

# Synthesis characterization and adsorption study of new resin PVC8-hydroxyquinoline-5-sulfonic acid with toxic metals

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**Abstract:** A new chelating copolymer (8HQ-pvc) was prepared through condensation reaction of 8-hydroxyquinoline -5-sulphonic acid with poly (vinyl chloride) in the presence of pyridine as catalyst. This newly developed resin (8-HQ-pvc) has been used to prepare a series of six polymeric chelates by using Cr(III), Co(II), Ni(II), Cu(II), Cd (II) , Hg(II) and Pb(II) ions. Both the parent chelating resin and its metal chelates have been systematically investigated in detail to elucidate the chemical structure by micro elemental analysis and spectral methods(IR,  $^1\text{H}$  -  $^{13}\text{C}$  NMR, and Uv-Vis) spectra, as well as the isometric studies to deduce the average molecular weights of repeated unit in polymeric metal complexes.. In addition to these magnetic susceptibility measurements of the solid metal complexes of PVC-8HQ and the molar conductance of thier solutions in DMSO solutions have been measured to investigate the stereo chemical structures. The chemical structure of metal chelates on the basis of elemental and IR data suggests that the bi dentate (8HQ-pvc) resin coordinate to metal ions through oxygen atom of SO<sub>3</sub>-H group by replacing H atom and nitrogen of the quinolone ring. Ion exchange properties of the newly resin were studied for Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> ions in aqueous solutions. Batch equilibrium method was employed over wide PH range and interval times and showed that PVC-8HQ resin showed a higher selectivity toward Cr<sup>3+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions.

**Keywords:** PVC, Chelating Properties of Resin and 8-Hydroxyquinoline

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## 1. Introduction

Selective chelation of specific metal ions to bring specific properties to the modified material, such as enhanced thermal stability, multiphase physical responses, compatibility, impact response, flexibility, and rigidity is a field of active research<sup>(1)</sup>. A number of ligands including polydentate amines, crown ethers, phosphates and bipyridines have been bound with mainly poly(styrene-divinylbenzene)copolymers<sup>(2)</sup>.

These studies are mostly concerned with ion-binding and catalytic aspects. Very little Synthesis of polymer-bound chelating ligands and the information appears to exist as to whether, and to what extent, such organic compounds can influence the properties of the macromolecule<sup>(3)</sup>. Recently, scientists were able to modify PVC, one of the most versatile plastics , by introduction aromatic and heterocyclic moieties

through halogen displacement reaction . PVC, thus modified, showed improved overall photochemical stability and optical properties<sup>(4)</sup>. A number of ligands including polydentate amines, crown ethers, phosphine and bipyridines have been bound with mainly poly (styrene-divinylbenzene)<sup>(5)</sup>. The facial chlorine displacement from PVC indicated the possibility on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes<sup>(6)</sup>. This article will describe the modification of PVC with anchoring ligand and study its optical properties.

Contamination of water resources by heavy metals has been serious environmental worldwide problem. Heavy metal pollution exists in waster effluents of many industries such as metal plating facilities .fertilizer industry, mining operations tanners, paints and pigments. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders<sup>(7)</sup>. It is

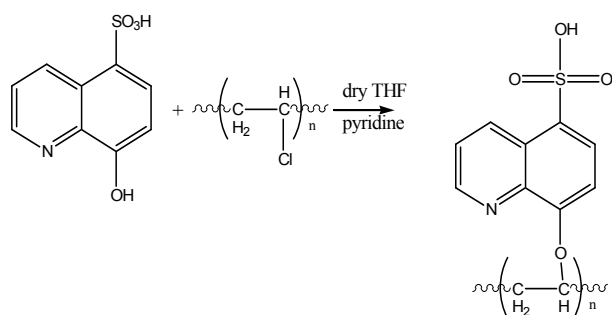
also known that heavy metals are carcinogenic. Therefore it is necessary to treat such toxic metals containing wastewater before discharging<sup>(8)</sup>. Among the conventional methods to remove heavy metals from wastewater include chemical precipitation, ion-exchange, membrane filtration, the adsorption has attracts attention as the results of new material type, available for the application of heavy metal removals. The adsorption involving chelation of metal ions to functional groups of adsorbent is a very efficient way to inactivate and remove metal ions and chelating resins characterization by functional groups containing O, N and / or S and P donor atoms coordinate to different metal ions<sup>(9,10)</sup> have been widely studied mostly by experimental methods modification of polymers such as polymethylmethacrylate polystyrene, PVC with derivative having heterocyclic ring or functional groups (isomethine C=N, hydroxyl groups -OH- and others.) will be helpful to act as chelating resin for toxic metals<sup>(12,13)</sup>. R. N Singru and co-worker<sup>(14)</sup> have been established new resin modified from poly(vinyl chloride) with 1,3,5-Tris(8-quinolin-ox-methyl)-2,4,6-trimethylbenzene, as ion selective electrode.

The present paper explored the newly eco-friendly synthesized polymer resin-pvc-8-hydroxy-quinoline-5-sulphonic acid (PVC-8HQ) in the light of its chelating properties on the basis batch equilibrium method towards Pb(II), Cd(II), Hg(II), Ni(II), Cr(III) and Cu(II) ions.

## 2. Experimental

The chemical 8-hydroxyquinoline-5-sulphonic acid and purified PVC by tetrahydrofuran (T.H.F.) and absolute ethanol are AR grade and chemically pure which is purchased from Fluka. Solvents like dry THF, Ethanol, *N,N*-dimethylformamide were used without distillation. 8-Hydroxyquinoline-5-sulphonic acid (0.04 mole, 8.44 gm) was suspended in dry THF (50 ml) and added to (0.5 gm, 0.04 mole) of poly(vinyl chloride), and three drops of pyridine in (25 ml) THF. The mixture was refluxed for about 6 hrs. until pale yellow precipitate of new resin formed, then filtered and washed with T.H.F. and finally ethanol to afford 80% yield of the resin, scheme (1),

The physical data of the prepared PVC-complexes are found in Table (1).



**Scheme (1).** Synthesis of p.v.c-8HQ-resin

## 3. Synthesis of PVC Ligand Complex

A general procedure can be adopted for the preparation of all the metal complexes as follows: PVC-L-MII complexes were obtained by dissolving 0.5 mole of the appropriate transition metal salt in ethanol and dissolving 1.5 mole of PVC-L dissolved in THF, colored precipitates were obtained then the precipitate was filtered, washed with excess of absolute ethanol. Scheme (1) shows reactions for the synthesis of PVC-L-MII polymer<sup>(15)</sup>.

## 4. Characterization of Modification Co Polymers and their Metal Complexes

Electronic absorption spectrum of resin in DMSO (spectroscopic grade) and metal chalets solutions were recorded on Shimadzu double beam spectrophotometer in the range of 200-800 nm. Infra-red spectra of 8H-Q-PVC resin and its metal chalets were recorded on Shimadzu 1601 pc spectrophotometer. F.T.IR on KBr and CsI. Pellet, region of 4000-400 cm<sup>-1</sup>. Nuclear magnetic Resonance (NMR) spectra of newly synthesized resin (PVC-8HQ) have been scanned on Bruker Advanced 400 NMR spectrometer using CDCl<sub>3</sub> at Al-Bait University, Jordan.

