Synthesis, Characterization and Antimicrobial Study of Polycyclicacetal Derived From PVA and Its Complexes with (Cu^{+2}, Ni^{+2}, Zn^{+2} and Ag^{+1})

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Abstract

Polymer metal complexes of poly vinyl alcohol acetal and Cu^{+2}, Ni^{+2}, Zn^{+2} and Ag^{+1} were synthesized from the reaction of PVA with 4-methoxybenzyldehyde. All compounds were characterized by FT-IR, UV-Visible, TGA, DTA, TG and *Biological activity*. The results showed that Polycyclicacetal behaved as bidentate through its oxygen atom of hydroxyl (O-H) groups of modified PVA. The tetrahedral geometrical was suggested for Cu^{+2}, Zn^{+2} and Ag^{+1} complexes and octahedral geometrical Ni^{+2} complexes. The ligand and its metal complex showed good activity against different types of bacteria.

تحضير وتشخيص مع دراسة المضادات البكتيرية لمعقدات فلزات متعددة حلقة الاسيتال المشتقة من بولي فينايل الكحول مع معوضات البنزالديهايد

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الكلمات المفتاحيه:بولي فاينيل الكحول, البولي اسيتال الحلقي,بوليمرات المضادات المكروبية, معقدات البوليمر.

الخلاصه

ضمن البحث حضيرالليكاند لحلقة الاسيتال المشتقة من بولي فاينيل الكحول مع بارا ميثوكسي بنزالديهايد كما م حضيرمعقداته لكل من ايونات النحاس (II) والنيكل (II) والخارصين (II) والفضة (I). شخص البولي اسيتال ومعقداته المحضرة بواسطة طيف الاشعة حت الحمراء (FT-IR) وطيف الاشعة فوق البنفسجية والمرئية (UV-Visible) والتحاليل الحرارية مع الاستعانة بخواصها الفيزيائية. واظهرت النتائج با الليكاند هو ثنائي المخلب من خلال ناسق ذ ي أوكسجين مجموعة الهايدروكسيل لبوليمرات PVA المحورة. ووفقاً لطرائق التشخيص المشار اليها أعلاه. فا الشكل الهندسي المقترح لمعقدات البوليمر المحورمع ايونات Cu^{+2}, Zn^{+2}, Ag^{+1} رباعي السطوح ولايونات Ni^{+2} ثماني السطوح. وضمنت الدراسة كذلك دراسة أثير الليكاند المحضر ومعقداته كمواد مثبطة ووجد ا المعقدات المحضرة لها فعالية عالية على انواع مختلفة من البكتريا.

Introduction

Antimicrobial polymers present promising class of therapeutics with unique characteristics for fighting microbial infections [1]. These materials are capable of inhibiting and killing the growth of microbes on a surface or surrounding environment. They have an inherent capacity to display antimicrobial activity and they can act as a backbone to incorporate small biocides and antibiotics to display their activity [2,3].

PVA is synthetic polymer with many properties such as, biodegradable, biocompatible, water-soluble have many medical applications such as wound dressings, artificial skin, coatings, transidermal patches, cardiovascular devices, and drug delivery systems. Moreover, it has good barrier properties against scents, oils, and fats. The physical characteristics of PVA are dependent on its method of preparation by hydrolysis or partial hydrolysis of poly(vinyl acetate) [4,5].

The acetals of poly (vinyl alcohol) (PVA) are obtained by acid catalyzed modification of PVA with various aldehydes [6]. Acetals of PVA are important industrial products that find various application in the aviation and automobile industries as well as in biomedical fields [7, 8].

Experimental

Poly (vinyl alcohol) M.W72000 was obtained from Aldrich and all reagents and solvents were obtained from BDH and used without further purification.

Synthesis of Poly vinyl acetal

PVA (1.5 gm) was dissolved in 25 ml of hot distilled water at 90°C,the solution was mixed in (250ml) round bottle with (50% Methanol), (10% Acetic acid) , (5% Sulphuric acid) after that three different percentages (5%, 8%, 10%) of (1.1 g/1mmole) 4- Methoxybenzaldehyde (L) were added to the solution ,and then magnetically stirred at 40°C for 24hrs, the resulting mixture was neutralized by adding few drops of (5N) NaOH solution. The crude product was washed with distilled water and acetone many times .The product is dried at 40°C for12hrs [9].

