

Study of Adsorption ability for (Bis-(acryloylamino-methyl)-Phosphinic acid) toward Ni (III) ion
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Abstract

Study of the adsorption of nickel ion (II) with Bis-(acryloylamino-methyl)-Phosphinic acid from its aqueous solution at pH 6 was performed. The effect of different parameters such as temperature and pH values wear evaluated. It was observed that the rise in temperature decrease the adsorption of nickle ion (exothermic). The applicability of the Freundlich model for the data was tested, and the best media was at pH 6. Various thermodynamic quantities namely ΔH , ΔS and ΔG were computed from the equilibrium constant values.

Keywords: phosphinic acid; complex; nickel (II); adsorption; thermodynamic parameters.

الخلاصة

تمت دراسة الامتزاز لايون النيكل الثنائي من محلوله المائي بواسطة الكاشف Bis- (acryloyl-amino-methyl)-Phosphinic acid) تمت دراسة تاثير كل من درجة الحرارة والدالة الحامضية. بينت الدراسة ان عملية امتزاز ايون النيكل الثنائي تقل بزيادة درجة الحرارة (عملية باعثة للحرارة). كما بينت الدراسة ان ايزوثيرم امتزاز ايون النيكل مع الكاشف يطابق معادلة فريند لش وان افضل وسط لامتزاز ايون النيكل هو عند الدالة الحامضية pH 6 . تم حساب قيم الدوال الترموديناميكية الاساسية مثل قيم الانثالبي ΔH , الانتروبي ΔS وطاقة كبس الحرة ΔG من معرفة قيمة ثابت الاتزان.

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Introduction

Adsorption on solid surfaces is a complex phenomenon. Most catalytic surfaces are not uniform. They consist of sites with abroad distribution of adsorption energies and irregular surface patterns. The density of sites may be extremely low or so high as to form a continuum. The adsorbed molecules may be mobile or immobile. They may be independent of each other or they may interact with their nearest neighbors or even with more distant ones, and, as a result, undergo phase transformations. The forces binding foreign molecules to a surface may be physical Vander Wall's attraction forces and the forces developed by dipoles and ions as they approach surfaces; or they may be equivalent to the forces in chemical bonds involving molecular orbital overlap^[1]. Gonzalez and M.Streat [1983]^[2] studied uranium sorption in phosphoric acid solution using levestrel resins containing DEHPA: di (2-ethylhexy) phosphoric acid and TOPO: tri n-octylphosphine oxide based on the homogeneous diffusion model. They indicated that the particle diffusion is rate controlled. R.S Juang have reported

[1999]^[3] preparation, properties, and sorption behavior of impregnated resins containing acidic organophosphorus extracts. Macroporous resins for the recovery and selective separation of Cu^{II} and Zn^{II} ions is studied.

Kazunori and co-workers [2001]^[4] clarify the metal ion selectivity of the phosphonic acid resin named RSPO, in which the functional groups were introduced into phenyl groups of macroporous poly(styrene-co-divinylbenzen) matrix, the distribution of kinds of metal ions from (0.0001 mol/l) solution of each metal ion onto RSPO was studies in nitric acid, hydrochloric acid, sulfuric acid and phosphoric acid. Soon Woo and co-worker's [2002]^[5] have reported the separation of zinc ions from aqueous solutions using modified silica impregnated with CYANEX 272(di-2,4,1,4,-trimethylpentyl phosphonic acid).

CYANEX 272 was immobilized on a silica surface after it was treated with dichlorodimethylsilane and chlorotripropylsilane. The resulting absorbent prepared showed an excellent selectivity for zinc ion in aqueous solutions and was stable under acidic conditions. Shiau Yeh and co-workers [2005]^[6] have reported adsorption equilibrium of zinc ions from aqueous sulfate solution on Amberlite XAP-2 resins impregnated with extratant Cyanex 272 as adsorbent. The effect of parameter such as modifier addition, solution pH, ionic strength, and temperatures on the sorption equilibrium was examined by batch

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experiments. The adsorption was also conducted in a column operation. The loaded Zn in the column can be completely and rapidly recovered by stripping with 1.0 M HNO₃.

T.Ogata and co-workers [2006]^[7] reported the synthesis of hydrogel beads having phosphonic acid groups and its adsorption ability for Lanthanide ions.

Experimental

Chemicals

Reagent grade, commercially available, chemicals were used with out further purification. Nickel (II) chloride hexa hydrate (1000mg/L), 37% hydrochloric acid and triethylamine are used in this work .The ligand H₃L¹ (Bis-(acryloylamino-methyl)-phosphinic acid has synthesis via Mannich reaction from the reaction of paraformaldehyde and acrylamide with phosphinic acid at reflux temperature in under nitrogen atmosphere^[8].

