



Identification and Investigation of the Chelating Activity of Some Phenolic Polymers Derived from Mefenamic Acid



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NEW phenol formaldehyde resin synthesized from multi steps, the first step converts mefenamic acid to their ester ethyl 2-((2,3-dimethylphenyl) amino) benzoate (T_1) by reaction with ethanol catalyzed by sulfuric acid as a catalyzed. The hydrazide derivatives 2-((2,3-dimethylphenyl) amino) benzohydrazide (T_2) prepared through the reaction ester(T_1) with hydrazine hydrate in ethanol. Third step Prepared of some Schiff bases phenolic [T_3 - T_5], (E)-2-((2,3-dimethylphenyl) amino)- N' -(4-hydroxy-2-methylbenzylidene) benzohydrazide (T_3), (E)-2-((2,3- dimethylphenyl) amino)- N' -(3-hydroxy-2-methoxybenzylidene)benzohydr azide(T_4) and(E)- N' -(2,4-dihydroxy-6-methylbenzylidene)-2-((2,3-dimethylphenyl) amino) benzohydrazide (T_5) finally prepared the phenol formaldehyde resins [T_6 - T_7]. The chelating ability of these polymers was studied to extract some metallic ions such as Co^{+2} , Fe^{+3} , Ni^{+2} by using batch equilibrium method. The different factors are studied, loading capacity, pH and time. All the synthesized compounds were characterized by using by various spectroscopic techniques such as FTIR, 1H NMR as well as DSC.

Keywords: Mefenamic acid, Chelating, Thermal analysis (DSC), Loading Capacity (LC).

Introduction

Aromatic aldehydes react smoothly under moderate conditions and low temperatures in or without an appropriate solvent, When aromatic amines are condensed with aromatic aldehydes[1], the drawing groups of the electrons in the para site are barren in the amines, reducing the reaction speed while increasing the reaction rate in the case of aldehyde compensation[2], When intensifying aromatic amines with ketones, especially aromatics, they require high temperature, longer reaction time and auxiliary factor, as well as

water displacement[3]. Other characteristics of the right-hand vehicles are often colored[4], and it has the ability to form colored complexes with most metal ions transitional[5-6]. Chelate resins can be prepared containing the azomethine group the group responsible for the formation of the complex with many different element ions [7-10]. Chelated polymers are used to remove some ions of non-degradable elements in industrial water [11-13], as well as in the manufacture of selective electrodes used in ion membranes [14-17].

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Received 7/6/2019; Accepted 20/8/2019

DOI: 10.21608/ejchem.2019.13353.1836

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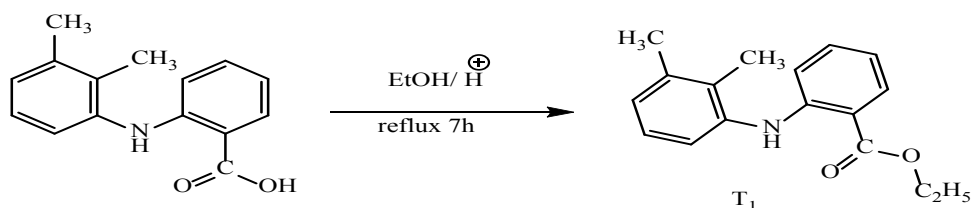
Instruments and synthesis methods

FTIR spectra of all compounds were recorded on Cary FTIR 600 Series Spectrophotometer using KBr pellets in the range 4000-400 cm^{-1} . The experimental values of ^1H and ^{13}C NMR spectra for the studied compounds were scanned on a Bruker 500 MHz spectrometer with a field gradient to operating at 500 MHz for proton observation using Dimethylsulphoxide(DMSO- d_6) as solvent and tetramethylsilane (TMS) as internal standard. The differential scanning calorimetry were carried out using (DSC Q1000V9.9 Build), the sample (4-5.7mg) in a sealed aluminum pan heating from 0 to 200 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}$ and

under nitrogen flow of 20 cm^3/min . Indium was used as standard for calibrating the temperature.

Preparation ethyl 2-((2,3-dimethylphenyl) amino) benzoate (T_1):

In a 100mL round bottom flask, (2.4129gm, 0.01 mol) of the carboxylic acid in dissolved in 50 ml of absolute ethanol and add 2 ml of concentrated sulfuric acid as catalyzed. The mixture reflux for (7 hours) and then wash with sodium bicarbonate solution, ester was extracted (20 x 3 mL) of diethyl ether. The organic layer dried then evaporates the solvent, the product crystallized from ethanol, (Fig.1).

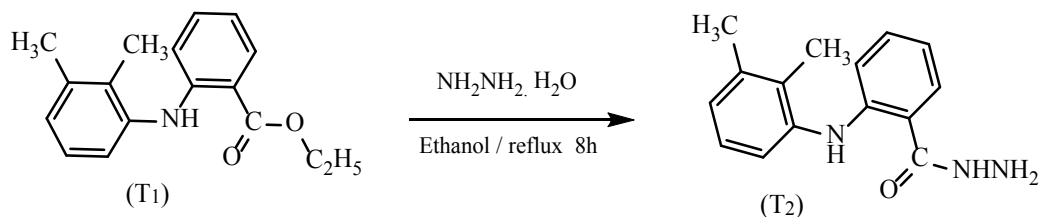


figure(1)

Preparation of 2-((2,3-dimethylphenyl) amino) benzohydrazide (T_2):

To a (2.6934gm, 0.01mol) of compound T_1

in 25 mL ethanol, 6mL of hydrazine hydrate, the mixture was heated under reflux with stirring for 8 hours. The mixture cooled to get white solid product then dried and recrystallized from ethanol, melting point (191-193) $^{\circ}\text{C}$, (Fig.2).



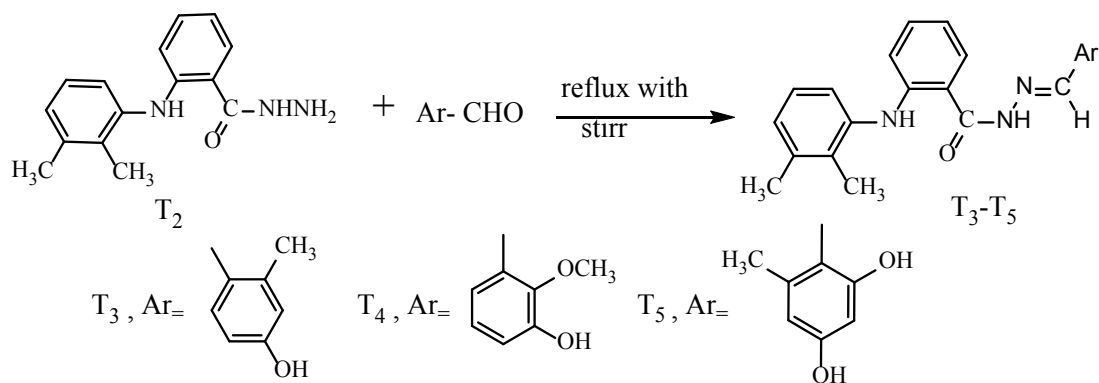
figure(2)

General Procedure for the synthesis of [T_3 - T_5]

In a suitable round flat bottom flask (0.001 mol, 0.255gm) of the compound (T_2) in 50ml ethanol, (0.001mol) of the appropriate benzaldehyde was added. the mixture was heated under reflux with stirring for 6 hours. cooled to get white solid product then dried and recrystallized from ethanol. Table (1) shows some physical properties of compounds [T_3 - T_5], (Fig.3).

