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Characteristics of Polyaniline synthesized in green medium Averrhoa bilimbi fruit extract

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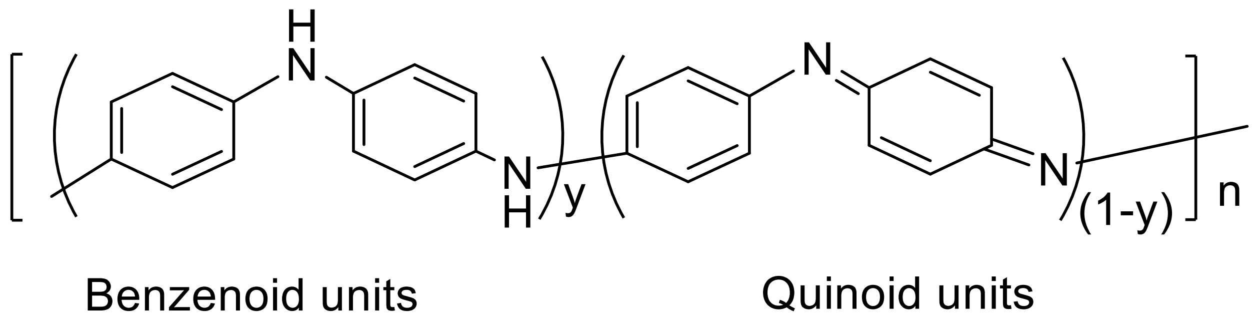
Abstract

Organic semiconductors are one of the active research fields in chemistry having promising applications in science and technology. These are used extensively in nano electronic circuits. In recent years, centre of attraction of researchers is the development of proficient green chemistry methods for the synthesis of nano particles. Green synthesis focuses on minimizing hazardous chemicals and maximizing the use of natural resources. In this work a green medium of Averrhoa bilimbi fruit extract was used for the synthesis of polyaniline (PANI). Properties of the prepared sample were analysed and were compared with the sample prepared in the mineral acid HCl.

INTRODUCTION

Polyaniline, one kind of conducting polymer has been playing a great role in the field of electronics. It captured the intense attention of the scientific community due to the discovery of its high electrical conductivity. Amongst the family of conducting polymers and organic semi-conductors, polyaniline has many attractive properties such as lightweight, conductivity, mechanical flexibility and low cost[1]. It has three distinct oxidation states with different colours and has an acid/base doping response. This latter property makes polyaniline an attractive for acid/base chemical vapour sensors, supercapacitors and biosensors. The different colours, charges and conformations of the multiple oxidation states also make the material promising for applications such as actuators, super capacitors and electro-chromic devices[2-4]. Polyaniline has been historically considered as a battery material but its intrinsic pseudo capacitive behaviour has shifted the energy storage potential to supercapacitor. An interesting feature of polyaniline, is the versatility in manufacturing electrical conducting yarns, antistatic coatings, electromagnetic shielding, and flexible electrodes[5].

General structural formula of PANI is represented in the Figure 1.



$$\mathbf{0 \geq y \leq 1}$$

Figure 1. General structure of PANI

The three stable and isolable oxidation states of polyaniline are Leuco-emeraldine (fully reduced), emeraldine (half oxidized) and pernigraniline (fully oxidized) where the value of y becomes 1, 0.5 and 0 respectively [6]. Emeraldine base is blue in colour, protonated salt is green, the pernigraniline base is violet, pernigraniline salt is blue and the leuco-emeraldine base is colourless. Conductivity of polyaniline is due to the protonation of imine N-atoms which results the formation of corresponding salts. Among the three forms, emeraldine salt is the conductive form of polyaniline[7]. The conductivity of these polymers can be varied by chemical manoeuvring of the polymer backbone, by the nature of the solvent, by the degree of doping and change in the pH of the solvent [8].

Averrhoa bilimbi (Irumban puli, Figure 2) is a local fruit in South India which has high oxalic acid content. This tree belongs to Oxalidaceae family. The bilimbi fruit is very juicy and extremely sour in taste. In this work PANI is synthesized in the green medium, bilimbi fruit extract and conventional solvent HCl. Properties of the samples compared to analyse the efficacy of the green medium.

Figure 2. Averrhoa bilimbi

EXPERIMENTAL MATERIALS AND METHODS

All the chemicals used for the synthesis of PANI such as aniline, HCl, acetone and ammonium peroxy disulphate (APS) were purchased from Merck chemical company and were of high purity. Aniline is used after double distillation.

Procedure

Polyaniline was prepared by oxidative polymerization of aniline using ammonium peroxy disulphate(APS) oxidant in HCl and in green medium bilimbi fruit extract.

