with speed 300 rpm at temperature 20 C° a (293 K) for 240 min to optimize best pH value for other experiment.

Removal percent was calculated through the following equation:-

$$\text{Removal\%} = \frac{Co-C}{C0} \times 100 \qquad (1)$$

Batch sorption experiments

Equilibrium isotherm experiments were carried outto determine the effect of adsorbent dosage at the desired pH values , constant contact time , constant temperature ,and variable Ze mass dosages (0.1 ,0.2 ,0.3 .0.4 and 0.5) g were added in individual samples of 50 ml in 100 ml plastic containers of Ni and Pb solution with 100 mg/l as initial concentration and mixing by shaker at 300 rpm for 240 min. the analyses of samples were done by ICP after filtration of each samples using filter paper type -------

The effect of temperature on the Ni and Pb sorption progress was studied by changing the temperature (20 ,35, and 50) C° (293 , 308 and 323) K respectively in each equilibrium isotherm experiments where each experiment was done at different constant temperature, where controlling of temperature was done by a blowing hot air through isolated area where the shaker place in and desired temperature is fixed by setting display and adding of adsorbent was done after time contacting with hot air to get wanted temperature of the solution.

Sorption capacity represent amount of adsorbate mass per adsorbent mass which is calculated by the following equation (2):-

$$q_e = \frac{(Co-C)V}{m} \qquad (2)$$

Kinetic studies

The influence of time contact on the sorption capacity of Ze and percent removal of Ni and Pb individually in 500 ml flask with 250 ml of Ni or Pb with initial concentration 100 mg/lby adding 2.5 g of Ze adsorbent at desired pH and 20 Co (293 K) , the mixing was achieved by magneticstirrer with speed of 300 rpm and contact time 240 min, the sampling process was done by drawing 5 ml during interval time (15, 30, 60, 120, 180, 210 and 240) min ,filtration of each sample was done to separate any suspended solids.

Results and discussion

Effect of pH

Figure 1 shows the effect of removal percent %of Ni and Pb with initial concentration in sorption process with Ze at different pH values (3, 4, 5, 6.5) and tempreture 20 C(293 K) where increasing of removal percent of Ni and Pb at increasing pH value (low acidity) of solutions [1][5] due to the repulsive force between the H+ at high pH with positive ions (Ni and Pb) which cause competition to exchange with available sites [6] and high density of H+ at low pH will decrease efficiency of Ziolite to attract of positive ions of Ni and Pb by formation more positive electrostatic repulsion between Ni and Pb and the exchangeable site at surface of Ze , it is mean increased pH value will act as naturalization of acidity effect by decreasing more free protons H+ and Ze became favorable for positive ions due to available negative sites above pH 4.5 [7], but in this study for Ni removal % was best value (78.1)% at pH 6.5 while for Pb removal% (97.04) which be depended at pH 5 as optimum due to at pH 6.5 there are appearance of suspended white solid which became as settled with time and that refers to chemical precipitation of lead as $Pb(OH)_2$ [8,9]

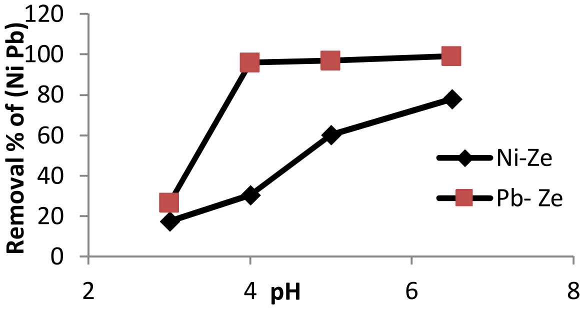


Fig.1 Effect of pH value on the removal percent of Ni and Pb at Co (50mg/l) by Zeolite3A at dose (0.2 g) and temp (20 C^o) with 300 rpm

