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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL PROPERTIES OF COMPLEXES OF POLY(VINYLPYRROLIDONE) WITH NICKEL(II) AND COPPER(II) - A COMPARATIVE STUDY

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Abstract: Nickel compounds mainly find their use as catalysts. Bacteriostatic compounds, fungicides and some food preservatives contain copper compounds. Poly(vinylpyrrolidone) is a water soluble polymer having many eco-friendly uses due to its unique properties like low toxicity, biological compatibility, comparatively inert behavior towards many compounds, complex forming ability, resistance to thermal degradation in solution, film forming ability etc., In the proposed work, the transition metal complexes of poly(vinylpyrrolidone) - copper and poly(vinylpyrrolidone) - nickel were prepared by using aqueous solution of PVP (30K) and alcoholic solution of hydrated copper chloride and hydrated nickel chloride at room temperature with different molar composition. Polymer-metal complexes in the solid state were obtained by evaporation of the solvent. They were characterized by solubility studies, spectral analysis such as FTIR, ^{1}H-NMR and ^{13}C-NMR, thermal analysis by DSC studies and magnetic properties by VSM technique. A comparative study of the spectral data of the complexes helps in optimizing the conditions for the preparation of these eco-friendly complexes. Another important field of application of these polymers is in the development of antimicrobial agents. Poly(vinylpyrrolidone), as a polymer, does not exhibit any antimicrobial activity. The PVP – metal complexes prepared were checked for the antimicrobial property with different bacteria and fungi by Agar Well Diffusion method. The antimicrobial polymers have many advantages such as chemical stability, nonvolatile nature and capacity to permeate through skin, etc., over the conventional antimicrobial agents with low molecular mass.

Index Terms – Polymer-metal complexes, copper chloride, nickel chloride, FTIR, NMR, DSC, VSM.

I. INTRODUCTION

It is found that the complexes formed by transition metal ions with a potent ligand like poly (vinylpyrrolidone) are more active and effective than the individual metal and the ligand separately. In the proposed work we have selected water soluble salts of nickel and copper [10-15] for complexing with poly (vinylpyrrolidone) (abbreviated as PVP ligand. Nickel based catalysts meet wide range of requirements of most of chemical reactions and therefore often the preferred choice. Copper compounds are used as bacteriostatic substances, fungicides and food preservatives. PVP is a water soluble polymer having many eco-friendly uses which are the results of its unique properties like low toxicity, bio-compatibility, comparatively inert behavior towards salts and acids, complexing ability, resistance to thermal degradation in solution and film forming ability [1-7]. In the light of these facts, the overall objective of this research was to synthesize environment friendly polymer – metal complexes of poly (vinylpyrrolidone) in much easier way and characterize them so that the use of these complexes widens the area of applications.

Antimicrobial polymers act as polymeric biocides by inhibiting the growth of micro-organisms such as bacteria or fungi [8-9]. The pathogens selected included two gram +ve bacteria, two gram –ve bacteria and three fungi. If the polymer happens to be eco-friendly as in the case of PVP, it is even safer to substitute the conventional ones by antimicrobial polymers.

II. EXPERIMENTAL

2.1. Materials and Methods: 10 mL of 0.5 M aqueous solution of hydrated chloride salts of nickel (II) and copper (II) were stirred constantly at room temperature, with 50 mL of 25 % (w/v %) aqueous solution of PVP – 30K for about 10-12 hours, on a magnetic stirrer, till the volume of the solution was reduced to half of the initial volume. Thickened gum like semisolid was poured into Petri plates and dried in hot air oven at slightly above room temperature i.e. at 35-40 ºC for 15-16 hours. After the attainment of constant weight, the solid lumps were collected in air tight bottles.

Few other samples of PVP – metal (II) complexes were prepared by taking 50 mL each of 10 %, 25 % and 40 % (w/v %) aqueous solutions PVP – 30K and 10 mL each of 0.1 M, 0.5 M and 1.0 M aqueous solutions of hydrated metal (II) chloride (Table 1), to optimize the relative molar ratio of the two reactants for the synthesis.

