Facile Synthesis and Characterization of Polyaniline (PANI-Mn) Nano-catalyst by using Oxidative Polymerization

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ABSTRACT

Nano-catalyst is rapid growing field which involves the use of nanomaterials as catalyst for a variety of homogeneous and heterogeneous catalysis application. Nano catalytical system allow the rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. An efficient doped polyaniline-manganese metal Nano-catalyst was synthesized by chemical oxidative polymerization method. The polymerization of aniline was carried out in presence of Ammonium persulphate as oxidizing agent. During the reaction aniline monomer undergo oxidation and forms Polyaniline. Doping was done with help of Manganese dichloride. The detailed morphological and structural analysis reveals the manganese nano particle was uniformly distributed in polyaniline. The structural analysis was carried out by using Fourier Transform Infrared Spectroscopy, Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), X-Ray diffraction technique. The peak obtained in spectra confirm the synthesis of Nano-catalyst. The average particle size was calculated by Scherrer formula. Which was found in nanometer range. The present paper reports the facile synthesis of Polyaniline-Mn Nano-catalyst and its confirmation.

KEYWORDS: Polyaniline, $MnCl_2$, TEM, SEM, FT-IR.

INTRODUCTION

Polyaniline is a conducting polymer and organic semiconductor of the semi-flexible rod polymer family. The compound has been of interest since the 1980s because of its electrical conductivity and mechanical properties. Highly conductive polymer are used as electrode materials for super capacitors. The polymers having poly conjugated structures and they possess poor electrical conductivity but oxidized polymers shows excellent electrical conductivity. The polyaniline is unique properties among all polymers. Polyaniline having various application in Polymer electronics.[1]The unique properties such as electrical, optical and photoelectrical as well as easy to synthesis with great environment stability therefore its very useful in commercial field.[2-3] The polyaniline (PANI) has much practical application such as light emitting device,[4]electrode,[5-6] sensor device,[7-8] light weight batteries and surgical instruments.[9]electromagnetic interference shielding materials.[10]It used in corrosion protecting agent in the paint industries,[11]in solar cells,[12]The polyaniline shows various oxidation states when it is half oxidized it is called Emeraldine base, fully oxidized it is called pernigraniline and in fully reduced state leucoemeral.

The doping of polyaniline increase the catalytical properties therefore many researcher are attracted toward the doping of polyaniline. After doping the Nano composite is formed which is used as catalyst for organic and inorganic synthesis. The ammonia-Doped polyaniline-Graphitic nitride Nanocomposite as a Heterogeneous Green Catalyst for Synthesis of Indole-substituted 4H-Chromenes.[13] The Effect of Mn^{2+} as a redox additive on ternary doped polyaniline-metal nanocomposite: an efficient dielectric material.[14] The Synthesis and Characterization of Polyaniline/Mn3O4 Reduced grapheme oxide Nanocomposite and they had studied the electrical and dielectical properties.[15] The polyaniline/Nanomaterials Composite is used for removal of Heavy Metals by adsorption[16] The polyaniline based magnesium nanoferrite composite is efficient photo-catalyst for photo degradation of Indigo Carmine in aqueous solution.[17] some researcher done the Synthesis and Characterization of Polyaniline-$CaCu_3Ti_4O_{12}$ Nano crystal composite.[18]Polyaniline-Copper oxide Nano-composite: Synthesis and Characterization.[19] The Nanocomposites exhibits electrolytic and gas sensing properties[20]The PANI-Mn Nanocomposite exhibit good cycling stability as well as a high capacitance close to 207 Fg^{-1}. [21] In this present paper we successfully synthesize Polyaniline-Mn Nano-catalyst by simple, facile polymerization methods. The prepared sample were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), X-Ray diffraction technique.

EXPERIMENTAL

The chemicals used such as aniline, ammonium persulphate, ammonia, manganese dichloride, ethanol, concentrated Hydrochloric acids were of analytical grade, The Distilled water used for experimental work.