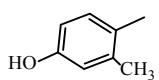
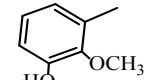
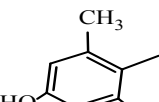
Method of preparation chelating resins [T_6 - T_8]:

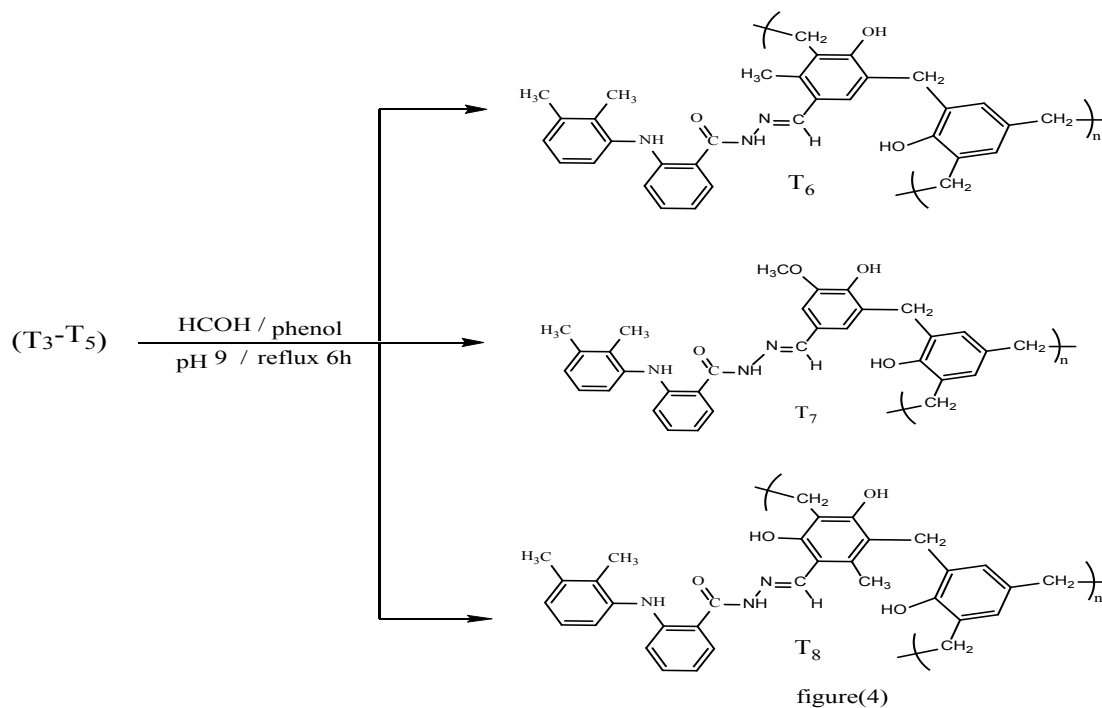
In round flat bottom flask 0.005mol of synthesized compounds [T_5 - T_3] dissolved in 50mL THF then added 7mg phenol, and 25 mL Formaldehyde, the acidity of mixture adjusted at pH 9 by sodium hydroxide solution, then heated under reflux 16 hours. Cool, Evaporation the solvent the residue poured in porcelain dish and heat at 250 $^{\circ}\text{C}$ for 6 hours to complete the polymerization, (Fig.4).



figure(3)

TABLE (1): Some physical properties of prepared compounds [T₃-T₅]

COMP.	Radical	Molecular Formula	Melting Point (°C)	Yield %	Product Color
T3		C ₁₇ H ₂₃ N ₃ O ₂	183-185	58	White
T4		C ₁₇ H ₂₃ N ₃ O ₃	196-198	52	White
T5		C ₁₇ H ₂₃ N ₃ O ₃	188-190	46	Brown



figure(4)

Preparation of standard solutions for element ions:

Prepare the standard solutions by dissolving the necessary weights of the metal nitrate in the least possible amount of water with the addition

of 2 mL of concentrated nitric acid or concentrated hydrochloric acid and according to the salt used. Then complete the volume to 500 mL with non-ionic water. Table (2) shows the weights used salts of the elements for the preparation of standard solutions 1000 ppm in metal ion.

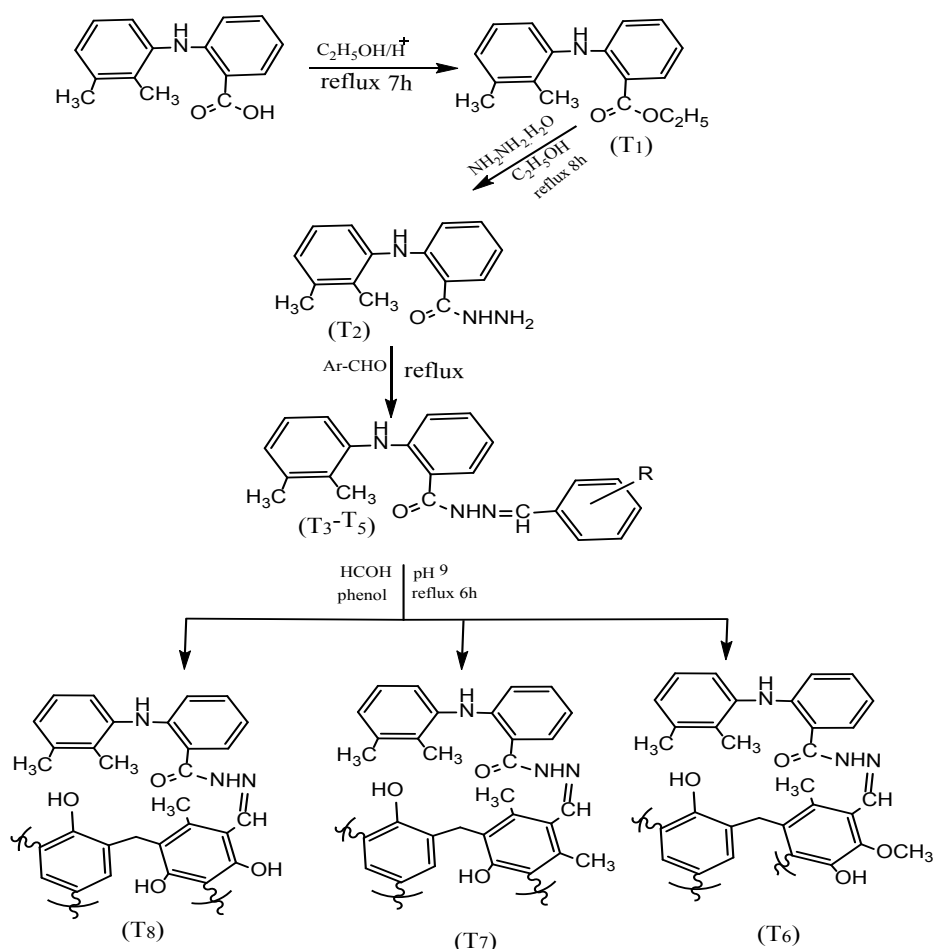
TABLE (2) Weights used for salts of each element necessary to obtain (500 ml) of solutions at a concentration of (1000) ppm.

