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## Synthesis, characterization and biological applications of poly meta amino phenol and its nano compound

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### ABSTRACT

The polymer and the nano compound of meta aminophenol was prepared by oxidative chemical polymerization in acidic medium using potassium dichromate as an oxidant at 0°C and they were characterized by FT-IR, UV-VIS, SEM, TEM, TGA and DSC. The conductance was measured and found to be semiconducting in nature. From the thermal analysis it is evident that the poly nano compound is thermally more stable than the corresponding polymer. The resulting polymer and its nano compound were analyzed for its antioxidant activities using DPPH assay and the antibacterial activities were measured by agar well cut diffusion method against two bacterial stains *Staphylococcus aureus* (gram +ve) and *Escherichia coli* (gram -ve). From the result it is evident that the antioxidant and antibacterial activities of poly meta aminophenol nano compound were greater than the corresponding polymer and they were concentration and the time dependant. The increased activities of poly nano compound may be due to its smaller size which increases the surface area and these properties can be considered in the field of biomaterials in biomedical areas.

**Keywords:** Aminophenol, DPPH assay, Antibacterial, Surfactant, Polymerization.

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### INTRODUCTION

Conducting polymers have been widely applied due to its high conductivity, excellent electrochromic property, electrochemical reversibility and stability in aqueous solutions. The investigations on the synthesis and application of conductive polymers have become one of the most active research areas. Amongst the investigated polymers, Polyaniline (PAN), Polypyrrole (PPY), Poly O-Phenylenediamine (POPD), Poly (aminophenol) (PAP) have recently been paid a lot of attention for its application in biochemistry, biosensor and the immobilization of protein and enzyme [1]. Aminophenols are interesting electrochemical materials since, unlike aniline [2]

and other substituted anilines [3], they have two groups ( $-\text{NH}_2$  and  $-\text{OH}$ ) which can be oxidized. Therefore, they can show electrochemical behavior resembling anilines [2-4] and phenols [5, 6]. 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 [7].

The monomer m-aminophenol [8-10] had been used very little and due to many controversies on polymerization mechanism and properties of the final polymer product, it was reported that poly (m-aminophenol) [8, 10, 11] synthesized from acidic medium is insoluble in organic solvents even after dedoping. Based on spectral evidence [8], ladder type structure is the more acceptable one. There is almost no report in the literature on chemical polymerization of aniline derivatives in basic medium. Electro polymerized 2-aminophenol [12, 13] in alkaline hydro alcoholic medium and they got polyether having  $-\text{NH}_2$  group intact. In another study, meta-aminophenol was electro polymerized in both acidic and basic medium [14].

The ability of conducting polymers to act as reducing agents and scavenge free radicals, and in this sense to act as antioxidants, is considered. Phenolic antioxidants in the diet are thought to offer protection against cardiovascular diseases and cancers where the onset of the disease involves oxidative damage caused by excessive levels of free radicals [15]. Poly aniline and substituted poly anilines have already been examined for their use as antioxidants in rubber materials [16]. However, their antioxidant ability in biological media needs to be examined to assess their likely activity in biomedical applications [17]. 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 [18]. 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 [19].

The extensive literature survey shows that lots of work has been carried out in conducting polymers especially their applications in the fields of electrochemical sensors, solar cells, electrochemical devices, coating in corrosion control, applications in rechargeable batteries, electro catalysis, super capacitors, bio medical application etc. No attempt was made to study the antioxidant and antibacterial activities of conducting polymers especially in meta amino phenol. Hence an attempt was made to synthesis, characterize the poly meta amino phenol and its nano compound and to study their biological applications prepared by chemical oxidative method. The resulting conducting polymer and its nano compound were subjected to antioxidant and antibacterial studies.

## MATERIALS AND METHODS

All chemicals used in the present investigation are of Analytical Reagent (AR) grade and used as received.

**Preparation of poly Meta amino phenol**

The poly Meta aminophenol was synthesized in acidic medium using standard procedure [20]. Monomer (m-aminophenol) was initiated by the drop wise addition of the oxidizing agent (potassium dichromate) and Conc. HCl as a dopant under constant stirring at 0-3<sup>0</sup>C. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for 5hrs, after that the reaction vessel was placed in the refrigerator for overnight. The product was filtered and washed with distilled water until the filtrate was colourless. Finally the polymer was dried and powdered.

**Preparation of poly Meta aminophenol nanocompound**

The poly meta aminophenol nano compound 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 [21]. 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 [22].