Synthesis of Polyaniline: Here we used oxidative polymerization of aniline. The 0.5 M aniline monomer(99%) solution and 0.5 M ammonium persulphate (APS) was prepared in 0.5M Concentrated hydrochloric acid solution, In two separate beakers. These two were mixed slowly with constant stirring, this mixture kept in ice bath maintaining the temp below 0-6 ºC for 4-5 hours, [22] Without stirring to settle the powder, The dark suspension becomes green in color. This reveals that polymerization reaction started, the complete polymerization reaction was carried out at 0–6 ºC for 10-12 Hours. The green colored residue like paste was obtained. The final product was washed several times with D.W. and acetone for removing short chain molecule of aniline. Finally the dark-green powder is dried at 70^{o}C for 6-8 Hours in Oven. The final product was grinded to form a green powder is known as conducting PAni and it was used for further process.

Synthesis of PANI-Mn Nano-catalyst: After formation of Polyaniline Emeraldine Salt (ES) the accurate amount of 0.2 M solution of Manganese chloride (MnCl2) slowly and carefully dissolved in polyaniline.[23] The Polyaniline Manganese chloride solution was kept in R. B. flask and kept for stirrer with the help of hot plate with magnetic stirrer (700 RPM) about 4-5 hours. The dark green suspension is formation in the R. B. flask after that this R B flask was kept in Ice bath for overnight. After filtration the product were washed with 2 times with distilled water and 3 times with ethanol. The prepared Nano catalyst was kept in hot air oven for 7 hours at 70^{0}C. In this method the Nano particle of Mn is uniformly distributed in Polyaniline. There is formation of Nano catalyst having dark green color.

Fig- 1. Product in Ice Bath

Fig- 2. Filtration of Product

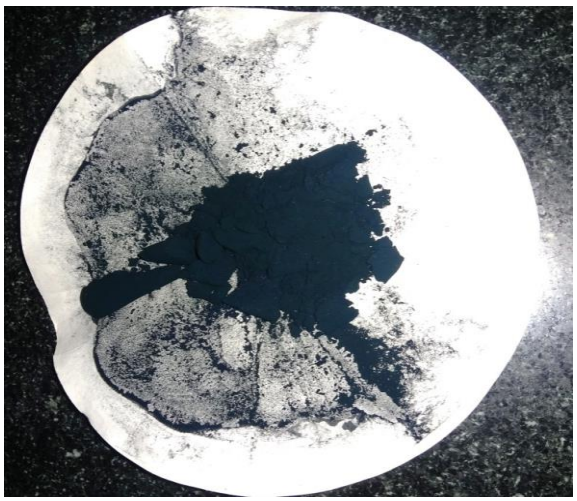

Fig-3. Dark Green color Nano-catalyst

RESULT AND DISCUSSION:

X-Ray Diffraction analysis of PANI-Mn Nano-catalyst: X-ray Diffraction analysis was obtained from Bruker D8 Advance service (Powder XRD) using CuKα (Kα =1.54056 Å) radiation. The diffracto meter was operated at 40.0 kV and 35.0 mA. The Scanning type is coupled 2θ with a 57.60 s total time per step was used. Detector name LynxEye. Compute crystallite- Yes. Powder X-ray diffraction pattern was recorded.

The crystalline structure of the Polyaniline was investigated on the basis of X-ray diffraction analysis. The Polyaniline gives four different peak at room temp(25^{o}c) i.e. 14.026^{0}, 20.037^{0}, 25.446^{0} , 27.118^{0} respectively as show in Fig-4. Diffraction peak were obtained at 2 θ= (25) 25.446^{0} is due to PAni-Mn Nanocomposite. The Inter planar distance value obtained is 3.53A^{0} hence diffraction peak at 2 θ of the nano-materials of thin film has been calculated on the basis of Debye Scherer Equation. (D= kλ /β cos θ) where k is the shape of factor (0.89); D is the average crystallite size ; λ is the wavelength of X-ray radiation used (1.54060A^{0}); β is the full width at half maximum ; θ is the diffraction angle.[24] The average crystallite size value obtained is 43.16 nm on the basis of XRD data.

Table-I: The XRD Data of Polyaniline-Mn Nano composite.

