Synthesis Characterization and Analytical Applications of New Chelating Resin of Formaldehyde-condensed Phenolic Schiff base.

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Abstract

A new chelating phenolic Schiff base containing phthalate imide pendant group resin was synthesized by three steps. The first step includes synthesis of 2-(4-aminobiphenyl-4-ylcarbamoyl) benzoic acid (1), Via reaction of pthalic anhydride with benzidine. In the second lines, the compound that we obtained in the first step was reacted with o-hydroxybenzaldehyde to obtain phenolic Schiff base 2-(4'-(2-hydroxybenzylideneamino) bephenyl-4-yl carbamoyl) benzoic acid (2) The third step includes prepared resin during intensification Schiff base derived with formaldehyde inan alkaline middle. Thepthale amice acid, Schiff base and resin were characterized by various instrumental techniques like FT-IR, ^{1}HNMR ,^{13}CNMR and elemental analysis, thermal behavior of the polymer was investigated by DSC and TGA.SEM analysis of polymer shows the amorphous structure of polymer. The chelating behaviors was examined against Ni (п), Cd (п), Cr(ш)and Pb(п). using patch method in different conditions like treatment time and pH at room temperature. The resin shows a good loading capacity.

Key words: phenolic schiff bases, formaldehyde Chelating Resin, pthale amice acid, Thermal Studies

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Introduction

Ecological defilement has twisted into one of the most remarkable problems threading our world. [1] Heavy element ion rest an earnest ecological problem face-off the world for defilement because of the use of metal ion as accelerator in different manufacture operation [2, 3]. Chelating rosin together different functional grouping containing N, O, P and S in the polymer metal ion have extensively studied [quadruplet ,5]. Chelating resin of Schiff base towards different metal ion have been published investigating a variety of biological, clinical and industrial application programmer [1-4]. The Schiff bases were discovered by Hugo Schiff since 1864 when reported the condensation of carbonyl compound with primary amines. Schiff bases fulfill from aromatic aldehydes ortho – substituted with hydroxyl group have initially trigger the researcher utility because of their capability to act accordingly bi dentate ligand for changeover metal ion [6-8]Schiff pedestal Chelating resin with oxygen, nitrogen donor atoms mote are found to take possession of very goodness selectivity for changeover alloy ions and screening negligible likeness for alkaline and alkaline earth alloy element [9,10] This shuffling the resin beneficial for elimination of trace engrossment of metal ions[11,12] .Many reports have spill discuss the Chelating possession of Schiff base resins across various metal ions[13-19]. The effect of PH ,inter-group communication time , chemical social system of resin, concentrations of the metal ion were inspected to uncovering out their metal uptake feature .In the sitting paper , we characterize the synthesis of phenolic Schiff base resin derived of 2-(4'-(2-hydroxybenzylideneamino)bephenyl-4-ylcarbamoyl)benzoic acid with formaldehyde The resin has been field for sorption of Atomic number 28 (п), CD(п) , Cr(ш)and lead(п) of hydrous solution .To this aim, several element affects the Chelating such as PH handling judgment of conviction . The rejuvenate competence has been studied by using nitric acid

Experimental

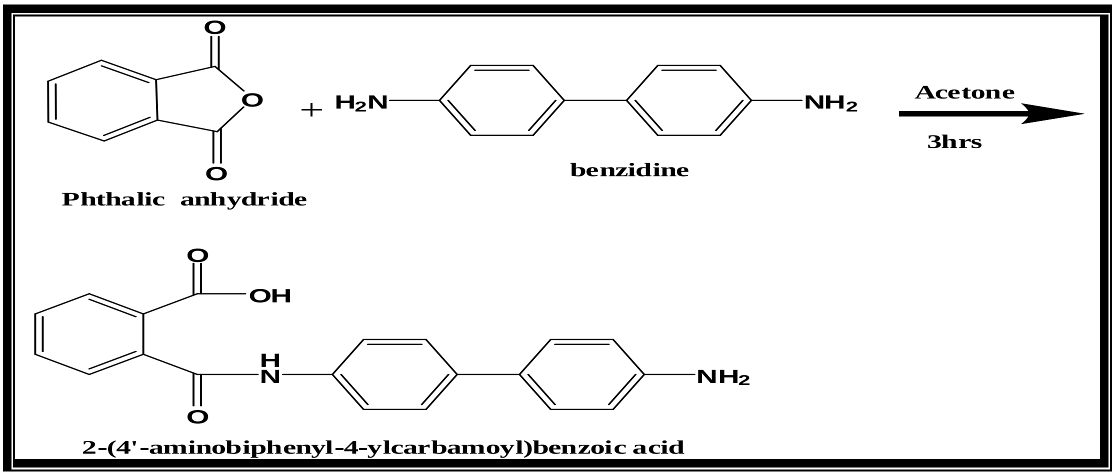
Materials

Benzeden (99.8% (99. eight % ,fluka), Phthalic anhydride(99.5% , B.D.H) , (99.8%, Na bicarbonate(99.octonary %, RTEDEL-DEHAEN AG) , Sodium hydroxide(solid)(98%, Fluka) , Glacial acetic acid(99.5%, B.D.H) , O-Hydroxybenzaldehyde (99%, B.D.H) , formaldehyde(37%, B.D.H) , Nitric acid(98%, Fluka) , acetone(99%, Fluka) , Nickel(Two)chloride dehydrate (98%, B.D.H) , Chromium(III) chloride dehydrate(98%, B.D.H) , Lead Nitrate(98%, H.W), oxalic acid(98%,B.D.H).

II -2- Measurements FTIridium spectrum of synthesized chemical compound carry out in Shimadzu FT-IR 8300 series spectrophotometer. 1HNMR, ^{13}CNMR (300 MHZ) spectra was recorded using (Ultra shield, Burke, Switzerland CDCL3+THF). Elemental Depth psychology is recorded by Micro approximation proficiency Euro EA 3000single ..Amount of metal ions was estimated by atomic engrossment Spectrophotometer technique Emission Spectrophotometer Shimadzu (A-A680).

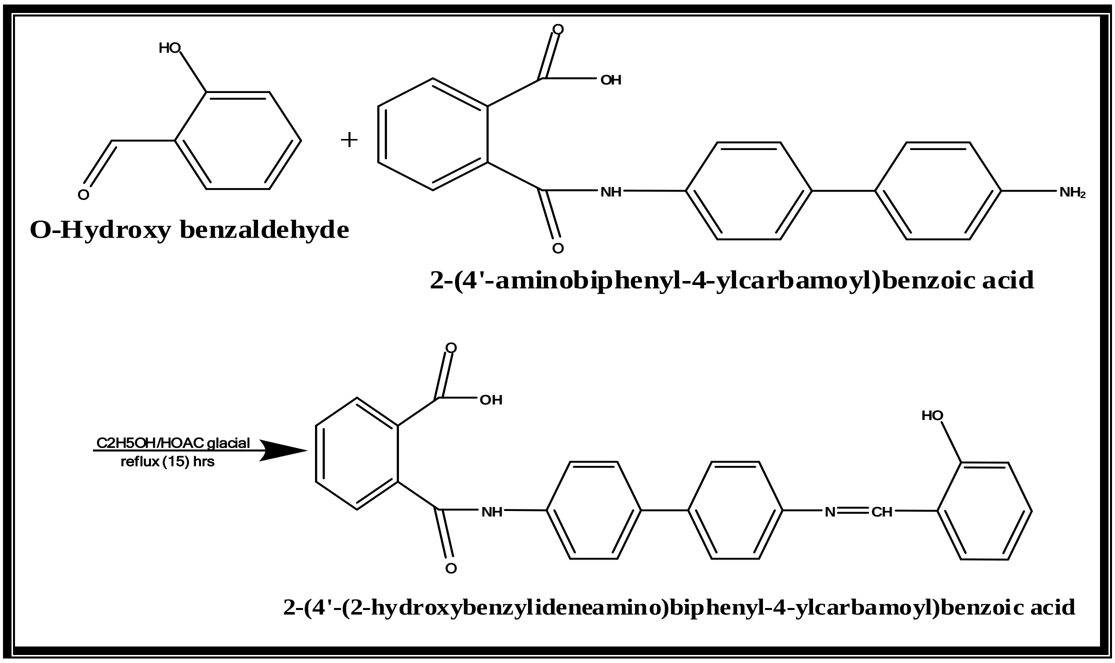
2-3. synthesis of 2-(4-aminobiphenyl-4-ylcarbamoyl) benzoic acid (1)

