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Synthesis, Characterization and biological activities of polymer and chitosan-metal oxides Nano composites

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Abstract- **Nanocomposites, a high performance material exhibit unusual property combinations and unique design possibilities. With an estimated annual growth rate of about 25% and fastest demand to be in engineering plastics and elastomers, their potential is so striking that they are useful in several areas ranging from packaging to biomedical applications. Being environmentally friendly, applications of nanocomposites offer new technology and business opportunities for several sectors of the aerospace, automotive, electronics and biotechnology industries. In this work, the four polymer-metal oxides (V_2O_5) and chitosan (CHIN) based metal oxides nanocomposities (V_2O_5 and In_2O_3) were synthesized using chemical methods. All the nanocomposites were characterized by various spectral techniques like UV-Vis absorption, photoluminescence, FT-IR, XRD, DSC and AFM studies. The chitosan-metal oxides nanocomposites were further characterized by FESEM study. The AFM studies shows that the prepared polymer - V_2O_5 nano composites and Chitosan - metal oxide nanocomposites sizes in the range from 51 to 112nm and 55 to 115nm respectively. The FESEM studies shows that both the chitosan-In_2O_3 nanocomposite and chitosan-V_2O_5 nanocomposites have nano rock and stone like structures respectively. Their antibacterial and antifungal studies were also carried out for chitosan- metal oxides nanocomposites. However chitosan-V_2O_5 nanocomposite has higher antibacterial activity than chitosan-In_2O_3 nanocomposite.**

Keywords: Nanocomposites, chitosan, polymers and nanorock structure.

I. INTRODUCTION

A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nano-scale repeat distances between the different phases that make up the material. Ajayan *et al.*[1] note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix. The vanadium pentoxide (V_2O5) / carbon nanofiber composites (CNFCs) were prepared from polyacrylonitrile / V_2O_5 in N,N-dimethylformamide by a simple electrospinning method, and their electro chemical properties as supercapacitor electrodes were investigated[2]. Nanocrystalline transition metal oxides (TMOs) have been the topic of research for decades due to their technological applications like lithium-ion batteries, photocatalytic degradation, etc. and fundamental aspects like surface-to-volume ratio, increased chemical reactivity, special optical properties and exceptional electronic properties [3].

TMOs find application in various fields like catalysis [4], electrochromism [5], energetics [6] and energy storage devices [7]. Nano structured vanadium pentoxide/carbon (V_2O_5/carbon) composite powders with enhanced specific capacitance were synthesized by the spray pyrolysis technique[8]. Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. chotosan obtained from the deacetylation of chitin is a natural, abundantly available cationic polysaccharide [9]. It has various commercial and biomedical uses [10]. Chitosan is a well-known polysaccharide that can be used as thickening agents in the food industry and in drug release system in pharmaceutical applications. Over recent years, hybrid materials based on chitosan have been developed, including conducting polymers, metal NPs, and oxide agents, due to their excellent properties of individual components and outstanding synergistic effects [11].

Chitosan is a polysaccharide characterized by the presence of hydroxyl and amino functional groups in its chains. From the chemical point of view, it has the ability to interact with metal ions, organic halogen substances, and biological molecules, through a variety of mechanisms including chelation, electrostatic attraction, and ion exchange. For these reasons, chitosan has been successfully used in environmental applications, such as the removal of contaminants from wastewater [12].

II. EXPERIMENTAL PROCEDURE

Preparation of polyaminothiophenol (PATP)-V2O5 nanocomposites:

The preparation of PATP- V_2O_5 was carried out by dissolving 1mL of aminothiophenol in 20mL of dil.HCl and it was stirred for about five minutes. To the stirring solution, 1g of V_2O_5 powder was added and it was continued to stir for about half an hour. After half an hour of stirring, 2mL of H_2O_2 was added and continue to stirring till the colour of the solution turns to dark green. The dark green precipitate thus obtained was filtered, washed several times with water and air dried at room temperature.