The synthetic route of target compounds is shown in figure (1)

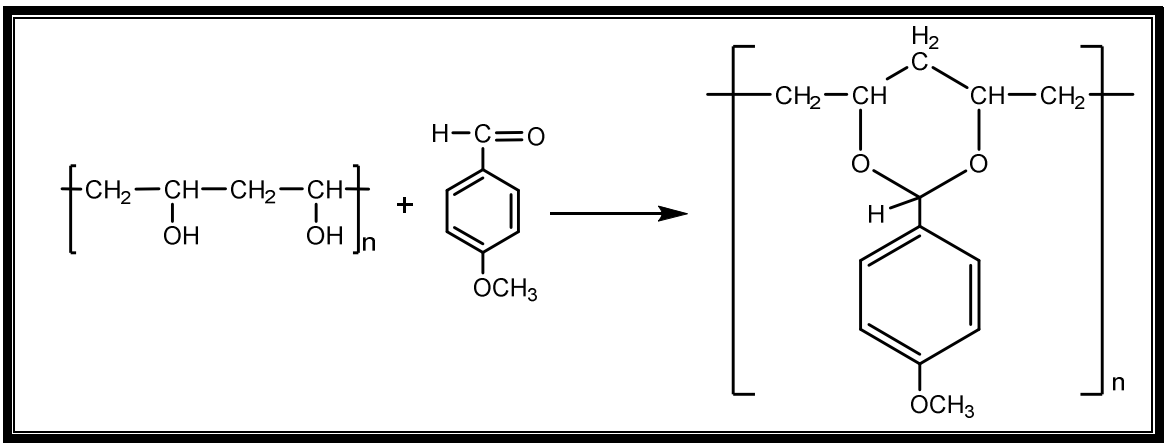


Figure (1) synthesis of poly cyclic acetal (L)

Preparation of polycyclic acetal metal complexes

(0.6 g/1mmole) of modified polymer ligand was mixed with (0.2g/1mmole of $ZnCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $AgNO_3$) was dissolved in 20 ml of DMSO stirred and heated at 60°C for12 hrs. After cooling, the complexes washed with Ethanol, and dried at 60°C in vacuum for 24 hrs [10]. The synthetic route of target compounds is shown in figure (2).

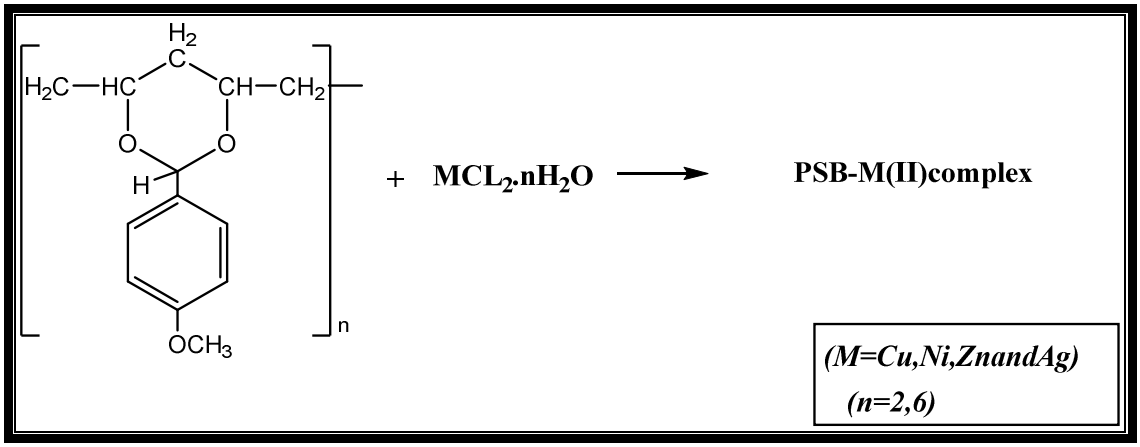


Figure (2) preparation of polymer metal complexes

Results and Discussion

Poly cyclic acetal and its metal complexes were prepared from the reaction of PVA with 4-Methoxybenzaldehyde and characterized by FTIR, UV-Visible spectroscopy and Thermal analysis. The white ligand was formed and it was soluble in DMSO solvent. Table (1) shows physical properties of the ligand and its metal complexes with (Cu^{+2} Ni^{+2} ,$Zn^{+2}$and Ag^{+1}).