The method used the same in literature with some modification [20,21,22] In a 150 cubic centimeter flask equipped with a magnetic bar abettor, drooping funnel shapeand ebb condenser, was of put option (0.01mole) of pthalic anhydride and (25ml) of dry acetone, when all anhydride had been dissolved by hustle, a solution of (0.01mole) of Benzeden in(25ml) of dry acetone was allowed to run out of the free fall funnel drop prudent. The salmagundi was stirred at (0-5 c°) for 3hrs. The precipitate was filtered off and washed with solvent and recrystallized of DMF. When purification of the generated amice acid was purified by dissolving it in sodium hydrogen carbonate solution (5%), The solution was filtered and acidified with dilute hydrochloric acid, the phthalateamice acid was precipitate and then washed with frigidness water. acetone and then prohibitionist.



Scheme (1): Synthesis of (amice acid) (1)

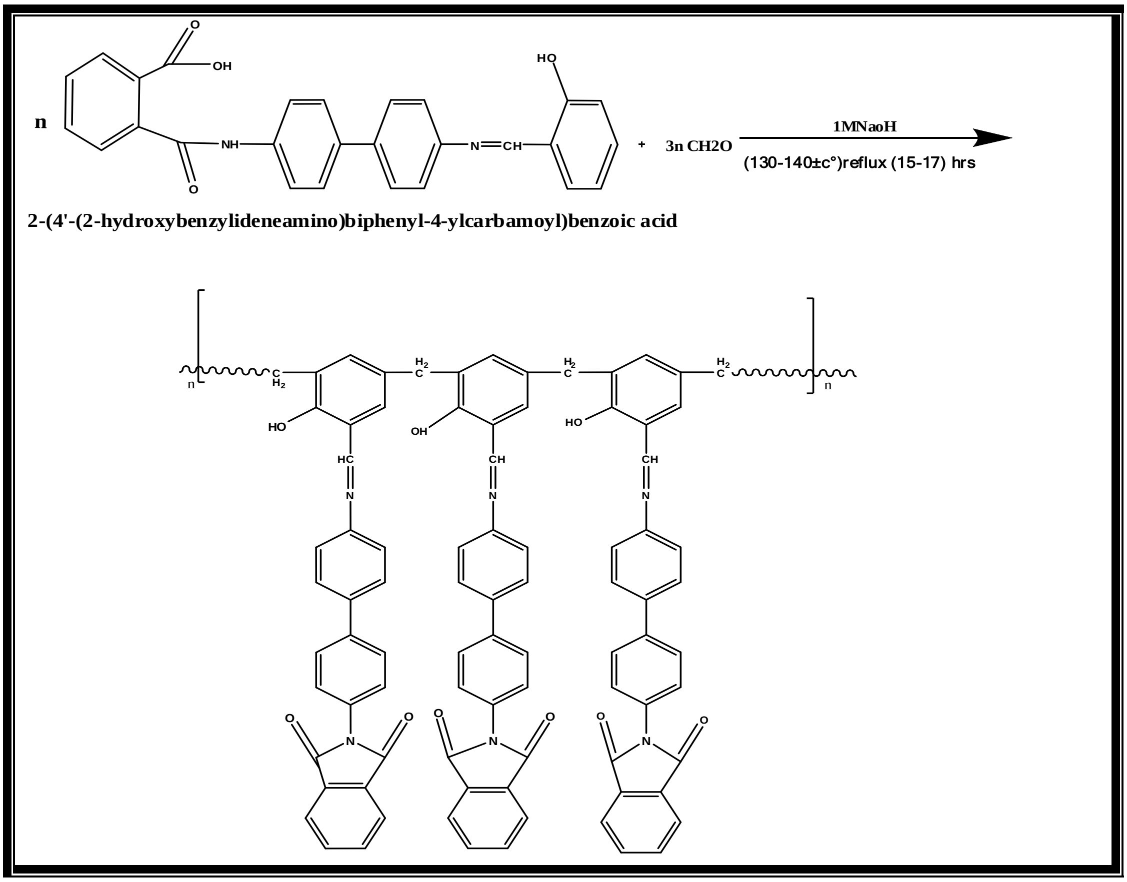
2-4. Preparation of phenolic Schiff base monomer (2) The (deuce) The chemical compound (2) was prepared according to the methods mentioned in the literatures [23,24] A mixture of compound (1) (0.01mole) and (0.01mole) of O-Hydroxybenzaldehyde in(30ml) of absolute ethyl alcohol and (2-3) bead curtain from glacial acidic acid was refluxed to15 hrs .with stirring . The resulted variety was cold to room temperature and the obtained precipitate was filtered dried then recrystallization from DMF.



Scheme (2): Synthesis of phenolic Schiff base[2]

2-5.Preparation of the phenolic Schiff base- formaldehyde chelating resin (3)
The method acting used same in literature with some modification [25, 26] the new phenolic Schiff base- formaldehyde resin was synthesized by capsule polymerization. In three necks volumetric flask, mixed Schiff {foundationbottombasic} monomer (2) (0. 01mole) was

hanging in 20ml {drinking waternormal water} at room temperature and a minimum volume of 1M NaOH solution was then {put into included with included in} dissolve it. formaldehyde(0. 012mol) was added to the alkaline Boot base al-Qaeda solution and the mixture was refluxed in a petroleum {shower bathroom bath tub} at (130-140 c?) for (15-17hrs) the {botanicalplant} rest soluble in the response mixture as a blackish John Brown anticipation of the resin was load out by balance the alkaline resin solution. using 0. 1M oxalic acid solution. The {blackdimly litshadowy} precipitate acquired was filtrated, washed repeatedly with deionized water.



Scheme (3): Structure of the phenolic–Schiff base formaldehyderesins.

2-6. deductive reasoning of metallic element solution:Set from standard {metallicsteelmaterial} solution(Ni2+, Cd2+, Pb2+, Cr3+)were prepared by weighting of confirmed of metal debris (Nicl2. 6H2O, Cdcl2. 2H2O, Pb(NO3)2, Crcl3. 6H2O) respectively in the non ionic {drinking water|normal water}[27] in {focus attention attentiveness} 1000and 100ppm with different PH(2-8)by using(1MHCL)and (1MNaOH)forcommand the PH.