NO	Molecular formula	Weight in (500 ml)
1	Co (NO ₃) ₂ .6H ₂ O	2.961mg
2	FeCl ₃	1.312mg
3	Ni (NO ₃) ₂ .3H ₂ O	2.132mg

Results and Discussion

A number of compounds derived from ester

and then to the chelate polymers are shown and the scheme 1 below shows the prepared compounds.



H¹ NMR spectra of (T₁).

The magnetic resonance spectra of the T₁ showed a signal at 0.91 ppm was due to the ringing of CH₃ protons. AS well as a two a single signal at 2.09 ppm and 2.28 ppm are associated to the protons of (2CH₃) interlocking benzene ring. The appearance

of a signal at 5.11 ppm belonging to the protons of the group (-OCH₂), With two signals at the range 7.11-7.87 ppm due to the resonance of aromatic rings (Ar-H), and the appearance of a single signal at the chemical shift 10.57 ppm associated of the proton resonant group (NH) (Fig .5).

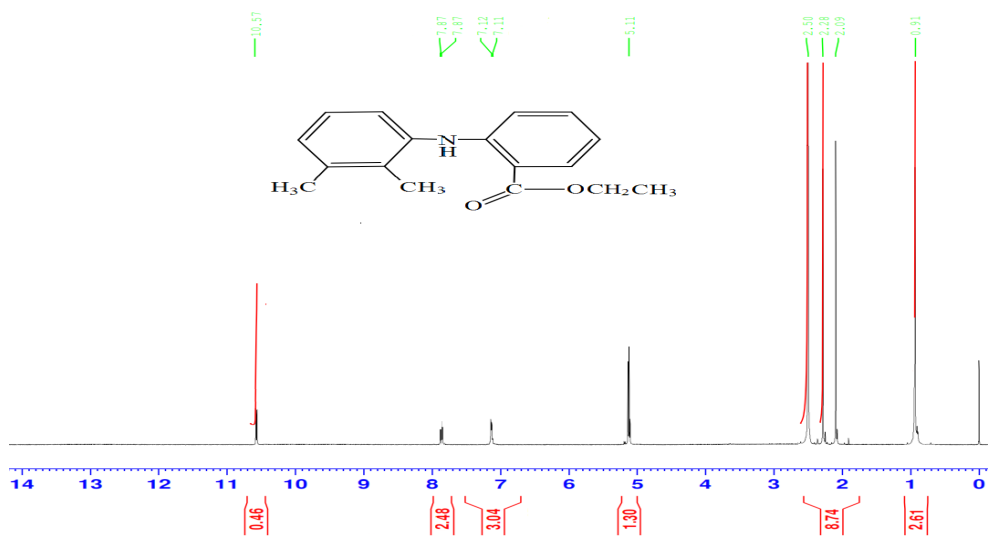


Fig. 5. ¹H-NMR spectrum of the T₁

H¹ NMR spectra of (T₂).

The spectrum of the T₂ compounds showed the disappearance of some signals at the chemical shift 0.91 ppm and 5.11 ppm, which are due to the group (-OCH₂CH₃). Appearance new signals

at the chemical shifts 4.90 ppm and 11.71 ppm for the protein resonance groups NH₂ and NH. As well as signals at 1.44 ppm and 2.69 ppm for proton group protons (2CH₃) associated with the benzene ring, 7.27-7.58 of the aromatic protons (Ar-H), (Fig.6.).

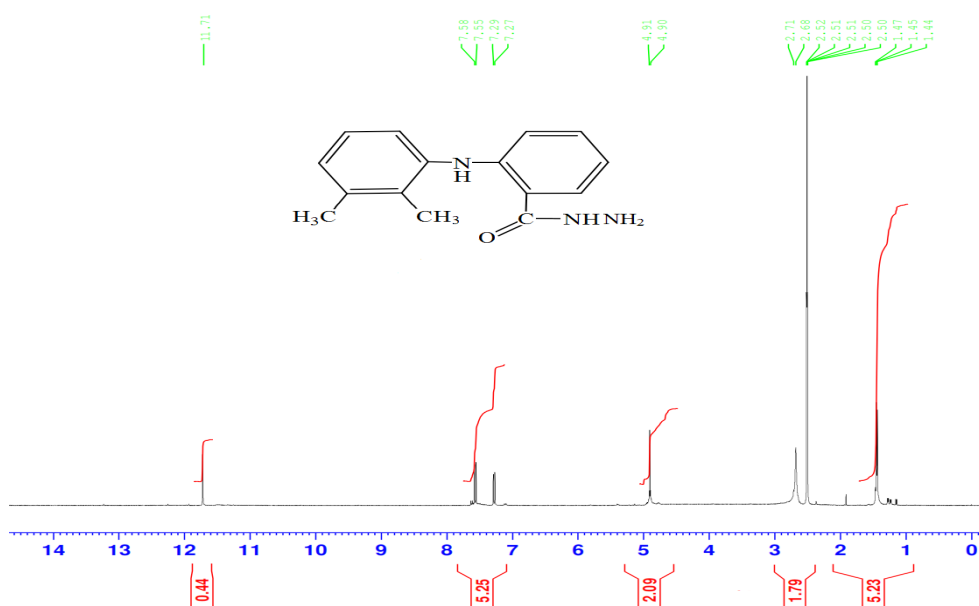


Fig. 6. ¹H-NMR spectrum of the T₂.

FTIR analysis of compounds of (T_3, T_4).

FTIR spectra are shown in (Fig. 7) and (Fig.8), the bands at 3332-3583 cm^{-1} was attributed to the bending mode of the NH group, and the disappearance of the NH_2 peak was observed. The spectra showed a band within the range 3009-

3046 cm^{-1} as a result of the vibration of C-H and aromatic bands. The range 2747-2918 cm^{-1} was attributed to the vibration of C-H. 1702-1720 cm^{-1} is due to the vibration of the carbonyl group $\text{C}=\text{O}$. The peaks at 1648-1653 cm^{-1} and 1498-1569 cm^{-1} due to the vibration of $\text{C}=\text{N}$ group and $\text{C}=\text{C}$ bond respectively.

