Plant Archives Vol. 20, Supplement 2, 2020 pp. 2670-2672 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

STRUCTURAL CHARACTERIZATION OF POLYANILINE

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Abstract

Conducting Polyaniline has been prepared with chemical oxidative polymerization method. In this work $K_2Cr_2O_7$ has been used as an oxidant which helps in the polymerization of the conducting polyaniline. The various characterization techniques like X-ray diffrectometery (XRD), Fourier Transform Infrared (FTIR) Spectroscopy have been used to analyze the structure of polyaniline. These characterizations have been done for the conformation of emeraldinr salt formation of polyaniline. Emeradine salt form of polyaniline also physically distinguished with the appearance of green colour when it was protonated with the acidic dopant. Therefore , 1M HCl was used during the synthesis of polyaniline.
Keywords: Polyaniline, Pot.dichromate ($K_2Cr_2O_7$), chemical oxidative polymerization, Hydrochloric acid.

Introduction

Polymers are well known for their class of sensitivity of heat, flexibility, and insulating nature of folded polymeric chains (Mostafaei *et al.,* 2012). It was the great surprise for the scientific community when conducting polymers replace the metal in various materials application. The exploitation of properties of conducting polymers changed the world. The conducting polymers perform as unique candidates for number of applications like sensors, electromagnetic interference shielding, corrosion and super-capacitors etc. The versatility of material in these applications is due to the matrix incompatibility, weight and integrality of the environment (Kumar *et al.,* 2016). Along with light weight material, resistant in corrosion other properties were also made-to-order for development. There are number of conducting polymers which exist like polypyrrole, PEDOT: PSS, polyfluorenes, polythophene (Song *et al.,* 2013; Sharma *et al.,* 2015, 2016, 2017, 2018; Kumar *et al*., 2010, 2013, 2014, 2015, 2019). The electrically conducting polymers were initially exposed in 1976. In 1970s, polyacetylene was the chief conducting polymer which was accidentally prepared by the scientist Shirakawa. In 1976, three scientists Hideki Shirakawa, Alan MacDiarmid and Alan Heeger, collectively worked on polyacetylene (PA) for their electrical property. They have improved the electrical conductivity up to the six orders of magnitude when it was treated with reluctant iodine. It was found that the conductivity were improved from 10^{-4} S/cm to 10^{2} S/cm. It was the great change in the electrical conductivity. This phenomenon of improvement in conductivity with reductant is known as doping. Among all these conducting polymers polyaniline has the greater kind of attraction due to ease of processibility, environmental stability, less expensive and processability. In consort with these qualities of polyaniline its morphology is also very attractive. It exists in granular, fibrillar, both granular and fibrillar, tube and rod form. These types of morphology tuned the property in better ways which are helpful in the application part.

The different structures of polyaniline have unlike stabilities, shades and electrical conductivity. It is well known that Leucoemeraldine has no colour as described through absorption spectroscopy (absorption band at 343 nm) in N-methylpyrrolidone (NMP) solvent (Mudila *et al.*, 2018, 2019, 2016, 2018; Boeva *et al.*, 2014; Kumar *et al.*, 2018). Meanwhile this material comprises merely amino groups and benzene; it gradually oxidizes in air and existing as insulating polymer. It is expected that Leucoemeraldine might be oxidized in medium (merely acidic) to the electrically conducting emeraldine salt (ES). The second existing structure i.e Pernigraniline is made up of irregular amino-benzene along with quinone-diimine trashes. For the reason that the quinone-diimine is not stable in the company of pernigraniline nucleophiles and specifically water its salts forms freely go moldy in presence of air. The ES form of polyaniline is shaped during the protonation of the EB (emeraldine base) with acids like organic and inorganic. When polyaniline in the state of EB is cured by means of acids, protons mainly cooperate by the imine atoms of N: therefore, gives an impression of poly-cation. Since charges (positive) confined on adjacent N atoms rise the energy of polymeric structure, the density of electron inclines to undergo reorganization (Kumar *et al.* 2017).

Materials and Methods

Reagents and chemicals

Chemicals Used: Aniline, HCl and Potassium dichromate ($K_2Cr_2O_7$), Polymethylmethacrylate, ethanol, petridish containing Mercury, dichloromethane (DCM).

Synthesis of polyaniline (PANI)

Chemicals Used: Aniline, HCl and Potassium dichromate ($K_2Cr_2O_7$) Add 5.0 millilitre of aniline monomer into 100 millilitre of aqueous hydrochloric acid (1M). Then, stir the solution so that solution gets dissolve completly. Now, place the solution in ice bath at 0 degree temperature. Then, add the solution of $K_2Cr_2O_7$ dropwise for half an hour. On addition, dark suspension of aniline changes its colour into green. Now place the solution at 20 degree for 24 hour. Then, filter the reaction solution using wattman paper and washes with 1M HCl solution. Now dry the materials at 50°C in the oven. PANI is formed in a green powder form.

