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Removal of Nickel Ions from Aqueous Solutions by Using Insolubilized Humic Acid: Effect of pH and Temperature

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A batch adsorption system using insolubilized humic acid was investigated to remove Ni(II) from aqueous solutions in single component system at different temperature and pH values and at constant ionic strength. The experimental data were fitted to the Langmuir, Freundlich and Redlich-Peterson isotherm models to obtain the characteristic parameter of each model, in order to determine the best fit isotherm for each system. The Redlich-Peterson model was found to well represent the measured adsorption data. The results, which were analyzed by the three models showed temperature and pH dependence. The derived adsorption constants (log a_L) and their temperature dependence from Langmuir isotherm have been used to calculate the corresponding thermodynamic quantities such as the free energy of adsorption, heat and entropy of adsorption. The thermodynamic data indicate that Ni(II) adsorption on to insolubilized humic acid is entropically driven and characterized by physical adsorption.

Key Words: Adsorption, Isotherm models, Insolubilized humic acid, Nickel, Thermodynamic quantities.

INTRODUCTION

The hazard to human life from the effects of various metal ions has received extensive attention in the past twenty years. There are several methods to treat the metal contaminated effluents such as precipitation, ion exchange, adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost treatment. However, these methods are unable to achieve the standards recommended by international water standard bodies[1]. Adsorption processes have been accepted as one of the most appropriate and effective separation processes for a wide variety of applications, for the purification of drinking water and wastewater; it can remove metals over a wider range of pH values and at lower concentration than can alkaline precipitation. The adsorbent used most widely for industrial applications is activated carbon. However, it is an expensive material despite its ability to be regenerated. Since activated carbon is expensive, an alternative inexpensive sorbent able to drastically reduce the cost of a sorption system has always been a subject of research[2, 3]. Therefore, in recent years extensive studies have been undertaken to

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find low-cost adsorbents to remove pollutants from drinking water and aqueous effluents. Heavy metals produced and released during agricultural and industrial activities may pose a serious threat to the environment; they are not biodegradable and tend to accumulate in living organisms, causing various disorders. The sorption of metal ions from aqueous solution plays an important role in water pollution control and in recent years, there has been considerable interest in the use of low-cost natural adsorbents such as humic substances for this purpose[4–14].

Humic substances are widespread in soils, natural waters, rivers and lakes and sea sediments. These macromolecular substances are formed as a product of chemical and biological transformation of animal and plant residues. Humic substances have been shown to be heterogeneous, consisting of numerous oxygen-containing functional groups and fractions (humic acids, fulvic acids and humin) with different molecular weights. Humic acids (HA) are considered natural electrolytic organic compounds of complex structures including condensed aromatic rings with a large number of attached carboxylic and hydroxyl groups. The structure of this biopolymer is still not clearly defined. Humic acids have great capacity to bind metal cations. The binding or complexing of metal ions by humic substances plays an important role in metal toxicity, mobility and bioavailability in the environment. The removal of metal ions from wastewaters has received considerable attention in recent years[15, 16].

Nickel is an essential micronutrient for some marine algae, but micro-molar Ni^{2+} is toxic. However interaction of Ni^{2+} with organic matter has not been much studied for that, the removal of nickel ions from wastewaters has received considerable attention in recent years[17, 18].

The environmental significance of this work is that it elucidates the Ni(II) binding characteristics of insolubilized humic acid (IHA). In the present study, insolubilized humic acid from Al-Azraq was prepared, to avoid the soluble state of this natural HA in alkaline media and to be able to study the adsorption behaviour of this insolubilized Al-Azraq humic acid with nickel at different pH and temperature values. It was found that Azraq Oasis is the richest place in Jordan with humic acid and it is an important environmental site, because it is an important water reservoir, that supplies water to many cities in Jordan[15, 16] . The adsorption behaviour of Azraq HA for heavy metal ions has never been studied before in Jordan. This has encouraged us to carry out this research. This paper forms a part of our research program for studying and developing the adsorption behaviour of these toxic metal ions by using natural matter. The objective of this work is to study the possibility of the IHA from Al-Azraq for the removal of Ni(II) from the aqueous media. Variables of the system include Ni(II) concentration, pH and temperature. Langmuir, Freundlich and Redlich-Peterson isotherms have been compared at pH 4, 5 and 6 to avoid hydrolysis of metal ions and carbonate formation[15, 16, 19].

Adsorption isotherms

The relationships between adsorbent and adsorbate described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium can be described by adsorption isotherms. There are three types of isotherms:

Langmuir isotherm model: Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as

$$q_e = \frac{q_{max} a_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g^{-1}) at equilibrium, C_e is the final concentration in the solution (mg L^{-1}), q_{max} is the maximum adsorption at monolayer coverage (mg g^{-1}) and a_L is the adsorption equilibrium constant which is related (mg g^{-1}) to energy of adsorption (L mg^{-1}).

