Study of Enhancement of Bio-Compatibility of Argon Plasma Irradiated: Polycarbonate Ag Nanocomposites Polymer Membranes

Narendra Kumar Agrawal
Department of Physics
Malaviya National Institute of Technology,
Jaipur, 302017, India.
E-mail: research.nka@gmail.com

Ravi Agarwal
Centre for Converging Technologies
University of Rajasthan,
Jaipur, 302004, India.

Gautam Aashish Kumar
Centre for Converging Technologies
University of Rajasthan,
Jaipur, 302004, India.

Y. K. Vijay
Department of Physics
University of Rajasthan,
Jaipur, 302004, India.

K. C. Swami
Department of Physics
Malaviya National Institute of Technology,
Jaipur, 302017, India.

***Abstract*— Nano particles of silver were synthesized from Coriandrum sativum plant extract and characterized (to ensure nano range particle size distribution) using UV-Vis spectrophotometer, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction and Scanning Electron Microscope. These Nanoparticles were used as nano composites for polymer. Solution casting and spin coating method, was used to prepare Ag-Polycarbonate nanocomposite polymeric membranes of 35 micron. Argon plasma irradiation was done for these membranes. These membranes were characterized by different technique such as Atomic Force Microscopy and Fourier transform infrared spectroscopy before and after plasma treatment. The selectivity for bacterial growth of these membranes depends upon thickness, ion dose, etching time and chemical nature. The plasma treatment modifies the bio-adoptability of membrane and creates active site to enhances the bacterial growth. This shows use of Argon plasma treatment for improving Bio-Compatibility of nanocomposite polymer membranes.**

Keywords*— Ag nanoparticles, Polymer Nano Composites, Synthetic Membrane, Plasma Treatment, Plasma Etching.

I. INTRODUCTION

Metallic nanoparticles are traditionally synthesized by wet chemical synthesis where chemicals used or by-products generated are often toxic and flammable [1]. Since noble metal nanoparticles are widely used in biomedical applications [2]. It shows a growing need to develop environmentally friendly processes for nanoparticle synthesis that do not use toxic chemicals. Biological and biomedical methods of nanoparticle synthesis using micro-organisms, plants including algae, fungi, bryophyte, pteridophyte etc [3] have been suggested as possible ecofriendly alternatives to chemical and physical methods [4]. Among the various noble inorganic metal nanoparticles, silver nanoparticles have received substantial attention for various reasons – like transmission [5], refractive index [6], high electrical conductivity by cross linking [7], catalysis [8] and antimicrobial activities [9]. Use of silver metal ions for their sustained antifungal, antibacterial and antiviral effects has been practiced [10]. In the present study Ag NPs were synthesized using Coriandrum sativum plant extract and characterized with various characterization techniques like UV-Vis spectrophotometer, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction and Scanning Electron Microscope.

Polymers have become very important materials in modern manufacturing processes and offer wide varieties of electrical, physical and mechanical properties applicable in various applications like solar cell synthesis [11], biomedical device synthesis [12] and other biological purposes [13]. But it is also well known that permanent bonding [14], coating, printing etc. [15] are difficult or not possible on many polymers without surface pre-treatment [16]. Therefore, surface treatment of polymers have significant benefits in the specific requirements of surface properties while retaining bulk mechanical and physical properties unaltered [17]. The physical and chemical surface modifications of polymeric materials without alteration of the bulk properties are of great interest in artificial skin development [18].The complex nature of plasma due to presence of ions, neutrals and radiation in the discharge makes low-temperature plasmas widely useful in a growing number of materials fabrication processes including the etching of complex patterns and surface modifications of polymeric membranes.

Plasma surface treatment usually refers to a plasma reaction or plasma etching that either results in modification of the

molecular structure of surface, or atomic substitution. Plasma treatment is a useful tool in the modification of surface properties [19]. The accelerated electrons from the plasma have sufficient energy to induce cleavage of chemical bonds in membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization [20]. The use of low pressure plasma enables surface and chemical modification of polymer materials [21]. Various plasma components such as electrons, ions, radical etc. are involved in this process. These components react with the exposed surfaces. Since some parts of surface are exposed to energies higher than the characteristic bond energy of polymers, these parts undergo scission reactions and form new bonding configurations on the surface. Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites on the surfaces which are subjected to post-reaction [22]. Glow-discharge plasma technique is particularly useful for functionalization of surfaces as it is possible to modify the outermost surface layer by this technique. Functionalization of polymer surfaces has been recognized as a valuable tool to improve their adhesion properties. Additionally, weak boundary layers and surface contaminants are also removed during modification. These factors improve the adhesion properties of the surface and improve bio-Compatibility of polymer.