Preparation of polyaminobenzoic acid (PABA)-V_2O_5 nanocomposites:

The preparation of PABA- V_2O_5 was carried out by dissolving 1.56g of p-aminobenzoic acid in 20mL of dil.HCl and it was stirred for about five minutes and the colour of the solution was pale brown. To the stirring solution, 1.56g of V_2O_5 powder was added and stirring is continued for half an hour. After half an hour of stirring, 2mL of H_2O_2 was added and continue to stirring till the colour of the solution turns to dark reddish brown. The dark brown precipitate thus obtained was filtered, washed several times with water and air dried at room temperature.

Preparation of chitosan / V_2O_5 and In_2O_3 nano composites:

The Chitosan/metal oxides nanocomposites was prepared by mixing vanadium oxide (V_2O_5) and In_2O_3 with chitosan in the ratio 3:2 in water and the aqueous mixture was kept for 24hr. The mixture was stirred well with 4g of sodium dodecyl sulfate at 70˚C for five hours. Then the mixture was calcined at 200˚C to get chitosan/ metal oxide nanocomposites.

III. RESULTS AND DISCUSSION

XRD analysis of PATP-V_2O_5 and PABA-V_2O_5 nanocomposites

The X-ray diffraction pattern for PATP-V_2O_5 nanocomposite is given in the Fig 3.**1.1(a)** and it shows that the high intensity peaks at the range 2θ value from 15.38° to 32.34°. The crystalline sizes of the nano composites were calculated from Debye-Scherrer formula, $D=0.94l/\beta \cos\theta$ where λ is the wavelength of Cu $K_{\alpha1}$ radiation (λ=1.5406 Å), β the full width at half maximum of peak and θ is the diffraction angle obtained from 2θ value. The average size of the nanocomposites was calculated to be 11.0 nm and from the XRD data, PATP-V_2O_5 nano composite is semi crystalline in nature. The X-ray diffraction pattern for PABA-V_2O_5 nanocomposite is given in the Fig 3.**1.1(b)** and it shows that the high intensity peaks at the range 2θ value from 11.98° to 50.44°.The particle size is 15.7 nm which is calculated from the Scherrer's formula and from the XRD data, PABA-V_2O_5 nanocomposite is amorphous.

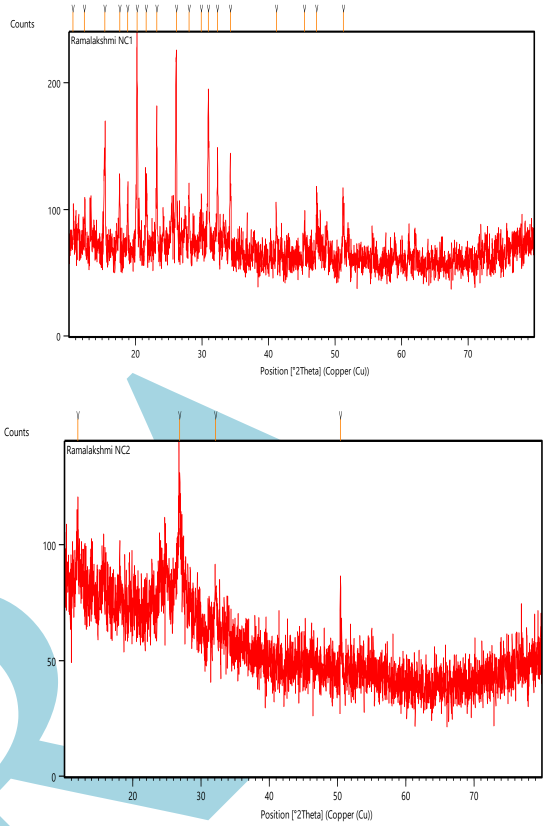
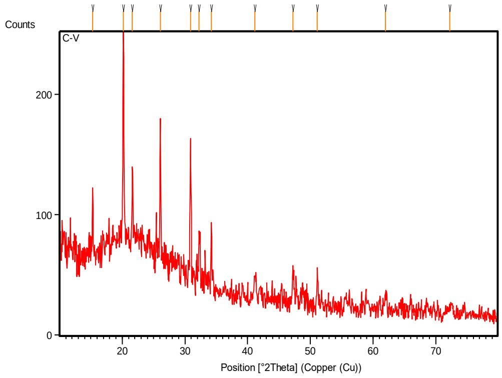