**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<sup>7</sup>-10<sup>8</sup> cells/mL after the incubation period they were used as an inoculum. An about 0.1ml of suspension containing 10<sup>8</sup> Colony Forming Unit (CFU / mL) of bacterial strains was used to study by Agar well cut diffusion method [23]. 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 inhibition zone was compared with the standard Gentamycin.

**Characterization**

FT-IR spectra were recorded in the mid IR region between 4000cm<sup>-1</sup> to 400cm<sup>-1</sup> using Thermo Nicolet Model 6700. UV-Vis spectra were recorded from 200-800nm using systronics double beam UV-Visible spectrophotometer 2201. 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<sup>-1</sup> under nitrogen atmosphere with gas flow rate of 90 ml min<sup>-1</sup>. Differential Scanning Calorimeter (DSC) analysis were carried out in a waters Q2000 V24.4 built 116 thermal analyzer between 10°C to 400°C at a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere with gas flow rate of 90ml min<sup>-1</sup>. 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

### FT-IR analysis

The FT-IR spectrums of the synthesized polymer m-aminophenol (PMAP) and its nano compound prepared in the presence of SDS are shown from Fig 1. Both for polymer and its nano compound, the pattern of the curve is almost the same. A broad band appear in the region  $3690\text{--}1833\text{cm}^{-1}$  is due to the stretching of aromatic C–H, hydrogen bonded –OH, and –NH– groups. The –OH group is hydrogen bonded with nearest nitrogen of –NH group present in the polymer chain through the  $\text{H}_2\text{O}$  molecule present in the sample. So -OH absorption band appears at about  $3425\text{cm}^{-1}$  as a broad peak. There is a band at  $1050\text{cm}^{-1}$  due to bending vibration of aromatic C–O–H group present in the polymer. The stretching peaks of –NH and –C=N groups appear at around  $1620\text{--}1625\text{cm}^{-1}$  for both MAP and MAP/SDS. In the case of MAP/SDS, the presence of  $\text{SO}_3^-$  group is confirmed by appearance of a band around  $576\text{cm}^{-1}$  is attributed to degenerate bending mode of the  $\text{SO}_3^-$  group [24] and the peak around  $2800\text{--}3000\text{cm}^{-1}$  are due to the – $\text{CH}_2$  stretching of the SDS.

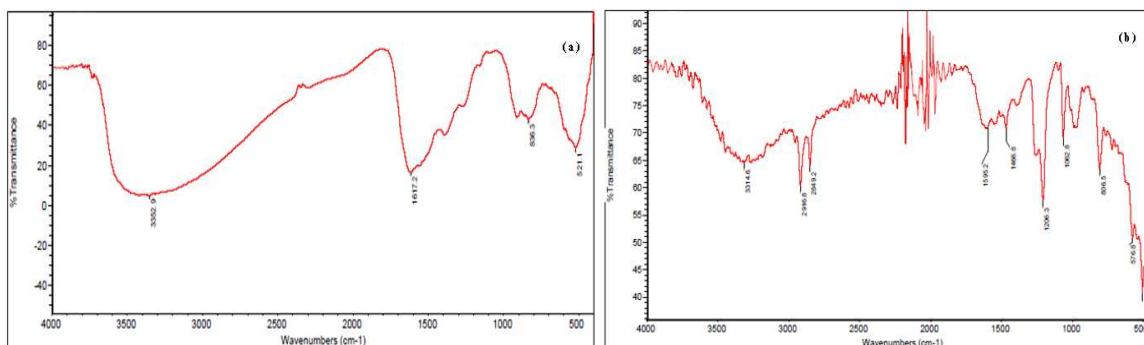
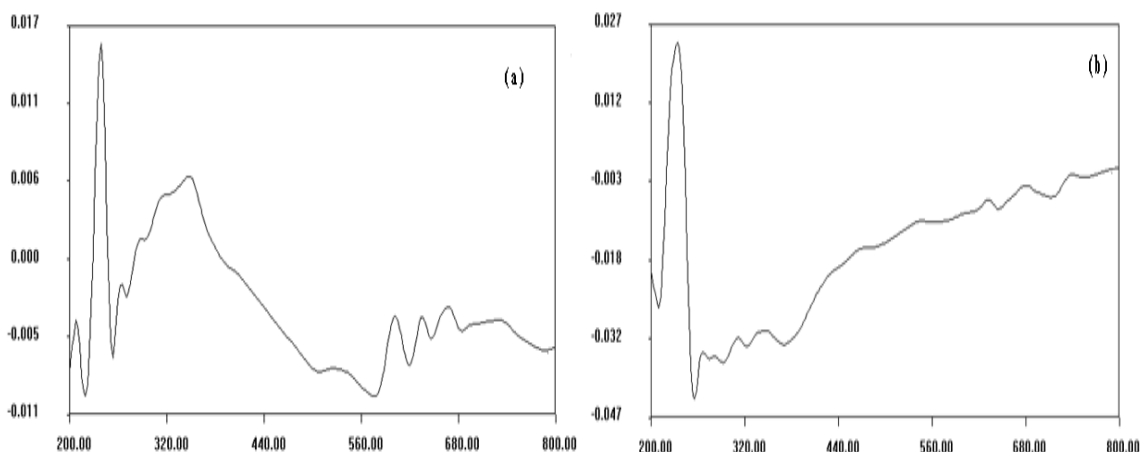


