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Research Article

SYNTHESIS, CHARACTERIZATION AND ANTI-MICROBIAL STUDIES OF KEGGIN ANION DOPED BIO-POLYMERS

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ABSTRACT

Six Keggin $[XM_{12}O_{40}]^{n-}$ anions doped bio-polymers namely S1, S2, A1, A2, R1 & R2 (starch, agar-agar, moringa resin) is synthesized and characterized using various techniques like Scanning Electron Microscope (SEM) and FT-IR spectra, which shows the presence of prominent functional groups. The anti-microbial test with Gram positive and Gram negative (*Staphylococcus aureus & E-coli*) cell activity has been examined. The conductivity studies was also been studied.

INTRODUCTION

Polyacid is one of the most interesting areas in Inorganic chemistry, exhibiting at various promising properties and applications. Polyacids have a molecular weight as well as temperature response over doped polymer material (Y. Wang *et al.*, 2016). Polyacid (PA) is shown as an effective study in last decades of geometric and electronic structural property. Polyacid doped bio-polymers which have three major challengesin ions pairing, such as stability, selectivity and reactivity (Kazuyoshi Ogasawara *et al*., 2016; S.M. Lauinger *et al*., 2017). Polyacid based catalysis, shows their chemistry is stable, but also progress in the Polyacids. Polyacid (PA) is a sub-division of MO (metal oxide) with specific, unique physical and chemical properties, as well as prospective applications like structural materials, medicines, catalysts. In addition, Polyacids synthesis of salts likes, (a) Keggin anion; (b) Lindquist anion. Polyacid, Metal oxides, zeolites, clays are efficient material have been used as a solid acid catalyst (Eugenio Coronado *et al*., 1998; Sheldon R A *et al*., 1999). The conducting polymers enhance the performance for both host and guest of metal nanoparticle (Mitsutani A, *et al*., 2002). The recent progresses of molecular and doped polymers are emerging in areas such as surface, electronic, energy, environment, life science, etc. (R Gangopadhyay *et al*., 2000; W Yu-Fei Song *et al.,* 2012). 'Mn' ion has multiple levels and most effective properties like light reflective property, bond strength, symmetry and lattice relaxation (Gholamyan S *et al.,* 2017). Efficiency and selectivity in the states of the catalysts of transition metal which enhance extremely imperative for the new energy technology (Isabel C.M.S. Santos *et al.,* 2017).A composite of polyacid doped bio-polymers (Starch, agar-agar) showa new division of applications (Tao Wei *et al.,* 2017). Starch is the next abundant natural polymer after cellulose because of it chemical structure. The starch bio-polymer gives chemical and enzymatic modifications into novel functionalities. It is natural, biodegradable convert into sugar and organic acids. It has industrial chemical, thermoplastic, biofuels and food packaging applications (Jasim Ahmed *et al.,* 2016).

Polyacid doped bio-polymers givean important studies, suchas agar-agar (A1, A2), Starch (S1, S2), Moringa Resin (R1, R2). Therefore, it is found that the polyacid doped bio-polymers exhibit the high catalytic activity to a new properties and applications. Gram positive (*Staphylococcus aureus*) and Gram negative (*Escherichia coli*) test is also examined (C.Maria Magdalane *et al.,* 2016). Unconventional type of manganese based polyacid has been synthesized and its properties, structure, growth mechanism and optical are studied (Kaustav Bhattacharjee *et al.,* 2015). The polyacid doped conducting

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polymer composites has various applications such as energy conversation, energy storage, etc. (Sven Herrmann *et al.,* 2015). The polyacid reactivity with biomolecules was a promising factor due to the condition such as temperature, acidity and solvent. Therefore, modification of biomolecules in polymers (starch) gives a prominent and controlling mechanism of various activities (S Sadjadi *et al.,* 2017). However, the selectivity had insufficient materials, which is found to be a minor drawback for the PA. Interactions between Keggin structure polyacid and natural biomolecules have promising effective study.