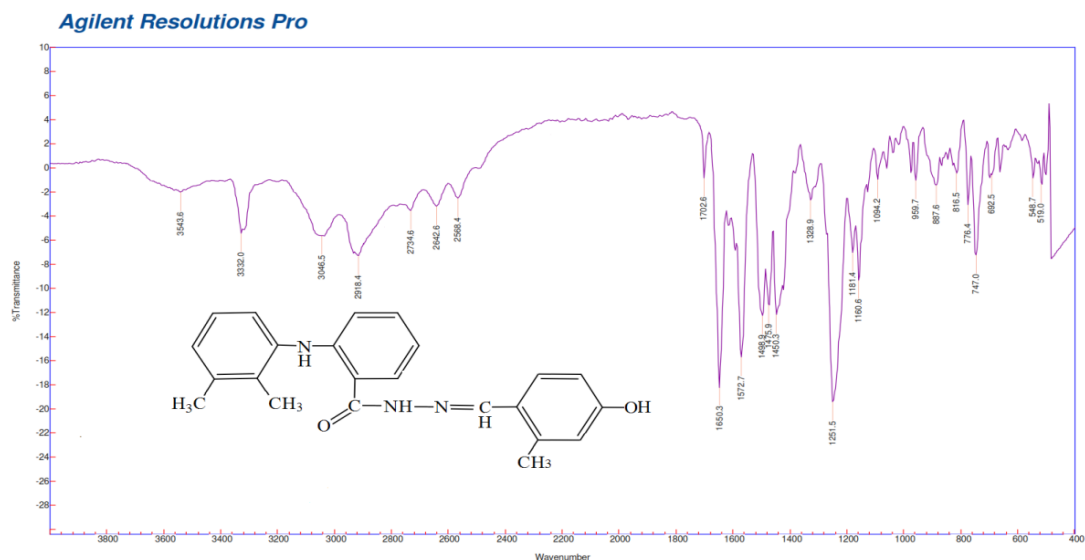


Fig. 7. FTIR spectrum of the T_3

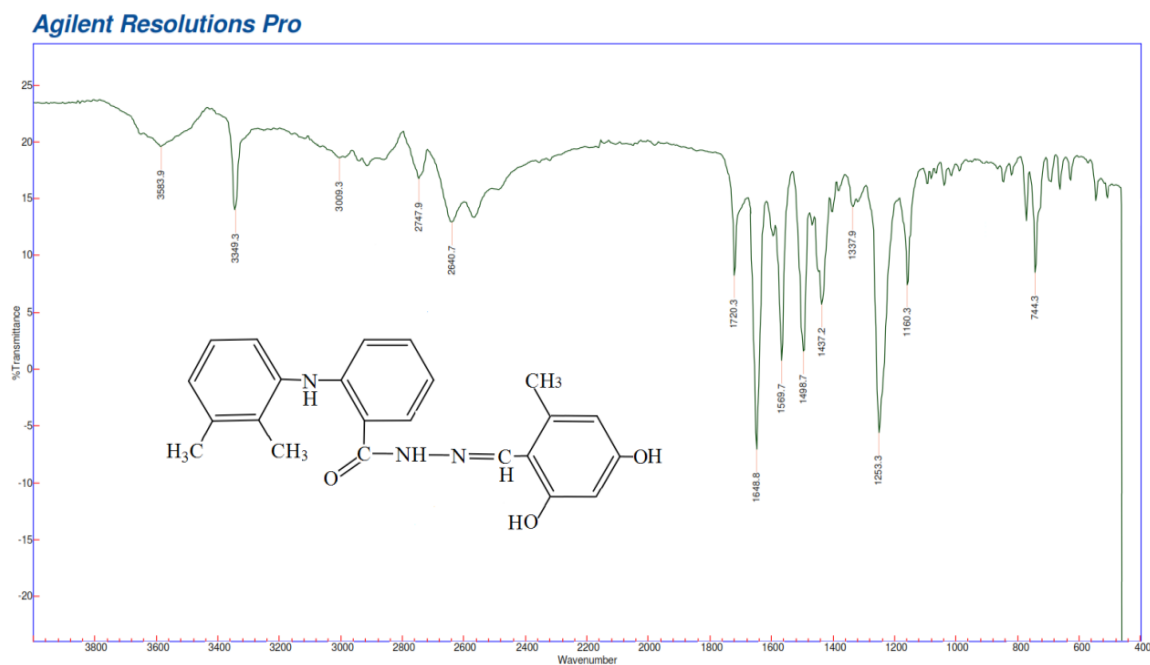


Fig. 8. FTIR spectrum of the T_4 .

Discussion of NMR spectra of $^1\text{H-NMR}$ for compounds prepared from $[T_3-T_5]$.

The spectrum of the two compounds (T_3 and T_4) showed a single indication at the chemical shift 1.82ppm and 2.27 ppm) for the proton groups (2CH_3) associated with the benzene ring, the appearance of the spectrum is a single signal at 4.50ppm of the resonant protons group ($-\text{OCH}_3$). As well as the appearance of signals within the

range of displacement 7.67-7.89ppm belonging to aromatic proton rings (Ar-H), and the emergence of a monotonous signal ranging from 8.85ppm to the proton resonant group of azomethane ($\text{N} = \text{CH}$). The appearance of a single signal at the displacement of 9.51ppm due to the resonance of the (OH) group, and emergence of a single signal at displacement 9.79ppm was attributed to the proton resonance group (NH). Fig. 9.

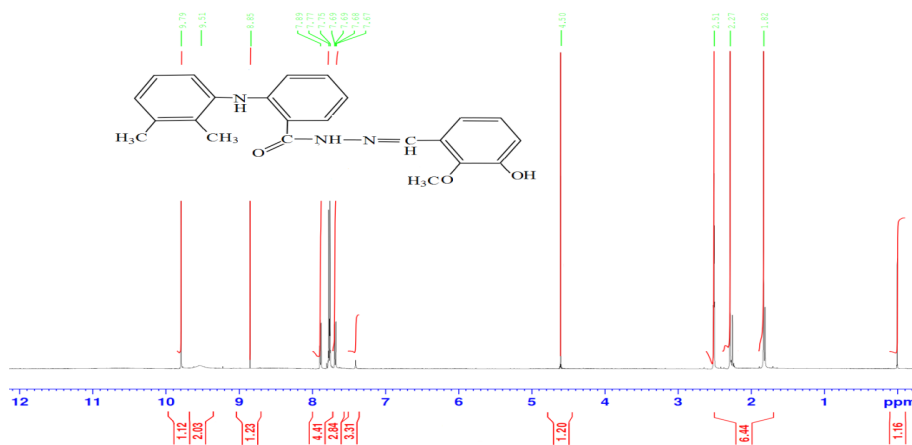


Fig. 9. $^1\text{H-NMR}$ spectrum of T_4 .

The T_5 spectrum showed three unilateral signals at the chemical displacement 1.50ppm, 2.11ppm and 2.28 ppm due to the resonance of proton groups (3CH_3) associated with the benzene rings, as well as signals within the displacement range 7.89-7.67ppm of the proton resonance (Ar-H). The appearance of a single signal at

8.60ppm belonging to the proton resonant group azomethine ($\text{N} = \text{CH}$), with a single signal at the displacement of 9.89ppm, which is due to the proton resonance (OH). The appearance of a mono signal at 11.29ppm was attributed to the Proton resonance group (NH). Notes (Fig. 10).

