A Novel Hybrid Organic-Inorganic Cdo Doped Poly-O-Toluidine Polymer Nanocomposite For Gram Positive Anti-Microbial Activity

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Abstract: An organic-inorganic hybrid Poly-o-toluidine-CdO (POT-CdO) nanocomposite has been synthesized by Insitu chemical oxidative polymerization method. The prepared pure POT and POT-CdO (50%) polymer nanocomposite are characterized by using FTIR, UV-Vis, XRD, SEM, EDAX and antimicrobial activities. In FTIR spectra reveals the information of functional groups (N-H, C-H, C-C, C=C) in pure POT and POT-CdO (50%) nanocomposites also confirm interaction between POT and CdO nanoparticle, The optical absorbance of pure POT and POT-CdO was measured in the range of 250-1000 nm. This absorption spectrum shows two absorption bands centered at 316, 622 nm (pure POT) and the optical band gap energy is (3.93 eV, 1.99 eV) and 314, 613 nm are observed in POT-CdO (50%) nanocomposite and the optical band gap energy is (3.95 eV, 2.02 eV). The XRD pattern of pure POT shows the amorphous nature and the XRD pattern of POT-CdO nanocomposites reveals high crystalline material. The SEM micrograph of POT has porous and irregular structure and POT-CdO nanocomposites are highly agglomerated and form cluster spherical shaped morphology due to Vander Waals force of attraction, the morphology of the material has been confirmed with the formation of organic-inorganic nanocomposite material. The EDAX spectrum of pure POT and POT-CdO nanocomposites C, S, O and Cd elements are present in different weight percentage. The antibacterial activity of pure POT and POT-CdO nanocomposites against gram positive and gram negative were observed using agar well diffusion method. It was also found that POT-CdO has enhanced antibacterial activity compared to pure POT.

Index Terms: Poly-O-toluidine (POT), Cadmium oxide (CdO), Nanocomposites, Antibacterial activity

1. INTRODUCTION

In the recent decades, Conductive polymeric materials have been occupied more important and pivotal position in the field of scientific and technological areas [1-3]. A novel of hybrid organic-inorganic materials present one of the most hastily augments areas of the conducting polymers [4-8]. Hybrid used to modify organic polymeric material or to modify inorganic materials that exhibit very different properties from the original component [9-10]. Among the entire conducting polymers poly (o-toluidine) [11-12] and its derivatives such as polyanline (PANI) [13-14] and poly-o-anisidine are most promising polymeric material which are frequently used because of its easy synthesis, flexibility, high electrical conductivity, thermal stability, environmental stability, electrochemical, optical, electrical properties and other medical field applications[15]. Polypyyrole (PPy) [16] and polyanline (PANI) [17-19] is by far the most investigated conducting polymer. However, major problem related to its successful utilization lays in its poor mechanical properties and process ability due to its insoluble nature in common organic solvents [20-21]. The common way to change the physical and chemical properties of polymer is to substitute the polymer chain with special chemical groups like $–CH_3$,$-C_2H_5$, -OH, $-OCH_3$ [22] etc. Poly-o-toluidine has attracted considerable attention as they exhibit better solubility in many solvents and better processability than PPy and PANI [23-28]. The aim of our work is to synthesize and characterize the POT and doped with cadmium oxide (CdO) by insitu chemical oxidative polymerization method. In the order of investigate the properties of POT and doped with CdO. The sample has been characterized by FTIR, XRD, UV-Vis, SEM, EDAX and antibacterial activities were investigated. Hence an attempt has been made to synthesize POT and to study their biological applications.

2. Experimental

2.1 Synthesis of Poly-o-toluidine-CdO nanocomposites

Pure POT and POT-CdO nanocomposite are synthesized by using chemical oxidative polymerization and Insitu chemical oxidative polymerization method respectively. ortho-toluidine [1M] act as a monomer was dissolved in de-ionized water at room temperature, then a sulfuric acid ($H_2SO_{4)}$ [1M] was added to the above suspension solution and the inorganic material cadmium oxide (CdO) [1M] is added which this solution was magnetically stirring for 1hr. After 1hr the polymerization reaction is performed by adding to the oxidant ammonium per sulphate (APS) [0.5M] solution under vigorous stirring. After a 24hrs reaction time, the obtained green precipitate is filtered and washed using de-ionized water, and acetone and ammonia solution until obtaining a dark blue precipitate is filtrate. Obtained the resultant residual was dried thoroughly in an oven at 60 ˚C for 24hrs, then grinded and sieved in pestle mortar to get powder form.