In this paper we have carried out detailed study to identify the effect of Argon plasma for improving biocompatibility of nanocomposite polymer membranes. Nano particles of silver were synthesized from Coriandrum sativum plant extract and characterized (to ensure nano range particle size distribution) using UV-Vis spectrophotometer, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction and Scanning Electron Microscope. These Nanoparticles were used as nano composites for polymer. Solution casting and spin coating method, was used to prepare Ag-Polycarbonate nanocomposite polymeric membranes of 35 micron. Argon plasma irradiation was done for these membranes. These membranes were characterized by different technique such as Atomic Force Microscopy and Fourier transform infrared spectroscopy before and after plasma treatment. The plasma treatment modifies the bio-adoptability of membrane and creates active site to enhances the bacterial growth. This shows use of Argon plasma treatment for improving Bio-Compatibility of nanocomposite polymer membranes.

II. EXPERIMENTAL

The plant material were collected from university campus and washed with sterile distilled water. The plant extract was prepared by taking 35 g of thoroughly washed plant material in a 500-mL Erlenmeyer flask with 200 mL of distilled water, and then boiling the mixture for 10 min in a water bath. The leaf broth was then cooled and filtered through Whatman No.1 filter paper (pore size 25 μm). For preparation of silver nanoparticles, 20 mL of the prepared plant extract was added to 200 ml of 1mM silver nitrate solution and incubated in a rotary shaker for 2 h. The color of the solution changed from light yellow to brown indicating the formation of silver nanoparticles. UV-Vis spectrum of NPs was taken using UV-Vis spectrophotometer SHIMADZU 1800. FTIR Analysis was done using FTIR spectrophotometer (IR Affinity-1 Shimadzu) in the range of 4000- 400 cm-1 for knowing the possible functional groups present with synthesized Ag NPs. Scanning Electron Microscopic (SEM) analysis was done using Hitachi S-4500 SEM machine. X'Pert Pro x-ray diffractometer (PAN alytical BV, The Netherlands) operated at a voltage of 45kV and current of 40mA with Cu k(α) radiation of wavelength 1.54059 Å were used to record X-ray diffraction Pattern.

Polycarbonate granules (2mm, 0.02 gm. Each, obtained as commercial grade from Loxim Polymers, Jaipur) were used to prepare flat sheet membranes by solution cast method. Dichloromethane of extra pure grade was used as a solvent for preparing 10% polymer solution.

Solution-casting method was used for preparation of polycarbonate membranes (both doped and pristine). Polycarbonate granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution. Agitation of the solution is important, since the solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution. The process is carried out at room temperature for around 2-3 hours till a clear solution is formed. The solution was then put into flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10 –12 h. The films so obtained were peeled off using forceps.

3.5 % Ag doped polycarbonate membranes was also prepared by solution casting method (Fig 1). Polycarbonate solution was prepared in the same way as mentioned above for pristine membranes. Ag nanoparticles were dispersed in the solvent dichloromethane using ultra-sonicator. This dispersed solution was then added to the polycarbonate solution and stirred for around 30 minutes. The solution was then put into flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10-12 hours. The films so obtained were peeled off using forceps.

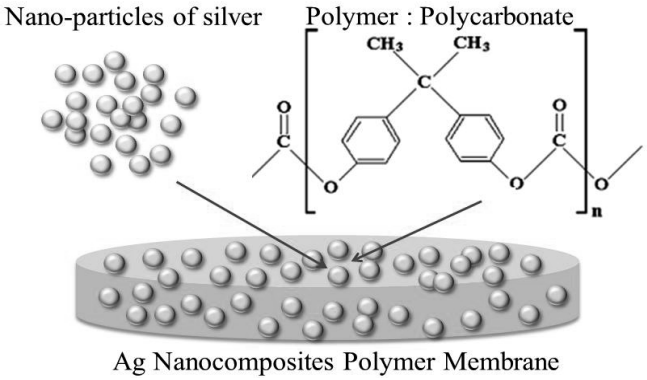


Fig. 1. Schematic diagram for preparation of Ag Nano composites polymer membranes.

Plasma treatment consists of a source chamber with the complete power supply, connected to a vacuum system. The magnet is positioned to get a magnetic field (0.5 K. Gauss)

inside the source chamber. Argon gas used for generate plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes at10 cm distances. The confined plasma in the chamber is used for surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge. The chamber is first evacuated to a base pressure of 10^{-10} torr and working pressure is maintained at 10^{-7} torr by admitting argon gas. The current in the upper and lower electrodes is maintained at few mA at 1.2 KeV. In this study we have used argon plasma. The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and then refilled with low-pressure argon gas to create glow discharge plasma. The gas is then energized by direct current. The energetic species in plasma include ions, radicals, electrons and meta-stable photons in short-wave UV range. DC glow discharge is generated by applying a high voltage between two electrodes in presence of magnetic field.

