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Facile Preparation and Characterization of Polyaniline-iron Oxide Ternary Polymer Nanocomposites by Using “Mechanical Mixing” Approach

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ABSTRACT. Polymer science and technology has received momentous research consideration in last some decades. An effortless and cost-effective access to the synthesis of a nanocomposite material of polyaniline (PANI)-iron oxide Fe₃O₄ nPs has been improved. Polyaniline-iron oxide (PANI-nFe₃O₄) nanocomposites were synthesized by increasing the wt% of nano iron oxide (nFe₃O₄) with in the presence of PANI materials. Mechanical mixing method is used in the preparation of PANI-nFe₃O₄ nanocomposites material. The chemical structure of pure PANI and PANI-nFe₃O₄ nanocomposites is characterized by using Fourier Transform infrared spectroscopy and it is also used to analyze the stretching vibration, wavenumber shifting and chemical structure changes of nanocomposites. The optical properties were characterized by using UV-Visible spectroscopy and the band gap value of pure PANI, PANI-nFe₃O₄ (50%), PANI-nFe₃O₄ (100%) are 3.284 eV, 3.214 eV and 3.201 eV respectively; it was observed that the band gap value of nanocomposites decreased with increase in the concentration of Fe₃O₄ nanoparticles. Crystalline nature of pure PANI and its nanocomposites were analyzed by using the X-Ray diffraction spectroscopy. pure PANI has amorphous nature. By increasing the iron oxide nPs the amorphous nature of pure PANI decreases while its crystalline nature increases. The bacterial growth (E-Coli and staphylococcus aureus), the resultant increase in the zone of inhibition due to increase in the weight % of Fe₃O₄ nPs were studied using antibacterial activity.

Introduction. In recent research, the preparation of conducting polymer nanocomposites (CPnCs) has obtained a great deal of interest in physics and chemistry materials research community because of different potential applications of these materials in chemical sensing, polymer batteries catalysis, energy storage, solar cells, light emitting diode (LED), organic light emitting diode (OLED) and medical diagnosis etc., [1]. The synthesis of organic-inorganic nanocomposites has become the subject of extensive studies. The nanocomposites containing organic polymers (polyaniline, polypyrrole, polythiophene, poly-o-toluidine etc.) and inorganic particles in nano metal oxide (nFe₃O₄, nNiO, nSb₂O₃, nZnO, nTiO₂, nCuO, nCrO₂, nV₂O₅ and nAl₂O₃ etc.) provide an entirely new class of materials with novel properties. Nowadays, syntheses of new CPnCs with improved mechanical properties, processability, or heat resistance in comparison to corresponding pure conducting polymers alone, as well as the studies of their electrical, optical, magnetic, and catalytic properties constitute a great scientific challenge [2]. Polyaniline (PANI) is one of the most extensively studied conducting polymers because of its simple synthesis and doping-dedoping chemistry, low cost, high conductivity, excellent environmental stability, and wide potential applicability, erasable optical information storage, shielding of electromagnetic interference, microwave and radar

absorbing materials, indicators, catalysts, electronic and bioelectronic components, membranes, electrochemical capacitors, electrochromic devices, nonlinear optical, electromechanical actuators, antistatic and anticorrosion coatings, high specific capacitance and electroactivity etc., The nanosized metallic particles have attracted attention of the materials community due to their unique properties [3]. In the present work, PANI-nFe₃O₄ nanocomposites were prepared by increased Fe nanoparticles in the presence PANI and different contents of Fe nanoparticles. PANI is a conducting polymer that contains positively charged amine/imine groups on its polymer chain, which may favor adhesion onto the Fe surface.

