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Comparative Study of Electrochemical properties of Synthesized PANI and PANI/Ni-NPs / Aloe-Vera thin films Biocomposite.

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Abstract:

This study deal with comparative observation of synthesized polyaniline films on glass subtract by chemically oxidative polymerization technique and synthesized polydisperse nickel nano particles(NiNPs) Stabilized on Aloe Vera Leaf Extract. The secondary phytochemical of plant extract polyphenols stabilizing and capping agentsfor the more stability and conductivity enhancement property.We synthesized PANI-Ni-NPs. Aloe Vera leaf extract and metal salt nickel chlorides dopant for the thin film composite formation on the glass substrate and studied their U.V. FTIR and Electronic microscopy Characterizationfor their comparative study of Electrochemical Behavior and current voltage Characteristics. The four-probe instrumentation indicate that the PANI-NiNPs modified electrode was good conductivity and stability on glass substrate (Resistivity = $1.305x10^4\Omega$) compared to that of the PANI thin films electrode (Resistivity =$1.024x10^5$ Ω)

Key word: Polyaniline, Conductivity, I-R Characterization, Thin film and PANI-Ni-NPs, Biocomposites

Introduction:

The polyaniline exhibits excellent characteristic such as good electrical conductivity also environmental stability and aneasy synthetic route. This characteristics property polyaniline applied in several area such as sensor, actuator, battery storage, electronic application has been reported [1-2]. Recent development in this field that nano-sized PANi/metal composites/hybrids exhibit even better characteristics as compared to the single homopolymer.There are numbers of different technique to Synthesized hybrids polymers composites like chemical oxidative polymerization, Electrochemical polymerization, spraying technique, coating systems,one-pot synthesis techniques, thin films coatingto Synthesis such conducting polymer/metal nanocomposites [3-4].

In this study we reported the synthesis PANI-Ni-NPs -Aloe Vera hybrids thin films composites on glass substrate via simple chemical oxidative polymerization technique by using ultra sonicator. The Ni-NPs are first synthesized through the reduction of Nickel chlorides salts with Aloe -Vera leaf extracts of polyphenol. How ever the Aloe-Vera polyphenol has not reported yet to, its utility as a nanoparticle fabrication precursor hybrid. The Aloe-Vera plant has large antioxidation property are due to the fact that it contains largequantities of polyphenols.It is believed that these polyols can play a vital role as stabilizers/capping agents in the production of the Nickle nanoparticles. The Novelty of this works is that plant extract polyols as well as flavonoids are used to stabilize the nano particle in formation of thin films on glass substrate and their utility for electrochemical characterizations in different application as sensor or biosensors.

2. Materials and Methods

2.1 Materials and chemical

Aniline and Ammonium oxysulphides from Sd -Fine chemical are used. Aniline distilled prior to used, The Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$, >98%) was from Sd-Fine chemicals.Aloe-Vera was bought from a local college medicinal garden. Double Distilled deionized water (DDW) was from the analytical laboratory, Chemistry Department, was used for all aqueous preparations.

2.2 **Extraction of Aloe-Vera gel and Ni -NPs synthesis**

We are collected the one fresh leaves of Aloe-Vera was bought from a local college medicinal garden and remove the hard green coat from leave by using knife, the after near about 10 g semi liquid parts gel and 10 ml of doble distilled water are mixed in 100ml beaker by using ultra sonicator for 20 minutes. The resultant supernatant was collected, filtered and stored at 10 ℃ before use. The NiNPs were prepared by adding 0.1 M Nickel II chloride solution to the Aloe-Vera extract (supernatant at ambient temperature) in a series of 1:1,1:2,1:3 and also 4:1,3:1, 2:1 volume ratio. The mixture was hand shaken for 1 min and allowed to stand at room temperature for 30 minutes in ultra sonicator at 40 to 90 ℃ to prepare the nanoparticles.