The above equation can be rearranged in the following linear form

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{a_L q_{max}} \tag{2}$$

The linear form can be used for linearization of experimental data by plotting C_e/q_e *vs.* C_e. The Langmuir constants q_{max} and a_L can be evaluated from the slope and intercept of linear equation[20, 21].

The effect of isotherm shape can be used to predict whether a sorption system is favourable or unfavourable.

According to Hall *et al.*[22], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is defined by the following relationship:

$$K_R = 1/(1 + a_L C_0) \tag{3}$$

where C_0 is the initial concentration of the metal ion concentration in mg/L.

The parameter K_R indicates the shape of the isotherm accordingly.

Values of K_R	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The plateau on each isotherm corresponds to monolayer coverage of the surface by the metal ions and this value is the ultimate sorptive capacity at high concentrations that can be used to estimate the specific surface area (*S*) of IHA using the following equation:

$$S = (q_{max} NA)/M \tag{4}$$

where *S* is the specific surface area, m^2/g of adsorbent; q_{max} is the monolayer sorption capacity (mg g^{-1}); N is Avogadro number, 6.02×10^{23}; A is the cross-sectional area, m^2; M is the atomic weight of the metal[23].

Freundlich isotherm model: Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as

$$q_e = K_F C_e^{1/n} \tag{5}$$

where q_e and C_e have the same definitions as in eqn. (1), K_F is a Freundlich constant representing the adsorption capacity (mg g^{-1}) (L $mg^{-1})^n$ and n is a constant depicting the adsorption intensity (dimensionless). This equation is conveniently used in the linear form by taking the logarithms of both sides as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

A plot of $\ln q_e$ *vs.* $\ln C_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants which are K_F and 1/n can be determined from the slope and the intercept[20, 24].

Redlich-Peterson isotherm: The above models described isotherms with two parameters, but Redlich-Peterson model describes a three-parameter isotherm; its non-linear equation is expressed as follows

$$q_e = \frac{q_{max} a_R C_e}{1 + a_R C_e^{bR}} \tag{7}$$

where q_e and C_e have the same definitions as in eqn. (1), a_R is the Redlich-Peterson isotherm constant (L mg^{-1}) and b_R is the Redlich-Peterson isotherm exponent.

The linearized form of eqn. (7) is

$$\ln\left(K_R\left(\frac{C_e}{q_e}\right) - 1\right) = b_R \ln C_e + \ln a_R \tag{8}$$

Three isotherm constants, K_R, b_R and a_R can be evaluated from the linear plot represented by eqn. (8) using a trial and error optimization method.

At low concentrations, the Redlich-Peterson isotherm approximates to Henry's law and at high concentration, its behaviour approaches that of the Freundlich isotherm[20].

From the first isotherm model, heat of adsorption of Ni(II) on to IHA can be calculated from the temperature dependence of the equilibrium adsorption constant a_L by the Clausius-Claperyon's equation

$$\frac{\partial \log a_L}{\partial (1/T)} = -\frac{\Delta H_{ads}}{2.303R} \tag{9}$$

A plot of $\log a_L$ *vs.* 1/T should be linear with slope equal to $-\Delta H/(2.303R)$ and with intercept equal to $\Delta S/(2.303R)$[25]. These quantities are related *via*

$$-RT \ln a_L = \Delta G_{ads} = \Delta H_{ads} - T\,\Delta S \tag{10}$$

EXPERIMENTAL

Instrumentation

Dissolved metal ion was determined by using atomic absorption spectrophotometer Unicam, model 929. The metal ion was determined with the aid of an air-acetylene flame. The separation of the liquid phase from the solid phase was established by filtration (45 μm) followed by centrifugation using Sigma 2-3 centrifuge. All the samples were shaken on shaker with water bath GFL model 1083. pH-meter Metrohm model 744 and analytical balance Scaltec were used.

The average particle size for IHA was determined by using Fritsch particle sizer 'analysette 22'.

A stock solution (1000 mg/L) of Ni(II) (BDH, AnalaR) was prepared by dissolving an appropriate quantity of the metal nitrate powder in 0.1 M HNO_3 (BDH, AnalaR). The metal ion, Ni(II) stock solution was prepared in 0.1 M $NaNO_3$ (BDH, AnalaR); to keep the ionic strength constant, a range of Ni(II) concentrations from 10 to 120 mg/L were used. The metal ion solution was adjusted to the desired pH by adding 0.1 M NaOH (GCC) and/or 0.1 M HNO_3 solution. The pH was chosen in the range where no precipitation of metal hydroxide takes place.