Results and Discussion

X-ray diffractometery

Figure 1 shows X-ray pattern of polyaniline prepared by Rx^n. The figure indicates that the chains are strongly disordered. Two broad peaks were observed at around 2θ of 20^0 and 25^0. These can be assigned as the (020) and (200) reflections of PANI in its emeraldine salt form. Polyaniline displays merely a peak at 2θ = 25^0 which indicate the semicrystalline nature of the polymer (**Figure 1**) (Shaban *et al.* 2018; Kumar *et al.* 2017).

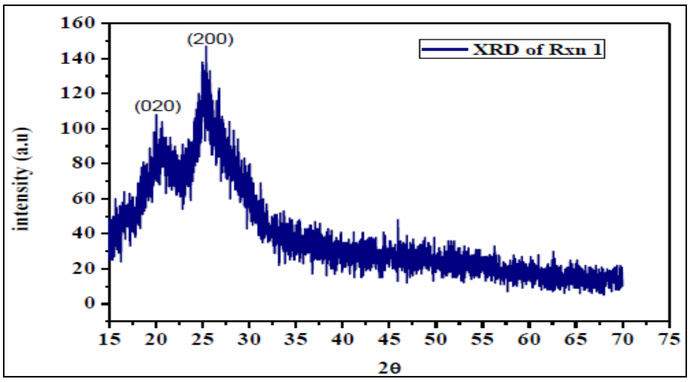

Fig. 1 : X-Ray Diffraction pattern of PANI

FT-IR spectra

It has been observed from figure 2 that there are six principal absorptions band at 1504, 1482, 1306, 1245.9, 1148 and 803 cm^{-1} which correspond to the formation of polyaniline. The intense peaks observed at 1482 and 1504cm^{-1} are corresponding to the stretching vibration of C-C ring. It has also been found that the peaks 1245.9 cm^{-1} and 1306 cm^{-1} relate to symmetric component of the C-C and N-H bending (or C-N) stretching modes. The bands which have been observed at 803 cm^{-1} and 1148 cm^{-1} accredited to the out-of-plane and in-plane C-H bending modes, respectively (Figure 2).

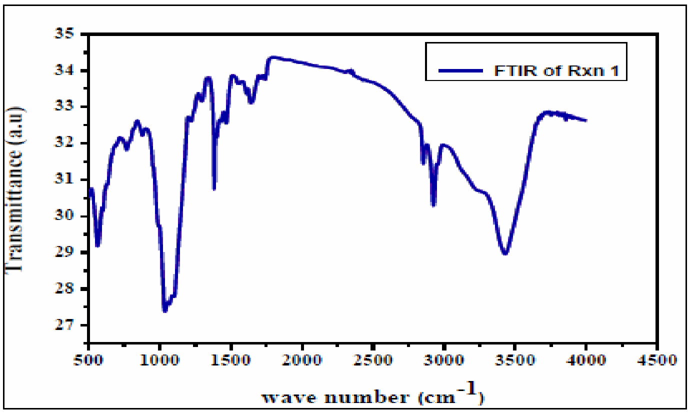

Fig. 2: FTIR Spectra pattern of PANI

The peak of polyaniline emeraldine salt also displays about 3460 cm^{-1}, 1653 cm^{-1}, 684 cm^{-1}. The observed band at 3460 cm^{-1} may possibly be credited because of the stretching mode of NH_2, however the peak at 1653 cm^{-1} correspond to the NH_2 vibration (bending). The wagging for NH_2 is explained by the 684 cm^{-1} band. The conducting structure of PANI is also explained by the band detected nearly 1246cm^{-1}. It understood that bi-polaron structure for conducting PANI assigned for stretching vibration of C-N. The observed band at 1580 cm^{-1} authorizes the occurrence of imine in protonated form. The peak observed at 590 – 700 cm^{-1} expose the stretching peak for C-Cl. (Puthirath *et al.* 2015; Palaniappan *et al.* 2008).

Conclusions

PANI has been successfully prepared by oxidative polymerization method in aqua medium. The synthesized conducting polyaniline was characterized by using XRD and FTIR spectroscopy. X-ray reveals that prepared material has the semi-crystalline nature. The oxidant $K_2Cr_2O_7$ was used for the oxidation purposes which assist in the polymerization of the polyaniline.

