Biocidal and Antistatic Performance of fabric modified with Polyaniline Microtubes: An Efficient Material for Waste Water Treatment.

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Abstract

Present paper describes the antistatic and biocidal performance (i.e.removal of *E.coli* and Total coliform (TC) bacteria) of fabric modified with polyaniline microtubes. Polyaniline coated fabric has been developed by chemical oxidative polymerization of aniline in presence of naphthalene sulphonic acid as a dopant. Coating of polymer on fabric material was carried out during polymerization in different concentration. Conducting polymer coated fabrics were characterized by TGA analysis, FTIR spectroscopy and XRD analysis and conductivity measurement, which indicate that the inclusion of polyaniline microtubes into the fabric matrix. Scanning electron microscopy (SEM) revealed the surface morphology of the material. Evaluation of the membrane for antimicrobial activity (removal of Total coliform and *E.coli*) has been carried out by membrane filtration method. M-Endo broth was used for selectively isolated coliform bacteria from water using membrane filtration method. Data will be compared with uncoated fabric and polyaniline doped with benzene sulphonic acid. Results revealed that polyaniline microtubes coated fabric showed upto 75-85 % reduction of E.coli and Total coliform bacteria from waste water. Moreover, Antistatic performance of the polyaniline impregnated fabric was investigated by John Chubb Instrument. The static decay time of the coated fabric was found to be in the range 0.9 to 10.2 s on recording the decay time from 5000 V to 500 V. The effect of morphology on antisatic and biocidal properties has also been explained.

Keywords: Conducting polymer, Waste Water, Biocidal Property, Antistatic study.

1.0 Introduction:

Conducting polymers represent an important class of materials with potential applications in number of devices like electrode materials in energy storage devices [1, 2], anticorrosive materials [3-5], sensor technology [6-8], solar cell [9,10], shielding of equipments from electromagnetic interference [11,12], One of the most important applications of these materials which are attracting considerable attention in the most recent times is dissipation of electrostatic charge [13,14] and antimicrobial applications [15] etc.Electrostatic charge has become an important issue within the electronic components such as chips carriers, data storage devices and computer internals. Antistatic protection is also required for parts where relative motion between dissimilar materials occurs such as weaving machine arms, aeroplane tyres etc [16]. Conventional polymers (i.e.insulating polymers) as well as insulation materials commonly being used for packaging of various electronic equipments but due to their insulating nature, these materials failed to dissipate the static charge. The generation of static electricity on the materials leads to a variety of problems in manufacturing and consumer use. Moreover, electronic components are vulnerable to damage from electrostatic discharge. The accumulated static charge may lead to sparking or explosion. Hence, some antistatic act is essential to continuously drain the charges from the electronic packaging material, thus the challenge is to convert inherently insulating materials to a product that would present an effective antistatic properties. Among polyaniline is one of the most promising intrinsically conducting polymers, because of its good environmental stability and high electrical conductivity, which can be reversibly controlled by a change in the oxidation state and protonation of the imine nitrogen groups. The commercial exploitation of most of the applications based on polyaniline is closely linked to the lack of its mechanical properties and poor processability. There are many reports on the synthesis of conducting polymer blends based on polyaniline and different insulating polymers for antistatic applications [17-19]. Better mechanical properties could be attained by incorporation of conducting polymer in insulating materials like Polyethylene, polystyrene and polypropylene and, but the blend with poor conductivity has been observed. Incorporation of polyaniline in insulating polymer via blending has carried out but the resultant materials with better mechanical properties could be achieved at the rate of conductivity. There are many papers based on the synthesis of conducting polymer blend/composites for antistatic applications [17-19] but only a few brief reports are available on the antistatic fabrics [20-25]. Since, antistatic materials should have better mechanical properties, flexibility and moderate electrical conductivity. Different polymers such as polyaniline and polypyrrole have been coated over the surface of the fabrics and resulting materials were found to be of better mechanical properties, flexibility, stitch ability of fabric. Faez et al. [26] have suggested that conductivity range from 10^{-11} to 10^{-2} S/cm is considered suitable for an effective antistatic packaging application. According to Electronic Industries Association (EIA) standards 541, in electrostatic protected environments, the optimal surface conductivity should be in the range of 10^{-6} to 10^{-10} S/cm. However, by modifying the polyaniline in to tubular structure and incorporation of it into fabric, mechanical properties and acceptable conductivity can easily be achieved [27, 28]. These conducting polymer polyaniline microtubes were also found to be more effective for antimicrobial applications as compared to polyaniline prepared by conventional method. Fabrics coated with metal nanoparticles for biocidal application have been extensively reported [29, 31].