The investigation of the present ideashows the synthesis of Polyacid and manganese containing polyacid doped bio-polymers were prepared and characterized. The SEM morphology may reveal formation of Polyacid and manganese containing polyacid doped bio-polymers. The most advantageous feature of Polyacid is the possibility of the stability and structural changes in atomic/molecular levels. Thus catalysts were obtained, structurally characterized by using Scanning Electron Microscope (SEM) and Fourier Transform Infrared spectroscopy (FT-IR). The anti-microbial test is performed to investigate the effect of polyacid doped bio-polymers. The impendence spectra for manganese containing polyacid doped bio-polymers conductivityhas also examined. Hereafter, Polyacid and Manganese containing polyacid are mentioned as a PA and Mn-PA respectively. In this paper, the synthesis and characterization of polyacid doped bio-polymers have been discussed. The Schematic presentation of PA and Mn-PA doped bio-polymers is given in the Fig.1.

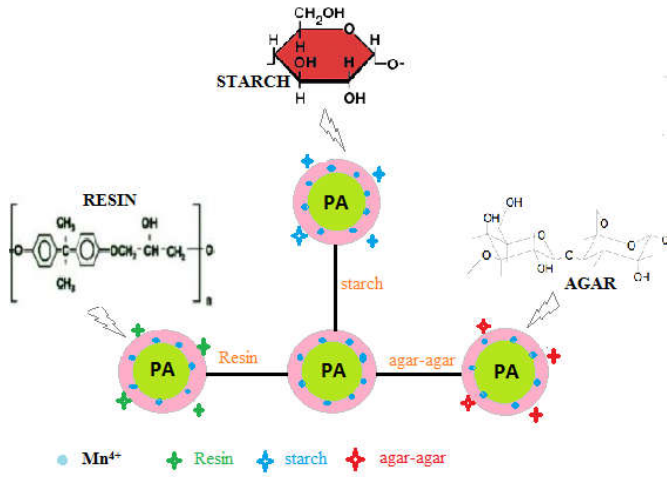

Figure 1 Schematic presentation of PA and Mn-PA doped bio-polymers.

MATERIALS AND METHODS

Materials

Ammonium molybdate, disodium hydrogen phosphate, Magnesium sulphate, $K_2S_2O_8$ are purchased from Merck.

Synthesis of PA doped bio-Polymer

2g of $(NH_4)_2MoO_4$ is dissolved in 15 ml of H_2O and 1g of Na_2HPO_4 is added to this solution with continuous stirring.In this hot solution, 1 ml of Conc. HNO_3 is added dropwise with constant stirring. To this contains, (J. Arichi *et al.,* 2010) 2g of starch (S2) solution is added continuously with stirring. The other two compounds were prepared using the solution of agar-agar (A2) and Moringa resin (R2) respectively, instead of starch (S2) solution. The formed PA doped bio-polymers is filtered and dried.

Synthesis of $PMo_{11}MnO_{40}$ doped bio-polymers

Mn-PA doped bio-polymers were prepared by adding $MnSO_4$ solution (1g, 10 ml) containing $K_2S_2O_8$ oxidant (0.5 g, 10 ml) by mixing the solution of ammonium molybdate (2g, 10 ml). To this acidified solution, 1g of Na_2HPO_4 is added with continuous stirring and heated. To the prepared Mn-PA ($PMo_{11}MnO_{40}$) solution, bio-polymers (S1, A1&R1) starch, agar-agar and Moringa resin are added with continuous stirring. The formed products are filtered and dried.

Characterization studies

FT-IR spectra were obtained SHIMAZDU usingKBr pellets. The morphology and size of PA and Mn-PA doped bio-polymers were scanned through scanning electron microscope (JOEL JSM 6390). XRD are obtained by SHIMAZDU 6000. Anti-microbial activities were also studied for polyacid doped bio-polymers.