2.3 Synthesis of PANI films.

The aniline was double distilled prior to used then in 100ml, we have taken glass substrate andoptimize the stoichiometric ratio of both chemicals that is 2ml of aniline and 0.5 M ammonium peroxydisulphate under continuous stirring at room temperature and kept in ultrasonicates for 20 minutes then cool it below -10 ℃ freezers for 12 hours to obtained homogenous stable thin film formation.

2.4 Synthesis of PANI-Ni NPs of Aloe-Vera films.

The optimize stoichiometric concentration of 2ml aniline and 0.01, 0.02, 0.03, 0.04 upto 0.1 M Concentration of Ni-NPs of Aloe-Vera extract solution added to in series of 100 ml beaker with glass substrate to oxidized with 0.5 M ammonium peroxydisulphate under continuous stirring at room temperature and kept in ultrasonicates for 20 minutes then cool it below -10 ℃ freezers for 12 hours to obtained homogenous stable thin film formation. The thin films substrates wash with deionized water kept to dry at room temperature with drier. The Figure shown in Fig 1.1 and 1.2 is that Synthesis of PANI-Ni NPs of Aloe-Vera films before oxidation and after oxidation the formation Biocomposites films of PANI-Ni NPs. Fig 1.3 indicate the formation of thin films of PANI-Ni NPs on Glass substrate.

Fig 1.1 and 1.2 before oxidation and after oxidation the formation Biocomposites films of PANI-Ni NPs.

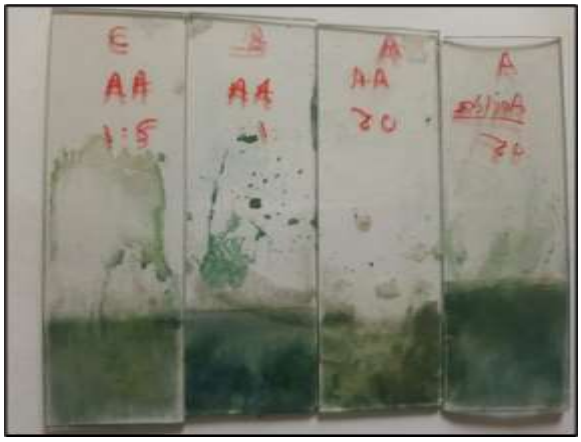

Fig 1.3. Optimization PANI-Ni NPs of Aloe-Vera films

2.5 Electrochemical Characterization of the PANI-Ni NPs of Aloe-Vera films

The PANI-Ni NPs of Aloe-Vera films were prepared by Chemical oxidative polymerization method are Characterized by U.V.-Visible spectroscopy was recorded on UV- VIS Spectrophotometer Carry Agilent Tech at Department of chemistry SGBAU, Amravati. In case of UV- VIS Spectroscopy transition that results in the absorption of electromagnetic radiation in UV-VIS Absorption Region are Spectrum of transition between electronic levels.

Infrared spectroscopy is the analysis of infrared light interacting with molecule. This can be analyzed in three ways by measuring abortion, Emission and reflection. It is used to determine functional group in molecule FTIR Spectroscopy measure the vibration atoms and based in this it is possible to determine functional groups. The following IR spectra were recorded on Bunker Alpha-T FT IR Spectrometerat Department of chemistry SGBAU, Amravati.

Olympus electron microscope is used for thin and observation of stability as well as granular or tubular size nanoparticles of PANI/Ni-NPs /Aloe-Veragranules at Department of Botany. The conductivity and Current -Voltage characterization was carried out by using four probe Instrumentation.