Equilibrium isotherm results

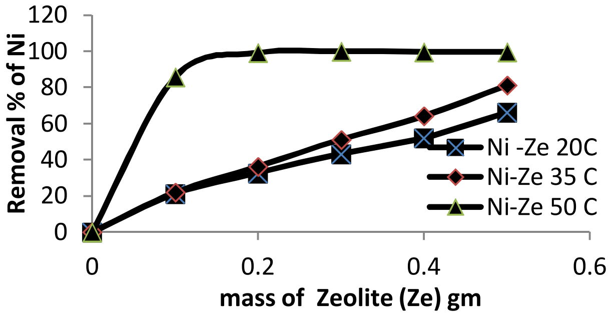
The Effect of Adsorbent mass and temperature

Figure 2-a show removal % of Ni increased at increasing zeolite mass and increasing temperature , at increasing adsorbent mass of Ze (0.1-

0.5) g at pH 6.5 , initial Ni concentration 100 mg/l and different temperature (20 ,35, and 50) C° (293 , 308 and 323) K which were (21.26 - 66.13)% , (21.86 - 81.11) % and (85.73- 99.55)% respectively this is due to increasing in exchangeable site on the surface of Zeolite 3A [10][11]while effect of temperature show clear increasing of removal %at temperature (20-35) C° were (21.26 – 21.86)% , (32.77 – 36.29)% , (43.33-51.2)% ,(52.1-64.1)% and (66.13-81.11) at Zeolite dosage (0.1, 0.2, 0.3 0.4 and 0.5) g respectively, due to the increasing the temperature will increase the ability of ions to have a kinetic accelerating to exchange with sites on the outer and inner surface of zeolite [2] and reach the microproses into zeolite particles[12],while at temperature 50 C (323 K) the curve show a high removal (85.73) at dosage of Zeolite (0.1) g comparing with other temperature and approximately equal removal % (99.1- 99.8) % for other dosage (0.2-0.5) g and this point shows clear explain of effect increasing temperature on increasing of Ni removal % which related to increasing of energy in the system

Figure 2-b show removal % of Pb increased at increasing zeolite mass and increasing temperature , at increasing adsorbent mass of Ze (0.1-0.5) g at pH 5 , initial Pb concentration 100 mg/l and different temperature (20 ,35, and 50) C° (293 , 308 and 323) K which were (57.83-99.87)% , (80 – 99.23)% and (89.3 – 99.55)% respectively due to available exchangeable site on the zeolite surface with clear effect of increasing temperature at amount of removing of Pb from solution [2] and remark that (0.2-0.3) shows a suitable dosage for all temperature in case of removal of Pb by zeolite[10]

(a)



(b

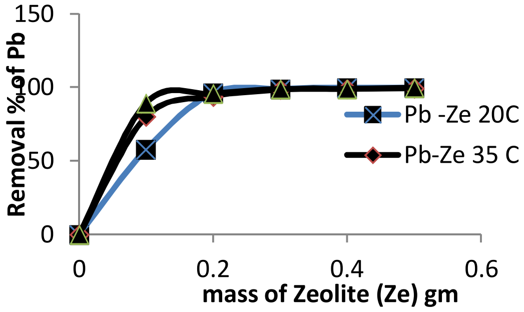
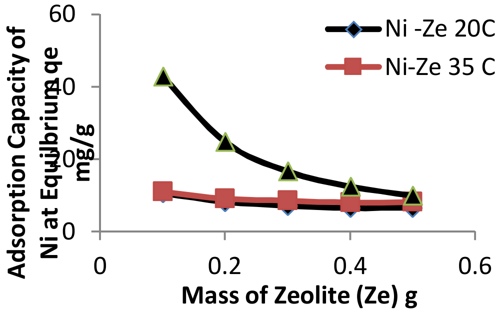
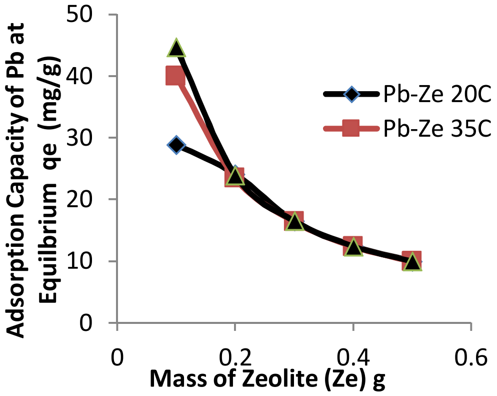