## 5. Ion-Exchange Properties

The ion exchange properties of the 8H-Q-PV resin have been determined by the batch equilibrium method<sup>(16)</sup>. 8-Hydroxyquinoline-PVC was prepared and transformed to suitable grains after motorized.<sup>(17)</sup>

## 6. Adsorption Experiments

Batch adsorption experiments were conducted in 100 ml flasks, each of which contained (250-1500) ppm of metal solution prepared with, Cd(NO<sub>3</sub>).4H<sub>2</sub>O, Cr(NO<sub>3</sub>).3.9H<sub>2</sub>O and Cu(NO<sub>3</sub>).2.2H<sub>2</sub>O. A 0.25 gm amount of 8HQ-PVC resin was added into a flask, containing all contents shaken in a thermostatic water-bath shaker operated at 25°C and 120 rpm and 90 min shaking (BS-11 digital, JEIO TECH, Korea, (20-185) rpm, (-10\_120 °C) ±0.5 °C. Samples were taken from the flask at appropriate time intervals as necessary and the concentration of metal ions in the sample were analyzed with UV-visible spectroscopy, at maximum absorption (λ<sub>max</sub> nm) table (4). After an experiment, the resin was separated from solution by filtration,

## 7. Effect of PH on Metal Ion Exchange Capacity

To study the effect of pH on the metal ion uptake, it is necessary to buffer the resin and the solution used. To do this, buffer soluble of pH range 2-10 were prepared from 0.15 M phosphoric acid and 0.15 M sodium phosphate<sup>(18)</sup>. A pH

meter (HANA, HI 8417, Fugle) was used to measure the PH. A different sets of weight ( $0.25 \pm 0.001$ g) dry resin were equilibrated with buffer in differed stopped bottle for 24 hrs., so that resin attained desired pH value<sup>(19-20)</sup>.

## 8. Results and Discussion

The analytical data (C.H.N.M) show the proposed formulas for metal chelate of PVC8HQ- as shown in table (1). All the solid metal chelates of PVC-8HQ with  $\text{Cr}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  were soluble in DMF and DMSO.

The measurements of molar conductance ( $\approx 30\text{--}45 \text{ S.cm}^2 \text{ ml}^{-1}$  for  $\text{M}^{\text{II}}$  and  $75 \text{ S.cm}^2 \text{ ml}^{-1}$  for  $\text{Cr}^{\text{III}}$ ) in DMSO, showed that these chelates are non-electrolytic, except  $\text{Cr}^{\text{III}}$ (8HQ) which showed electrolytic behavior, of in 1:1 ratio<sup>(21)</sup>.

The magnetic moments of  $\text{Cr}^{\text{III}}$  (3.5 BM) revealed the present of three unpaired electrons which agree with octahedral environments around  $\text{Cr}^{\text{III}}$  ion, as well as the magnetic moment of  $\text{Cu}^{\text{II}}$ , chelate<sup>(22)</sup>. As well as the orange  $\text{Ni}^{\text{II}}$  complex showed diamagnetic properties, which confirms the square planer geometry around (II) ion<sup>(23)</sup>.

Table (1). Elemental analysis data of 8-HQ-pvc

Compound	Expected formula	Molecule <sup>(a)</sup> weight	C% Calc. (Found).	%H Calc. (Found.)	%N Calc. (Found)	%S Calc. (Found)	Intrinsic viscosity $\eta$	Metal%
PVC-8HQ.	$\text{C}_{13}\text{H}_{15}\text{NO}_4\text{S}$	281	55.50 (55.31)	5.37 (4.81)	4.98 (5.71)	11.40 (10.02)	-	-
Cr-PVC-HQ	$\text{C}_{29}\text{H}_{45}\text{ClCr}_2\text{N}_2\text{O}_{12}\text{S}_2$	817	42.62 (41.31)	5.55 (3.11)	5.24 (5.33)	7.85 (7.04)	0.63	12.72 (11.12)
Ni-PVC-HQ	$\text{C}_{29}\text{H}_{37}\text{ClNi}_2\text{N}_2\text{O}_8\text{S}_2$	759	45.92 (4.34)	4.92 (4.03)	3.69 (3.33)	8.45 (8.01)	-	15.47 (14.45)
Cu-PVC-HQ	$\text{C}_{29}\text{H}_{45}\text{ClCu}_2\text{N}_2\text{O}_{12}\text{S}_2$	840	41.45 (42.33)	5.40 (4.61)	3.33 (3.59)	7.63 (6.56)	0.69	15.12 (14.01)
Cd-PVC-HQ	$\text{C}_{29}\text{H}_{37}\text{ClCd}_2\text{N}_2\text{O}_8\text{S}_2$	866	40.22 (38.01)	4.31 (4.88)	3.33 (3.41)	7.41 (7.01)	0.72	25.96 (24.23)
Hg-PVC-HQ.	$\text{C}_{29}\text{H}_{37}\text{ClHg}_2\text{N}_2\text{O}_8\text{S}_2$	1042	33.41 (32.01)	3.58 (2.98)	2.69 (2.71)	6.15 (5.79)	-	38.49 (36.98)

A=average molecular weight of repeated unit in g/mol.

Table (2). <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra of 8HQ-Ppvc-resin

Expected chemical shift (ppm)	Nature of proton assigned	Observed chemical shift (ppm)
3.00-3.5	$\text{CH}_2\text{-CH}$	3-3.3 (multiple)
7.5-8.5	Aromatic proton (Ar-)	7.9- 8.20
9-10	Proton of phenolic-OH-	No signal
9.0- 10.0	Proton of $\text{SO}_3\text{H}$	9.5(singlet)

### 8.1. <sup>1</sup>HNMR and <sup>13</sup>CNMR

The NMR spectra of PVC-8HQ resin in  $\text{CDCl}_3$  solvent revealed that the copolymer gave different pattern of <sup>1</sup>HNMR spectra, table 2, since it possesses set of proton having different electronic environment. The chemical shift (ppm) observed at (7.4-8.20) ppm is assigned to de shielding protons of aromatic ring. The signal in the 9.5ppm region may be due to proton of  $-\text{SO}_3\text{H}$  group confirming displacement reaction of P.V.C with 8-hydroxyquinoline-5-sulphonic acid via attacking  $-\text{OH}$  group of high basicity on carbon bearing chlorine atom of poly(vinyl chloride), Scheme 1.. The much down field chemical shift for  $\text{SO}_3\text{H}$  indicate clearly the intermolecular hydrogen bonding with adjacent groups in the same

copolymer<sup>(24)</sup>. However, the absence of signals of protons of  $-\text{OH}$  group (8-position) in the new copolymer indicates the substitution reaction of PVC *via* departure of hydrogen chloride gas in assistance of  $-\text{OH}$  group, Figure (1). <sup>13</sup>CNMR spectra of new resin display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton. The <sup>13</sup>CNMR spectrum of 8 HQ-PVC resin is shown in figure (2), and the peak positions are assigned according to the literature<sup>(25)</sup>. The absorptions at 160, 153, 159, 172, 142, 136, 148, 125 and 119 ppm with respect to  $\text{C}_1$  to  $\text{C}_9$  of the aromatic quinolone ring<sup>(26)</sup>, while absorptions at 40 and 60 ppm may be assigned to  $-\text{CH}_2$  and  $\text{CH-}$  of vinyl group linked to quinolone ring in position 8 via hydroxyl group. Table. (2)

