Research Article Adv. Mat. Lett. 2014, **5**(10), 562-568 ADVANCED MATERIALS *Letters*

www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2014.572 Published online by the VBRI press in 2014

Effective antimicrobial filter from electrospun polyacrylonitrile-silver composite nanofibers membrane for conducive environment

Anisha Chaudhary, Ashish Gupta, Rakesh B. Mathur, Sanjay R. Dhakate*

Physics and Engineering of, Carbon, Division of Materials Physics and Engineering,
CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi 110012, India

*Corresponding author. Tel: (+91) 11 45608257; Fax: (+91) 11 45609310; E-mail: dhakate@mail.nplindia.org

Received: 09 January 2014, Revised: 08 June 2014 and Accepted: 28 June 2014

ABSTRACT

Electrospun nanofibers based antimicrobial filter were examined for their capability to build conductive environment. An antimicrobial agent, silver nitrate ($AgNO_3$), was added to the nanofibers membrane for its ability to prevent growth of microorganisms over the filter media. In this direction in the present investigation the different fractions of silver nanoparticles were in-situ synthesized in PAN solution and then polyacrylonitrile (PAN)-silver composite nanofibers membrane filter was prepared by electrospinning technique. The resultant solution and PAN-silver composite nanofibers was characterized by UV–visible spectroscopy, scanning electron microscope, atomic force microscope and X-ray diffraction. Antibacterial property of PAN silver composite nanofibers were investigated against gram positive *Staphylococcus aureus* and gram negative *Escherichia coli* microorganisms. The formation of clear zone suggests that composite nanofibers containing silver nanoparticles show strong antibacterial activity and it increases with increasing silver content in the composite nanofibers. The PAN-silver composite nanofibers sheet was also examined for filtration of microorganisms and dust particles. It was observed that PAN-silver composite nanofibers filter proven to be an excellent filter for creating microorganism and dust free hygienic environment. Thus electrospun PAN nanofibers filters containing an antibacterial agent can be a promising solution for effective microorganism filtration from indoor air in hospitals or other places which are more prone to bacterial infections. Copyright © 2014 VBRI press.

Keywords: Electrospinning; composite nanofibers; nanoparticles; antibacterial activity; filtration.

Anisha Chaudhary completed her M.Tech. in Nanoscience & Technology from G.J. University, Hisar, India. Presently she is pursuing her PhD (Engg.) from AcSIR-NPL, Delhi, India. Her research activities have been focused in the field of nanofibers & carbon based materials such as carbon nanofibers, CNTs and pitch based Nanomaterials.

Ashish Gupta (M. Tech.) is CSIR-Senior Research Fellow and perusing PhD in Engineering from Academic of Scientific and Innovative research- CSIR at National Physical Laboratory, New Delhi, INDIA. His research Interests are in electrospinning of polymeric, metal oxide and carbon nanofibers and their use for energy, filtration and biomedical applications.

Sanjay R. Dhakate is Senior Principal Scientist, Physics and Engineering of Carbon, CSIR –National Physical Laboratory, New Delhi India. He is working on various forms of carbon materials for structural and energy applications such as carbon fibers, carbon foams, carbon-carbon composites, electrospun nanofibers, graphene, polymer nanocomposites etc. He published his research work in various International repute journals. He is also senior editor of Journal of Nanoscience Letters.

Introduction

The air filtration process includes filtration of dust particles, pollen, water or oil aerosols, mold spores, volatile organic compounds and hydrocarbon or other vapors and thus represents a wide area **[1]**. In addition to these contaminants air contain microorganisms which can spoil or otherwise cause harm to the product or the living beings **[2]**. These microorganisms are main cause of indoor air contaminations in hospitals. The contaminated indoor air consequences in the greater risk to the patients to acquired infection. Ishida et al reported that in the hospital airborne bacteria are primary source for post-operative infection. Most of these bacteria became resistant to common antiseptics which are used in hospitals. The microorganisms that are often related to the hospital acquired infections are *Pseudomonas sp., Staphylococcus aureus, Micrococcus sp., Proteus sp., Escherichia coli, Bacillus cereus, Cladosporium sp., Enterobacter, Aspergillus sp*., and viruses. *Pseudomonas aeruginosa* has been developed intrinsic resistance to many antibiotics and found particularly associated with nosocomial infection. The preventive measures often taken in nosocomial infections includes adequate cleaning effective use of disinfectants, antiseptics, sterilization and isolation of patients from infectious diseases. However, very less attention is paid to contaminated indoor air which is potentially responsible more to hospital acquired infections. In order to meet the firm purity specifications, high quality sanitary applications with sterile air filtration products are required. Since, checks for the occurrence of germs normally involves complex and tedious procedure, precautions for contamination control become the primary objective **[2]**. A number of studies are conducted on air filtration, which proves the presence of living microorganisms on the surface of the filter media. Together with harmless microorganisms a nod of pathogenic species are isolated from air filters. Out of which the Pseudomonas aeruginosa is the most dangerous bacterial species **[3]**. *Aspergillus spp., Cladosporium spp., Penicillium spp., Rhizopus spp., Alternaria spp*., etc. are some of the fungal pathogens found in air filters. These pathogens produce mycotoxins which are generally situated inside or over the surface of spores and are more risky to human health. Apart from this certain strains can produce more than eight forms of mycotoxins. Mycotoxins, if inhaled can increase the chances of occurrence of cancerous diseases because mycotoxins have potential to impair the immune system and affect the lungs. They can also initiate the allergic reaction and cause skin and eyes irritation. In order to avoid the microbial growth in air filters with special care and precautions, it becomes essential to use an antimicrobial agent which can inhibit the microbial growth in filters, thus reduces bio contamination level in the treated air **[4]**. Since ancient time silver is the most extensively employed inorganic antibacterial agents capable of killing microorganisms, prevent infections and spoilage of products **[5]**. It is safe, nontoxic but quite effective in minute concentrations **[6]**. Probability of developing the resistance against silver is very low as metal can cover a wide range of targets in microorganisms. In this way they would develop instantaneously a series of mutations to defend themselves **[5-7]**. There are various methods for the synthesis of the silver nanoparticles such as chemical reduction, photo reduction, thermal decomposition, and reverse micelles chemical reduction **[8]**. For the synthesis of silver nanoparticles from the liquid phase the reduction via a reducing agent is the most effective one **[9]**.

