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Synthesis, characterisation and biological applications of conducting poly (*p*- amino phenol) and its nano compound

Thenmozhi G[a], JayaKumar D[a], Mohanraj Gopalswamy[b] and Jaya Santhi R[a]*

[a]*P G & Research Department of Chemistry, Auxilium College, Vellore, Tamil Nadu, India*
[b]*Department of Physics , Martin Luther University of Halle-wittenberg, Halle(saale), Germany*

ABSTRACT

The oxidative chemical polymerizations of para aminophenol was synthesized in acidic medium using potassium dichromate as an oxidant at 0^0C and its nano compound was synthesized using an anionic surfactant Sodium Dodecyl Sulphate. They were characterized by FT- IR, UV-VIS, ^{1}H-NMR, TGA, SEM and TEM. The formation of benzenoid and quinonoid structure was confirmed from the FT-IR, ^{1}H-NMR and UV studies and the thermal studies confirms that the poly nano compound is more stable than the corresponding polymer. The conductance was measured and found to be semiconducting in nature. The resulting polymer and its nano compound were analyzed for its antioxidant activities using DPPH assay and the antibacterial activities by agar well cut diffusion method against two bacterial stains Staphylococcus aureus (gram +ve) and Escherichia coli (gram-ve). The antioxidant and antibacterial activities of poly (p–aminophenol) nano compound is greater than the corresponding polymer and they were concentration and the time dependant. The increased activities of poly nano compound may be due increase in surface area because of its smaller size and these properties can be considered in the field of biomaterials in biomedical areas.

Keywords: Aminophenol, Antioxidant, Antibacterial, Surfactant, Polymerization.

INTRODUCTION

After the successful synthesis of poly acetylene by shirakawa and co-workers [1], conducting polymers have attracted much scientific and technological interest in recent years because of their many possible applications. A signification portion of these studies has been devoted to polyaniline and this constitutes a large family of polymers which are formed by oxidative either electrochemically or chemically of aniline or its derivatives [2]. Aminophenols are interesting electrochemical materials since, unlike aniline [3] and other substituted anilines [4], they have

two groups ($–NH_2$ and–OH) which can be oxidized. Therefore, they can show electrochemical behavior resembling anilines [3-5] and phenols [6, 7].

In polymerization of aminophenol, the relative position of amino and hydroxyl group is important. The reported electrochemical properties of the three positional isomers (ortho, meta and para) are strongly different. P- Aminophenol is a well-known compound which, in its simple form or derivative [8] has been used as redox agent in photography. In neutral media, it is oxidized to complex oligomeric dyes that could be used in enzymatic assays [9]. Taj et.al [10] has studied the electro polymerization of p-aminophenol on a platinum electrode which yields a soluble electro active polymer in organic solvents.

Recently, conducting polymers are being considered for a range of biomedical applications, including the development of artificial muscles [11], controlled drug release [12] and the stimulation of nerve regeneration [13]. Low cytotoxicity and good biocompatibility of these materials are evident from the growth of cells on conducting polymers and from the low degree of inflammation seen in test animals over a period of several weeks [14]. Conducting polymers are redox-active, they are potential materials to act as reducing agents and scavenge free radicals. Poly aniline and substituted poly anilines have already been examined for their use as antioxidants in rubber materials [15]. However, their antioxidant ability in biological media needs to be examined to assess their likely activity in biomedical applications [16].

Recently, serious infections of microbe have become a social problem. Therefore, safe extermination of microbe is very important to human health care. During the last two decades, continuous effort has been made to develop the Polymers with antimicrobial function [17]. Generally, polymeric antimicrobial agents have following advantages. It is believed that they are non volatile, chemically stable, and do not permeate through the skin .As a result, the application of polymers with antibacterial activities will be a major step toward a healthier living. On the other hand, though hundreds of thousands of polymeric compounds have been prepared, few of them were of visible antimicrobial activities [18].

The extensive literature survey shows that some work has been carried out in aminophenol and their application in different field. But no attempt was made to synthesize conducting poly (*P*-amino phenol) and its nano compound and its biomedical applications. So we have under taken to synthesis poly (*P*- amino phenol) by chemical oxidation method and its nano compound using SDS as an emulsifier. The prepared compounds were characterized by spectroscopic techniques and its biological applications like antioxidant and antibacterial studies were carried out.