Green method using Averrhoa bilimbi fruit extract as solvent

10-15 fresh fruits of unripe Averrhoa bilimbi were collected, washed with distilled water, wiped and cut into small pieces. These pieces were crushed in a mortar, squeezed to get the juice and filtered. Filtrate of bilimbi fruit extract was collected in a clean beaker. Dissolved 3.92g [0.4M] aniline in 100ml bilimbi fruit extract placed in an ice bath and stirred well, using a magnetic stirrer. Solution of 9.12 gm (0.4M) APS dissolved in 50ml bilimbi fruit extract was added slowly (dropwise) to the aniline solution with constant stirring. After the complete addition of the oxidant, stirring was continued for about two hours. Kept the solution overnight and filtered the green precipitate of polyaniline. It was washed with distilled water and then with acetone to remove unreacted aniline. Precipitate was heated at 50°C for two hours. Samples were prepared taking different ratios of aniline and APS as per the Table.1. The experiment was repeated and samples were synthesized using the solvent HCl also.

Table 1. Oxidant/ Aniline ratio

Aniline	**APS**	**Oxidant/Aniline ratio**
0.4M	0.4M	1
0.4M	0.6M	1.5
0.4M	0.8M	2

The samples prepared from the two media were characterized by FT-IR spectroscopy, Scanning Electron Microscopy, DC conductivity measurements and UV-Visible spectroscopy.

RESULTS AND DISCUSIONS

Table 2 represents the yield of PANI (g) formed in the two media. It shows that maximum amount of polyaniline is formed when aniline-oxidant ratio is 1:1.5. It also shows that the amount of polyaniline formed by green method is slightly less compared to the conventional method.

Table 2. Yield of PANI

Sl.No	**Oxidant/ Aniline ratio**	**HCl**(g)	**Bilimbi Juice**(g)
1	1:1	3.5883	3.0387
2	1:1.5	4.9856	4.1248
3	1:2	4.0572	3.6342

IR Studies

Figure 3 and 4 show IR spectra of representative samples (ratio 1:1.5)of PANI from HCl and bilimbi fruit extract respectively. Both the figures show all the characteristic absorption bands of polyaniline. Band at 1116 cm^{-1} is due to out of plane bending vibration of C-H bond of para substituted benzene ring which confirms the conjugated π system present in PANI. Band at 1295 cm^{-1} is due to C-N stretching. The bands at 1485 cm^{-1} and 1560cm^{-1} corresponding to C=C stretching vibrations of benzenoid and quinanoid C=N respectively. Presence of these bands confirms the formation of PANI in the conductive emeraldine form.The band observed at around is 3425 cm^{-1} is due to N-H stretching.