In recent years, nanofibers, particularly polymeric nanofibers, have gained significant prominence in commercial air filtration applications due to their superior ability to enhance filtration efficiency of different forms of filter media **[10]**. As compared to woven form nonwoven nanofibers mat possess a small pore size with high surface area, and high aspect ratio. This, together with the advantage of low density and highly interconnected porous structure, makes nanofibers suitable for a number of filtration applications **[11]**. There are different approaches of nanofibers production, but the most versatile process is the electrospinning. This novel process have drawn immense interest because of the unique properties of electrospun nanofibers such as the high surface area, high porosity, high aspect ratio **[12-15]** and it can prepare low cost nanofibers with high yield. Electrospun nanofibers with this novel functionality can be produced by the addition inorganic materials to the polymeric system **[16, 17]**. For the preparation of metal polymer nanofibers composite either the silver nanoparticles are synthesized inside the polymer matrix (in-situ reduction) or they are dispersed separately in the polymer matrix. But in situ reduction of silver nanoparticles is better choice as compared to the dispersion of nanoparticles in polymer matrix, which is quite difficult task and has more chances of agglomeration of nanoparticles **[18]** and consequently has low bioavailability with diminished antimicrobial activity. In-situ reduction results in more uniform dispersion because polymer molecules have a stabilizing effect on the silver nanoparticles **[19-21]**.

PAN is the choice of polymer because of it high strength, high thermal stability and good solvent properties **[22-24]**. Whereas for preparing spinable PAN solution, N, N-dimethylformamide (DMF) has been selected as solvent it can also act as reducing agent and reduce the silver ions to the zero valent metal without the need of any further external reducing agent **[25]**. Together with DMF, PAN molecules stabilize the as formed silver nanoparticles and thus prevent their agglomeration. In this investigation the silver nanoparticles were in-situ synthesized in the polymer matrix and electrospun into PAN-Ag composite nanofibers. These composite nanofibers membrane were studied for antimicrobial activity with as filter to create protective environment in hospitals.

Experimental

Materials

PAN co-polymer having Poly acrylonitrile with a 6% monomer methyl methacrylate was used as source for the fabrication of nanofibers. DMF of 99% purity (B. Pt. = 157^{o}C) and silver nitrate ($AgNO_3$) were purchased from Fisher Scientific. *Staphylococcus aureus*-MTCC-1809 and *Escherichia Coli*-MTCC-40 purchased from IMTECH, Chandigarh. The chemicals used during the studies were of analytical grade and used as received without further purification.

Preparation of PAN solution containing Ag ions

8 weight % of PAN solution was prepared in organic solvent DMF through sonication for 50 min and magnetic stirring for 5 h at room temperature. Then $AgNO_3$ (0.05–1wt. % calculated on the basis of PAN weight) was added in the solutions. The PAN/DMF solutions **[26]** containing silver salt was stirred for overnight at 40^{o}C. During the stirring process, the beakers were covered with aluminum

foil in order to prevent the unwanted reduction of silver ions. Later on silver ion reduction in the solutions mixture was carried out by exposing to light for 4 h. During the irradiation yellow color of the PAN/DMF solution containing silver salt was observed with the naked eye which indicates Ag nanoparticles.

Electrospinning of PAN/AgNO$_3$ solution

The electrospinning of PAN and PAN/$AgNO_3$ solution was carried out on Espin-Nano instrument procured from PICO, Chennai **[27]**. The PAN-$AgNO_3$ solution was poured into a syringe equipped with a stainless steel needle tip and electrospun into nanofibers at flow rate of 0.2ml/h. The voltage used for electrospinning was 15 kV. The distance between the needle tips to collector was 20 cm and speed of rotation of collector was 2000 rpm.