3. Result and Discussion.

3.1. U. V. Visible of PANI and PANI/Ni-NPs / Aloe-Verafilms.

The U.V.-Visible spectroscopy was studied in range between 200nm to 700nm after dissolution of PANI and PANI/Ni-NPs / Aloe-Verathin films in DMSO solvents. The spectrum shows a prominent peak at absorption maxima of 292 nm which has been assigned to the $\pi \rightarrow \pi^*$ transitions of the Aloe-Vera polyols. The high absorbance value of 1.5 obtained indicates a high concentration ofthe polyols in solution.A broad peak extending from 260-380 nm with absorption maxima at 298 nm was seen. Such observationis characteristic of transition metal elements where the observed broad peaks are due to transitions within the filled and unfilled d-orbitals of metal salts by influence from other external factors.

The new peak formed was slightly shifted bathochromically compared to the 292 nm peak of the Aloe-Vera extracts. This peak at 290 nm and the smaller hub at around 350 nm have been shown to be due to the presence of the Ni-NPs nanoparticles in the Ni (II) state. It means the reluctant polyols within the matrices successfully reduced the Ni (II) ions to the Ni zero states also indicating the formation of theNi-NPs/polyols hybrid. The reduction of the prominent extract peak at 292 nm indicates the polyols were actually involved in the reduction process and the consequent formation of a new compound the PANI/Ni-NPs / Aloe-Vera film composite as shown in figure 3.1.

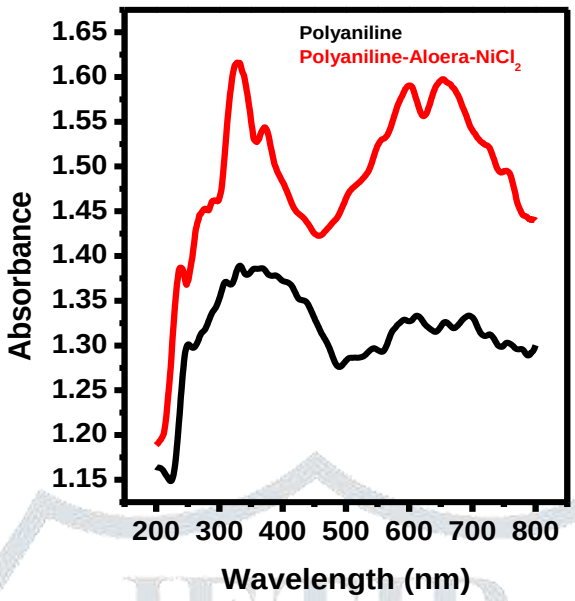

Figure 3.1. U. V. Visible of PANI and PANI/Ni-NPs / Aloe-Vera film

3.2.FT-IR spectra of PANIand PANI/Ni-NPs / Aloe-Vera films.

FT-IR spectra of PANI solid exhibited the characteristicabsorption bands of emeraldine salt at 1518 and 1616 cm^{-1}, whichcorrespond to the C- C stretching vibration of benzenoid (N -B-N)and quinonoid (N =Q= N) ring, respectively [5]. The peaks in therange of 1300–1400 cm^{-1} as arise from C-N stretching vibrationsof the secondary aromatic amines, while the intense absorptionpeak at 1193 cm^{-1} is associated to the B- NH -B and protonatedQ =NH^{+}-B stretching modes of PANI chains [6]. The vibrationalfeatures at 519, 593 and 838 cm^{-1} correspond to the aromaticring deformation (C-C stretching modes) and C- H out-of-planebending mode of 1,4-disubstituted benzene ring, respectively [7].

Compared with the pure PANI in figure 3.2.1 and figure 3.2.2 of the hybrid PANI/Ni-NPs / Aloe-Vera composite materials indicated a considerable red shift (∼15–20 cm^{-1}) of theN-B-N and N =Q=N vibrational bands at ∼1501 and ∼1600 cm^{-1}respectively, suggesting interaction of PANI chains with anionic heteropolyacids. The IR spectra of the hybrid samples indicate thepresence of Ni-Od (terminal bonds) and Ni-Ob -Ni (bridge bonds between the corner-sharing NiCl octahedra; M = Ni) stretchingvibrations at ∼972–988 and ∼879–890 cm^{-1} respectively [8,9]. However, these absorption bands are considerably red-shifted (∼10 cm^{-1}) compared with theNi-Nps -Aleo vera, suggesting strong binding of Ni-Nps –Aleovera units to the polymer network. The intense absorption bands at∼1140 and ∼1080 cm^{-1} observed in the samples of Ni-Nps –Aleovera and PANI–Ni-Nps -Aleovera are ascribed to the clusters, respectively. The PANI–Ni-Nps sample exhibits the corresponding Ni-Clvibration band of cluster at ∼804 cm^{-1}.