Table – 1: Molar compositions of PVP and hydrated metal chloride solutions for the synthesis of PVP – M (II) complexes where M = Ni, Cu.

PVP↓ / Salt Solution→	0.1M	0.5M	1M
10 % (w/v)	PM-1	PM-4	PM-7
25 % (w/v)	PM-2	PM-5	PM-8
40 % (w/v)	PM-3	PM-6	PM-9

Complexes thus obtained were characterized by solubility studies, spectral analysis - FTIR, ^{1}H-NMR and ^{13}C-NMR, thermal analysis by DSC and VSM analysis. The samples were studied for their antimicrobial activities.

2.2. Solubility Test: The complexes were insoluble in non-polar solvents like acetone, diethyl ether, n-hexane, n-heptane, toluene, carbon tetrachloride and 1, 4 – dioxane.

2.3. FTIR Spectral Analysis: Based on the FTIR spectral data, we can conclude that the interaction between PVP and metal through oxygen atom of ketone (C=O) group is maximum with nickel whereas interaction through nitrogen was found to be significant in copper complex.

Table – 2: Nature of interaction between PVP and metal ion during the formation of complexes

Sample	CNC Stretching	N-C Stretching	C=O Stretching
PVP – 30K	**1443.5**	**1292.1**	**1663.4**
PVP–Ni(II)	1441.5	1292.1	1651.7
PVP–Cu(II)	1438.6	1291.1	1662.3

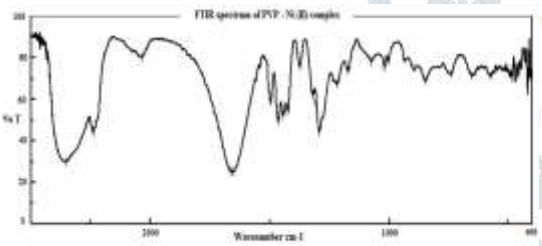


Fig. 1

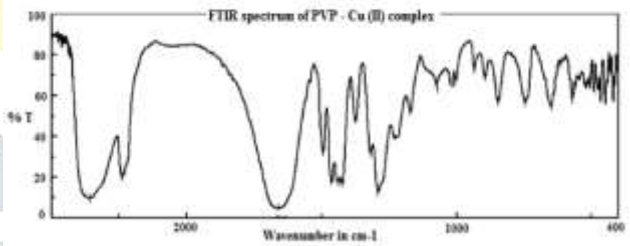


Fig. 2

2.4. The ^{1}H-NMR spectrum of PVP – Ni (II) complex (Fig. 3) indicates that,

- Main chain methylene proton ($–CH_2–$) of PVP resonate at $\delta = 3.15$ ppm
- Methine proton (– CH –) of PVP resonate at $\delta = 3.75$ppm
- Methylene protons of the side chain (i.e., pyrrolidone ring) in PVP signal at $\delta = 1.86$ ($–^{4}CH_2$) ppm, $\delta = 1.63$ ($–^{2}CH_2$) ppm and $\delta = 1.32$ ($–^{3}CH_2$) ppm respectively.

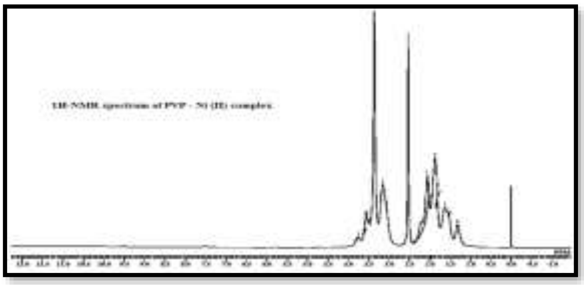


Fig. 3

The ^{1}H-NMR spectrum of PVP – Cu (II) (Fig. 4) complex indicates that,

- Main chain methylene proton ($–CH_2–$) of PVP resonate at $\delta = 3.15$ ppm
- Methine proton (– CH –) of PVP resonate at $\delta = 3.53$ ppm
- Methylene protons of the side chain (i.e., pyrrolidone ring) in PVP signal at $\delta = 1.87$ ($–^{4}CH_2$) ppm, $\delta = 1.63$ ($–^{2}CH_2$) ppm and $\delta = 1.31$ ($–^{3}CH_2$) ppm respectively.