III. Result and Discussions

Fig. 2 shows surface plasmon resonance peak of pure Ag nanoparticles at 413 nm monitored by measuring the UV-Vis spectrum of the reaction medium after 2 hours of completion of reaction. After the complete reduction of Ag+ ions by the plant extract, nanoparticles were filtered, dried, mixed with KBr in a ratio of 1:10 and then analyzed by FTIR spectrophotometer (IR Affinity-1 Shimadzu) in the range of 4000- 400 cm^{-1} for knowing the possible functional groups responsible for the formation of silver nanoparticles (Fig. 3.). The absorption bands as obtained are classified as (1) 783 cm^{-1}, the stretching vibration of Ag NPs (b) 1220-1286 cm^{-1}, the C=C unsaturated (c) 1680-1720 cm^{-1}, the C=O stretching vibration (d) 3100-3160 cm^{-1}, the CH_3 stretching vibration of aromatic compound. Biosynthesized silver nanoparticles were further confirmed by the characteristic diffractions planes of silver at 212, 121, 101 and 002 at diffraction angles (2θ) 38.9º, 44.5º, 64.4º, 77º respectively (JCPDS files No. 21-1272) (fig. 4). Higher value of FWHM is sufficient to confirm the nano range particles. Average Crystalline size is determined using Scherrer's formula comes out between 30-40 nm calculated using XRD profile. The XRD patterns study indicates the formation of silver (Ag) nanoparticles contained a mixed phase, cubic (44.5º and 77º) and hexagonal structures (peaks at 38.9º and 64.4º) 2θ angle, after comparing form JCPDF data base) of silver nanoparticles. Morphology, particle size and particle size distribution was also calculated using Scanning Electron Microscope (Fig. 5). As individual particle can easily identified form SEM image shows no aggregation in NPs with particle size ranging 30-40 nm as calculated by XRD.

LABOMED microscope is used for recording optical images. The micrographs are stored in computer through CCD camera which is attached to the computer with standard software (Pixel View, Fig 6) In case of pristine membrane there is very smooth surface but plasma treatment increase its porosity and roughness. Nano composite membrane is comparatively having high porosity but plasma treatment again increases its porosity and roughness.

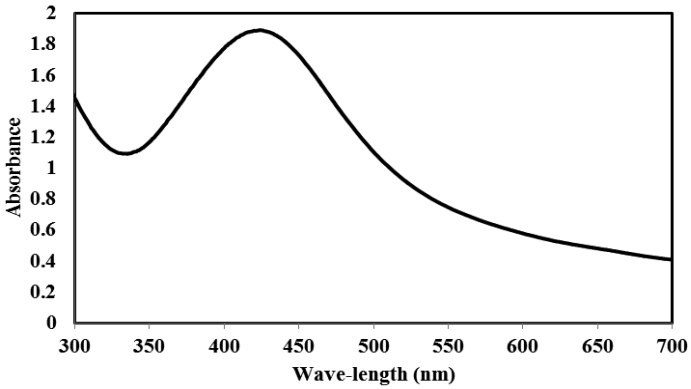


Fig. 2. UV-Vis absorption spectrum of silver nanoparticles.

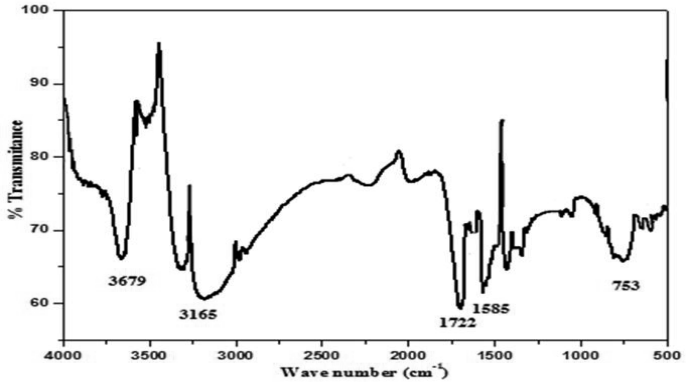


Fig. 3. FTIR spectra of vacuum dried powder of silver nanoparticles.