FTIR – characterization of PVA Poly cyclic acetal and its metal complexes

The FTIR spectra for prepared ligand and its *(Cu^{+2}, Ni^{+2}, Zn^{+2} and Ag^{+1})* complexes confirms the formation of the polyacetal. The assignment of the characteristic bands is summarized in Table (2).

The (FT-IR) spectrum of the ligand (L), shows bands at (3483) cm^{-1}, (2839-2920) cm^{-1} and (1111) cm^{-1} due to stretching frequency ν(O—H), ν(C—H

aliphatic),and ν(C—O—H) respectively groups of starting material (PVA). The spectrum of the ligand (L) displays anew band at (1173) cm^{-1},(1616) cm^{-1} and (3414) is for stretching frequency of ν (C—O) acetal group, ν(C═C aromatic) and ν(C—H aromatic) confirm the formation of the ligand (L) [11].

The FT-IR spectra of all the prepared complexes exhibited broad band at range (3395– 3688) cm^{-1}, that may be attributed to ν(O-H) group in starting material, and the band at range (3630- 3765) cm^{-1}, that may be attributed to ν (O-H) water molecules, and these bands at a weak bands at(833-995) cm^{-1}refered to coordinates water (aqua).

Assignment of proposed coordination sites is further supported by the appearance of bands at [(1385) cm^{-1} and (1288) cm^{-1}] which could be attributed to ν (Ag-ONO_2) asymmetrical and symmetrical for L complex respectively, in this work; we expect these complexes as neutral molecules.

Electronic spectra of the polycyclic acetal and its metal complexes

The UV-Vis spectrum of ligand (L) Figure(3) displays one absorption peak at (276 nm, 36232 cm^{-1}) which could be attributed to ($\pi\rightarrow\pi^*$). The UV-Vis spectrum of [CuL] complex displayed two absorption peaks, the first peak at (285 nm, 35080 cm^{-1}) refer to intra-ligand and the other at (927 nm, 10787 cm^{-1}) was attributed to ($^2T_2\rightarrow{}^2E$) which was a good evidence for Cu^{+2}tetrahedral structure.

The electronic spectrum of [NiL] complex exhibited four absorption peaks at [(278 nm,35971 cm^{-1}), (301nm,33223cm^{-1})] refer to intra-ligand, which it's splitting because of coordination with metal ion .While the new two peaks at [(840 nm,11905 cm^{-1}),(967nm,10341cm^{-1})] were attributed to (d-d) electronic transition type$^3A_{2g(F)}\rightarrow{}^3T_{1g(F)}$,$^3A_{2g(F)}\rightarrow{}^3T_{2g(F)}$ respectively, Which were a good agreement for octahedral formula for Ni^{+2}complex.

The UV-Vis spectrum of [Zn L] complex and [Ag L] exhibited two peaks at [(275 nm, 36364 cm^{-1}), (271nm, 36900 cm^{-1})] refered to intra-ligand and new peak of [AgL_3] at (459 nm, 21786 cm^{-1}) was attributed to C.T electronic transition type M→L which were a good agreement for tetrahedral formula for $Zn^{+2}$and Ag^{+2}complexes. The electronic spectra for ligand complexes are summarized in Table (3) together with electronic transition and suggested geometrics.

Thermal analysis

The thermo gravimetric (DSC⁄ TGA) for pure PVA, Ligand and its metal complexes Cu^{2+},Ni^{2+} ,Zn^{+2} and Ag^{1+} ,was measured in temperature range from 0 ˚C up to 600 ˚C with a constant rate of 10°C⁄ min^{-1}.Table (4) shows the thermal decomposition of the ligand-metal complexes.