MATERIALS AND METHODS

All chemicals used were of analytical grade, supplied from Sigma-Aldrich and used as received. The solvents were purified using Vacuum Rotary Evaporator under reduced pressure and their boiling point was checked for their purity.

Preparation of poly Para amino phenol

The poly para aminophenol (PPAP) was synthesized by chemical oxidative method in acidic medium using standard procedure [19]. Monomer (*P*-aminophenol) was initiated by the drop wise addition of potassium dichromate as an oxidizing agent and conc. HCl as a dopant under constant stirring at 0-3^{0}C. After complete addition of the oxidant, the reaction mixture was continued to stir for five hours and the reaction vessel was placed in the refrigerator overnight. The product was filtered and washed with distilled water until the filtrate was colourless and the polymer was dried and powdered.

Preparation of poly Para aminophenol nanocompound

The poly para aminophenol nano compound (PPAP/SDS) was prepared by chemical oxidation *insitu* method as mentioned above with slight modification using Sodium Dodecyl Sulphate (SDS) as an emulsifier.

Antioxidant Activity

The antioxidant activity was carried out in triplicate according to the method of Blois (1958) with the slight modification [20]. Briefly, 25mg /L solution of DPPH radical (Aldrich) in methanol was prepared and then 2mL of this solution was mixed with different concentration like 50, 60, 70, 80, 90, 100 µg / mL of sample solution to achieve the final volume of 3mL. The absorbance was measured at 517nm for different concentration at different time intervals at room temperature. Decrease in the absorbance of the DPPH solution indicates an increase of the DPPH antioxidant activity. The antioxidant activity was calculated using standard equation [21].

Antibacterial Activity

Sterile Nutrient broth was inoculated with freshly isolated bacterial culture and incubated for 24h at 37°C. The bacterial suspension was found to be approximately 10^7-10^8 cells/mL after the incubation period they were used as an inoculum. An about 0.1ml of suspension containing 10^8 Colony Forming Unit (CFU / mL) of bacterial strains was used to study by Agar well cut diffusion method [22]. The polymer and its nano compound were taken at different concentrations like 50, 75 and 100µg / mL and their zone of inhibitions were monitored after 24 hours and the zone of inhibition was compared with the standard Gentamycin.

Characterization

FT-IR spectra were recorded in the mid IR region between 4000cm^{-1} to 400cm^{-1} using Thermo Nicolet Model 6700. UV-Vis spectra were recorded from 200-800nm using systronics double beam UV-Visible spectrophotometer 2201. ^{1}H-NMR spectra of the samples were recorded in a BRUKER AVANCE II- 600MHz instrument using d^6 - DMSO as solvent at 298K. Thermo Gravimetric Analysis (TGA) was carried out using on waters Q5000 V3.10 built 258 thermal analyzer 10°C to 350°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere with gas flow rate of 90ml min^{-1}.The conductance of the synthesized polymer and its nano compounds were measured by Keithley four probe nanovoltmeter. The particle morphology of the nano compound was determined by Scanning Electron Microscopy (SEM) using JSM 5800, JEOL. The nano compound particle size was measured by Transmission Electron Microscopy (TEM) using Zeiss 900 electron microscopy. The microscope was operated at an acceleration voltage of 80Kv and a magnification of 20,000X was used for imaging.

RESULTS AND DISCUSSION

Solubility Test

The solubility of the polymer and its nano compound in different solvents are presented in table 1. From the table it was clear that the PPAP and its nano compound are completely soluble in DMSO and they are partially soluble in THF, DMF, methanol and acetone but insoluble in n-hexane.

Table 1: Solubility test for the synthesized Poly *P*- Amino Phenol and its nano compound

Solvent	PPAP	PPAP/SDS
DMSO	++	++
DMF	+	++
THF	+	-
Methanol	+	+
Acetone	-	+
Hexane	-	-

++ Excellent + good - not soluble

FT-IR Analysis

The FT-IR spectrums of the synthesized poly (*P*-aminophenol) and its nano compound prepared in the presence of SDS are shown from Fig 1. For the polymer and its nano compound, a broad peak appeared in the 3500-2000cm^{-1} region and these absorption bands are due to stretching of aromatic C-H, -NH_2 stretching, -OH stretching (where applicable) etc. A broad band at 3415cm^{-1} appears for P*P*AP, this may be due to the merging of two individual absorption peaks from the stretching vibrations of –OH group and –NH_2 group. The two peaks at 1602 and 1387cm^{-1} are attributed to the C=C stretching vibrations of benzene and quinone rings respectively. The peak at 1258cm^{-1} is assigned to the C-N stretching vibrations, because the C-N stretching vibrations in aromatic amines are in the range of 1280-1180cm^{-1} [23]. In the case of PPAP/SDS, the presence of SO_3^- group is confirmed by appearance of a band around 576cm^{-1} is attributed to degenerate bending mode of the SO_3^- group [24] and the peak around 2800-3000cm^{-1} are due to the –CH_2 stretching of the SDS.