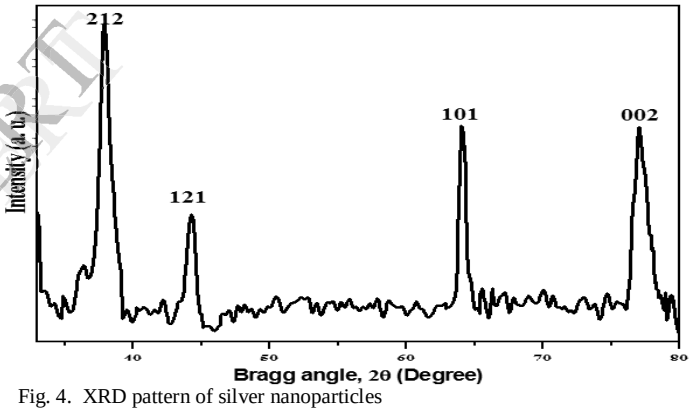


Fig. 4. XRD pattern of silver nanoparticles

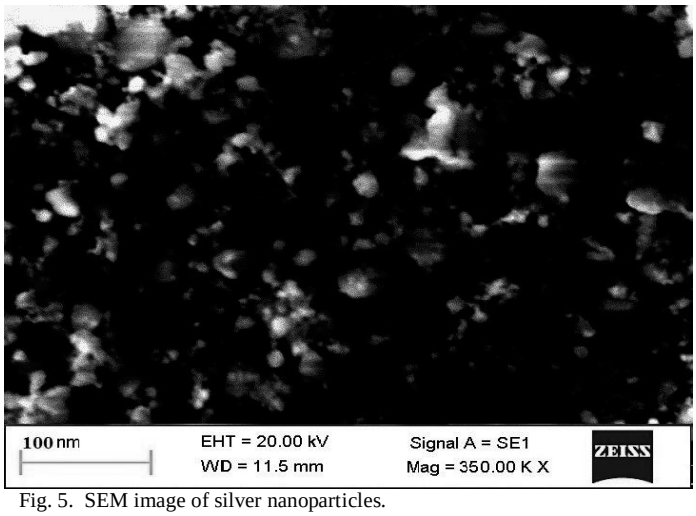
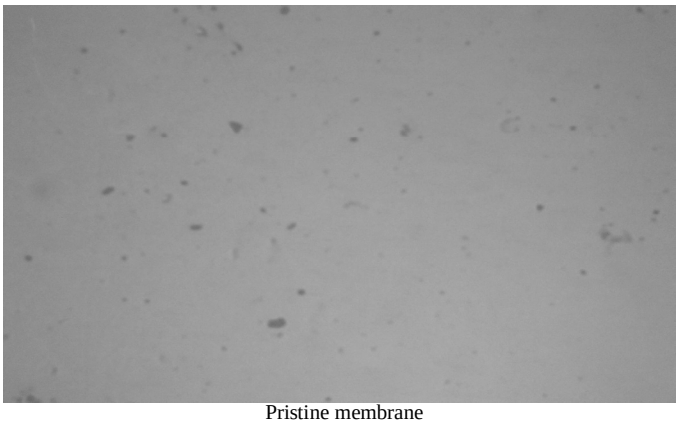
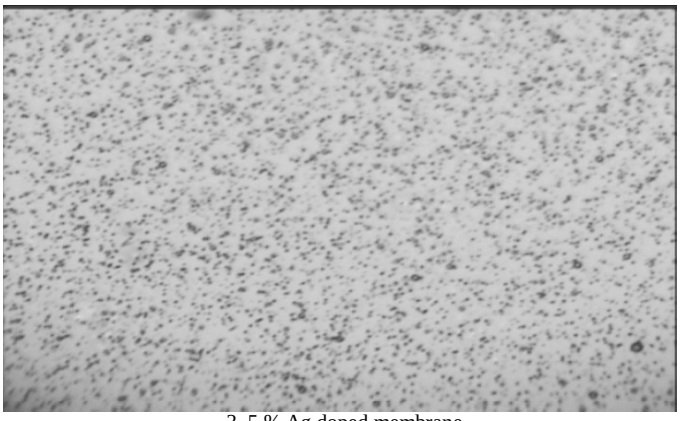


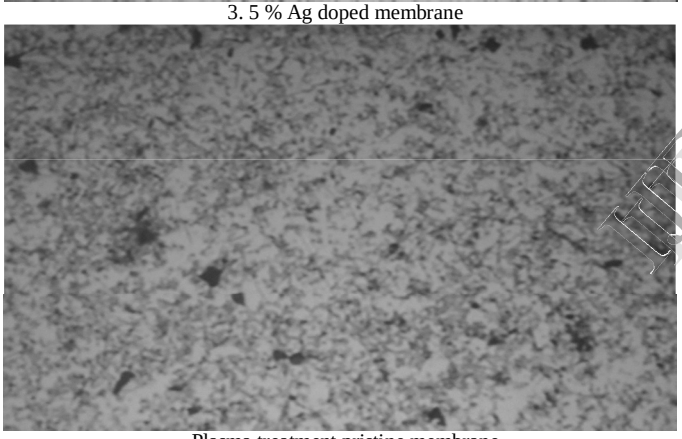
Fig. 5. SEM image of silver nanoparticles.