3. Result and Discussion

3.1 FTIR Characteristics

The FTIR spectra of pure POT and POT-CdO (50%) nanocomposite are shown in Fig.1. The characteristic bands peak of 3431.17 cm^{-1} pure POT and 3426.57 cm^{-1} POT-CdO (50%) due to the presence of N–H stretching mode. The band at 2925.97 cm^{-1} of pure POT, 2928.27 cm^{-1} POT-CdO (50%) is associated with C–H stretching in methylene group. The peak positions related to corresponding chemical bonds are listed in Table.1.

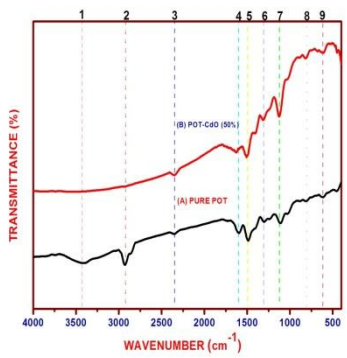


Fig.1 *FTIR spectra of pure POT and POT-CdO (50%) nanocomposites*

Wavenumber(cm^{-1})		*Band characteristics*
Pure POT	*POT-CdO (50%)*	
3431.17	*3426.57*	*N-H Stretching Vibration*
2925.97	*2928.27*	*C-H stretching due to substituent methyl group*
2353.32	*2350.25*	*C=C Stretching Vibration*
1599.74	*1622.79*	*C-N Stretching of quinoid Rings*
1490.11	*1513.11*	*C-N Stretching of benzeniod rings*
1302.64	*1313.79*	*Aromatic C-N Stretching indicating secondary aromatic amine group*
1113.71	*1124.44*	*C-H in plane bending vibration*
817.03	*815.50*	*Paradisubstituted aromatic rings indicating polymerization*
616.81	*596.25*	*C-H out of plane bending vibration*

Table: 1 *FTIR Wavenumber region of pure POT (A) and POT-CdO (50%) (B) nanocomposite*

The presence of the pure POT and POT-CdO (50%) in the vicinity of 1490.11 cm^{-1} and 1513.11 cm^{-1} are assigned to the nonsymmetric C_6 ring stretching modes. The higher frequency vibration at 1599.74 cm^{-1} and 1622.79 cm^{-1} has a major contribution from the quinoid rings while, the lower frequency mode at 1490.11 cm^{-1} depicts the presence of benzeniod rings. The presence of these pure POT and POT-CdO (50%) bands clearly shows the interesting phenomenon specifies there is a good interaction between POT and CdO and also confirmed the doping of CdO in the POT polymer matrix.

3.2 XRD Analysis

The XRD pattern of pure POT and POT-CdO (50%) nanocomposite are shown in Fig.2. The pure POT, the XRD pattern indicates which are attributed to amorphous nature. In POT-CdO nanocomposites exhibited sharp peak indicates the semi-crystalline nature of the material and the sharp crystalline peaks of POT-CdO nanocomposites are reduced the amorphous nature of POT. This suggests that the changes in overall crystalline of nanocomposite are due to blending of inorganic precipitate CdO into polymer matrix.

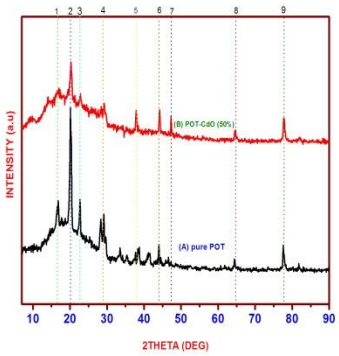


Fig.2 *XRD pattern of pure POT (A) and POT-CdO (50%) (B) nanocomposites*

Pure POT					
Peak No	2 Theta (Deg)	FWHM (Deg)	d Spacing (Å)	Crystal size (nm)	Average Crystal Size (nm)
1	16.6393	0.89860	5.32359	9.34	19.27
2	20.1473	0.58030	4.40388	14.53	
3	22.6449	0.46770	3.92349	18.11	
4	29.0943	0.50480	3.06677	16.99	
5	29.7000	0.28000	3.00559	30.68	
6	38.4835	0.71570	2.33740	12.29	
7	43.9553	0.37060	2.05828	24.16	
8	46.4650	0.43000	1.95278	21.02	
9	77.6004	0.40480	1.22932	26.32	

