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Enhancement of specific capacitance and catalytic activities of MnO2 nanoparticles assisted with PVA and PVP

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Abstract : In this present study, MnO_2 nanoparticles were synthesized by hydrothermal method and along with MnO_2 nanoparticles doped with poly Vinyl Alcohol (PVA) and poly Vinyl Pyrrollidone (PVP) nanoparticles. The synthesized nanoparticle's specific capacitance properties were analyzed by AC impedance and cyclic-voltametric techniques. Catalytic activities of MnO_2, with PVA and PVP assisted nanoparticles on dye removal capacity were done on rhodamine-B dye. The size of these nanoparticles from SEM study observed that all of these nanoparticles were in the nanoscale range. The results of these study reveals that with respect to specific capacitance value of MnO_2 assisted PVA nanoparticles have shown very high value (1235 F/g) when compared with Pure MnO_2 (164F/g) and MnO_2 assisted with PVP (151 F/g) nanoparticles. The SEM study of PVA assisted MnO_2 nanoparticles has dense spindle shape with high surface to volume ratio compared with other nanoparticles was the main reason for having high specific capacitance value. The size of the synthesized nanoparticles was calculated by powder XRD study and it is observed that among the three nanoparticles, the pure MnO_2synthesized particles has very low size reduction (10.12 nm) compared with other nanoparticles. The effective catalytic activity of MnO_2 nanoparticles on dye removal (rhodamine-B) depends on small size of the nanoparticles.
Key words : MnO_2, surfactant PVA/PVP, Rhodamine-B.

1. Introduction

Metal nanoparticles have different physical and chemical properties (e.g., lower melting point, higher specific surface areas, specific optical properties, mechanical strengths and specific magnetization) its bulk materials. The nano-MnO_2 has great potential applications in an environment protection field as a new generation of environmental friendly catalyst **[1]**. Manganese oxide is one of the most interesting material, which has a wide variety of structure with large surface area. The diverse structures, chemical properties of manganeseoxide are taken advantage in potential applications such as cation-exchange. Manganese dioxide has been applied in the super capacitors by Goodnough group in 1999 **[2]**.The study of MnO_2 has larger pseudo and well specific capacitance and is a suitable electrode material for electro chemical capacitors. Thus many investigators have studied the electrochemical properties of MnO_2 for applications in super capacitors.

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For example the MnO_2 filmprepared by using dip coated sol-gel method contains the specific capacitance up to 698 F/g **[3]**.Manganese oxide nanoparticles (MnO_2) can be utilized for advanced materials in batteries as well as other application such as, water treatment and imaging contrast agents. High capacity lithium ion batterie **[4-6]**, lithium air battery for their advantage of low cost earth abundance, Environmental friendliness and superior performance in high energy capacity. So for variety of chemical methods are available to synthesize MnO_2 nanoparticles, including thermal decomposition, co-precipitation **[7]**, simple reduction **[8,9]**, solid -phase process hydrothermal method **[10]** etc., In this paper we synthesized MnO_2 nanoparticles, MnO_2 assisted with poly vinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) nanoparticles by hydrothermal method and compare their specific capacitance values and also we investigate the catalytic activities of the synthesized nanoparticles.

2. Experimental Sections

2.1. Hydrothermal synthesis of MnO_2 nanoparticles

In a typical synthesis of MnO_2 nanoparticles by hydrothermal method about 0.5g of $MnCl_2$was mixed with 50mL of ethanol and heated at 73^0C and then 0.10g of $KMnO_4$ was added to the above solution. The mixture was carried out for four hours by Refluxing. After 4hours the resulting particles are filtered and then impurities are removed using ethanol (three times). The nanoparticles are kept under the microwave oven for 24hrs. The sample was taken from the oven and then dried.

$3MnCl_2 + 6\ KMnO_4 + C_2H_5OH \rightarrow 9MnO_2 + 6KCl + 3H_2O + 2CO_2\uparrow$

2.2.Preparation of PVA / PVP assisted MnO_2 nanoparticles

Similarly PVA / PVP assisted MnO_2 nanoparticles were synthesized under hydrothermal method by the addition of both PVA and PVP for about 0.15g to the reacting mixture.

3. Results and Discussions

3.1 X-ray Diffraction (XRD) Studies

The XRD pattern and various parameters were calculated from 2θ values of XRD for MnO_2, MnO_2 assisted with PVA and PVP nanoparticles. The XRD spectra of the MnO_2, MnO_2 with PVA and PVP are shown in the figure3.1.A strong diffraction peak at 2θ =36.79° was due to presence of MnO_2 nanoparticles and 2θ=36.52° for PVA assisted with MnO_2 nanoparticles, 2θ =36.4° for PVP assisted with MnO_2 nanoparticles. From XRD spectra the crystalline size of the MnO_2 was for 10.12 nm and the MnO_2 with PVA was13.15 nm and MnO_2 with PVP was 37.03 nm respectively (using Expert High Score software).