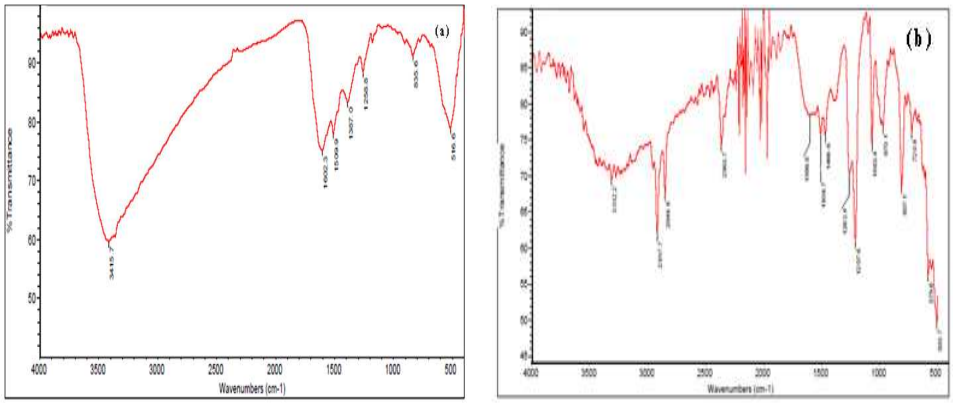

Fig 1: FT-IR spectrum of a) PPAP (b) PPAP/SDS

UV-Vis Spectral Analysis

The UV-Vis spectra of PPAP and PPAP/SDS were recorded in DMSO and are shown in Fig 2. In the synthesized polymer and its nano compound, the first absorption band appears in the region of 238-389nm is assigned to the $\pi - \pi^*$ transition of the benzenoid ring. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The absorption band at 589 and 632nm was believed to be $n - \pi^*$ transition, which correspond to non-bonding lone pair electron transitions of hetero atoms like nitrogen and oxygen respectively. PPAP/SDS additionally has other two peaks around 468 and 740nm are assigned to the polaron transitions. From the UV-Vis spectral characterization, it is clear that some polarons are obtained in the π - conjugated backbone of the polymer by the addition of an emulsifier SDS [25]. The observation of polaron bands is consistent with a high degree of doping and good solubility of the polymer nano compound.