Zone inhibition test for antimicrobial activity

The Zone inhibition test for antimicrobial activity was carried out with gram positive bacteria *Staphylococcus aureus* and gram negative bacteria *E. coli*. Microbes were inoculated from the stock culture in 300 mL nutrient broth having composition peptone (5g/L), NaCl (5g/L), beef extract (1.5g/L), yeast extract (1.5g/L) in separate test tubes. Then tubes were plugged with cotton, wrapped with aluminum foil and incubated for 24 h at 37^{o}C. Next day the nutrient agar solution was autoclaved for sterilization and poured in the disposable petri plates under laminar air flow so as to exclude the microbial contamination which might come during the experiment. When the agar gets solidified, each microbial solution was spread over the solidified agar plates and fixed weight of nanofibers having varying conc. of silver placed over agar plates. The controls for each bacterium were also prepared with using streptomycin antibiotics. Plates were then sealed with parafilm and incubated again for 24 h at 37^{o}C. Next day zone surrounding the nanofibers membrane were obtained and area was measured.

Air filtration efficiency test

Fig. **1** illustrates schematic diagram of the bacterial filtration testing apparatus. It consists of glass chamber with open mouth and having an outlet at the bottom of the apparatus. For the filtration test the sterile glass dish containing the nutrient solution (as mentioned earlier) for the growth of microorganisms was placed inside the chamber. The open surface of chamber was covered with the PAN-silver (Ag) composite nanofibers membrane. Vacuum was applied from the bottom of the apparatus to ensure the flow of the air through the nanofibers membrane over the glass plate. The glass plate was continuously monitor for two month and was compared with the glass plate placed inside the chamber without nanofibers filter membrane.

Characterization Techniques

The morphology of nanofibers membrane was studied by SEM using Model EVO M-10 of Zeiss. Chemical composition near the surface was measured by energy dispersive X-ray analysis (EDAX). UV-Visible absorption spectroscopy of the silver nanoparticles containing PAN/DMF solutions from 300 to 700 nm were carried out on a UV–visible spectrophotometer (Model 160UV shimadzu). The composite nanofibers membrane was characterized by X-ray diffractometer (RIGAKU, Tokyo, Japan). The surface topography of nanofiber membrane was observed by Atomic force microscopy (Scanning probe microscope, SPM-V) Veeco instruments Inc., USA. In the AFM, the force-transducer is a deflecting cantilever on which a sharp tip is mounted. Cantilevers exhibit force constants around 0.1 N/m. in contact imaging, the measurement of cantilever deflection is performed directly (quasi statically) as the tip was being scanned over the surface.

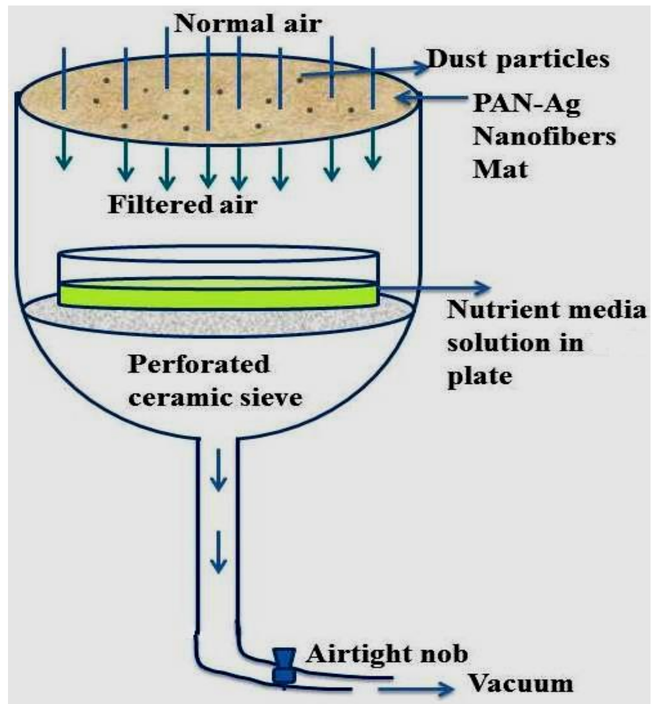

Fig. 1. A schematic drawing of the microorganism's filtration testing apparatus.

Results and discussion

Morphology of PAN and PAN-Ag composite nanofibers

Fig. **2** shows the SEM images of PAN and PAN-Ag composite nanofibers. The PAN nanofibers with uniform morphology and the nanofibers diameter is in the range of 200 -300 nm (**Fig**. **2a**). On the other hand, in case of PAN-Ag composite nanofibers, Ag nanoparticles randomly distributed over the surface of the PAN nanofibers and entrap between the polymeric chains and as consequence increase in composite nanofibers diameter as compared PAN nanofibers. The composite nanofibers surface morphology changes from smooth to rough surface and nanofibers have diameter in the range of 600 to 900 nm. In some cases the diameter of nanofibers is very large , this might be due to the fact that during electrospinning the Ag particles are unite or agglomerate in the syringe tip and sometime it suddenly drop down with nanofiber ejection. (**Fig**. **2b, c**).