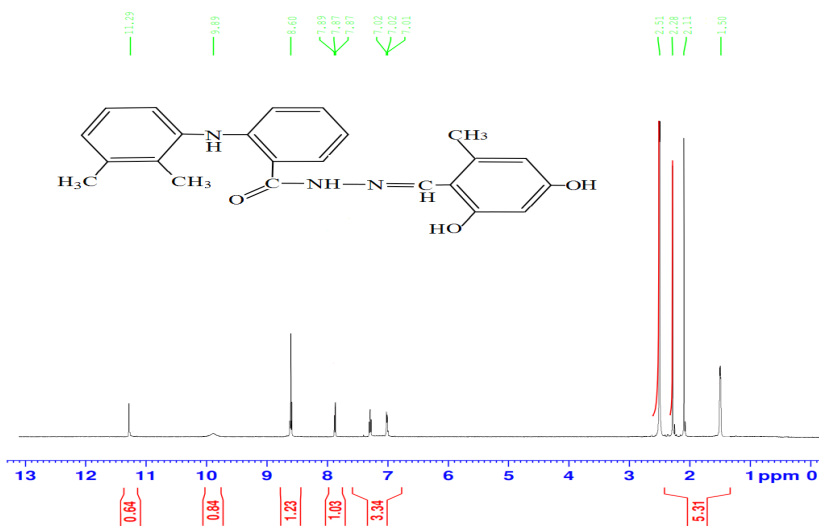


Fig. 10. $^1\text{H-NMR}$ spectrum of the T_5 .

Differential scanning calorimetry (DSC) of compounds [T₆-T₈].

Differential scanning calorimetry of polymers (T₆ - T₈) was recorded from (0 -200)°C at rate of 10°C. DSC is valuable method to give some information about structure of compound. First it is important to note that all these compounds are crystalline in nature because the (T_c) and (T_m) were observed. While purely amorphous compounds will only undergo a glass transition

The (T₆) compound showed the glass transition (T_g) at 91.63 °C, (T_c) at 108.25 °C and melting at 124.89 °C. While both T₇ and T₈ shows the glass transition at lower temperature compared with T₆ were the (T_g) observed at 38.39 °C and 35.31 °C respectively. The low temperature (T_g) indicated the flexible nature of the compounds at these temperatures and many be indicated that both T₇ and T₈ exist in cis form where the double bond in cis form reduce the energy barrier for rotation of adjacent bonds. Note figures 6, 7 and 8.

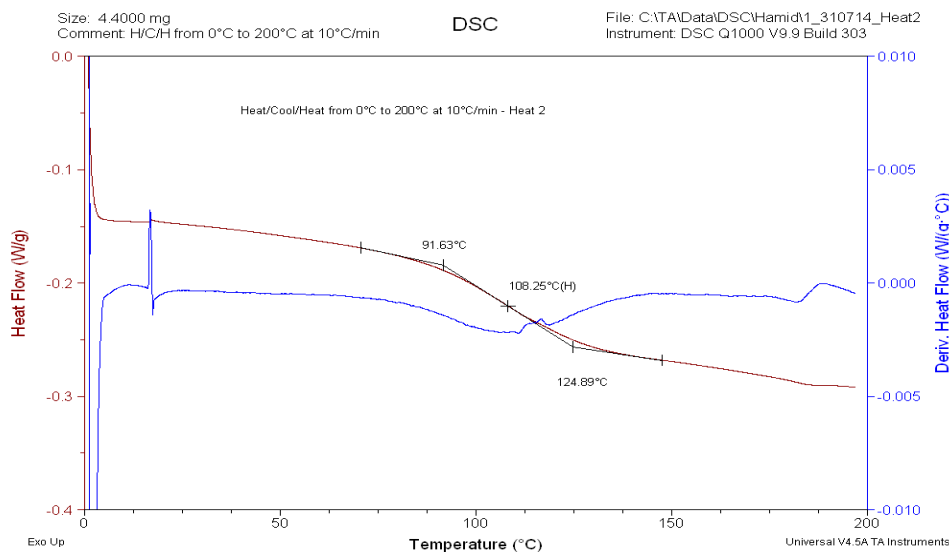


Fig. 7. DSC thermogram for polymer [T₆]

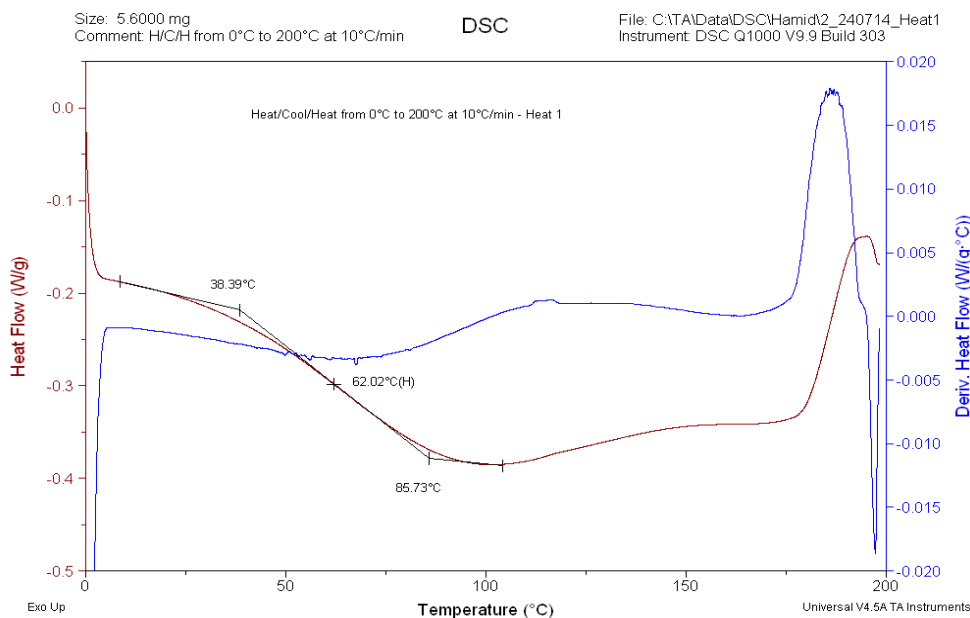


Fig.8. DSC thermogram for polymer [T₇]

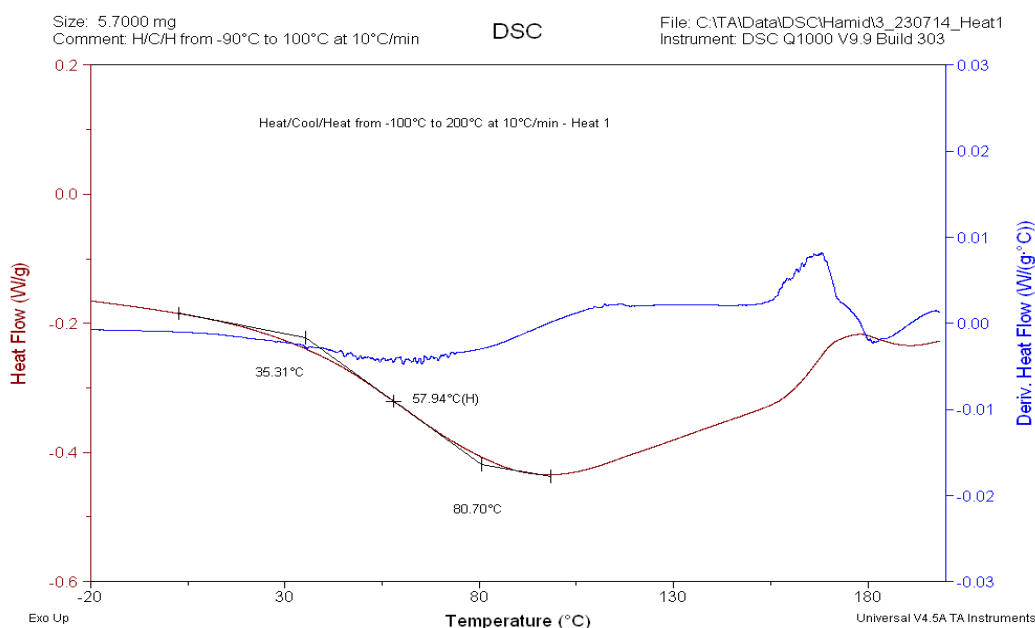


Fig.9. DSC thermogram for polymer [T₆]