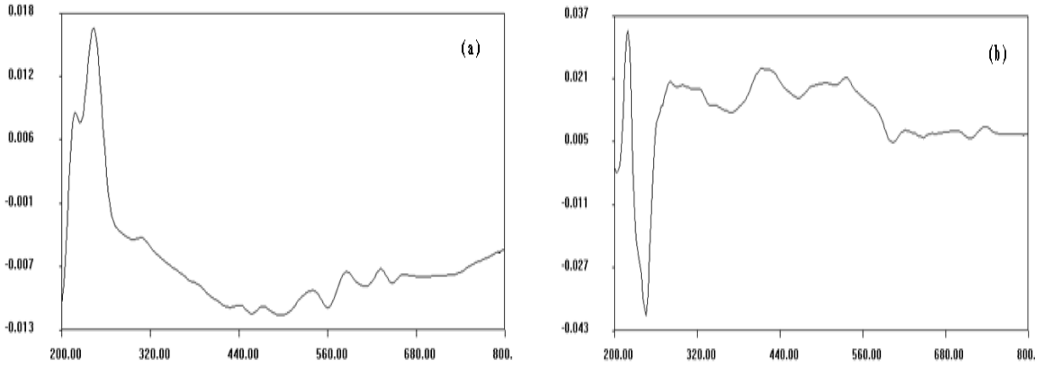

Fig 2: UV-Vis absorption spectrum of a) PPAP (b) PPAP/SDS

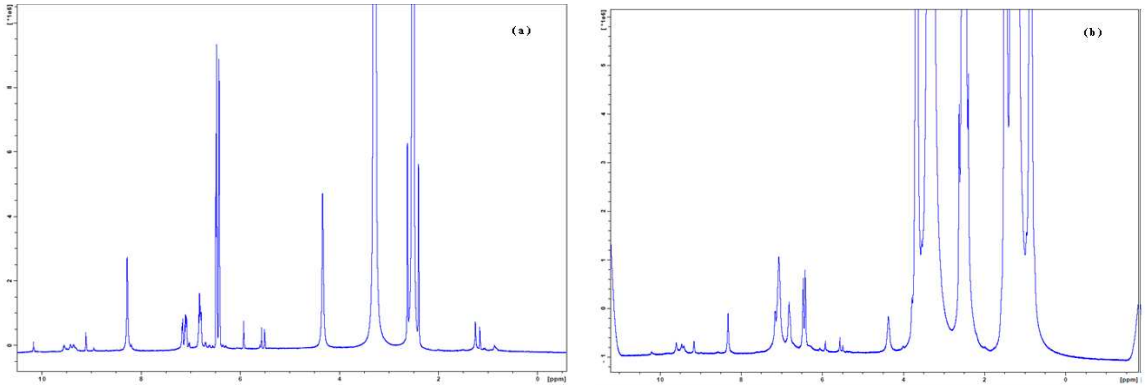

Fig 3: ^{1}H-NMR Spectra of a) PPAP (b) PPAP/SDS

^{1}H-NMR Spectral Analysis

The ^{1}H-NMR Spectra of the synthesized polymer and its nano compound taken at 25^0C using D^6-DMSO as solvent are given in Fig 3. In the ^{1}H-NMR Spectra of PPAP and its nano compound, the chemical shift is observed for three aromatic hydrogen atoms in the regions of 6-8δ. In PPAP, three positions of the benzene rings are engaged due to substitution and the other three positions are free [26]. A weak chemical shift appears at 5.53 δ due to the terminal $–NH_2$

group [26] and around 9.0 δ the chemical shifts appear for OH (hydrogen bonded and > NH (within the chain) in the ^{1}H-NMR spectrum of PPAP polymer and its nano compound. The aliphatic region is very similar for all SDS dopant polymers and shows signals around 0 - 4 δ for CH_2 protons. The protons present in -CH_3 group of DMSO appears at 2.5 δ and a broad peak appears at 3.7 δ due to the protons present in the water molecule, which is present in the sample as well as in the solvent [19].

Thermo Gravimetric Analysis

The Thermo gravimetric analysis of polymer and its nano compound are shown in Fig 4. The thermal stabilities of polymer are inevitably lower than the polymer nano compound. It is generally known that three weight-loss steps are observed in the TGA measurements for Poly aniline and their derivatives [27]. Thus, the first weight-loss observed up to 110°C should be due to loss of residual water molecules/moisture present from the polymer matrix [27, 28]. The second stage observed within the temperature range of 110-250°C, should be related to removal of dopant molecules from the polymer structure [27, 29]. The weight-loss observed after the removal of the dopant molecules should correspond to the complete degradation and decomposition of the polymeric main chain [27, 30]. From the TGA analysis (fig 4) it may be said that the polymer are thermally stable up to 270°C. But when SDS is added with polymer, there is no complete degradation up to 350°C. From this result it was clear that the PPAP is less thermally stable than PPAP/SDS.

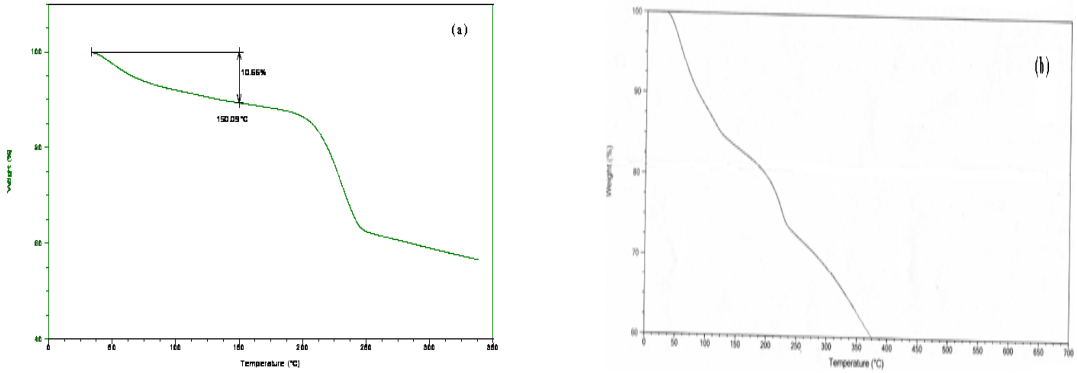

Fig 4: TGA of a) PPAP (b) PPAP/SDS

Electrical Conductance

The synthesized Polymer and its nano compound showed the conductance values 1.69 x10^{-6} and 1.72 x10^{-6} respectively. From the values it is evident that the synthesized polymer and its nano compound are of semi conducting nature.

