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Morphological and Mechanical Characterization of Electrospun Ag Nanospecies Decorated Polyacrylonitrile (PAN) Membrane for Water Purification

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Abstract

Membrane development includes a wide array of technological fields, which includes interaction phenomena, materials engineering, chemical engineering, and process and product design. The majority of the global issues relating to water, air, energy, healthcare, and subsequently global warming can be resolved with the help of advancements in membrane technology. Currently, electrospun polymeric fiber membranes are dominant products because of their broad spectrum of materials and process-dependent architecture with desirable physico-chemical properties for diverse applications.In this work, dual membranes, one having amphiphilic/antibacterial and photocatalytic properties and another having antibacterial and hydrophobic properties, are being fabricated using electrospinning. Hexadecyltrimethylammonium bromide (CTAB) loaded electrospun PAN nanofibers treated with aqueous $AgNO_3$ become amphiphilic/photocatalytic and antibacterial. For the first membrane, freshly prepared electrospun nanofibers of PAN fabricated from its DMF solution were treated with $AgNO_3$ solution. Similarly, for the second membrane, CTAB dispersed in PAN solution was subjected to electrospinning and the as-fabricated membrane was treated with $AgNO_3$ in the dark to obtain an AgBr loaded PAN fiber. The AgBr-loaded PAN shows amphiphilic, photocatalytic, and antibacterial characteristics. Therefore, designing the dual membrane, upper with AgBr/PAN and lower with Ag/PAN, can be applied to obtain pure water if water is contaminated with dyes, bacteria, and oil.

Keywords

Silver nanoparticles, Silver bromide, Polyacrylonitrile, Dimethylformamide, Electrospinning

1. Introduction

Water is an important resource for human survival, and there have been numerous developmental activities that have led to the contamination of water resources. Industrialization is one of the key contributors to the contamination of water resources. There are numerous cases of oil spills that occur during transportation and the discharge of industrial waste [1]. If left unchecked, this has had a serious negative impact on the ecological environment and marine ecosystem, as well as posing a threat to the entire human society. Filtration is an important step to ensure that our water resources do not get contaminated by chemicals and pollutants. So, it is crucial to develop a filtration separation system that would separate the inorganic and organic solvents from the water as well as the harmful pathogens.[2]

Polyacrylonitrile (PAN) is a synthetic resin which is formed from the polymerization of acrylonitrile which can be used to produce a variety of products and is used as a precursor for the manufacture of high quality carbon fibers [3]. N, N-Dimethylformamide (DMF) is a member of the family of formamides, also a polar aprotic hydrophilic solvent with a high boiling point is used by industries as a solvent for the production of fibers [4]. Hexadecyltrimethylammonium bromide (CTAB) is amphiphilic in nature and an effective antiseptic agent against fungi and bacteria, which can lower the surface tension of the liquid and can be used for the removal of heavy metal ions [5]. Silver nitrate ($AgNO_3$) is an antiseptic inorganic compound which inhibit the growth of gram-negative and gram-positive bacteria along with some species of fungi. Combining $AgNO_3$ with CTAB in PAN fibers forms AgBr which is an excellent antiseptic agent. The composite created also becomes amphiphilic which can separate water contaminated with oil, dyes, and harmful pathogens.

Here, we developed a composite PAN electrospun nanofibrous membrane with varying concentration of CTAB decorated with Ag nanospecies (by reduction of $AgNO_3$ solution) capable of oil water separation and purification. The nanofibrous membrane were characterized and their mechanical properties, filtration properties, antibacterial properties and photocatalytic activities were measured.

2. Experimental

2.1 Materials used

Composite nanofibers were obtained using Polyacrylonitrile (PAN, d:1.184g/mL at 25°C, MW: 150,000, Sigma Aldrich Chemistry), Hexadecyltrimethylammonium bromide (CTAB, MW:364.45 g/mol, mp 248-251°C, assay >=99%, Sigma Life Science), N, N Dimethylformamide (DMF, MW: 73.09, Thermo Fisher Scientific), Silver Nitrate ($AgNO_3$, MW: 169.87 g/mol, assay >=98.5%, Merch Life Science Private Limited), Sodium borohydride ($NaBH_4$, MW:37.83, assay >=98%, Himedia Laboratories Pvt. Ltd.) were purchased and utilized.

2.2 Fabrication of fibers and modification

10% by weight PAN were dissolved in DMF solution followed by addition of different amounts of CTAB to the solution (0.5%, 1%, and 2%) was dissolved and kept in the ultrasonic cleaning machine for particle dispersion. The following conditions were maintained: 15KV applied voltage, 25cm distance from the tip to the collector, flow rate of 1.5ml/hr, temperature maintained at room conditions, with drum rotation speed maintained at 500rpm. CTAB-PAN composite nanofibers were immersed 25 ml of 1×10^{-3} N $AgNO_3$ solution, kept in dark for 24hrs, washed and vacuum dried for 24hrs.

