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RESEARCH ARTICLE

Synthesis , Characterization & Analytical study of anew Schiff base derive from substituted aniline and Their Complexation with Zn^{+2} , Cu^{+2} & Cd^{+2} ions ,Copolymerization and their biological study.

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Abstract

Some new Schiff base compounds were prepared through the reaction between salicyldehyde and subsituted aniline .These compounds were characterized by FTIR &CHN analysis .Complexation of these Schiff base with some transition metal nitrates in alcoholic solution were done and the result shown that the M:L ratio is (1:2). On other hand these compounds were polymerized via condensation polymerization with resorcinol and formaline solution in basic medium .,their ability for complexation with Zn ,Cu &Cd ions were examined by using Flame photometry the result shown that the ability of metal complexation in the order of Zn+2 >Cu+2 >Cd+2 .Thermal studies of these copolymers were done using TGA and DSC techniques , The result shown that these copolymers have good thermal stability .Finally the biological studies showed no activity towards two kinds of bacterial while all the prepared Schiff base gave positive test .

INTRODUCTION

Hugo Schiff condensation (the condensation between an aldehyde and an amine) leading to Schiff base in 1864.(1)the Schiff base ligands are able to coordinate metal ions through imine nitrogen and other group usually linked to aldehyde.(2) The compounds containing an azomethine group (-CH=N-) are known as imines,anils or Schiff base .Schiff base derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many field (3-4). Schiff base ligands are known as (privileged ligands) being active, well designed and easy to prepare through the aldehyde –amine condensation(5)when two equivalents of salicylaldehyde are combined with one equivalent diamine a particular chelating Schiff base is produced which is also called a(Salen ligand) (6)which have four coordinating sites & two sites open ,Salen are very much like porphyrins but areeasire to prepare(7). Schiff base as chelating ligands have attracted great interest and various uses in different fields .Schiff base and their metal complexes have been found to be biological active in the view of antibiotic (8), antimicrobial (9),antifungal (10) ,and antitumor (11) ,properties. In organic Schiff base complexes have key role in catalysis of a variety of organic reaction such as reductive carbonylation (12) ,polymerization (13) ,decarboxylation (14) ,and oxidation (15) ,In inorganic chemistry Schiff base have been widely applied for development of coordination chemhstry. The aim of this study reports preparation of Schiff bases derived from salicyladehyde with serious of aniline derivative ,Study its ability to determine the transition element-complexs then polymerization these Schiff bases and study its capacity to pull these transition element ions at different PH and Time .Finally the biological studies of these Schiff base& copolymers with two kinds of bacterial

2-Material & method :

2-1 Chemical Material :

4-chloro- 2- methyl aniline (Aldrich) , 3-chloro-4 methyl aniline (Aldrich) , p-chloro aniline (Aldrich) , salicylaldehyde (RDH) , Hydrated copper nitrate (fluka) , Hydrated cadmium nitrate (fluka) , Absolute ethanol (RDH) , Resorcinol (fluka) , Formalin (H &W) , Sodium hydroxide (merk) , Hydrochloric acid (BDH) , Cupric Nitrate (standard solution 1000ppm (BDH)) , Cadmium Nitrate (standard solution 1000 ppm (BDH)) , Zinc Nitrate (standard solution 1000 ppm (fluka)) .

2-2 Instrument used :

- Infrared spectrophotometer / Schimadza ., Electro Thermal melting point / Ucego dital (Jenway) ., Uv-Vis. Spectrophotometer (single beam) / Engineering managemient Co . LTD (uk). , Sensitive Balance / Germany ., CHN Elemental., Atomic Absorption Spectrometer (QCB 933 Plus)., TGA (perkin) ., DSC (Perkin Elemer DSC-6) .

2-3 Method :

Synthesis of salicylidene-4-chloro-2-methyl aniline (I): 5.64 g (0.04 mol) of 4-chloro-2-methyl aniline was dissolve in 20 ml Absolute ethanol & mixed with equivalent amount of salicylaldehyde 4.88 g (0.04 mol) [mole ratio 1:1] dissolve in 20 ml ethanol containing two drops of glacial acetic acid , the resulting mixture was heated for 5 minute about 50 C° then the mixture transfer to 100 ml round flask on magnetic stirrer in ice bath for (1-2) h , the color solid crystal product was formed , then separated by filtration , purified by recrystallization from ethanol , and then dried .

Synthesis of salicylidene-3- chloro-2-methyl aniline (II): 5.64 g (0.04 mol) of 3-choro-2-methyl aniline was dissolved in 20ml Absolute ethanol and mixed with equivalent amount of salicylaldehyde 4.88 g (0.04 mol) dissolved in 20 ml ethanol containing 2 drops of glacial acetic acid , the resulting mixture was heated to about 50C° for 5 min , transfer the mixture to 100 ml round flask kept on electrical magnetic stirrer in ice bath for , the colored solid crystal produced was formed and then separated by filtration , purified [16,17] by recrystallization from and then dried .

Polymerization of Schiff base :

Synthesis of copolymer Schiff base I & II,Both dissolve in few amount ethanol at 40C° , 100 ml Formaline (Solution 35%) was added to the mixture and heated with continuous stirring on hot plat magnetic stirrer ,Few drops of 10% NaOH was in order to keep the PH=9-10 , high viscosity of the result mixture indicate the polymerization takes place, after complete copolymerization (3 hr at 60C°) , the mixture was cooled and neutralize by adding 10% phosphonic Acid and the paste was remove, washing three time with disteld water and drying under vacume to give red viscuse material this was thermal curing at different temperature first at 75C° for 3h , Second at 120C° for 2h and finally post cure in order to complete copolymerization at 150C° for 1.5h

3- Result and Discussion :