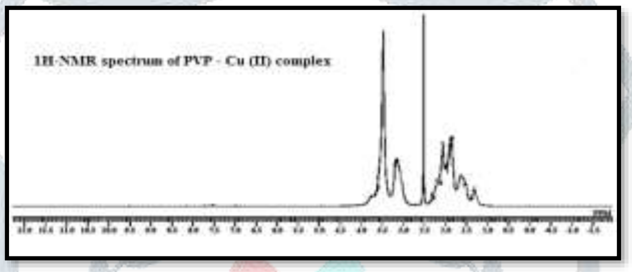


Fig. 4

2.5. ^{13}C NMR (100 MHz DMSO-d6) spectrum of PVP – nickel (II) complex (Fig. 5) indicates that the methylene carbons ($^{2}CH_2$, $^{3}CH_2$, $^{4}CH_2$) of side chain resonate and produce peaks in the range of 17.8 ppm to 33.7ppm. The carbonyl carbon ($^{1}C=O$) produces peak at $\delta = 173.6$ ppm

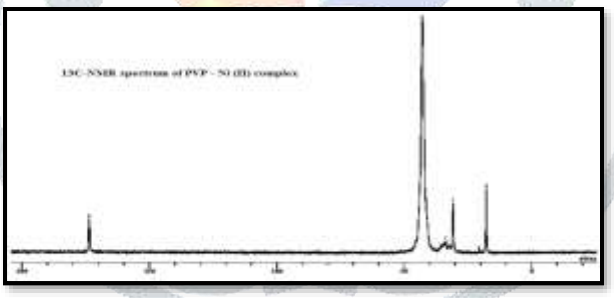
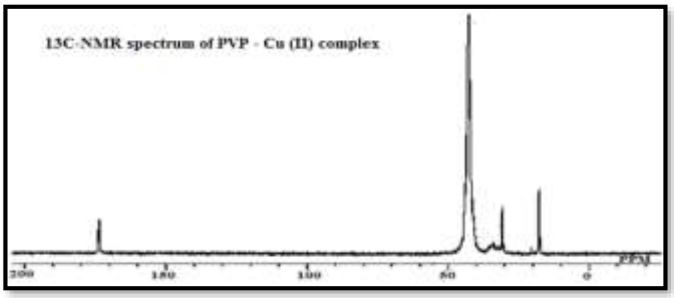