Scanning Electron Microscopy and Transmission Electron Microscopy

The morphology of the synthesized poly (*P* - aminophenol) nano compound was measured by SEM and is shown in Fig 5. From the figure it was evident that the morphology of the resultant nano compound is flakes in shape. The size of the synthesized poly PAP nano compound measured by transition electron microscopy is given in fig 6. The result clearly indicates that the

size of the nano compound is found to be 25-42nm at 12K with the magnification of 20,000x. This confirms that the synthesized PPAP/SDS falls under the category of nano compound.

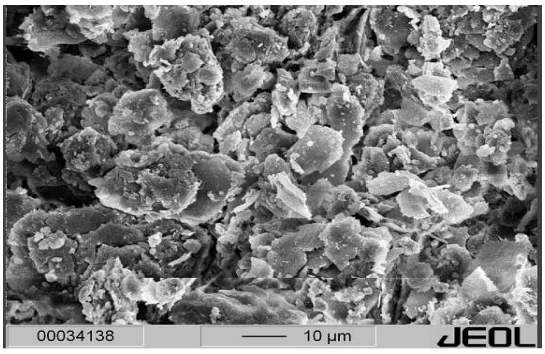

Fig 5: SEM image PPAP/SDS

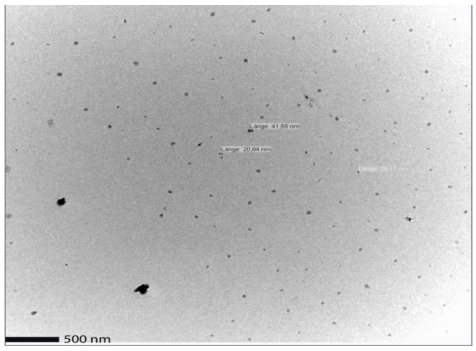

Fig 6: TEM Image of PPAP/SDS

Antioxidant Activity

The antioxidant activities of polymer and its nano compound were carried out by DPPH assay and their values are given in table 2.

From the value it is evident that the antioxidant activity increases with increase in time and concentration for the polymer and for its nano compound. The antioxidant activities of PPAP at zero and 80 minutes with the maximum concentration of 100µg/mL are 27.03±0.25 and 50.70±0.36 where as for PPAP/SDS it was 43.70±0.36% and 68.53±0.25%. Antioxidant activities of poly nano compound were slightly higher than the corresponding polymer. The regression analysis value is ≈ 0.977 for polymer and its nano compound and this shows that there was a good linearity between the concentration and the absorption of the polymer and its nano compound. The antioxidant activities were compared with standard L - ascorbic acid. The antioxidant activities of the polymer and its nano compound have significant implication for their inclusion as biomaterials in biological media. This property may be particularly beneficial in tissues suffering from oxidative stress, where the ability to lower excessive levels of reactive radical species is desirable. The study clearly indicates that the antioxidant activity of nano compound increases as the surface area increases. So it can be believed that poly nano compound with high surface area have stronger ability to scavenge free radicals than that of the polymer.

Antibacterial Activity

The antibacterial activities of PPAP and PPAP/SDS were investigated against *Staphylococcus aureus* and *Escherichia coli* which were gram positive and gram negative bacteria and their zone of inhibition are given in table 3 at the concentration of 50, 75 and 100 µg/ mL.