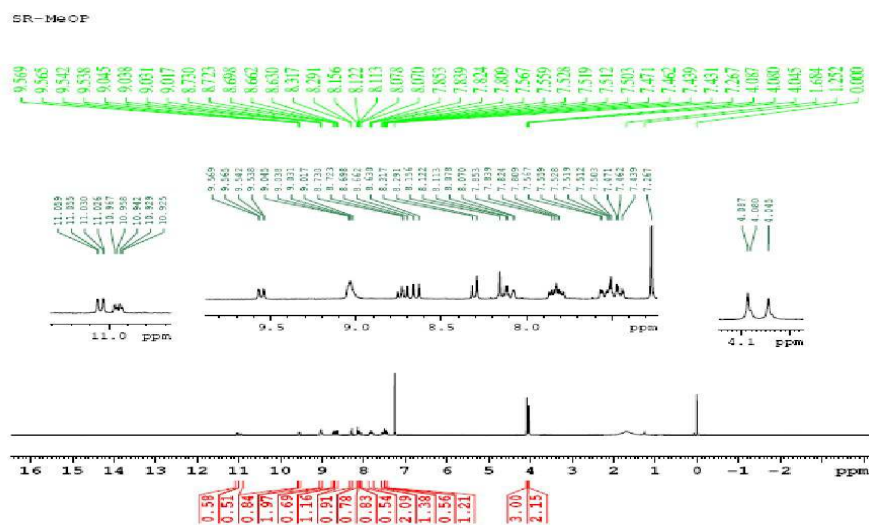


Figure (1).  $^1\text{H}$  NMR spectra of 8HQ-pvc resin in  $\text{CDCl}_3$ .

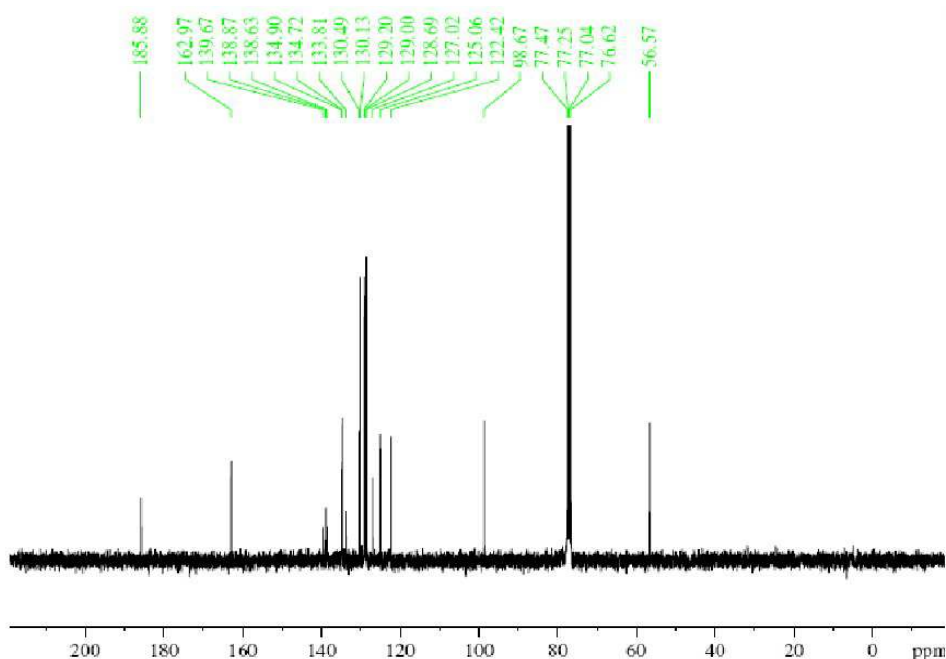
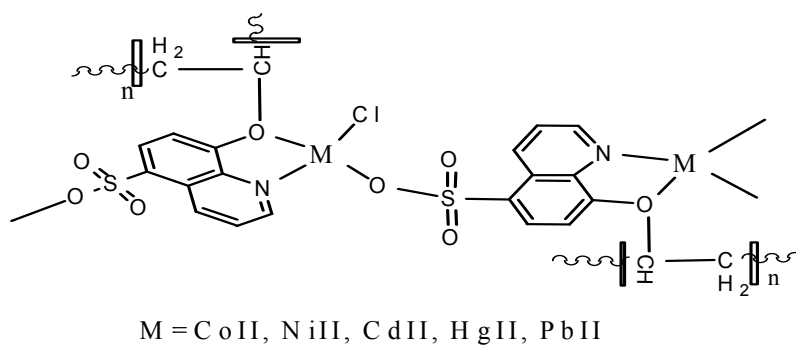
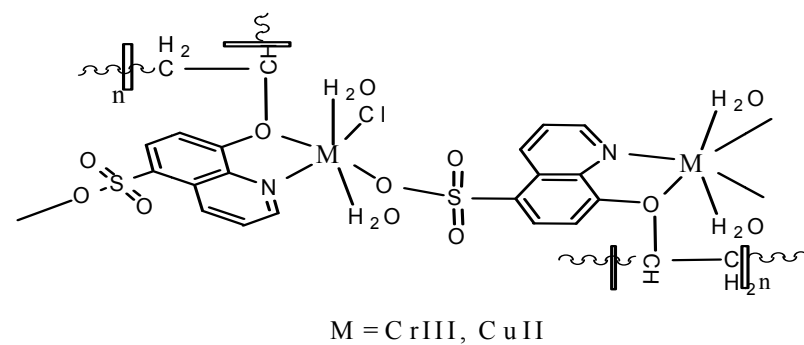


Figure (2).  $^{13}\text{C}$  NMR spectra of 8HQ-pvc resin in  $\text{CDCl}_3$ .