Fig 1: FT-IR spectrum of (a) PMAP (b) PMAP/SDS

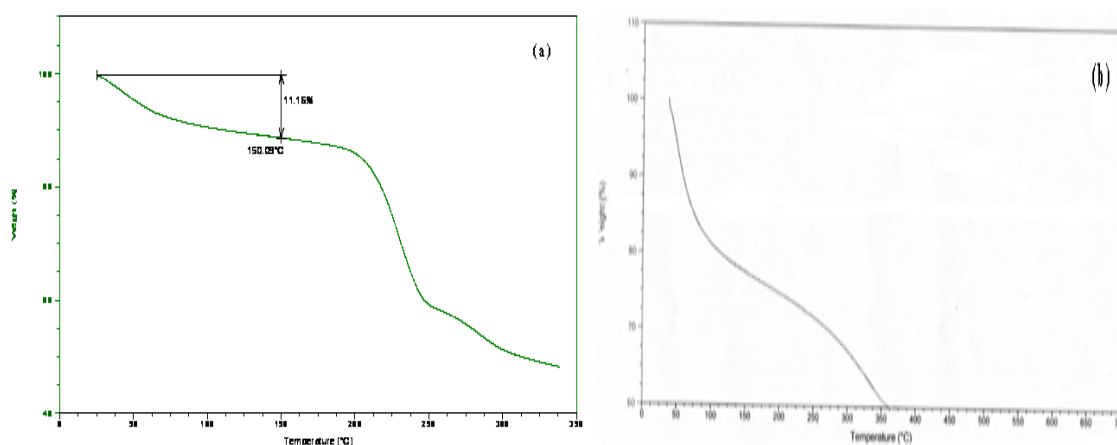
### UV-Vis spectral analysis

The UV-Vis spectra of PMAP and PMAP/SDS were recorded in DMSO is shown in Fig 2. In the synthesized polymer and its nano compound, the first absorption band appears in the region of  $238\text{--}389\text{nm}$  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  $632\text{nm}$  was believed to be  $n - \pi^*$  transition, which is correspond to non-bonding lone pair electron transitions of hetero atoms like nitrogen and oxygen respectively. PMAP/SDS additionally has other two peaks around  $468$  and  $740\text{nm}$  are assigned to the polaron transitions. From the UV-Vis spectral characterization, it is clear that some polarons are obtained in the  $\pi$ -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 (a) PMAP (b) PMAP/SDS**

### Thermo Gravimetric Analysis

The Thermo gravimetric analysis of polymer and its nano compound are shown in Fig 3. The thermal stabilities of polymer are inevitably lower than that of polymer nano compound. It is generally known that three weight-loss steps are observed in the TGA measurements for Poly aniline and their derivatives [26]. 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 [26, 27]. The second stage observed within the temperature range of 110-250°C, should be related to removal of dopant molecules from the polymer structure [26, 28]. The weight-loss observed after the removal of the dopant molecules should correspond to the complete degradation and decomposition of the polymeric main chain [26, 29]. From the TGA analysis (fig 3) 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 PMAP is less thermally stable than PMAP/SDS.

**Fig 3: TGA of (a) PMAP (b) PMAP/SDS**

### Differential Scanning Calorimetry

The thermal transition of PMAP was measured with differential scanning calorimetry and compared with that of PMAP/SDS, and the results are shown in fig 4. The glass transition temperature ( $T_g$ ) of PMAP was found to be 235.19°C. In PMAP and PMAP/SDS, the two

endothermic peaks around 62°C and 112°C are due to the expulsion of free and bonded water and dopants from the polymeric matrix. The melting transition temperature of the polymer MAP was observed in the temperature range 247.06°C. PMAP/SDS is unable to melt below 350°C and this clearly indicates that the nano compound is thermally more stable than the corresponding polymers, which are also substantiated by TGA analysis.