Table 2: Antioxidant Activities of Poly P - amino phenol and its nano compound

S.No	Conc (µg/mL)	Time (mins)	Antioxidant *(%)*	
			PPAP	PPAP/SDS
1	50	0	19.97±0.15	24.73±0.21
	60		21.53±0.25	28.70±0.36
	70		22.77±0.25	33.93±0.25
	80		24.00±0.30	36.07±0.31
	90		25.97±0.25	39.70±0.36
	100		27.03±0.25	43.70±0.36
2	50	10	24.13±0.15	28.70±0.30
	60		27.43±0.32	33.70±0.30
	70		28.53±0.25	36.47±0.35
	80		29.47±0.25	40.47±0.35
	90		31.04±0.27	42.93±0.31
	100		32.87±0.45	47.50±0.30
3	50	20	25.66±0.41	32.55±0.25
	60		31.74±0.07	35.60±0.36
	70		32.83±0.21	38.73±0.25
	80		33.43±0.49	43.80±0.26
	90		34.97±0.42	46.57±0.31
	100		36.03±0.25	51.00±0.20
4	50	30	27.54±0.39	34.35±0.33
	60		35.02±0.23	37.40±0.40
	70		35.78±0.26	42.00±0.30
	80		36.89±0.36	46.50±0.20
	90		38.00±0.44	49.93±0.21
	100		39.17±0.50	54.88±0.11
5	50	40	30.02±0.36	36.93±0.45
	60		37.27±0.25	38.66±0.31
	70		39.00±0.20	45.03±0.25
	80		39.57±0.40	48.65±0.33
	90		40.64±0.41	53.43±0.38
	100		42.27±0.21	57.72±0.28
6	50	50	31.93±0.31	38.65±0.31
	60		38.38±0.28	40.73±0.31
	70		40.67±0.35	47.52±0.38
	80		42.00±0.20	52.00±0.30
	90		43.20±0.30	56.91±0.10
	100		44.00±0.20	61.60±0.26
7	50	60	34.23±0.25	40.53±0.31
	60		40.55±0.25	43.03±0.15
	70		42.55±0.33	49.66±0.35
	80		43.67±0.30	54.60±0.40
	90		45.00±0.20	60.43±0.35
	100		45.93±0.25	63.37±0.47

8	50	70	35.76±0.24	41.75±0.22
	60		41.86±0.15	45.57±0.35
	70		44.63±0.21	53.60±0.40
	80		45.54±0.31	57.47±0.29
	90		46.61±0.27	63.50±0.36
	100		48.41±0.27	66.10±0.36
9	50	80	36.97±0.25	42.60±0.46
	60		42.97±0.25	47.43±0.40
	70		46.27±0.25	55.80±0.20
	80		47.86±0.12	60.97±0.96
	90		48.87±0.32	67.03±0.15
	100		50.70±0.36	68.53±0.25

Table 3: Antibacterial activities of Poly P-amino phenol and its nano compound at 24 hrs

Staphylococcus aureus (mm)			*Escherichia coli* (mm)	
Conc (µg / mL)	PPAP	PPAP/SDS	PPAP	PPAP/SDS
50	6	7	6	7
75	8	10	7	11
100	9	11	8	13

The polymer and its nano compound inhibited the bacterial stains at different levels. The zone of inhibition increased as the concentration of the polymer and its nano compound increased. Depending on the measured values with the zone of inhibition including the well in millimeter, the antibacterial activity can be classified into the following types: > 12mm zone of inhibition- high sensitive, 9-12mm zone of inhibition – moderate sensitive, 6-9mm zone of inhibition - less sensitive and < 6mm zone of inhibition – bacterial resistant [31]. From the table value it was evident that polymer and its nano compounds are moderately sensitive towards *Staphylococcus aureus* and *Escherichia coli* and the sensitivity increased as the concentration increased. The zone of inhibition for poly Para amino phenol against *Escherichia coli* was 8 mm but for its nano compounds the inhibition zone increased to 13 mm and this shows that PPAP/SDS is highly sensitive towards *Escherichia coli* than PPAP. The zone of inhibition was compared with the positive control (Gentamycin) whose inhibition zone was 29mm. The antibacterial activity is in accordance with the literature value which shows that the polymer containing phenol derivatives with one, two, or three hydroxyl groups exhibited good antibacterial activities [32].

CONCLUSION

In this work, we have synthesized conducting polymer, poly para amino phenol and its nano compound by chemical oxidative polymerization method and they were characterized using different spectroscopic techniques. The antioxidant and antibacterial capacity of the conducting polymer and its nano compound were investigated and compared with the standard. The activities increased as the time and the concentration increased. The high antioxidant and antibacterial activities of the conducting polymer and its nano compound could be considered to

be included as biomaterials in biological media. Further research could pay way for the development of novel drugs to control diseases and infections.

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