Chelation competency of (leash): the Chelation competence of (3) polymer resin was estimate via flock { residuum horse sense of balance constancy} method. The finely group polymer was used to determine its alloy ion uptake capability for specific metal ion such as (Ni2+, Cd2+, Pb2+, Cr3+) in the variant of their chloride salt aqueous solvent , metal ion binding capacity for the polymer was studied under two various experimental shape . The {performance delivery setup} frame-up} adopted on eliminate of metal ion by {trembling banging moving} of the polymer (0. 1g) and (10ml) resolution having (100ppm) {metallic steel material} stuff } ion concentration for 24h at higher PH[28]. The salmagundi was then filtered off and {cleaning cleansing were} collected and then the amount of {metallic steel material} ion was estimated by using atomic engrossment spectrophotometer.

{Repair Recovery Refurbishment} of metals ions from chelating resin: Reactivation of the dry loading {resin was flora was} carried out by {trembling banging nervous-looking} with 10 {ml cubic centimeters} (3MHNO3) at different time. Following {purification filtering}, the metal ions {focus tending heed} in the {acidity result chemical p} solution were calculated via atomic absorption using standard solution roundabout way for the {metallic steel material} in same {acidity solution chemical p} {focus attention attentiveness}. of recuperation {metallic steel material} ions concentration ability {determine estimate compute} the Recovery proportion[29]

effect of handling time at ultimate capableness for lode chelating resin (three some): competence of lode chelating resin (tierce)to selection {metallic steel material} ions as it was noted that growing treatment time for the resolution of the subject area ions growing on us from the chelating resin capableness , though the ions orbit {balance sense of balance stableness } after about (10h)and {the amount of the turn of how much} load capability turn away a few bit till they reach 24h of treatment Tabular array - 4 and Fig. 5shows the {impact result} of time in treatment on the load {ability capacity functionality } of the chelating {botanical plant} (3) ions(Ni2+, Cd2+, Pb2+, Cr3+) in PH scale {analyzed researched examined}.

Effect of pH on the analytical competency from(3): The study shows that pH was with {substantial significant extensive} effect in the {weight unitfillinsert} {capacity of capacity for} the chelating {botanical plant life} {to any or allfor allto all or any} studied ion. {ThisThat} has been spotted that ingeneral , a higher shipmentcapability of the rosin {for people for the for anyone} ion are at the highest pHstratum utilized in the {research review analysis} of each ion (Fig. 6).

Results and discussion

In the first synthetic stape we prepared new p-amino phthaleamicacid(1)This compound was then used in preparation of new phenolic Schiff base radical (2) The phenolic Schiff base resin(3) rosin (tern ion) was intended by condensation the Schiffsubstructuremonomer with formaldehyde in alkaline center of attention . This polymer was deliberately excerption on bid to study the consequence of construction on the uptake capability from metal ion .Table 1 displays the physical preparations of phthaleamic acid, phenolic Schiff base and phenolic Schiff base resin.

Characterization of the synthesized compounds:
Physical preparations of the N-Substituted phthale amic acid, phenolic Schiff base and the resin is shown in Table (1)

Table (1): Physical self-control of prepared compounds (1-3)

Compound	Color	Melting points ◦C	Yield %	Recrystallization Solvent
1	Off white	280°c	95%	DMF
2	Yellow	230-235°c	97%	DMF
3	dark – brown	abouve300°c	-	DMSO

CHN analysis:

The elemental analysis of the N-Substituted phthaleamic acid and the resin is shown in Table 2.

Table (2): Elemental analysis data of the N-Substituted phthaleamic acid and the resin is shown in.

Compound	Calculated/ Found		
	C%	H%	N%
(1)	72.28 (71.739)	4.81 (4.981)	8.433 6.991)
(3)	56.05 (56.206)	4.55 (4.918)	16.379 (16.393)

3.1.3. FT-IR spectroscopy:

The chemical structure of the phthaleamic acid, phenolic Schiff base and the phenolic Schiff base resinidentified byFTIR, 1HNMR and 13CNMR spectral data[26,30].FTIR spectrum of compound (1) appeared strong preoccupancy bands at 3100-2700 Cm $^{-1}$ and 3356 cm^{-1} due to δ (O-H)carboxylic and δ (N-H) amide. Other absorptions appeared at 1712 cm^{-1}, 1651cm^{-1}and 1612 cm^{-1} due to δ (C=O) carboxylic, δ (C=O) amide and δ (C=C) aromatic respectively.
FTIR spectra of the new Schiff bases (2) appeared a broad absorption band of phenolic-OH and δ (N-H) amide appeared at 3421and absorption band at2830-3100cm^{-1}due tocarboxylic –OH
appearance of clear strong absorption band at(1620) cm^{-1} due to δ (C=N) imine. Other absorption bands appeared at (1523-1571) cm^{-1} ,(1282) cm^{-1} which were attributed to asym aromatic and δ (C-O)respectively.

FTIR spectra of thephenolic Schiff base resin (3) showed a broad absorption band of phenolic-OH and gave broader and less intense peak Absorption peak 2783 cm^{-1} due to methylene δ (CH2) linkage in the resin the peak at 2922cm^{-1} is assigned to aromatic δ (C-H),Other absorption bands appeared at(1784)cm^{-1},and 1595 cm^{-1} are attributed to δ(C=O) imide and aromatic ring δ (C=C) stretching vibrations.