POT-CdO (50%) nanocomposites					
Peak No	2 Theta (Deg)	FWHM (Deg)	d Spacing (Å)	Crystal size (nm)	Average Crystal Size (nm)
1	14.3000	2.57140	6.18877	3.25	4.66
2	20.0607	2.32140	4.42270	3.63	
3	22.6000	3.20000	3.93118	2.65	
4	28.8200	1.96000	3.09533	4.37	
5	37.9464	1.59290	2.36924	5.51	
6	44.1700	1.82000	2.04877	4.92	
7	47.1750	1.75000	1.92503	5.18	
8	64.6500	1.60000	1.44056	6.14	
9	77.7500	1.70000	1.22733	6.27	

Table: 2 *Crystalline properties of pure POT and POT-CdO (50%) nanocomposites*

The crystallite size D of pure POT and POT-CdO (50%) is estimated from the Scherrer's equation [32] given as

$$D = K\lambda / \beta \cos\theta$$

Where D is the mean crystallite size (nm), K is the shape factor (K = 0.9), λ is the wavelength of the X-rays (0.154056 nm for CuKα radiation), θ is Bragg angle and β is half of its maximum intensity (in radians). The crystallite size D measured using Scherrer's formula are tabulated shown in Table.2: The XRD pattern indicates the diffraction peaks at the angle of 20.06°, 22.60°, 28.82°, 37.94°, 44.17°, 64.65°, and 77.75°. The average crystallite size is 19.27 nm for pure POT and 4.66 nm for POT-CdO (50%) nanocomposites. The XRD pattern clearly reveals the incorporation of POT and CdO nanoparticles.

3.3 UV-Vis analysis

UV-Vis spectra are used to find qualitative information and the optical properties about pure POT and POT-CdO (50%) nanocomposite. The optical band gap energy (E_g) are obtained by using the fundamental law, $Eg=hc/\lambda_{max}$, where λ_{max} is the maximum absorption wavelength in nm. UV-Vis spectra of pure POT and POT-CdO nanocomposites are shown in Fig.3. The spectrum of pure POT show that there are two absorption bands at 316 and 622 nm, which are assigned to π-π* transition of the benzenoid ring and n-π* excitation of benzenoid to the quinoid ring in the polymer chain and the band gap energy are 3.93, 1.99eV. The POT-CdO nanocomposite spectrum also appeared two absorptions peaks and the wavelength range at 314, 613 nm and the band gap energy 3.95 and 2.02 eV respectively. The E_g value POT-CdO nanocomposites compared to the pure POT the band gap value is increased in the nanocomposites sample. The pure POT the peak intensity of the nanocomposites is increased with increasing the Cd ion concentration. This blue shifting and peak intensity phenomenon of the absorption peak in POT-CdO nanocomposites may be due to the doping effect. It is also observed that there is a blue shifting of the peak for the POT-CdO nanocomposites, only because of some interaction between the quinonoid ring of POT and CdO nanoparticles.

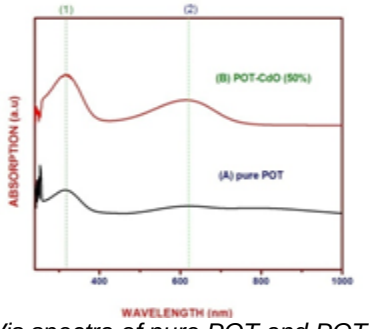


Fig: 3 *UV-Vis spectra of pure POT and POT-CdO (50%) nanocomposites*

S.No	Sample Name	Wavelength (nm)	Electron Transition	Band gap energy (eV)
1	Pure POT	316.00 622.00	π-π* n-π*	3.93 1.99
2	POT-CdO (50%)	314.00 613.00	π-π* n-π*	3.95 2.02

Table: 3 *UV-Vis spectra of pure POT (A) and POT-CdO (50%) (B) nanocomposites*

3.4 SEM analysis

The surface morphology of the pure POT and POT-CdO (50%) nanocomposites are characterized by SEM. It is clear from the photographs that after binding of organic polymer compound of POT with inorganic nanoparticle CdO the morphology of the material has been changed with the formation of POT-CdO nanocomposites