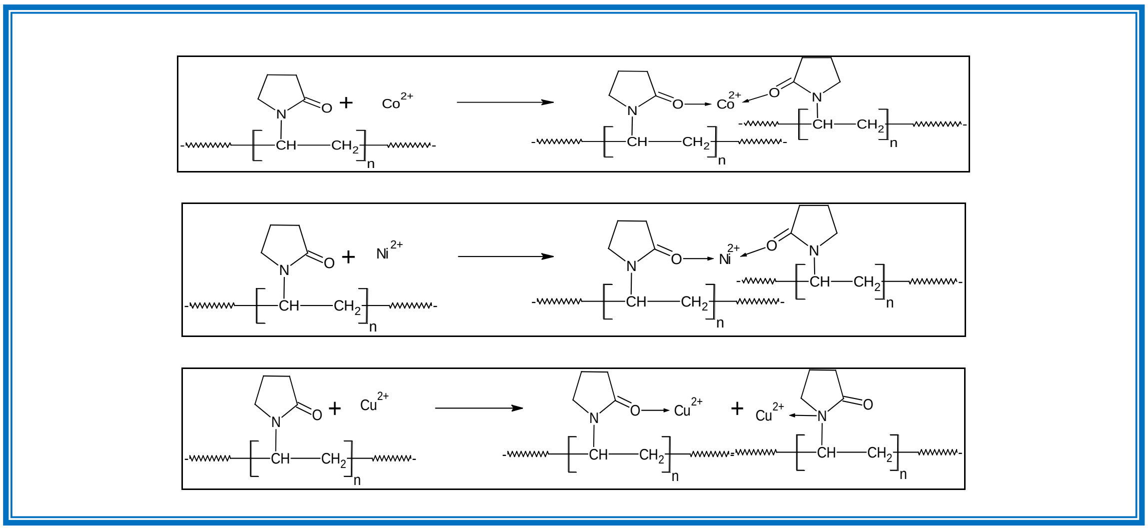
Fig. 5

^{13}C NMR (100 MHz DMSO-d6) spectrum of PVP – Cu (II) (Fig. 6) complex indicates that the methylene carbons ($^{2}CH_2$, $^{3}CH_2$, $^{4}CH_2$) of side chain resonate and produce peaks in the range of 17.93 ppm to 34.48 ppm. The carbonyl carbon ($^{1}C=O$) produces peak at $\delta = 173.9$ ppm



(Fig.6)

Based on the above spectral data, the possible structures of the complexes may be given as shown in the following scheme.



2.6 Thermal Analysis – Differential Scanning Calorimetric (DSC) Studies

Tg of a polymer changes when different degrees of polymerization are observed or when the additives are inserted. Tg of PVP-30K from literature is 163ºC.

Thermogram of PVP- Ni (II) complex shows two glass transition temperatures one at 35.5ºC and another at 57.7 ºC. The deviation in the Tg value of the PVP – Ni complex from that of pure PVP indicates that there is interaction between PVP and nickel ions. The complex melts (Tm) at 97.1ºC. DSC study facilitates us to evaluate the heat capacity of the given polymeric compound. The area under the peak gives the heat capacity of the complex which is equal to 682.7 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

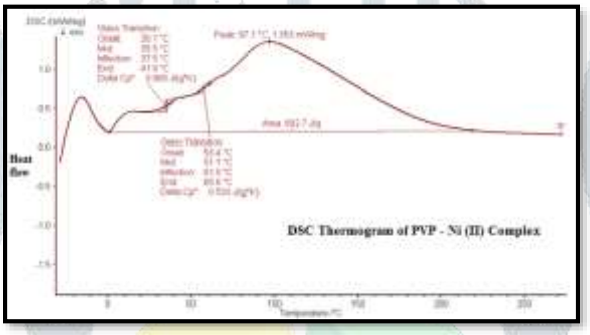


Fig. 7 : DSC thermograms of PVP – Ni (II) complexes

Thermogram of PVP – Cu (II) complex shows that its Tg is 51.0ºC. The deviation in the Tg value of the PVP – Cu (II) complex indicates that there is interaction between PVP and copper ions. The complex melts (Tm) at 140.8ºC. DSC study facilitates us to evaluate the heat capacity of the given polymeric compound. The area under the peak gives the heat capacity of the complex which is equal to 120.04 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

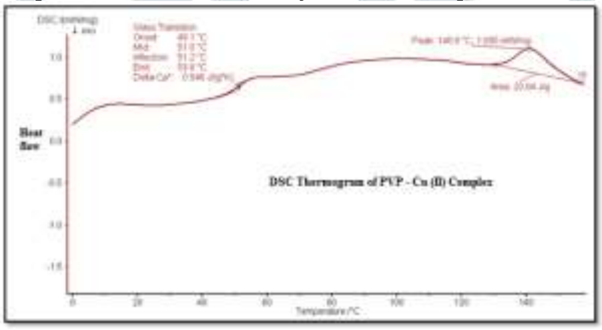


Fig. 8 : DSC thermograms of PVP – Cu (II) complexes

2.7. Magnetic Properties – Vibarating Sample Magnetometric Studies

VSM curve of the PVP – Ni (II) complex shows linear magnetization of the sample (Fig.9). As the applied field (H) varies between positive and negative values, the dipole moment realign without randomness, showing that the complex is isotropic. The sample reaches saturation around 15000 G. But at H = 0, magnetization, M is also zero. Hence there is no residual magnetization. Consequently, it may not turn into a permanent magnet for the given domain. It is only paramagnetic.

The magnetization curve of PVP – Co (II) complex obtained by VSM studies is shown in the Fig. 9 and 10.