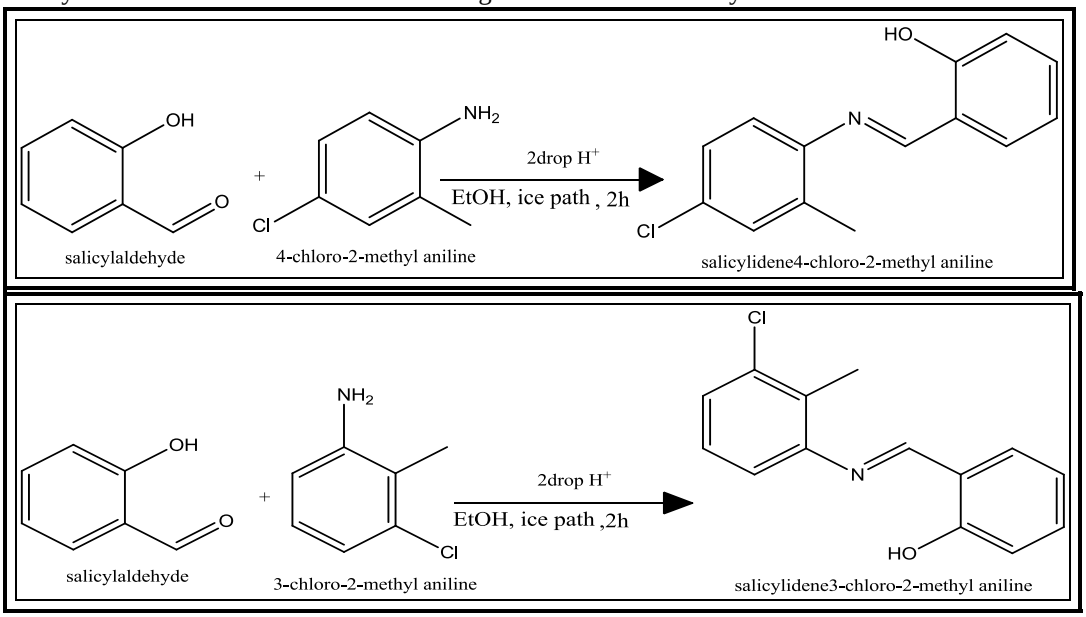
Table (1) the physical properties for the prepared Schiff bases:

Compound	Molecular weight	Yield	color	Physical Property	M.P.	Formula molecular
I Salicylidene -4-cloro-2-methyl aniline	245 gm/mol	77.5% 7.6 gm	Orange	Lattice Crystal	44-46	$C_{14}H_{12}ONCl$
II Salicylidene -3-choro-2-Methyl aniline	245 gm/mol	75.5% 7.4 gm	Pale Yellow	Needle Crystal	94-95	$C_{14}H_{12}ONCl$

Table (2) starting material used in polymerization of Schiff base in basic medium

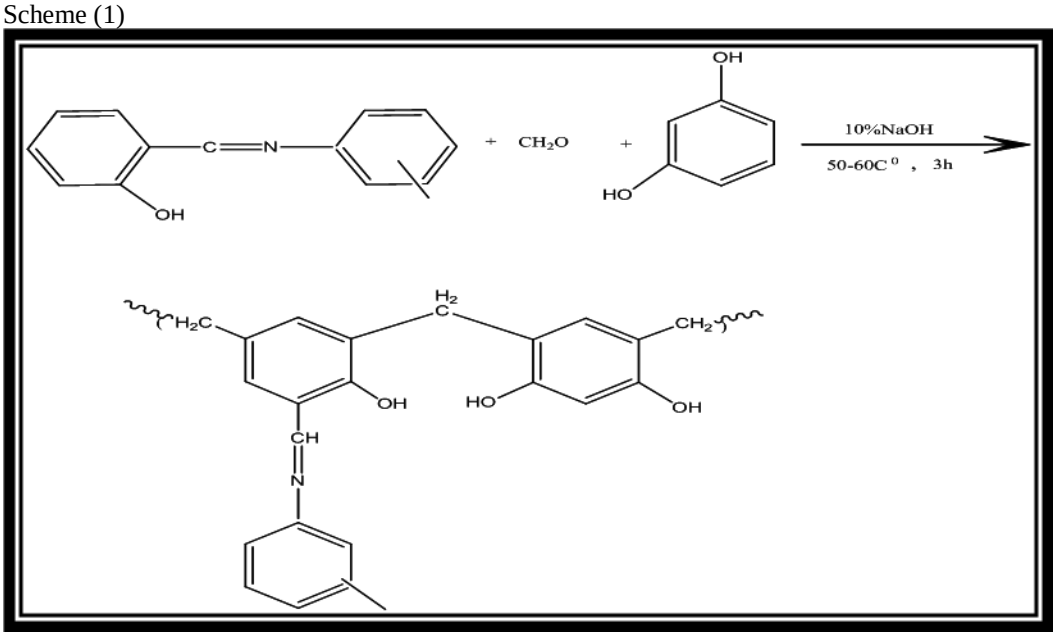
No. of Copolymer	Weight and Moles of Schiff base	Weight and Moles of resorsenol	Volume used of formain
Cop.I	**4 gm / 0.3 mole Of Schiff base I**	**5.98 gm / 1 mole**	**100 ml**
Cop.II	**4 gm / 0.3 mole Of Schiff base II**	**5.98 gm / 1 mole**	**100 ml**

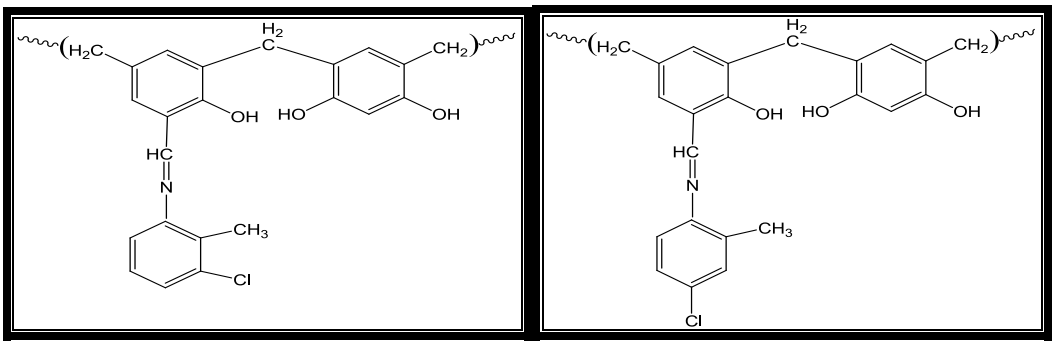
The synthesis rout of these Schiff base through the reaction of aldehyde and aromatic amine as shown below:



These compounds are prepared through the reaction of aldehyde group and amine group at low temperature in acidic medium, In the case of the polymerization of these two Schiff base , resorcinol and formalmaline solution were used in basic medium and the expected structure of these two copolymers are shown below :

Scheme (1)





Copolymer I **Copolymer II**

3-2 CHN Analysis and FTIR Study :

The result of CHN analysis provide good support for the structure of the prepared Schiff base and the data in table (3) are very near expected the chemical structure of compounds

Table (3) CHN data for new Schiff bases :

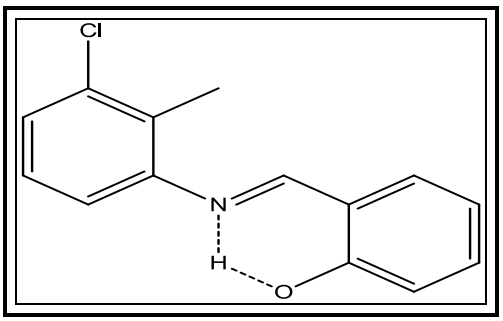
Compound NO.	**Molecular formal**	% Experimental and(calculated)		
		% C	% H	% N
I	$C_{14}H_{12}NOCl$	68.44 (67.79)	4.92 (4.43)	5.7 (5.42)
II	$C_{14}H_{12}NOCl$	68.44 (68.09)	4.92 (4.69)	5.7 (5.53)

On the other hand the FTIR spectra are shown in Fig (1,2) while the essential bands of compounds are listed in the table (4)

Table (4) characterstic band of new Schiff bases :

IR spectra	**I**	**II**
O-H str	**3514.06**	**-------**
C-H str (aromatic)	**3055.03**	**3066.61**
C-H str (assy) for CH_3	**2923.8**	**2983.67**
C-H str (sym) for CH_3	**2723.3**	**2854.45**
C=N	**1620.09**	**1618.17**
C-N	**1361.65**	**1365.51**
C=C	**1577.6 1488.94**	**1560.30 1494.73**
C-O	**1276.79**	**1274.86**

The spectrum of compound (I) shown abroad band at (3444-3514) cm^{1} which attributed to hydroxyl group , which for compound two is disappeared due to covalent with nitrogen atom to form cyclic structure as shown below :



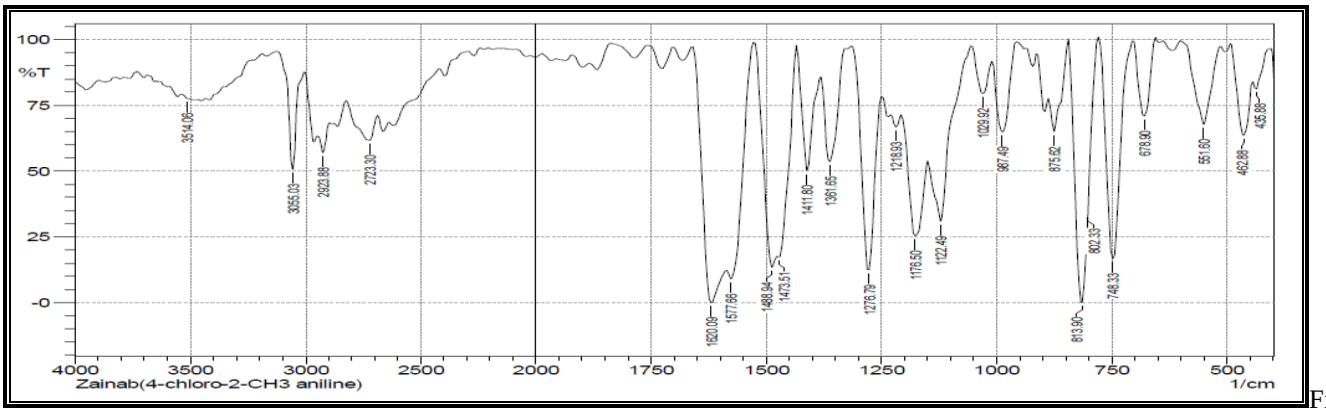


Fig (1) : FTIR Spectrum for Schiff base (I)

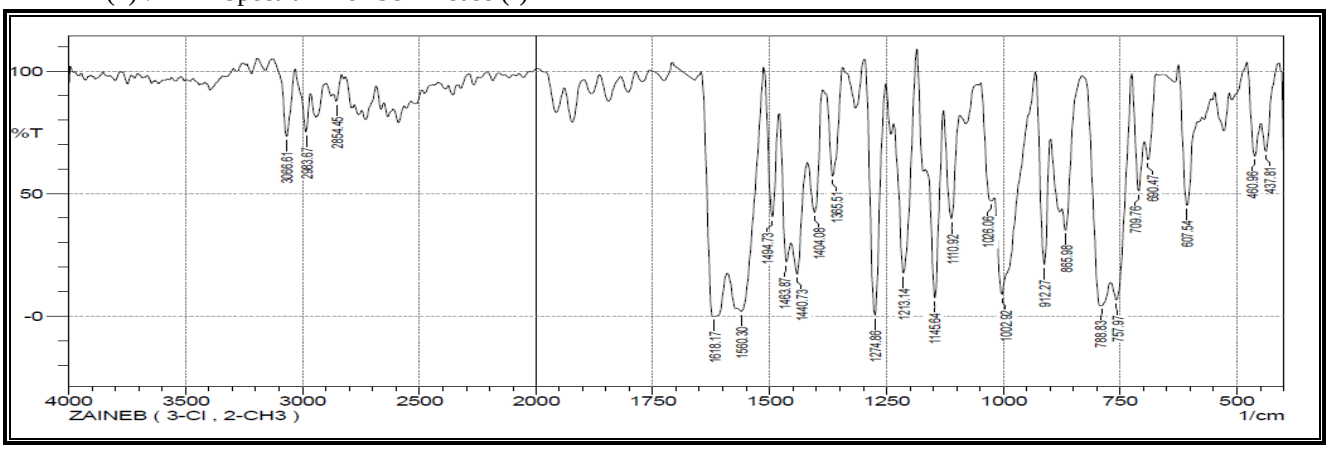


Fig (2) : FTIR Spectrum for Schiff base (II)

Table 5 : λ_{max} of shiff base

Schiff base	λ_{max} Cu complex
I	395 nm
II	405 nm

The optimum condition appointment series of Cu complex with Schiff base was prepared to get the best concentration of metal ion and Schiff base by using molar ratio method , uv-vis spectra of the resulting solution of various M^{+2} concentration / constant concentration of Schiff base mole ratio were recorder until the desired mole ratio was reached (2×10^{-4} M) , then the concentration of metal ion (2×10^{-4} M) was kept constant and the concentration of the ligand (2×10^{-4} M) was then added in different volume [18,19] , λ_{max} for each ligand and ligand-complex was recorded from (200-700) nm .