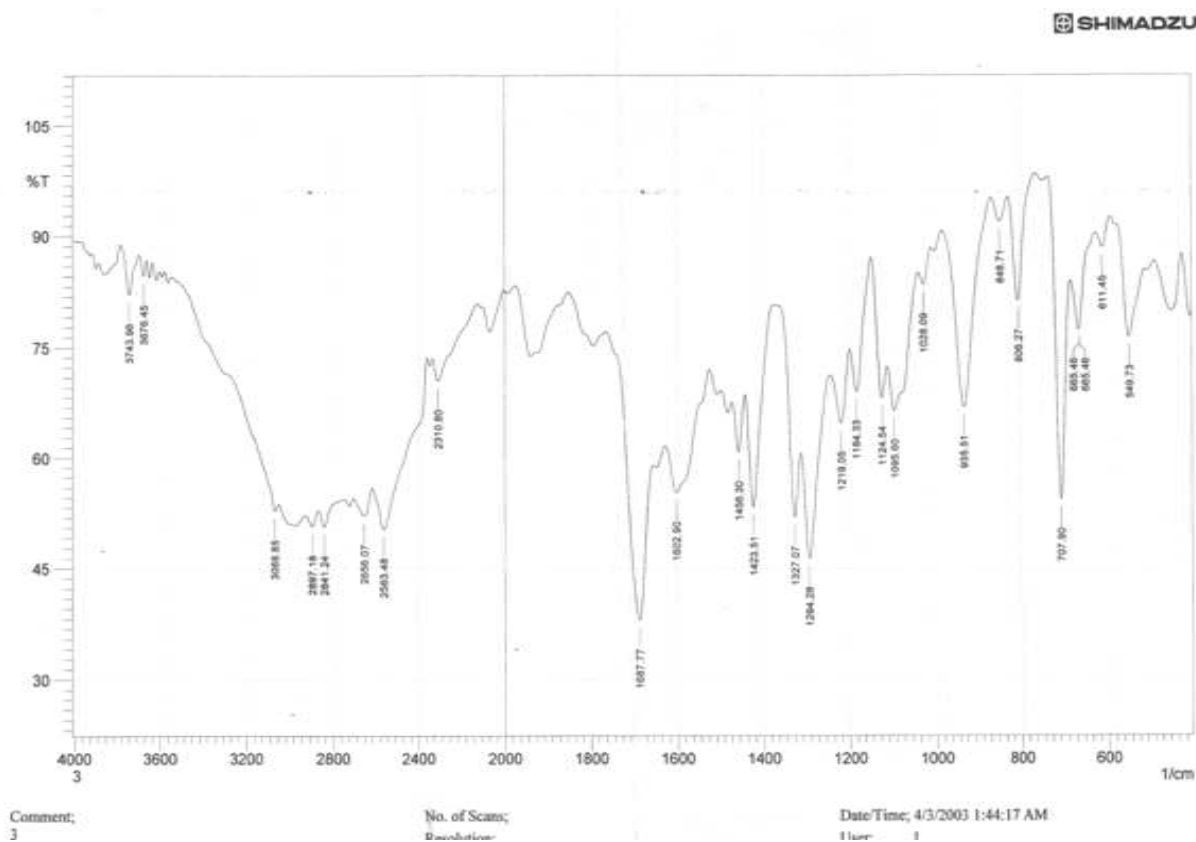
## 8.2. IR Spectra

The FTIR spectrum of (8HQ-PVC)resin, with its metal chelates are presented in figures (3 and 4). The IR spectrum of PVC-8HQ resin showed broad band appeared in the region  $3676\text{cm}^{-1}$  may be assigned to the stretching vibration of the intermolecular hydrogen bonded phenol- $\text{SO}_3\text{H}$  group. The presence of strong band at  $1687\text{cm}^{-1}$  and  $1602\text{cm}^{-1}$  indicate the  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  group in quinolone ring<sup>(26)</sup>, which up on complexation, the absorption of  $\text{SO}_3\text{-H}$  group was disappeared in the infrared of all metal chelates, this confirms the coordination of PVC-8HQ resin with metal ion through deprotonation depending on the high acidity of sulfonyl groups attached directly to phenyl moieties<sup>(27)</sup>. The depression in the wave numbers of ( $\text{C}=\text{N}$ ) may be explained

on the basis of drift of lone pair density of azomethine nitrogen ring toward metal ion<sup>(28)</sup>. The IR spectra of the all complexes showed new bands in the far IR ( $430\text{-}549\text{cm}^{-1}$  and  $456\text{-}530$  corresponding to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  vibrations. Furthermore, the far-infrared spectra of all polymeric metal complexes showed weak bands in the  $300\text{-}385\text{cm}^{-1}$  that are assigned to  $\text{M-Cl}$  bonds<sup>(29)</sup>, and hence investigates the participation of  $\text{Cl}^-$  ion in completion the coordination numbers of central metal ions, scheme 2<sup>(30)</sup>. Furthermore, the strong absorptions at  $1426\text{cm}^{-1}$  and  $1456\text{cm}^{-1}$  are attributed to methylene  $\text{CH}_2\text{-CH}$  bridge of P.V.C. bonded directly with quinoline ring<sup>(31)</sup> confirming substitution reaction with hydroxyl group in position (8) of hydroxyl-5-sulphonic acid-quinolone<sup>(32)</sup>.



*Scheme (2). Coordination patterns of PVC-8HQ Resin with metal ions*



*Figure (3). Infrared spectrum of PVC-8HQ resin KBr disc.*

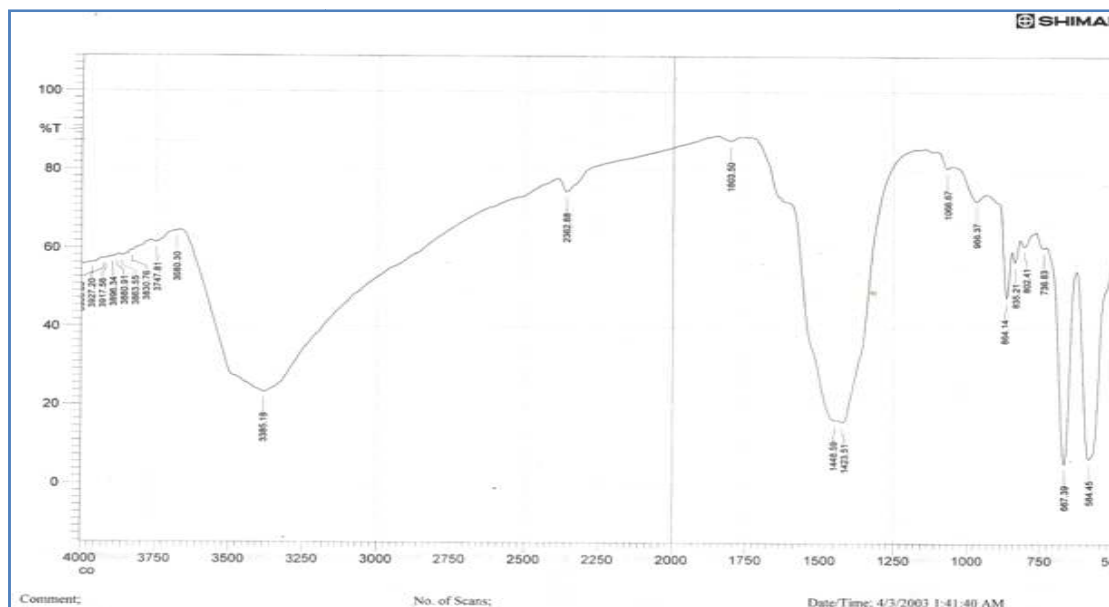


Figure (4). Infrared spectrum of Cu(II)-PVC-Q-chelatein CsI disc.