On the basis of literature it is observed that use of these metal and metal oxide nanoparticles are found to be quite expensive. Most of the literature was concerned with metal/metal oxide nanoparticles-coated cotton for antimicrobial application. But only few articles are concerned with only polyaniline microtube coated fabrics for antistatic and antimicrobial applications. The coating of conducting polymers on insulating fabric leads to reduce in its electrical conductivity than that of powder form of polyaniline. In order to achieve the fabric with acceptable conductivity and good mechanical properties, we have modified the morphology of polyaniline into tubular form by changing the reaction condition and nature of dopant. Therefore, in the present paper we have used cost effective and highly efficient PANI-microtubes impregnated fabrics as antistatic encase material and biocidal applications. Such polymer impregnated fabrics were found to be ideal for large area antistatic materials like sheeting, floor covering, and awning etc. Moreover, use of conducting polymer impregnated fabrics also a prospective method to recover the drawback of polyaniline and creating new materials with specific properties for the desired application at low cost. The use of cotton fabric as an insulating matrix for the PANI is very attractive because of its good mechanical properties and better interaction with conducting polymers. In the present paper, we have achieved the conducting polymer polyaniline with moderate conductivity and good mechanical properties by modifying its morphology and using fabric as an insulating substrate. These materials have been used for antimicrobial and antistatic applications.

Present work is based on the synthesis of PANI microtubes by using naphthalene sulphonic acid as a dopant. Incorporation of these polymers in fabric material was carried out during polymerization. The effect of the tubular morphology of polyaniline on electrical, thermal and antistatic antimicrobial properties has also been investigated in the present work and the properties have also been compared with polyaniline synthesised by using conventional dopant like BSA.

2.0 Experimental

2.1 Synthesis of PANI-microtubes impregnated fabric

The cotton fabric was allowed to soak in the aqueous solution of 0.1 M aniline (AN) and 1.0 M naphthalene sulphonic acid (NSA) or Benzene sulphonic acid (BSA). Reaction was initiated by drop wise addition of oxidant (i.e Ammonium peroxydisulphate) with constant stirring for about 3-4 hr.After deposition of PANI- on fabric, the fabric was thoroughly washed with deionised water to remove loosely bonded polymer particles, unreacted monomer and dopant. It was allowed to dry under 50 ^{o}C. Remaining residue of PANI in the reaction vessel, was filtered, washed and dried.

It was observed that polyaniline synthesised in BSA medium showed globular granule like morphology but in presence of naphthalene sulphonic acid, it showed tubular morphology as shown in SEM micrographs.

3.0 Characterization:

The structure of the nanocomposite was characterized by Fourier Transform Tnfrared (FTIR) Spectrometer (Nicolet 5700 FTIR, USA) in KBr pellets in the range of 400-4000 cm^{-1}. TGA (Mettler Toledo TGA/SDTA 851e, Switzerland) was used to investigate the thermal stability of polymers in nitrogen atmosphere. A heating rate of 10^{o}C/min and a sample size (in the form of fine powder) of 10±2 mg were used in each experiment. Scanning Electron Microscopy (SEM; Leo S-440, Germany) was employed to observe morphology of the samples and perform EDX analysis. A conductivity measurement of powdered samples as well as polymer coated fabric was carried out by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter, Germany).