Fig 3.1.1 XRD behavior of (a) PATP-V_2O_5 (b) PABA-V_2O_5 nanocomposites

XRD behaviour of CHIN -V_2O_5 and CHIN- In_2O_3 nanocomposites

The X-ray diffraction pattern for CHIN-V_2O_5 nano composite is given in the Fig **3.1.2 (a)** and it shows that the high intensity peaks at the range 2θ value from 15.27° to 34.18°.The particle size is 13.7 nm which is calculated from the Scherrer's formula. The X-ray diffraction pattern for CHIN- In_2O_3 nanoparticles is given in the Fig **3.1.2(b)** It shows that the high intensity peaks at the range 2θ value from 10.96° to 37.79°. The particle size is calculated as 13.2 nm using Scherrer's formula and which is crystalline in nature.



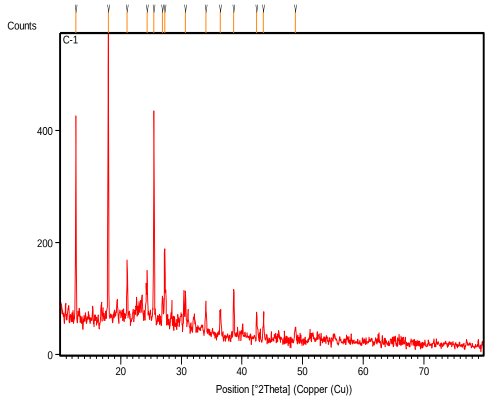


Fig.3.1.2 XRD behavior of (a) CHIN-V2O5 (b) CHIN-In2O3 nanocomposites

FT-IR Spectrum OF PATP- V_2O_5 and CHITOSAN-In_2O_3

The FT-IR spectrum of PATP- V_2O_5 is given in Fig 3.**2(a)** The IR bands corresponding to the –NH stretching vibration mode is shifted to the lower wavenumber and become broader in the IR spectra of PATP- V_2O_5, corresponding to pure PATP. This indicates that -NH stretching of PATP is involved in the assembling of vanadium oxide and also the bands between 400-1050 cm^{-1} show the presence of vanadium oxide particles in the PATP. The FTIR spectra of the CHIN-In_2O_3 is given in the Fig 3.2. (b). It exhibits characteristic IR bands of the functional group corresponding to pure CHIN and In_2O_3 nanoparticles. The IR bands corresponding to the –NH and OH stretching modes are broader and stronger peak at 3446 cm-1 which indicated the strong interaction between these groups and In_2O_3. The absorptions around 500 is due to In_2O_3 nanoparticles[13].