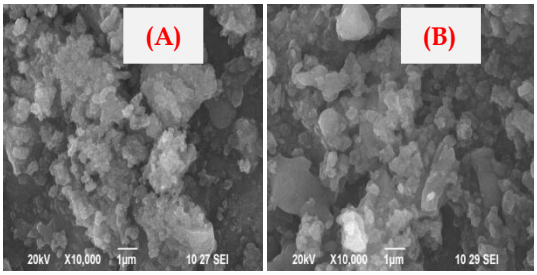
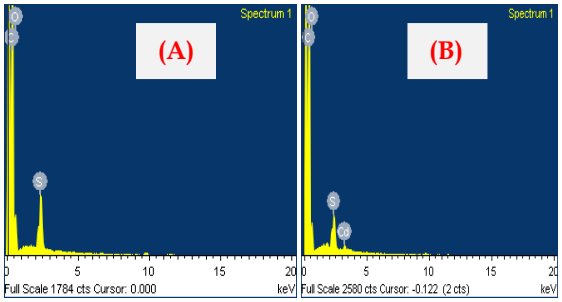


Fig: 4 *SEM micrographs of pure POT (A) and POT-CdO (50%) (B) nanocomposites*

The micrograph obtained at different magnifications reveals a flaky like with few a cluster structures which are seen in the SEM image. The photograph of the POT doped with CdO reveals crystalline as well as amorphous regions. The crystalline regions with shaped edged particles and lamellar sides were found to be interspersed in the amorphous regions containing of particles with no well defined the shapes.

3.5 EDAX

The elemental analysis was carried out in order to know about the chemical composition of polymer with various elements such as C, O and S present in pure POT. The carbon element of pure POT (76.64%) and POT-CdO (50%) (76.59%) the weight % of carbon element is decreased with adding of CdO nanocomposite, and the peak intensity decreased this changes clearly observed in the spectrum. Similarly the weight % of oxygen element in order of pure POT and POT-CdO (50%) nanocomposite are 21.12% and 21.10% respectively. Sulfur element is decreased with adding of CdO nanoparticles were obtained it is clearly listed in Table 4. Finally the Cd element is increased with increasing the weight 0.99% of CdO nanoparticle this results indicate the CdO is presence in nanocomposite and high interaction between POT and CdO nanoparticles.



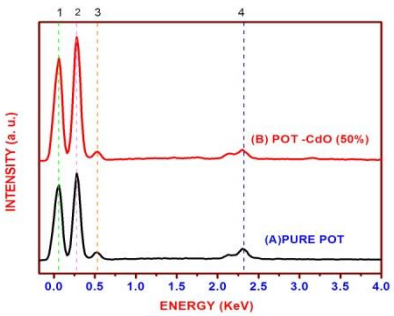


Fig: 5 *EDAX spectra of pure POT (A) and POT-CdO (50%) (B) nanocomposites*

S.No	Sample Name	Elemental composition (Wt %)			
		C	O	S	Cd
1	Pure POT	76.64	21.12	2.24	-
2	POT-CdO (50%)	76.59	21.10	1.32	0.99

Table: 4 *Summary of the elemental composition related to pure POT and POT-CdO (50%) nanocomposites*

3.6. Antibacterial activities

The antimicrobial activities of pure POT and POT- CdO (50%) nanocomposite were investigated using agar well diffusion method using nutrient agar media. Microorganisms obtained from IMTECH like Gram positive organisms like Bacillus cereus MTCC 430 & Staphylococcus aureus MTCC 3160; Gram negative organisms such as Escherichia coli MTCC 1698 and Klebsiella pneumonia (MTCC10309) were used. The pure POT sample does not shown any antimicrobial activity against both Gram positive as well as Gram negative organisms where as POT-CdO (50%) shows the antimicrobial activity against both organisms as shown in the Fig.6, & 7. The POT-CdO (50%) exhibit highest antimicrobial activity at 100µl concentration .In E.coli POT-CdO (50%) shows antimicrobial activity which is equal to the test antibiotic i.e., Erythromycin where as in K.pneumonia, POT-CdO (50%) shows the antimicrobial activity which is higher than the test antibiotic as shown in the Table.5. A show the results indicates that POT-CdO (50%) can be used against E.coli and K.pneumonia as an alternative to conventional antibiotics. Conducting POT and its composites are believed to be useful as an antibacterial agent, self-clean as well as multifunctional material for improving the human health and living environment.