Analytical measurements

A selective study of resins towards elements

The maximum loading capacity of the resins to the studied elements at the maximum treatment time 24 hours and the highest pH of the metal ion solution, where the solution is clear and non-turbid and at room temperature, is the optimal condition used for the study of selective renal resins. The process is treated with 0.1gm of resins with element ions, which are 100ppm in isolation for 24hour and at the highest acidic function of the element ions solution. The filtration process is performed and the concentration of each ion

in the leachate is performed mediated Atomic absorption spectrometry to determine the number of ions associated with different resins studied [T₆-T₈].

Factors Affecting polymer Loading Capacity [T₆ - T₈].

The factors influencing the resin loading capacity (T₆ - T₈) were the treatment time and the acidic function by adding 0.1 g to 10 mL ions (Cu⁺², Fe⁺³, Cd⁺²) at a concentration of 100 ppm and at a time of (1-24) hours and pH (1- 6) .As shown in Tables 3, 4 and 5, Figures (10-18).

TABLE (3): Number of milligrams of ions (Co²⁺, Fe³⁺, Ni²⁺) drawn by (0.1mg) of chelated resin [T₆] as a function of time in different acidic functions.

Ions	pH	Loading Capacity of ion				
		mg ion /mg resin				
		Time(hour)				
		1	4	7	12	24
Co ²⁺	1	0.8	1.9	2.6	3.9	4.9
	3	0.3	1.5	3.1	5.4	6.2
Fe ³⁺	2	0.9	2.3	3.7	4	5.8
	3	0.6	1.7	2.8	4.7	6.5
Ni ²⁺	1	0.4	1.4	2.1	3	4.9
	4	1.2	2.6	3.8	5	6.5

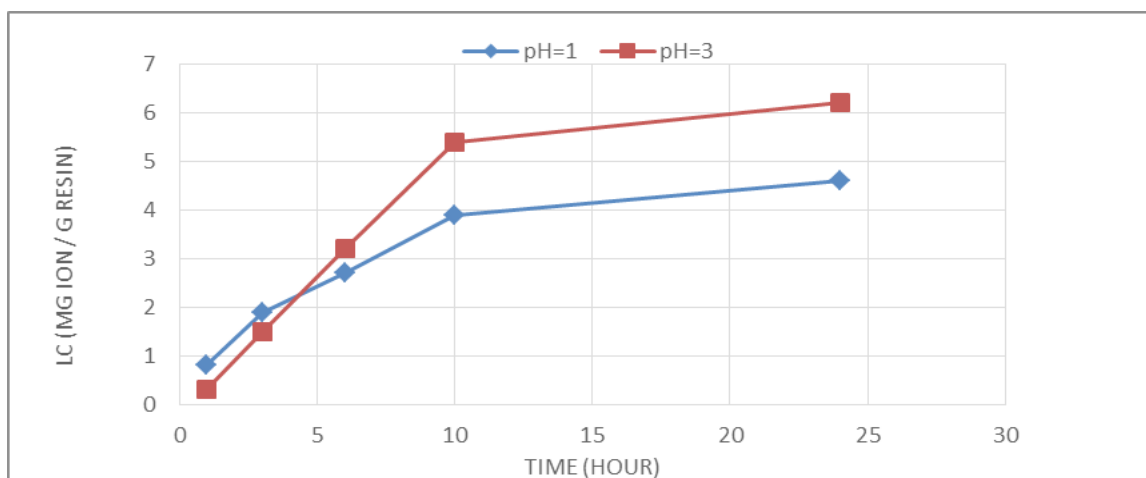


Fig. 10. Number of mg / ions (Co^{+2}) withdrawn by (0.1gm) of the polymer [T_6] as a function of time in different pH (=1, 3).

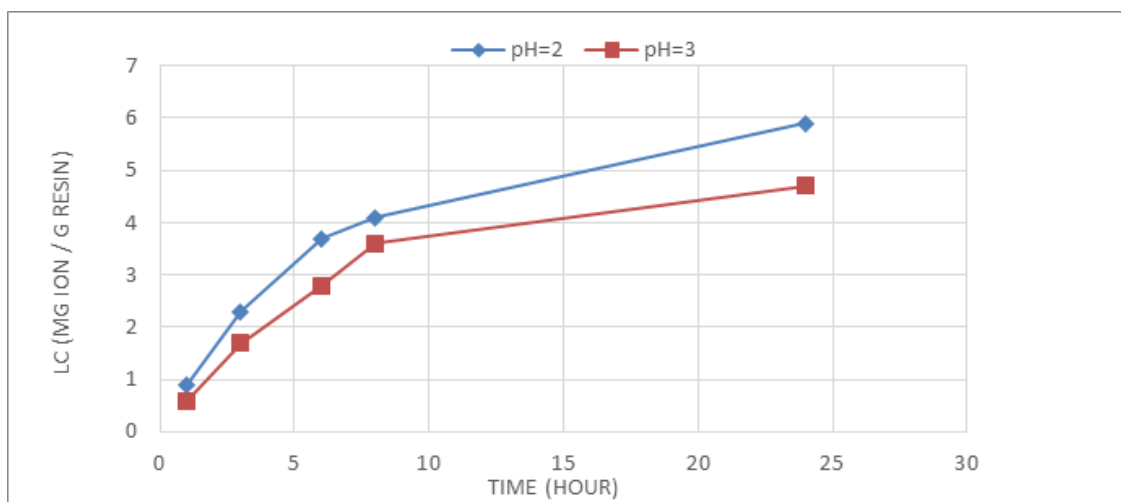


Fig. 11. The number of milligrams of ions (Fe^{+3}) withdrawn by (0.1gm) of the polymer [T_6] as a function of time in different acidic functions in (pH = 2, 3).