RESULTS AND DISCUSSION

FT-IR

Fig.2a and 2b shows that FT-IR bands of PA and Mn-PA doped bio-polymers reveal the presence of PA and bio-polymers.

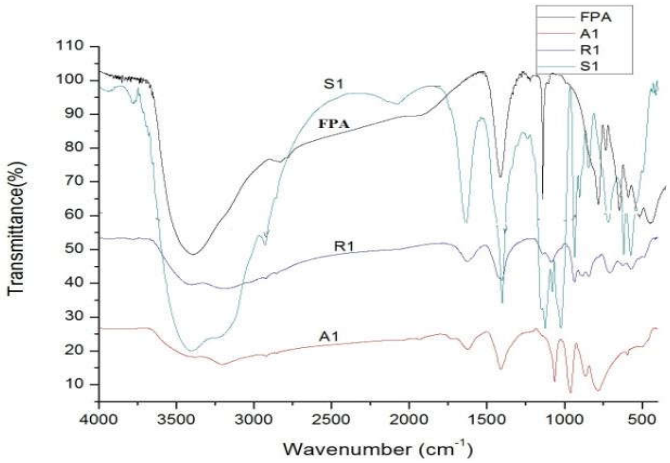

Figure 2 (a) IR spectrum of Mn-PA doped bio-polymers PA, A1, R1 and S1.

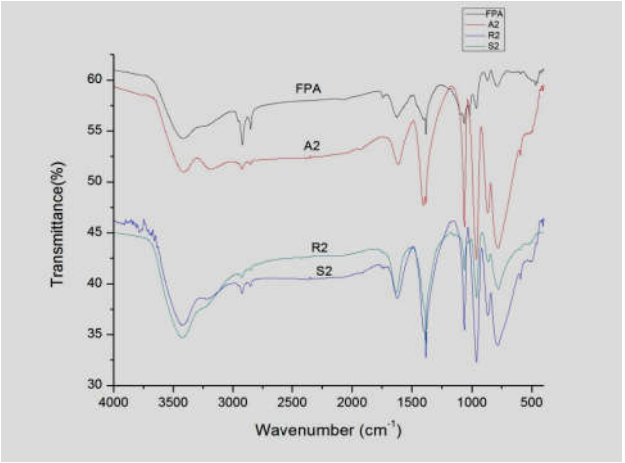

Figure 2 (b) IR spectrum of PA doped bio-polymers PA, A2, R2 and S2.

The IR spectral data are given in Table.1. Mn-PA doped bio-polymers (A1, R1 & S1) exhibit intensive three characteristic peaks, which are approximately at 960, 780 and 1061 cm^{-1} indicating a stretching vibration as assigned to Mo-O_t, Mo-O-M_O and P-O bonds (t, terminal; c, corner-sharing); these sharp peak splits indicates that the PA structure was maintained after immobilization.

Table 1 IR data for PA AND Mn-PA doped bio-polymers

PAPA doped bio-polymers		Mn-PA doped bio-polymers	Tentative assignment
1061	1061	1062	P-O
960	961	962	Mo-O_b
780	780	782	Mo-O-M_O
-	3413	3415	O-H

[a]In cm^{-1}, polymers like Starch (S), Agar-agar (A), Moringa resin (R), (b, terminal oxygen; c, bridging oxygen between corner-sharing) assignments based on Ref. 19.

The one at 962 cm^{-1} split into three spectral peaks which indicate the presence of Mn in the PA lattice (Mn-PA) as shown in (Fig. 2a). The one at 3413-3415 cm^{-1}peak in the IR spectra is assigned to O-H stretching as shown in (Fig. 2a and 2b). Fig.2b shows PA doped bio-polymers (A2, R2 & S2) in which peaks at 1062 cm^{-1} is stretching frequency P-O. Theone at 782 cm^{-1} is due to edge-bridge bonds Mo-O-M_O. The one at 962 cm^{-1} is the stretching of Mo-$O_t$bond. This vibrating peak revealed that the PA doped bio-polymers; structure is remaining intact after ion exchange between bio-polymers.