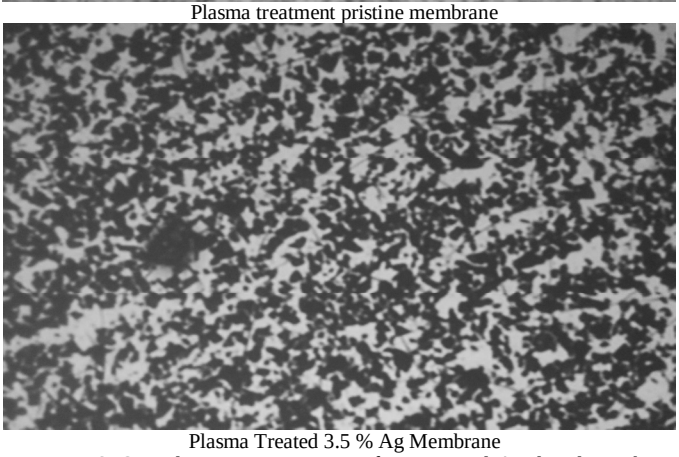
Pristine membrane



3. 5 % Ag doped membrane

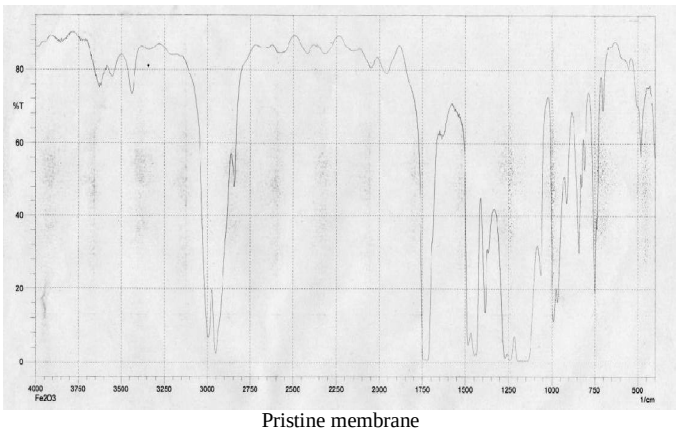


Plasma treatment pristine membrane

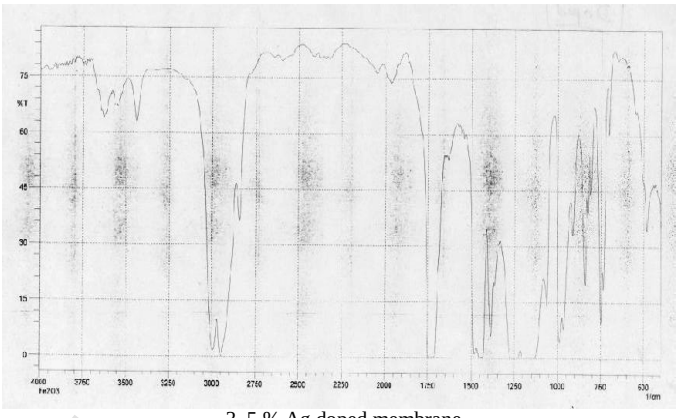


Plasma Treated 3.5 % Ag Membrane

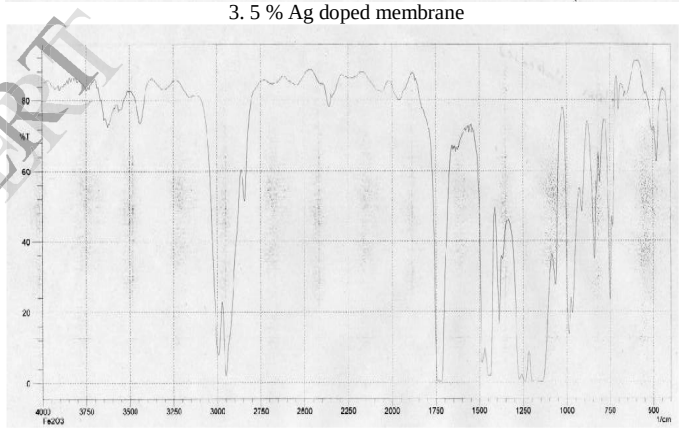
Fig. 6. Optical microscope images of pristine and Ag doped membranes both plasma treated and untreated.



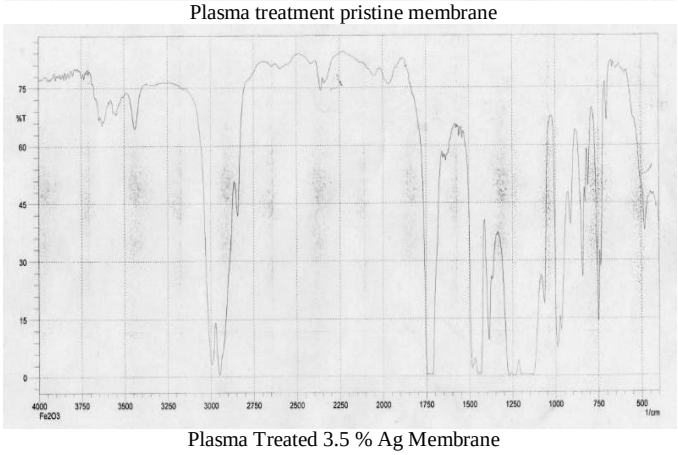
Pristine membrane



3. 5 % Ag doped membrane



Plasma treatment pristine membrane



Plasma Treated 3.5 % Ag Membrane

Fig. 7. FTIR spectra of pristine and Ag doped membranes both plasma treated and untreated.