Fig. 2 Effect of Zeolite dose on the removal percent of Ni and Pb at Co (100 mg/l) by Zeolite3A at and different temp. with 300 rpm speed

Figure 3 a and b show relation of sorption capacity qe which calculated by equation 2 and zeolite mass at different temperatures, the results show decreasing of qe with increasing of mass at all temperature with clear greatest values at 50 Co (323 K) due to increasing zeolite mass will effect low proportional of exchanged Ni and Pb to available exchangeable site at constant volume[13] For Ni sorption the q_e values show clear effect at 50 c 323 K while equals responses at other temperatures but for Pb sorption the qe values shows increasing with different values at (0.1-0.2) g of zeolite at all temperatures , while no effect was detected for dosage of zeolite more than 0.2 g at all temperatures this due the nature of thermodynamic behavior of Ni and Pb adsorption



(a)



(b)

Fig.3 Effect of Zeolite dose sorption capacity) of Ni and Pb at Co (100 mg/l) by Zeolite3A and different temp. with 300 rpm speed of Zeolite at different dosage and temperatures for (a) Ni and (b) Pb.

Equilibrium isotherm models results

Table 1 shows results of concentration at equilibrium Ce and sorption capacity qe of Ni an Pb of equilibrium isotherm experiments at different temperatures at different dosage mass of zeolite.

Table-1 values of zeolite 3A dosage related to concentration and sorption capacity

Mass of Ze g	Ni -Ze 20C		Ni-Ze 35 C		Ni-Ze 50 C	
	Ce (mg/l)	qe mg/g	Ce (mg/l)	qe mg	Ce (mg/l)	qe mg/g
0.1	78.74	10.6	78.14	10.93	14.27	42.8
0.2	67.23	8.2	63.71	9.1	0.9	24.7

0.3	56.77	7.2	48.8	8.5	0.113	16.6
0.4	47.9	6.5	35.9	8	0.339	12.4
0.5	33.87	6.6	18.89	8.1	0.45	9.9
Mass of Ze g	Pb -Ze 20C		Pb-Ze 35 C		Pb- 50 C	
	Ce (mg/l)	qe mg/g	Ce (mg/l)	qe mg	Ce (mg/l)	qe mg/g
0.1	42.17	28.9	20	40	10.7	44.7
0.2	3.784	24.	6.2	23.45	4.35	23.9
0.3	0.95	16.5	1.7	16.4	1.14	16.5
0.4	0.19	12.5	1.2	12.4	0.96	12.4
0.5	0.13	10	0.77	9.9	0.45	10

Langmuir Isotherm Model by this equation (3) refers to homogenous nature of adsorbent to form monolayer of adsorbate on the surface of adsorbat which used for evaluating of sorption capacity qe as a maximum value for the adsorbate[14][15]

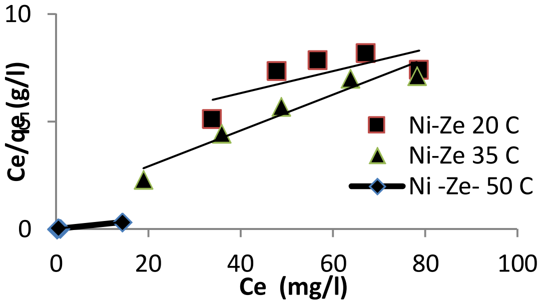
$$qe = \frac{K_l Ce}{1 + q_{th} Ce} \quad (3)$$

Where Ce is concentration at equilibrium mg/l , qe sorption capacity at equilibruim mg/g , K_l langmuir constant l/g and q_{th} theoretical maximum sorption capacity mg/g.