### 8.3. UV-Visible Spectra

The electronic spectra of PVC-8HQ in DMSO solution, Table.(3) showed distinct peaks at 225nm and 336nm are assigned to  $\pi-\pi^*$  and  $n-\pi^*$  transition of chromophoric groups of S=O, C=N and C=C<sup>(33)</sup>. The absorption spectra of copper (II) chelate exhibited bands at 365nm and 550nm assuming tetragonal distortion in the molecule, since the broadening in the region 550 may be assigned to overlapping of two transitions  $B_1g^2 \rightarrow B_2g^2$  and  $B_2g^2 \rightarrow E_g^2$ , respectively<sup>(34)</sup>. The green solution of Cr(III) chelate in DMSO showed two weak bands in 400-600 nm regions, which may be assigning to  $A_2g^4 \rightarrow T_1g^4$  and  $A_2g^4 \rightarrow T_1g^4(F)$  transitions<sup>(34)</sup> respectively suggesting octahedral geometry around Cr(III) ion. The orange solution of Ni(II) chelate displayed, a well discernable bands at 413 and 455nm, assignable to  $A_1g^1 \rightarrow B_1g^1$  and  $A_1g^1 \rightarrow B_1g^1$  transitions respectively, then, these are consistent with square planer symmetry around  $Ni^{+2}$  ion<sup>(35)</sup>.

The white of solution of Hg (II) chelate showed high intensity bands in 335 and 355nm concerning the  $\pi-\pi^*$  and intra- ligand charge transfer, which agrees well with tetrahedral environment around Hg (II) ion<sup>(34)</sup>.

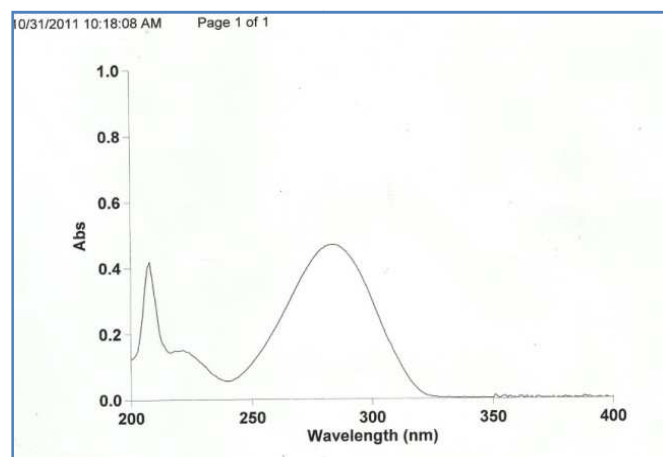


Fig. (6.A). Electronic spectrum of Ni( 8HQ-pvc ) in DMSO Solution.

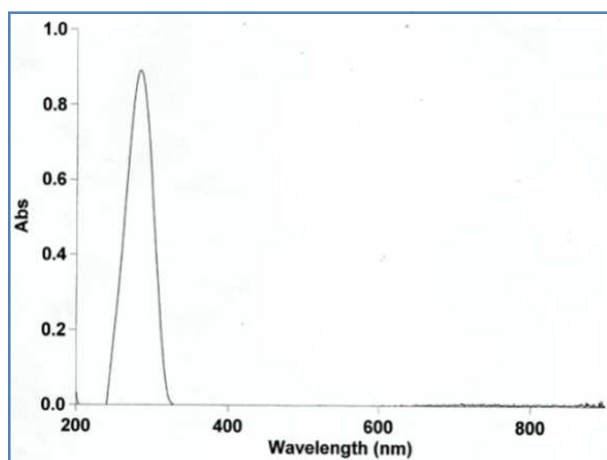


Figure .(5). Electronic spectrum of 8HQ-pvc resin in DMSO Solution.

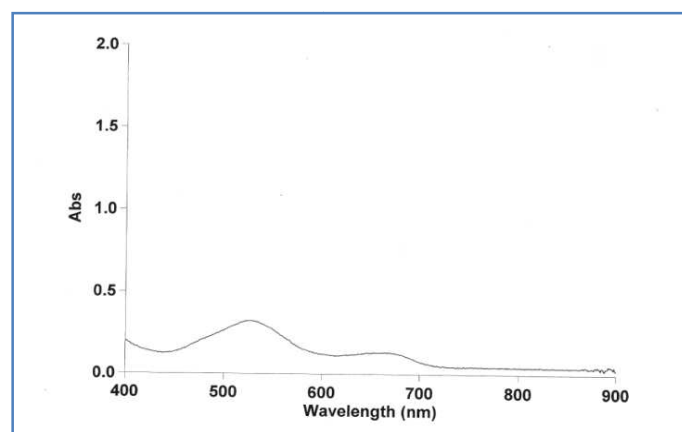


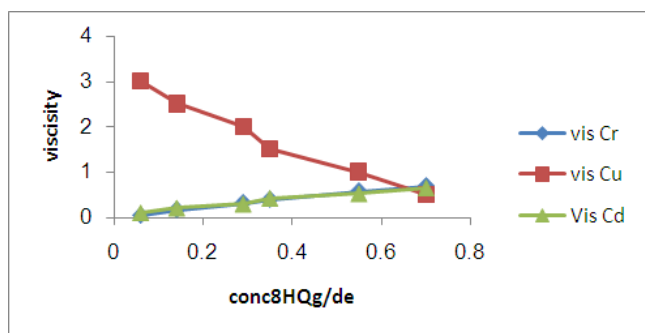
Fig. (6.B). Electronic spectrum of Ni( 8HQ-pvc ) in DMSO Solution

**Table (3).** UV-Visible spectra, molar conductance and magnetic moments of polymeric metal complexes

Compound	$\lambda_{nm}$	$cm^{-1}$	$\Sigma_{max}$ (molar $^{-1}$ . $cm^{-1}$ )	Assignment	$\mu_{eff}(B.M)$	Proposed geometry	S $cm^2.mol^{-1}$
8H Q-PVC.	225 336	44444 29761	23002 30433	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$			11
[CrIII(8H Q) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> Cl]	250 400 600	40000 24213 16666	43210 120 90	C.T $^4A_2g(F \rightarrow ^4T_1g(F))$ $^4A_2g(F) \rightarrow ^4T_2g(F)$	3.05	Octahedral	75
NiII(8H Q) <sub>2</sub> (H <sub>2</sub> O)	554 413	25000 24100	23000 55	$^1A_1g \rightarrow ^1B_2g$ $^1A_1g \rightarrow ^1B_2g$	0.0	Square planar	45
CuII(8H Q) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	365 550	27390 18181	31200 130	C.T $^2B_1g(F \rightarrow ^2B_2g(F))$ $^2B_2g(F) \rightarrow ^2Eg(F)$	1.29	Distorted-Oh	30
CdII(8H Q) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	304	23894	18770	MLCT. C.T	0.0	tetrahedral	41
HgII(8H Q) <sub>2</sub> (H <sub>2</sub> O)	235 355	25974	20550	$\pi \rightarrow \pi^*$ C.T	0.0	tetrahedral	40
PbII(8H Q) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>			19870	C.T	0.0	tetrahedral	32

#### 8.4. Viscometric study

Isometric measurements were carried out in *N,N*-dimethylform amide solution at 25C<sup>0</sup> using a TuanFouss<sup>(36)</sup>, table(4) reduced viscosity versus concentration, (0.5- 3.0 %) of 8-HQpvc, Cu<sup>II</sup>-8-HQpvc, Cr<sup>II</sup>-8-HQpvc complexes were plotted for each set of data Figure(7). The intrinsic viscosity<sup>(36)</sup> was determined by the corresponding liner plots. The following equations were used to determine Huggins<sup>(37)</sup>.

