Synthesis , Characterzation and analytical study of polymer derive from extracted (Hibiscus Sabdariffa) leaves plant with 8-hydroxyquinoline

تحضير وتشخيص ودراسة تحليليه لبوليمرات مشتقة من مستخلص أوراق الكجرات مع هيدوكسي ـ كوينولين

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Abstract :

Commerical Hibiscus sabdariffa is known for delicacy and also for medicinal properties .The
present paper deals to study the extraction in aqueous solution of leaves shows best results in which phenolics have been found to be present more in leaves , the extracting result was cured with different percentages of (8-hydroxyquinoline)(2%, 4% , 6%) , polymerization takesplace in presence of formaldehyde . The grinded resin was characterized by (IR),DSC and CHN analysis . The resin was used as a chelating polymer for the investigation of loading capacity (L.C) of [Bi^{+3} , Fe^{+3}, Ni^{+2}] from their diluted solution (100ppm) , The (L.C) of the resin was determined using (uv-v) spectrophotemetry as a function of both shaking time & pH . The metal ion solution optimum L.C. of the resin was found as following order .

$Bi^{3+} > Fe^{3+} > Ni^{2+}$

Keywords : Hibiscus sabdariffa , leaf, Spectrophotemetry , polymerization

الخلاصة :

ورق شاي الكجرات يستخدم لاغراض تغذية وطبية . تم استخلاص المركبات الفينولية في محيط مائي المتواجدة بصورة كبيرة في أوراق النبتة عملت مع الفورمالديهايد مع نسب مختلفة من هيدروكسي كوينولين (6% ، 4% ، 2%) . ثم بلمرت هذه المونيمرات على حمام زيتي بدرجة 70°C . درست كفاءة هذا الراتنج بعد تشخيصه بتقنية I.R و CHN وDSCمع عدد من الايونات من محاليلها المخففة (100 ppm) بأتباع التقنية المطيافية UV-visible لتعيين طاقة التحميل الاستيعابية لكل من Ni^{2+} ، Fe^{3+} ، Bi^{3+} كدالة للزمن والدالة الحامضية فكانت النتائج كما يلي :- $Bi^{3+} > Fe^{3+}$
سعة تحمل الراتنج Ni^{2+} كانت قليلة جداً تكاد تكون معدومة .

Introduction :

Hibiscus Sabdariffa belongs to the family Malvacea . It an annual herb cultivated for its leaves and stem[(1)] . The physic –chemical characteristics of Hibisucs . Sabdariffa was studied and it was characterized as highly acidic fruit. With low sugar content[(2)] . Phenolics were detected in leaves, have attracted a great attention in relation to their beneficial effects on health , several experimental studies have revealed biological and pharcological properties of phenolics compounds and bioflavonoid that have excellent antioxidant properties[(3)] . Phenolic are active in curing kidney & stomach problems as well as helpful as anti –inflammatory in action[(4)] . Many part of the plant is reported to be used as treatment for several diseases such as hypertension and urinary tract infection and its effect on raised blood pressure[(5)]. Or on blood lipid lowering[(6)]and it found that (Hibiscus Sabdariffa) infusion has positive effects on BP in type II diabetic with mild hypertension[(7)].

The aim of the present invesgation was to study the polymerization of phenotilled water for 24hr. in mechanical shaker. Polymerization takeplace with 8-hydrexyquinoline inpresance of formaldehyde .

This resin was used as chelating polymer for investigation of L.C. metal ions of (Bi^{3+}, Fe^{3+}, Ni^{2+}) using (UV-visible) Spectrophotometer.

Experimental

i)Materials: Commerical (Hibiscus Sabdariffa), (2) All Starting materials were purchased from fluka , B.D.H. and Merck

Instrumentation : FTIR-8400S – Fourier Tranform infrared spectrophotometer were recorded On Shimadzu.,Balance, Sensitive Balance , BL / 5005 / Sartorious ,pH – meter – H durgeasol Co./Berman, Lab – Therm Shaker / Adolf Kuhner AG., (uv-v) Spectrophotometry recorded On Shimadzue.,DSC-60 Differential Scanning Calorimeter Shimadzu.,C.E-440 Elemental Analyzer,EXETER

ii) Preparation of analytical Resin :

A multy neck top reaction vessel equipped with mechanical stirrer , digital thermometer and condenser . The reaction was charged with (8 g) of extracted leaves H_2O/ NaNO3(highly phenolic acid contained) as a monomer and (3g) of 8-hydroxyquinoline in presence of formaldehyde (20ml) then 10% NaOH was added until the (pH = 9 – 10). The reaction system was heated in an oil bath at 70°C for 3Hr. The reaction was continued until the mixture reach its gel form . The reaction was stopped and the last product was neutralized with 10% H_3PO_4 .

(iii) Chelating efficiency :

The Chelating efficiency of resin toward the metals ions were studied [Bi^{3+} , Fe^{3+} , Ni^{2+}] by bath method[8] . By treating (0.1gm) resin with (25ml) metals ion solution (100 ppm) using mechanical shaker at room temperature . The resin was filtered and the concentration of the ions in the filtrate was determined by using UV-visible spectrophotometer. The extraction chelating efficiency was examined at several pH and time .