The pure PVA film showed three main stages of the weight loss , first one from 198-340.67˚C devoted to evaporation of the volatile compounds ,mainly water and weight loss about -48.13%, The second stage is from 340.67- 435.961˚ C (decomposition of side chain of pure PVA) and weight losses about-14.07% .The last one is from 435.961˚C to 594.67˚C(decomposition of the main chain of PVA) and weight losses about -22.37%. The DSC curve, for pure PVA film shows a glass transition temperature ,Tg of 63^0C, exothermic peak in 195˚C at crystalline temperature ,a broad endothermic peak regarded to the polymer melting at 214.5˚C these temperature were lower than PVA grains probably due to plasticization effect of water .The begin in 247-594.67 ˚C.

TGA curves of ligand (L) show four steps of a continuous mass loss. The first-step is 30-320.59˚C with -37.260% mass loss of volatile compounds. The second and third steps are 320.59-397.47˚C and 397.47-478.02˚C (decomposition of side chain of ligand) and weight loss about -31.202% and -14.708% respectively. The last- step 478.02 -593.1˚C with weight loss about -17.068%. The same figure showed glass transition temperature Tg at 63˚C. Exothermic peak for crystalline temperature at 108˚C .The endothermic peak regarding to the polymer melting at 243˚C.The degradation ligand L3 starts in 295˚C and ends at 594 ˚C.

The TGA thermo gram of Cu-ligand, Figures was characterized by two decomposition steps in the range [(55-219.38˚C) and (219.38-592.22˚C)] and weight losses about [(-37.85%) and (-44.33%)] respectively.

The DSC curve of Cu-ligand showed a glass transition temperature Tg of 78˚C. Crystalline temperature at 140˚C and Cu complex melting at 159˚C. The degradation of Cu-L begin from 285-592.02˚C.

The TGA thermo gram of Ni-ligand, was characterized by the three decomposition steps in the range of [(40-171.96˚C) and (171.96-320.71˚C)], and [(320.71-592.02˚C)] and weight loss about [(-14.39%), (-31.81%)] and [(-38.52%)] respectively.

The DSC curve of Ni-ligand, showed a glass transition temperature of 68˚C.Crystalline temperature point at 181˚C and the complex melting at 213˚C. The degradation of Ni-L begin from (313-592.02) ˚C.

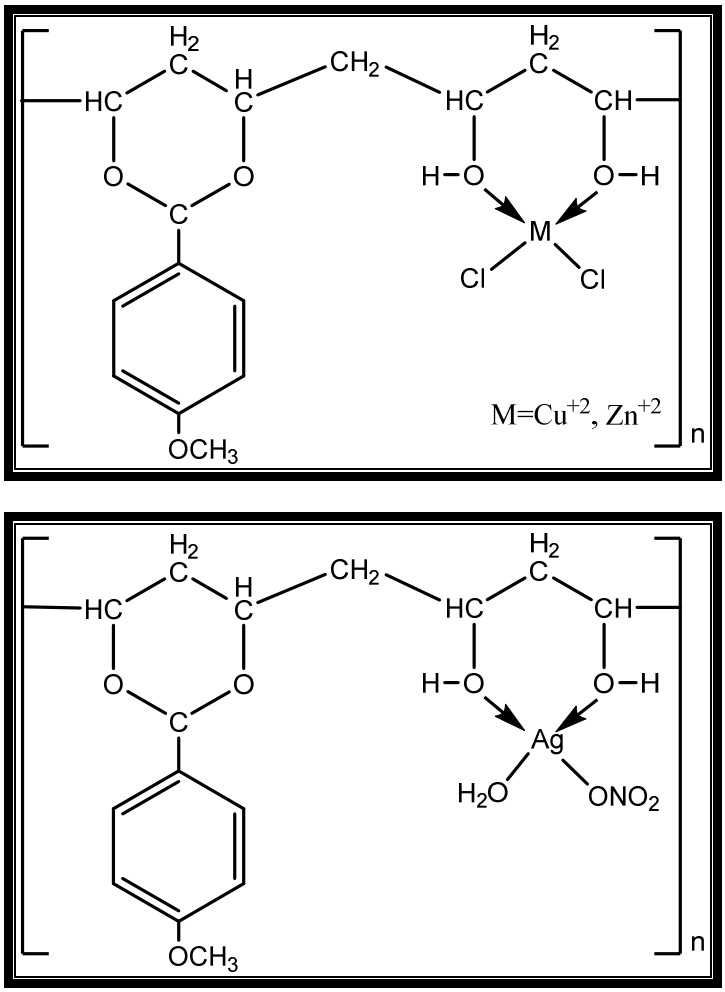
The TGA thermo gram of Zn-ligand, was characterized by two steps, the first-step [(41- 303.09˚C) with weight loss about -44.1% and second step 303.09 –594.07˚C with weight loss about -44. 38%.