**Figure(7).** viscometric plot of Cr(III), Cu and Cd(II) complexes

According to above relation, HQ-PVC, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Cr<sup>3+</sup> a plot of the *via* concentration (g/dl), were liner with slopes of K1 and K2 respectively. Intercepts on the viscosity function axis gave valid in both plots. The calculated values of the constants k<sub>1</sub> and k<sub>2</sub> for the intrinsic viscosity satisfy the relation k<sub>1</sub>+k<sub>2</sub>=0.6 favorably<sup>(36)</sup>. It was observed that the (8HQ-pvc), Cd (8HQpvc), Cu (8HQpvc) and Cr (HQ) chelates having showing a higher value of  $[\eta]$ .

$$\eta sp/c = [\eta] + K_1[\eta]^2 \quad (3)$$

$$\frac{\ln \eta_{rol}}{c} = [\eta] - K_2[\eta]^2 \quad (4)$$

A according to above relations, a plots of

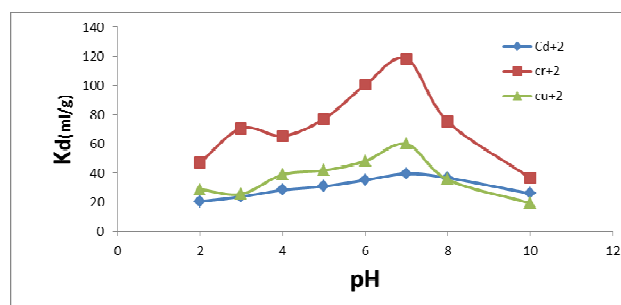
$(\eta sp)_c$  and  $\frac{\ln \eta_{rol}}{c}$  against concentrations of resin 8HQ-pvc and its chelates with Cr(III) and Cu(II) were liner with slope k<sub>1</sub>+k<sub>2</sub>, figure(7).

**Table (4).** isometric plots of 8HQpvc, Cr(III), Cu(II) and Cd(II) chelate

vis Cr	vis Cu	Vis Cd	con 8HQg/de
0.69	0.5	0.65	0.701
0.58	1	0.52	0.55
0.4	1.5	0.42	0.35
0.33	2	0.29	0.29
0.18	2.5	0.2	0.141
0.058	3	0.095	0.06

#### 8.5. Distributions Ratios of Metal Ions of Different values of PH

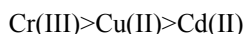
The effect of PH on the amount of metal ions distributed between two phases can be explained by the results given in Figure (8), Table (5). The data obtained from effect of PH on the removal of metal ions from aqueous solutions indicate that the relative amount of metal taken up by 8-HQpvc resin increases with increasing PH of the medium<sup>(37)</sup>.

**Figure(8).** effect of PH on distribution constant of metal ions adsorption

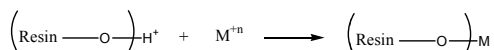
The study was carried out to a definite PH value for the particular metal ion to prevent hydroxide formation of the



metal ions at higher PH. In the case of Cu(II) and Ni(II) ions, the highest distribution ratio (D) (390-400) of PH $\approx$  7.0 whereas the highest value for (D) for Hg(II) and Cd(II) at PH=6.0. The results of this study help in selecting the optimum PH for selective uptake of a metal ion from a mixture of different ions<sup>(38)</sup>. The order of distribution ratio of metal ions measured in PH range 2 to 10 is found to be:



The (8 HQ-PVC) resin is considered as cationic exchange resin, therefore, the exchange may be expressed as:



Therefore the tendency of Cr<sup>+3</sup>, Ni<sup>+2</sup>, Cu<sup>+2</sup>, Cd<sup>+2</sup>, Hg<sup>+2</sup> is much more faster toward increasing the deportation of -OH phenolic and form strong covalent band of the type chelate.



### 8.6. Adsorption Isotherms

The equilibrium experimental data were correlated with Langmuir and Freundlich isotherm models

The studying the adsorption behavior of high concentrations of metal ions, isotherms for the adsorption of Cr(III), Cu(II) and Cd(II) were obtained by batch method. The isotherms of metal ions can be described by Freundlich equation:-

$$\log q_e = \log k + 1/n \log C_e \quad (1)$$

[ $q_e$  is the amount of metal ion adsorbed per gram of adsorbent ( $\text{mg.g}^{-1}$ ),  $C_e$  is equilibrium the concentration is metal ion solution ( $\text{mg.lit}^{-1}$ ) and the value  $n$  and  $K$  are Freundlich constants  $n$  gives an indication of favorability and  $k$  the capacity adsorbent. The liner plot of  $\log C_e$  vs.  $\log q_e$  shows that adsorption follows Freundlich isotherm model. figure(9-10) and table (7). The Langmuir isotherm is represented by the following equation:

$$C_e/q_e = 1/q_{\text{max}} + C_e/q_{\text{max}}$$

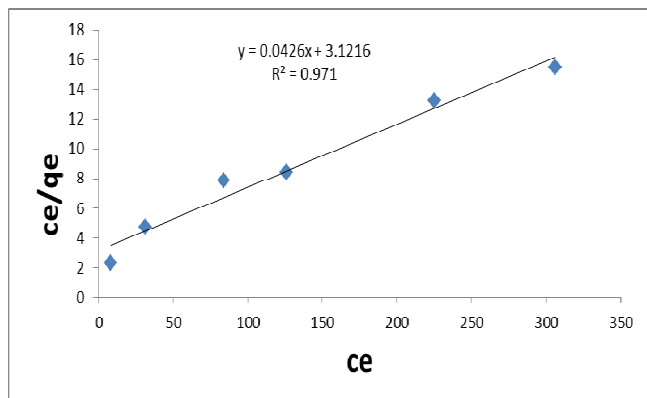


Figure (9). Langmuir adsorption of Cr(III)