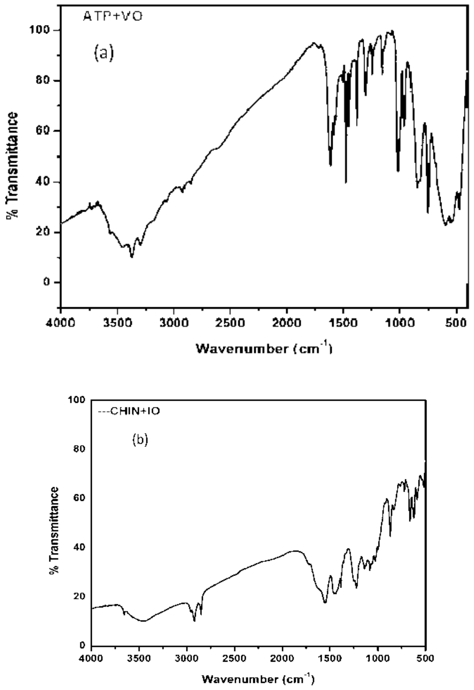


Fig 3.2FT-IR spectra of (a) PATP- V_2O_5 (b) CHIN-In_2O_3

UV-visible absorption spectra of PATP-V_2O_5 and PABA-V_2O_5

The UV-visible absorption spectrum of the PATP- V_2O_5 nanoparticle in aqueous medium is shown in the Fig 3.3 (a). It has a peak at 350 nm shows a red shift compared to the polymer and a blue shift compared to vanadium oxide which shows the formation of polymer vanadium nanocomposites. The UV-Visible spectrum of the PABA- V_2O_5 nanocomposite in aqueous medium is shown in the Fig 3.3(b)**.** It has a peak at 268 nm shows a red shift compared to the polymer and a shoulder at around **2**07 nm which is due to the formation of polymer vanadium nanocomposites.

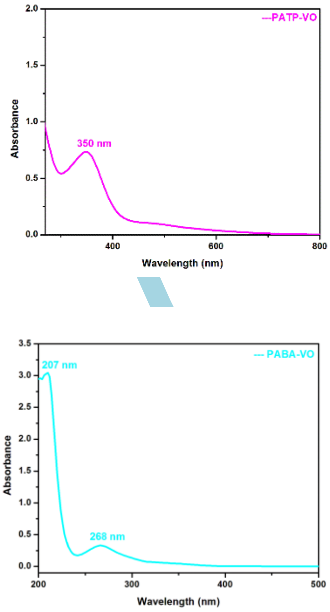


Fig 3.3 UV-Vis absorption spectra of (a) PATP-V2O5 (b) PABA-V_2O_5

Photoluminescence spectra of CHIN- In_2O_3 and CHIN-V_2O_5

The PL spectra of Chitosan- Indium oxide nanocomposite is shown in the Fig 3.4(a). The peak intensity of CHIN-IO is around 682 nm and for IO is around 533 nm. It is noticed that CHIN-IO nanocomposite's intensity get enhanced due to the binding of chitosan with indium oxide, corresponding to pure indium oxide respectively. The PL spectra of Chitosan-Vanadium oxide nanocomposite is shown in the Fig 3.4(b). The peak intensity of CHIN-VO is at 424.4 and for VO is at 372.7. It is noticed that CHIN-VO nanocomposite's intensity get enhanced due to the binding of chitosan with vanadium oxide, corresponding to pure vanadium oxide respectively.

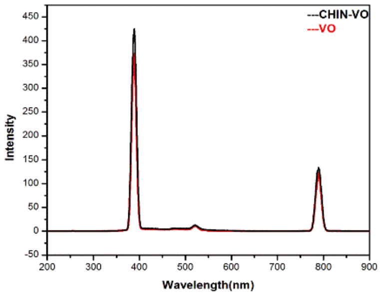


Fig 3.4 PL spectra of (a) Chitosan -In_2O_3 (b) Chitosan - V_2O_5

Differential scanning calorimetric study of PATP-V_2O_5 and PABA-V_2O_5 nanocomposites

The DSC thermogram for the poly amino thiophenol-V_2O_5 nanocomposite is shown in the Fig 3.5 (a) with the temperature range from 50 to 450^{0}C and from the DSC thermogram the glass transition temperature (Tg), crystallization transition temperature (Tc) and melting point (Tm) are determined and which are given below.

Glass transition temperature (Tg) = 60^{0}C,
Crystallization transition temperature (Tc) = 102^{0}C, 185^{0}C.
Melting point (Tm) = 108^{0}C, 132 ^{0}C and 408 ^{0}C .

The DSC thermogram for the polyaminobenzoic acid-V_2O_5 nanocomposite is shown in the Fig 3.5 (b). with the temperature range from 50 to 450^{0}C and from the DSC thermogram the glass transition temperature (Tg), crystallization transition temperature (Tc) and melting point (Tm) are determined and which are given below.
Glass transition temperature (Tg) = 150^{0}C
Crystallization transition temperature (Tc) = 240^{0}C
Melting point (Tm) = 274^{0}C and 403^{0}C.