The DSC curve of Zn-ligand, showed a glass transition temperature of 65˚C respectively. Crystalline temperature point at 152˚C and the complex melting at 195˚C. The degradation of Zn-L begin from 335-594.07˚C.

The TGA thermo gram of Ag-ligand , was characterized by three steps, the first step is 38-187.16°C with weight loss about -15.52%, the second step is 187.16-313.61°C with weight loss about -29.8%, the third step is 313.61-396.53°C with weight loss about -19.53%.

The DSC curve of Ag-L showed a glass transition temperature Tg of 74°C. Crystalline temperature point is at 172°C, the complex melting at 172°C. The degradation of Ag-L begin from 356-396.53°C.

According to the above - mentioned analysis, the suggested structures for the prepared complexes are illustrated in figure (3)



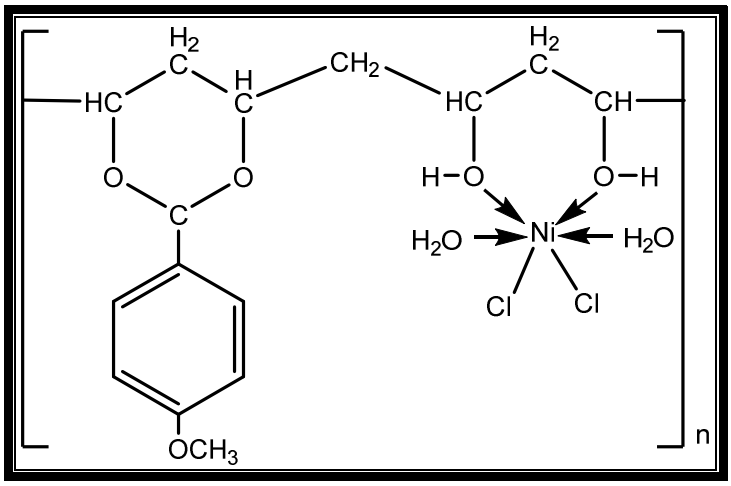


Figure (3) Suggested structure of prepared complexes

Antimicrobial studies

The synthesized ligand and its metal complexes were tested *in vitro* against bacteria: *Staphyloccus aureus*, *E-coli*, and *Burkholderiacepacia and Bacillus subtilis* The inhibition zone of the ligand and its metal complexes were given in Table (5) The biological activity of the ligand [L], was tested on four types of pathogenic bacteria using inhibition method [12-15]. Two types of bacteria were gram positive *Staphylococcus aureu*and *Bacillus subtilis*. The second two were gram negative *Escherichiacoli* and *Burkholderincepacia*. The ligands did not show any inhibition diameter against any type of the four bacterial, neither after 24 hrs.

