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Research Article

SYNTHESIS AND CHARACTERIZATION OF SULFUR- POLYANILINE (SNPs-PANI) NANOCOMPOSITE AND ITS POTENTIAL APPLICATION AS ANTIBACTERIAL

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ABSTRACT

Sulfur nanoparticles (S NPs), Polyaniline (PANI), S NPs- PANI nanocomposite were synthesized by a simple, cost effective, minimal equipment facilities and more environment-friendly methods. Sulfur nanoparticles (SNPs) were synthesized in different acidic (oxalic acid and hydrochloric acid) media in presence of surfactant (CTAB) by acid catalyzed precipitation of sodium thiosulfate. The synthesized products were analyzed by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). XRD pattern reveals that the particles were in orthorhombic crystal form and the particle size was 65 nm in oxalic acid medium. The polymerization of aniline was held *in situ* condition and with exposure of S NPs on to the PANI a new nanocomposite was obtained. The XRD pattern and the EDS spectrum give evidence of the formation of S NPs-PANI nanocomposite by showing characteristic peaks of S NPs and PANI both. In addition, these synthesized products were executed for antibacterial test of some diarrhoeal and non-diarrhoeal pathogens. The obtained results showed that S NPs- PANI nanocomposite has enhanced antibacterial activity than SNPs, PANI and also the extensively used antibiotic ciprofloxacin and cotrimoxazole due to synergistic effect of S NPs and PANI.

INTRODUCTION

The emerging infectious diseases and the development of drug resistance in the pathogenic bacteria and fungi at an alarming rate is a matter of serious concern. Therefore, there is always a pressing demand to discover novel strategies and identify new antimicrobial agents from natural and inorganic substances to develop the next generation of drugs or agents to control microbial infections. In the recent times, the advances in the field of nano sciences and nanotechnology has brought to fore the nano sized inorganic and organic particles which are finding increasing applications as amendments in medicine and therapeutics industries.

Nanoparticles usually ranging in dimension from 1-100 nm have unique physic-chemical and biological properties which can be manipulated suitably for desired applications. It is found that the biological processes also occur at the nano scale and due to their amenability to biological functionalization; the NPs are finding important applications in the field of medicine (MacNaught *et al*, 1997). The antimicrobial activity of the NPs is known to be a function of the surface area in contact with the microorganisms. The small size and the high surface to volume ratio *i.e.* large surface area of the NPs enhance their interaction with the microbes to carry out a broad range of probable antimicrobial activities.

However, it has been demonstrated that the antimicrobial property of metal NPs composites with polymer been extensively explored (Taylor *et al*,2013, Lu *et al*, 2007, Jiang *et al*, 2007, Sun *et al*, 2007, Lopeandia *et al*, 1994. Yadav *et al*, 2012) but the antimicrobial property of nonmetals nanocomposite remain an undeveloped area. Polymer nanocomposites are materials in which nanoscopic inorganic particles are dispersed in an organic polymer matrix in order to significantly improve the performance and properties of the polymer.

From the ancient times along with other uses of bulk form of elemental sulfur, it is extensively used as pest killer in agriculture field and in different therapeutic purpose. The polymer polyaniline (PANI) has attracted great attraction for their scientific interest. It is the mostly studied conducting and biodegradable polymer and some polyaniline based core-shell nanocomposite such as Ag/PANI, Ni/ PANI and Si/ PANI have been well demonstrated and in some studies their antimicrobial efficacy is also found (Corriu *et al*, 2009). Now realizing the importance of S NPs and PANI in their application, we set up a target to develop a novel protocol for synthesis of S NPs, their

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dispersion on to conducting PANI and to examine the antimicrobial activity of S NPs, PANI, S NPs- PANI composite.

MATERIALS AND METHODS

Chemicals

Analytical grade chemicals and solvents were used throughout the work. The monomer aniline was distilled twice prior to its use in polymerization reactions. Double distilled water (H_2O) was used as solvent to prepare most of the solutions utilized in this work except for optical analysis where N, N- dimethyl form amide (DMF) was employed as solvent. The important chemicals and solvents utilized throughout the experiments are- Aniline (Merck, Germany), Sulphuric acid (97%) (Merck, Germany), Sodium thiosulfate ($Na_2S_2O_3$) (Merck, India), Hydrochloric acid (HCl) (Merck, Germany), Oxalic acid ($H_2C_2O_4$) (Merck, India), Ammonium peroxydisulfate (Merck, Germany), Cetyltrimethyl ammonium bromide (CTAB) (Merck, Germany).

Preparation of sulfur nanoparticle (S NP)

S NPs was synthesized through the disproportionation reaction in two different acidic media oxalic acid and hydrochloric acid media by following two different routes e.g. in presence of surfactant, CTAB and in absence of surfactant.