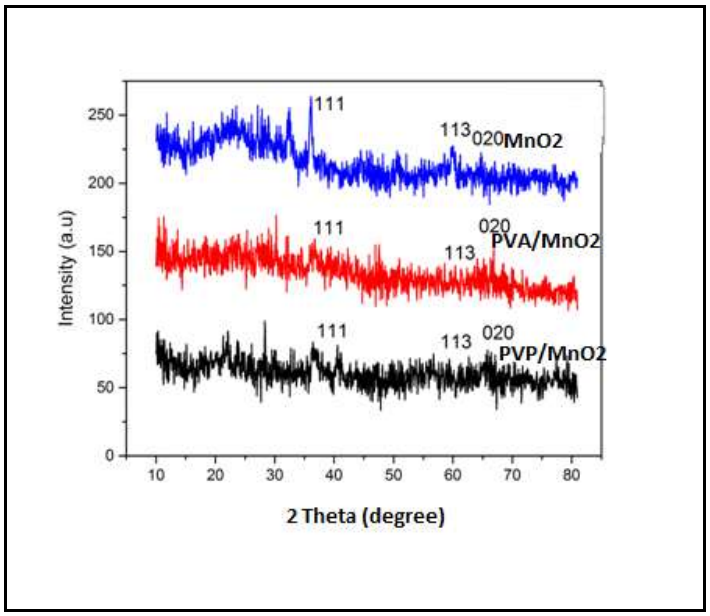


Fig-1. XRD Pattern of MnO_2 , PVA/PVP on MnO_2 nanoparticles.

$$D = K\lambda / \beta COS\theta \qquad (1)$$

Where, K is the Scherrer constant, which is related to the crystallite shape and are the radiation wavelength and Bragg's angle, respectively and is the full width at half maximum of the diffraction peak.

3.2 . Scanning electron microscope (SEM)

The SEM studies gives the information about surface morphology of the MnO_2, MnO_2 with PVA and MnO_2 with PVP nanoparticles as shown in the fig 3.2 which forming cloudy, this indicates MnO_2 nanoparticles are agglomerate with high magnification.