The results of the antibacterial activity show that the ligand and its metal complexes showed weak to good activity comparing with the control (DMSO). [16-18] The increase in biological activity of the metal complexes may due to the effect of the metal ion on the normal cell process. A possible mode of action by increasing the toxicity may be considered in the light of (Tweedy's chelation theory) [19]. Chelation considerably reduces the polarity of the metal ions because of the partial sharing of the metal positive charge with the donor groups and the possibility of delocalization of p-electron within the whole ring system that is formed during the coordination. Such chelation could enhance the lipophilicity of the central metal atom, and hence increasing the hydrophobic character and liposolubility of the complex favoring its permeation through the cell membrane lipid layer. This process enhances the rate of uptake/entrance, and thus the antimicrobial activity of the testing compounds. Accordingly, the antimicrobial activity of the three metal complexes can be referred to the increase in the lipophilicity which will deactivates respiration processes enzymes and probably the other cellular enzymes, which play a vital role in metabolic pathways of the tested microorganisms [20].

Table (1) Physical properties of the ligand with metal ions (Cu^{+2}, Zn^{+2} Ni^{+2} and Ag^{+1})

Symbol	*colors*
PGM (L)	White
Cu L	Dark Green
Ni L	Green
Zn L	Light Yellow
Ag L	Dark Brown

Table (2) Infrared spectral data (cm^{-1}) for the ligands and complexes

Comp.	υOH_{alcohl}	υOH Coordinate	υCoordinateH_2O	υ(C-H) aliph.	υ(C-H) arom.	υ(C-O) Acetal group	υ_{asym}(Ag-ONO_2)	υ_{sym}(Ag-ONO_2)	M-O
L	3483	---	---	2839-2920	3414	1173	---	---	---
Cu L	3395	3685	991	2909-2986	3075	1173	---	---	432
Ni L	3410	3765	953	2870-2943	3260	1173	---	----	444
Zn L	3466	3760	995	2916-2936	3005	1173	---	---	447
Ag L	3414	3680	949	2913-2940	3800	1173	1385	1250	463

Table (3) Electronic spectral data of ligand and it's complexes and molar conductance for all complexes

Compound	λ (nm)	$V^{-}cm^{-1}$	Assignment	Suggested structure	Fig.
L	276	36232	$\pi \rightarrow \pi$	---	3

Cu L	285 927	35088 10787	Intra-ligand $^2T_2 \rightarrow {}^2E$	Tetrahedral	4
Ni L	278 301 840 967	35971 33223 11905 10341	Intra-ligand Intra-ligand $^3A_{2g(f)} \rightarrow {}^3T_{1g(f)}$ $^3A_{2g(f)} \rightarrow {}^3T_{2g(f)}$	Octahedral	5
Zn L	275	36364	Intra-ligand	Tetrahedral	6
Ag L	271 459	36900 21786	Intra-ligand C.T	Tetrahedral	7

Table (4) characterization parameter of thermal decomposition of polymer compound

Comp.	**DSC**				**TGA**			
	Tg/°C	**Te/°C**	**Tm/°C**	**Td/°C**	**Step**	**Ti/°C**	**Tf/°C**	**Wt.Los%**
PVA	63	195	214.5	247	1	198	340.67	-48.139
					2	340.67	435.96	-14.071
					3	435.96	594.67	-22.372
PVA-L	63	108	243	295	1	30	320.59	-37.349
					2	320.59	397.47	-31.202
					3	397.47	478.02	-14.708
					4	478.02	593.1	-17.068
PVA-L-Ag	74	172	225	356	1	38	187.16	-15.52
					2	187.16	313.61	-29.81
					3	313.61	396.53	-19.53
PVA-L-Cu	78	140	159	285	1	55	219.38	-37.85
					2	219.38	592.22	-44.33
PVA-L-Ni	68	181	213	313	1	40	171.96	-14.39
					2	171.96	320.71	-31.81
					3	320.71	592.02	-38.52
PVA-L3-Zn	65	152	195	335	1	41	303.09	-44.10
					2	303.09	594.07	-44.38

Table (5) Inhibition diameter in millimetre for the ligand complexes after 24 hrs

ComPound	*Burkholderia cepacia*	*Esherichia coli*	*Staphylococcus aureas*	*Bacillus subtilis*
L	---	---	---	---
Ag3	**14mm**	**11mm**	**12mm**	**12mm**
Ni3	**12mm**	**12mm**	**_**	**12mm**
Cu3	**21mm**	**_**	**16mm**	**30mm**
Zn3	**25mm**	**15mm**	**15mm**	**20mm**