$Na_2S_2O_3 + 2HCl = 2NaCl + S\downarrow + H_2O + SO_2$
$Na_2S_2O_3 + (COOH)_2 = Na_2CO_3 + S\downarrow + H_2O + SO_2$

Synthesis of polyanline (PANI)

In a typical synthesis experiment of PANI, the aniline monomer was dissolved in 1.0 M HCl solution. 2.2 M ammonium dipursulfate was slowly added drop wise into the aniline HCl solution with a constant mechanical stirring at a temperature of 0-5 °C for 2-3 hour which results green suspension, indicating the formation of insoluble polyaniline in its emeraldine salt (ES) form. It was then filtered with Whatmann filter paper through vacuum and rinsed several times with distilled water.

Synthesis of S NPs-PANI nanocomposite

The composite of PANI with SNPs was synthesized by in situ chemical oxidation polymerization. In a typical synthesis experiments, 0.05 gm of SNPs were dissolved in 0.1 M DMSO solution and ultrasonicated over 1h, then transferred into a flask with an ice bath. The S NP was added with the aniline monomer and the total process for preparation of PANI was repeated. Then it was filtered off and was dried in a vacuum at 50°C for 24 hour resulting powder of sulfur-Polyaniline nanocomposite.

Characterization

The particle size of S NPs was characterized through X-ray diffractrometre (XRD) with scanning rate of 0.01^0/s in the 2θ range from 20^0 to 40^0. The size and shape of S NPs was observed by scanning electron microscope (SEM). The PANI was characterized through infra red spectrometer (IR). The formation of S NPs-PANI nanocomposite was confirmed by XRD, IR and EDS spectrometer. EDS spectrometer is used to judge the purity of the entire synthesized product

Antibacterial Test

Susceptibility of isolates to S NPs, PANI and S NP-PANI composite was measured *invitro* by employing well diffusion method. This method allows for the rapid determination of the efficacy of a drug by measuring the diameter of the zone of inhibition that results from diffusion of the agent into the medium surrounding the well. Mueller Hinton agar (MHA) medium (beef extract 2 g l^{-1}, acid hydrolysate of casein 17.5 g l^{-1}, starch 1.5 g l^{-1} and agar 17 g l^{-1}). Four to five bacterial colonies were inoculated into 3 ml of Mueller Hinton broth (MHB) and incubated at 37°C for three hours. The broth culture was adjusted to 0.5 McFarland standards ($8X10^8$ CFU/ml of broth). A cotton swab was dipped into broth containing young culture of bacteria and was streaked evenly in three directions over the entire surface of the MHA plate for uniform inoculums to obtain confluent growth. The plate was then allowed to dry for 3 to 5 minutes. Wells were made into MHA. S NPs, PANI and S NP-PANI nanocomposite were then applied to the wells of the inoculated plates with micropipette. Within 5 min after the plates were placed in an incubator at 37°C.After 16 to 18 h of incubation, inhibition zone diameter around disc was measured in mm.

RESULTS

The particle size of sulfur differs on different factor e.g. concentration of the acids, nature of the acids and presence of surfactants. Among the inorganic acids in hydrochloric acid media the synthesized particle size of S NPs was least and in organic acid e.g. oxalic acid media the particle size was found smaller. In presence of surfactant CTAB, the particles formed in the smallest size.

XRD analysis of S NPs

The presence of strong and sharp diffraction peaksin the Figure-1 indicated that the synthesized nanoparticles were highly crystalline in nature. The determination of the mean particle diameter (D) was done by the XRD analysis using

Debye-Scherrer formula $D = \frac{k\lambda}{\beta Cos\theta}$

Where, D is the particle's diameter, k is the Scherrer constant usually taken as 0.89, λ is the wavelength of the X-ray radiation (0.154056 nm for Cu Kα), and β is the full width at half maximum of the diffraction peak measured at 2θ.

However, there is distinct difference in the peak intensity of the sample prepared in hydrochloric and oxalic acid media. As in absence of surfactant the estimated crystallite size was more than 100 nm. But in presence of surfactant, CTAB the particle size synthesized in oxalic acid was approximately 65 nm which was shown Figure-1 (a). Here the value of β is 0.00215and 2θ value is 23.39^0. The obtained result was similar to other researchers (Chowdhury *et al*, 2011, 2013).

All detectable peaks could be indexed to S orthorhombic phase with S_8 structure, without obvious characteristic reflection peaks from other impurities, revealing the high purity of the as-synthesized products. The characteristic highest peaks at 23.39^0 correspond to (1, 1, 1) crystalline plane.

XRD Pattern for S NPs-PANI nanocomposite

Most of the conducting polymers are reported to be extremely poor crystalline and therefore it leads to the diffuse diffraction pattern as exhibited in Figure-1 (b). From Figure-1 (b) it can be seen that peak intensity of S NPs-PANI nanocomposite was decreased than PANI.