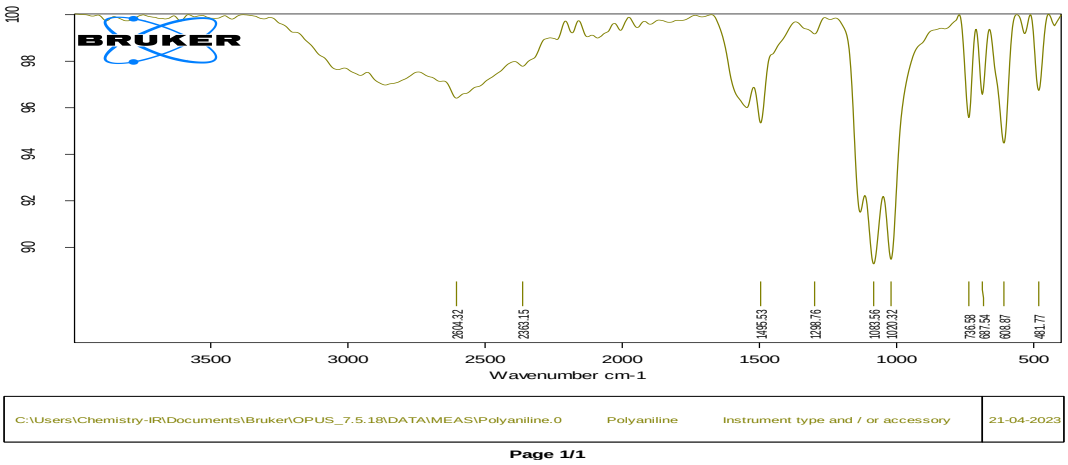

Fig 3.2.1 FTIR Spectrum of Polyaniline

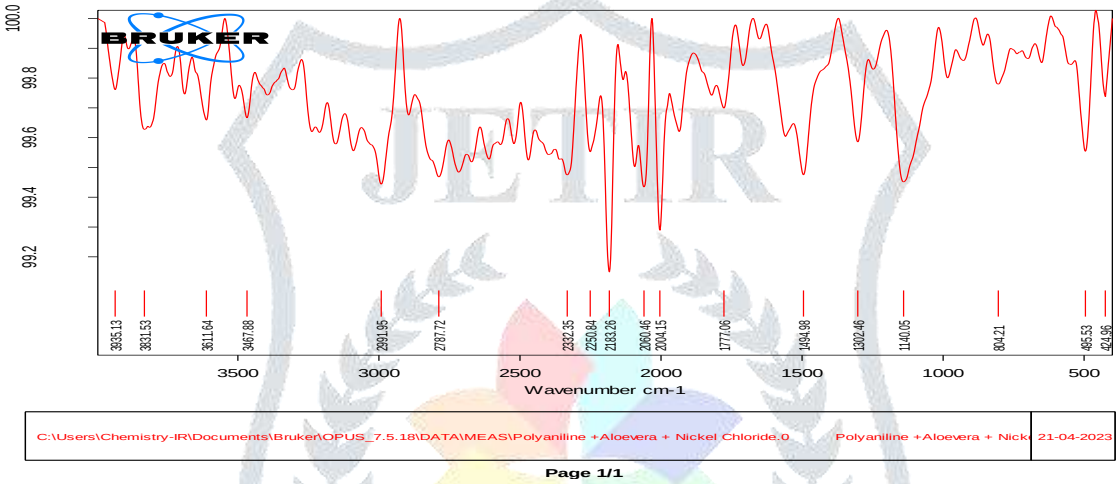

Figure 3.2.2 FTIR Spectrum of PANI-NiNps AloeVera

Sr.	Assignments	PANI-NiNpsAloeVera Observed Value (cm^{-1})	PANI Observed Value(cm^{-1})	Literature value (cm^{-1})
1	O-H Stretching Aromatic Polyol ring	3631, 3611		~3560
2	N-H Stretching Aromatic ring	3467,	3300	~3400
3	C-H stretching vibration aliphatic	2991	2968.	~2930
4	diazonium salts	2787	2604	~2740
5	asymmetric NH+=)	2332,2183	2363,	~2156
6	N-B-N and N =Q=N vibrational bands at ~1501 and ~1600 cm−1 benzenoid unitsC=C	1777, 1494	1496, 1296	~1600, ~1300
7	Intense absorption Ni-Nps	1140,1080.	1083,1020	~1080 cm−1
8	Ni -Od (terminal bonds) and Ni -Ob -Ni (bridge bonds between (M = Ni)	804,		~972–988 and ~879–890 cm−1
9	Para, ortho substituted aromatic rings	495	736,608	519, 593

3.3. **Electron microscopy of PANI and PANI /Ni-NPs / Aloe-Vera films.**