References

Boeva, Z.A. and Sergeyev, V.G. (2014). Polyaniline: synthesis, properties and application. Polymer Science, Ser. C, 56(1): 144-153.

Kumar, A. K. (2010). Ruthenium (III) catalyzed oxidation of D(+)Galactose and Lactose by alkaline potassium bromate, International Journal of Pure and Applied Chemistry, 5(1) p. 2010.

Kumar, A.; Jangir, L. K.; Kumari, Y.; Kumar, M.; Kumar, V. and Awasthi, K.; (2016). Electrical behavior of dual-morphology polyaniline. *Journal of Applied Polymer Science* ,133,p. 44091.

Kumar, A.; Kumar, V. and Awasthi, K. (2017). Polyaniline-carbon nanotube composites: preparation methods, properties and applications. Polymer-Plastics Technology and Engineering, 57(2): 70-97.

Kumar, A.; Kumar, V.; Kumar, M. and Awasthi, K, (2017). Synthesis and characterization of hybrid PANI/MWCNT nanocomposites for EMI applications. Polymer Composite, 39(11): 3858-3868.

Kumar, A.; Kumar, V.; Sain, P.K.; Kumar, M. and Awasthi, K. (2018). Synthesis and characterization of polyaniline membranes with secondary amine additive containing N, N'-dimethyl propylene urea for fuel cell application. International Journal of Hydrogen Energy, 43(47): 21715-21723.

Kumar, A.K. (2010). Aquachlororuthenium (III) Catalyzed Oxidation of some Sugars by Alkaline Potassium Bromate: A kinetic Study, Alfa Universal-An International Journal of Chemistry, 1(2): 87-95.

Kumar, A.K. (2013). Comparative Study of Kinetics of Catalyzed Oxidation of D (+) galactose and lactose by Ruthenium (III) in Alkaline Medium. Oriental Journal of chemistry, 29(2): 815-821.

Kumar, A.K. (2013). Phenobarbital: A New and Effective Corrosion Inhibitor for Mild Steel in 1 M HCl Solution. Asian Journal of Chemistry, 25 (17): 9808-9812.

Kumar, A.K. (2013). Spectral Study of Ruthenium (III) Catalyzed Oxidation of Maltose by Potassium Permagnate in Acidic Medium, Oriental Journal of chemistry, 29(2): 441-450.

Kumar, A.K. (2013). Theoretical Approach to the Study of Some Plant Extracts as Green Corrosion Inhibitor for Mild Steel in HCl Solution, 29(1): 277-283.

Kumar, A.K. (2014). Comparative study of Ruthenium (III) catalyzed oxidation of D(+) Xylose both in acidic and alkaline medium. Oxidation Communications 37(1): 179–192.

Kumar, A.K. (2014). Magnetite nanoparticle green synthesis from Canola oil. Oriental journal of chemistry 30(2): 553-558.

Kumar, A.K. (2014). Partial Molar Volumes of Aluminium Chloride, Aluminium Sulphate and Aluminium Nitrate in Water-rich Binary Aqueous Mixtures of

Tetrahydrofuran, Oriental journal of chemistry, 30(4): 2037-2041.

Kumar, A.K. (2015). A Comparative Study of Interactions between Protein (Lysozyme) and Ionic Surfactants (SDS, CTAB) in Aqueous Rich Mixtures of DMSO At Different Temperatures, Research Journal of Pharmaceutical, Biological and Chemical Sciences 6(1): 721-729.

Kumar, A.K. (2015). Transport studies of alkaline earth metal chlorides in binary aqueous mixtures of sucrose at different temperatures, Journal of Chemical and Pharmaceutical Research, 7(1): 255-261.

Kumar, A.K. (2019) An investigation on mitigation of corrosion of mildsteel by Origanum vulgare in acidic medium, Bulletin of the Chemical Society of Ethiopia, 33(1): 159-168.

Kumar, A.K. (2019). Electrochemical behavior and Computational analysis of Phenylephrine for corrosion inhibition of Aluminium in acidic medium, Metallurgical and Materials Transactions A, 50(1): 468-479.

Mostafaei, A. and Zolriasatein, A. (2012). Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods. Progress in Natural Science Materials International, 22(4): 273-280.

Mudila, H, Zaidi, M.G.H.; Rana, S. and Alam, S. (2016).Comparative electrochemical study of sulphonated polysulphone binded graphene oxide supercapacitor in two electrolytes. Carbon Letters, 18(1): 43-48.

Mudila, H.; P. Prasher, M. Kumar, H. Kapoor, A. Kumar, M. Zaidi and A. Verma (2018). An insight into Cadmium poisoning and its removal from aqueous sources by Graphene Adsorbents, International Journal of Environmental Health Research, 29(1) p. 1-21.