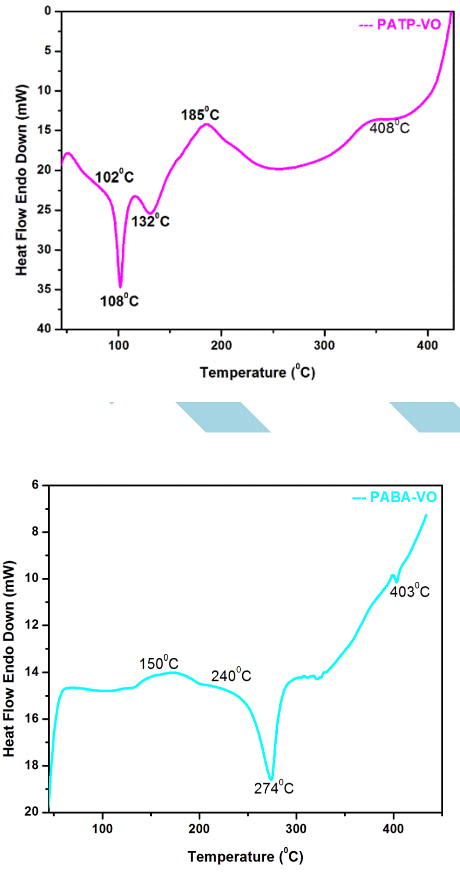


Fig 3.5 (a) DSC of PATP- V_2O_5 (b) PABA- V_2O_5 nanocomposites

Atomic Force Microscopy study of PATP -V_2O_5 and PABA -V_2O_5 nanocomposites

The AFM image of PATP -V2O5 nanocomposite (Fig 3.6.1(a)) are shown below. The PATP -V2O5 nanocompoosite size is in the range of 54 to 112 nm. The AFM image of PABA -V2O5 nanocomposite (Fig 3.6.1 (b)) is shown below. The PABA -V2O5 nanocompoosite size is in the range of 51 to 102 nm. This confirms that the particles are in the nanosize range.

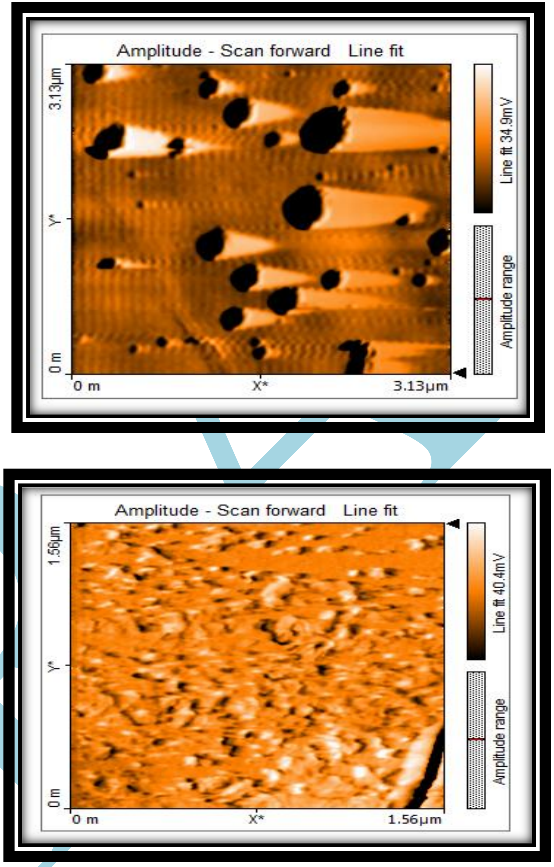
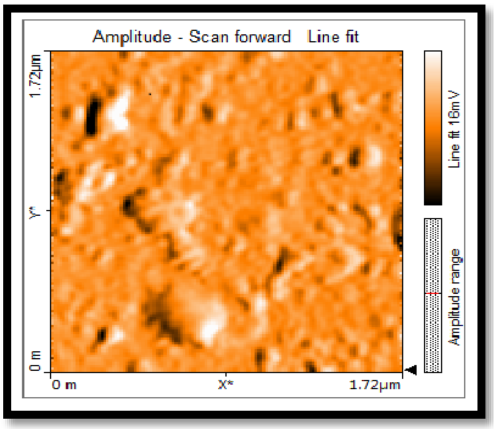