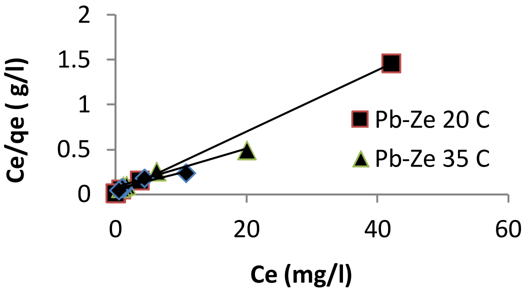
Equation 3 can be rearrangement by linear regression formula as following.

$$\frac{Ce}{qe} = \frac{1}{q_{th} K_l} + \frac{Ce}{q_{th}} \quad (4)$$

Plot of $\frac{Ce}{qe}$ vs Ce for equation (4) as a linear relation to evaluate the q_{th}andK_l by intercpt and slope of line equation by Excel , Figure 4 a and b represent linear form of Langmuir isotherm curve for Ni and Pb respectivel



(a)



(b)

Fig. 4 Linearization of Langmuir equilibrium isotherm model for (a) Ni and (b) Pb.

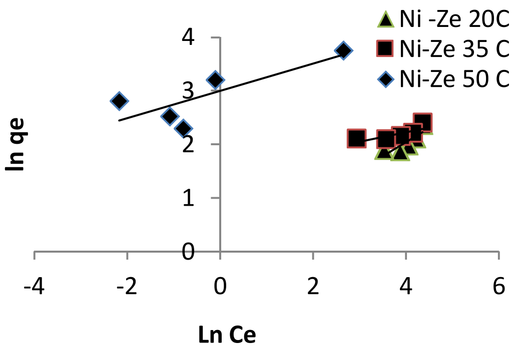
Freundlich isotherm model by equation (5) refers to heterogeneous nature of adsorbent to form multi-layers of the adsorbed matters on the surface of adsorbent.[16,17]

$$qe = K_f Ce^{1/n} \qquad (5)$$

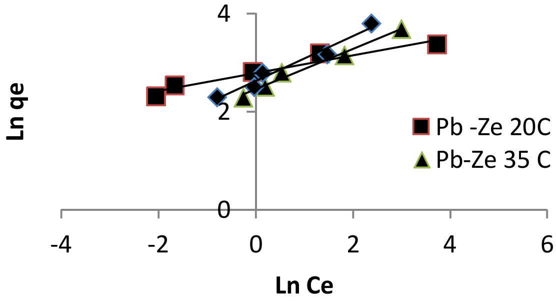
Where Ce is concentration at equilibrium mg/l , qe sorption capacity at equilibrium mg/g , K_f Freundlich constant [(mg/g)(l/mg)$^{1/n}$ and n constant refers to sorption intensity . Logarthmetic of equation 5 to get linear relation between (ln qe vs ln Ce) as following:

$$Lnqe = lnK_f + \frac{1}{n} \ln Ce \qquad (5)$$

Where values of n and K_f can be obtained by solpe and intercept of line using Excel. As showen in Fugre 5 a and for Ni and Pb respectively.



(a)



(b)

Fig. 5 Linearization of Freundlich equilibrium isotherm model for (a) Ni and (b) Pb

Table 2 show the Langmuir and Freundlich Constants and sorption capacity to comparing between experimental and theoretical sorption capacity q_{ex} , q_{th} by Langmuir model and any applied model for calculating the theoretical values, the Average Relative Error (ARE) was applied to determine the validity of any model equation (7)[18]

$$ARE = \frac{|qth - qex|}{qex} 100 \qquad (7)$$

Table 2 Langmuir and Freundlich equilibrium isotherm models parameters.