The actual integration and the structurization effect of the Aloe-Vera polyphenols/flavanoids were observed in the Electron microscopy images obtained. .The rod or fiber like morphologies are obtained by suppressing secondary growth. It has been shown that PANI first forms fibers in figure 3.3.1; however, with the progress of the polymerization, the formed fibers serve as the scaffolds for the further growth of PANI and finally develop to a particle form. The average particle sizes with variation in polymerization can be seen that for polymerization time, rod-like particles are present. With increase in polymerisation duration, rod-like particle become less abundant and more spherical/globular particles are seen due to the presence of Aleo-Vera polyol that is polyphenol immersed with or coagulant of Nickel metal atoms are present in formation of Polymeric thin of PANI /Ni-NPs / Aloe-Vera films in figure 3.2.2 .The nickel metal morphology in figure 3.2.3. favors the formation globular particles.

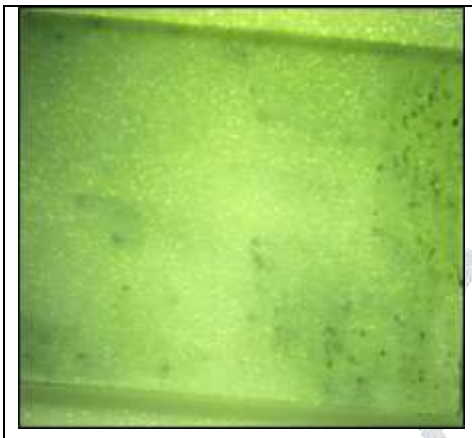

Figure 3.3.1.Electron microscopy morphology PANI

Figure 3.3.2 Electron microscopy morphology PANI /Ni-NPs / Aloe-Vera.

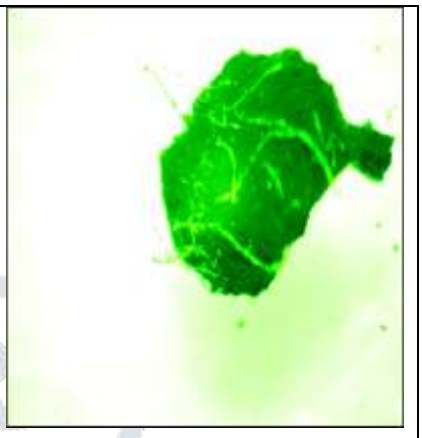

Figure 3.3.3 Electron microscopy Image Nickel metal.