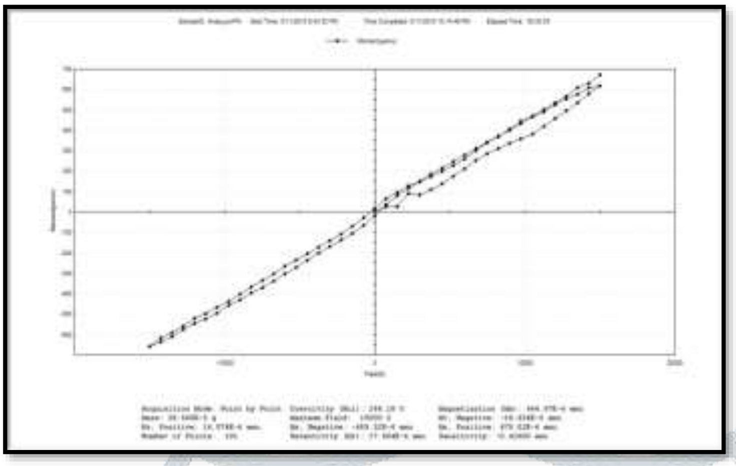


Fig. 9: The magnetization curve of PVP – Ni (II) complex

PVP – Cu(II) complex exhibits permanent magnetism as it shows non-zero residual dipole moment even at null fields (Fig. 10). As the applied field increases, magnetization also increases but for higher values of H, there is a decrease in μ. Similarly, as –H increases –μ becomes small and attains saturation. Hence PVP – Cu (II) complex shows permanent magnetism at lower fields and paramagnetism at higher fields.

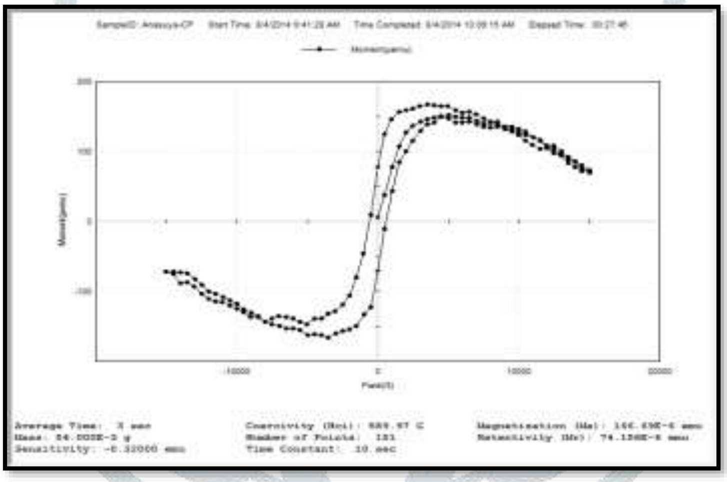


Fig. 10: The magnetization curve of PVP – Cu(II) complex

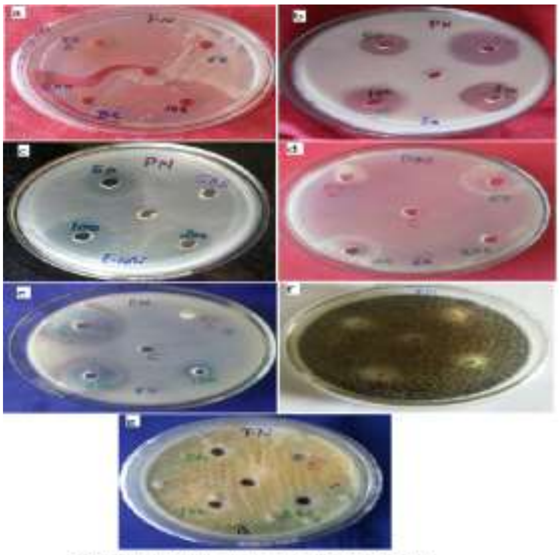
2.8. Antimicrobial Studies:

‘Agar well diffusion’ method is employed for antimicrobial studies. Streptomycin sulphate was used as the standard antibacterial. The standard antifungal used was Fluconazole.

The inhibition zones in mm for PVP-Ni and PVP-Cu complexes (Figures 11 and 12) are given in the tables 3 and 4.