Fig 3.6.1 AFM image of (a) PATP -V_2O_5 (b) PABA -V_2O_5 nanocomposite

Atomic force microscopy study of chitosan- In_2O_3 and chitosan- V_2O_5 nanocomposites

The AFM images of Chitosan- In_2O_3 nanocomposite (Fig 3.6.2(a)) and Chitosan-V_2O_5 nanocomposite (Fig 3.6.2(b)) are shown below. The Chitosan -In_2O_3 nanocomposite is in the range of 55 to 107 nm and Chitosan-V_2O_5 nanocompoosite size is in the range of 67 to 115 nm.



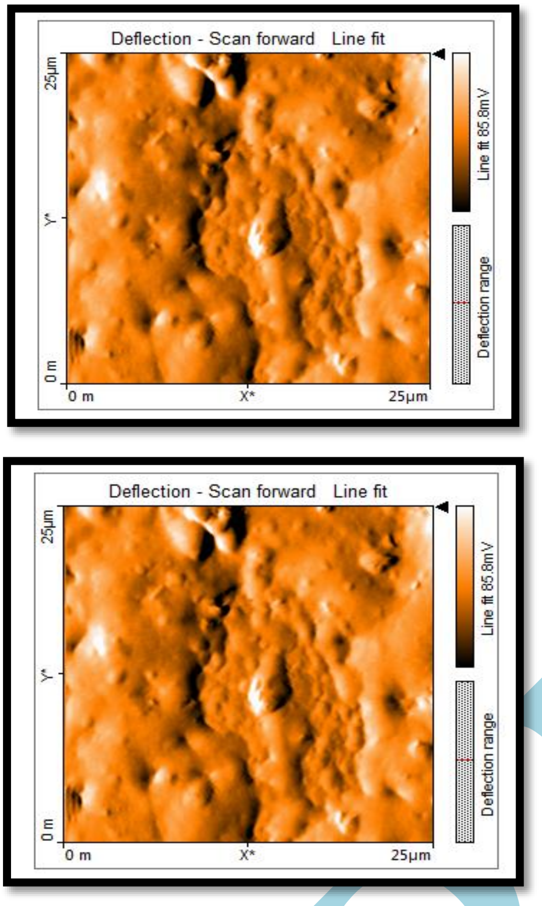


Fig 3.6.2 (a) AFM image of Chitosan- In2O3 (b) Chitosan- V2O5 nanocomposites

FESEM OF CHIN- In_2O_3

The FESEM of Chitosan- In_2O_3 and Chitosan-Vanadium Oxide nanocomposites are shown in the following Fig 3.7(a) and 3.7(b). The surface morphology of CHIN- In_2O_3 and CHIN- V_2O_5 nanocomposite are given and it is noticed that the nanocomposites are nanorock and stone like structures respectively.