3.1 Antimicrobial and Antistatic activity measurement

The antimicrobial activity of cotton coated with PANI was tested against Gram negative and Gram positive bacteria. A small piece of uncoated, PANI coated cotton was added to a tube containing 5 ml of freshly prepared brain heart infusion broth (BHIB) (HiMedia, Mumbai, India) that is inoculated with *E. coli* and *S. aureus* (these are clinical isolates provided by the Department of Microbiology, JNU, New Delhi India). The tubes were incubated at 37°C for 24 h. The turbidity of the test tubes was compared visually to an uninoculated (control) BHIB tube. A 0.5 ml of each tube was diluted to 100 ml distill water and the fractions were placed on m-Endo broth medium that is selective media for *E.coli* growth. All the samples were incubated at 37°C for 24 h. After incubation, the colonies that have grown were identified. Colonies grow in specific colour and were manually counted. *E.coli* bacteria form pink colonies with a metallic sheen on m-Endo broth medium containing lactose. Each experiment was repeated three times and counted total number of *E.coli* using colony counter in term of colony forming units (CFU) under magnifying glass and express as CFU/100ml.

E.coli density in m-Endo browth medium was calculated as;

$$\text{E. coli}\ /100\text{ml} = \frac{\text{Coliform colonies counted}}{\text{Volume of sample (ml)}} \times 100$$

Eq.1.0

Moreover, reduction percentage (R %) of *E.coli* bacteria from coated and uncoated cotton fabric can also be calculated using following equation;

$$R\,(\%) = \frac{B - C}{B} \times 100$$

Eq.1.1

Where ‘B’ is the CFU/100 ml without treatment and ‘C’ is CFU/100 ml with treatment (using PANI, impregnated fabric).

The measurement of static decay time of uncoated and polymer coated fabrics was carried out on John Chubb Instrument, U.K. (JCI 155 v5) charge decay test unit at room temperature on recording the decay time from 5000 V to 500 V.

4.0 Results and discussion

4.1 FTIR Spectra

Fig.1 shows the FTIR spectra of PANI microtubes. PANI showed a main characteristics band around 815 cm^{-1} due to the out of the plane C-H bending vibrations and is indicative of the para coupling i.e. the polymerization occurs at 1-4 position. The band at 1035 cm^{-1} corresponding to S=O stretching mode of the $-SO_3$ group of naphthalene sulphonic acid splits into two bands. The bands around 1125 cm^{-1} and 1160 cm^{-1} are due to the symmetric SO_2 stretching and SO_3 stretching in PANI. The peaks around 1565 and 1461 cm^{-1} are characteristic stretching bands of nitrogen quinoid (N=Q=N) and benzenoid. (N-B-N) and are due to the conducting state of the polymer.