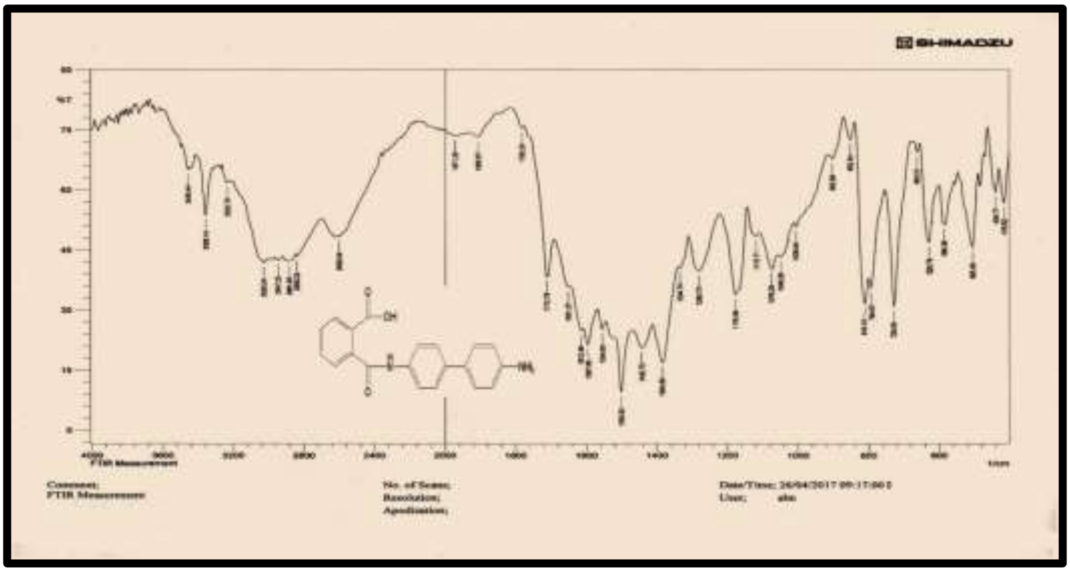


Figure (1): The FT-IRspectrum of the phthaleamic acid

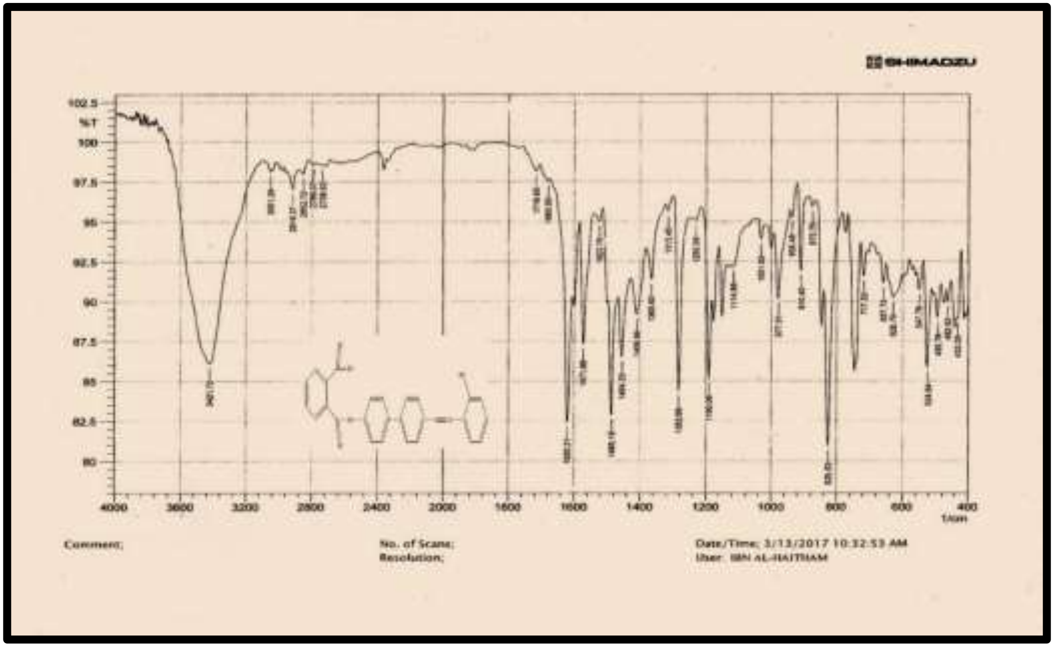


Figure (2): The FT-IR spectrum of the phenolic Schiff base.

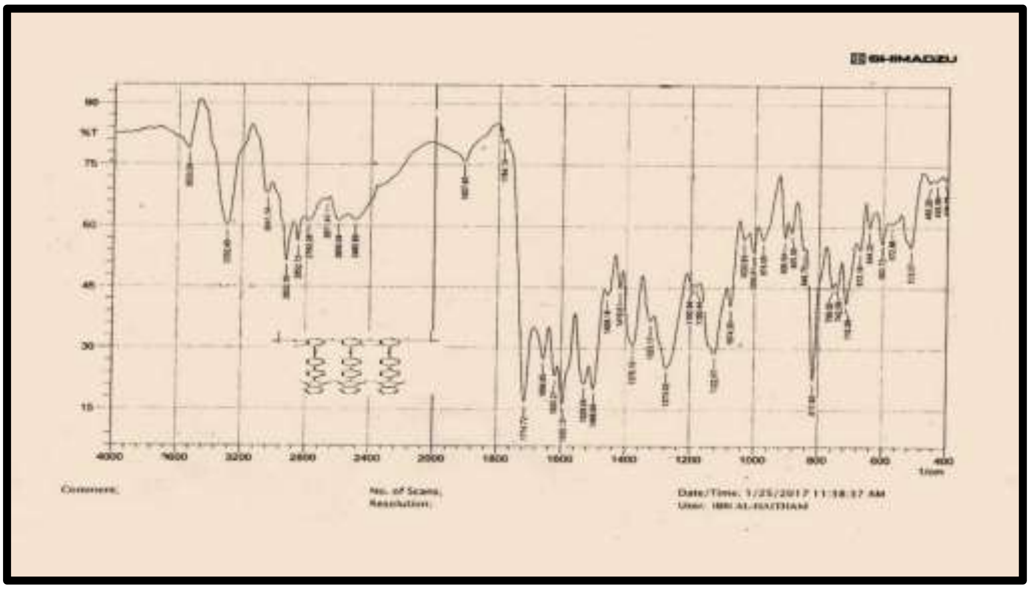


Figure (3): The FT-IR spectrum of the phenolic Schiff base resin.

^{1}H-NMR spectrum of compound (1) appeared signals at δ = (7.91-8.74) ppm belong to aromatic and NH amide protons and a clear signal at δ = 11.96 ppm due to (O-H) carboxylic, ^{1}H-proton magnetics of compound (2) appeared a clear signal at observed at δ =12.32 ppm ,11.92 ppm and10.96 are due to carboxylic –OH, phenol –OH and NH amide protons and signal at δ =8.74 ppm belong to imine protons signals multiple at δ = (7.91) ppm due to aromatic protons.

^{1}H-NMR spectrum of compound (3) showed a clear signal atδ = 11.95ppm due to phenolic-(O-H) and signal at δ =3.21 ppm due to methylene (CH2) linkage in the resin signal at δ =8.21 ppm belong to imine protons signals multiple at δ = (7.96) ppm due to aromatic protons .

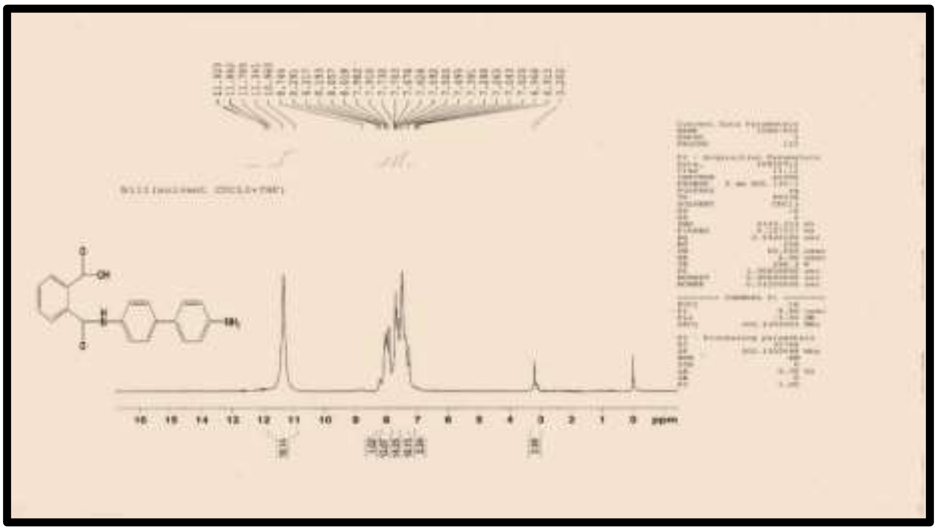


Figure (4): The ^{1}H NMR spectrum of the phthaleamic acid.