Temprrture C^o (K)	Langmuir isotherm model		Freundlich isotherm model	
	Ni- Ze	Pb- Ze	Ni- Ze	Pb- Ze
20 (293)	q_{th} gm/g 19.6 $K_{l\ l/g}$ 0.012	q_{th} gm/g 29.41 K_l l/g 2 R^2 0.999	K_f [(mg/g)(l /mg)$^{1/n}$ 0.94	K_f [(mg/g)(l /mg)$^{1/n}$ 16.22

	R^2 0.536 q_{ex} gm/g 10.6 ARE 84.9	q_{ex} gm/g 28.9 ARE 1.76	n 1.905 R^2 0.717	n 5.52 R^2 0.987
35 (308)	q_{th} gmlg 12.05 K_l l/g 0.0672 R^2 0.934 q_{ex} gm/g 10.93 ARE 10.2	q_{th} gm/g 47.6 K_l l/g 0.42 R^2 0.947 q_{ex} gm/g 40 ARE 19	K_f [(mg/g)(l/mg)$^{1/n}$ 4.5 n 6.52 R^2 0.616	K_f [(mg/g)(l/mg)$^{1/n}$ 11.68 n 2.45 R^2 0.982
50 (323)	q_{th} gm/g 45.45 K_l l/g 1.222 R^2 0.993 gm/g 42.8 ARE 6.19	q_{th} gm/g 55.56 K_l l/g 0.316 R^2 0.90 q_{ex}gm/g 44.7 ARE 24.3	K_f [(mg/g)(l/mg)$^{1/n}$ 20 n 3.94 R^2 0.637	K_f [(mg/g)(l/mg)$^{1/n}$ 13.92 n 2.19 R^2 0.967

The result in above table 2 show a good fitting with highest R^2values more than 0.9 of Langmuir model for Pb sorption at all temperature but for Ni sorption were showd only at temp. (35 and 50) C° whilea good R^2 values by Freundlich with 1> n values <10 as a favorable type of isotherm [15,19] for sorption of Pb by zeolite at all temperatures mean the sorption of Ni as monolayer as a homogeneous sorption while multi-layer sorption of Pb by zeolite with heterogeneous adsorption. ARE values show decreasing for Ni sorption at temperature increasing with best value at 50 C(323 K) while for Pb sorption ARE values recorded lowest value at low temperature which suggested a good fitting of Langmuir model results with experimental results.

Thermodynamic parameters of adsorption

Evaluation of sorption at different temperature to investigated the thermodynamic parameters which aim to determine the nature of sorption according to the its spontaneously of reaction, exothermic or endothermic behavior and system randomly by evaluate Gibbs energy ΔG(Kj/mol), Enthalpy ΔH (Kj/mol)and Entropy ΔS (Kj/mol K) respectively[15,20] which were evaluated by the following equation (8 and 9).

$$\Delta G = -RT \, \mathrm{Ln} \, K \qquad (8)$$

$$\Delta G = \Delta H - T \, \Delta S \qquad (9)$$

Where K = Langmuir constant (l/mol) which equle to (l/g multiple by molecular weight of metal) , evaluation of ΔG values can be obtain directly by substitution of K values , temperature (K) and R gas constant (0.008314 Kj/mol.K) , while ΔS and ΔH were evaluated by linear regression of ΔG versus T by determine the slope and intercept of line by Excel as showen in Figure and Table 3.

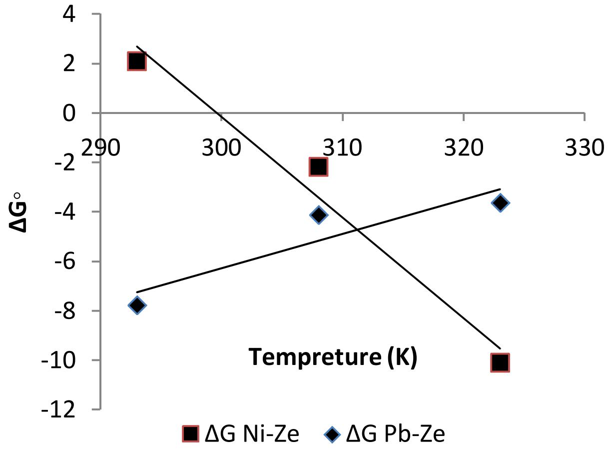


Fig. 6 linear relation of temperatures and Gibbs energy ΔG

Table 3 Thermodynamic parameter for equilibrium sorption of Ni and Pb by Zeolite 3A Ze