Pos [^{0}2Th]	Height t [cts]	FWHM [^{0}2Th]	d- Spacing [A^0]	Rel. Int [%]
25.446	26	1	3.49760	100.00

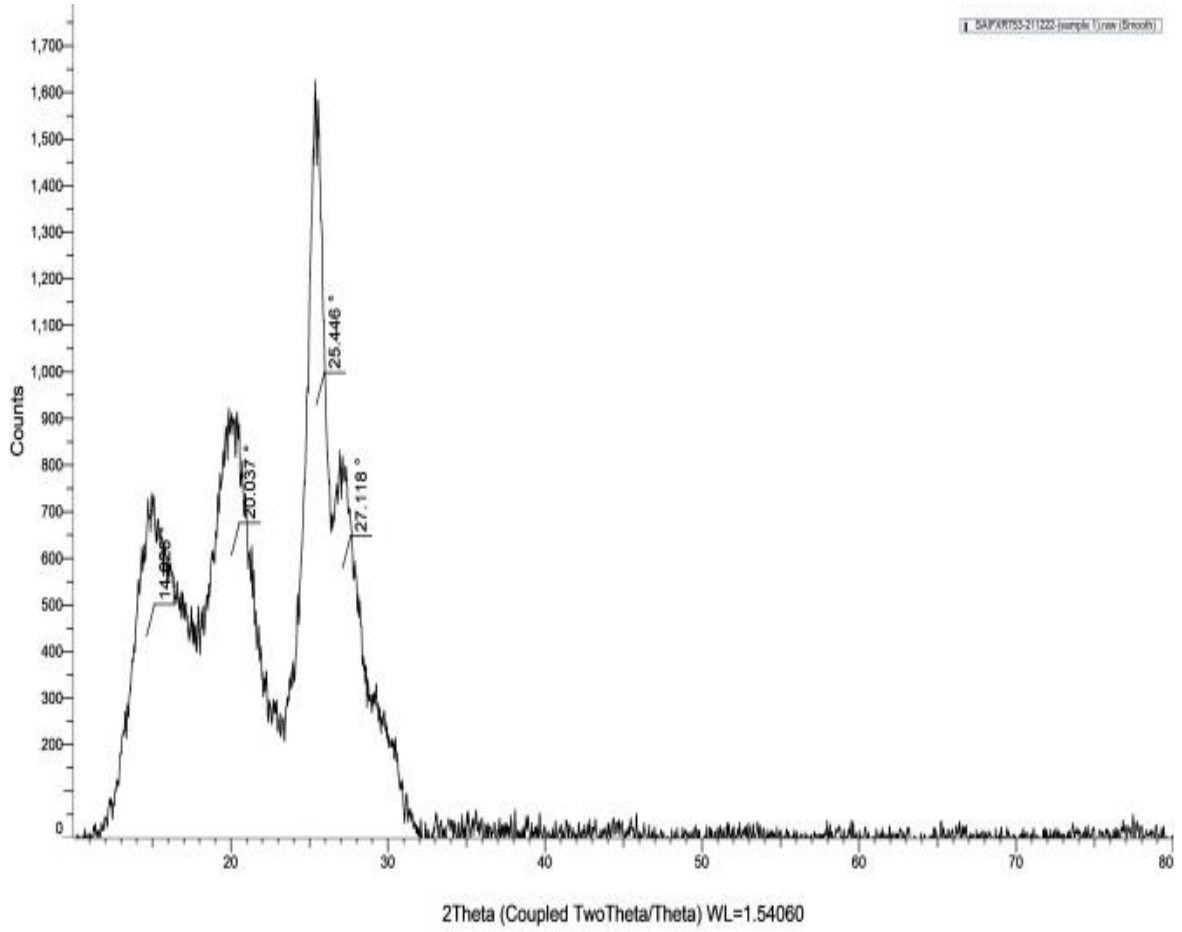

Fig-4. XRD pattern for PAni-Mn

Fourier- transforms infrared spectroscopy (FT-IR) Analysis: The prepared Polyaniline-Mn Nano-catalyst was identified by IR spectroscopy. The sample was run in the wavelength 4000-900cm^{-1}. The FTIR spectra of synthesized pure polyaniline-Mn presented In following fig-5. The absorption peak at 3443.49 cm-1 is due to –OH group of absorbed water molecules. The distinctive peak at 1608.35 and 1562.24 cm-1match to the quinoid ring and benzene ring respectively. The band is in the range 1224.30 to 1460.30 cm-1 corresponds to C-N stetching band of an aromatic amines. The typical band of polyaniline base (N=Q=N stretching band) was observed at 1111.61 cm-1. The peak band close to 794.93 to 901.17 cm-1 are characteristics of the p-substituted chain of polyaniline. The band close to 1145 cm-1 is described as characteristics of the conducting polymers due to the delocalization of electrical charges caused deprotonation. It shows the band characteristics of B-NH-Q or B-NH-B refer to the benzoic-type ring and Q to the quinoid-type rings.