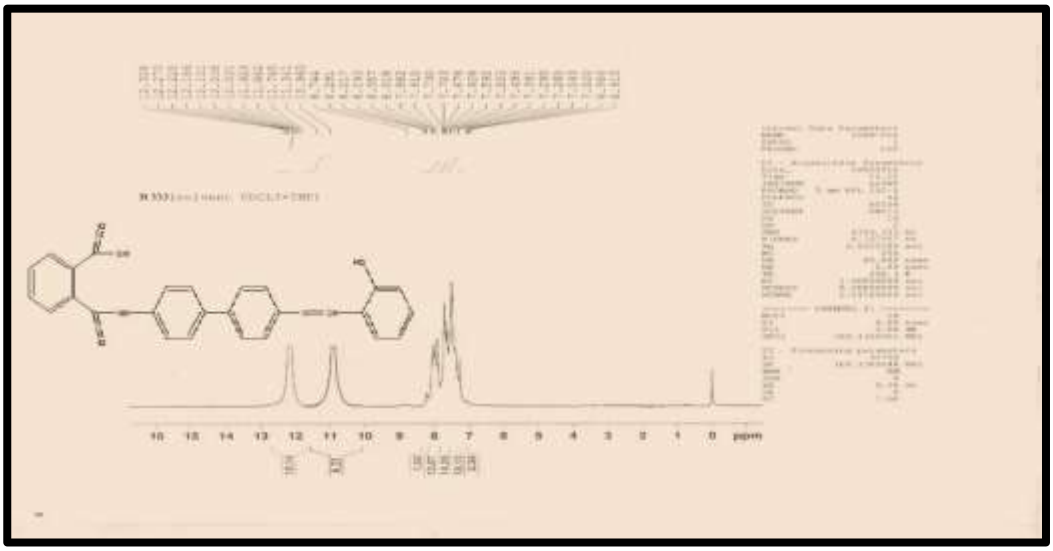


Figure (5): The^{1}H NMR spectrum of the phenolic Schiff base.

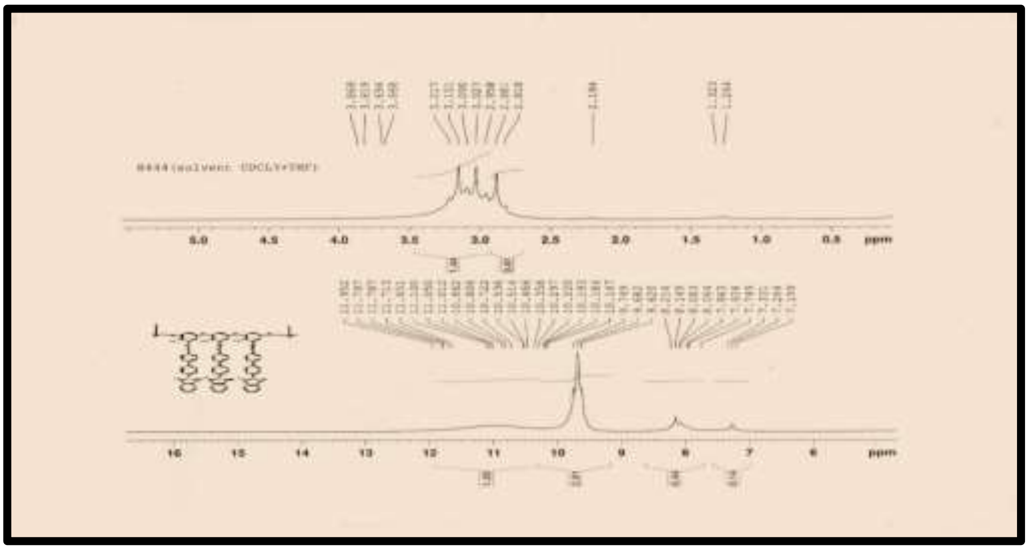


Figure (6): The ^{1}H NMR spectrum of the phenolic Schiff base resin

While^{13}C-NMR spectrum of (1): showed signals at δ = (147.56), 161.92 and 162.50 ppm due to aromatic carbons, (C=O) amide
And (C=O) carboxylic respectively establishment.
^{13}C-NMR spectrum of (3):The signals observed at 160.36 ppm are due to the azomethine carbonsand 116.68 ppm due to aromatic carbonsand signaling at 38.45 ppm due to methylene(CH2) linkage in the resin signal at 161.64 ppm due to(C=O)imid carbons.

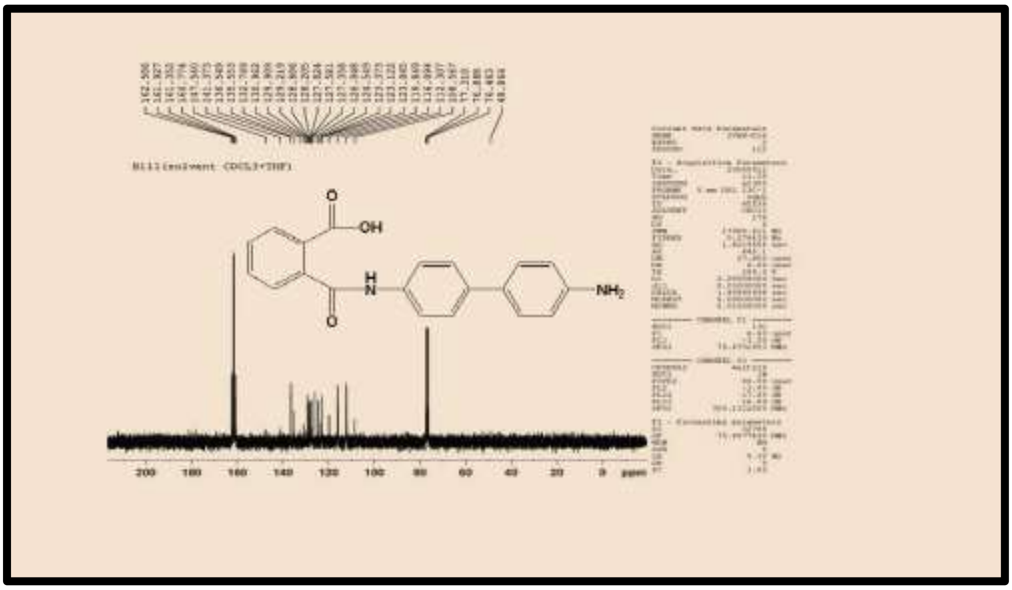


Figure (7): The ^{13}C NMR spectrum of the phthaleamic acid.