Experimental. All of the chemical reagents used in this experiment were A.R. grade. The monomer aniline (ANI) and sulphuric acid (H₂SO₄) as dopant were used as received. The polyaniline was synthesized by chemical oxidative polymerization under static condition in a lower temperature (0- 5 °C). Sulphuric acid (H₂SO₄) as a dopant was dissolved in about 500 mL of deionized water and the solution was well stirred in round-bottomed flask. Monomer aniline was added in the above suspension solution and keeps stirring for 0.5 hrs. After 0.5 h ammonium peroxydisulfate (NH₄)₂S₂O₈ as an oxidant was added drop wise slowly, until good degree of polymerization is achieved which results in green coloured solution. The entire mixture was continuously stirred well at 0-5 °C and the reaction was continued for another 24 h overall time speed of rotation was maintained at 600 rpm. The product was filtered and washed with deionized water, ethanol and acetone and by using ammonia solution the emeraldine salt form of polyaniline is change the emeraldine base form, then dried under vacuum at 70 °C for 24 h. PANI-nFe₃O₄ nanocomposites were prepared using different (50 and 100 %) wt % of nFe₃O₄ with respect to polyaniline which are referred as PANI-nFe₃O₄ nanocomposites. The molar ratio of polymer (PANI) and metal oxide (nFe₃O₄) was for the preparation of PANI-nFe₃O₄ (50 %) nanocomposites by using mechanical mixing method and similarly the samples were prepared in the different wt % of nFe₃O₄ nanoparticles PPy-nFe₃O₄ (100 %) by the ratio 1:0.50 and 1:1, respectively.

Result and discussion.

FTIR Spectra. The surface functional groups have been verified and the structural information on all the nanocomposites materials and transmittance of polyaniline in the PANI-nFe₃O₄ nanocomposites was identified by FTIR spectral investigation. The FTIR spectrum of pure PANI and PANI-nFe₃O₄ (50%, 100%) nanocomposites are clearly showed in Fig.1. In the FTIR spectra of pure PANI (Fig.1a) eight sharp, broad absorptions peaks are obtained. The first peak the band at 3417 cm⁻¹ attributed to N-H stretching vibration and the transmittance for this peak is 53.66 [4]. The second peak is observed at 1586 cm⁻¹ assigned to C=C stretching mode of vibration for the quinoid unit and transmittance peak value is 34.05 [5]. The bands 1499 cm⁻¹ is attributed to C=C stretching vibration for the benzoid unit this peaks is third peak of the spectrum of pure PANI and the transmittance value (54.38). This above two peaks of the pure PANI spectrum the second peak (C=C quinoid) is very strong peak and the third peak (C=C benzoid) very weak peak. The band at 1399 cm⁻¹ is attributed in C-N stretching vibration (Q=N-B) and transmittance is (41.48) [7]. The fifth absorption band of pure PANI spectrum is assigned at 1316 cm⁻¹ and this band observed in C-N stretching of the secondary aromatic amine and which transmittance band value are 61.90 [6].

The six peaks at 1123 cm⁻¹ are assigned to in-plane bending modes of C-H stretching and the seventh peak obtained at 817 cm⁻¹ to out-plane bending modes of C-H stretching vibration. The absorptions at lower wavenumber (622 cm⁻¹) belong to the nFe-O and nFe-O-nFe vibration modes of nFe₃O₄ nPs [7]. FTIR Spectrum of PANI-nFe₃O₄ (50%, 100%) nanocomposites both is similar to pure PANI. This two nanocomposites spectrum also have eight bands are obtained. In PANI-nFe₃O₄ (50%) nanocomposites the stretching vibrations at 3414, 1587, 1497, 1396, 1307, 1131, 830 and 620 cm⁻¹ this region were assigned at N-H stretching vibration, C-H stretching vibration (quinoid), C-H stretching vibration (benzoid), C-N stretching vibration, C-N (Secondary aromatic amine), C-H in-plane bending mode, C-H out plane bending mode, Fe-O-Fe stretching vibration respectively, (Fig.1b) prove the presence of emeraldine base state of PANI in our synthesized nanocomposites [9].