(iv) Determination of Fe^{3+} [9]

The filtrate of experiment of Fe^{3+} was controlled by dilute ammonical solution at PH (2-3) , (5ml) of 10% 5-Sulphsalysalic acid (w/v %) was added then adjust the pH= 9 by (1 M) ammonia solution . transfer to (50ml) volumetric flask and dilute to mark with distilled water . (uv-vis) spectrophotemetry as a function of both shaking time and pH of metal ion solution at λmax=425nm

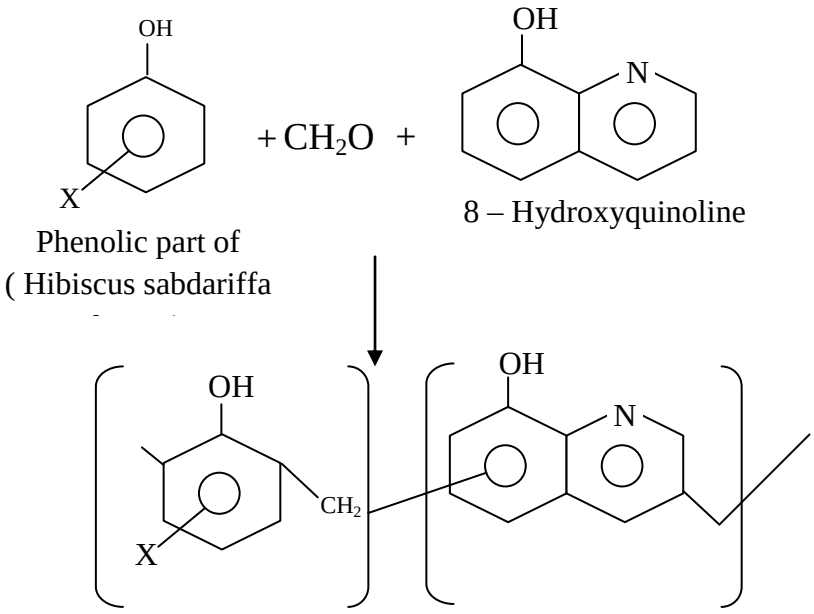
(v)Determination of Bi^{3+} [10]

The filtrate of experiments of Bi^{3+} transfer to 50ml volumetric flask after addition of (5ml) of (50%) H_2SO_4 (%v/v) and (2%) ascorbic acid (w/v) was added then (10ml) of (20%) (w/v %) potassium iodate . Complete the volumetric flask to the mark with distilled water . (L.C) of the resin was determined using UV-visible spectrophotemtry for each elements was calculated from the difference of concentration before & after treatment .

Result and Discussion :

The obtained product was characterized by various techniques I.R. and thermal analysis (DSC),the I.R spectra was recorded the spectra were shown in fig(1) for (Hibiscus sabdariffa) polymerization, hydroxyl band are related to group of hydroxy at 3382 cm^{-1} as wide band , at 1791 cm^{-1} related to carbonyl group C= 0, 1629 cm^{-1} related to benzene ring, 1070 – 1097 cm^{-1} related to C – O – C linkage group . The literature review refer to the expected structure of (Hibiscus Sabdariffa) while is the repeating unit contains , Tanins , Alkaloids , Phenolic molecules . So the polymerization take place due to phenolic groups using different percentage of 8 – HQ (2% , 4% , 6%). In the presence of formalin solution (35%) and 10% sodium hydroxide solution , The FTIR spectra shown in Figs (2, 3 , 4 cm^{-1}) related to C = C of the benzene ring , also bands at (116 – 1068 cm^{-1}) conterbuted to other linkage (C – O – C) on the other hand band at 2937 due to – CH_2 – group . Also of the copolymerization occur the behavior of the resulting product differs from the original compounds , so after curing by heating , the proposed structure of the final product as below :

Formula expected for copolymer result from the intercalation of the three copolymers are



The results obtained during the study showed that the resin has remarkable ability of chelating efficiency toward the metal ions studied was in the following order :

$Bi^{3+} > Fe^{3+} > Ni^{2+}$

The optimum conditions toward pH and trcatment time for extraction metal ions were obtained typical results as show in figs (9-14)

The best conditions of the loading capacity of the resin from (2% , 4% , 6%) , 8-hydroxy quinoline with Bi^{3+} was found to be as show in table (1) .whear as gave result Ni+2 compaired with Fe+3 in table2. From the result of differential scanning calorometry (DSC)study,the thermogram of the isolated material in fig(5)show the glass transition temperature (Tg)at 76C°,also there is an endothermic peak at 150C° may be due to melting temperature, while the thermogram as in fig(6),show shift in (Tg)to about 134C°, which indicate the reaction of isolated material with 8-hydroxy quinoline(2%)forming acopolymeric material with new (Tg).the same result obtain when addition of 4% and 6% of 8-hydroxy quinoline ashown in fig(7-8).i.e in fig(3)the (Tg) is 132C° while its about 138C° when the percentage of 8-hydroxy quinoline is 6%.also fig(4) show exothermic peak at >300C° which attributed to decomposition of the copolymer .Finally all the measurement occure at N2 atmosphere and at heating rate 10C°/min.

Formula expected for ter polymer result from the reaction of three monomers,the result from CHN analysis indicate the expected structure except for carbon due to type of (X)group in the unit of Hibiscus sabdarrifa[11,12]. Table (1): show the results of CHN analysis.