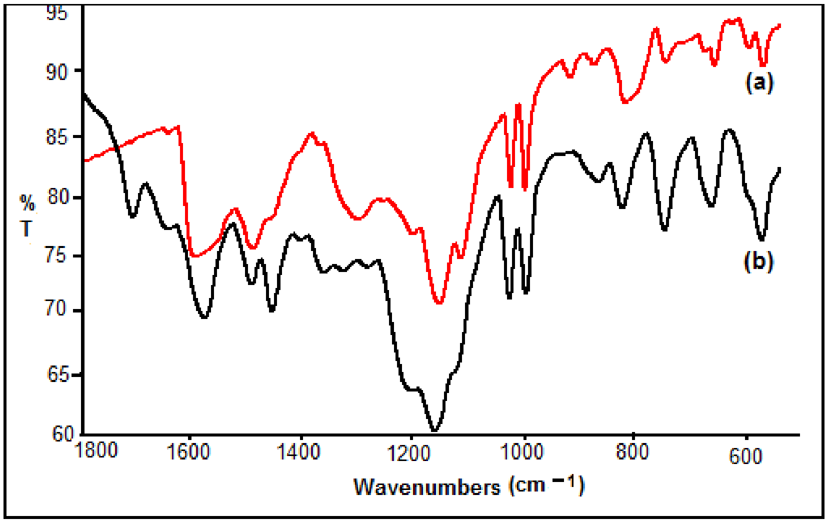

Fig.1 FTIR spectra of (a) PANI-NSA and (b) PANI-BSA

4.2 Conductivity Measurement

Room temperature conductivity of BSA doped and NSA doped PANI a powder sample was found to 0.95 and 2.50 S/cm respectively. After incorporation of PANI into cotton fabric, conductivity value at room temperature was found to decrease from 2.50 to 1.0×10^{-8} S/cm in case of PANI-NSA and from 0.95 to 1.0×10^{-11} S/cm in PANI-BSA due to the interaction of conducting phase (i.e PANI with insulating phase (i.e. cotton fabric). Insulating nature of the cotton fabric hinders the mobility of charge carrier throughout the composite. Thus the conductivity of the polymer coated fabric is lower than that of powder form of polymer. Moreover, it has also been observed that the conduction mechanism and transportation of charge carrier in the coated fabric depends on the morphology of polymer, their loading level and mode of dispersion of the conducting materials.

4.3 Thermo gravimetric analysis

Fig. 2 shows the thermo-gravimetric curves (TGA) of PANI. The TGA curve of BSA and NSA doped PANI indicates first weight loss at 100-110°C may be attributed to the loss of water and other volatile species. The weight loss in the second step at about 180°C involves the loss of dopant ions as well as onset of degradation of polyaniline backbone. It was observed that the PANI was thermally stable up to 180-190 °C, which indicates that these nanocomposites can also be used for melt blending with conventional thermoplastics such as polyethylene, polypropylene, polystyrene etc. for antistatic packaging materials.

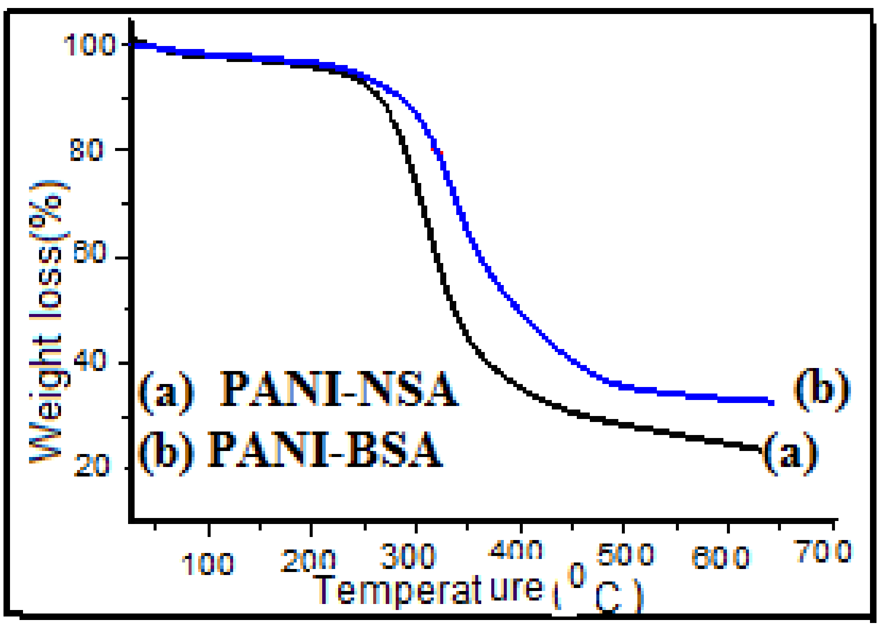

Fig.2 TGA analysis of PANI-NSA and PANI-BSA

4.4 X-Ray Diffraction analysis

Fig.3 shows the X-ray diffractogram of PANI preapared by using BSA as dopant and and NSA doped PANI microtubes. The weak reflections of PANI were centered at 2θ values of approximately 56.2^o, 49^o, 65 ^{o} and 78^o. These are characteristic of amorphous nature of PANI doped with BSA. But in case of PANI doped with NSA, The sharp diffraction peaks were observed; these peaks indicate the slight crystalline nature of polyaniline microtubes.