In addition, the broad and appearance of sharp peak indicates the presence of crystalline S NPs in the composite. There is a distinct difference between the XRD pattern of PANI and SNPs-PANI nanocomposite which is indicated by combined spectrum in Figure -1(b).

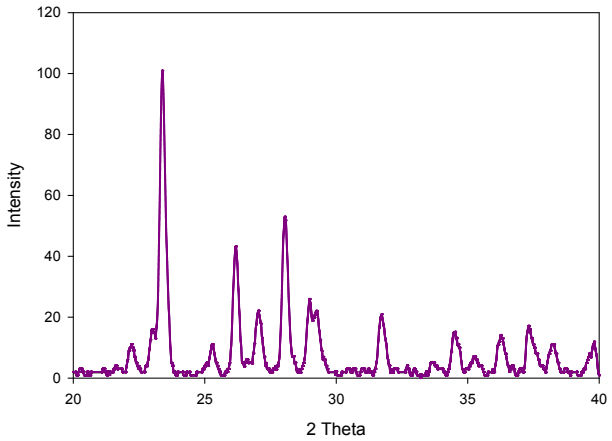

Figure-1(a) XRD pattern of S NPs in Oxalic acid medium and in presence of CTAB surfactant.

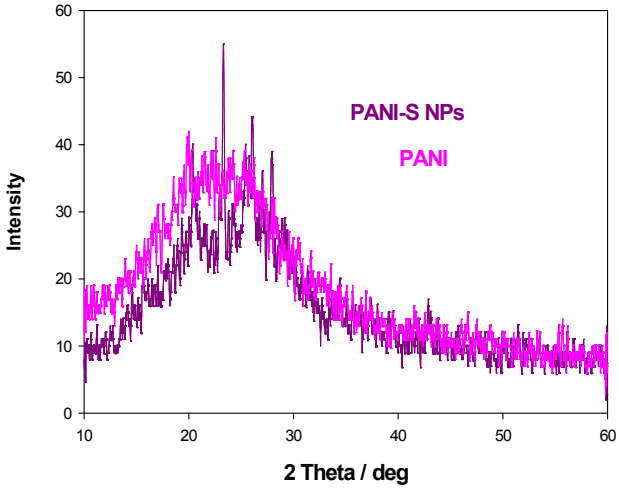

Figure-1(b) XRD of S NPs-PANI nanocomposite

Scanning Electron Microscopic (SEM) Analysis

The SEM images of S NPs synthesized in hydrochloric acid and oxalic acid media in presence or absence of surfactant, CTAB was taken. In presence of CTAB, closer focusing on the aggregated structures showed that each aggregate is a collection of tinier and solid compact which has size of around 65±10 nm on average. Though not completely homogenous, the size distribution is uniform, with no huge crystals of bulk sulfur and the particles are in less aggregated state.

In the presence of CTAB, the particles are found in more isolated state. The probable reason behind it is that the monomer CTAB molecules are adsorbed on the sulfur particle surface through its tail group. As a result, after the adsorption of the ionic surfactant molecules, a charge is developed on the particle surface. Therefore, agglomeration tendency of the particles are reduced due to the electrostatic repulsion between the particles adsorbed by ionic surfactants.

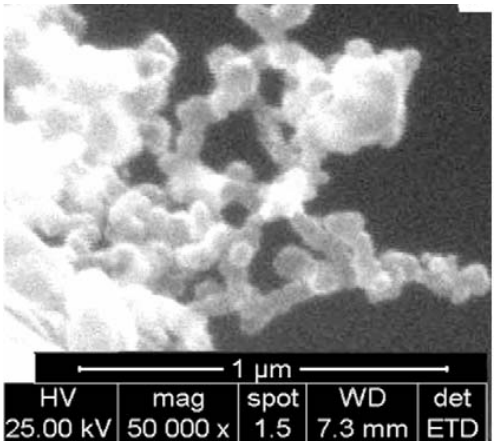

Figure-2 SEM image of the as prepared S NPs in oxalic acid medium in presence of CTAB

Fourier Transform Infrared Spectroscopic (FT-IR) Analysis

It is worthwhile to mention here that the observed IR spectra are consistent with the previous studies and discussed according to the frequency region. Aromatic ring breathing, N-H deformation and C=N stretching all give absorption band at 1600-1580 and 1510-1500 cm^{-1}.