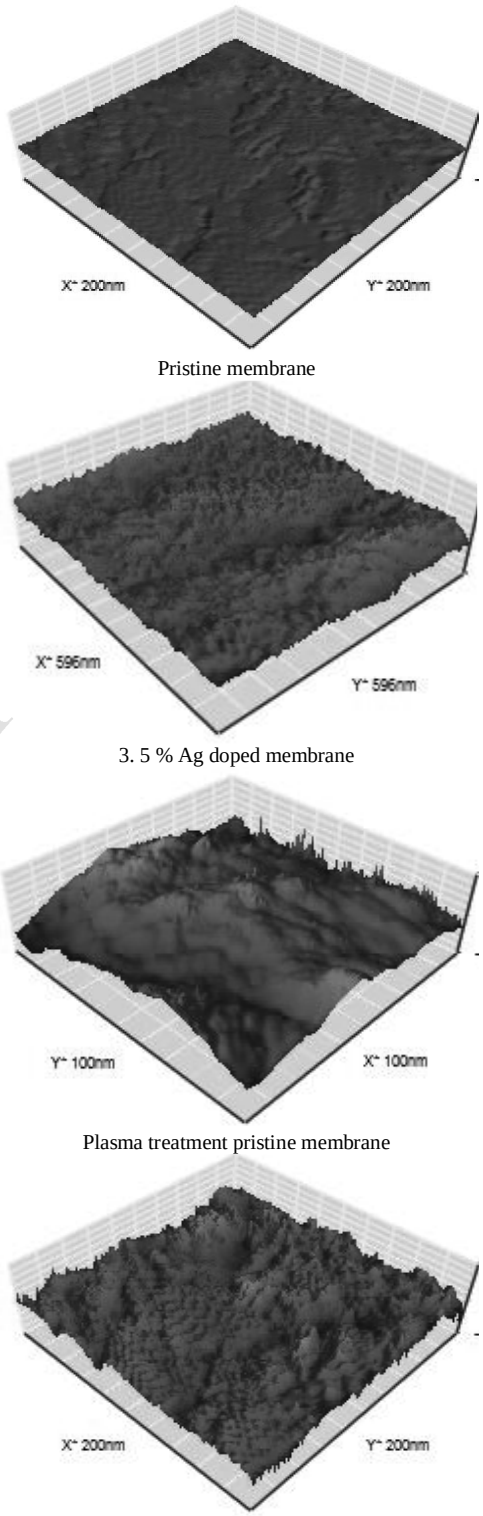
FTIR spectra are obtained on FTIR spectrometer. In present case, Nicolet Megna IR 550 single beam FTIR spectrometer is used at Rajasthan University, Jaipur. FTIR is used to gather both the information about the structure of a compound and as an analytical tool to measure the purity of the compound. The FTIR images of the pristine and 3.5% doped (untreated and plasma treated) membranes are as shown in the Figure 7. We notice certain characteristic differences in the peaks at certain wavelengths. These wavelengths are indicators of change in the chemical bonding and structure of the samples due to plasma treatment. It is observed from FTIR spectra that the C-C and C-H bands have been decreased after plasma treatment. It indicates that cross linking phenomenon enhanced during plasma treatment. While Ag is showing its characteristic peak in 783 cm^{-1} for nano composite membrane (Fig. 7). We investigated the surface morphologies of Ag Nano composite polycarbonate membranes using AFM. AFM images of films are shown in Fig. 8. Plasma treated nano composite membrane can be compared with untreated one which shows improve in porosity and roughness after plasma treatment.

To study bio-compatibility of plasma treated nanocomposite polymer membranes in terms of bio-adoptability, E.coli bacteria were chosen. The autoclaved membrane was mounted on liquid nutrient Agar (Autoclaved) media by streaking and spreading and few drops of E.coli bacteria solution was spread on membranes. Membranes were kept at 37º C in the incubation chamber for 48 hrs and then they were studied under optical microscope (fig. 9). Polymer film is non-porous without plasma treatment; this polymer film was acting as a passive layer between base support and food (media). This results into no growth on the surface of polymer film but Ag casted films show little growth of bacteria due to some porosity present in membranes. But when polymer film is made porous by plasma treatment and experiment is repeated to compare the bacterial growth on porous polymer films as separating media for bacteria and food. Enhanced growth was found for plasma treated samples. This shows plasma treatment increase bio-adoptability of nanocomposite polymer membranes i.e. polymers membranes become more bio-compatible after plasma treatment.

IV. Summary and Conclusions

There was a change in color of the solution from green to brownish as the plant extract was mixed in the aqueous solution of the silver ion complex; this gives the primary indication of formation of silver nanoparticles. A typical absorbance peak at 413 nm of silver nanoparticles was obtained due to the surface Plasmon vibrations of silver nanoparticles. Biosynthesized silver nanoparticles were further confirmed by the characteristic peaks observed in XRD profile and morphological and structural view under the scanning electron microscope. The XRD study indicates the formation of silver (Ag) nanoparticles with four intense characteristic peaks and SEM image of silver nanoparticles show average particle size of 30-40 nm.

Pristine polycarbonate membranes and polycarbonate membrane doped with Ag nanoparticles (3.5 weight percent) were prepared by solution cast method. Plasma treatment techniques applied here have shown considerable improvement in porosity and roughness after plasma treatment. Polymer crosslinking also get enhanced after plasma treatment. High bacterial on plasma treated polymer membranes shows increase of bio-adoptability and bio-compatibility after plasma treatment makes them suitable for many biomedical applications.