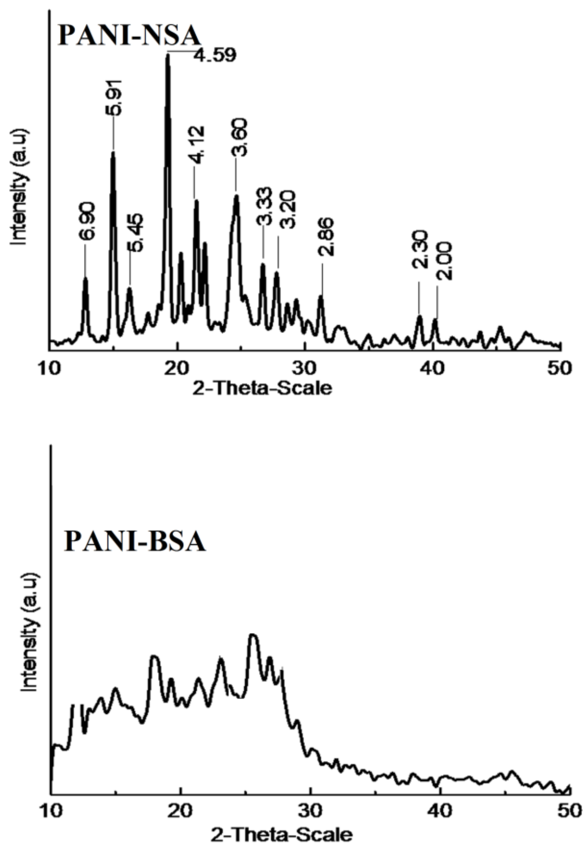

Fig.3 XRD spectra of PANI-NSA and PANI-BSA

4.5 Morphological Characterization of Polyaniline-NSA and Polyaniline-BSA

Fig.4 shows a typical SEM image of the PANI doped with BSA and PANI doped with NSA. SEM image of PANI-BSA revealed the spherical morphology. While SEM image of PANI-NSA showed tube like morphology. The dimension of the tube was found to be about 1.0 µm.

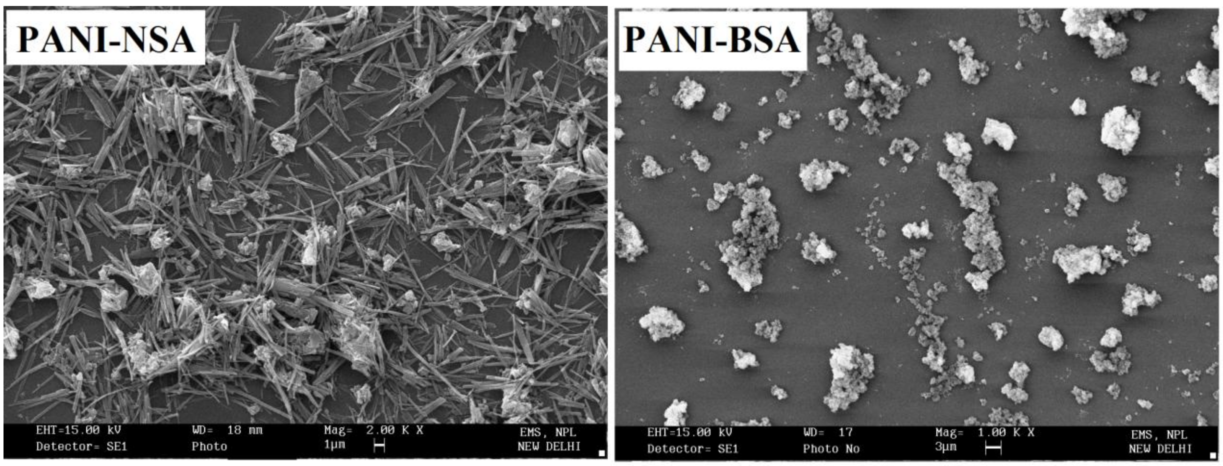

Fig. 4 SEM image of conducting polymer containing different dopant

4.6 Antistatic Measurements

Antistatic behaviour of uncoated, PANI-BSA granules coated and PANI-NSA (tubular morphology) coated fabrics was investigated by using John Chubb Instrument. Samples of uncoated and conducting polymer coated fabrics were cut in to pieces of 15 x 15 cm^2 were used for measurement of static decay time on john Chubb Instrument by measuring the time on applying a high corona positive voltage of 5000 V and recording the decay time on going down to 500 V at 10% and 50 % cut-off.