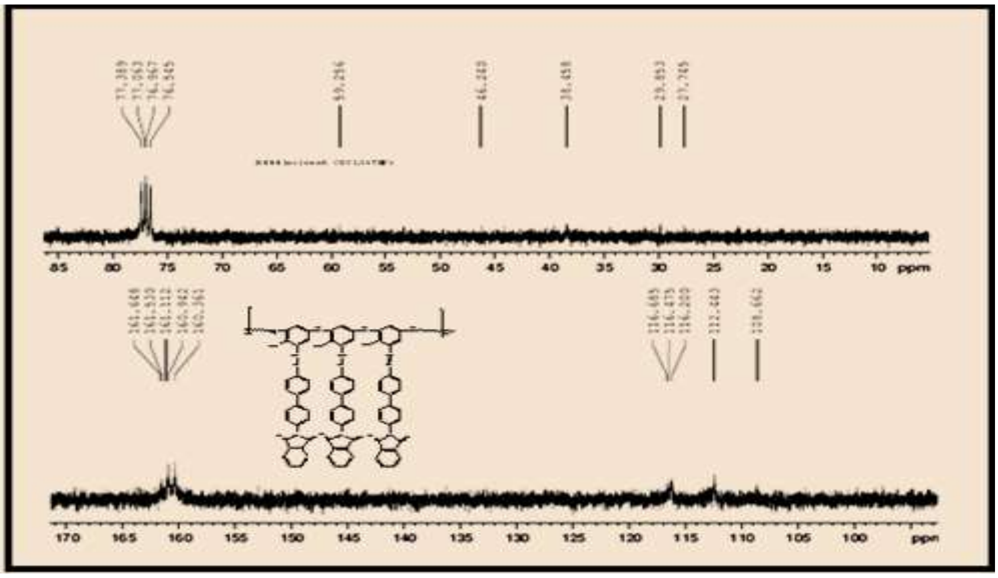


Figure (8): The ^{13}C NMR spectrum of the phenolic Schiff base resin

Thermal properties:
Thermal properties of the prepared polymer that is glass transition temperature and thermal stability were evaluated by the first derivative CAT scan calorimetry and thermo gravimetric The solvent are summarized in Table 3.

Table (3): Thermal properties for resin

Polymer code	Glass transation temperature Tg[◦c]	TGA		
		Polymer Onset Decomposition Temperture (POD)◦c	Decomposition temperature after ten minutes(Td10)◦c	Temperature of Completepolymer Pyrolysis (TCP)◦c
[C.P]	110	241.13	370.7	593.48

All the studied polymer spring analogous DSC visibility For no melting endow thermos , and with a obvious deoxyephedrine transition what prove their amorphous nature . The existence for the imide grouping s is one of the factors accountable for high school price of Tg of the chelating resin. The lowest Tg was observed for synthesized polymer. What is not a model position? Generally, polymer containing further functional groupin polymer serial publication display brings down Tg, because of a reduction in the intermolecular interactions inter alia polymer string [31,32].

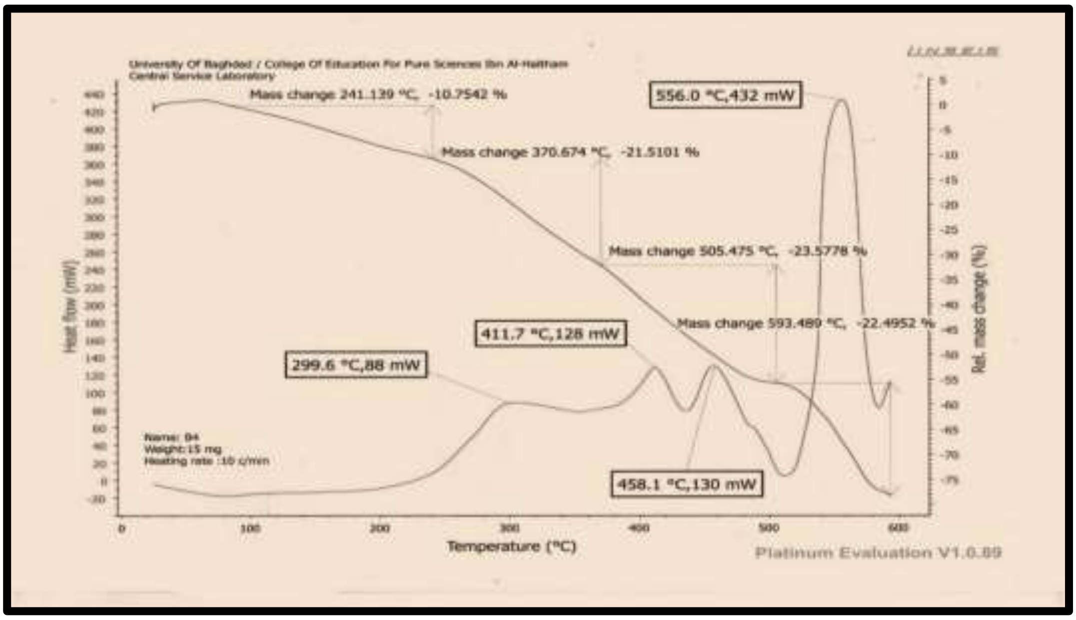
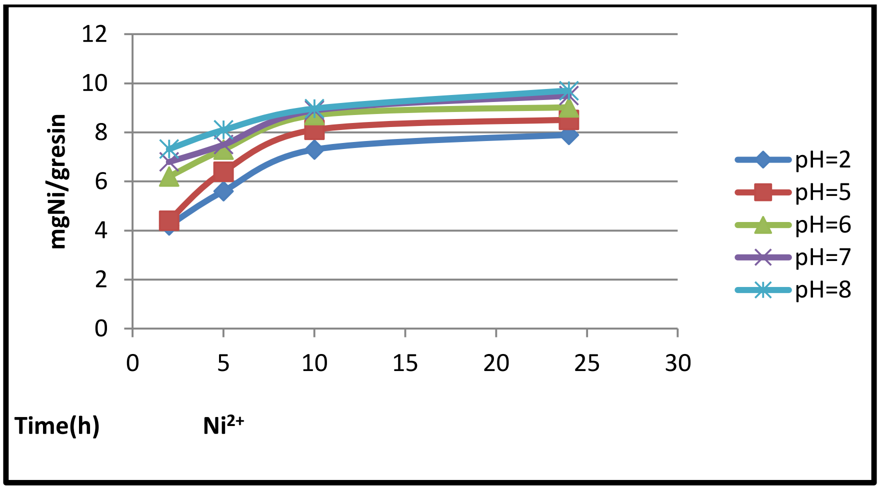


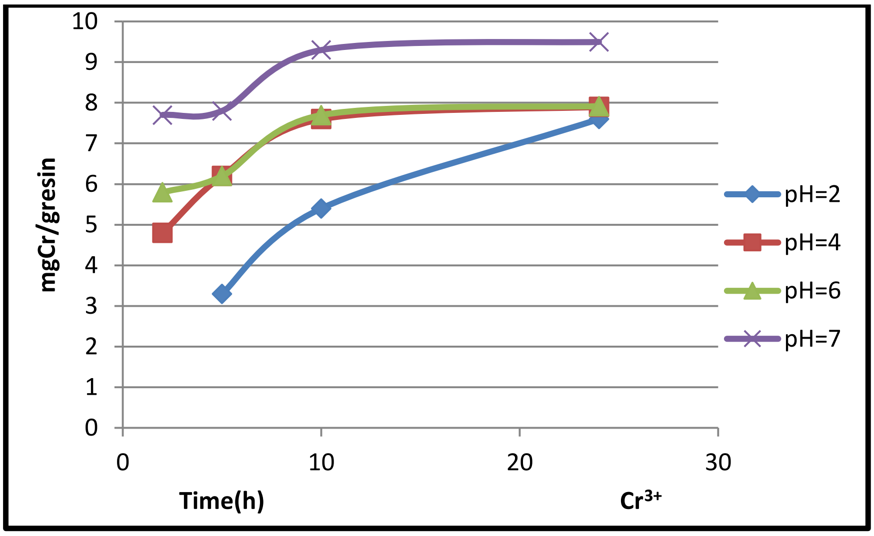
Figure (9): DSC, TGA thermogram of (3) resin