	%C	%H	%N
Predicated % content	76.9	5.1	5.2
Result	70.6 ±2.640	4.792 ±0.03	4.837 ±0.095

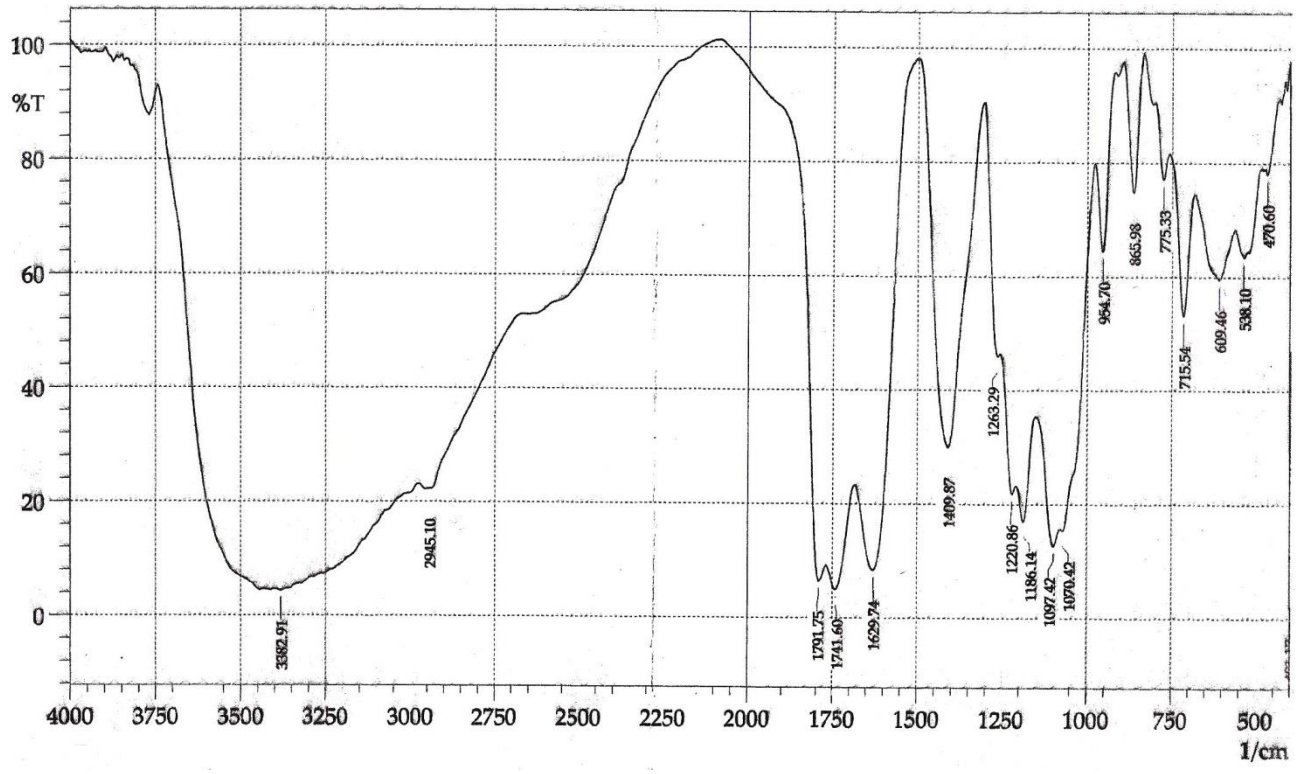
Table(1)CHN Data analysis for isolated material with 4% 8-hydroxy quinoline

	2%	4%	6%
L.C	22.5	13.5	15
Best PH	2.5	2.5	4.5
Time (hr)	24	24	6

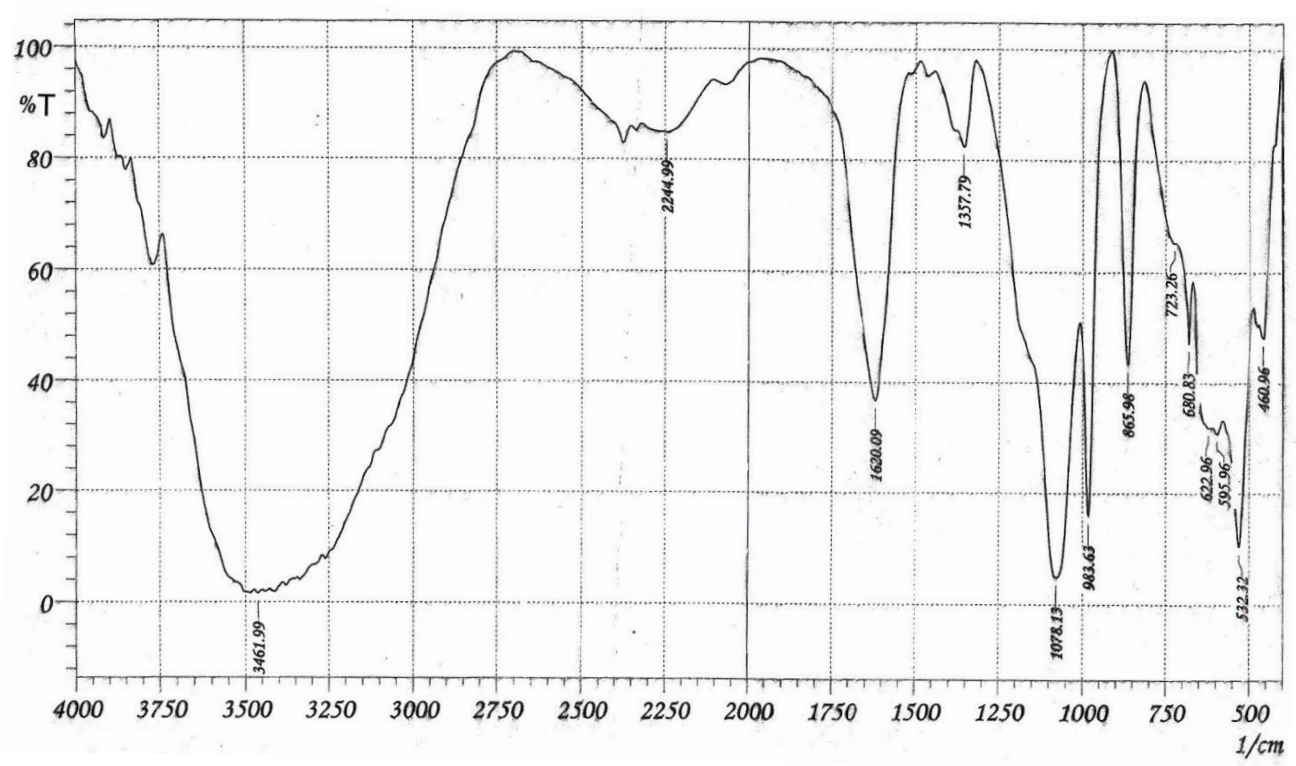
Table (2) : The chelating eff. Data of resin with Bi^{3+}