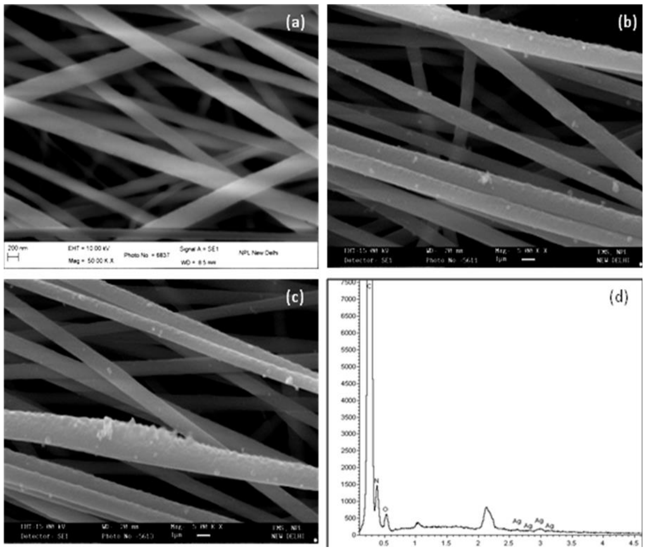

Fig. 2. SEM micrographs of (a) PAN, (b and c) PAN-Ag composite nanofibers and its EDAX spectrum (d).

The chemical composition of PAN-Ag composite nanofibers is measured EDAX. In this during the preparation of spinable solution, $AgNO_3$ added in such a manner in the final PAN-Ag composites nanofiber membrane Ag content will be 0.5 %. From the EDAX spectra of PAN-silver composite nanofibers (**Fig**. **2d**) it is observed that it consist of carbon 61.36%, nitrogen 37.90%, oxygen 0.23% and Ag 0.5%. The incorporation of silver nanoparticles in PAN nanofibers has adverse effect on the surface morphology and roughness of nanofibers. This is confirmed by AFM. **Fig**. **3** shows the AFM image of PAN/Ag composite nanofibers, it shows the mat type morphology of nanofibers membrane.

It is observe that brighter regions in nanofibers mat (**Fig**. **3b**) are due to the Ag nanoparticles entrap in the polymeric chain or nanoparticles over the surface of the PAN nanofibers. In **Fig**. **3**, insert 3D topography image gives information of surface parameters such as the root mean square (Rq) and mean roughness (R_a). The PAN nanofibers have Rq 358 nm and Ra 287 nm. However, PAN-Ag composite nanofibers having Rq 585nm and Ra 454 nm values which are higher as compared to that of PAN nanofibers, this is due to entrapment of Ag nanoparticles in the polymer chain and Ag particles on the surface of PAN nanofibers. These observations are in agreement with SEM study of PAN- Ag composite nanofibers.

UV visible Spectroscopy

Fig. **4**. shows the UV –visible spectra of an 8 wt. % PAN/DMF solution containing 0.5 wt. % $AgNO_3$ which is used to determine the synthesis of Ag nanoparticles in PAN DMF solution under 4 h light irradiation. It shows that Plasmon absorption peak observed at wavelength of 430 to 440nm. The absorption peak for silver nanoparticles in the range of 2 to 50 nm is appearing as in wavelength range between 400 to 450nm. There is a change in the absorption spectrum and wavelength with the course of irradiation.