This interesting phenomenon specifies there is a good interaction between PANI and $n\text{Fe}_3\text{O}_4$ and also confirmed the doping of Fe in the PANI. For PANI- $n\text{Fe}_3\text{O}_4$ nanocomposites, the shifting of peaks at lower wavenumber is mainly due to the π - π conjugated interaction between the benzene ring of PANI and the metal oxide, indicating a strong interaction between PANI and the $n\text{Fe}_3\text{O}_4$ nPs [10].

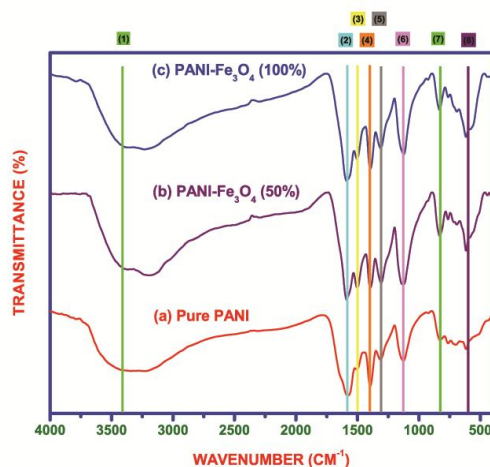


Fig. 1. FTIR spectra of pure PANI (a) and PANI- $n\text{Fe}_3\text{O}_4$ (50, 100%) nCs (b) and (c).

UV-Vis Spectra. UV-Vis spectra of pure PANI and PANI- Fe_3O_4 nanocomposites are shown in Fig.2, the optical properties of the PANI and the nanocomposites of UV-visible absorption spectroscopy analyses were performed. The spectrum of pure PANI show that there are two absorption bands of PANI at 328 and 627 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. The band gap was calculated by means of the Tauc equation

$$\alpha h\nu = B(h\nu - E_g)^n$$

where α is the absorption coefficient, h is the Planck constant, ν represents the photon frequency, B is a fitting parameter, E_g is the band gap, and n is the different possible electronic transitions responsible for the light absorption.

For PANI and its nanocomposites, $n = \frac{1}{2}$. The band gap was obtained by plotting the UV-Vis spectra as $(\alpha h\nu)^2$ vs $h\nu$ and extrapolating the linear portion of $(\alpha h\nu)^2$ vs $h\nu$ to zero, shown in Fig. 3 (a-c). The calculated E_g values were 3.284 eV for the pure PANI. Furthermore, compared with pure PANI, the absorption bands of the two nanocomposites both show a little blue shift about ± 4 nm. The blue shift of the band gap for the PANI- Fe_3O_4 (50, 100%) nanocomposites clearly indicates that the metal ions strongly bind with the PANI matrix chain.

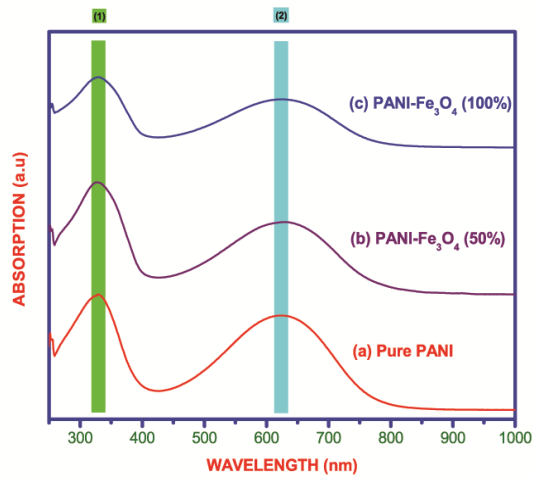


Fig. 2. UV-Vis Spectrum of Pure PANI (a) and PANI-Fe₃O₄ (50%, 100%) nCs (b), (c).