A fast response electrostatic field meter observes the voltage received on the surface of sample and measurements were to observe how quickly the voltage falls as the charge is dissipated from the sample's surface. Graphs obtained from these experiments have been shown in the Fig.5.

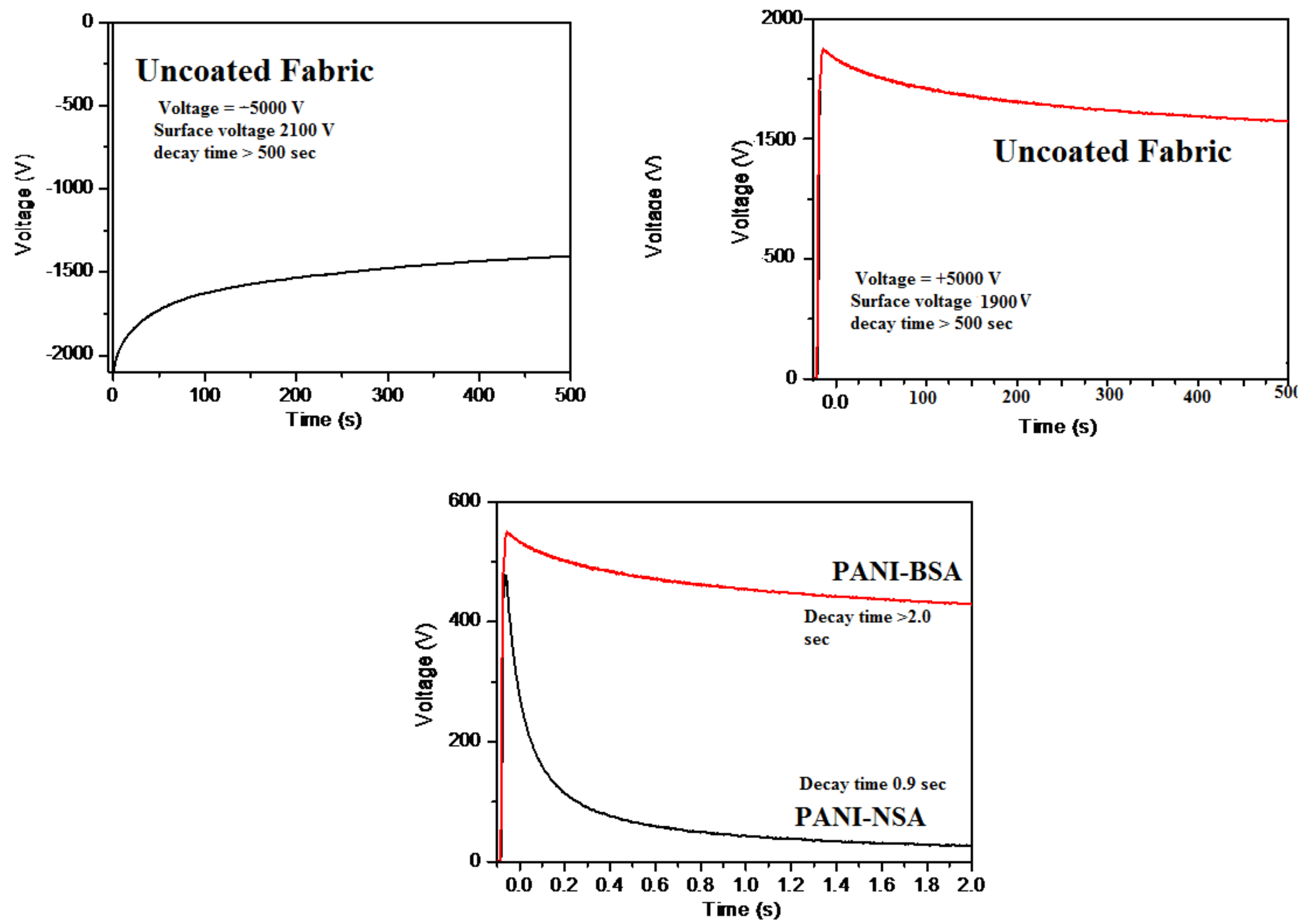

Fig.5 JCI graphs of uncoated and polymer coated samples

It shows the decay of surface voltage and decay time. When high corona voltage was applied on the surface of insulating material, only few voltage were drained away and larger amount of voltage were retained on its surface. This surface voltage decays at particular time. Moreover, the surface charge received by the fabric material was also calculated during the experiment. Hence the charge retention capability of conducting materials was found to be very low thus they quickly dissipate this surface charge. The static decay time of uncoated fabric was found to be very high on applying the positive and negative corona voltage of 5000 V. The peak at 2100 V indicates that the uncoated fabric has received 2100 V of voltage at the surface which dissipated very slowly and was not found to be able to dissipate it up to 10 % cut off as shown in the Fig. 5. Due to insulating nature of the material, a lot of charges were found to be retained on the surface of uncoated fabric. Fabrication of conducting polymer (i.e. PANI) on fabric matrix decreases the charge retention capability by reducing the decay time as shown in Fig. 5. This indicates that in case of PANI-BSA impregnated cotton fabric, the static decay time was > 2.0 sec. While the static decay time in NSA doped PANI impregnated fabric was found to be around 0.9 s on applying the voltage of +5000 V which showed remarkable reduction of static decay time at 10 % cut off. Any material which showed a static decay time less than 2.0 sec passes the criteria for its use as antistatic material. Based on above observations, we can say that polyaniline microtubes doped with naphthalene sulphonic acid can be used as an effective antistatic fabric.

4.7 Antimicrobial activity measurement against *E.coli* Bacteria

The antibacterial activity of PANI-BSA and PANI-NSA coated cotton fabric against *E. coli* microorganisms are shown in Fig.6. PANI-BSA coated samples showed less activity against bacteria (< 60 %) While, PANI-NSA impregnated fabric sample exhibits high activity with a great reduction of bacteria (80-85%), whereas the uncoated cotton did not show any antibacterial activity.