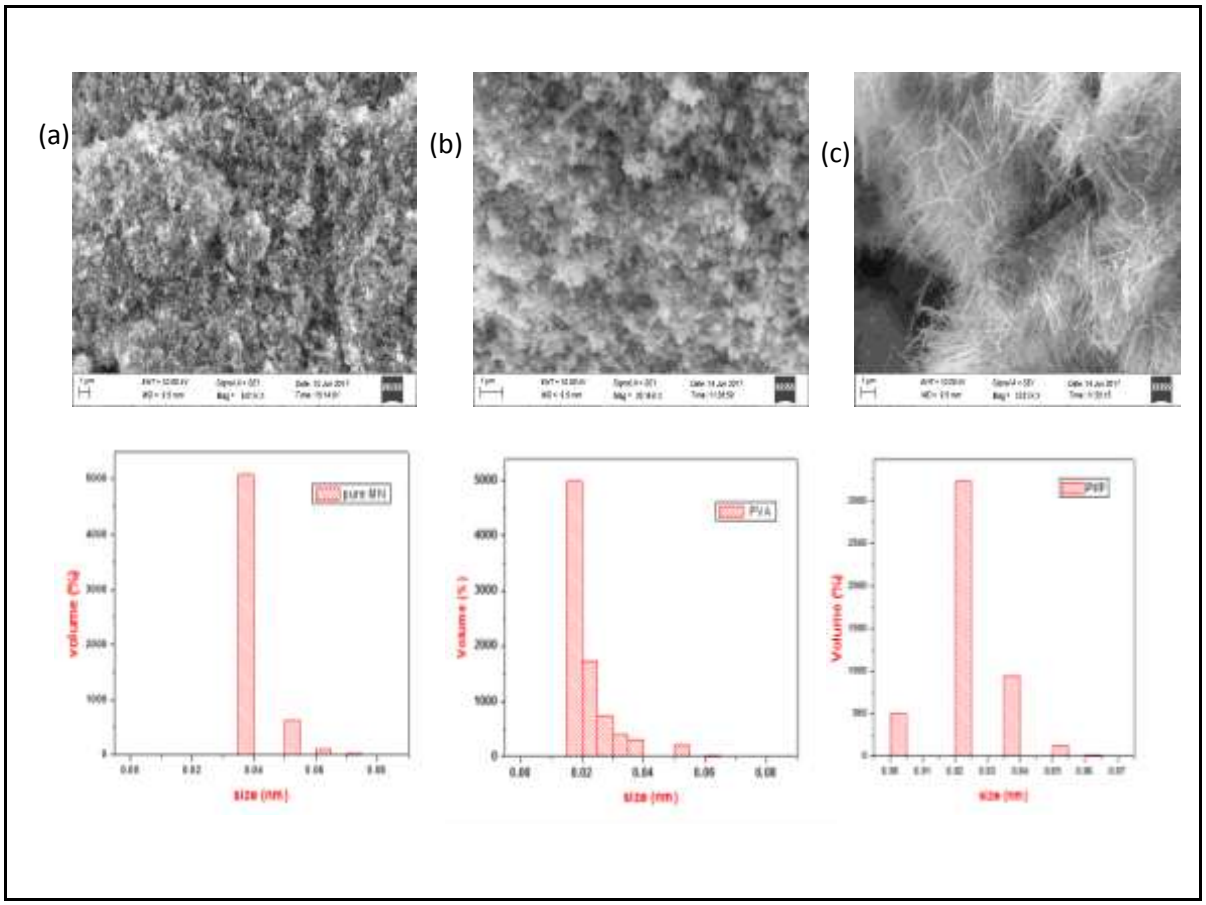


Fig-2. SEM image and Size Distribution of MnO_2 , PVA / PVP Assisted MnO_2 nanoparticles

From the size distribution analysis it was observed that the synthesized nanoparticles products are within the nanoscale range. The morphological images are observed in SEM analysis for MnO_2 and PVA/PVP assisted MnO_2 nanoparticles revealed that the growth of particle were very well organized.

3.3. UV-Visible absorbance spectra analysis:

UV-Visible spectrum was recorded using Perkin – Elmer lambda -35 UV-Visible spectrometer. The optical absorption spectra analysis is an important tool to obtain electronic band gap of synthesized nanoparticles MnO_2, MnO_2 with surfactant Poly vinyl alcohol and MnO_2 with surfactant poly vinyl pyrollidone nanoparticles in the range of 200-1200nm and is shown in this fig.3.3. The band gap energy was calculated by following formula

$$E_g = 1240/\lambda \text{ eV} \qquad (2)$$

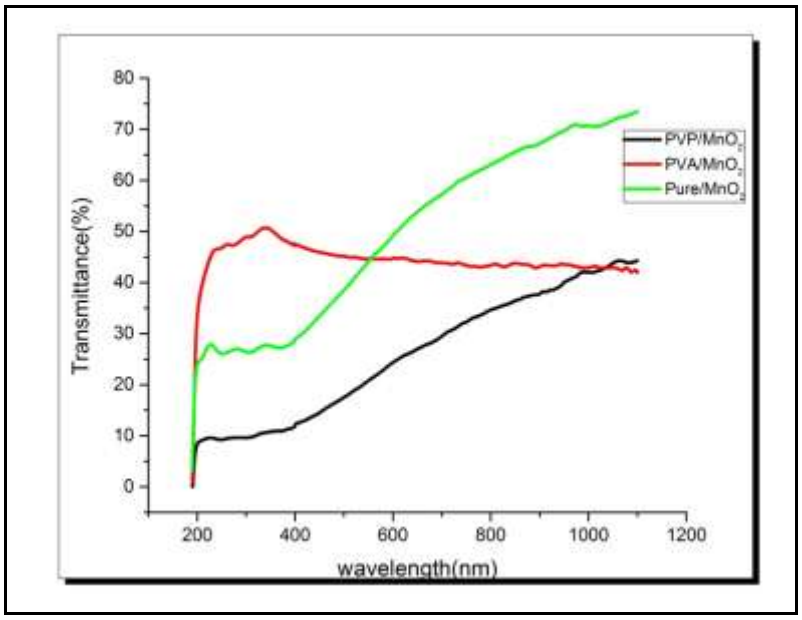


Fig.3. UV-Visible absorption spectrum of MnO_2, PVA/PVP on MnO_2 nanoparticles.

The lower cut-off wavelength of MnO_2, MnO_2 (poly vinyl pyrrolidone) and MnO_2 (poly vinyl Alcohol) nanoparticles was found to be 251, 243 and 249 nm respectively. The energy band gap was found to be 6.2, 5.16 and 6.04 eV.From the results, the pure Mno_2 particles band gap 6.2 eV, when poly vinyl alcohol embedded on the Mno_2 nanoparticles decreases because of the nature of polymers band gap decreases.

3.4. FT-IR spectrum analysis:

Infrared spectra are an important record, which provide more information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within definite range of frequency. The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to prime importance for the study of organic and semi organic compounds by spectral analysis. Fourier transform-Infrared (FT-IR) spectrometer has high resolution (HR) than ordinary infrared spectrometer (IR). The FT-IR spectrum of the sample was regarded using a Perkin-Elmer FT-IR spectrometer (Model: Spectrum RX1) using KBr pellet technique in the wave number range 4000-400 cm^{-1}.