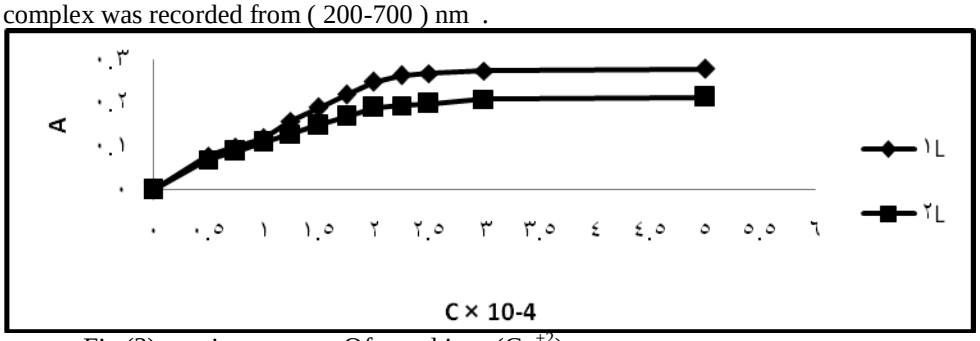


Fig (3) : optimum conc. Of metal ions (Cu^{+2})

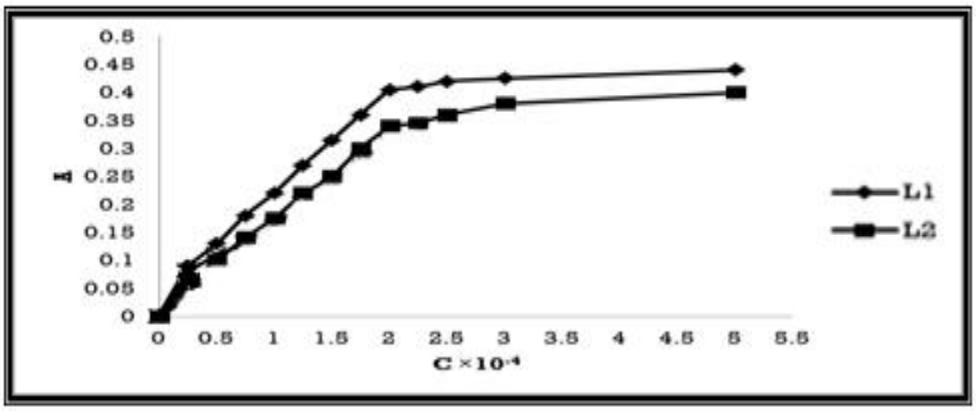


Fig (4) : The optimum conc. Of ligand .

3-3 Determination of expected structure of complex :

In order to determine the expected structure of the complex , mole- ratio method were used and the Fig (5) below show the ratio of L:Musing λ_{max} for each ligand-complex .

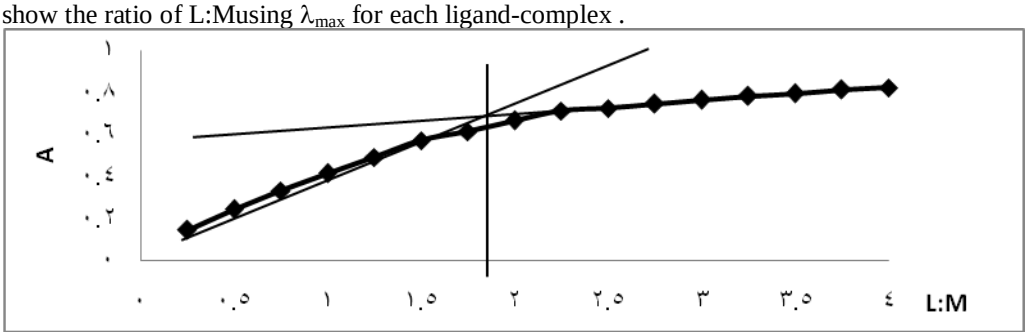


Fig (5) : mole ratio curve for Cu-Complex with Schiff base I

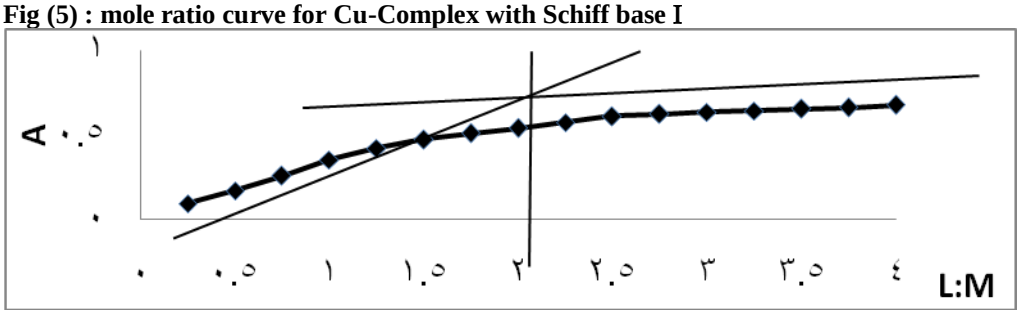


Fig (6) : mole ratio curve for Cu-Complex with Schiff base II

3-4 Determination the stability constant for Cu-Complex from the equation:

$$\propto = \frac{A_m - A_s}{A_m} \dots\dots\dots\dots 1$$

Where $\dot{\alpha}$ = degree of analysis

$\mathbf{A_m}$ = absorbance of equivalent amount of **L : M**

$\mathbf{A_s}$ = absorbance of excess amount of ligand with constant volume & metal[17] .

$$K = \frac{1-\propto}{4 \propto^3 C^2} \dots\dots\dots\dots 2$$

Table 6 :Show the value of some electronic parameters

complex	A_s	A_m	α	K
I	0.416	0.571	0.2714	10^8×4.5528
II	0.352	0.474	0.2573	10^8×5.4441

According to the result value it found that **Schiff base II > I** due to the Cl^- ion in p-position in Schiff base**I** which decrease the stability of complex because Cl^- is an accepter group [20], using mole ratio method ,these spectra show the ratio of **L:M** using λ_{max} for each ligand-Complex at its optimum concentration for each[21] , the following figs.(7,8) during our study it found that the **L : M** ratio was **2 : 1** according to that we can determine as shown in table (7) .