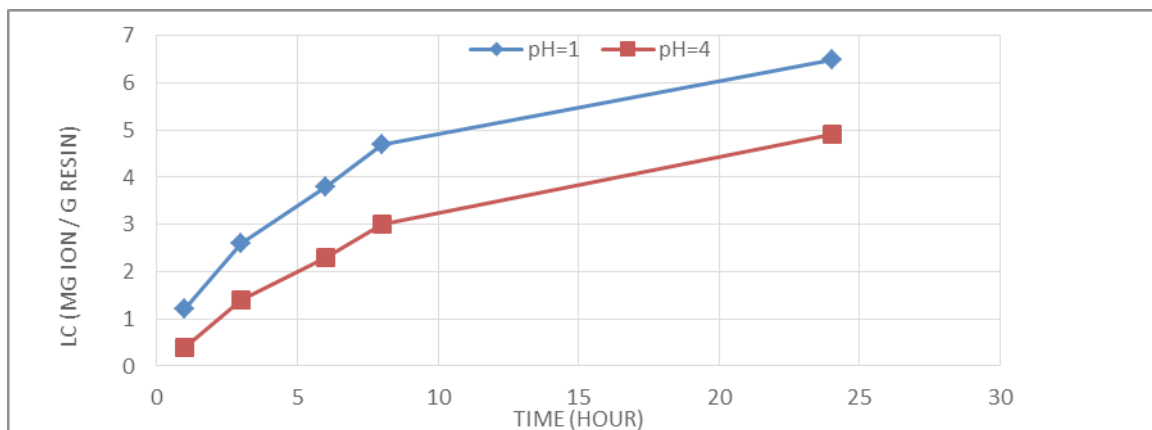


Fig. 12. The number of milligrams of ions (Ni^{2+}) withdrawn by (0.1gm) of the polymer [T6] as a function of time in different acidic functions in PH (1, 4).

TABLE (4): Number of milligrams of ions (Co^+ , Fe^{3+} , Ni^{2+}) withdrawn by 0.1gm of the renal resin [T_7] as a function of time in different pH.

Ions	pH	Loading Capacity of ion				
		mg ion /gm resin				
		Time(hour)				
		1	4	7	12	24
Co^{2+}	4	1.4	2.7	3.5	4.1	5.6
	2	0.2	1.3	2.8	3.4	4.6
Fe^{3+}	2	0.7	1.2	2.3	3.9	5.2
	5	1	2.5	3.6	4.8	6.7
Ni^{2+}	1	1.1	2	3.1	4.5	6.1
	6	1.6	2.9	4.4	6.3	7.8

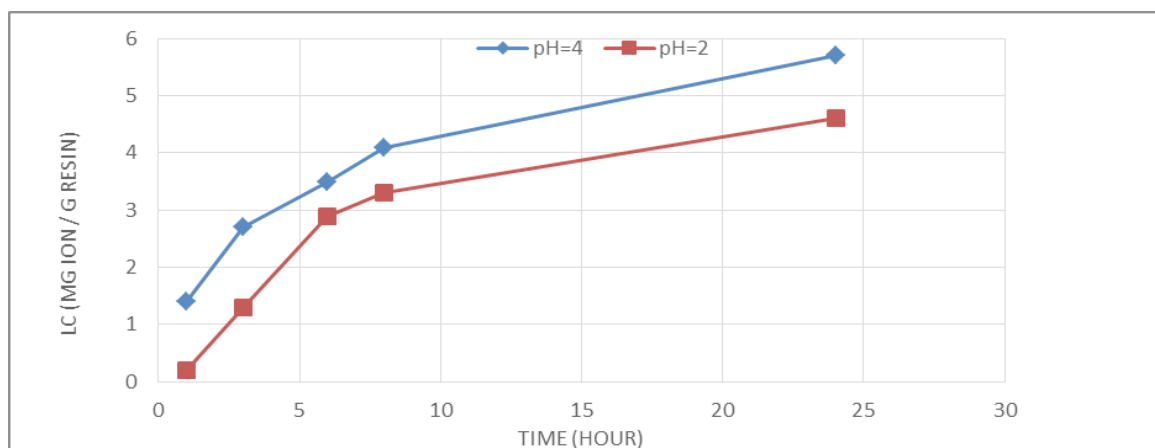


Fig. 13. The number of mg of ions (Co^{2+}) withdrawn by 0.1gm of the polymer [T_7] as a function of time in different acidic functions (PH = 2, 4).

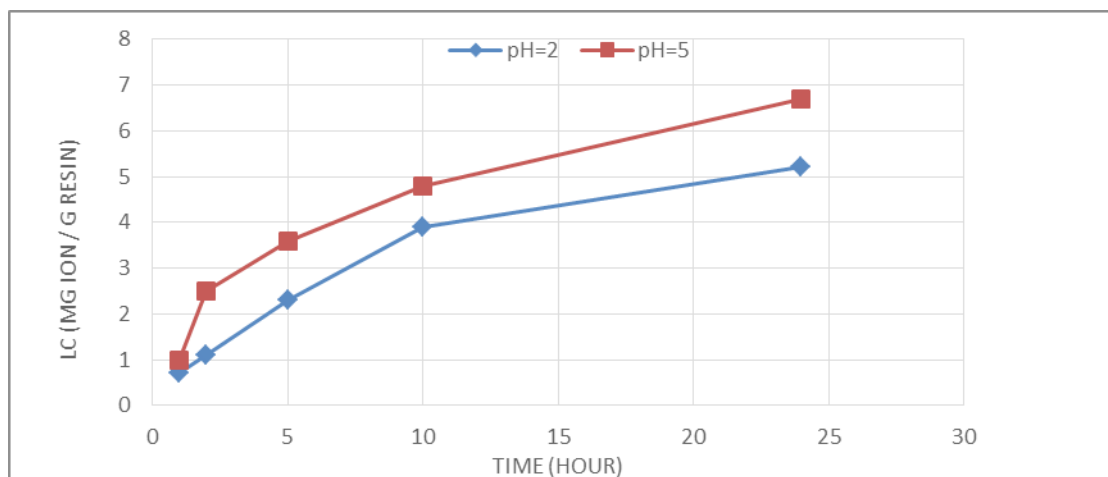


Fig. 14. Number of mg / ions (Fe^{3+}) withdrawn by (0.1mg) of the polymer [T_7] as a function of time in different acidic functions (PH = 2, 5).

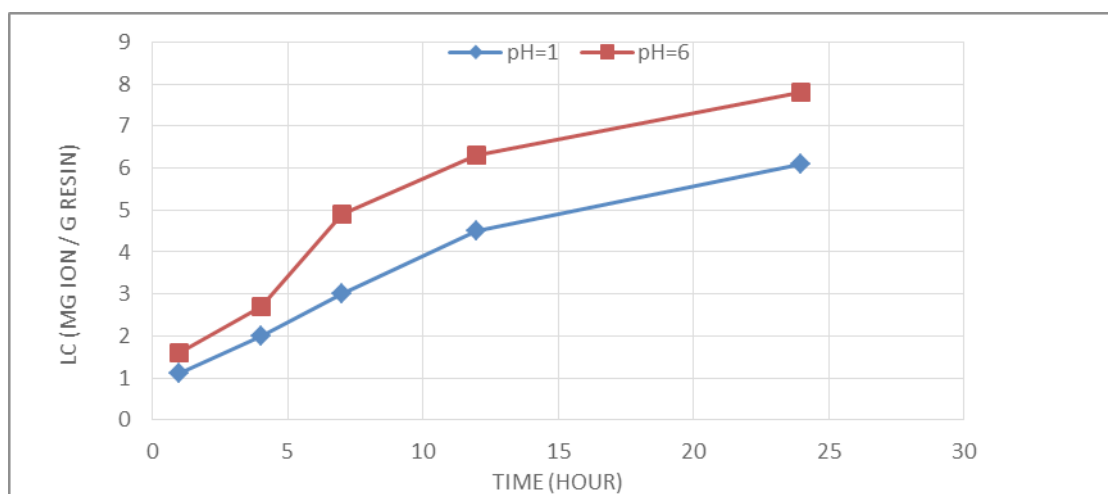


Fig. 15. The number of milligrams of ions (Ni^{2+}) withdrawn by (0.1gm) of the polymer [T_7] as a function of time in different acidic functions (PH = 1, 6).