[25] The absorption band lies below 502.70, 562.76,618.10,1003.01 and 1029.92 cm^{-1} spectral region indicate the all the substitution present in benzene ring as a result of the polymerization process. The clear shift was formed in the FT-IR spectra of Polyaniline –Mn composite. For example absorption peak at 820,1146 and 2945 cm-1 belong to un doped polyaniline[26] shifted to 794.93, 1111.35 and 2925.46 cm-1respectively. This shifting spectrum formed by Manganese metal cation become absorbed by as a result of electrostatic attraction of chlorine ions on the surface of polyaniline molecules.

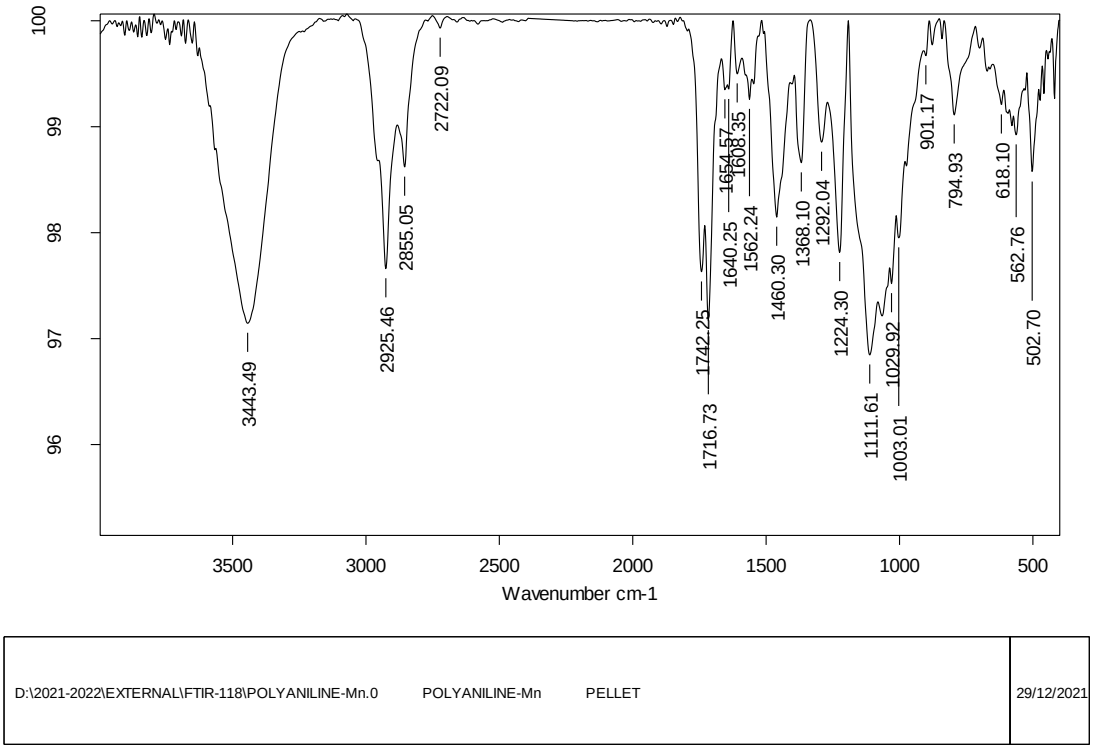

Fig-5. FT-IR Analysis of PANI-MN

Transmission electron microscopy (TEM 300kV): The HR-TEM (300kV) was recorded by using FEI, Tacna G2, F30, and Resolution Point: 2.0 Angstrom Line: 1.0 Angstrom, Accelerating potential: 300 kV. F Following fig- 6, 7, 8, 9 shows the TEM images of the synthesized Polyaniline-Mn Nano-catalyst synthesized by oxidative polymerization methods. The TEM analysis were done at 100nm, 200nm, 500nm. The TEM can be used to determine the size of Nano-particle and to examine homogeneity and size distribution.[27] It can be seen from the fig: that there is uniform distribution of Mn particle having size 43.16nm