Table (7) the expected structure of complexes

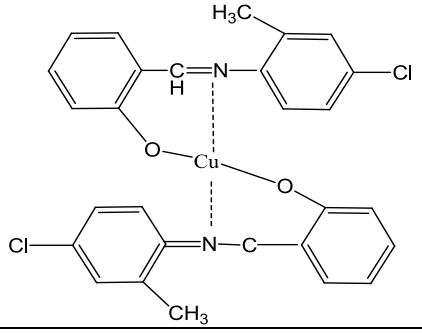
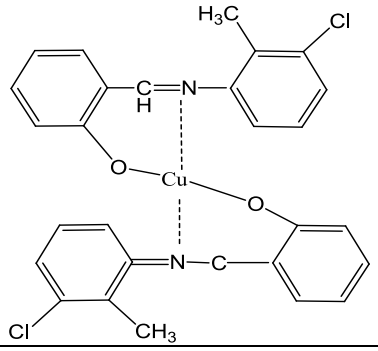
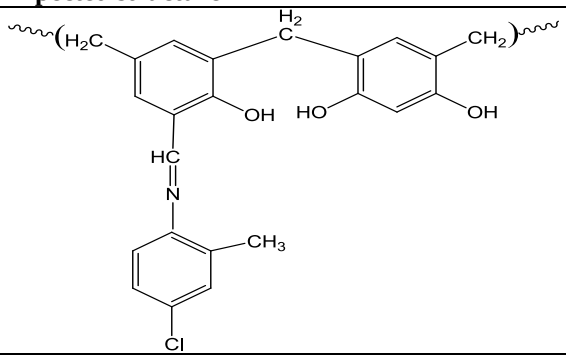
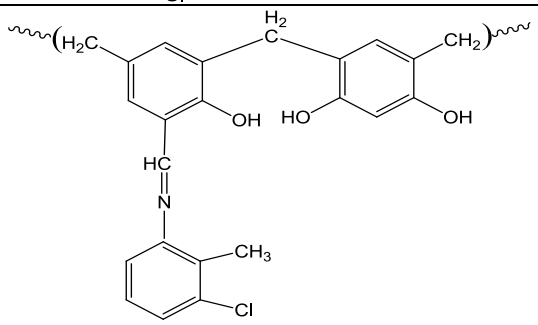
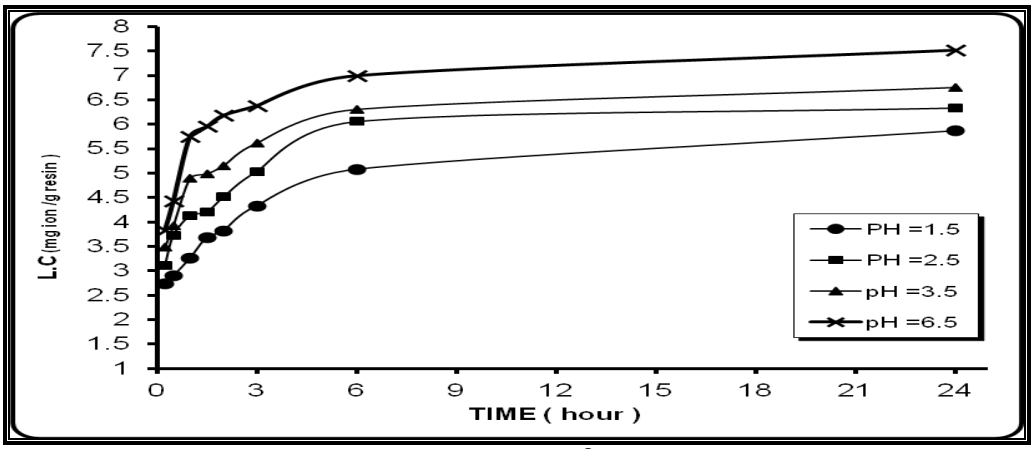
complex	Expected structure
I	
II	

Table (8) the expected structure of Copolymers .

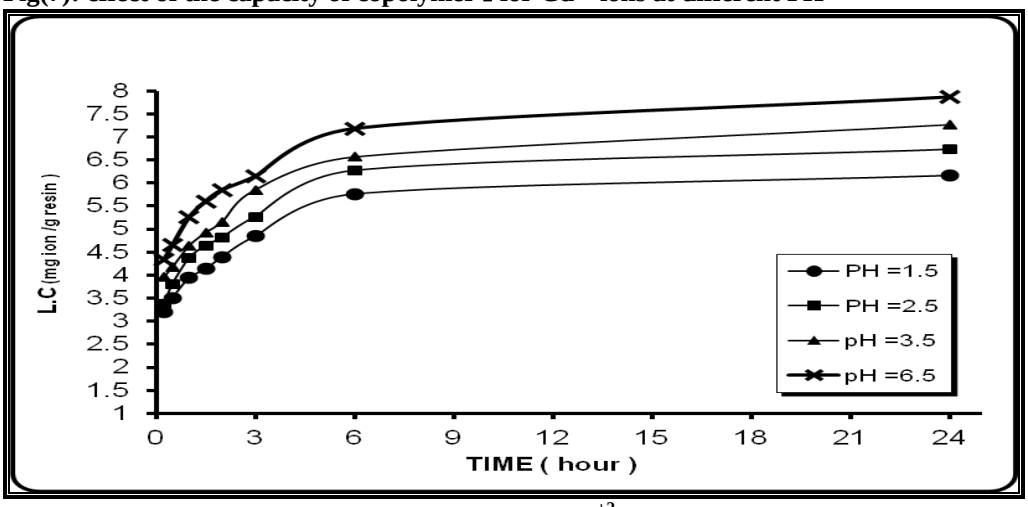
Copolymers	Expected structure
Cop.I	
Cop.II	