X-Ray Diffraction

Fig.3 show XRD patterns for the PA doped bio-polymersdisplay characteristic peaks as assigned to starch (S2) (2θ = 10°, 26°, 30°, 35.0° and 55.4°). For agar-agar (A2), one major peak is observed at 2θ = 20.59° (maximum intensity) which corresponds to the intermolecular interaction. Fig.3 shows XRD patterns for the PA doped bio-polymers display characteristic peaks as assigned to starch (S2) (2θ = 10°, 26°, 30°, 35.0° and 55.4°). For agar-agar (A2), one major peak is observed at 2θ = 20.59° (maximum intensity) which corresponds to the intermolecular interaction.

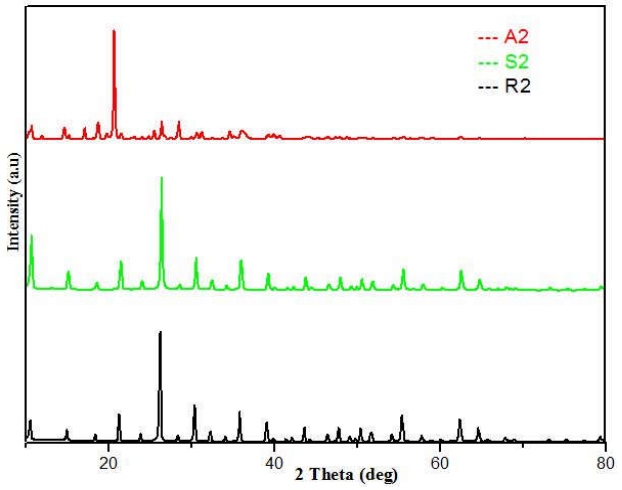

Figure 3 XRD patterns of PA doped bio-polymers (S2, R2 & A2).

The characteristicpeak also revealed that the PA structure is preserved after incorporation with bio-polymers. The results obtained in the XRD of PA doped bio-polymers show that powders made by wet-chemical exhibit the PA and bio-polymers characteristics with good crystal structure. There is no phase of the crystal structure is found.

Table 2 The Grain Size of Pa Doped Bio-Polymers

S. No	Samples	2θ Value	Grain size value(nm)
1	PA doped bio-polymers (S2)	10.62	2.8
		26.32	3.6
		35.94	3.7
2	PA doped bio-polymers (A2)	20.59	3.8
		26.30	3.4
		28.42	3.2
3	PA doped bio-polymers (R2)	26.15	3.7
		30.23	2.9
		35.10	3.3

Scanning Electron Microscope

Figure 4a and 4b showthat SEM morphologies of PA and Mn-PA doped bio-polymers (starch, Moringa resin and Agar-Agar) synthesized under the same conditions, respectively.S1 and S2 show that the spherical structureof the sample with the average diameterof 190, 175 ±10 nm.R1 and R2 show that uniform formation of granules is around 154, 99 ±10 nm. The bio-polymers (Agar-agar) form a Cluster of the stack showsthe structural change and the sizeof A1 and A2 around 98, 152 ±10 nm. Thus, the formed SEM morphology shows that thestructure of PA and Mn-PA in intact in doped bio-polymers.