Mudila, H.; Prasher, P.; Kumar, M.; Kumar, A.; Zaidi, M. G. H. and Kumar, A.; (2019). Critical analysis of polyindole and its composites in supercapacitor application. Materials for Renewable and Sustainable Energy, 8(2): 1-19.

Mudila, H.; Prasher, P.; Rana, S.; Khati, B. and Zaidi, M.G.H. (2018). Electrochemical Oxidation-Reduction and Determination of Urea at Enzyme Free PPY-GO Electrode. Carbon letters, 26(1): 88-94.

Palaniappan, S. and John, A. (2008). Polyaniline materials by emulsion polymerization pathway. Progress in Polymer Science, 33(7): 732-758.

Puthirath, A.B.; John, B.; Gouri, C and Jayalekshmi, S. (2015). Lithium doped polyaniline and its composites with $LiFePO_4$ and $LiMn_2O_4$-prospective cathode active materials for environment friendly and flexible Li-ion battery applications. RSC Advances, 5: 69220-69228.

Shaban, M.; Rabia, M.; Fathallah, W.; Mawgoud, N. A. El.; Mahmoud, A.; Hussien, H and Said, O, (2018). Preparation and characterization of polyaniline and Ag/ polyaniline composite nanoporous particles and their antimicrobial activities. Journal of Polymers and the Environment, 26: 434–442.

Sharma, P.K. (2015). Antimicrobial activities of substituted 2-aminobenzothiazoles, *Journal of Chemical and Pharmaceutical Research*, 7(3):p. 819-822

Sharma, P.K. (2015). Synthesis and antimicrobial activities of substituted phenylthioureas, *Journal of Chemical and Pharmaceutical Research*, 7(2): p. 133-139

Sharma, P.K. (2015). Synthesis and antimicrobial studies of fused heterocycles pyrimidobenzothiazoles, Journal of Chemical and Pharmaceutical Research, 7(1): 710-714.

Sharma, P.K. (2015). Synthesis of Bioactive substituted pyrazolylbenzothiazinones" Res.Chem.Intermed.; 41,(9): 6141-6148.

Sharma, P.K. (2015). Synthesis, spectral, energetic and reactivity properties of phenothiazines: Experimental and computational approach, Journal of Chemical and Pharmaceutical Research, 7(11): 462-473.

Sharma, P.K. (2016). Antibacterial and Antifungal activity of Piperazinylbenzothiazine, Der Pharma Chemica, 8(5): 191-193.

Sharma, P.K. (2016). Antibacterial, Antifungal and Antioxidant activities of substituted pyrazolylbenzothiazines, Der Pharmacia Lettre, 8 (11): 79-82

Sharma, P.K. (2016). Antibacterial, Antifungal and Antioxidant activities of substituted 4H-1,4-benzothiazines, *Der Pharma Chemica*, 8(11): 156-159

Sharma, P.K. (2016). Antifungal, Antibacterial and Antioxidant activities of substituted Morpholinylbenzothiazine, *Der Pharmacia Lettre*, 8 (11): 140-142

Sharma, P.K. (2016). Morpholinylbenzothiazine consider as bioactive compound, *Der Pharmacia Lettre*, 8 (4): 86-90

Sharma, P.K. (2017). A review on antimicrobial activities of important thiazines based heterocycles, Drug Invent. Today, 9(3) p. 23-25

Sharma, P.K. (2017). A Review: Antimicrobial agents based on Nitrogen and Sulphur containing Heterocycles. Asian. J. Pharm. Clin. Res.; 10(2): 47-49

Sharma, P.K. (2017). A review: Different approach of bioactive pyrimidobenzothiazoles synthesis, Drug Invent. Today, 9(3) p. 18-22

Sharma, P.K. (2017). A Review: Thiazines derivatives treated as potential antimicrobial agents, Asian. J. Pharm. Clin. Res.; 10(1). 43-46.

Sharma, P.K. (2017). Antimicrobial and antioxidant activities of substituted 4H-1, 4-benzothiazines AIP Conference Proceedings, 1860(1).

Sharma, P.K. (2018). Synthesis of Starting Heterocycles: 2-Aminobenzothiazoles, 2-Aminothiazoles and 2 Aminobenzenethiols – Potential Precursors for Macroheterocycles, Macroheterocycles 11: 316-321.

Song, E and Choi, J. W.; (2013). Conducting polyaniline nanowire and its applications in chemiresistive sensing. *Nanomaterials*, 3(3): 498-523.