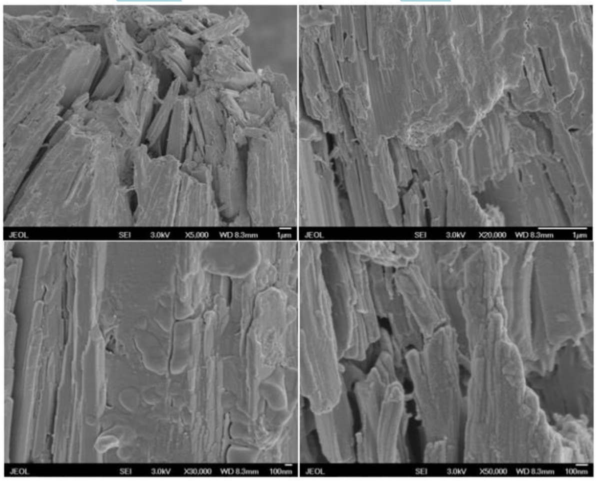


Fig 3.7 (a) FESEM of CHIN- In_2O_3 nanocomposite

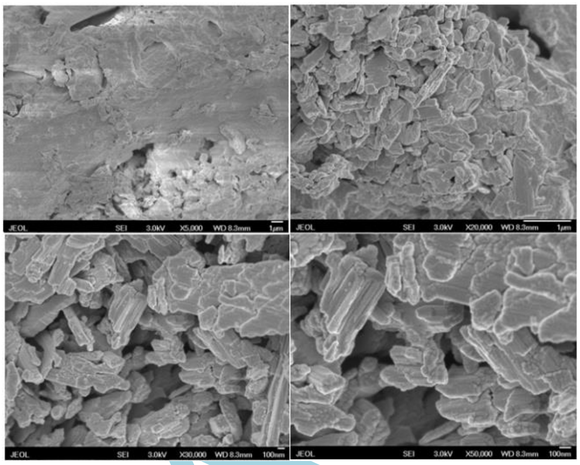


Fig 3.7 (b) FESEM of CHIN- V_2O_5 nanocomposite

ANTIBACTERIAL STUDIES

Bacteria such as *E.Coli, Pseudomonas aeruginosa, Salmonella typhi and Staph aureus* are investigated for the bacterial inhibition of Chitosan- V_2O_5 nanocomposite and Chitosan- In_2O_3 nanocomposite. The results are shown in the following table **I** and the antibacterial images are shown below from Fig 3.8(1 – 8). respectively

Table I: Antibacterial values for chitosan-V_2O_5 and chitosan- In_2O_3 nanocomposites

BACTERIA	CHIN-V_2O_5	CHIN-In_2O_3	CONTROL
E.coli	34mm	19mm	9mm
P.aeruginosa	24mm	24mm	20mm
Salmonella typhi	54mm	31mm	35mm
Staph aureus	26mm	19mm	14mm

From the result, it can be determined that CHIN-V_2O_5 and CHIN-In_2O_3 have good antibacterial activity, especially, the CHIN- V_2O_5 nanocomposite has higher antibacterial activity than CHIN- In_2O_3. Also, both the nanocomposites have higher inhibition rate towards Salmonella typhi bacteria.

ANTIFUNGAL STUDIES

Fungi such as Candida albicans, Candida parapsilosis, Candida tropicalis and Candida krusei are investigated for the fungal inhibition of Chitosan- V_2O_5 nanocomposite and Chitosan- In_2O_3 nanocomposite. The results are shown in the following table II and the antifungal images are shown below from Fig 3.9 (1- 6) respectively. From the table, it can be determined that CHIN-V_2O_5 and CHIN- In_2O_3 are inactive towards fungi. Hence, CHIN- V_2O_5 and CHIN- In_2O_3 nanocomposites does not have antifungal property.

Table II Antifungal values for chitosan-V_2O_5 and chitosan- In_2O_3 nanocompoosites

FUNGI	CHIN-V_2O_5	CHIN-In_2O_3	CONTROL *(Gentamycin)*
Candida albicans	19mm	13mm	25mm
Candida tropicalis	35mm	18mm	35mm
Candida parapsilosis	14mm	13mm	17mm
Candida krusei	18mm	21mm	-

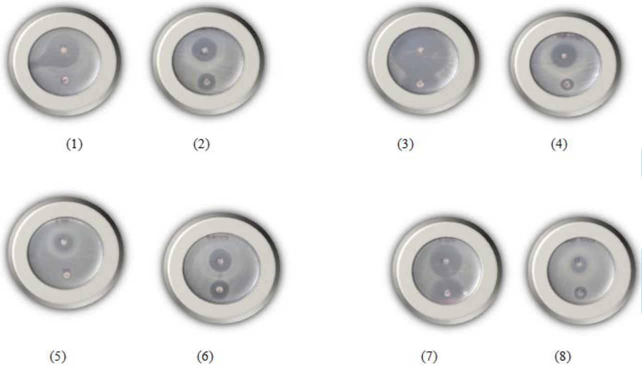


Fig 3.8 Antibacterial images of CHIN-V2O5 and CHIN-In2O3 using (1) & (5) E.Coli, (2)&(6) Pseudomonas aeruginosa, (3) & (7) S.Typhi, (4) & (8) Staph.aureus