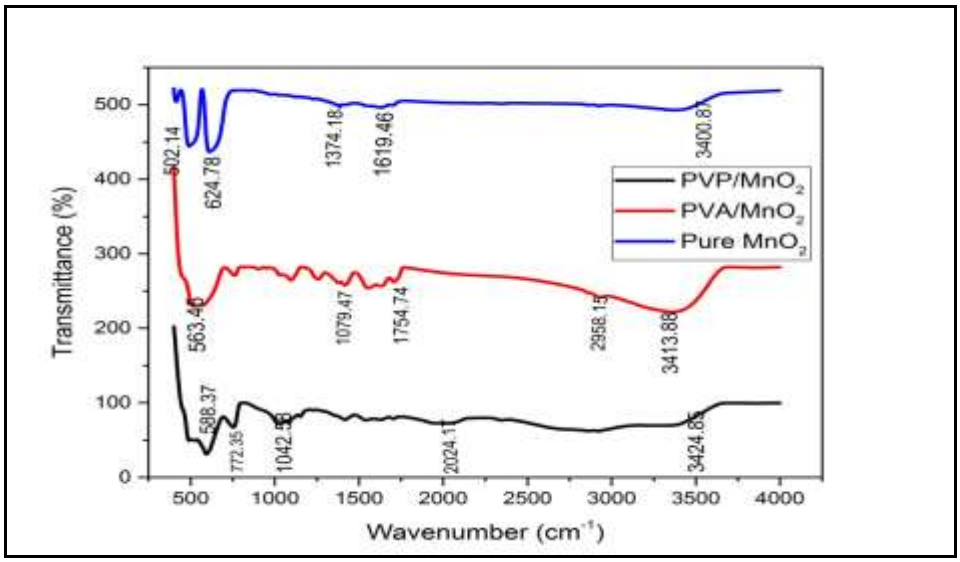


Fig-4. FT-IR Spectrum analysis of Pure MnO_2, PVA/PVP on MnO_2 nanoparticles.

The observed FT-IR spectrum of synthesized Pure MnO_2 , MnO_2(PVA) and MnO_2 (PVP) nanoparticles is shown **[fig.4].** The stretching vibrations of the water molecule is expected in 3387cm^{-1}. The absorption in the region 1700 – 1650 cm^{-1} is assigned to C=0 stretching of COOH group. The peak around at 523cm^{-1} of FT-IR spectra are assigned to C-Br stretching vibrations. The FT-IR assignments for the absorption peaks/bands of the synthesized sample of this work are assigned in the **Table 1.**

Table: 1. FT-IR assignments for MnO_2 nanoparticles

S.NO	Wave Number cm $^{-1}$			ASSIGNMENT FREQUENCIES		
	Undoped MnO_2	MnO_2doped with PVA	MnO_2doped with PVP	Bond	Functional Group	Intensity & type of vibration
1.	521.23	518.13	501.01	C-Br	Alkyl halides	Stretch-strong
2.	593.23	560.98	609.62	C-Br	Alkyl halides	Stretch-strong
3.	1417.02	1417.99	1384.65	C-H bend	Alkenes	Medium-variables, bending
4.	1536.70	1631.90	1628.33	N-H bend	1°amines	Medium-bending
5.	1707.46	1705.03	1704.88	C=O stretch	Alpha, beta-unsaturated aldehydes, ketones	Strong-stretch
6.	2923.95	2927.00	2925.39	C-H stretch	Alkenes	Medium-strong-stretch

3.5. Photoluminescence (PL)

The photoluminescence is an important tool to explore the optical energy band structures of the material. Generally the luminescence phenomenon that occurs in any material due to the intrinsic behavior. The emission spectra of the synthesized MnO_2, Poly vinyl alcohol embedded MnO_2, Poly vinyl pyrrollidone embedded MnO_2 nanoparticles was recorded in the range of 300-600nm using perkin-Elmer fluorescence spectrometer **(Model : LS45)** and shown in **[fig.5].**