Analytical study of Copolymers with Cd^{+2} , Zn^{+2} and Cu^{+2} according the effect of time on the capacity of the resin it found that for the two Copolymers , the capacity increase with respect to time and the time required to reach equilibrium state within (6 hours) ,

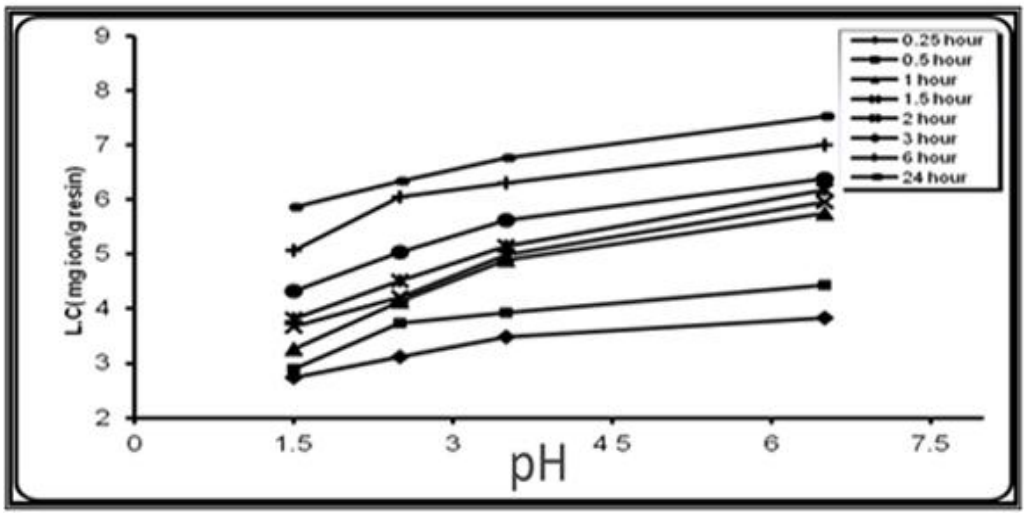
The highest capacity for Cd^{+2} with Copolymer **I& II** about (7.1 – 7.4) mg Cd^{+2} /g resin , whereas for copolymer **II** 5.98 mg Cd^{+2}/g resin , as shown in figure below .



Fig(7): effect of the capacity of copolymer I for Cd^{+2} ions at different PH



Fig(8) : effect of the capacity of copolymer II for Cd^{+2} ions at different PH



Fig(9) : change of capacity of copolymer I with Cd^{+2} with PH at different time

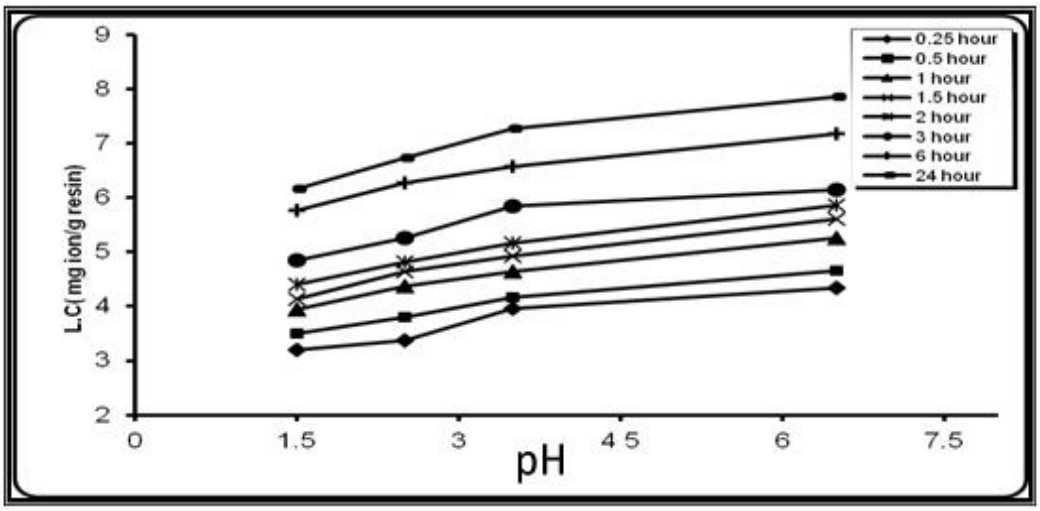


Fig (10) : change of capacity of copolymer Ⅱ with Cd^{+2} with PH at different time