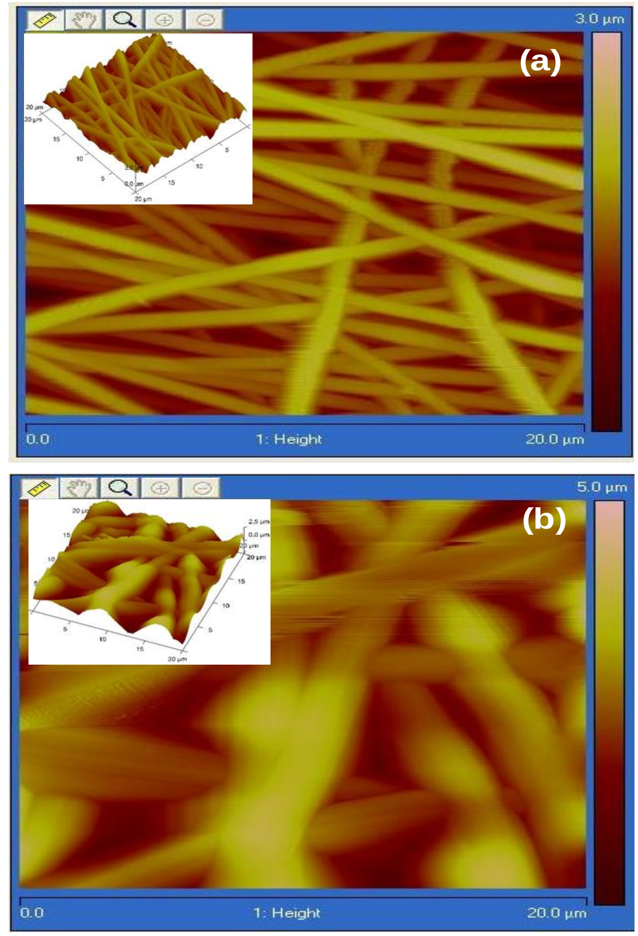

Fig. 3. AFM 2D and 3D (inset) images of (a) PAN as such (b) PAN/Ag composite nanofibers.

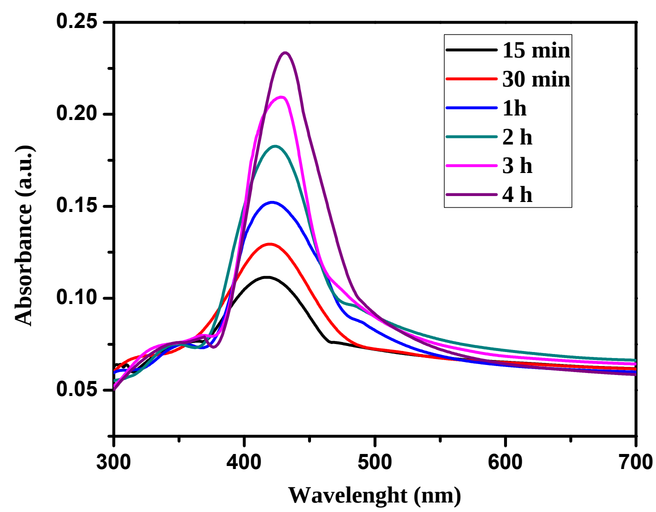

Fig. 4. UV–Vis spectra of 8 wt % PAN/DMF solution containing 0.5 wt % $AgNO_3$ in the course of 4 h of irradiation.

The intensity of the strong absorption peak appeared at about 416nm and start increasing with the irradiation time possibly due to the increase in the reaction process of silver ion reduction into silver nanoparticles. A significant increase in the wavelength with irradiation time is observed which confirmed the formation of nanoparticles of higher particles size with respect to time during the reaction process (**Fig. 5**).

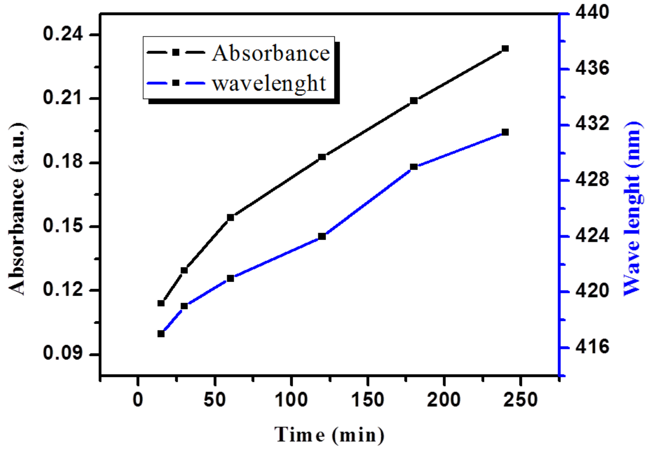

Fig. 5. Absorption maximum and wavelength of the absorption maximum of 8 wt. % PAN/DMF solution containing 0.5 wt. % $AgNO_3$ in the course of 4 h of irradiation versus irradiation time.

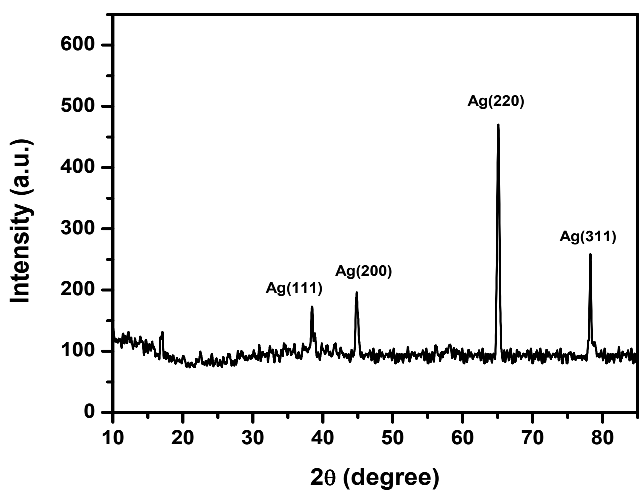

Fig. 6. XRD curves of PAN-Ag composite nanofibers.