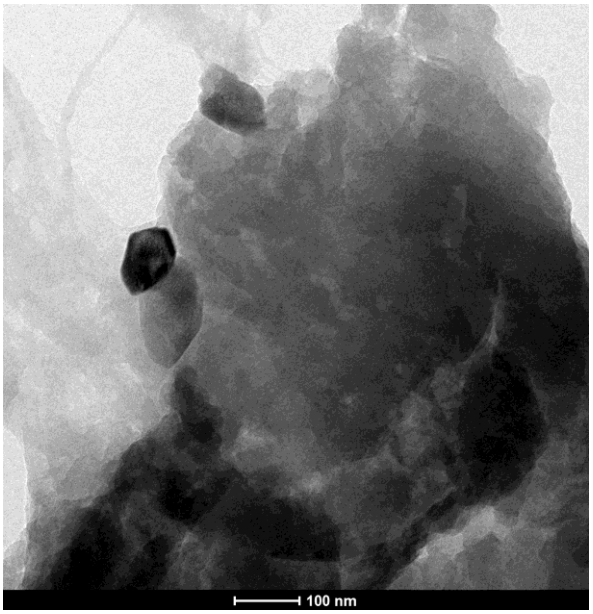

Fig-6. TEM Image at 200nm

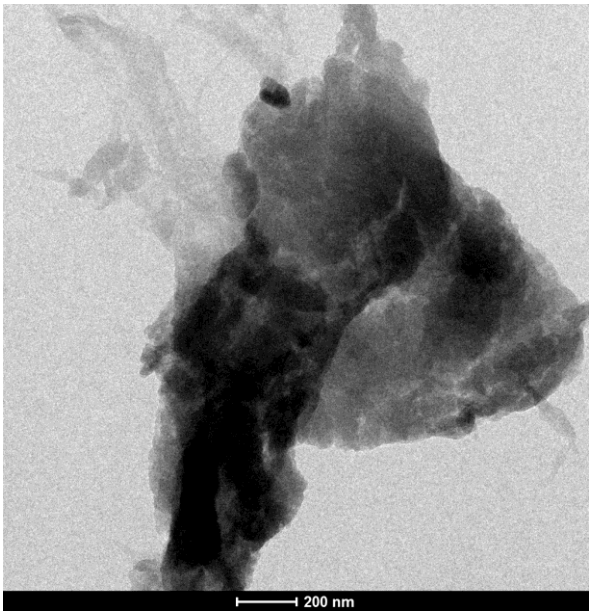

Fig-7. TEM Image at 100nm

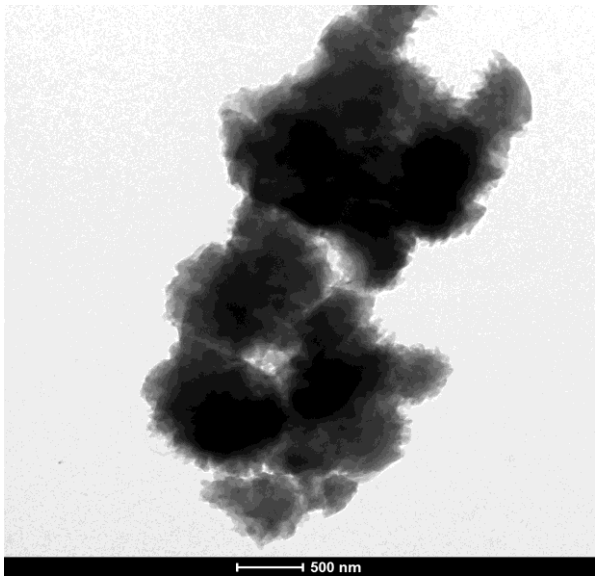

Fig-8. TEM Image at 500nm.