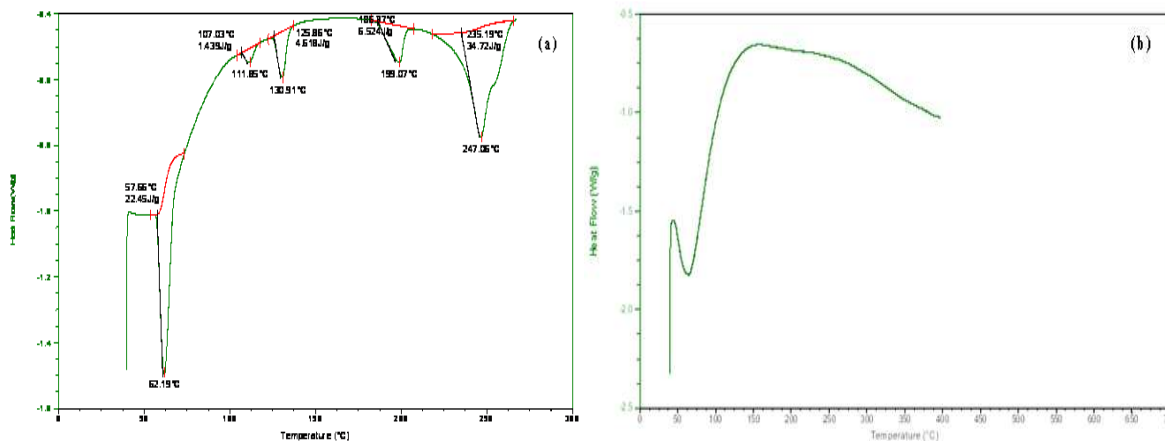


Fig 4: DSC of (a) PMAP (b) PMAP/SDS

### Scanning Electron Microscopy and Transmission Electron Microscopy

The morphology of the synthesized poly Meta 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 MAP nano compound which was 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 35-50nm at 12K with the magnification of 20,000x. This confirms that the synthesized PMAP/SDS falls under the category of nano compounds.

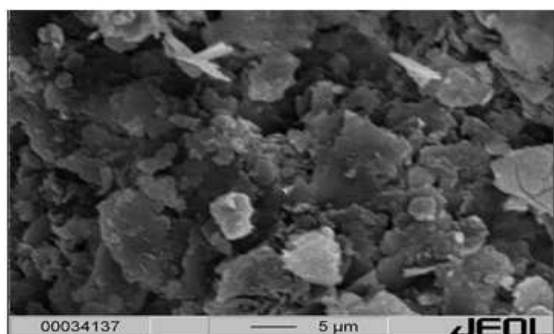


Fig 5: SEM image PMAP/SDS

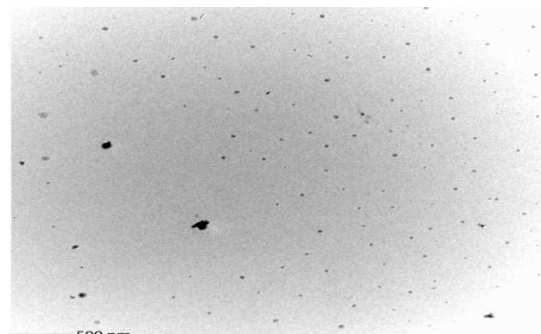
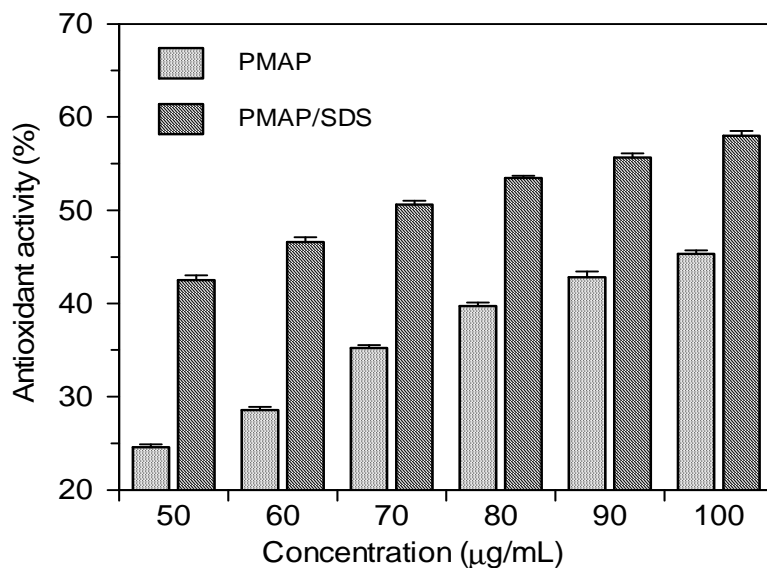