In-situ synthesis of Ag nanoparticles in PAN polymer matrix is confirmed by the XRD. **Fig. 6** shows the XRD spectra of PAN-Ag composite nanofibers. The spectra consist of four peaks which are corresponds to 110, 200, 220 and 311 crystal planes of silver nanoparticles at the 2θ values of 38.504°, 44.752°, 65.126°, 78.251° respectively. The peaks in the XRD pattern revealed the face-centered-cubic form of metallic silver resembled with standard values given in ICCD-JCPDS card no. 4-0787 with diameters in the range of 20 to 50nm.

Antibacterial activity

Antibacterial activity of PAN-Ag composite nanofibers is studied by the zone inhibition test using gram positive bacterium *staphylococcus aureus* and gram negative bacterium *E. coli*. **Fig. 7** shows the clear zone of inhibition surroundings the composite nanofibers disc having different concentration of silver nanoparticles but it is absent in PAN nanofibers disc which did not contain silver nanoparticles. The length of the zones are measured with help of the caliper scale and analyzed for different concentration of the silver containing nanofibers. It is observed that with the increase of silver ions concentration in the composite nanofibers, antibacterial activity increases while zone remains absent in the PAN nanofibers, this suggest that PAN nanofibers does not show antibacterial activity. Antibacterial activity in PAN-Ag composite nanofibers is found to be more against S. aureus compared to E.coli. With increasing the concentration of Ag in PAN-Ag composite nanofibers, it is found that zone inhibition length increases continuously (**Table 1**).

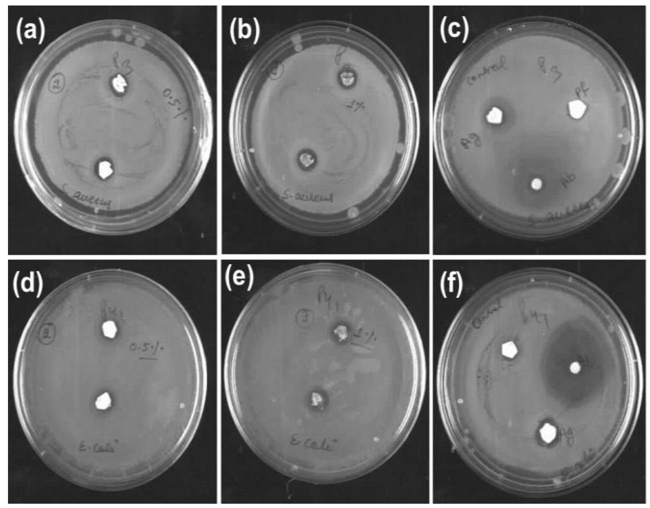

Fig. 7. Photographs showing zone of inhibition of the PAN/Ag composite nanofibers membrane against (a,b,c) S. Aureus and (d,e,f) E. Coli for 0.5, 1.0 and 0 wt % concentration of Ag.

Table 1. The zone length of inhibition for the PAN/Ag composite nanofibers membrane against S. aureus, and E. coli microorganisms.

Polymer nanofiber	Microorganisms	Zone of inhibition (mm)				Activity
		0.05% Ag	0.1% Ag	0.5% Ag	1% Ag	
PAN nanofibers	E. coli/S.aureus	0	0	0	0	No
PAN-Ag composite nanofibers	E. coli	10	13	16	17	yes
PAN Ag composite nanofibers	S.aureus	12	14	16	18	yes

The mechanism of the inhibitory effects of Ag on microorganisms is partially known. Some studies have reported that the positive charge on the Ag ion is crucial for its antimicrobial activity through the electrostatic attraction between negative charged cell membrane of microorganism and positive charged Ag nanoparticles **[28, 29]**. In contrast, it is reported that the antimicrobial activity of Ag nano-particles on gram-negative bacteria is dependent on the concentration of Ag nanoparticles **[30]** and is closely associated with the formation of pits in the cell wall of bacteria. Then, Ag nanoparticles accumulated in the bacterial membrane caused the permeability, resulting in cell death. However, it is difficult to explain antimicrobial activity using both positively and negatively charged Ag ions. Therefore, we expect that there is another possible mechanism, metal depletion may cause the formation of irregularly shaped pits in the outer membrane and change membrane permeability, which is caused by progressive release of lipopolysaccharides molecules and membrane proteins **[31]**.