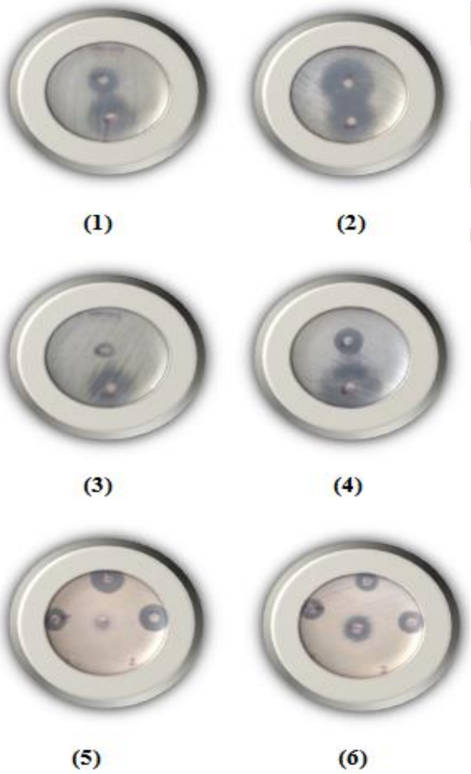


Fig 3.9 Antifungal images of CHIN-V2O5 and CHIN-In2O3 using (1) & (3) C.albicans (2) &(4) C.tropicalis (5) C.parapsilosis (6) C.krusei

REFERENCES

1.P.S.M.Ajayan,L.S.Schadler,P.V.Braun.,Nano composite science and technology. 2003, 3-527-3059-6.

2. Bo-Hye Kim, Chang Hyo Kim, Kap Seung Yang, Abdelaziz Rahy, Duck J. Yang. Electrochimica Acta, 83 2012, 335– 340.

3. A.Henglein, Chem Rev., 89, 1989, 1861-1873.

4. M. A. Zhen, B. Zhou, Y. Ren, Front. Environ. Sci. Eng., 7, 2013, 341–355.

5, D. T. Gillaspie, R. C. Tenent, A. C. Dillon, J. Mater. Chem. 20, 2010, 9585–9592.

6. J. Meyer , S. Hamwi , M. Kröger , W. Kowalsky , T. Riedl , A. Kahn, Adv.Mater. 24, 2012, 5408–5427.

7. X. Xia, Y. Zhang, D. Chao, C. Guan, Y. Zhang, L. Li, X. Ge, I. M. Bacho, J. Tu, H. J.Fan, Nanoscale 6, 2014, 5008–5048.

8. Bei Wang; Konstantin Konstantinov; David Wexler; Hao Liu; GuoXiu Wang. Electrochimica Acta.,54., 2009., 1420–1425

9. S.K. Janardhanan, R. Indumathy, B.U. Nair,Trans. Met. Chem. 33 (2008) 127-131.

10. A.A. Sunil, N.M. Nadagouda, M.A. Tejraj, J. Contr. Release., 100 (2004) 5-28.

11. L.H. Li, J.C. Deng, H.R. Deng, Z.L. Liu, L. Xin, Carbohydrate Res. ,345 (2010) 994-998.

12. Lalov, I.G.; Guerginov, I.I.; Krysteva1, M.A.; Fartsov, K, Water Res. 2000, 34, 1503–1506.

13. Bhadra, P., Mitra, M. K., Das, G. C., Dey, R., Mukherjee, S., Materials Science and Engineering C., 2011, 31 (5), 929–937.