Preparation of the adsorption surface

The ligand Bis-(acryloylamino-methyl)-phosphinic acid was washed with excessive amount of deionized water to remove the soluble materials, then dried and grounded at particle size of nearly (200) μm by using Laser diffraction particle size analyzer, Shimadzu SALD-2101.

Preparation of the standard stock solution of Nickle (II) Chloride

A standard stock solution of Nickel (II) (1000 mg/L) was prepared by dissolving (2.02g) of NiCl₂.6H₂O in (3ml) HCl (37%). The volumetric flask (500) mL was completed to filled mark with deionized water. Metal content was determined by an Atomic Adsorption Spectrophotometer ion(Shimadzu (A.A) 680G atomic).

Effect of pH

The effect of the pH initial solution on nickel sorption onto Bis-(acryloylamino-methyl)-phosphinic acid was studied at room temperature by varying the pH between 2.0 and 7.0 using HANNA pH211, as it show in Table (1).

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Equilibrium times of adsorption system

The time that is sufficient for the adsorption process to reach equilibrium at certain temperature was determined according to the following procedure: Volume of (10 ml) of an initially fixed concentration (50 ppm) of Ni(II) solution was shaken with (0.05g) of adsorbent at specified temperature 25°C using Thermo-stated shaker bath GCA/precision scientific Chicago, U.S.A. The concentration of Ni (II) ion solution was determined by atomic absorption at (5, 10, 15, 30, 45, 60, 75 minutes) until reaching equilibrium.

Adsorption isotherm

To determine the adsorption isotherm for Ni(II) solution on adsorbent surface the following procedure was carried out :-

(10ml) of Ni(II) aqueous solution of known concentration (2, 4, 8, 10 and 12 ppm), were added separately to volumetric flasks containing (0.05g) of the ligand at particle size of nearly (200) μm . At a certain temperature, the flasks were shaken in a thermostatically controlled shaker at a speed of (60 cycle per minute). For the required equilibrium time at pH6.

After the equilibrium time elapsed, the mixtures were allowed to settle and the clear liquids were filtered using filter paper (Whitman no. 50).

The metal solution was prepared as mentioned, and the Equilibrium concentrations were obtained by the used manner of comparing the experimental data with the calibration curve. The amount of metal ion adsorbed was calculated from the initial and final concentrations and the volume of solution. According to the following equation:-

$$X/M = V(C_o - C_e)/M$$

Where:

X= The quantity adsorbed (mg)

V= Volume of solution (L)

C_o= Initial concentration (mg/L) of metal ion.

C_e=Equilibrium concentration (mg/L)

M=Weight of adsorption (g) (ligand)

Adsorption uptake is expressed by the ratio **X/M** or **Q_e** which is defined by the quantity of adsorbate in (mg) held by (0.05 g) of surface

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Effect of temperature

Similar adsorption experiments were performed as mentioned at temperature (25, 50 °C) to estimate the basic thermodynamic functions.

Results and Discussion

Effect of pH

The results described in table(1) show that the sorption of nickel increases as the pH increases (Fig.1), from a low value of 7% at pH 2 with maximum of 66% at pH 6 and above that precipitation was noted, therefore pH 6 was selected for this study.

Equilibrium times of adsorption system

The time that is sufficient for the adsorption process to reach equilibrium at 25°C have been studied. This study shows that the time needed for pair adsorbent-adsorbate to attain equilibrium is (1) hr.

Adsorption process of Ni (II)

The adsorption of Ni (II) from aqueous solutions on the adsorbate surface has been studied initially at room temperature (25°C) as well as 50°C.

Table (2) shows the related results by the equilibrium concentration (C_e) and the quantity adsorbed on the ligand (Q_e).

Adsorption isotherm

Some adsorption isotherm may be interpreted as a combination of chemical and physical adsorption curve. However, no simple, or even complex explanation can be expected for the shapes of all adsorption isotherm^[9]. The shape of isotherm can be used to diagnose the adsorption mechanism and the nature of adsorption.

It is normally assumed that adsorption from solution is a continuous function of the concentration of the solution^[10]. Molecular interaction of the solution components with the adsorbent and with each other in the surface and bulk solutions affect the shape of the isotherm of adsorption from solution in a manner. If the nature of the interaction of the solution components with the adsorbent is similar, adsorption selectivity is not high.

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The general shapes of Ni(II) adsorption isotherm is shown in Fig.(2) , where the quantities adsorbed on the ligand (Q_e) are plotted as a function of equilibrium concentration (C_e) at 25 and 50°C.