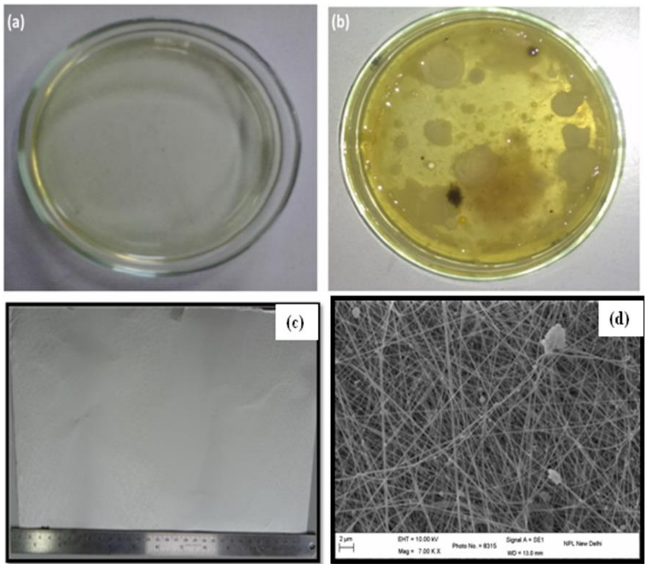

Fig. 8. Photographs showing glass disc plates containing nutrient media for the growth of microorganisms a) covered with PAN/Ag composite nanofibers membrane, b) without cover, c) PAN-Ag composite nanofiber membrane of size 30 cm x 20 cm and d) SEM image of PAN/Ag composite nanofibers showing dust particles over the nanofibers surface.

Air filtration test

PAN-Ag based nanofibers membrane filter synthesized and studied for a period of about 2 month (as shown in **Fig**. **1** setup) and found to have demonstrated potential for effective removal and retention of bacteria during air-filtration process for a longer period of time. From the experiment of microbial filtration (**Fig**. **8**), it shows that the glass plate placed in the glass chamber covered with the composite nanofibers sheet show effective filtration control on penetration of microorganisms in the nutrient solution. On the other hand the glass plates placed without nanofibers sheet covering in glass chamber is found to have profound microbial growth as well dust particles (**Fig**. **8b**). These results shows that silver nanoparticles based composite nanofibers have enormous potential to prevent the access of microorganisms through their surface to the interior of the nanofibers membrane. Not only it prevents access of microorganism but also stop various sizes of dust particles (air pollutant) to enter in the interior of membrane. The nanofibers layer thickness and diameter distribution can be varied according to the requirements. Since after the discovery of nanomaterial, miniaturization of technologies by using smaller size or nanoscale materials increase tremendously and as a result there is dust particles of nanosize suspended in the environment. On these nanoparticles microorganism can also be grow easily and bind with them due to it high surface area. Therefore, there is need of such a filter material that can not only retain smaller or nanosize dust particles but also protects the environment from microorganism. **Fig**. **8c** shows the composite nanofiber sheet of 30 cm x 20 cm, which can cover small window for air circulation. **Fig**. **8d** also shows different size of dust particles collected on the PAN-Ag composite nanofibers. It is found that the dust particles of size 500-1000 nm are collected on the PAN-Ag nanofiber filter membrane; also there are some big particles as well.

Conclusion

Electrospun PAN-Ag composite nanofibers were tested for antibacterial activity and show good antibacterial activity against *S. aureus* and *E. coli*. Air filtration test performed also confirmed the ability of composite nanofibers to filter dust and microorganisms. Microorganisms free air helps in providing the clean environment which can save many lives in hospitals where, the chances of bacterial infections after post surgery are common and for senior citizens who are supposed to be more susceptible to bacterial infections. Also the use of an antibacterial agent in nanofibers membrane prevents the growth of microorganisms in filters membrane and subsequently provides the hygienic filters. These membranes can also be used as antimicrobial wound dressing material.

Acknowledgements

Authors are highly grateful to Director, CSIR-NPL, for his kind permission to publish the results. Thanks Mr. Sood and J. Tawale for providing SEM characterization facility. Author also like to thanks Department of Science and Technology for financial support (SR/S2/CMP-10/2010). One of the author Ashish Gupta thanks CSIR for SRF fellowship.

Reference

1. Lubasova, D.; Netravali, A.; Parker, J.; Ingel, B. Nanocon Brno, *Czech Republic*, EU.**2012.**
2. Awosika, SA.; Olajubu, FA.; Amusa, NA. *Asian Pacific Journal of Tropical Biomedicine*. **2012**, *2*(6), 465.
   DOI: 10.1016/S2221-1691 (12)60077-X.
3. Ekhaise, FO.; Isitor, EE.; Idehen, O.; Emoghene, AO. *World J. Agric. Sci.* **2010**, *6*, 166.
4. Peska, EM.; Lebkowska, M. *Fibres & Textiles in Eastern Europe*. **2011**, *19*, 73.
5. Pal, S.; Tak, YK.; Song, JM.. *Applied and environmental microbiology*. **2007**, *73*, 1712.
   DOI: 10.1128/AEM.02218-06.
6. Raffiy, M.; Hussain, F.; Bhatti, TM.; Akhter, JI.; Hameed, A.; Hasan, MM. *J. Mater. Sci. Technol.* **2008**, *24*, 192.
7. Singh, M.; Singh, S.; Prasad, S.; gambhir, IS. *Digest Journal of Nanomaterials and Biostructures.* **2008**, *3*, 115.
8. Forough, M.; Farhadi, K. Turkish J. *Eng. Env. Sci.* **2010**, *34*, 281.
   DOI: 10.3906/muh-1005-30
9. Sarkar, A.; Kapoor, S.; Mukherjee, T. *Res Chem Intermed.* **2010**, *36*, 411.
   DOI: 10.1007/s11164-010-0151-4
10. Graham, K.; Ouyang, M; Raether, T.; Grafe, T.; McDonald, B.; Knauf, P. Presented at the 15th Annual Technical Conference & Expo of the American Filtration & Separations Society, **2002** April 9-12; Galveston, Texas.
11. Lev, J.; Holba, M.; Kalhotka, L.; Mikula, P. Kimmer, D. *International Journal of Theoretical and Applied Nanotechnology*. **2012**, *1*, 16.
12. Huanga, ZM.; Zhangb, YZ.; Kotakic, M.; Ramakrishnab, S. *Composites Science and Technology*. **2003**, *63*, 2223.
    DOI: 10.1016/S0266-3538(03)00178-7.
13. Sichani, GN.; Morshed, M.; Amirnasr, M.; Abedi, D. *Journal of Applied Polymer Science*. **2010**, *116*, 1021.
    DOI: 10.1002/app.31436.
14. Mahapatra, A.; Garg, N.; Nayak, BP.; Mishra, B.G.; Hota, G. *Journal of Applied Polymer Science*. **2012**, *124*, 1178.
    DOI: 10.1002/app.35076.
15. Bai, J.; Yang, Q.; Wang, S.; Li, Y. *Korean J. Chem. Eng.* **2011,** *28*, 1761.
    DOI: 10.1007/s11814-011-0006-8.
16. Wang, HS.; Fu, GD.; Li, XS. *Recent Patents on Nanotechnology*, **2009,** *3*, 21.