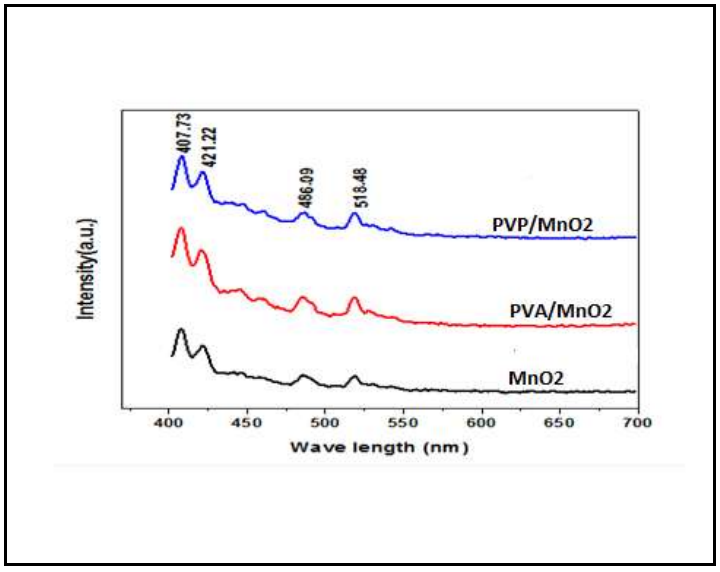


Fig-5. Photo-Luminescence spectrum of MnO_2 , PVA/PVP on MnO_2 nanoparticles.

Photoluminescence (PL) in Nano particles is the phenomenon in which electronic states of solid one excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material.There emission peaks are observed at 407.21 and 421.22 nm and in strong violet region for the above these case. weak blue band emission were observed at 486 and 518.58nm indicates that weak green band emission .It is confirmed that the nano particles emit UV light,violet and green fluorescence light.

3.6. Elementalanalysis (EDAX)

Energy dispersive X-ray analysis (EDAX) is a micro-analytical technique which is used to obtain useful information regarding to the chemical composition of the MnO_2 nanoparticles. In this work, the MnO_2 nanoparticles were subjected to EDAX analysis using the instrument energy dispersive X-ray micro analyzer.

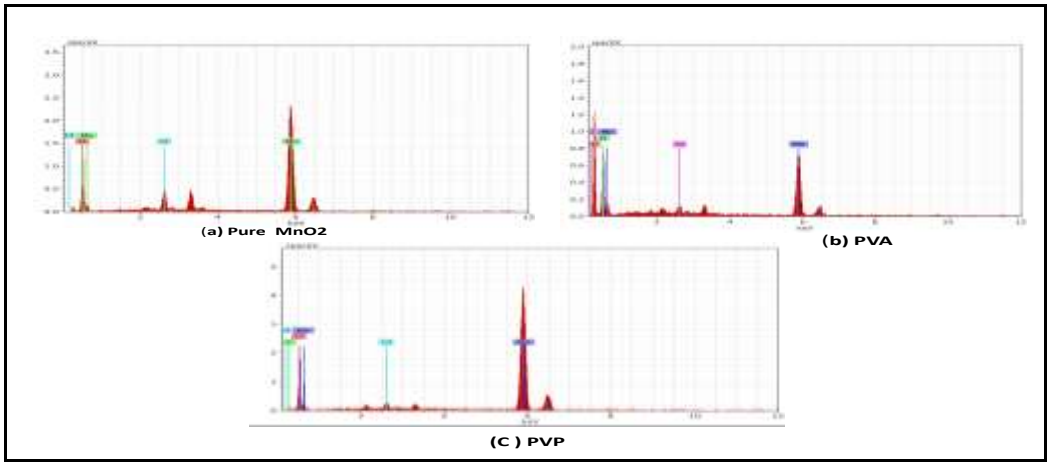


Fig -6. EADX images of nanoparticles of MnO_2 , PVA/PVP on MnO_2 nanoparticles.

The EDAX spectrum of the MnO_2 nanoparticles is depicted in **[fig.6].** The recorded spectrum confirms the formation of the title compound.The presence of the elements in different proportions are indicated by the respective peaks.

3.7.CYCLIC VOLTAGRAM (CV)

3.7.1. Electro chemical behavior of MnO_2 PVA, PVP assisted MnO_2 Nanoparticles

Electro chemical behavior of MnO_2nanoparticles with surfactant and without surfactant were studied by using CV. Thereare relations between structure, Morphology and electro chemical reactivity has been established and therefore it can be predicted in different structural form of the MnO_2nano particles will exhibit different electro chemical behavior. The electrical conductivity was calculated using formula

ó=I/E (mho) (4)

I = current (A) , V=Potential (v)

The electrical conductivity of pure MnO_2nanoparticles 17.675 milli mho, the electrical conductivity of MnO_2 with surfactant PVA 50.819 milli mho and of MnO_2 surfactant of PVP 24.32 mho.

3.7.2. Impedance analysis

The impedance analysis of pure MnO_2 nanoparticles the values of R and C_{dl} like 5908.1 ohm and 4.979 farad. The values of R and C_{dl} 3582.7 ohm, 9.443 farad and 6688 ohm,4.993 farad for MnO_2 embedded with PVA and PVP respectively.Cyclic Volta gram taken at scan rate 2 mv unit lower cut off potential from the fig3.6.It can be seen that during cathodic scanning cycle, the peaks are observed at 0.3V and 1.2V which corresponds to the match with MnO_2nanoparticles. Fig3.6 the Cathodic potential was observed at 0.3 V which indicates, that the MnO_2 nanoparticles are present in thesesamples. The CV curves of MnO_2 nanoparticles measured in the scan range of 1.8 to 1.7V.