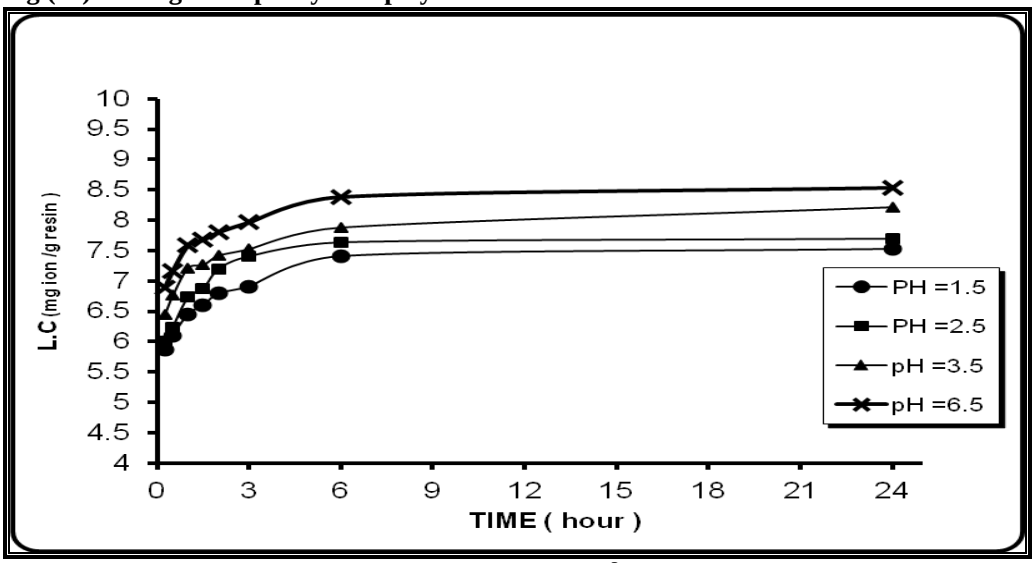
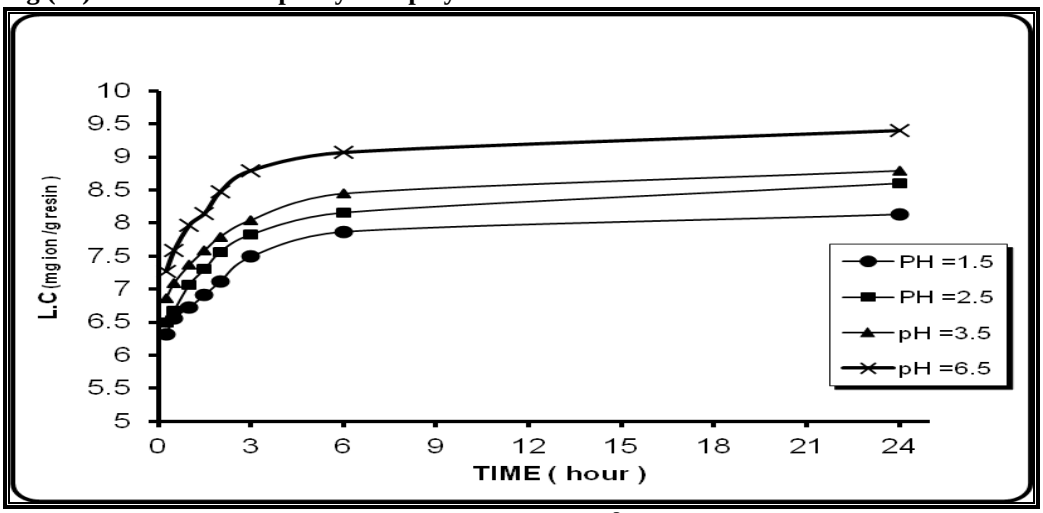
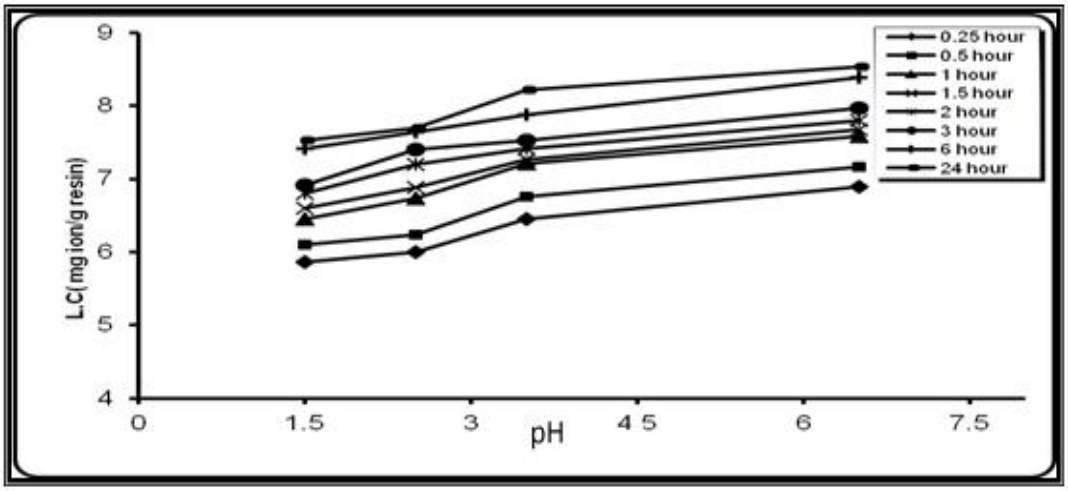


Fig (11) : effect of the capacity of copolymer Ⅰ for Cu^{+2} ions at different PH



Fig(12) : effect of the capacity of copolymer Ⅱ for Cu^{+2} ions at different PH



Fig(13):change of loading capacity of copolymer I with Cu^{+2} with PH at different time