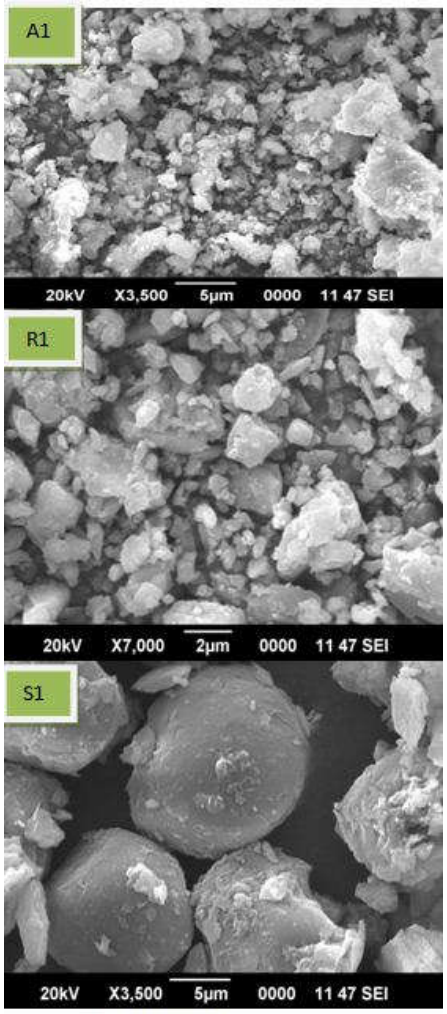

Figure 4 (a)

Figure 4 (a) SEM images of Mn-PA doped bio-polymers (A1, R1 & S1).

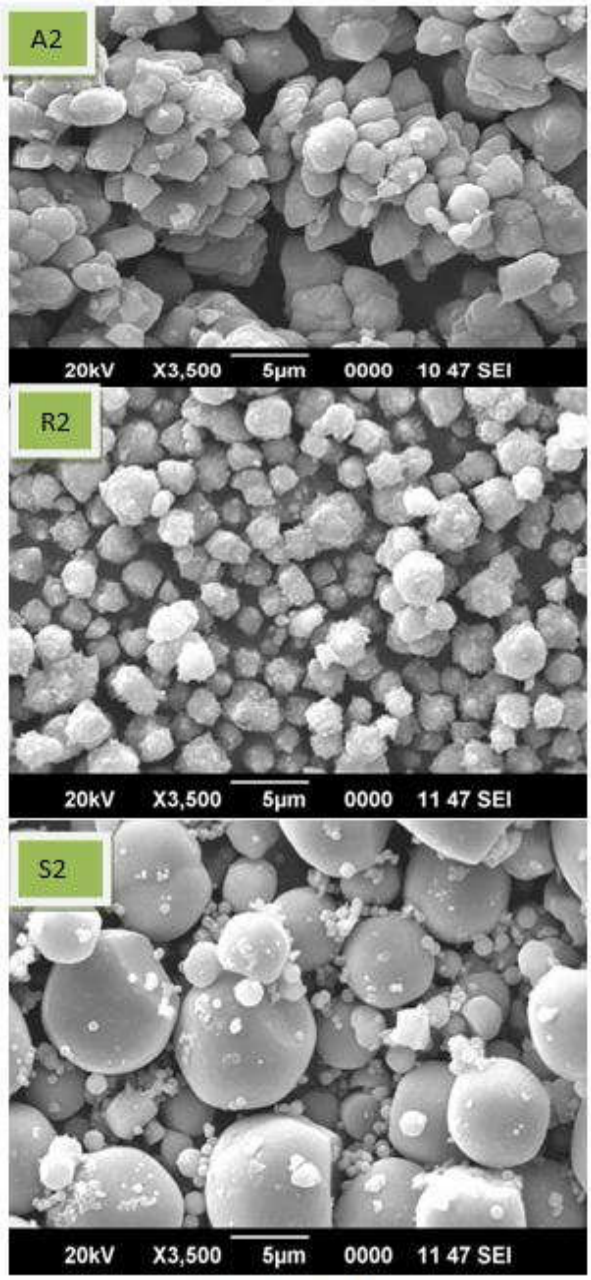

Figure 4 (b)

Figure 4 (b) SEM images of PA doped bio-polymers (A2, R2 & S2).