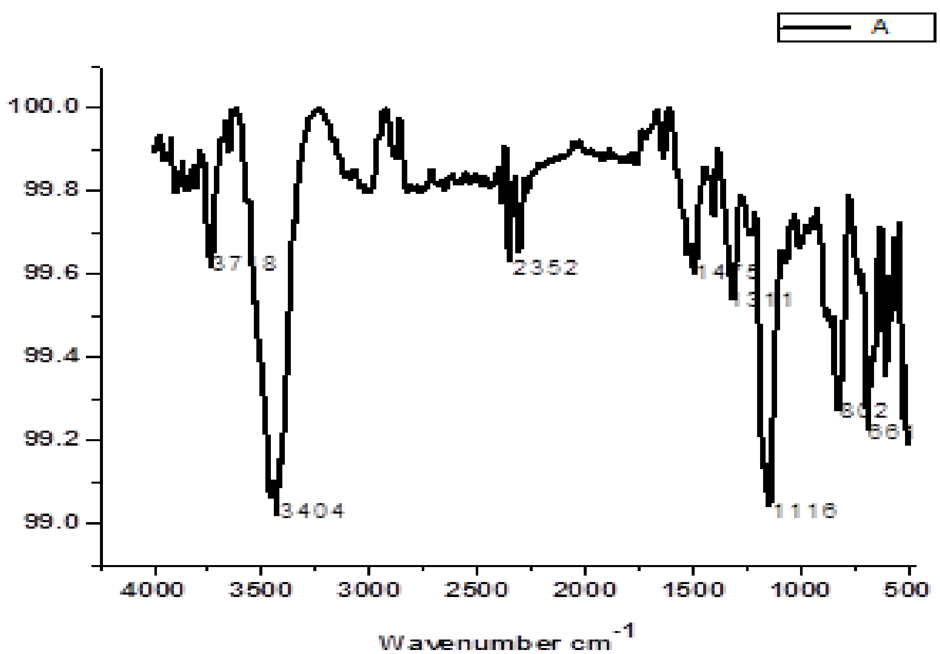


Figure 3. IR Spectra of PANI from HCl

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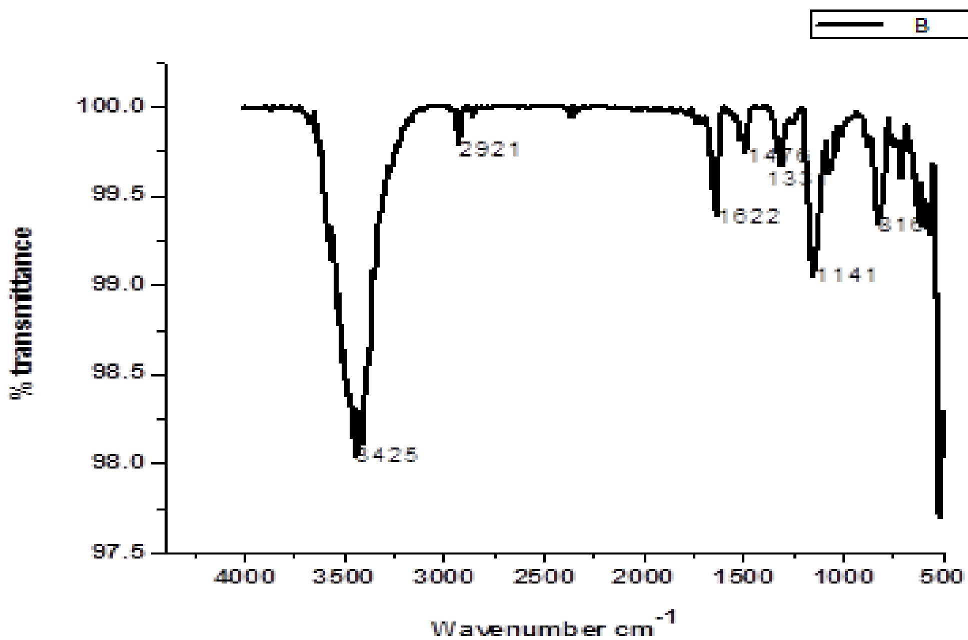
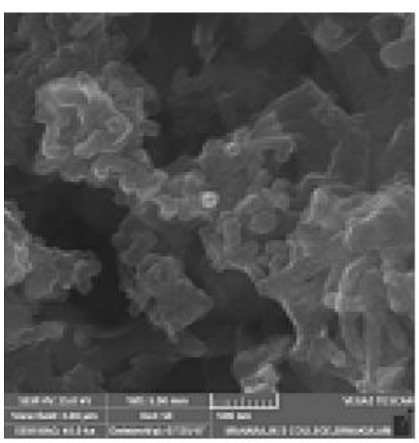


Figure 4. IR Spectra of PANI from bilimbi fruit extract

SEM Analysis

The SEM images of the samples are shown in Figure 5 and 6. It is clear from the SEM images that the sample prepared using bilimbi fruit extract exhibit well defined morphology and homogeneity (spherical particles) than that prepared in HCl. Thus it is clear that solvent affects the size and surface morphology of the sample and thereby properties of the sample.