{SyntheticConditionalDeductive} chelating resin efficiency: {situation circumstances scenario} of the analytical {proficiencyexpertise} of the chelating resin is one of the farthest substantial application in analytical chemistry, where the selective chelating rosin for specified elements of the existence of other {is dependent will depend will depend on} on various active, {revolutionary major significant} in the chelating {botanical plant}, as per the {character characteristics mother nature} of the corpuscle -giving and this lead-in to the use of chelating resin as selective {shuttingfinal} off of various ion to the {enthrallconsumeastound}. {You findwill discover} sundry technique used in the retainerof analytical competency of chelating resin. The preferable of these techniques used for this aim are atomic absorption spectroscopy which {can be used is employed} in this study. the analytical competence of the chelating resin (3) across several ions(Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}) have been {researchreviewanalysis}. Aftershakiness 10ml of identical metal ions, a solvent concentration(100ppm)with 0. 1g of chelating resin for interval of 24 {they wouldl} has shown rejoinder ion towards polymer.

Table (4): issue of milligrams of ion dragged by (0.1g)of the chelat Polymer [3] as a function of time in different pH

Ions	PH	Capacity mg/g resin loading			
		Time (hr.)			
		2	5	10	24
Ni^{2+}	2	4.2	5.6	7.3	7.9
	4	4.4	6.4	8.1	8.51
	6	6.2	7.3	8.7	9.02
	7	6.8	7.5	8.9	9.5
	8	7.32	8.1	8.97	9.7
Cr^{3+}	2	3.3	5.4	7.6	7.6
	4	4.8	6.2	7.6	7.9
	6	5.8	6.2	7.7	7.92
	7	7.7	7.8	9.3	9.5
Cd^{2+}	2	3.8	4.2	6.5	7.9
	4	4.1	4.4	6.8	8.2
	6	4.5	4.8	7.1	8.6
Pb^{2+}	2	4.94	5.3	5.5	7.7
	4	5.42	6.54	8.84	9.5
	6	5.75	7.38	9.3	9.62


12
10
8
6
4
2
0
0
5
10
15
20
25
30
mgNi/gresin
pH=2
pH=5
pH=6
pH=7
pH=8
Time(h)
Ni^{2+}


10
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3
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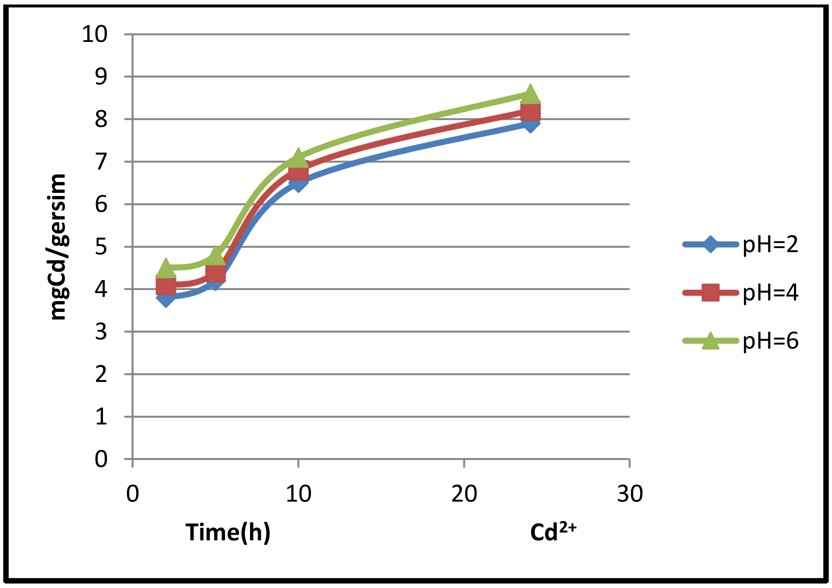
mgCr/gresin
pH=2
pH=4
pH=6
pH=7
Time(h)
Cr^{3+}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pH=4
pH=6
Time(h)
Cd^{2+}

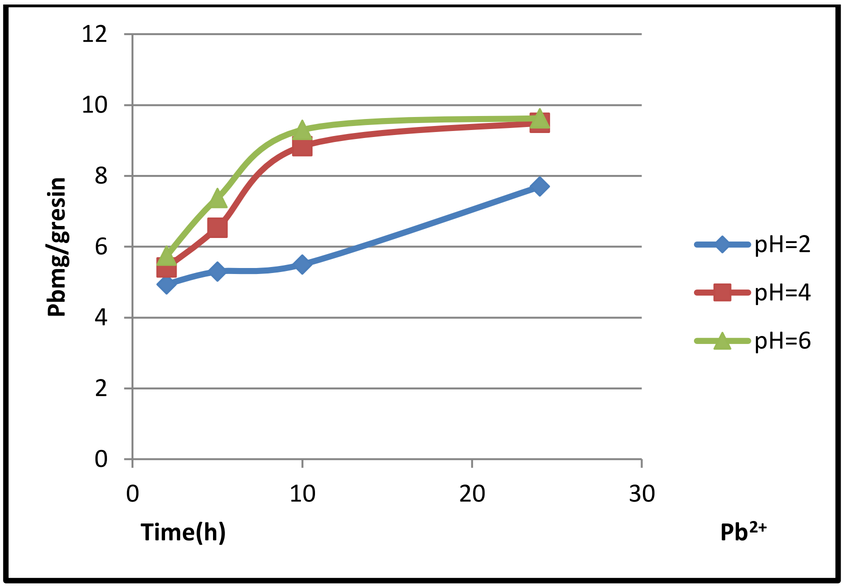
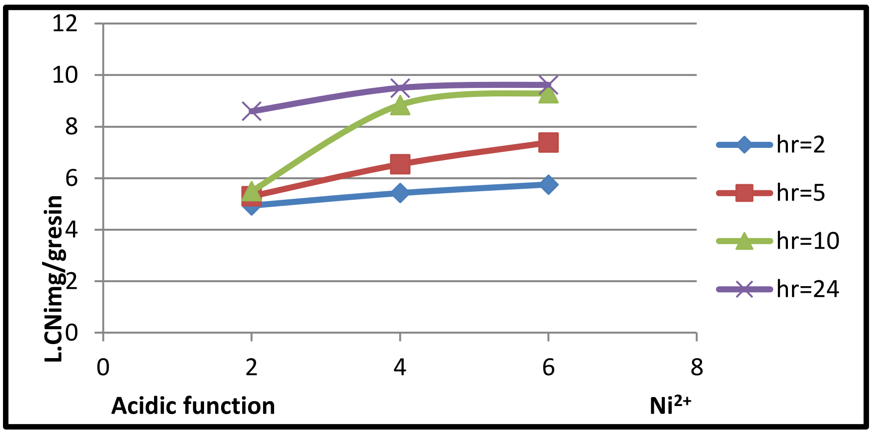
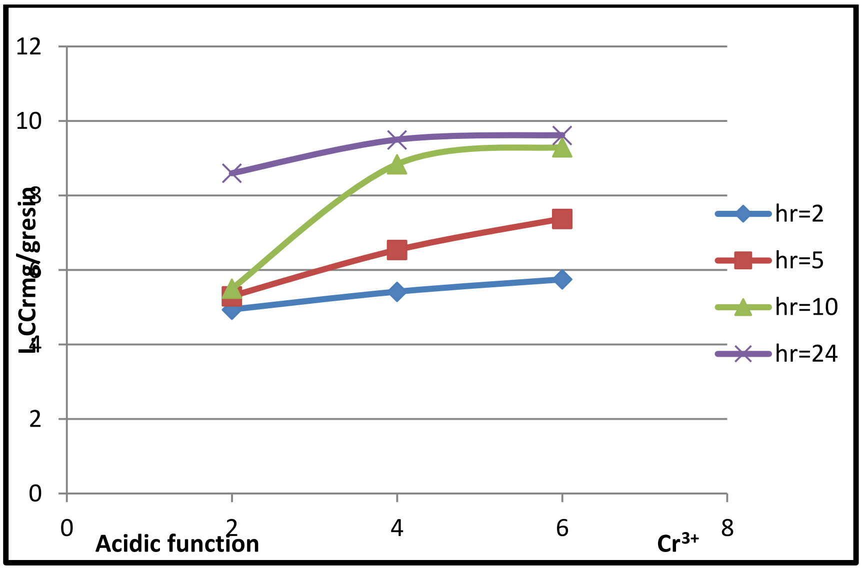
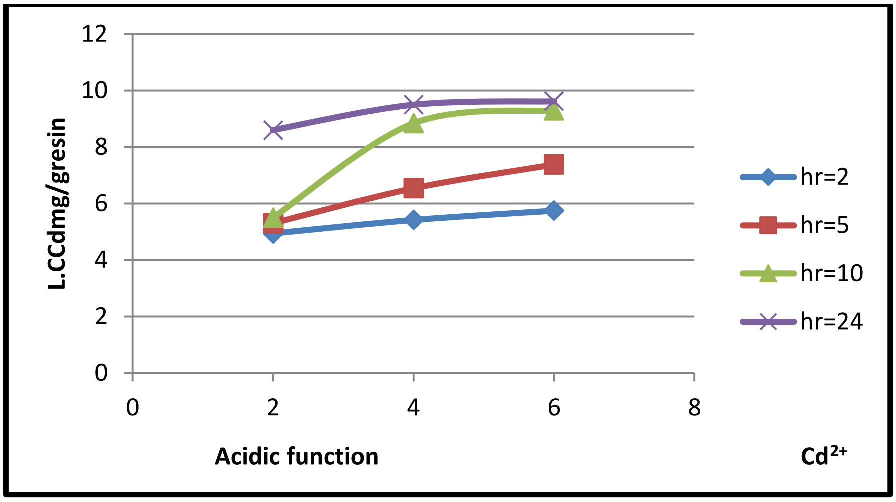