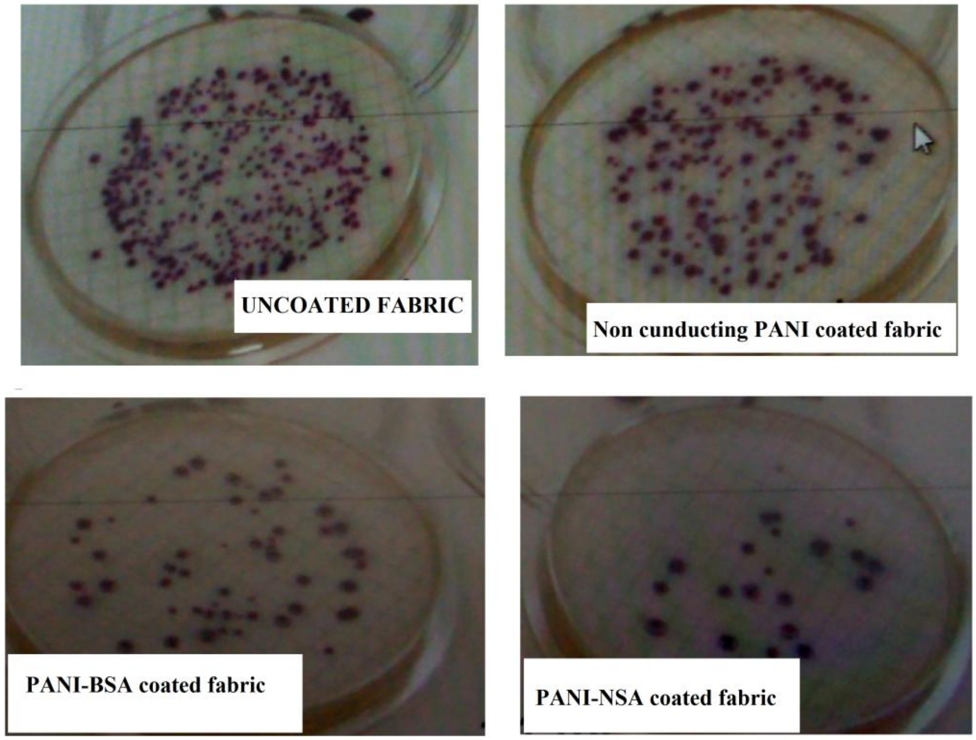

Fig. 6 The antibacterial activity of uncoated, PANI-BSA and PANI-NSA coated cotton fabric against *E. coli* microorganisms

5.0 Effect of morphology on Antistatic and biocidal properties of polyaniline

In conducting polymer coated fabric, the level of interaction between the two components such as polyaniline and insulating material, mode of dispersion of polyaniline and their morphology, influence the electrical and mechanical properties of the blends [24,25]. Interconnection of conducting phase in the non-conducting matrix such as cotton fabric creates a conducting path along the matrix. Moreover, it has also been observed that the conduction mechanism and transportation of charge carrier in the coated fabric depends on the loading level and mode of dispersion and morphology of the conducting materials. BSA doped PANI showed the granular globule like morphology and these granules seem to be embedded in the insulating matrix during coating. Conductivity value of PANI/BSA coated fabric was found to be in order of 10^{-11} Scm^{-1}

but in case of PANI/NSA coated fabric, the surface conductivity was found to be in the order of 10^{-8} Scm^{-1}, which is suitable for their use in ESD protection applications. Hence, it may be presumed that when the sufficient amount of conducting material is loaded in the polymer matrix, the conducting particles come closer and form linkage which makes an easy path for conduction of charge carrier throughout the fabric. While in the case of very low loading of conducting material in fabric matrix, the gap between conducting particles in the insulating matrix is large with the result that no conduction path in the fabric is established. More importantly it was noticed that, the conductivity of coated fabric also depends on the morphology of the conducting material when same loading level is used.

The tubular or fibre like morphology of conducting materials which form a network in the whole fabric which facilitate the conduction of charge carrier through the continuous structure of the chain of conducting material in the insulating matrix. Moreover it was also observed that, very low loading of conducting material in the insulating matrix decrease the conductivity. Hence conducting polymer coating on cotton fabric was carried out to achieve better and optimum absorption of conducting polymer in to fabric. Proper absorption and tubular morphology of polyaniline further favours the electrical, antistatic and antimicrobial performance of fabric material.

6.0 Conclusions

Conducting polymer PANI microgranules and microtubes were prepared by chemical oxidative oxidative polymerization method in the presence of BSA and Naphthalene sulphonic acid as dopant respectively. Formation of Polyaniline was confirmed by FTIR spectrum, XRD analysis, TGA, conductivity measurement and morphological characterization. Fabrication of PANI micro tubes on cotton fabric was carried out during polymerization that showed optimal conductivity and good thermal properties, Moreover, coated fabrics of these material successfully used for effective static protection application. These nanocomposites impregnated fabric showed a remarkable static decay time i.e. 0.9 sec which is less than 2.0 sec. Hence, various attractive features in PANI microtubes like better thermal stability, conductivity and antistatic performance make them a promising candidate for their use not only in antistatic encapsulation material but also for various electrical and electronic applications. Moreover, these materials can also be used as antibacterial fabrics in the form of protective and medical cloths and bed spreads, and many other purposes like water filter for waste water treatment to minimize the chance of bacterial infections.

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