Preparation of insolubilized Humic Acid

Adsorbent: Humic acid was isolated from O horizon of a soil from the Al-Azraq Oasis, which is located in the eastern desert of Jordan. A detailed description of the method of isolation and purification is given by Khalili[26]. Insolubilized HA was prepared by taking this highly soluble HA and heating it at 330°C for 1 h. The heating caused a too rapid dehydration (condensation) between acidic groups; after heating the HA was treated with 2 M $CaCl_2$ solution and was converted from sodium salt to calcium. The obtained insolubilized HA was ground and washed repeatedly with 1 M HNO_3 solution and with distilled water. The IHA was converted from the hydrogen form to sodium form with 1 M $NaNO_3$ solution and rinsed with distilled water and dried at 80°C. After drying, the average particle size for this IHA was measured to be 63 μm; the IHA was stored in an airtight glass bottle. It was found to be insoluble in water up to pH 10.[5]

Adsorption experiments

With the aim of avoiding any contamination, all glassware used for each experiment was cleaned in detergent first and then soaked with 10% HNO_3 for 24 h and finally rinsed with deionized distilled water. Batch adsorption experiments were conducted by introducing exact volume (10.00 mL) with known initial concentration of Ni^{2+} into glass bottles at an ionic strength of 0.1 M $NaNO_3$ containing accurately weighed amounts (10 mg) of the adsorbent. The concentration of the adsorptive solution ranged between 10–120 mg/L. The glass bottles were shaken by using shaker water bath at constant temperature and pH until adsorption equilibrium was established. The pH of the mixtures was maintained with 0.1 M NaOH and/or 0.1 M HNO_3 solution. All the experiments were performed at five different temperatures 25, 35, 45, 55 and 65°C ± 0.1°C and at three different pH values 4, 5 and 6. The results showed that equilibrium was reached in 24 h. The adsorbent was then removed from liquid phase by filtration followed by centrifugation. The equilibrium concentration of Ni(II) was determined by flame atomic absorption spectrophotometer (AAS). All the experiments were carried out in duplicate and only mean values are presented.

RESULTS AND DISCUSSION

The isotherm is characterized by the initial region, which is represented as being concave to the concentration axis. The isotherm is beginning to reach a plateau, which can be described by the Langmuir isotherm as shown in Fig. 1, at different pH and at different temperatures. The linear experimental isotherm constants were obtained for the sorption of Ni^{2+} onto the IHA for the three adsorption models at both pH 5 and 6. At pH 4 no specific removal of Ni^{2+} was observed and at different temperatures are presented in Tables 1 and 2 together with the correlation coefficient R^2 and are illustrated in Figs. 2–4.

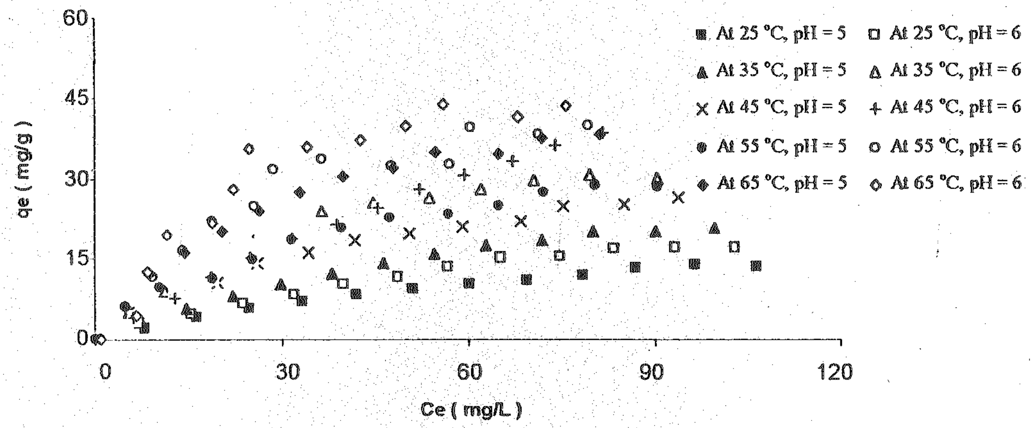

Fig. 1. Adsorption isotherms of Ni^{2+} on to IHA in 0.1 M $NaNO_3$ solution at different temperature and pH values