Figure (10): issue of milligrams ions(Ni2+,Cd2+, Pb2+,Cr3+) puff by (0.1g) of the chelat polymer [3] as a function of time in different pH.







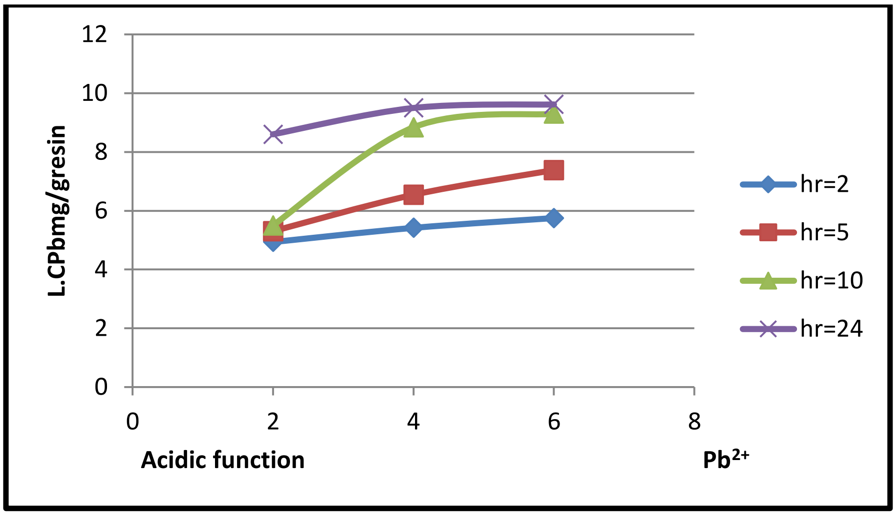


Figure (11): Effect of pH on the load capability ofchelate polymer(trinity)on metal ions (Ni^{2+},Cd^{2+}, Pb^{2+},Cr^{3+}) in different intervention times

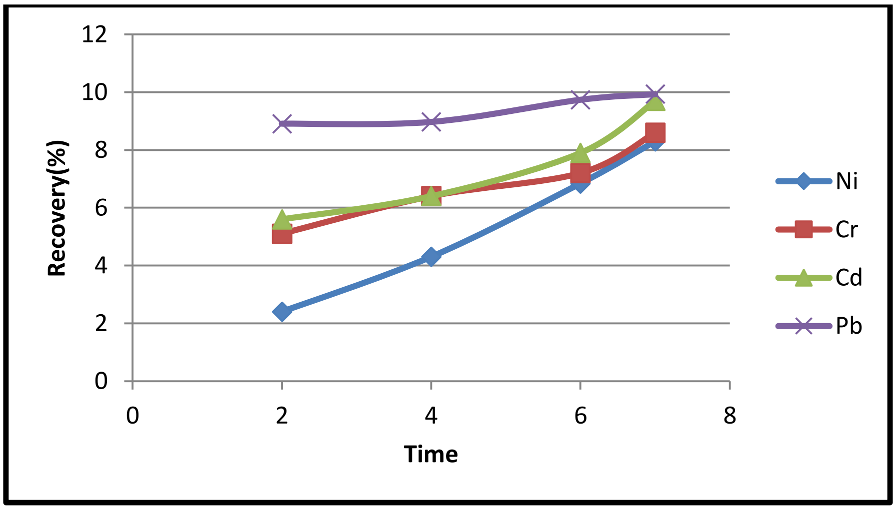


Figure (12):%Recovery (Ni^{2+},$Cd^{2+,}$ Pb^{2+},Cr^{3+}) in the different times

{Summary Bottom line Realization}: - the chelating resin prepared from Schiff {foundation bottom basic} monomer.and formaldehyde {proof facts data} the major power to work as chelating rosin where its extractive {value will depend on value is determined by advantage will depend on advantage is determined byworth will depend onworth is determined by} the number of chelating mathematical group {qualified proficient skilled} since the coordinating connectedness from the crew azomethine (CH = N) and phenol OH. Capacity of the chelating resin in the extraction of {metal material precious metal} {aspectfactor} ion {will depend onis determined by} manifold operator, inclusive the size of metal ions and nature of the {hyperlinkwebsite link} amidst chelating resin and ions. Capacity of the chelating resin synthesis increased with increased sharply {TraditionalTime-honoredCommon} Greek valance. {With thisThrough this From this} {Concern thoughtaccount}, it is establish the towering extractive worthiness of the resin is when the bill pH =8 where the requisite midfield command to a fragmentary; sectional melting of the {botanical plant}, {resulting inultimately causingbringing about} the plight of separate the resin {packedfilledcrammed} metal ions.

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