Temp. K	Ni -Ze			
	ΔG (Kj/mol)	ΔH (Kj/mol)	ΔS (Kj/mol K)	R^2
293 K	2.064	+121.8	+0.406	0.97
308 K	-2.24			
323 K	-10.1			
	Pb-Ze			
Temp. K	ΔG (Kj/mol)	ΔH (Kj/mol)	ΔS (Kj/mol K)	R^2
293 K	-7.78	-47.9	-0.138	0.838
308 K	-4.2			
323 K	-3.62			

From results of table 3 thermodynamic parameters show endothermic reaction of Ni sorption due to positive Enthalpy ΔH value and positive ΔS value which refers to increased randomness of the Ni-Ze sorption process due to get increasing of negative value of ΔG at increasing of temperature to get spontaneous sorption of Ni [10] and this results meet with Langmuir equilibrium isotherm curve at (323 K) and explain the effect of temperature to increase Ni uptake by Zeolite 3A.For Pb sorption the thermodynamic parameters show negative ΔH value refers to exothermic adsorption[1][15] and decreased degree of randomness due to negative ΔS value even the nature of Pb sorption is spontaneous adsorption[16] according to ΔG negatives value which was decreased at increasing of temperature which must not be more than (343 K) where value of TΔSbe equal to ΔH which lead to non spontaneous sorption and this result meet to good fitting of equilibrium results at all temperatures with best result at (293K) of Langmuir equilibrium isotherms curves and explain effect of increased temperature on nature of Pb adsorption.

Kinetic study

sorption capacity at variable time explain the mechanism of sorption where the transport of adsorbate onto an adsorbent by four rate processes; bulk transport, film transport ,inter particale transport and adsorption[17], kinetic modeling aim to investigate the mechanism of sorption and potential – controlling process such as mass transfer and chemical reaction like pseudo first and second order models and intera-particle diffusion model[18][10].

Figure shows sorption capacity as function of time for sorption of Ni and Pb in batch kinetic experiment at desired condition there are increasing in sorption capacity at first 60 min then there slow step of increasing in uptake to reach the equilibrium at (180 -240) min.

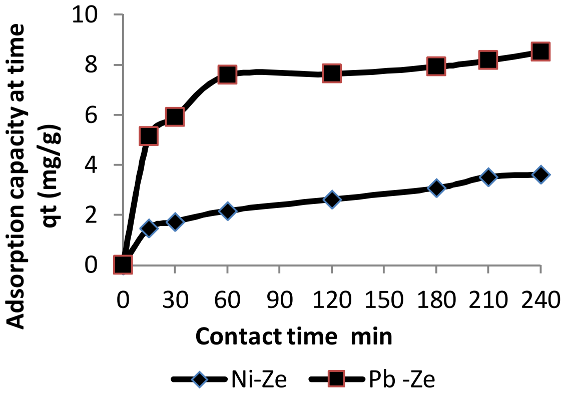


Fig. 7 sorption capacities at different contact time at 20 °C , Zeolite dosage (2.5 g) , 250 ml individual solution of conc. 100 mg/l and pH (5).

To determine kinetic rate sorption of Ni and Pb by zeolite there are three model will be examine the result to investigate the mechanism of adsorption.