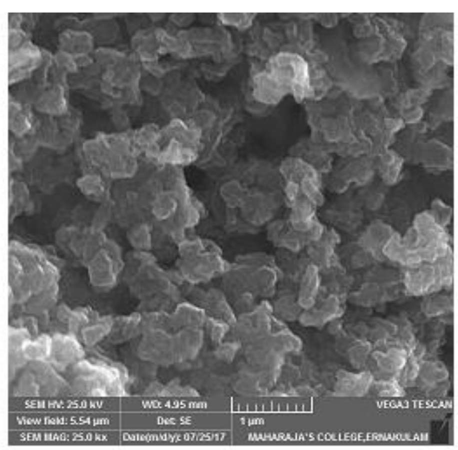


Figure 5 SEM micrograph of PANI from HCl

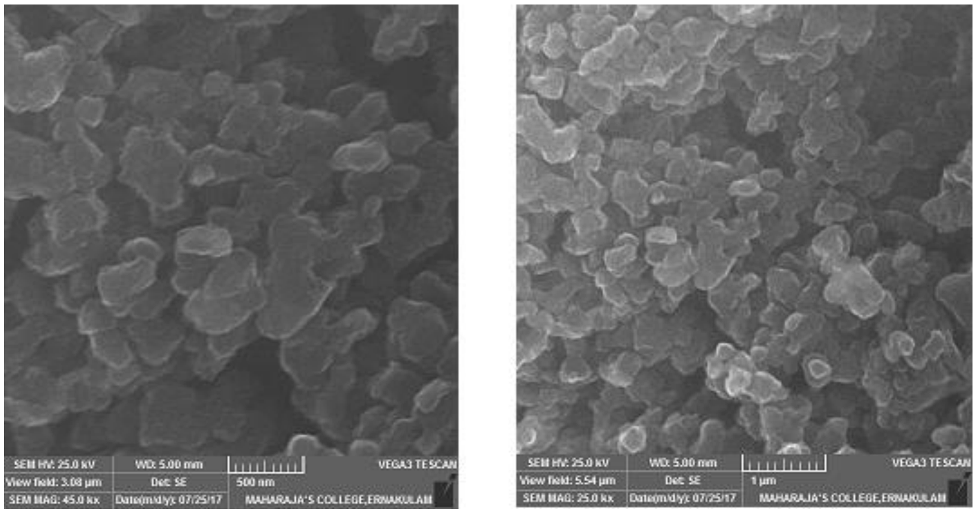


Figure 6. SEM micrograph of PANI from bilimbi fruit extract

DC conductivity analysis

DC conductivity values of the samples are depicted in the Table3. In all the three ratios better conductivity is observed for the samples in the green medium. This may due to increased conjugation of PANI which may arise from better conformation of homogeneous particles.

Table 3. DC conductivity

Sl.No	**Oxidant/ Aniline ratio**	**HCl S/cm**	**Bilimbi Juice S/cm**
1	1:1	6.1×10^{-4}	8.6×10^{-4}
2	1:1.5	1.87×10^{-3}	3.7×10^{-3}
3	1:2	4.59×10^{-3}	6.2×10^{-3}

UV Analysis

Figures 7 and 8 represent the UV- Visible spectra of different samples prepared by conventional method and green method respectively. All spectra show three absorption peaks (i)

340 nm π-π* transition of benzenoid structure of PANI, (ii) the peak at 440 nm corresponding to the polaron band to π* in the PANI chain (iii) at 700-900 nm π-polaron band. They exhibit similar pattern in the absorption spectra except shift in their wavelength around 700 nm. The absorption peaks of the samples in the green method show a red shift in the polaron band region. It may due to the formation of more charge carriers delocalised in the polaron band region.

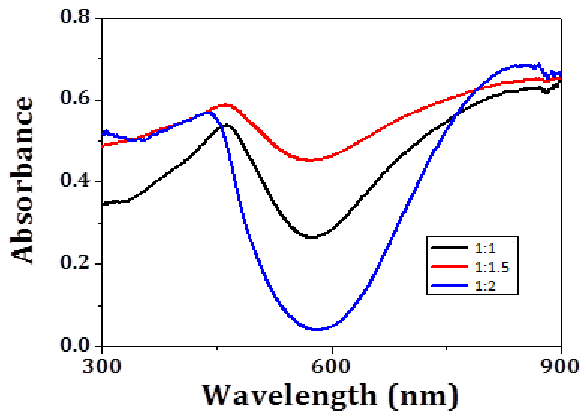


Figure 7. UV-Visible Spectra of PANI in HCl

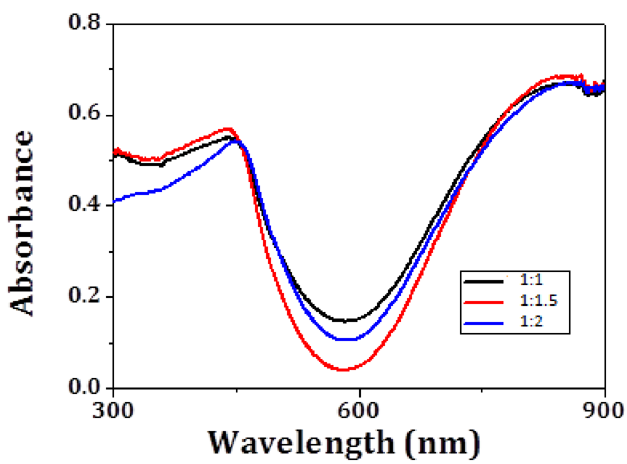


Figure 8. UV-Visible Spectra of PANI in bilimbi fruit extract

CONCLUSIONS

In this work polyaniline is synthesized by oxidative polymerisation of aniline using ammonium peroxy disulphate as oxidising agent in dilute HCl and bilimbi fruit extract media. IR studies confirmed the formation of polyaniline in the most conductive emeraldine salt form. SEM analysis showed better homogeneity for the sample in the green medium and UV spectrum showed better conjugation. DC conductivity value of the green sample is found greater than that in the conventional medium. Thus we can conclude that bilimbi fruit extract is an effective natural resource for the preparation of conductive polyanilne.

Acknowledgements

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