TABLE-1

CHARACTERISTIC PARAMETERS AND DETERMINATION COEFFICIENTS OF THE EXPERIMENTAL DATA ACCORDING TO THE LANGMUIR, FREUNDLICH AND REDLICH-PETERSON EQUATIONS FOR THE ADSORPTION OF Ni^{2+} ON IHA AT pH 5 AND IONIC STRENGTH 0.1

Temp. (°C)	Langmuir			Freundlich			Redlich-Peterson			
	q_{max} (mg g^{-1})	a_L (L mg^{-1})	R^2	n	KF (L g^{-1})	R^2	q_{max} (mg g^{-1})	a_R (L mg^{-1})	b_R	R^2
25	25.1889 ± 0.0013	0.01111 ± 0.0163	0.9904	1.4725 ± 0.0212	0.6105 ± 0.0846	0.9913	27.4342 ± 0.0019	0.2751 ± 7.E-05	1.0283 ± 2.E-05	1.0000
35	38.7597 ± 0.0014	0.01212 ± 0.0170	0.9524	1.3931 ± 0.0222	0.8443 ± 0.0839	0.9906	34.7493 ± 0.1500	0.2394 ± 0.0359	0.9842 ± 0.0564	0.9713
45	43.1034 ± 0.0011	0.01660 ± 0.0174	0.9785	1.6147 ± 0.0242	1.6758 ± 0.0896	0.9849	50.2109 ± 0.0037	0.1968 ± 7.E-05	1.0151 ± 2.E-05	1.0000
55	47.1698 ± 0.0019	0.01810 ± 0.0207	0.9556	1.6639 ± 0.0280	2.0786 ± 0.1019	0.9788	62.5169 ± 0.0829	0.1610 ± 0.0004	1.0427 ± 0.0013	1.0000
65	52.0833 ± 0.0005	0.03359 ± 0.0217	0.9937	1.7094 ± 0.0329	3.2717 ± 0.1143	0.9693	79.2972 ± 0.0019	0.1461 ± 2.E-05	1 0328 ± 7.E-06	1.0000

TABLE-2
CHARACTERISTIC PARAMETERS AND DETERMINATION COEFFICIENTS OF THE EXPERIMENTAL DATA ACCORDING TO THE LANGMUIR, FREUNDLICH AND REDLICH-PETERSON EQUATIONS FOR THE ADSORPTION OF Ni^{2+} ON IHA AT pH 6 AND IONIC STRENGTH 0.1

Temp. (°C)	Langmuir			Freundlich			Redlich-Peterson			
	q_{max} (mg g^{-1})	a_L (L mg^{-1})	R^2	n	KF (L g^{-1})	R^2	q_{max} (mg g^{-1})	a_R (L mg^{-1})	b_R	R^2
25	32.8947 ± 0.0023	0.01124 ± 0.1378	0.9524	1.2684 ± 0.0342	0.5099 ± 0.1309	0.9524	34.9199 ± 0.0227	0.2245 ± 0.1500	1.0216 ± 0.0693	0.9560
35	51.0200 ± 0.0020	0.0186 ± 0.0850	0.9331	1.4655 ± 0.0388	1.6636 ± 0.1405	0.9686	55.8337 ± 0.0002	0.1717 ± 0.0010	0.9945 ± 0.0003	1.0000
45	–	–	–	1.12777 ± 0.0360	0.8218 ± 0.1246	0.9967	–	–	–	–
55	55.5556 ± 0.0010	0.0316 ± 0.0479	0.9709	1.9008 ± 0.0543	4.3492 ± 0.1939	0.9124	66.4984 ± 0.0052	0.1711 ± 0.0302	0.9722 ± 0.0085	0.9993
65	58.1395 ± 0.0011	0.04203 ± 0.0481	0.9641	2.2065 ± 0.0436	6.5614 ± 0.1583	0.9391	96.8931 ± 0.0164	0.1465 ± 0.1117	1.0461 ± 0.0332	0.9900