Pseudo First Order model (Largergren Model)

Largergren model, proposed in 1898, assumes a first order sorption kinetic and can be represented by the Equation (10). [19,20]

$$\log(q_{exp}-q_t) = \log q_{th} - \frac{K_1}{2.303}t \qquad (10)$$

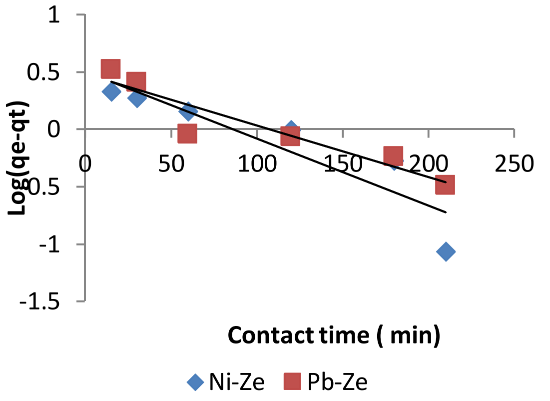
The values of log (q_{exp}– q_t) were linearly correlated with *t.* The plot of log (q_{exp}– q_t) versus t should give a linear relationship from which K_1 and q_{th}can be determined from the slop and intercept of the plot, respectively.

Pseudo second order model.

The pseudo second-order sorption kinetic rate Equation is expressed as Eq (11):

$$\frac{t}{q_t} = \frac{1}{K_2\, q^2{}_{th}} + \frac{t}{q_{th}} \qquad (11)$$

The plot of (t/q_t) and t of Eq (11) should give a linear relationship from which q_{th} and K_2 can be determined from the slope and intercept of the plot, respectively.



The Intra-particle diffusion model

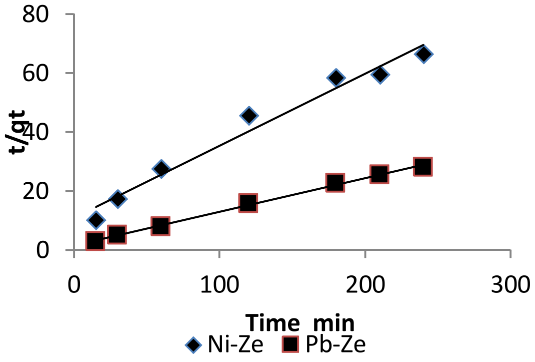
The possibility of intra-particle diffusion of adsorbate onto the adsorbent by using the intra-particle diffusion model Eq (12).

$$qt = K_3 t^{0.5} + C \qquad (12)$$

Where: q_t is the amount of dye adsorbed (mgg^{-1}) at time t; C (mg/g) is a constant and K_3 is the intra-particle diffusion rate constant ($mgg^{-1}\ min^{-1/2}$). The plots of the amount adsorbed, q_t versus $t^{1/2}$ with slope represent the value of K_3 [21]

Figure 8- a, b and c show the linear relations of equations to pseudo first and second order and intreparticles models respectively with constants and ARE% for experimental and theoretical sorption capacity shown in table

(a)



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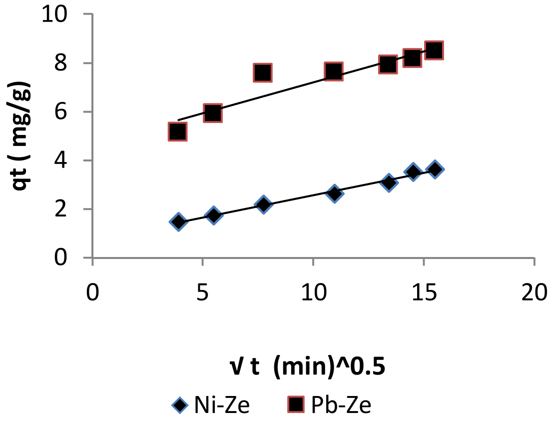

(c)

Fig. 8 Linearization curves of Kinetic models (a) Pseudo first order (b) Pseudo second order (c) Intra particle diffusion.