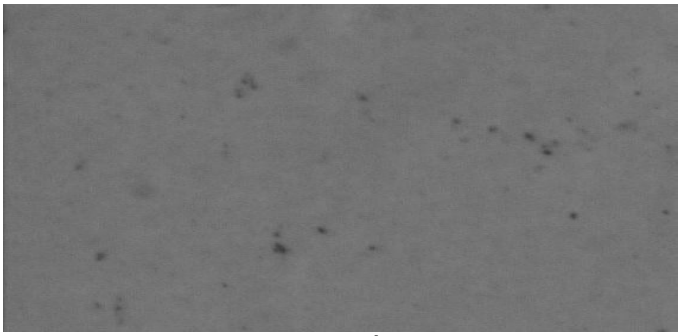
Pristine membrane

3. 5 % Ag doped membrane

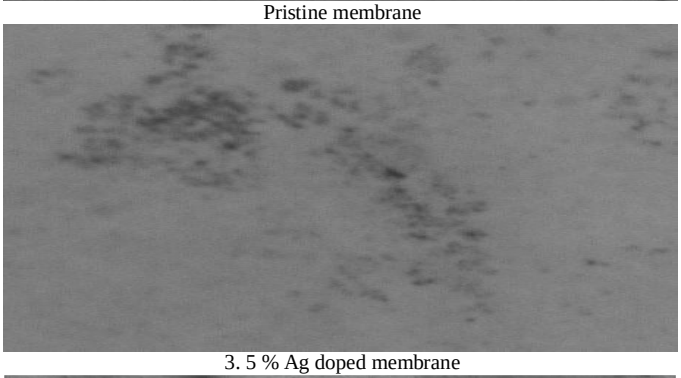
Plasma treatment pristine membrane

Plasma Treated 3.5 % Ag Membrane

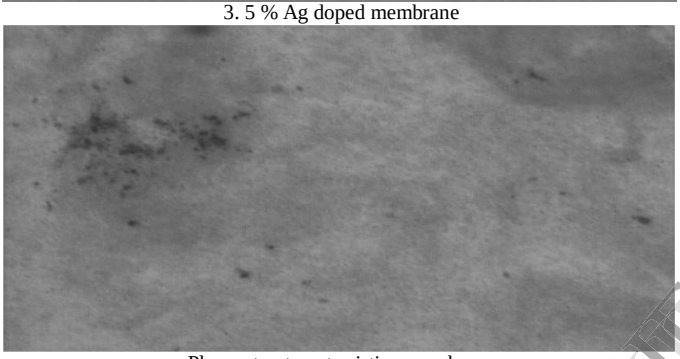
Fig. 8. AFM images of pristine and Ag doped membranes both plasma treated and untreated.



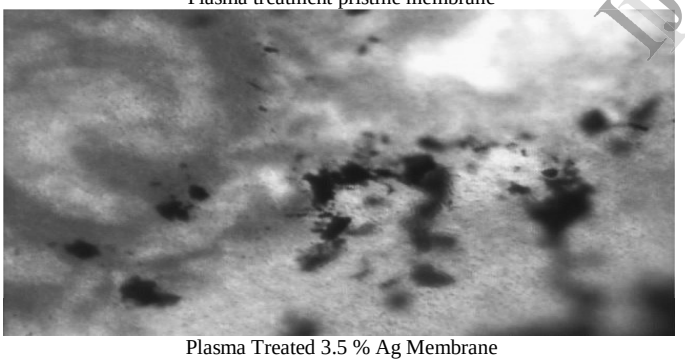
Pristine membrane



3. 5 % Ag doped membrane



Plasma treatment pristine membrane



Plasma Treated 3.5 % Ag Membrane

Fig. 9. Study of bio-adoptability and bio-compatibility of Ag nanocomposite polymer membranes before and after plasma treatment.

ACKNOWLEDGMENT

Authors wish to thanks and acknowledge Ms. Priti Agarwal for helping in synthesis of Ag nano particles. We are thankful to Department of Physics, MNIT and UOR for providing facility of FTIR and SEM analysis. Authors are also thankful to Jawaharlal Nehru Memorial Fund, New Delhi, India and INSPIRE DST, New Delhi, India for providing Scholarship to Mr. Narendra Kumar Agrawal and Ravi Agarwal respectively to carry out this work.

REFERENCES

[1] Y. Sanchuan, L. Xuesong, L. Jingqun, W. Dihua, L. Meihong and G. Congjie, Surface modification of thin-film composite polyamide reverse osmosis membranes with thermo-responsive polymer (TRP) for improved fouling resistance and cleaning efficiency, Separation and Purification Technol. 76, 283-291 (2011).

[2] B. Bagra, P. Pimpliskar and N. K. Agrawal, Bio-Compatibility, Surface & Chemical characterization of glow discharge plasma modified ZnO Nanocomposite Polycarbonate, proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings, Patiala India, Dec. 17-21 (2013).

[3] P. Pimpliskar, B. Bagra, A. Sharma, S. Khandwal and N. K. Agrawal, An Innovative Approach for Efficient and Reusable Catalization for Synthesis of α, β-Unsaturated Compounds Using Polymer - NPs Composites as Catalyst, proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings, Patiala India, Dec. 17-21 (2013).