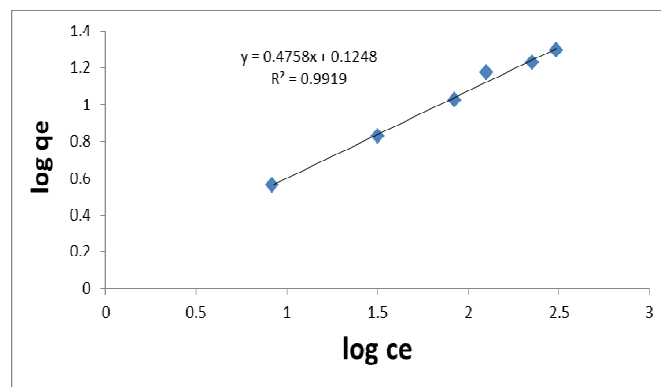
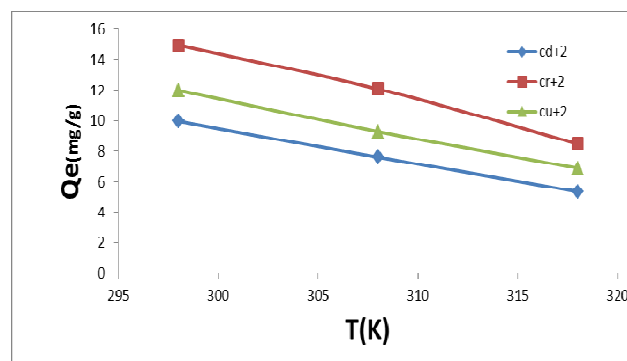


Figure (10). Freundlich adsorption of Cr(III)

Where  $C_e$  is the equilibrium concentration ( $\text{mg/L}$ ),  $q_e$  is the amount adsorbed at equilibrium time ( $\text{mg/L}$ ), and  $q_{\text{max}}$  and  $b$  are Langmuir constants related to the adsorption capacity and energy respectively. The plot of  $C_e/q_e$  versus  $C_e$  is linear. This result shows that the adsorption of metal follows Langmuir isotherm model. Figure (11), Table(5,6)



Figure(11). Vant Hoff's plot for adsorption metal ions on P.V.C-8HQ.

Table (5). Distribution ratio ( $K_d$ ) of different metal ions as function of the PH of 8HQ-Pvc resin Distribution ratio of ratio of  $M^{+2}$  at different PH

PH	$K_d\text{Cr(III)}$	$K_d\text{-Cu(II)}$	$K_d\text{-Cd(II)}$
2	47.32	29	20.63
3	70.88	25.8	23.95
4	65.65	39.1	28.56
5	77.09	41.9	31.01
6	100.44	48.3	35.31
7	118.52	60	39.68
8	75.49	35.7	36.84
10	36.82	19.5	26.2

Distribution ratio ( $k_d$ ) of different metal ions  $M^{+2}$  at different PH

$$D = \frac{\text{Amount of metal ion absorbed.}}{\text{amount of metal ion in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin gm}}$$

[Cr(NO<sub>3</sub>)<sub>3</sub>] .9H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>.2H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O



**Table (6).** Effect of the temperature on the maximum adsorbed quantity for adsorption of the three metals on 8HQ-Pvc resin surface

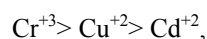
T (K)	Quantity of Adsorption		
	Cr(III)	Cu(II)	Cd(II)
298	14.95	12	9.96
308	12.1	9.3	7.62
318	8.5	6.9	5.37

**Table (7).** Adsorption values of the three metals ions on 8HQ-Pvc resin surface from aqueous solutions

	C0 mg/l	A	Ce	R%	Qe(mg/g)
Cr <sup>3+</sup>	100	0.005	8.33	91.67	3.66
	200	0.0190	31.66	84.17	6.73
	350	0.0503	83.83	76.04	10.64
	500	0.0757	126.16	74.76	14.95
	650	0.135	225.0	65.38	17.00
Cu <sup>2+</sup>	800	0.1849	306.16	61.73	19.75
	200	0.0063	78.75	60.62	4.85
	400	0.015	187.5	53.12	8.50
	600	0.0201	250	58.33	14.00
	800	0.033	412.5	48.43	15.50
Cd <sup>2+</sup>	1000	0.046	575	42.5	17.00
	1200	0.053	662.5	44.79	21.50
	250	0.0112	112	55.20	5.52
	500	0.0251	251	49.80	9.86
	800	0.0443	443	44.62	14.28
	1000	0.0595	595	40.50	16.20
	1200	0.0691	691	42.41	20.36
	1500	0.0837	837	44.2	26.52

### 8.7. EstimationRate of Metalion Uptake as a Function of Time

The rate of metal adsorption was determined to find out the shortest period of time within which equilibrium could be achieved as while operating as close to equilibrium condition as possible. As shaking time increases the polymer (8 HQ pvc) gets more time for adsorption, hence uptake increases. Figures(9-10), shows that rate of metal non uptake follows the order:



The sequence of rate metal ion uptake indicates that the rate is directly proportional to size of the metal ion. For example Cr<sup>+3</sup> has more change and small size, therefore equilibrium is attained within 90 minutes, while other ions Ni<sup>+2</sup>, Cu<sup>+2</sup> and Pb<sup>+2</sup> have nearly equal cationic size, having same charge, therefore required 120 minute, to attain

equilibrium while, Cd<sup>+2</sup>, and Hg<sup>+2</sup> and Pb<sup>+2</sup> have large atomic size, therefore requiring 125 minute to attain equilibrium. The trend is in good agreement with earlier workers<sup>(35)</sup> comparing to soft acids Pb<sup>+2</sup>, Cd<sup>+2</sup> and Hg<sup>(36)</sup>Figure(9).

### 8.8. Adsorption Process

In table(7), we have noticed that the three ions(Cr<sup>III</sup>, Cu and Cd<sup>II</sup>), the final pH decreases relatively to initial pH for different initial concentration used. This corresponds to an increase in the concentration of H<sup>+</sup> ions in the solution. This phenomena shows that the adsorption of metal ions by the Pvc 8-hydroxyquinoline -5-sulfonic acid surface is made by a process of ion exchange. Indeed, as indicated above the Pvc 8-hydroxyquinoline -5-sulfonic acid surface has a OH and SO<sub>3</sub>H group which is very reactive with Cd(II), Cu(II) and Cr(III), to form with them metal Avery stable complexes

A typical adsorption isotherms at given temperature was obtained by plotting qeVsCe for again 8HQ-pvc resin, equation<sup>(36)</sup>.

$$q_e = \left( \frac{C_0 - C_e}{d} \right) V \quad (3)$$

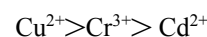
Where q<sub>e</sub> = the equilibrium metal ion concentration resin in mole /g

C<sub>0</sub>-C<sub>e</sub> = initial and equilibrium concentrations of metal ions under study in mole/lit.

V=volume of solution in liter, and d= weight of resin (8HQ- pvc) in g.

The Figures (9-14) clearly indicate that these isotherms are all of the favorable type referred to in literature<sup>(38)</sup> with increasing values of Ce, the values of qe of reaches the saturation level of the adsorbate on the adsorbent lie, formation of monolayer of the PVC-8HQ bonded with metal ions understudy. This value actually represents the maximum amount of metal ions that thePVC-8HQcould hold under a given set of experimental conditions. In order to verify to what extent the isotherms adhere to Langmuir and Freundlich adsorption isotherm representative plots of lnq<sub>e</sub>VslnC<sub>e</sub> for Freundlich (eq.1) and .1/q<sub>e</sub>vs 1/C<sub>e</sub>for Langmuir (equation 3) are accordingly shown in Figures (11). These plots indicate satisfactory adherence to isotherms within the range of concentrations employed in this work.