Table 4 Kinetic models parameters

Applied models	Ni	Pb
Pseudo First Order	K_1 (mg/g. min) 0.0115 q_{th} (mg/g) 3.19 R^2 0.824 q_{exp} (mg/g)	K_1 (mg/g. min) 0.0092 q_{th} (mg/g) 3.02 R^2 0.881 q_{exp} (mg/g) 8.5

	3.612 ARE 11.65	ARE 200
Pseudo Second Order	K (mg/g . min)$^{-1}$ 20.0055 q_{th} (mg/g) 4.1 R^2 0.971 q_{exp} (mg/g) 3.612 ARE 13.5	K2(mg/g . min)$^{-1}$ 0.0088 q_{th} (mg/g) 8.772 R^2 0.997 q_{exp}(mg/g)8.5 ARE 3.2
Intra-particle diffusion	K_3(mgg^{-1} min$^{-1/2}$) 0.184 C 0.717 R^2 0.988	K_3(mgg^{-1} min$^{-1/2}$) 0.254 C 4,667 R^2 0.864

Above result show Highest R^2 results with Pseudo Second Order more than with Pseudo First Order with a best ARE for Pb sorption by fitting of theoretical and experimental sorption capacity even accepted by Ni sorption [22 ,23] which mean that the chemical sorption is the controlled step [24] more than by diffusion across thin layer (film diffusion) where no rapid sorption during short time while good fitting by intraparticle diffusion model for Ni sorption than Pb step even though the pore diffusion is not controlled due to that the line do not pass through the origin [25] as indicator of limiting step by intra particle diffusion is invalided[21]

Conclusion

The results showed that the zeolite 3A can be used to remove Ni and Pb2+ ions from aqueous solutions at pH (6.5 and 5) respectively where are decreasing in sorption capacityand increasing percentage of removal at increasing zeolite 3A dosage with optimum dosage (0.2-0.3) g for Pb sorption at all temperatures and 0.2 g for Ni at 50 C (323 K). The equilibrium isotherm results show good fitting for both ions with Langmuir model while Freundlich model show good application for Pb sorption only.The temperature factor shows clear effect as dependent variable according to the thermodynamic parameters where sorption reaction was endothermic for Ni and exothermic for Pb where increasing temperature lead to increasing negative ΔG for Ni sorption and decreasing for Pb sorption . Kinetic study shows effect of contact time as an dependent factor on the sorption capacity by a good fitting with pseudo second model as a chemical sorption with no limiting step by intra particle diffusion model or pseudo first order models.

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الحراري والدراسة الحركية للنيكل والرصاص بطريقةالامتزاز بواسطةزيوليت التوازن3A

دراسة امتزاز النيكل Ni والرصاص بأستخدام الزيولايت نوع A3 عند تركيز 50 ملغم/لتر مع تغير الدالة الى الحامضيهللوصول الى القيمة المثلى المعتمدة في التجارب الوجبه حيث اجريت تجارب التوازن عند ثبوت الحرارة عند الداله الحامضية (6.5,5) لكل من النيكل الرصاص على التوالي وبتركيز 100 ملغم/ لتر وثبوت جرعة الزيولايت و تغير درجة الحرارة.

اظهرت النتائج تجارب التوازن الحراري تطابق مع موديل لانكمير بالنسبة للنيكل والرصاص بينما كان التطابق موديل فراندلش بالنسبة للرصاص حيث كانت افضل النتائج عند 323 لكن بالنسبة للنيكل و 293 بالنسبة للرصاص على اساس معامل الخطأ ARE بين النتائج النظرية و العملية

اظهرت نتائج تغير درجة الحرارة أن تفاعل ماص بالنسبة للنيكل بينما كانت بالنسبة للرصاص تفاعل باعث للحرارة.

تأثير عامل الزمن من خلال تطبيق تجارب الحركية عند ظروف 100 ملغم/لتر لتركيز المحلول و2.5 غرام من الزيولايت والنمذجة عند فترات زمنية مختلفة وكانت الناتئج تطابق موديل سيدو درجة ثانية اكثر من موديل سيدو درجة اولى للاشارة الى ان الامتزاز هو امتزاز كيمياوي من دون وجود تاثير للانتشار داخل جسيمات حبيبات الزيولايت.