3.7.3. Measurement of specific capacitance by cyclic voltametric study

Specific capacitance values for synthesized nanoparticles were calculated by applying the following formula; Specific capacitance

$$C_s = \int I_p \, \Delta t / 2m\Delta v \qquad (4)$$

Where C = Specific capacitance
M= mass of the nanomaterials
I_p = Peak current density
Δt – change in Time
Δv – window potential.

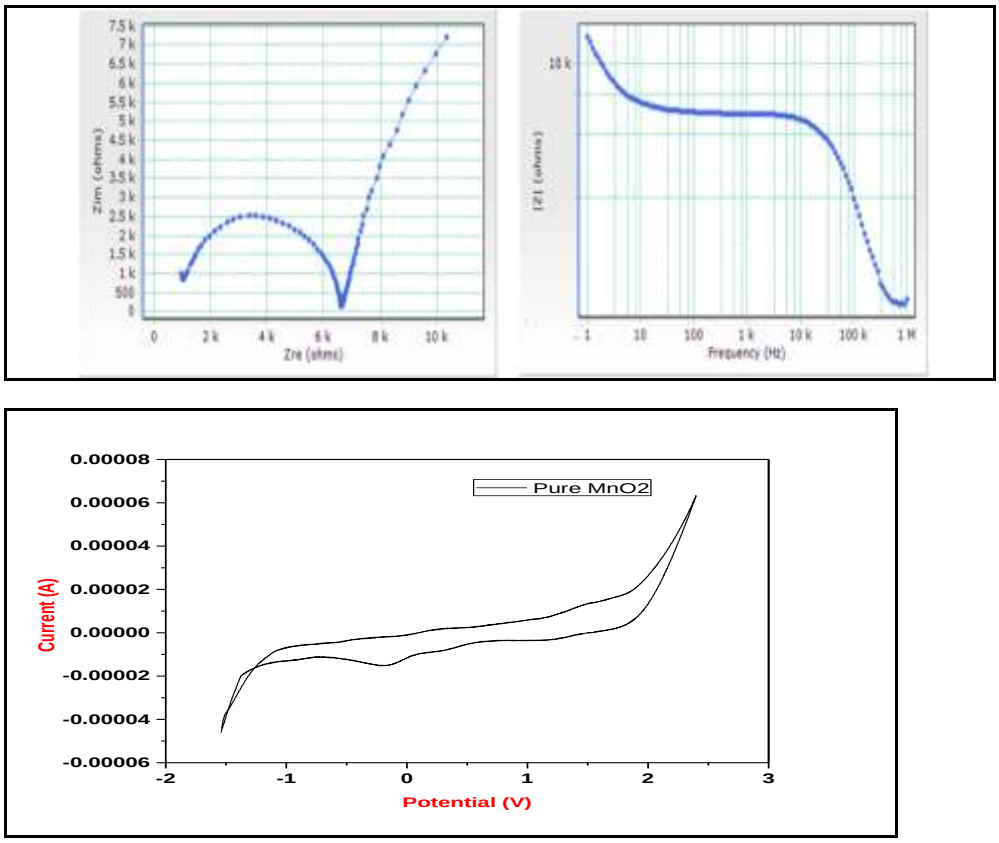
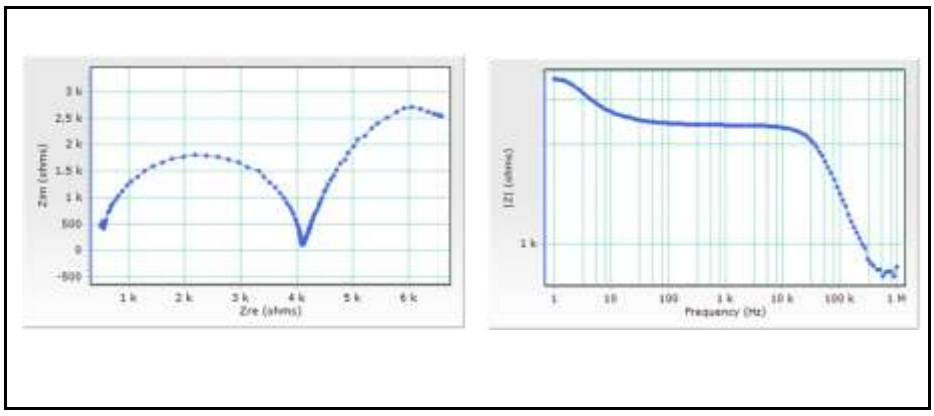