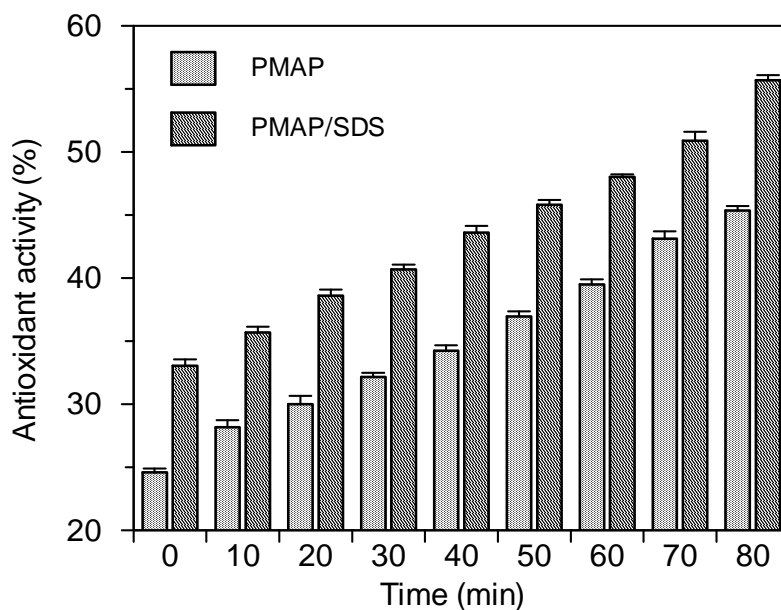
Fig 6: TEM Image of PMAP/SDS

### Electrical conductance

The synthesized PMAP and PMAP/SDS showed the conductance values  $1.68 \times 10^{-6}$  and  $1.70 \times 10^{-6}$  respectively. From the values it is evident that the synthesized polymer and its nano compound are of semi conducting nature.



**Fig 7: Antioxidant activities of PMAP and PMAP/SDS with different Concentration**



**Fig 8: Antioxidant activities of PMAP and PMAP/SDS with different time intervals**

**Antioxidant Activity**

The antioxidant activities of polymer and its nano compound were carried out by DPPH method. The antioxidant activity increases with increase in time and concentration for the polymer and for its nano compound were shown in fig 7 and 8. The antioxidant activity of PMAP at zero and 80 minutes with the concentration of 100µg/mL was 24.57±0.32 and 45.33±0.35 where as for PMAP/SDS it was 33.03±0.51% and 55.67±0.42% .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 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 PMAP and PMAP/SDS were investigated against *Staphylococcus aureus* and *Escherichia coli* and their zone of inhibition are given in table 1 at the concentration of 50, 75, 100  $\mu\text{g}/\text{mL}$ . 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 [30]. From the table 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 meta amino phenol against *Escherichia coli* was 13mm but for its nano compounds the inhibition zone increased to 17 mm for its nano compounds and this shows that PMAP/SDS is highly sensitive towards *Escherichia coli*. 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 which shows that the polymer containing phenol derivatives with one, two, or three hydroxyl groups exhibited good antibacterial activities [31].

**Table 1: Antibacterial activities of Poly m-amino phenol and its nano compound at 24 hrs**

Conc ( $\mu\text{g}/\text{mL}$ )	<i>Staphylococcus aureus</i> (mm)		<i>Escherichia coli</i> (mm)	
	PMAP	PMAP/SDS	PMAP	PMAP/SDS
50	6	7	7	8
75	7	8	9	11
100	8	13	13	17

### CONCLUSION

In the present study, we have synthesized conducting polymer, poly meta amino phenol and its nano compound in the presence of a surfactant SDS 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 ascorbic acid and gentamycin. The reasonable 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 by increasing the antioxidant and antibacterial activities by novel techniques.



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