	2%	4%	6%
L.C	24.25	24.29	22.8
Best PH	2	2	2
Time (hr)	24	24	24

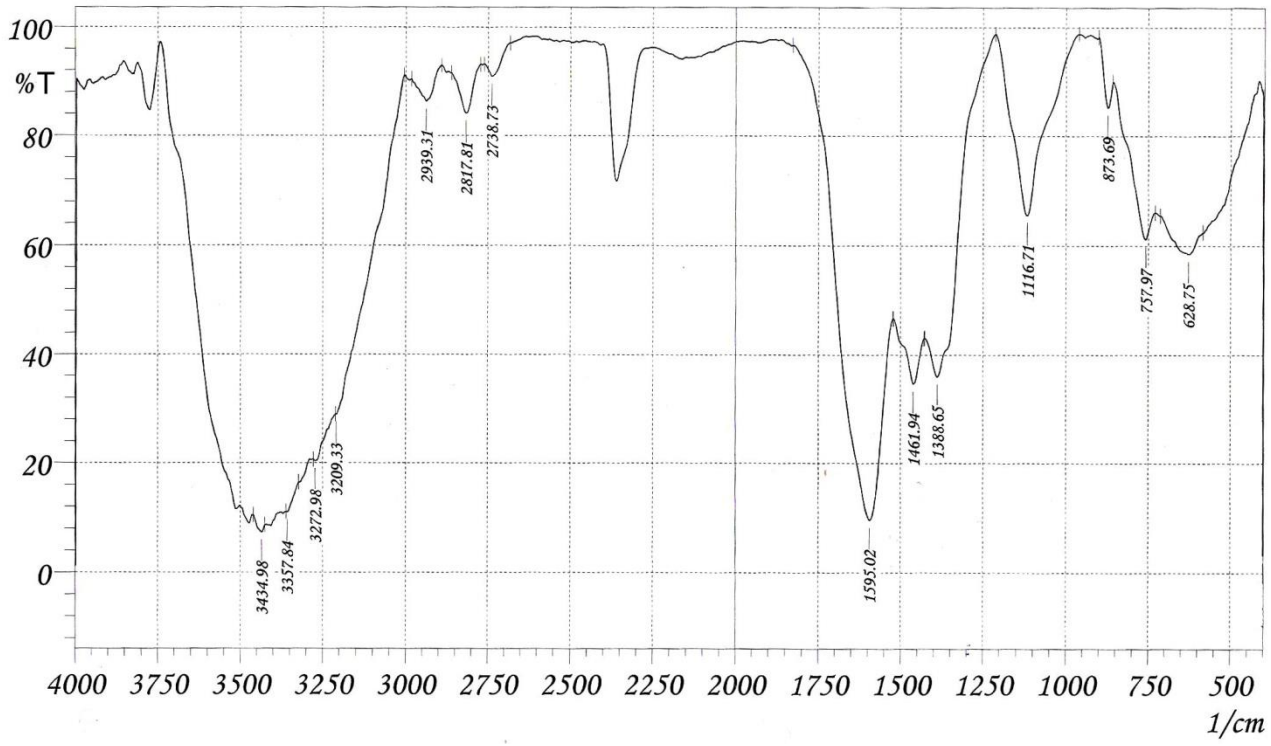
Table (2) : The chelating eff. Data of resin with Fe3+