DOI: 10.2174/187221009787003285.
17. Matulevicius, J.; Kliucininkas, L.; Martuzevicius, D.; Krugly, E.; Tichonovas, M.; Baltrusaitis, J. *J. of Nanomaterials*. **2014**, *2014*, 13.
DOI: org/10.1155/2014/859656.
18. Calinescu, I.; Patrascu, M.; Gavrila, AI.; Trifan, A.; Boscornea, C. *U.P.B. Sci. Bull Series B*. **2011,** *73*, 3.
19. Shi, Q.; Vitchuli, N.; Nowak, J.; Caldwell, JM.; Breidt, F.; Bourhamb, M.; Zhang, X.; McCord, M. *European Polymer Journal*. **2011**, *47*, 1402.
DOI: 10.1016/j.eurpolymj.2011.04.002.
20. Yu, D.; Zhou, J.; Chatterton, N.; Li, Y.; Huang, J.; Wang, X. *International Journal of Nanomedicine*. **2012**, *7*, 5725.
DOI: 10.2147/IJN.S37455.
21. Joe, Y.; Ju, W.; Park, J.; Yoon, Y.; Hwang, *J. Aerosol and Air Quality Research*. **2013**, *13*, 1009.
DOI: 10.4209/aaqr.2012.07.0191.
22. Rujitanaroj, P.; Pimpha, N.; Supaphol, P. *Journal of Applied Polymer Science*. **2010**, 116, 1967.
DOI: 10.1002/app.31498.
23. He, J.; Qi, K.; Zhou, Y.; Cui, S. *J. APPL. POLYM. SCI.* **2014,** *131*, 40137.
DOI: 10.1002/app.40137.
24. Zhang, L.; Aboagye, A.; Kelkar, A.; Lai, C.; Fong, H. J. *Mater Sci*. **2014**, *49*, 463.
DOI: 10.1007/s10853-013-7705-y.
25. Lee, DY.; Lee, KH.; Cho, BYKNI. *J Sol-Gel Sci Technol.* **2010,** *54*, 63.
DOI: 10.1007/s10971-010-2158-0.
26. Dhakate, S.R.; Gupta, A.; Choudhari, A.; Tawale J.; Mathur, RB. *Synthetic Metals* **2011,** *161*,411.
DOI: 10.1016/j.synthmet.2010.12.019.
27. Gupta**,** A.; Dhakate, S.R.; Pahawa, M.; Mathur, R.B.; Chand, S. *Process Biochemistry* **2013,** *48*, 124.
DOI: 10.1016/j.procbio.2012.09.028.
28. Dibrov, P.; Dzioba, J.; Gosink, KK.; Hase, CC. *Antimicrob Agents Chemother*. **2002,** *46*, 2668.
DOI: 10.1128/AAC.46.8.2668-2670.2002.
29. Dragieva, I.; Stoeva, S.; Stoimenov, P.; Pavlikianov, E.; Klabunde, K. *Nanostruct Mater*. **1999**, *12*, 267.
DOI: 10.1016/S0965-9773(99)00114-2.
30. Sondi, I.; Salopek-Sondi, B. *J Colloid Interface Sci.* **2004**, *275*,177.
DOI: 10.1016/j.jcis.2004.02.012.
31. Amro, NA.; Kotra, LP.; Wadu-Mesthrige, K.; Bulychev, A.; Mobashery, S.; Liu, G. *Langmuir*. **2000**, *16*, 2789.
DOI: 10.1021/la991013x.