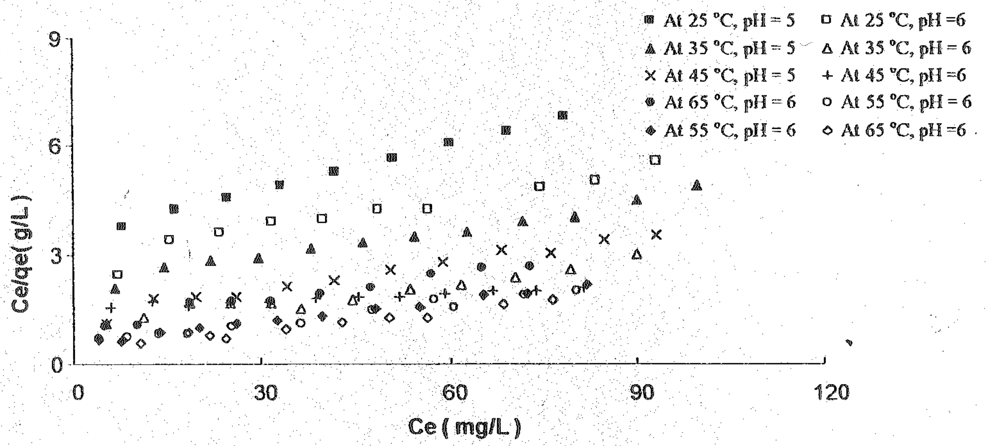

Fig. 2. Langmuir equation isotherms of Ni^{2+} adsorbed on to IHA in 0.1 M $NaNO_3$ solution at different temperature and pH values

Based on the correlation coefficient values for the three adsorption models they were found to be linear over the whole concentration range with high correlation coefficient values, which suggest that these isotherms provide a good model of the sorption system. It is clear that the Redlich-Peterson isotherm has best fit for the sorption of Ni^{2+} on IHA at various temperatures and pH. The equilibrium adsorption constants q_{max} and a_L were obtained by the least-square fit and were found to be increased by increasing temperature and pH values. The Langmuir isotherm is applicable to homogeneous sorption, where each nickel ion and IHA sorption process has equal sorption activation energy and it is applied to monolayer adsorption processes. The values of K_R for Ni^{2+} at different temperature and pH values are shown in Fig. 5.

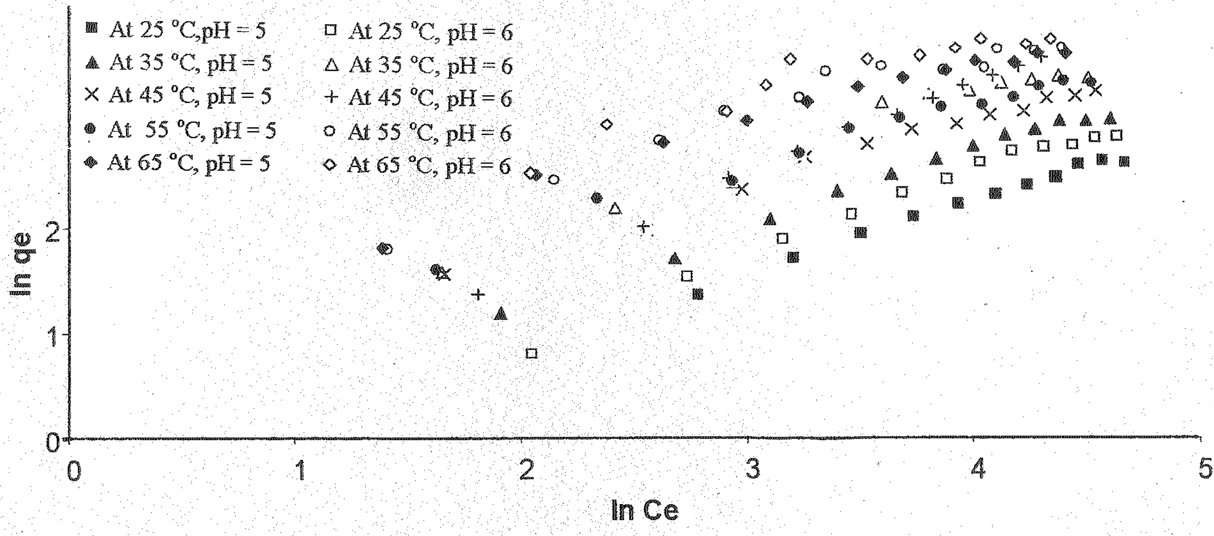

Fig. 3. Freundlich equation isotherms of Ni^{2+} adsorbed on to IHA in 0.1 M $NaNO_3$ solution at different temperature and pH values