[4] L. Zou, I. Vidalis, D. Steele, A. Michelmore, S.P. Low and J.Q. Verberk, Surface hydrophilic modification of RO membranes by plasma polymerization for low organic fouling; J. of Memb. Sci. 369, 420-428 (2011).

[5] N. K. Agrawal, N. A. Kumar, M. Singh, Y.K.Vijay and K.C.Swami, Plasma Surface Modification of Nano Composite Polymer Membranes: An Innovative Approach for Synthesis of Nano-Bio Materials, proceedings of 58th DAE-Solid State Physics Symposium, AIP proceedings, Patiala India, Dec. 17-21 (2013).

[6] L. Meihong, Y. Sanchuan, Q. Ming, P. Qiaoming and G. Congjie, Impact of manufacture technique on seawater desalination performance of thin-film composite polyamide-urethane reverse osmosis membranes and their spiral-wound elements, J. of Memb. Sci. 348, 268-276 (2008).

[7] H. Kanematsu, H. Ikegai and M. Yoshitake, Patents for Antibacterial Metallic Coating and Its Future Trend in Japan. Research Inventy, Int. J. of Eng. and Sci. 3(6), 47-55 (2013).

[8] A. Goyal, V. Sharma, A. Sharma, R. Agarwal, K. B. Sharma and S. L. Kothari, Synthesis, structural and optical study of CdS nanoparticles doped with different concentration of Cu, J. of Nano-and Electronic Physics 3 (1), 254-259 (2011).

[9] H. Kanematsu, H. Ikigai, and M. Yoshitake, Antibacterial Tin-Silver Plating by the Combination of Multistage Plating and Heat Treatment, J. of Appl. Surface Finishing 3, 114-118 (2008).

[10] P. Agarwal, R. Agarwal and N. K. Agrawal, Morphology and Crystallization of Size-Controlled Spherical Sliver Nanoparticles Synthesized Using Coriandrum sativum: A Greener Approach, proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings, Patiala India, Dec. 17-21 (2013).

[11] W. M. King, P. A. Cantor, L.W. Schoellenback and C. R. Cannon, High-retention reverse-osmosis desalination membranes from cellulose acetate, Membranes from Cellulose Derivatives, Interscience Publisher, New York (2001), P. 203-207.

[12] N. K. Agrawal, R. Agarwal, Y. K. Vijay and K. C. Swami, Characterization of N_2 Plasma Treated Nano Composites Polymer Membranes, J. of Mat. Sci. Surf. Eng. 1 (1), 4-7 (2013).

[13] P. Agarwal, A. Mehta, S. Kachhwaha and S. L.; Kothari, Green Synthesis of Silver Nanoparticles and Their Activity Against Mycobacterium tuberculosis, Adv. Sci. Eng. Med., 5(7), 709-714 (2013).

[14] J.K. Beasley, The evaluation and selection of polymeric materials for reverse osmosis membranes, Desalination, Interscience Publisher, New York (1997), P. 181–189.

[15] R. Agarwal, N. K. Agrawal and Ramvir Singh, Cicer arietinum Leaf Extract Mediated Synthesis of Silver Nanoparticles and Screening of Its Antimicrobial Activity, Adv. Sci. Eng. Med. 6 (2), 203-207 (2014).

[16] N. K. Agrawal, K. Awasthi, Y. K. Vijay and K. C. Swami, Synthesis and characterization of plasma treated TiO_2 Nano composites polymer membranes, J. of Adv. Electrochemistry "in press".

[17] K. Hyun and K. S. Soo, Plasma treatment of thin film composite reverse osmosis membrane, J. of Memb. Sci. 286, 193–201 (2009).

[18] N. K. Agrawal, M Singh, Y. K. Vijay and K. C. Swami, Synthesis and Characterization of Colloidal TiO2 Nanoparticles: Acquire Through Titanium Chloride Rich Solutions, Adv. Sci. Eng. Med. 6 (5), 595-602 (2014).

[19] N. K. Agrawal, R. Agarwal, Y. K. Vijay and K. C. Swami, Surface Modification of Ag Nano Composites Polymer Membranes by Glow Discharge Plasma, J. of Mat. Sci. Surf. Eng. 1 (1), 23-27 (2013).

[20] S. Goel and S. K. Mathew, Automated Detection, Characterization, and Tracking of Sunspots from SoHO/MDI Continuum Images, Solar Phys Solar Phys. 289 (4), 1413-1431 (2014).

[21] N. K. Agrawal, R. Agarwal, Y. K. Vijay and K. C. Swami, Plasma etching technology for Surface and Chemical Modifications of Aluminium and PMMA Nanocomposites, Adv. Sci. Eng. Med. 6 (6), xxx-xxx (2014).

[22] N. K. Agrawal, R. Agarwal, Y. K. Vijay and K. C. Swami, Reactive Polymer Surfaces for Cell Colonization, J. of Mat. Sci. Sur. Eng. 1 (1), xx-xx (2013).