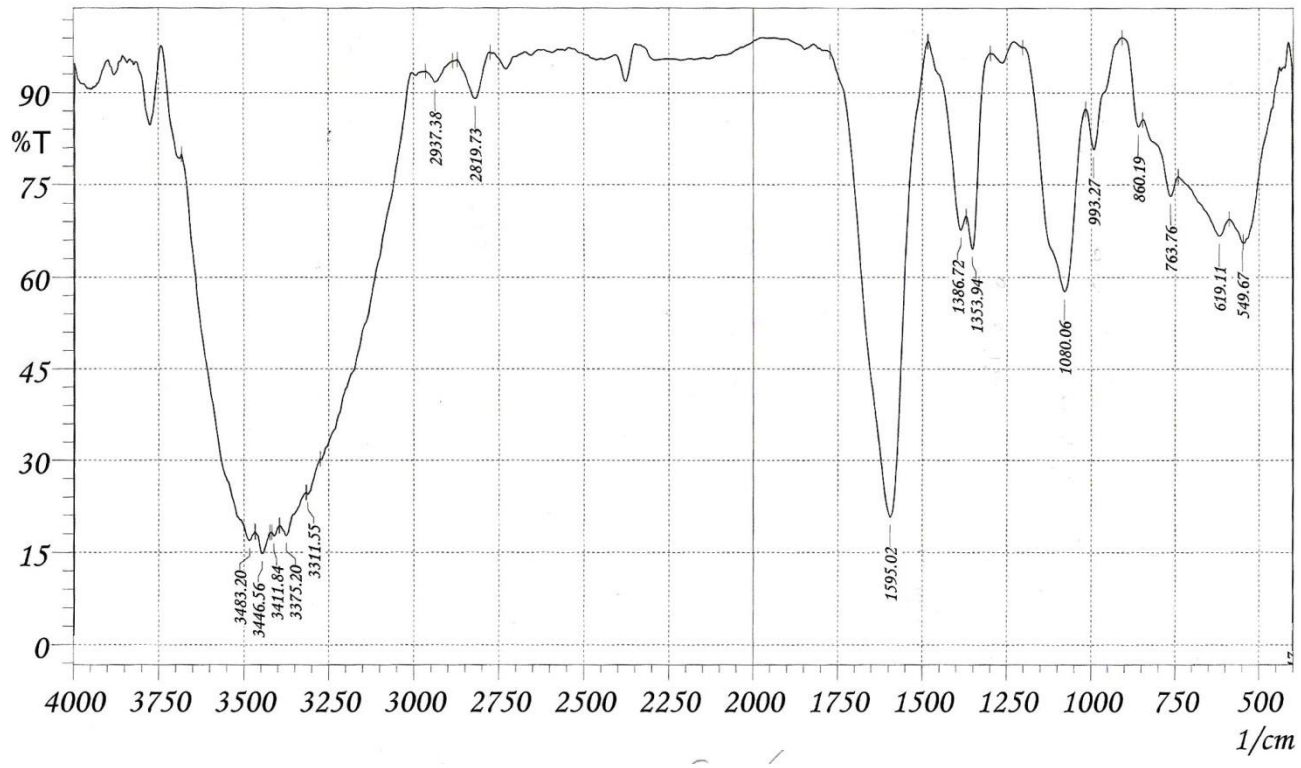
Fig(1) FT-IR spectrum For Hibiscus Sabdariffa copolymerization



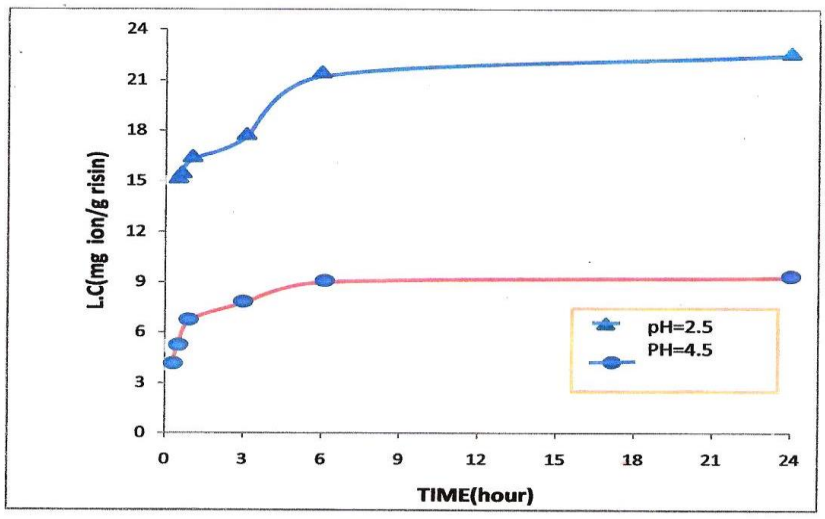
Fig(2)FT- IR spectrum For isolated material with 2% 8-hydroxy quinoline