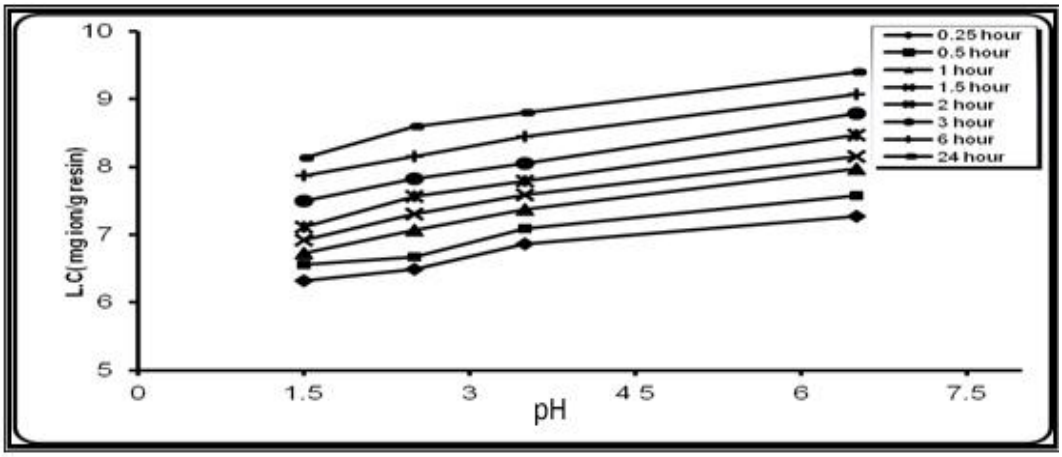


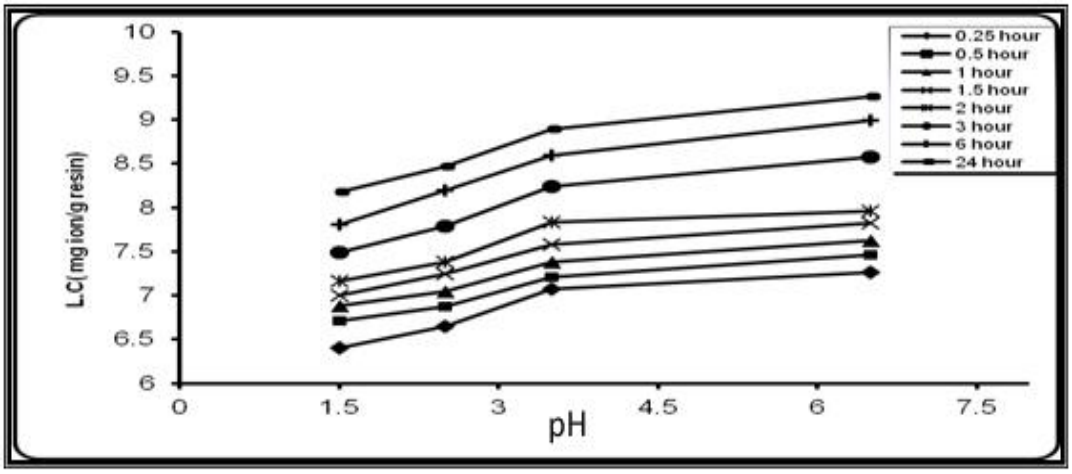
Fig (14) : change of loading capacity of copolymer II with Cu^{+2} with PH at different time

The highest loading capacity for the copolymer with Cu^{+2} ions as follow:

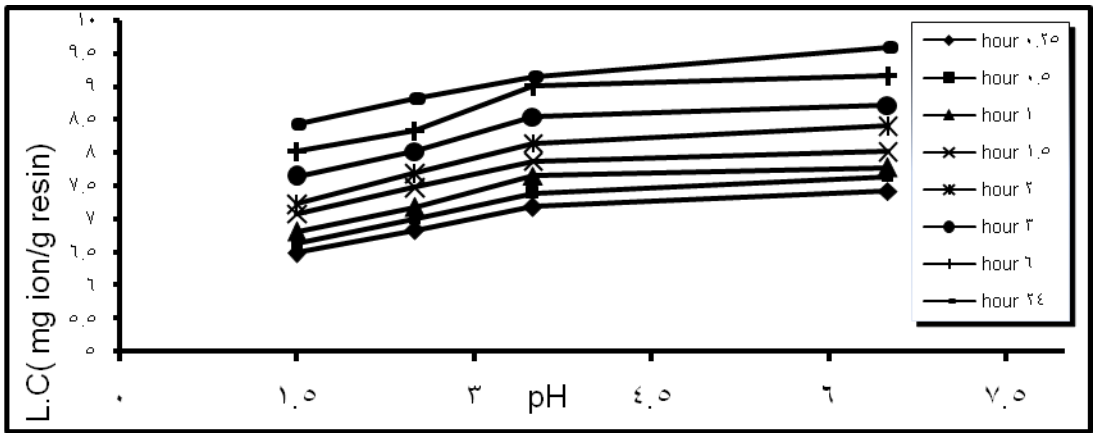
Cop II > Cop I

The highest loading capacity of copolymers with Zn^{+2} ions as follow

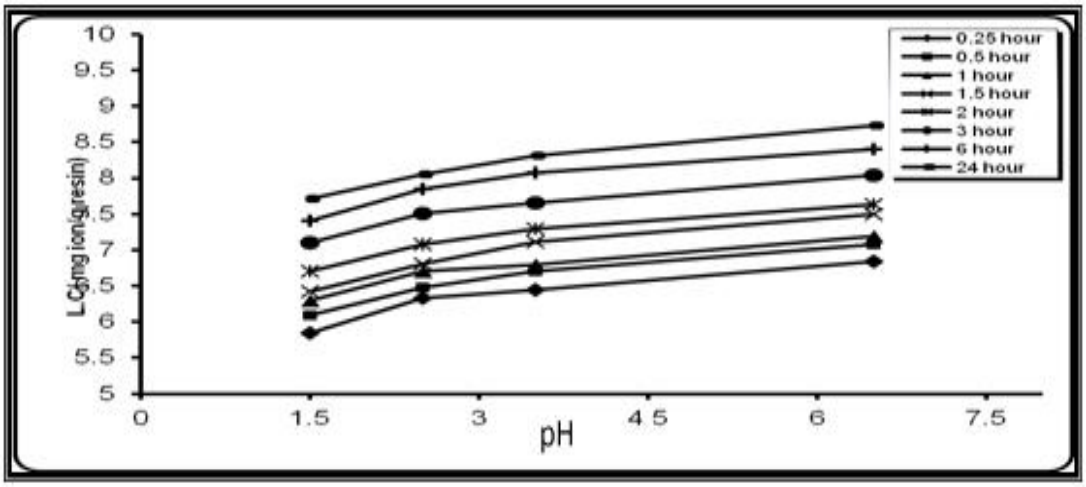
Cop II > Cop I



Fig(15) : Change of loading capacity of Copolymer I for Zn ions with respect to PH at different time



Fig(16) : Change of loading capacity of Copolymer II for Zn ions with respect to PH at different time



Fig(17) : Change of loading capacity of Copolymer III for Zn ions with respect to PH at different time

Table (9) the percent of regeneration ions from copolymer after 24 h .

copolymer	Copolymer I			Copolymer II		
PH	Cd	Cu	Zn	Cd	Cu	Zn
1.5	88.3%	88.1%	98.2%	88.2%	87.4%	96.2%
2.5	91.5%	87.2%	96.4%	92.1%	88.3%	95.1%
3.5	76.5%	68.4%	85.6%	82.5%	75.5%	87.3%
6.5	71.4%	65.2%	82.3%	71.3%	70.1%	85.2%

Finally the biological studies of all Schiff base gave positive tests to the ***Staphyl Cocus arueus*** but only **I Schiff base** gave positive test to the ***E.Coli bacteria ,*** the gram positive and gram negative bacteria were isolated from clinical sample and identified , the identity of all the strains was confirmed antibiotic sensitive test was studied by well diffusion method , the bacterial suspension was prepared and add to the well , using suitable technique , different weight of the Schiff base and it complexes were placed on the surface of colure and incubated at 37C° for one day , the average of inhibition zone was recorded

Bacteria	Schiff base	
	I	II
E.Coli	25 cm	--------
Staphylo Coccus aueur	13 cm	25 cm

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Conclusion:

New Schiff base compounds based on Salisalaldehyde and aniline derivative were prepared and characterization by FTIR , CHN , complexation of these compounds with some metals were done .

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