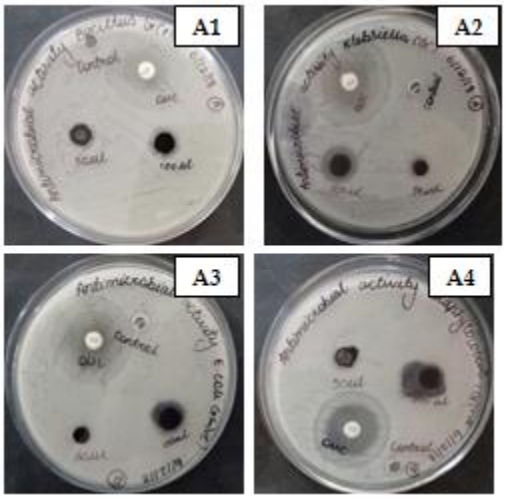


Fig.6 *Photographs of antimicrobial results of pure POT nanocomposites for Gram positive bacteria Bacillus cereus (A1), Staphylococcus aureus (A2), Gram negative bacteria Escherichia coli (A3), Klebsiella pneumonia (A4)*

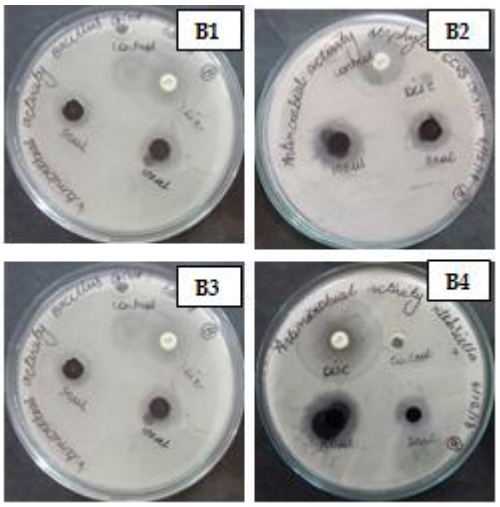


Fig.7 *Photographs of antimicrobial results of POT-CdO (50%) nanocomposites for Gram positive bacteria Bacillus cereus (B1), Staphylococcus aureus (B2), Gram negative bacteria Escherichia coli (B3), Klebsiella pneumonia (B4)*

Sample Name	Zone of Inhibition in Diameter (mm)							
	Gram positive				Gram negative			
	Bacillus cereus		Staphylococcus aureus		Escherichia coli		Klebsiella pneumonia	
	50 µl	100 µl	50 µl	100 µl	50 µl	100 µl	50 µl	100 µl
Pure POT	-	6	-	-	-	-	7	15
POT-CdO (50%)	12	17	17	21	15	22	15	22

Table: 5 *Photographs of antimicrobial results of pure POT (A) nanocomposites for Gram positive bacteria Bacillus cereus (A1), Staphylococcus aureus (A2), Gram negative bacteria Escherichia coli (A3), Klebsiella pneumonia (A4), and POT-CdO (50%) (B) nanocomposites for Gram positive bacteria Bacillus cereus (B1), Staphylococcus aureus (B2), Gram negative bacteria Escherichia coli (B3), Klebsiella pneumonia (B4),*

3.7 Conclusion

POT-CdO was successfully prepared by insitu chemical polymerization method .Ammonium per sulphate (APS) which act as oxidant and Sulfuric acid (H_2SO_4) which acts as dopant and the samples were name as a pure POT and POT-CdO (50%). From the characterization of prepared samples the following conclusions were arrived. The FTIR spectrum of as prepared composite confirms the molecular structure of synthesized samples. The XRD pattern of POT-CdO nanocomposites recorded the powder sample exhibited the sharp peaks which suggest semi-crystalline nature of the composite material. The UV spectra of the samples pure POT and POT- CdO (50%) are assigned to π-π*and n-π*transition. The maximum absorption peaks of the samples are observed at 613 nm and the corresponding band gap energy is found to be 2.02 eV. The scanning electron microphotograph (SEM) of pure POT and POT-CdO (50%) nanocomposites represent a flaky like feature with a cluster structures, the morphology of the material has been confirmed with the formation of organic inorganic composite material POT-CdO. The EDAX spectrum of POT-CdO nanocomposites gave C, O, Cd and S their weight%. The result indicates the existence of Cd and O from CdO, also C, O, and S from OT. The POT-CdO nanocomposites samples have been synthesized and their characteristics were analyzed, from the characterization techniques it was found that the properties of POT entirely changed due the addition of CdO. The pure POT sample does not shown any antimicrobial activity against both Gram positive as well as Gram negative organisms where as POT-CdO (50%) shows the antimicrobial activity against both organisms. POT-CdO (50%) can be used against E.coli and K.pneumonia as an alternative to conventional antibiotics. Conducting POT and its composites are believed to be useful as an antibacterial agent, self-clean as well as multifunctional material for improving the human health and living environment.

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