The shape of the isotherm of the Ni (II) on the ligand Bis-(acryloylamino-methyl) phosphinic acid was consistent with (S-type) on the Giles classification shown in Fig.(1). The S curve depending on Freundlich adsorption isotherm principles. This isotherm comes true with heterogeneous surfaces, so that the adsorption occur from different forces on different parts of the surfaces.

The ligand Bis-(acryloylamino-methyl) phosphinic acid have different binding sites, represented by the phosphinate group besides amino group. In acidic media, the ligand has the ability to bind metal ions through phosphinate group, while amino group still protonated. In neutral and basic media the ligand can binding through the phosphinate and amino group depend on the properties of the central ions. Besides, the ions differ in their soft/hard character and these results in different binding ability towards phosphinate.^[11]

The results showed an increase in adsorptive capacity of the ligand as the concentration of metal ions increased. Considering the hard/ soft character of ions and ligand, it is well known that the phosphinate group is a hard donor. On the other hand at pH 6 the metal ions have three species present in solution as suggested by Elliot and Huang⁽¹²⁾

1. M^{+2} (in very small quantity)
2. $MOH^- = M(OH)_2$ (in large quantity)

These species are adsorbed at the surface of the ligand either by ion exchange mechanism or by hydrogen bonding^[13].

Plotting of $\log C_e$ against $\log Q_e$ as shown in Fig. (3) for Ni(II) , give a straight line indicating that the data follow Freundlich equation. The constants of Freundlich equation are listed in Table (3) for Ni(II). The intercept K_f gives a measure of the adsorption capacity and the slope $1/n$ is an indicator for the intensity of adsorption.

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Effect of temperature

The effect of temperature on the adsorption extent of Ni (II) on the ligand Bis-(acryloylamino-methyl)-Phosphinic acid has been studied, at (25 and 50 °C).

The results showed decreased in the amount of ions with increasing temperature; hence the adsorption process appeared exothermic ^[14]. This corresponds to weakening of the attractive forces between the solute and the solid surface with increasing temperature.

Thermodynamic Parameter

The study of the **0.01** temperature effect on adsorption will help in evaluating the basic thermodynamic function (ΔH , ΔS , ΔG) of the adsorption process.

The equilibrium constant (K) for the adsorption process at each temperature was calculated from the equation ^[15] at (25) and (50) °C.

$$K = Q_e \cdot 0.05 / C_e \cdot 0.01$$

Table (4) listed the values of (K) equilibrium for Ni(II) at 25 and 50 °C

The enthalpies (ΔH) of adsorption of Ni(II) was calculated from the equation:

$$\ln [K_2/K_1] = -\Delta H^\circ / R [1/T_2 - 1/T_1] \dots \dots \dots (4-2)$$

The free energy for adsorption (ΔG) can be calculated from the equation:

$$\Delta G^\circ = -RT \ln K_{eq} \dots \dots \dots (4-3)$$

To get entropy values (ΔS), we follow Gibbs equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (4-4)$$

Table (6) shows the basic thermodynamic values of Ni(II) adsorption on the ligand surface.

The enthalpy of adsorption (ΔH) [Ni -ligand] systems was found to posses negative values indicating exothermic adsorption process ^[16], on the other hand the free energies was found positive values indicating that the process was non spontaneous. The function ΔS of Ni(II) adsorption on the surface of the ligand was found to be negative values, and shows that some structural exchange may occur between the active sites of the sorbent and metal^[17] .

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Table (1) The effect of pH values on the percentage quantity of adsorbate

pH	2	4	5	6	7
Qe%	7	23	38	66	58

Table (2) Adsorption value of Ni (II) on the ligand at two different temperatures

25°C						50°C	
No	C°	C _e (mg/L)	Log C _e	Q _e (mg/g)	Log Q _e	C _e (mg/L)	Q _e (mg/g)
1	2	1.25	0.25	0.15	-0.82	1.5	0.10
2	4	3.8	0.57	0.04	-1.39	3.2	0.16
3	6	5.5	0.74	0.1	-1.00	5	0.20
4	8	6.6	0.81	0.28	-0.55	6	0.40
5	10	8.6	0.93	0.28	-0.552	7.9	0.42
6	12	10.3	1.01	0.34	-0.46	9.9	0.42

Table (3) The Freundlich constants of k_f and 1/n

adsorbent	Ni		
[H ₃ L ¹]	k _f	1/n	R ²
	0.0501	1.424	0.299

Table (4) K_{eq} values for Ni (II) at 25 and 50C°

Ni		T C°
K ₁	0.165	25
K ₂	0.212	50

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Table (5) thermodynamic function of adsorption process of Ni (II) on the ligand surface at (25) and (50)°C.