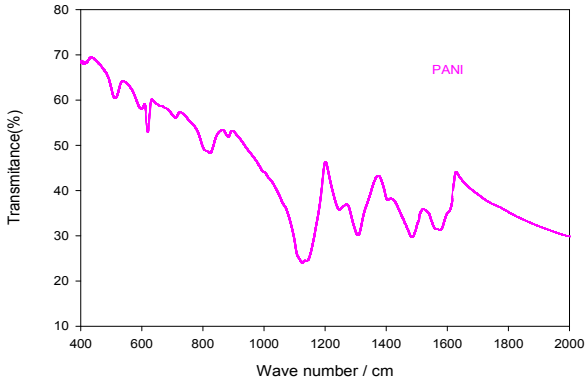

Figure-3 FT-IR Spectrum of PANI

The band formed in 1587 cm^{-1} band as a characteristic band of nitrogen quinine (Q).The intrinsic PANI shows three peaks: medium absorption at 1240 cm^{-1} and weak ones at 1380 and 1240 cm^{-1}. The 1315 cm^{-1} peak is rapidly strengthened by acid treatment. The band at 1160 and 1140 cm^{-1} was referred as "electronic like band". The 1220-500 cm^{-1} is the region in-plane and out of plane bending of C-H bonds on aromatic rings.

EDS Analysis

The synthesized nanoparticles, PANI and S NPs-PANI nanocomposite were characterized by EDAX for the evaluation of their composition and purity. Figure-4 shows the spectrum of the EDAX analysis of S NPs-PANI nanocomposite and proves the existence of carbon, nitrogen, oxygen and sulfur by showing the characteristic peaks for the corresponding elements. This is the evidence of the formation of S NPs-PANI nanocomposite as here is peak for sulfur along with other

elements of PANI. EDS spectrum of other products ensured the formation of pure products.

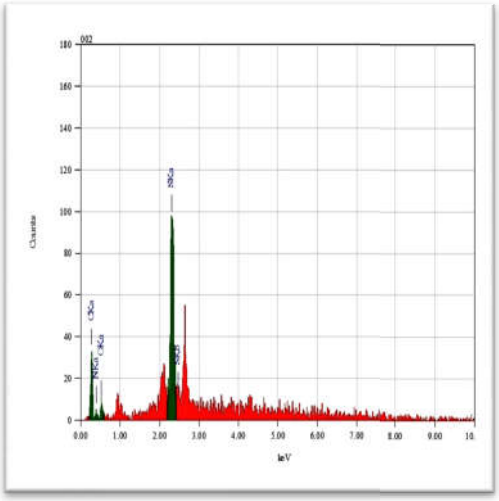

Figure-4 EDS Spectrum of S NP-PANI nanocomposite

Antibacterial Test

Antibacterial susceptibility test of four important and common diarrheal pathogens (*Eschericia Coli and VibirioCholarae*O1) and common non-diarrheal bacterial pathogens (*Streptococcus Aureous* and *Stephylococcus Typhi*) were taken for S NPs, PANI, S NPs-PANI nanocomposite and two common antibiotics e.g. cotrimoxazole and ciprofloxacin by standard disc diffusion method. S NPs, PANI, S NPs-PANI nanocomposite showed significant activity against to all mentioned bacteria. It is noteworthy to mention that S NPs-PANI nanocomposite were higher effective than others, even from the antibiotics. *Vibrio cholerae* O1 and *Staphylococcus aureus* showed resistant to the antibiotics cotrimoxazole and *Staphylococcus aureus* to ciprofloxacin.

Table Antibacterial activity (zone diameter) of SNPs, PANI and SNPs-PANI Composite agar well diffusion test

Bacteria Isolates	SNPs	PANI	SNPs-PANI nanocomposite	Cotrimoxazole	Ciprofloxacin
*Salmonella*Typhi	21.5	18.0	24.5	28	28
***Vibrio cholerae* O1**	16.5	14.5	**27.5**	**<7**	**26**
Eschericia coli	17.5	17.0	25.5	27	28
Staphylococcus aureus	20.0	18.5	**28.0**	**<7**	**≤10**

The different inhibition zone of SNPs, PANI and SNPs-PANI nanocomposite against the bacteria is given in Table. The enhanced antibacterial activity of S NPs-PANI nanocomposite was due to synergistic activities of the S NPs and PANI

CONCLUSION

In this research, S NPs (in presence of CTAB), PANI and S NPs- PANI nanocomposite were synthesized by a simple and cost effective method.

Antibacterial test were done by synthesized SNPs, PANI and PANI-SNPs nanocomposite and also comparison of antibacterial susceptibility test results of common antibiotics cotrimoxazole and ciprofloxacin. It was seen from the results that S NPs-PANI nanocomposite was more active than S NPs and PANI individually due to the synergistic effect of the S NPs and PANI. Additionally, the S NPs-PANI nanocomposite was also more susceptible than widely used antibiotics cotrimoxazole and ciprofloxacin. *Staphylococcus aureous* almost becomes resistant to the ciprofloxacin (inhibition zone less than 10) and cotrimoxazole (inhibition zone less than 7) whereas S NPs-PANI has susceptible toward it forming inhibition zone of 28.

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