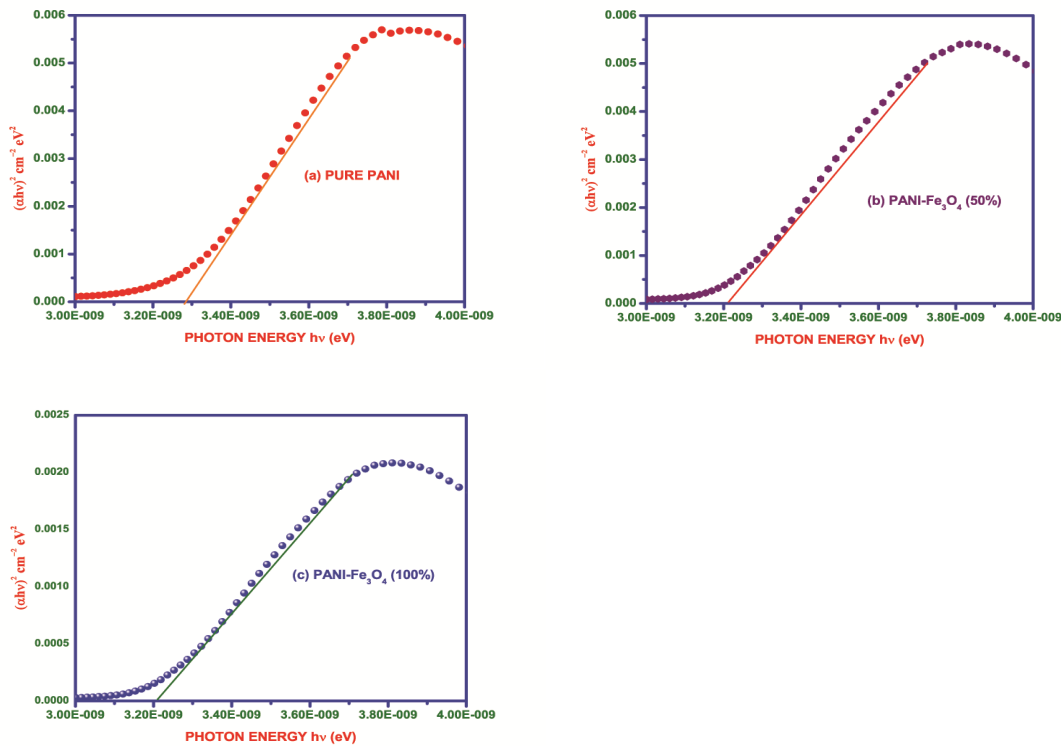


Fig. 3. Tauc Plot of Pure PANI (a) and PANI-nFe₃O₄ (50,100%) nCs (b), (c).

The E_g value of PANI-Fe₃O₄ (50%), PANI-Fe₃O₄ (100%) is 3.214 eV and 3.201 eV respectively; compared to the pure PANI the band gap value is decreased with increasing the wt % of dopant concentration in the nanocomposites samples and Tauc plot of pure PANI and nanocomposites is shown in Fig.3. In both the cases, the band gap is decreased by the incorporation of doping agents inside the materials. The comparison of pure PANI and nanocomposites the peak intensity of the nanocomposites is decreased with increasing the Fe ion concentration. This blue shifting and peak intensity phenomenon of the absorption peak in PANI-nFe₃O₄ nanocomposites may be due to the doping effect. It is also observed that there is a blue shifting of the peak for the PANI-nFe₃O₄ nanocomposites, only because of some interaction between the quinonoid ring of PANI and nFe₃O₄ nPs.

XRD Studies. Fig.4 (a-c) shows XRD patterns of the pure PANI and PANI-nFe₃O₄ nanocomposite. In case of pure PANI, a broad amorphous peak observed at 20.52° 2θ was assigned to the periodicity parallel to the polymer chain [8]. XRD of PANI-nFe₃O₄ indicated that the nanocomposite is crystalline and showed a XRD peaks. The crystallite sizes were estimated using the full width at half maxima of the XRD peaks. Using the Scherrer formula, the expression for the full width at half maximum of the XRD peaks can be expressed as

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

where K is the grain shape factor (0.89 for spherical), λ is the wavelength of CuK α (1.5406 Å), t is the thickness of the crystal and θ is the Bragg's angle.