Fig(3) FT-IR spectrum for isolated material with 4% 8-hydroxy quinoline



Fig(4) FT- IR spectrum For isolated material with 8-hydroxy quinoline



Fig(9)Effect of 2% L.C Resin as afunction of time at different PH for Bi+3 inos

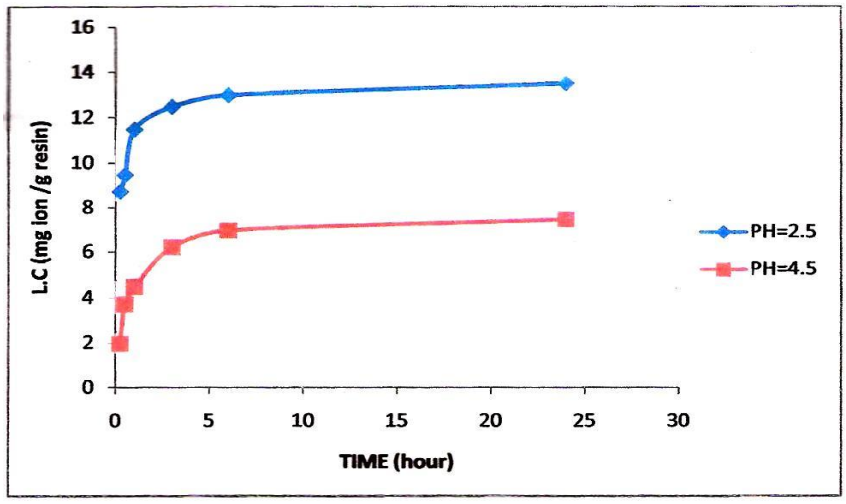
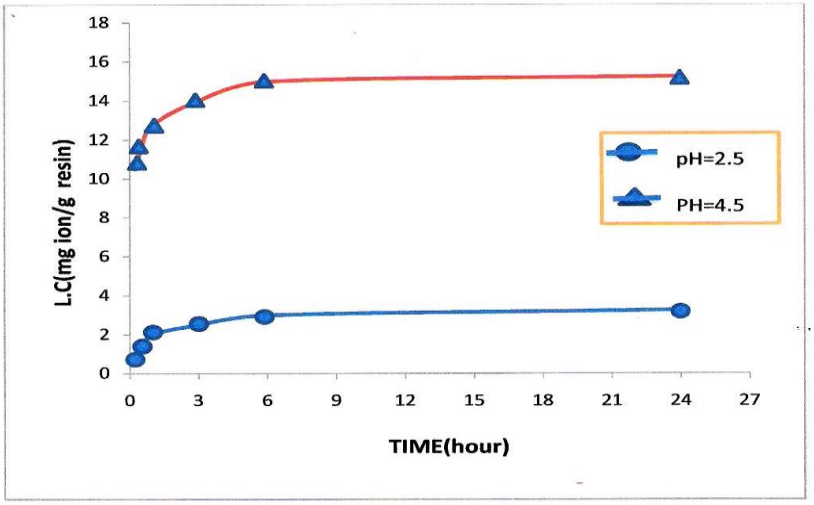
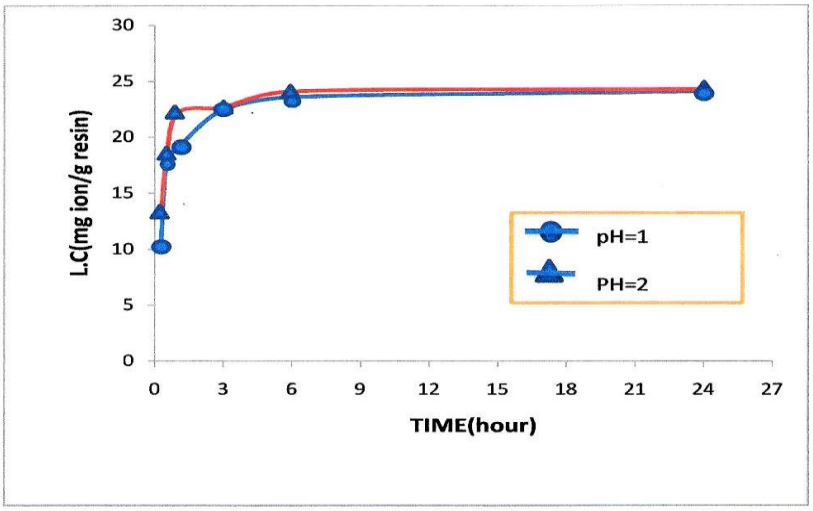


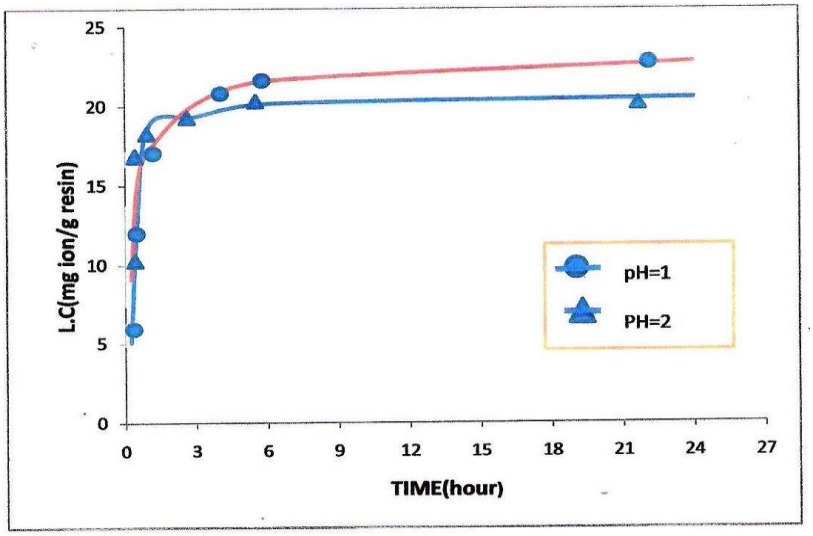
Fig (10)Effect of 4% L.C Resine as afunction of time at different PH for Bi+3 ions



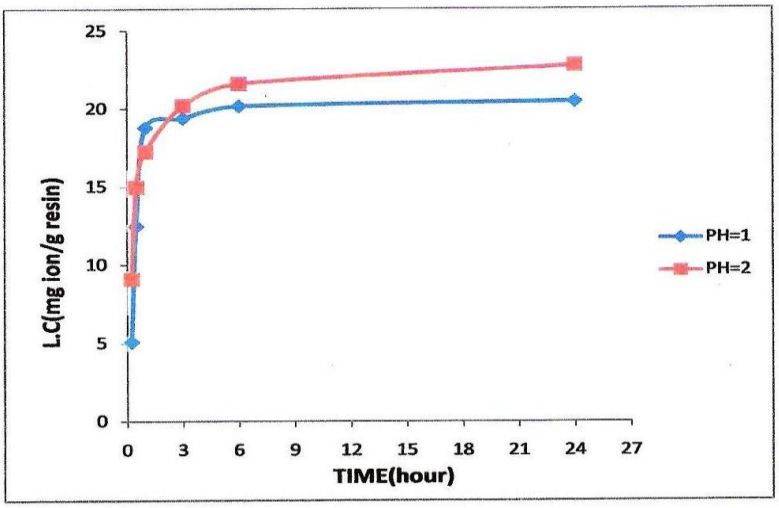
Fig(11) Effect of 6% L.C Resin as afunction of time at different PH for Bi+3 ions