Fig-7. Impedance and CV of Pure MnO_2 nanoparticles



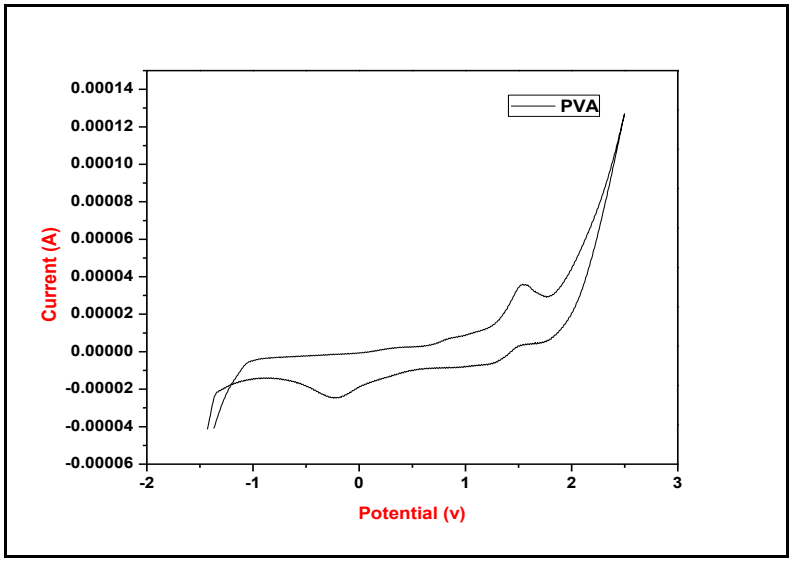
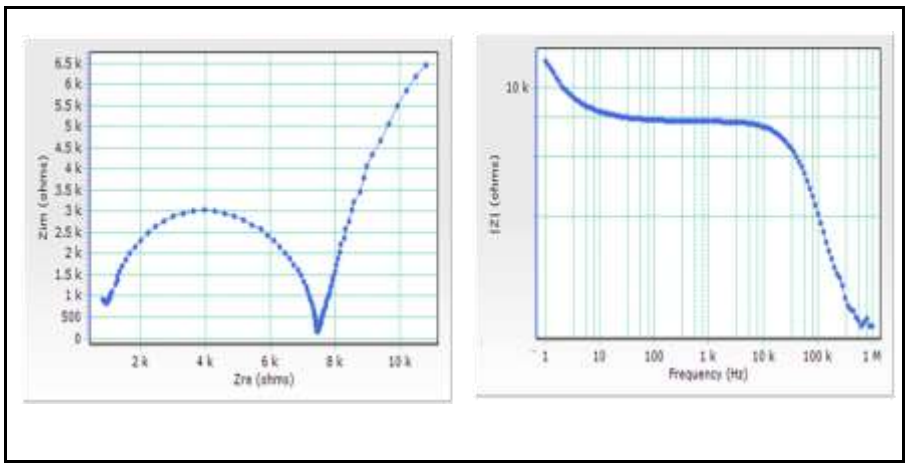


Fig-8. Impedance and CV of MnO_2 nanoparticles embedded with PVA



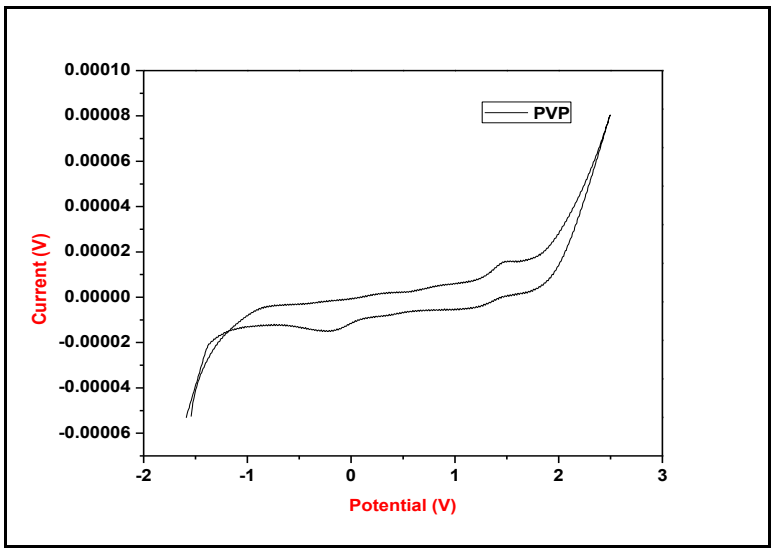


Fig-9. Impedance and CV of MnO_2 nanoparticles embedded with PVP

The specific capacitance of MnO_2 Nanoparticles and Pure MnO_2 are 164 F/g, surfactant with PVA 1235 F/g and surfactant with PVP 151 F/g.