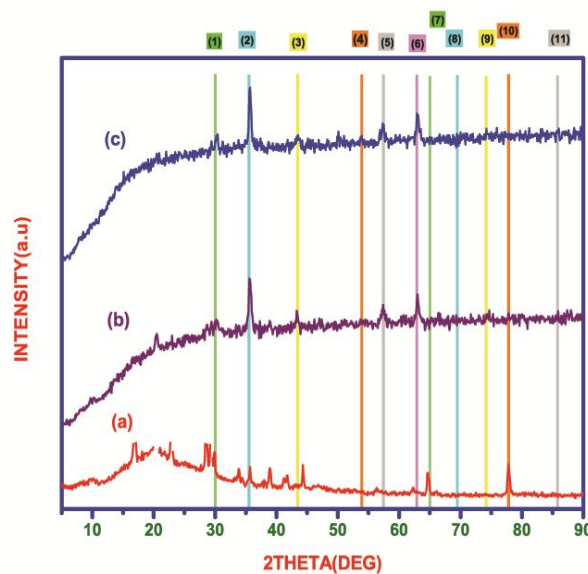


Fig. 4. XRD Pattern of Pure PANI (a) and PANI-Fe₃O₄ (50%, 100%) nCs (b), (c).

XRD patterns of PANI-nFe₃O₄ (50%) nanocomposites (Fig.4b) reveal the presence of crystalline nature with nFe₃O₄ nPs. A sharp peak appeared at the range of 20°~30.20-86.70 and for these range 11 sharp peaks for crystalline nature of nFe₃O₄ nPs. The crystalline peaks centered at 2θ≈30.20, 35.64, 43.29, 53.60, 57.29, 62.95, 65.31, 69.96, 74.34, 78.59, and 86.70° correspond to the (220), (311), (400), (422), (511), (440), (531), (620), (622), (444) and (642) crystal planes of the cubic structure of nFe₃O₄ nPs [9]. In the PANI-nFe₃O₄ (100%) nanocomposites of the typical diffraction peaks observed at 2θ=30.24, 35.66, 43.46, 53.74, 57.27, 62.98, 64.88, 69.68, 74.30, 77.39, and 86.70 correspond to the primary diffraction plane of the (220), (311), (400), (422), (511), (440), (531), (620), (622), (444) and (642) planes of the respectively [10]. The mean crystalline size of PANI-nFe₃O₄ (50%) and (100%) nanocomposites is 20.05 nm and 21.25 nm respectively. This result indicates that nFe₃O₄ nPs were embedded in PANI matrix. The peak intensity of crystalline nFe₃O₄ nPs gradually decreases with decreasing the amount of iron present in the system.

Antimicrobial Activity. Fig.5 shows the antibacterial photographs of pure PANI and PANI-nFe₃O₄ nanocomposites the antibacterial assay was used to determine the growth inhibition of bacteria. In E-Coli bacteria zone of inhibition for pure PANI is 10±0.2 mm and the nanocomposites 50% and 100% the zone of inhibition for E-Coli bacteria are 11±0.4 and 14±0.3 respectively. Compare the growth and zone of inhibition of E-Coli bacteria for pure PANI and nanocomposites which this parameter is

increased with adding $n\text{Fe}_3\text{O}_4$ nPs [15]. For this growth and zone of inhibition changes are confirmed the pure PANI and $n\text{Fe}_3\text{O}_4$ nPs are interact with each other. And similar changes were appeared at staphylococcus aureus bacteria for zone of inhibition value for pure PANI and PANI- $n\text{Fe}_3\text{O}_4$ nanocomposites.