Anti-microbial Activity

Antimicrobial experiment of PA doped bio-polymers (starch, Agar-Agar and resin) effectively acts on Gram positive and Gram negative cell activity. PA and Mn-PA doped bio-polymers were brought into test against Gram positive (*Staphylococcus aureus I and II*) and Gram negative (*Escherichia coli I and II*) as shown in Table.3 and 4. Thus, the listed of Gram positive and Gram negative activity of PA andMn-PA doped bio-polymers, as shown in Fig.5a, 5b with bar chart. In this experiment, the results haveconfirmed that the anti-microbial activity of three types of bio-polymers. The PA doped (starch) bio-polymer shows high Gram negative (*Escherichia coli I and II*) ±18 mm and±13;±12 mm (*Staphylococcus aureus I and II*) due to interaction of bio-polymer over PA which corresponds to enzymatic modifications.

Table 3 Anti-microbial activity of PA doped bio-polymers [Starch (A2), Agar-agar (A2) and Moringa resin (R2)]

Bacteria	Zone of Inhibition (in dm)		
	POM-Moringa resin	POM-starch	POM-Agar agar
Staphylococcus Aureus – I (Gram Positive)	±16.5 mm	±13 mm	±21 mm
Escherichia Coli – I (Gram Negative, Water Pathogen)	±13 mm	±18 mm	±12.5 mm

Table 4 Anti-microbial activity of Mn-PA doped bio-polymers [Starch (S2), Agar-agar (A2), and Moringa resin (R2)]

Bacteria	Zone of Inhibition (in dm)		
	POM-Moringa resin	POM-starch	POM-Agar agar
Staphylococcus Aureus – II (Gram Positive)	±16 mm	±12 mm	±20 mm
Escherichia Coli – II (Gram Negative, Water Pathogen)	±14 mm	±18 mm	±12 mm

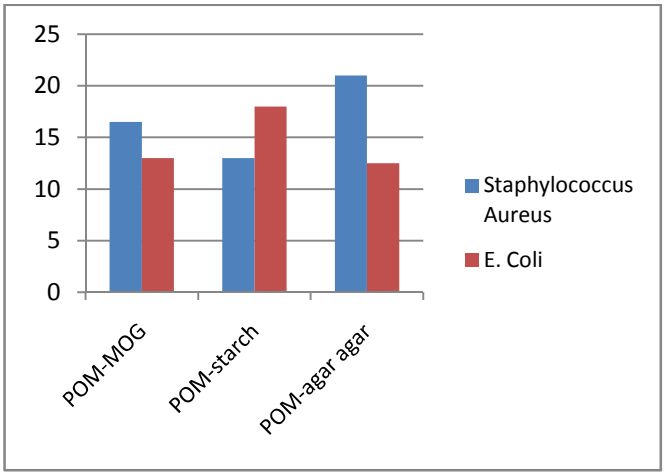

Figure.5a Bar chart of Anti-microbial activity of PA doped bio-polymers (S2, R2 & A2).

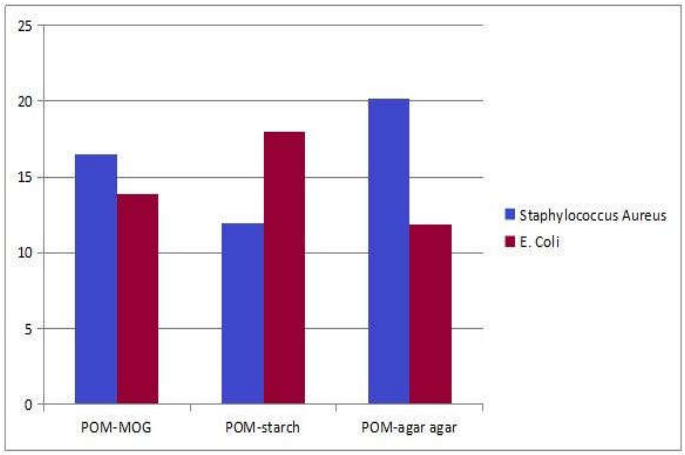

Figure.5b Bar chart of Anti-microbial activity of Mn-PA doped bio-polymers (S1, R1 & A1).