The high efficiency of PVC-8HQ resin to remove the metal ions especially Cr(III), Ni(II) and Cu(II), may be attributed to homogeneous distribution of active sites on the resin surface, since the displacement of hydrogen ions of -OH group in position (8), with metal ions understudy and nitrogen(N<sub>i</sub>) of quinolone ring tend to form five membered ring which is kinetically stable<sup>(37)</sup> and agree with sequins stability of metal complexes Irving Williamson<sup>(38)</sup>.



The maximum amount of metal ion adsorbed by 0.25 gm was calculated by Langmuir and Freundlich models

(equations 1, 3). The adsorption capacity of modified resin (8HQ-pvc) for metal ions is shown in table (8). As can be seen, the plots of Lagmuir and Freundlich models effectively describe the adsorption data with all R<sup>2</sup> values more than 0.98 for all ions.

$$(\% \text{Adsorption}) = [(C_0 - C_e)/C_0] \cdot 100 \quad (2)$$

Where C<sub>0</sub> is the initial concentration of metal ion in solution (mg. Lit-1), and C<sub>e</sub> is the concentration of metal ion in the filtrate (mg.lit-1).

### 8.9. Effect of Temperature on Cr (III), Cu (II) and Cd (II) Adsorption by PVC-Resin

The sorption experiments were repeated at various temperatures in range of 293 K, 298 K, 308 K and 318 K, the results are presented in fig(?) and table (1). The amount of Cr(III) ion adsorbed was 98.9 % at 298 K, whereas at 308 K it was 70.4 % and at 318 K the uptake of the metal ion had decreased to 66 %. Copper ion uptake by PVC-8HQ, followed a similar pattern of behavior with a sharp increase at 293 K (96 %), followed by sharp decrease, the amount of Cu(II) ion uptake 89 % at 298 K and 61 % at 318 K. Chromium ion show the same effect, but the uptake of the metal ion had decreased from 99.8 % at 293 K to 45 % at 318 K. It can be seen that the metal ions uptake follows a similar pattern, but the amount adsorbed at a particular temperature differ. These results indicate that the uptake of metal ions increases at lower temperature. The decrease of the uptake of heavy metal ions with increase in temperature may be due to that insufficient to retain the metal ions and the binding site. This could lead to desorption or cause the metal ions to bounce off the surface of resin instead of combining with it. Therefore, increase in temperature may be associated with decrease in the adsorption.

### 8.10. Thermodynamic Parameters of Adsorption

The effect of temperature on the adsorption extent of the three metal that's chose on PVC-8HQ surface has been studied at three different temperatures (25, 35, 45 and 37.5°C). The experimental data and the general shapes of the three metal adsorption are given in table (6) and figure () The results showed an increasing in the adsorption of metal ions on resin PVC 8-hydroxyquinoline -5-sulfonic acid with decreasing temperature, hence the adsorption process appeared to be exothermic <sup>(37)</sup> and this indicates the entity of absorption process as the adsorbed molecules diffused in the porous of the adsorbent, and increase the rate of the diffusing with decreasing temperature. Likely, the absorption process will be accompanied by the adsorption and get the sorption process (i.e. both the adsorption and the absorption could happen together and this phenomena could be seen clearly from the shape of the isotherms at high temperatures which differs completely in their shapes from the isotherms (25 and 35°C) as can be seen in figure (11).

On the other hand, the adsorption of Cr(III), Cu(II), Cd(II) on resin PVC-8HQ was decreased with the increasing

temperature, as it is shown in table (9) and this is consistent with the thermodynamic properties of adsorption and indicating exothermic process<sup>(39)</sup>. This could be interpreted as a result of weakening of attractive forces between the metal ions and the resin PVC-8HQ surface with the decreasing temperature.

There were no significant differences found in the amount of Cr(III), Cu(II), Cd(II) on resin PVC-8HQ surface at the studied range of different temperatures (25, 35, 45 and 37.5°C.) which indicates that the adsorption process for this Cr(III), Cu(II), Cd(II) in this range of temperatures would be temperature independent that means that the quantity adsorbed in the lowest temperature would not be desorbed perceptibly in the highest degree in the studied range of temperatures and the adsorbate-adsorbent interactive forces are relatively strong.

The equilibrium constant (K) for the adsorption process at each temperature is calculated as in the following equation:-

$$K = \frac{Q_e \times M}{C_e \times V}$$

Where Q<sub>e</sub> = the amount adsorbed in mg per one gram of adsorbent.

C<sub>e</sub> = the equilibrium concentration of the adsorbate expressed in mg/L.

M = the weight of the adsorbent (g)

V = the volume of the metal ions solution used in the adsorption process

The change in free energy (ΔG) could be determined from the following equation mentioned:-

$$\Delta G = -RT \ln K$$

Where R: the gas constant (8.314 J. mol<sup>-1</sup> deg<sup>-1</sup>).

T: the absolute temperature.

The change in enthalpy (the heat of adsorption (ΔH)) may be obtained from the following equation:-

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Where ΔH = enthalpy the maximum uptake of adsorption at a certain value of equilibrium concentration (C<sub>e</sub>) that was fixed for all temperature of study.

Table (9) showed values at different temperature. Plotting (ln K<sub>m</sub>) versus (1/T) should produce a straight line with a slope = (-ΔH/R) as shown in figure (11).

The change in entropies (ΔS) was calculated from Gibbs equation

$$\Delta G = \Delta H - T\Delta S.$$

## 9. Conclusion

PVC bound to 8-hydroxy-quinolin-5-sulphonic acid has been synthesized by chlorine displacement reaction between PVC and 8-hydroxyquinolin-8-sulphonic acid in presence of piperidine as catalyst. The polymeric metal complexes

of newly resin were prepared by direct interaction of PVC-8HQ copolymer and hydrated metal chlorides and nitrates of Cr(III), Ni(II), Cu(II), Pb(II) and Cd(II) ions.

We have choiced some highly toxic metal ions for studying the adsorption in aqueous solutions to attain optimum conditions to reach maximum removal of such toxic metal ions from water. The resultant polymer showed high efficiency for metal ions adsorption. The pH, temperature, time and resin content have great influence on the sorption. Cu (II) and Ni (II) ions removed at pH 8-9, This could be explained by at low pH, amine groups in the beads easily form protonation that induced an electrostatic repulsion for Cu (II), Ni (II) ions. At low pH of solutions increase H<sub>3</sub>O<sup>+</sup> concentration and intensifies the competition between H<sub>3</sub>O<sup>+</sup> and heavy metal ions for complexation sites. Whereas adsorption for Cr (III) ions at 7-8 decreased, this is due to the solubility of Cr (III) ions at high pH. Heavy metal ions accumulation from single ion solutions at pH 8-9 is in order; Cu (II) < Ni (II) < Cr (III). Whereas at low pH the order will be; Cr (III) < Cu (II) < Ni (II). The decreasing of total adsorption in multi element solutions indicates that a competitive inhibition may occur for Cr (III) by the other cations in the solution, with limited specificity related to ionic radii or tendency for complex formation, depend on pH of solution.

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