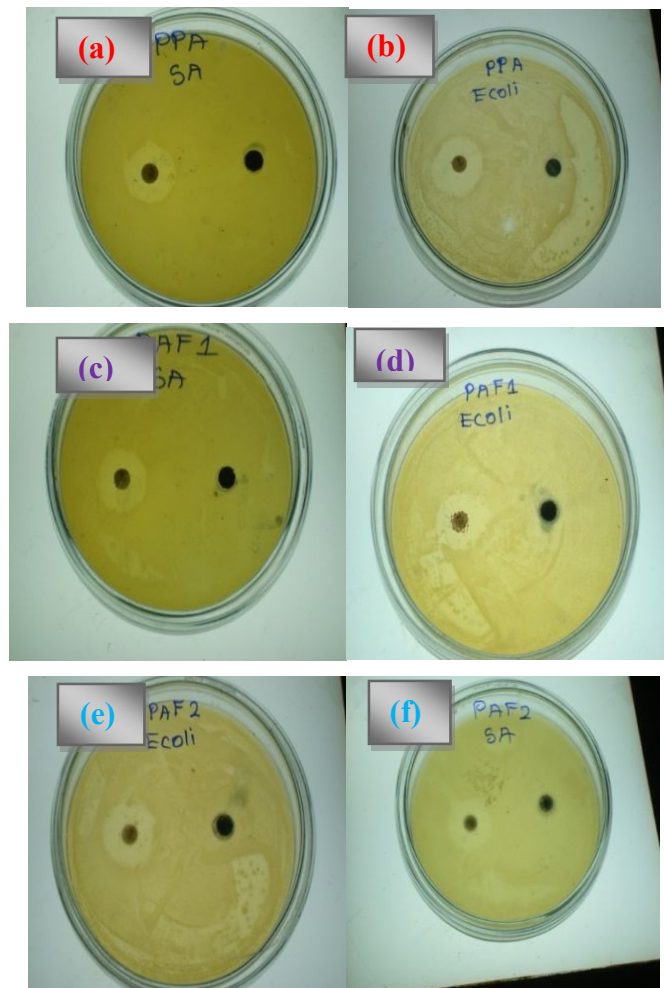


Fig. 5. Antibacterial activity photograph of pure PANI and PANI- Fe_3O_4 (50%, 100%) nCs, pure PANI (a) Staphylococcus aureus (b) E coli, PANI- Fe_3O_4 (50%) (c) Staphylococcus aureus (d) E coli and PANI- Fe_3O_4 (100%) (e) Staphylococcus aureus (f) E coli.

Summary. In summary, the synthesized polyaniline was adding the monomer aniline and oxidation agent ammonia peroxydisulphate (APS) by using chemical oxidative polymerization The polyaniline nanocomposites reinforced with different $n\text{Fe}_3\text{O}_4$ nPs loading levels have been successfully prepared by using mechanical mixing method. The nanostructure and chemical bonding state of the $n\text{Fe}_3\text{O}_4$ nPs modified PANI hybrids nanocomposites were systematically investigated using Fourier transform infrared (FTIR) spectra, UV-Vis spectra, X-ray diffraction spectroscopy, and antibacterial activity. FTIR spectroscopy of powdered samples mixed with potassium bromide and then pressed in pellets reveals only small changes in the PANI, viz., these nanoparticles were successfully incorporated in PANI, using a physical process with minimum risk of chemical contamination. The functional group of PANI- $n\text{Fe}_3\text{O}_4$ nanocomposites were analysis the Fe-O-Fe stretching vibration is gradually changed the peak intensity is increased with adding the Fe nanoparticles which this changes clearly explain the PANI and Fe nanoparticles highly interact for this simple method. UV-Vis and XRD analysis gave information towards the formation of pure PANI, PANI- $n\text{Fe}_3\text{O}_4$ nanocomposites.

The antibacterial activity confirmed for this nanocomposites materials are very useful in medical application.

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