Interestingly, agar-agar, PA doped bio-polymer (*Staphylococcus aureus I and II*) shows an effective and promising result than the other two bio-polymers. The Gram positive (*Staphylococcus aureus I and II*) zone of inhibition of ±21 and ±20 mm and Gram negative (*Escherichia coli I and II)*±12.5 mm; ±12 mm isshown in Fig.5a and 5b. And also the anti-microbial activity of resin, PA doped bio-polymers (*Staphylococcus aureus I and II*) of ±16.5 mm; ±16 mm and (*Escherichia coli I and II*)±13 mm; ±14 mm shows the normal effect on the zone of inhibition. The Gram-negative bacteria possess an outer layer with pores and which is not found in Gram-positive causes PA and Mn-PA doped bio-polymers exhibit a better bactericidal effect on the Gram-negative. The anti-microbial tests revealed that our compounds are interacting differently with the microbial targets, due to the differences in the microbial wall structures.

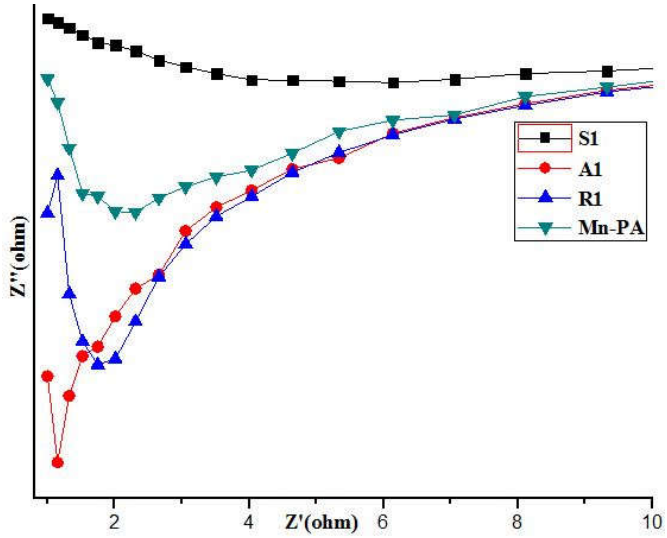

Figure 6 Impendence spectra of Mn-PA doped bio-polymers (S1, A1, R1 and PA) for conductivity.

Impendence Spectra

The impendence spectra of Mn-PA doped bio-polymers are S1, A1 & R1 (starch, agar-agar, and Moringa resin), whereas Mn-PA spectrum as ascendancy shown in Fig.6. The impendence spectra have high efficiencyin the higher frequency region due to the(+) and (–)ion exchange between Mn-PA and bio-polymers with the high presence of Mn^{+}. In lower frequency region, which shows decreases and increases of conductivity because of lack of sharing (+) and (–) ion charges. Conducting polymers give an impendence range as similar as magnitude which can be explained by the increased interfacial area and neural activity (Xinyan Cui *et al.,* 2001).

CONCLUSION

In summary, PA and Mn-PA doped bio-polymers are synthesized and characterized by using Scanning Electron Microscope and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. SEM image showsthat morphological structure on the PA and Mn-PA doped bio-polymers (Agar-Agar, Moringa resin and Starch) which are around ~190 nm. FT-IR shows thepresence of prominent peaks of functional groups, which is indicated in all samples. The anti-microbial activities of all synthesized samples were evaluated and they show comparable activity against Gram positive (*Staphylococcus aureus*) and Gram negative *(Escherichia coli*) in the zone of inhibition. The anti-microbial test of the PA and Mn-PA doped bio-polymer was assessed. The result in this study shows an effective alternative to antibiotic treatments.

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