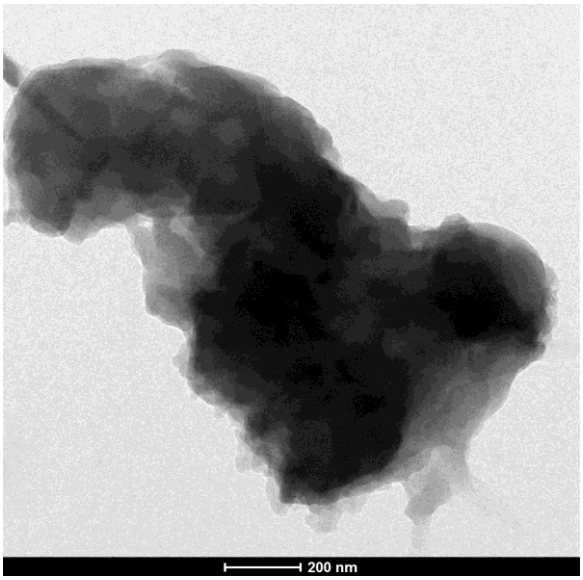

Fig-9. TEM Image at 200nm.

Scanning Electron Microscopy: Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) was taken by using JSM-7600F SEI Resolution: 1.0 nm at 15 Kv. The JEOL JSM – 7600F FEG-SEM combine two proven technology. The main objective of Scanning electron microscopy is to determine morphological features and surface characteristics of the compounds.

The Fig-10,11, show the SEM images of PANI-Mn Nano-catalyst at different magnification. The conducting polymers are highly sensitive towards temperature during recording of SEM. It can seen from the SEM images that particles are well defined in the size ranging in the nanometers. The high temperature creates a polymerization condition where the interfacial tension decreases with temperature,[28]It is seen to form polyaniline-Mn Nano rod morphology. Most of the particles are spherical in shape and slightly agglomerated.[29] The globular particle is produced with high surface.

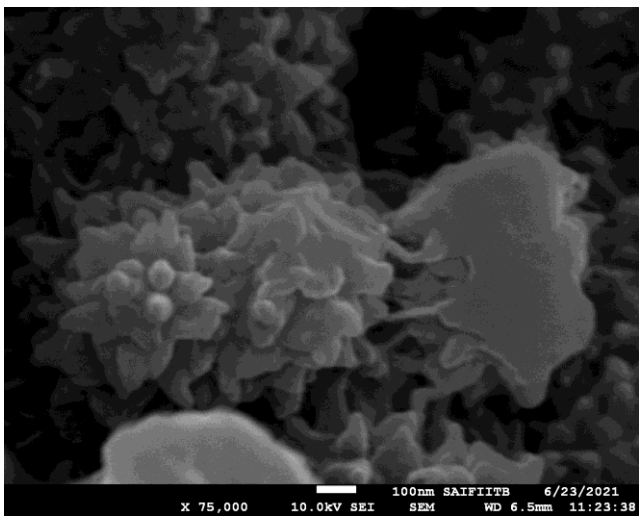

Fig-10. SEM Images at 100nm of PANI-MN

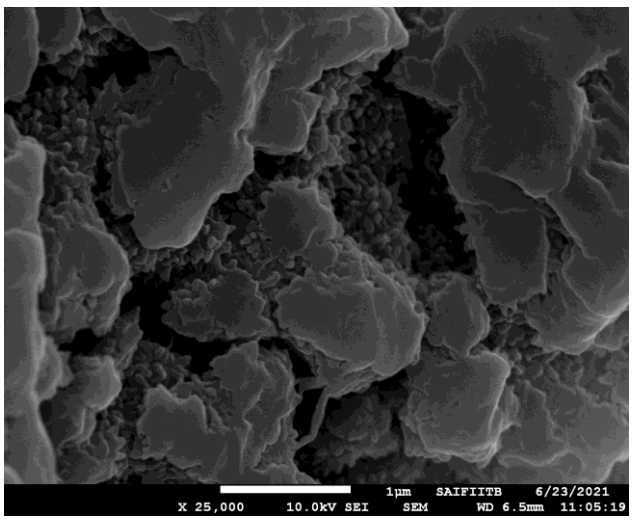

Fig-11. SEM Images at 1nm of PANI-MN

CONCLUSION

Polyaniline-Mn Nano-catalyst have been synthesized via oxidative polymerization methods and prepared sample were characterized by X-ray diffraction technique for determine crystalline size of Nano-catalyst PANI-Mn. The Functional group identification were determined from FT-IR spectrum. The surface morphology, shape was studied by TEM analysis. The Surface structure studied with the help of SEM analysis. All these results suggested that the Polyaniline-Mn Nano-catalyst is successfully synthesized.

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