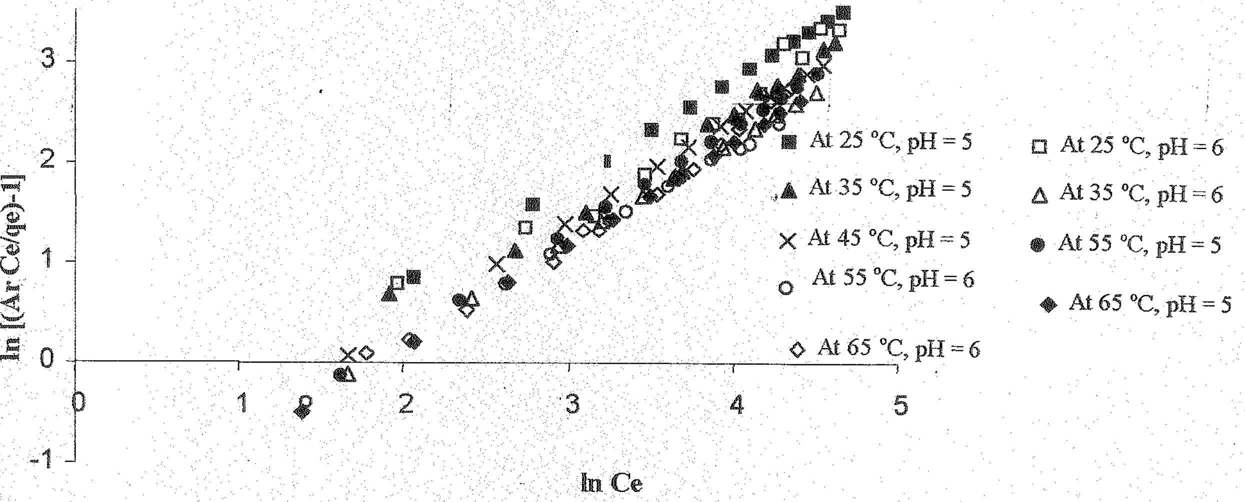

Fig. 4. Redlich-Peterson equation isotherms of Ni^{2+} adsorbed on to IHA in 0.1 M $NaNO_3$ solution

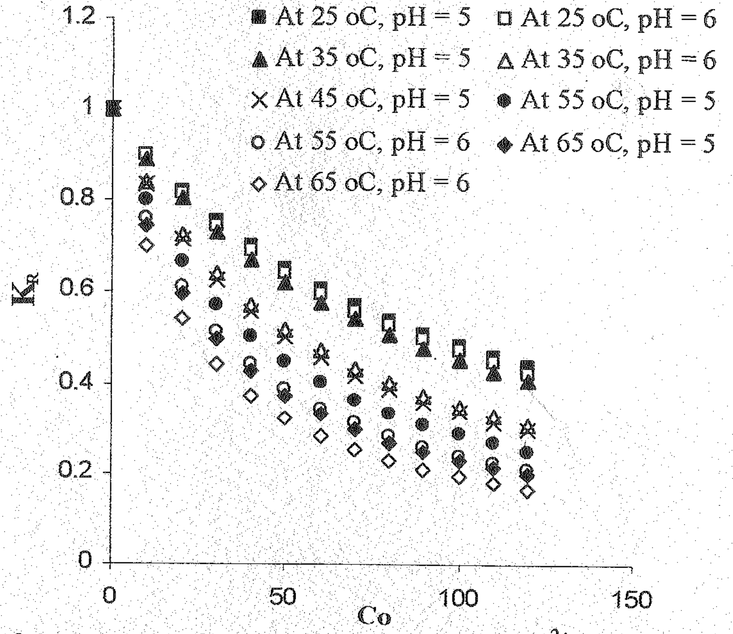

Fig. 5. Values of the separation factor, k_R for the sorption of Ni^{2+} by using IHA at different temperature and pH values (I = 0.1)

The K_R values indicate that adsorption was more favourable for the higher initial metal ion concentrations than the lower ones. However, the adsorption process became more favourable with increasing temperature and by increasing the pH. From Fig. 5 it was shown that the IHA would be an effective adsorbent for the removal of Ni^{2+} from aqueous solutions under the conditions that were used in this study. The linear isotherm constants K_F and 1/n for the Freundlich isotherm were also determined by the least-square fit, which are presented in Tables 1 and 2 (Fig. 3). The correlation coefficient values calculated in this case are high. In the case of the Freundlich isotherm, which is known to be applied to multilayer adsorption, the affinity of the adsorbent for metal ion can be measured by the parameter K_F. It was found that the values obtained for K_F follow the same order as those obtained for the maximum adsorption capacity when using Langmuir model. The examination of the plot suggests that the linear Freundlich isotherm is a good model for the adsorption of Ni^{2+} by knowing the R^2 values at both pH 5 and 6; it seems that at higher pH value there will be just one adsorption site[20, 27-31]. It was noticed that there is almost a positive correlation between the values of l/n with increasing the pH and the temperature. The lower value of l/n signifies that the forces which are exerted on the surface of the IHA during Ni^{2+} adsorption are weak. The Freundlich constant n also indicates the degree of favourability of adsorption; n should have values lying in the range of 1–10 for classification as favourable adsorption[32]. From the values of n that are reported in Tables 1 and 2 it was observed that n lies in this range.