3.4. Electrochemical Characterization

The I-V characterization measurement of the PANI and PANI /Ni-NPs / Aloe-Vera films was recorded by an indigenously developed computer controlled using four- probe method at room temperature. The current–voltage (I-V) characteristics of the synthesized PANI and PANI /Ni-NPs / Aloe-Vera thin films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig.3.4.1. reveals that the PANI and Fig.3.4.2. PANI /Ni-NPs / Aloe-Vera composites film has an ohmic behavior at room temperature. The four-probe instrumentation indicate that the PANI-Ni-NPs modified electrode was good conductivity and stability on glass substrate (Resistivity = 1.305x104 Ω) compared to that of the PANI thin films electrode (Resistivity =1.024x105 Ω) at room temperature.

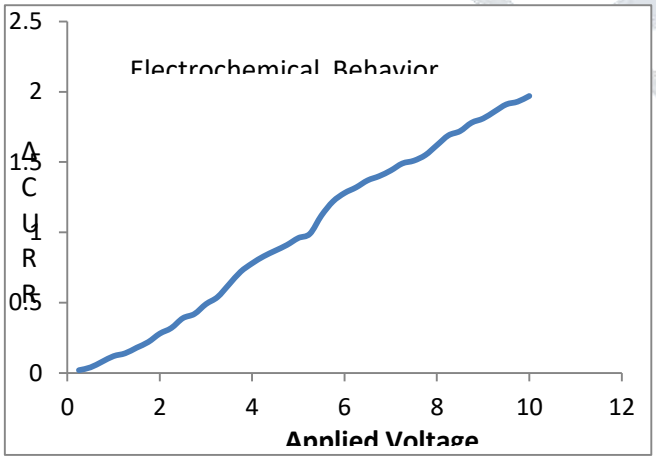

Fig.3.4.1. **Electrochemical** behavior the PANI

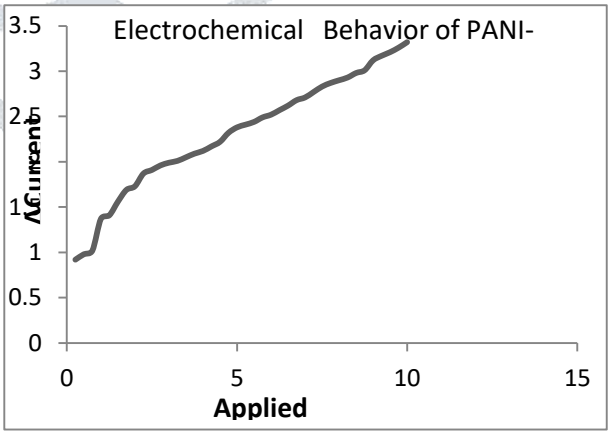

Fig.3.4.2. **Electrochemical** behavior PANI /Ni-NPs / Aloe-Vera

Conclusion:

This study comparesthe synthesis the PANI and PANI /Ni-NPs / Aloe-Vera films composite. The characterization techniques such as U.V, FTIR and EM analysis confirmed that Nickel chloride with Aleo Vera was successfully incorporated into the PANI matrix. Effect of different concentration of Nickel chloride with Aleo vera on structural, electrical and properties of PANI /Ni-NPs / Aloe-Vera films composite were studied. FTIR analysis showed good intermolecular interaction between PANI /Ni-NPs / Aloe-Vera matrix. The surface morphology of PANI /Ni-NPs / Aloe-Vera composite films was examined using EM analysis and the results confirm that Ni-NPs are homogeneously dispersed in PANI matrix. The synthesis composite films with Ni-NPs / Aloe-Vera doping showed highest conductivity with a value of $1.305x10^{-4}Scm^{-1}$. The results obtained in the present study for PANI and PANI /Ni-NPs / Aloe-Vera composite films observed electrochemical behavior which is linear.

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