TABLE (5): Number of milligrams of ions (Co^{+2} , Fe^{+3} , Ni^2) withdrawn by 0.1gm of the T_8 as a function of time in different acidic functions:

Ions	pH	Loading Capacity of ion				
		mg ion /gm resin				
		Time(hour)				
		1	4	7	12	24
CO^{2+}	1	0.2	1.5	2	3.2	4.2
	3	0.5	2.1	3.4	4.8	5.6
Fe^{3+}	2	0.6	2.2	3.6	5.1	6.9
	6	1.3	2.8	4.5	6.6	7.4
^{2+}Ni	4	0.4	1.7	3.3	4.9	5.6
	6	1.6	2.9	4.2	5.4	7.2

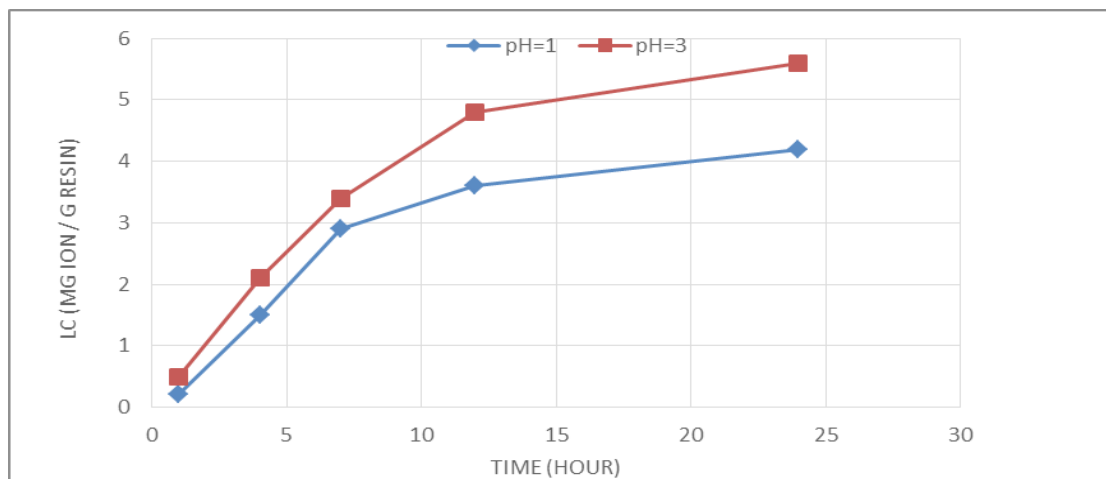


Fig. 16. The number of mg / ions (Co^{2+}) withdrawn by (0.1gm) of the T_8 polymer as a function of time in different acidic functions (pH = 1, 3)

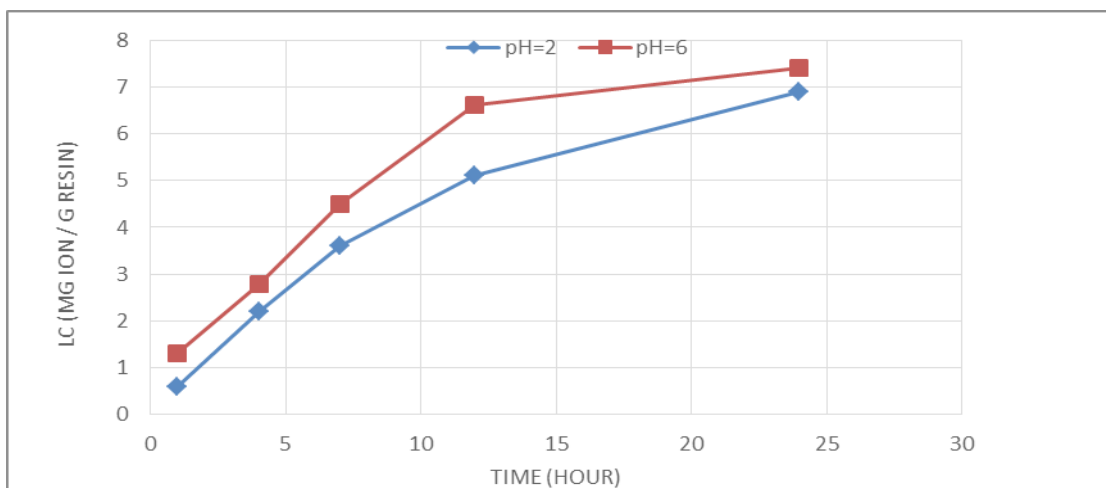


Fig. 17. Number of mg / ions (Fe^{3+}) withdrawn by 0.1mg of T_8 as a function of time in different acidic functions (pH = 2, 6).

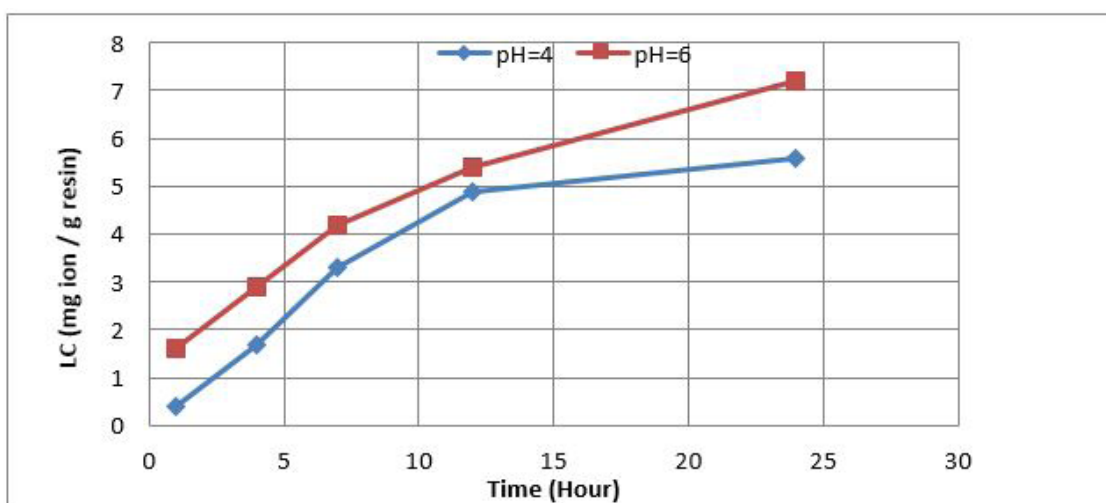


Fig. 18. The number of milligrams of ions (Ni^{2+}) withdrawn by (0.1mg) of the polymer [T_8] as a function of time in different acidic functions (pH = 4, 6).

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