2.3 Characterization

The 2D electrospun nanofibers were first characterised using an Olympus CX33RTFS2 optical microscope for the formation of Ag particles on the fibers. The presence of Ag NP and AgBr on the composite PAN fibers was further evaluated by using SEM-EDS mapping. To assess the antibacterial activity of various membranes toward gram-positive, gram-negative bacteria and fungi, the zone inhibition method was used. Triplicate samples of the developed membrane of CTAB-PAN fibers and silver-coated CTAB-PAN fibers were used with the PAN membrane used as a negative control and Kanamycin Antibiotic as a positive control for comparison.

3. Results and Discussion

3.1 Analysis under optical microscope

The magnified image of the pristine mat showed that there were no suspended PAN particles and the PAN fibers are compact structure. For the 3D PAN structure, the fibers are seen to be loosely packed due to the hydrolysis action. Visible inspection of fiber shows the color of Ag decorated mat changes to yellowish for the 3D PAN membrane [Figure 1]. The formation of beads in the fibers also increases with the CTAB concentration so the 1% PAN fiber has the best morphology.The alignment of the fibers increases as the concentration of CTAB in the fibers increases [Figure 2]. The coating of Ag decorated mat shows silver particles scattered in the pores as well as on the surface of the mat. It shows dense fibers packed with silver particles [Figure 3].

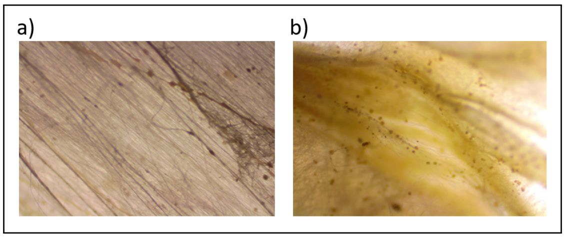

Figure 1: Optical image of a) pristine PAN and b) 3D PAN membrane

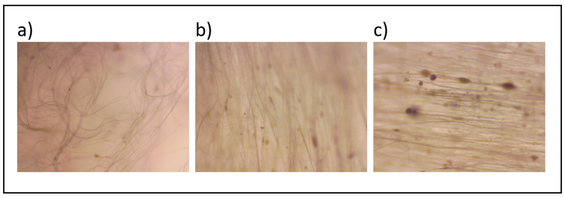

Figure 2: Optical image of a) 0.5%, b) 1% and c) 2% CTAB-PAN fiber

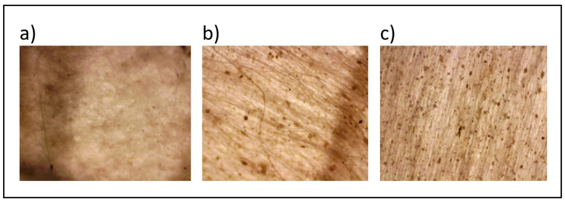

Figure 3: Optical image of a) 0.5%, b) 1% and c) 2% AgBr-PAN fiber

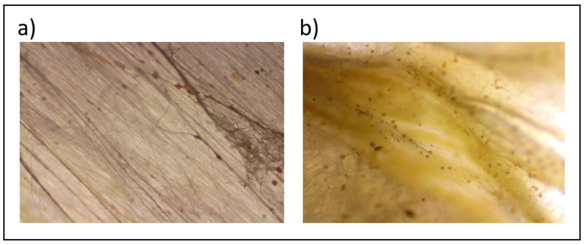

Figure 4: Optical image of a) pristine PAN and b) 3D PAN membrane

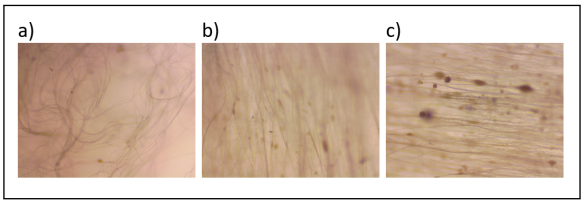

Figure 5: Optical image of a) 0.5%, b) 1% and c) 2% CTAB-PAN fiber

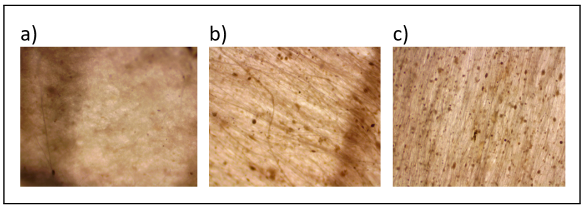

Figure 6: Optical image of a) 0.5%, b) 1% and c) 2% AgBr-PAN fiber

3.2 Membrane Morphology

The image of the pristine PAN mat shows the smooth surface of nanofibers while the image of the silver-decorated mat shows flaky silver deposits on the surface of the fibers.For the pristine PAN mat, the diameter of the fiber was determined to be 150.736 nm [Figure 4]. For the CTAB-PAN mat, the diameter of the fiber was determined to be 145.149 nm and we can confirm that CTAB particles has been embedded onto the PAN matrix [Figure 5]. For the AgBr PAN mat, the diameter of the fiber was determined to be 141.057 nm and we can confirm the formation of AgBr on the composite PAN fibers [6] [Figure 6].