3.8. Catalytic Dye Degradiations

3.8.1. MnO_2 catalyst performance of Rhodamine B dye

The catalytic efficiency of MnO_2, nanoparticles, $MnO_2$with PVA and MnO_2withPVP on Rhodamine B, were investigated in the presence of $NaBH_4$.the UV spectrum are recorded Rhodamine B dye are shows at the absorption peak around at (553 nm), which is correspond to n-π^* transition confirmed and shoulder peak exhibited at 523 nm.

The catalytic reaction was monitored spectro-photometrically by following degrees of absorption were gradually decreases with respect to periodic time interval.

% dye degradation = C_0-C_t / C_0*100 (5)

Where C_0- initial concentration of dye solution, C_t- illuminating dye concentration with respect time. The rate of degradation was calculated using the below equation

$Ln(C_0/C_t) = kt$ **(6)**

Where

T- Time, K- Rate constant

3.8.2. Effect of contact time

The rate of absorption of dye decreased with the increase in contact time 02 to 18minutes,0 to 12minutes and 0 to 14 minutes for pure MnO_2, MnO_2 embedded PVA and MnO_2 embedded PVP respectively, dye degradation are reached to an optimum value were the absorption occur equilibrium . The rate of absorption indicated that the removal of 25% of Rhodamine-B was observed in the first 2 minutes. The maximum absorption capacity of Rhodamine B on MnO_2 nanoparticles was obtained at 18minutes, 12minutes and 14minutes for a MnO_2 embedded PVA and MnO_2 embedded PVP respectively.

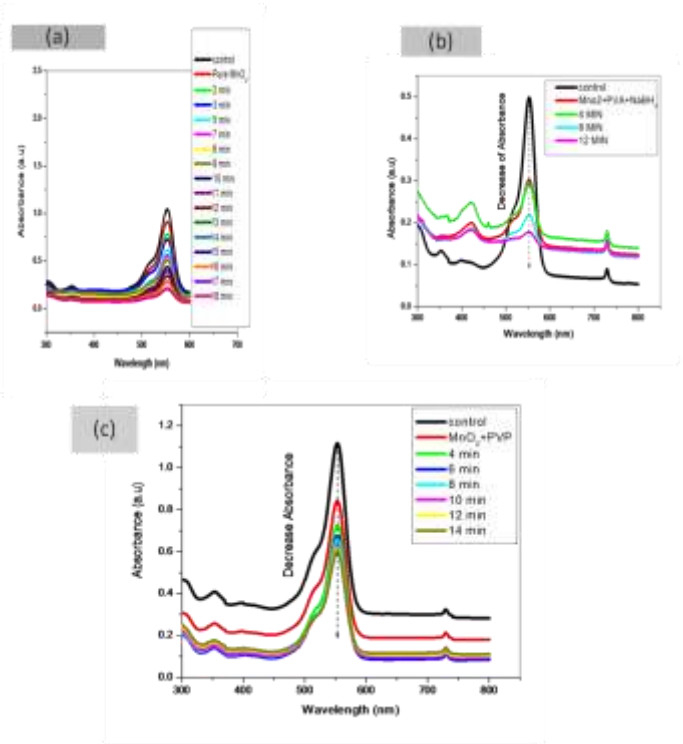


Fig-10. UV-visible of Rhoda mine B (a) Pure MnO_2, (b) PVA assisted MnO_2 (c) PVP assisted MnO_2 nanoparticles.

4. Conclusion

A good optical quality MnO_2nanoparticles was synthesized by hydrothermal method Grain size, dislocation density and micro strain are calculated from the XRD results of the MnO_2, MnO_2/PVA, MnO_2/PVP nanoparticles. FT-IR spectral studies confirmed that the various functional groups are present in the MnO_2 nanoparticles. The UV-Visible absorption spectra shows that MnO_2 nanoparticlesare transparent in the entire visible and NIR regions with lower cut-off wavelength at 250 nm. The band gap energy (Eg) for the MnO_2, MnO_2 / PVA, MnO_2/PVP nanoparticles was found to be 6.2, 6.04 and 5.16eV.

The catalysis activity of Pure MnO_2, MnO_2 / PVA and MnO_2 / PVP nanoparticles was investigated. The impedance analysis of pure MnO_2nanoparticles the values of R and C_{dl} are 5908.1 ohm and 4.979 farad. The values of R and C_{dl} 3582.7 ohm, 9.443 farad and 6688 ohm,4.993 farad for MnO_2 embedded with PVA and PVP respectively. The specific capacitance of MnO_2 Nanoparticles and Pure MnO_2 are 164 F/g, surfactant with PVA 1235 F/g and surfactant with PVP 151 F/g. Among these synthesized nanoparticles, MnO_2 nanoparticles were acting as a very good co-catalysis.

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