Table – 3: Inhibition zones (in mm) of PVP-M (II) complexes on pathogenic organisms

Test Sample	Volumes of the sample (μl)	Bacterial Strains				Fungal Strains		
		Bc	Sa	Ec	Ea	Fu	An	Pe
PN	50	30	18	20	21	22	10	-
	100	30	21	23	20	13	10	-
	200	30	24	26	20	24	8	-



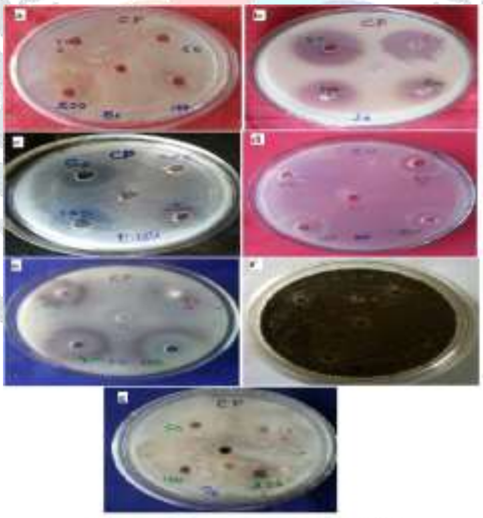
Photographic representation of antimicrobial test
a. *Bacillus pumillus*, b. *Staphylococcus aureus*,
c. *Escherichia coli*, d. *Enterobacter aerogenes*,
e. *Fusarium oxysporum*, f. *Aspergillus niger*,
g. *Penicillium sp*

Fig. 11

Table – 4: Inhibition zones (in mm) of PVP-Cu (II) complexes on pathogenic organisms

Test Sample	Volumes of the sample (µl)	Bacterial Strains				Fungal Strains		
		Bc	**Sa**	**Ec**	**Ea**	**Fu**	**An**	**Pe**
CP	50	18	30	18	20	14	-	12
	100	-	27	20	17	-	-	12
	200	35	25	20	18	-	-	12

***Bc**: Bacillus pumillus*, ***Sa**: Staphylococcus aureus*, ***Ec**: Escherichia coli*, ***Ea**: Enterobacter aerogenes*, ***Fu**: Fusarium oxysporum*, ***An**: Aspergillus niger*, ***Pe**: Penicillium sp*, '-': - inactive.



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a. *Bacillus pumillus*, b. *Staphylococcus aureus*,
c. *Escherichia coli*, d. *Enterobacter aerogenes*,
e. *Fusarium oxysporum*, f. *Aspergillus niger*,
g. *Penicillium sp*

Fig. 12

III. RESLTS AND DISCUSSION

Property	PVP-Ni (II) Complex	PVP-Cu (II) Complex
Colour	Olive green	Green
Interaction through	O – atom of keto group	Both from O - atom of keto group and N - atom of heterocyclic ring, but not simultaneously.
Molar composition for better interaction	Moderate PVP & lower M^{n+}	Higher PVP & lower M^{n+} favour interaction through O-atom whereas Higher PVP & higher M^{n+} favour interaction through N-atom.
Nature of the solid	Amorphous	Amorphous
Solubility studies	Both the complexes are soluble in polar solvents but insoluble in non-polar solvents	
Tg value	35.5ºC & 57.7ºC	51.0ºC
Heat capacity, Cp	682.7 J/g	20.04 J/g
Magnetic property	Isotropic & paramagnetic	Ferromagnetic at lower fields and Paramagnetic at higher fields
Anti - microbial activity	Active for all the bacteria and fungi selected except for Pe	Good antibacterial but not so effective as antifungal
Effect of solvent used for dissolving of metal salt	Nil	Nil

IV. CONCLUSION

The metal complexes of Ni and Cu with PVP were prepared in different molar compositions. FTIR spectra of all the complexes were taken and studied for the optimization of the conditions for better complexation of PVP with Metal. The variation in the stretching frequencies of C=O and C-N-C reveals the point of linkage of PVP with the metal. The ^{1}H- NMR and ^{13}C-NMR spectral studies also supplement the same. DSC and VSM studies reveal the amorphous nature and magnetic behaviour of the complexes. Antimicrobial studies show that the complexes are active against the selected pathogens.

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