The results, which are summarized in Tables 1 and 2 (Fig. 4) for the Redlich-Peterson equation, which incorporates both Langmuir and Freundlich isotherms, applies at low and moderate initial concentrations. The values of R^2 in both Tables 1 and 2 show that the Redlich-Peterson isotherm could describe the sorption behaviour of Ni^{2+} on to IHA surface over the concentration ranges studied; q_{max} represents the maximum adsorption per unit weight of adsorbent, not restricted to a monolayer of molecules as it was in the Langmuir isotherm. The Redlich-Peterson model considers, like the Freundlich model, heterogeneous adsorption surfaces as well as the possibility of multilayer adsorption. The b_R values should lie between 0 and 1 as we can see from Tables 1 and 2 that b_R nearly lies in this range. When $b_R = 1$, the Redlich-Peterson equation converges with the Langmuir isotherm[20, 28, 29]. Values of q_{max} calculated using the Redlich-Peterson isotherm show the same metal-IHA affinity order that was deduced from the application of Langmuir and Freundlich models. By calculating specific surface area (S) from eqn. (4), it was found that the value of S increases by increasing temperature and pH as shown in Table-3 which means that as the surface of adsorption increases, the capacity of the monolayer increases.

Effect of pH

The pH value of the solution is an important factor, which must be considered during the sorption studies. It is apparent that the adsorption capacity of Ni^{2+} increases by increasing the pH value as shown in Tables 1 and 2 for the three models at both pH 5 and 6. At pH 4 the results are not reported because there is no significant adsorption at this value of pH. Solution pH affects both IHA surface metal binding sites and the metal chemistry in water. At low pH value, the surface of the adsorbent is closely associated with H_3O^+. The surface of the IHA becomes positively charged and repulsive forces limit the approach of the metal ions[18, 33–35]; when pH increases, more protons are greatly combined with OH^- to produce H_2O. Free Ni^{2+} ion, which is $[Ni(H_2O)_6^{2+}]$ species, is present in the solution[36]. The increase in adsorption of Ni^{2+} is probably due to cation hydrolysis such as $Ni(OH)^+$. The affinity of this metal ion to the IHA surface can mainly be determined by the ability of this metal ion to form metal hydroxide species as shown in the following reaction.

$$Ni^{2+} + H_2O \rightleftarrows NiOH^+ + H^+$$

TABLE-3
SPECIFIC SURFACE AREA FOR Ni^{2+} AT DIFFERENT TEMPERATURES AT pH = 5 AND 6, IONIC STRENGTH 0.1

Temp. (°C)	pH = 5	pH = 6
	S (m^2/g of IHA)	S (m^2/g of IHA)
25	4.4411	5.7997
35	6.8337	8.9953
45	7.5996	–
55	8.3165	9.7950
65	9.1828	10.2510

The pK_1 which expresses the ability of the metals to form metal hydroxide species for the above reaction is 9.86 for zero ionic strength and 25°C can be taken as relative measures of the metal affinity for the oxide surface[37].

Since hydroxy complexes are adsorbed preferentially over uncomplexed cations[38], the basic structural units of humic acid are aromatic rings and alkyl chains contain a wide variety of functional groups (—COOH, —COH, —NH_2, etc). As the pH increases, more of these functional groups are exposed and carry negative charges with subsequent attraction of positively charged Ni^{2+}. These groups can bind strongly to metals and give humic acid a high adsorption capacity for metals; at higher pH the IHA surface starts to acquire a net negative charge creating a situation electrostatically favourable for higher adsorption of Ni^{2+} due to the increase in the concentration of hydroxyl ions[15, 39–41]. The higher the pH, the greater will be the dissociation of the functional groups —COOH and —COH to —COO^- and —CO^-. In such case adsorption occurs by electrostatic attraction of the negative charges with Ni^{2+} and the hydroxy cations[42–44].

When $Ni(OH)^+$ is formed, the adsorption process is rapidly completed by the interaction with the negative charge on the ionized phenolic and carboxylic groups on the IHA surface (≡IHA) and the mechanism of adsorption of Ni^{2+} onto IHA can be represented by the following surface complexation reactions:

$$\equiv IHACO^- + Ni(OH)^+ \longrightarrow \equiv IHACONiOH \qquad (I)$$

$$\equiv IHACOO^- + Ni(OH)^+ \longrightarrow \equiv IHACOONiOH \qquad (II)$$

Thermodynamic evaluation of the adsorption process

The adsorption mechanism (*i.e.*, chemical or physical) is often an important indicator to describe the type and level of interactions between the adsorbate and absorbent. If adsorption decreases with increasing temperature, this may indicate a physical adsorption and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in literature[45]. Nevertheless this is not sufficient to determine the type of adsorption. The type of adsorption may be determined through such thermodynamic quantities as ΔH_{ads}.[46] The adsorption process is composed of two contributions, enthalpic and entropic, which characterize whether the reaction is spontaneous. Examination of Table-4 and Fig. 6 reveals that ΔH_{ads} values, which are calculated from the Langmuir's equilibrium constants, are positive (indicative of the endothermic nature of the adsorption process for the present system). At the two pH values, the ΔH_{ads} values are smaller than the lower limit of chemisorption which is 42.0 kJ/mol, which means that the type of sorption of nickel on to IHA is physisorption (electrostatic attraction), rather than by chemical bonding. However, the free energy values (ΔG_{ads}) are very small and positive and decrease by increasing temperature; this indicates that better adsorption is obtained at higher temperature. Entropic contribution is even larger than the free energy of adsorption. Therefore, it is posible to say that the adsorption of Ni^{2+} on to IHA is entropically governed due to some structural changes in the adsorbent during the adsorption process[47–51]. The positive value of entropy reflects the affinity of the adsorbents for Ni^{2+} and

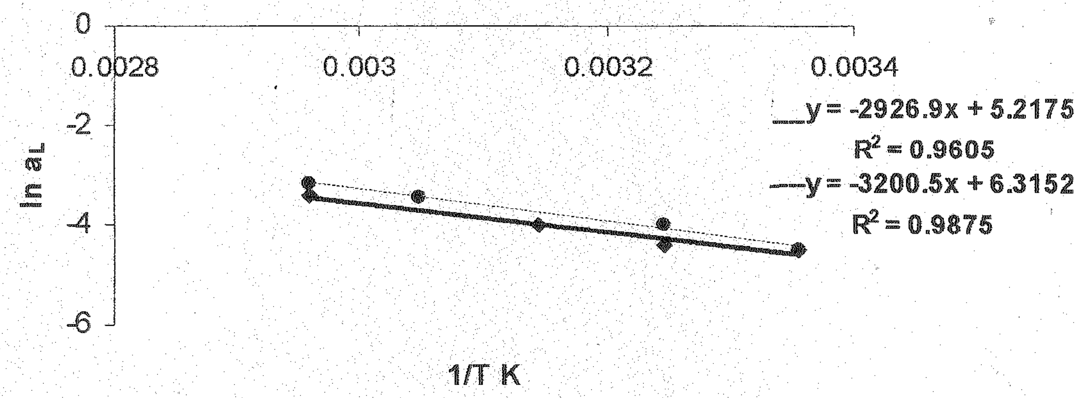

Fig. 6. Temperature dependence of log a_L for Ni-IHA, I = 0 (◆ pH 5; • pH 6)

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE REMOVAL OF Ni^{2+}
BY ADSORPTION ON TO IHA AT 298 K, pH 5 AND 6, IONIC STRENGTH 0.1

pH = 5			pH = 6		
ΔG (kJ eq^{-1})	ΔH (kJ eq^{-1})	ΔS (J eq^{-1} K^{-1})	ΔG (kJ eq^{-1})	ΔH (kJ eq^{-1})	ΔS (J eq^{-1} K^{-1})
11.1489 ± 0.0404	24.3342 ± 3.489	43.3783 ± 11.0945	11.1200 ± 0.3414	26.6090 ± 2.1182	52.5046 ± 6.6857

suggests some structural changes in Ni^{2+} and adsorbent. In addition, positive value of entropy shows the increasing randomness at the solid/liquid interface during the sorption of nickel on the IHA.

Conclusions

Nickel is regarded as one of the highly toxic metals in the environment. The removal of Ni^{2+} by the IHA was investigated by batch adsorption techniques. The interaction of Ni^{2+} with IHA has been performed under different temperatures and pH values by using three different isotherm models, Langmuir, Freundlich and Redlich-Peterson isotherms. Adsorption of Ni^{2+} is pH and temperature dependent and the regression analysis showed that the experimental data obtained in IHA-metal system fitted closely the Langmuir and Freundlich and Redlich-Peterson isotherms. It was found that the best correlation from these three models was obtained for Redlich-Peterson equation at pH 5 and 6. It was found that the capacity of adsorption increases by increasing the temperature and pH values.

The data obtained from adsorption isotherms at different temperature and pH values were fitted to Langmuir isotherm model to calculate thermodynamic quantities ΔG_{ads}, ΔH_{ads} and ΔS_{ads} .The results indicate that Ni^{2+} adsorption on to IHA is non-spontaneous, physical in nature and with entropy driven force. From these thermodynamic quantities, it was found that Al-Azraq humic acid is a suitable, low-cost adsorbent for the removal of Ni^{2+} from aqueous solution.

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