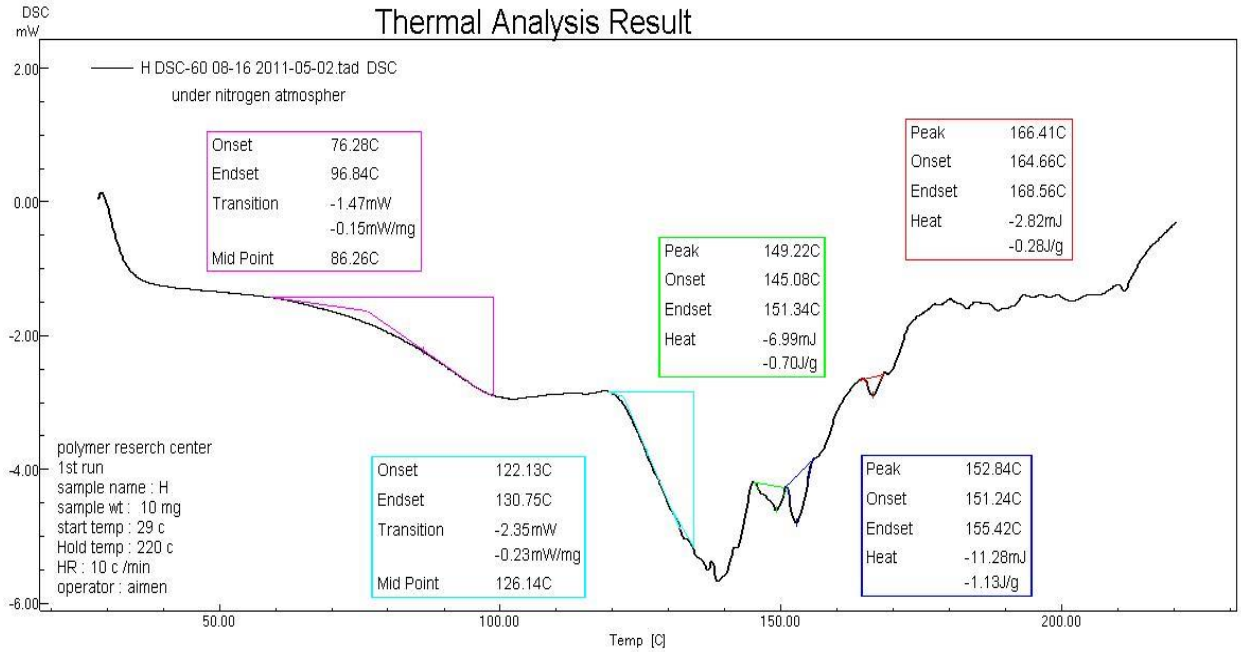
Fig(12)Effect of 2% L.C Resin as afunction of time at different PH for Fe+3 ions



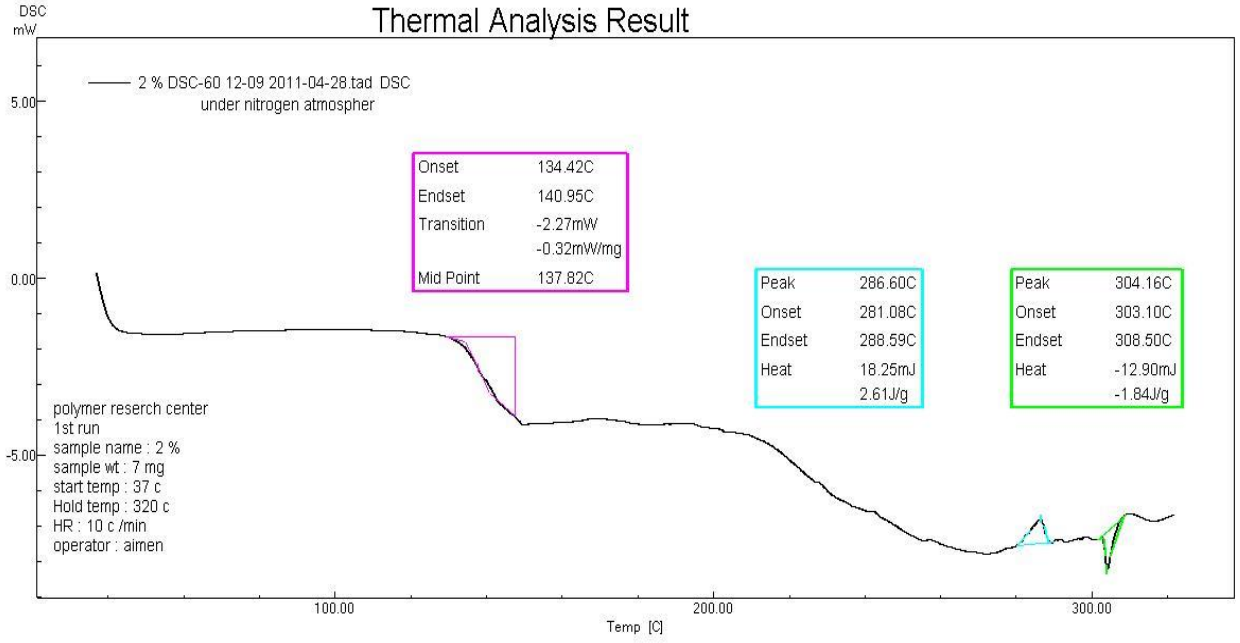
Fig(13)Effect of 4%L.C Resin as afunction of time at different PH for Fe+3 ions