Ion	ΔH° kJmol ⁻¹	ΔG° kJmol ⁻¹	ΔS° Jmol ⁻¹ k ⁻¹	T C°
Ni	-8.013	4.462	-41.06	25
		4.162	-37.68	50

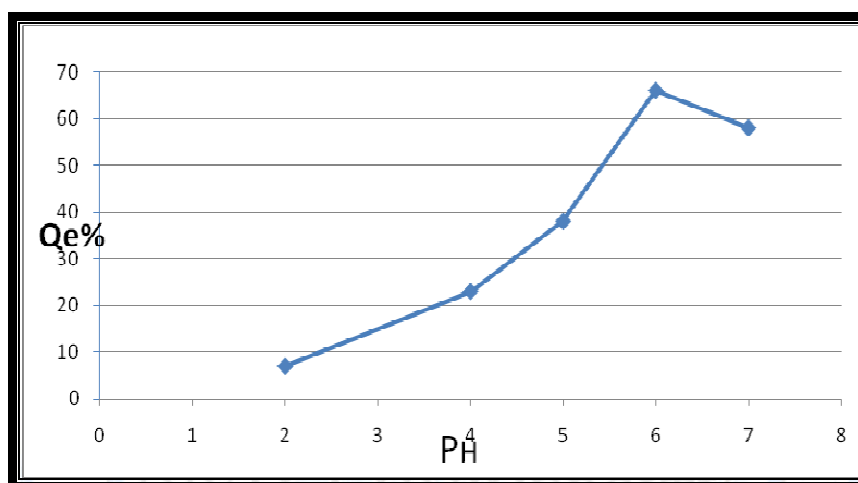


Fig.(1) The effect of pH

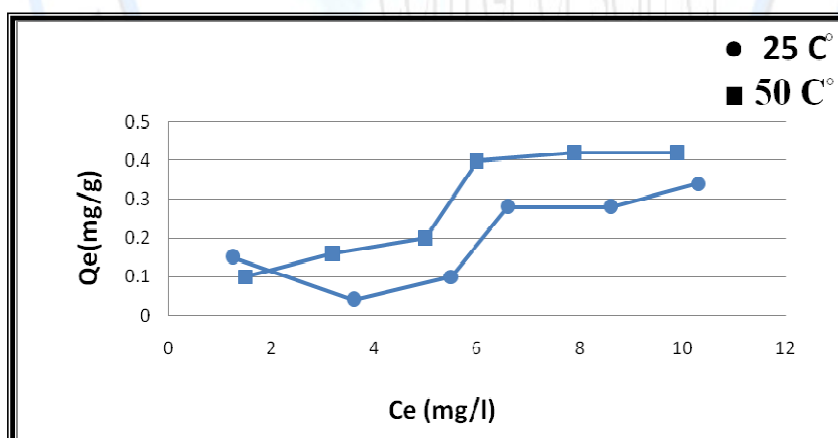


Fig (2) Adsorption isotherm of Ni (II) on the ligand at 25°C and 50°C

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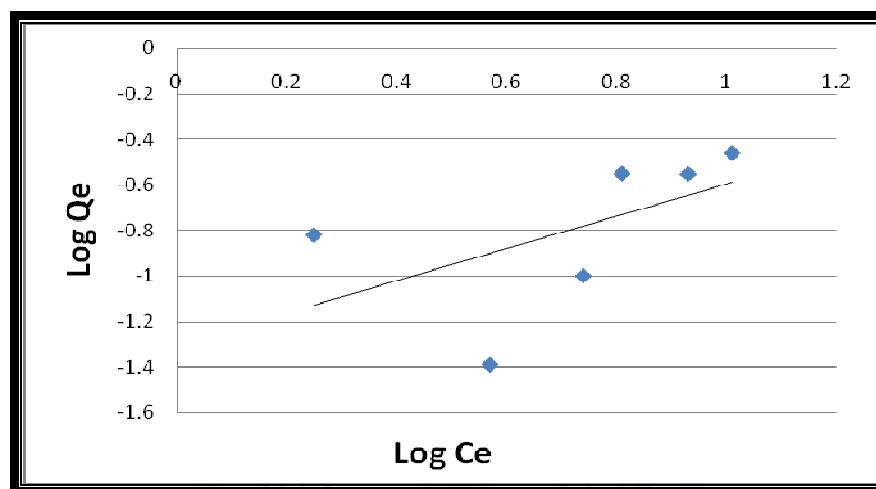


Fig. (3) Linear plot of Freundlich equation of the adsorption of Ni (II) on the ligand surface.