References

1. Santos M. R. , Fonseca A. C. , Mendonça P. V. (2016) Recent Development in Antimicrobial polymers AReview. **Materials** , 9, 599.
2. Muñoz-Bonilla A. Fernández-García M. (2012) Polymeric materials with antimicrobial activity. **Prog. Polym. Sci**.,*37* , 281 .
3. Timofeeva L., Kleshcheva N. (2011) Antimicrobial Polymers: mechanism of action, factors of activity and application" **Appl. Microbiol. Biotechnol.**, *89* , 475 .
4. Galya, V.T. Sedlar, I. itka (2008) Antibacterial Poly(vinyl Alcohol) Film Containing Silver Nanoparticles: Preparation and Characterization. **J. Appl. Polym. Sci.**, 110, 3178–3185.

5. Sedlarik, N. V. Saha, I. Kuritka, P. Saha (2007) Enviromentally Friendly Biocomposites Based onWWaste of the diery Industry and Poly vinyl alcohol. **J. Appl. Polym. Sci.,**106, 1869.
6. Fernandez, M. D.; Fernandez, M. J.; Hoces, P. J. (2006) Synthesis of Poly(vinyl Butyral)s in Homogeneous Phase and Their Thermal Properties. **Appl. Polym. Sci.,** 102,5, 5007.
7. Li, G.; Yi, Z., (2006).**China adhesives**, 15, 27.
8. Zhao, D.; Liao, G.; Gao, G.; Liu, F. (2006) Influences of intramolecular cyclization on structure and cross-linking reaction processes of PVA hydrogels. **Macromolecules,** 39, 1160-1164.
9. Poly vinyl acetal silver halide emulsion containing poly vinyl acetal color formers, patent,1953.
10. Jian,T.F. Zhoul J., Gao I. Xing Y.and Li X. (2011) Synthesis and characterization of chitosan- based Schiff based compounds with Aromatic substituent Group. **Iranian polymer Journal** 20(2), 123-136.
11. Reis E.F.D., Campos F.S. (2006) Synthesis and characterization of poly (vinylalcohol) hydrogels and hybrids for MPB70 protein adsorption**.** **Materials Res.g**(2):185-191.
12. Anacona J.R .(2006) Synthesis and antibacterial activity of some metal complexes of Lactams antibiotics, **J. coord. Chem.** 54: 355–365.
13. Petra D., Tatjano Z. and Boriset P. (2005) Synthesis and structure – activity relationships of potent antitumor active quinoline and naphthyridinr derivatives. **J. Inorg. Bio. Chemistry** 99(2):432- 422 .
14. Tauber S.C. and Nau R. (2008).“Immunomodulatoryproperties of antibiotics”, **Current molecular pharmacology**, 1, 68.
15. Sultana N. and Arayne M.S (2007) In vitro Activity of Cefadroxil, Cephalexin, Cephatrizine and Cefpirome in Presence Of Essential and Trace Elements. **Pakistan J. pharma.Sci.,** 20, 4, 305.
16. Awetz J. Melnick, And Delbrgs A. 2007, “Medical Microbiology**”**4th ed McGraw Hil-USA.
17. Neelam P., PoonamY., Jitendra S.,Chauhan, DeepaliC., Ankur J. (2011) Involvement of apoptosis in 17-oxo-17a-aza-D-homo-5-androsten- 3β-yl

phenyl acetate induced toxicity in mouse macrophages. **Scholars Research Library**, 3(1): 208-213.

18. Barry A.L., 1976, "The Antimicrobic Susceptibility test principle and practices", 180.
19. Tweedy B.G. 1964 **Phytopathology** 55, 910-914.
20. Wafaa M. Hosny*, Perihan.A. Khalaf-Alaa (2013) Potentiometric Study and Biological Activity of Some Metal Ion Complexes of Polyvinyl Alcohol (PVA) **Int. J. Electrochem. Sci.,** 8 , 1520 – 1533.