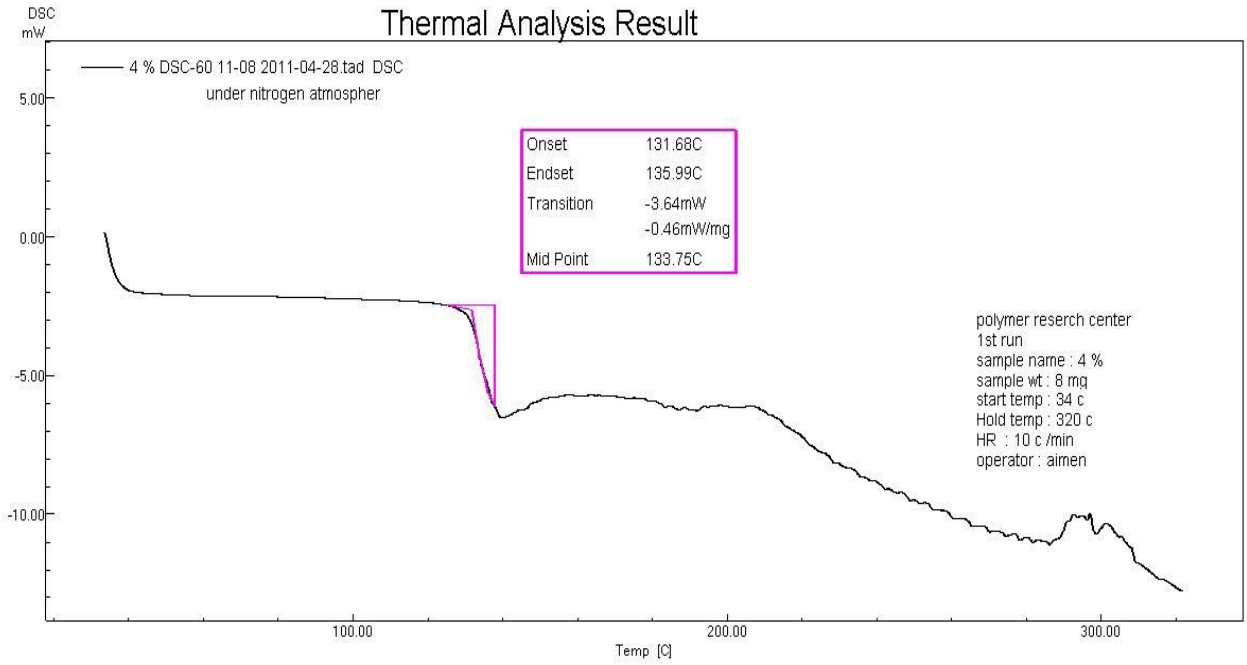
Fig(14)Effect of 6% L.C Resin as afunction of time at different PH for Fe+3 ions



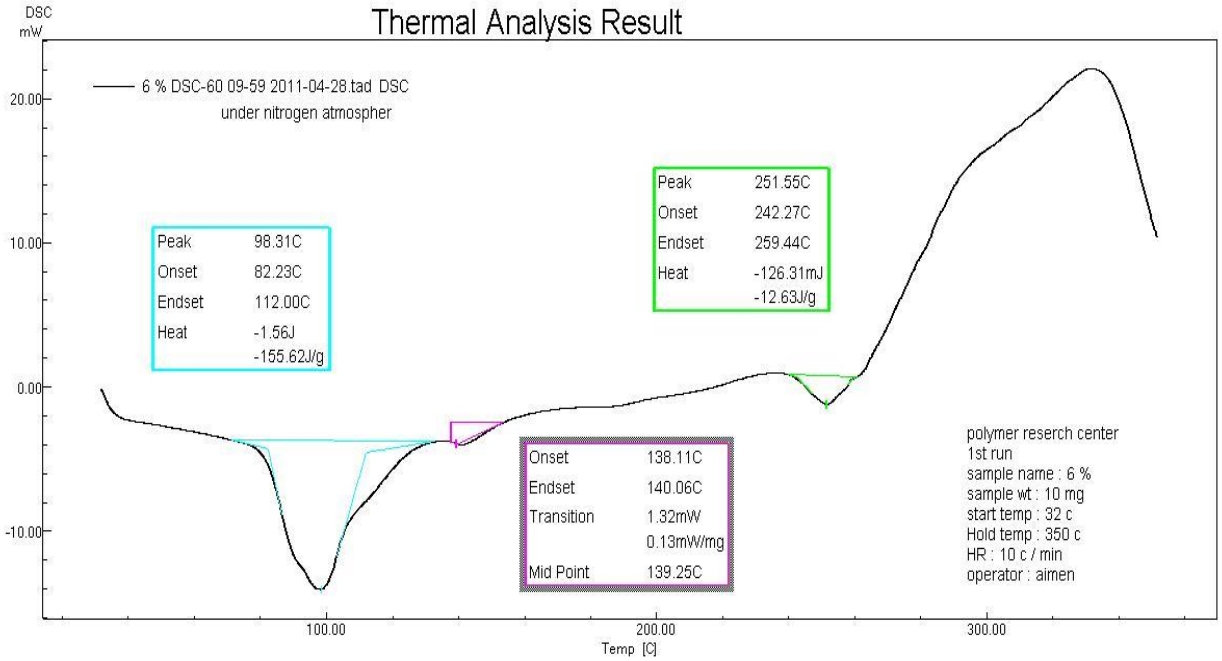
Fig(5) DSC Study for Hibiscus Sabdariffa polymerization



Fig(6) DSC Study for isolated material with 2% 8-hydroxy quinoline



Fig(7) DSC Study for isolated material with 4% 8-hydroxy quinoline



Fig(8) DSC Study for isolated material with 6% 8-hydroxy quinoline

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