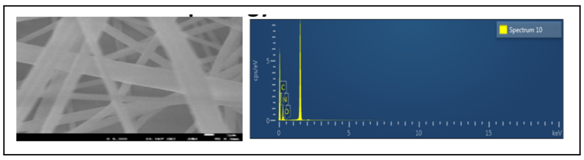

Figure 7: SEM and EDX of pristine PAN membrane

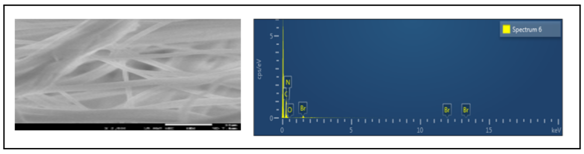

Figure 8: SEM and EDX of CTAB-PAN membrane

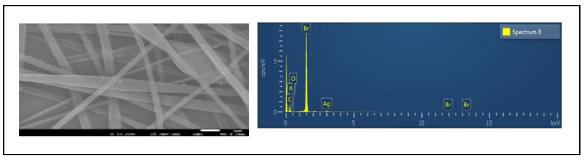

Figure 9: SEM and EDX of AgBr PAN membrane

3.3 FTIR analysis

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was used to determine the formation of composite PAN membrane. This analysis shows the molecular structure of the different samples, and interaction between the PAN molecules with added functionalities. Comparison of FTIR spectra of pristine PAN fibers with CTAB and AgBr [Figure 7] fibers clearly shows that some functionalities are added after the formation of composite PAN membrane [Figure 7]. The bands at 3618 cm^{-1} in the spectra show that phenol and alcohol group is present which corresponds to O-H stretching. The bands at 1631 cm^{-1} in the spectra show that the protein group is present which corresponds to the stretching of C-N and C-C. The band at 1448 cm^{-1} in the spectra show that the protein group have amide linkages with the stretching of N-H. The band at 1348 cm^{-1} show the stretching of nitro compound by the N=O bond. As specified by many studies, these groups play a crucial role in the stability of Ag nanoparticles [7].

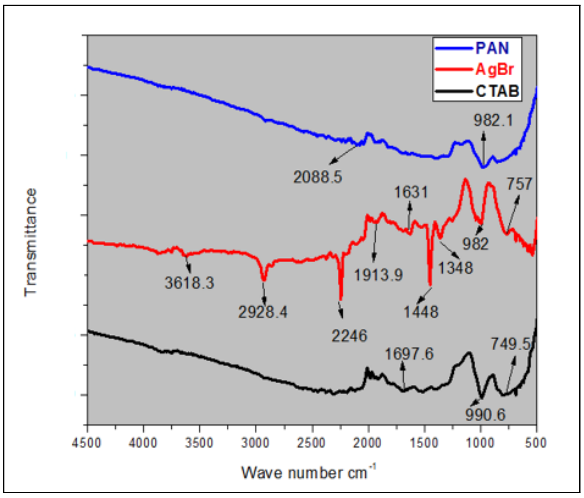

Figure 10: FTIR analysis

3.4 Contact Angle

The contact angle was found to be 101.25 ± 0.39 which means that the surface of PAN fiber is hydrophobic. For the AgBr PAN fiber, the water droplets were immediately absorbed by the surface of the CTAB-PAN fiber, making the surface hydrophilic [8] [Figure 8].

Table 1: Contact Angle and Surface Energy

Sample	Water Contact Angle [deg]	Surface Energy [mJ/m^2]
Pure PAN	101.25 ± 0.39	22.28 ± 0.24

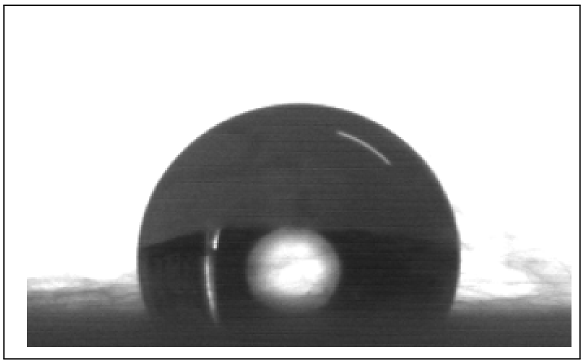

Figure 11: Contact Angle Measurement

3.5 Photocatalytic activity measurement

The photocatalytic properties of the CTAB-PAN fibers were determined by carrying out the degradation of the methylene blue (MB) dye solution in a photochemical reaction. The reaction was carried out in 100 ml borosilicate beakers under direct sunlight and under UV irradiation light at 365 nm. The experiments were carried out in the natural environment in the sunlight and inside the UV chamber. For the degradation experiments, 20 ml of MB dye (10ppm concentration) was reacted with the Ag doped CTAB-PAN fiber mats under the given conditions. The samples were taken at regular intervals of time, taking 2 ml of dye at a time, and the concentration of the dye dipped in the mats was measured by recording its absorbance at 665 nm with a UV–visible spectrophotometer (HP 8453 UV–vis spectroscopy system, Germany) [9]. The sample was reused, and the photocatalytic action of the reused sample was also determined. The graph shows that the reused modified Ag-Br PAN fiber has nearly the same efficiency as new and, therefore, the material can be considered to have good photocatalytic degradation activity [Figure 9].

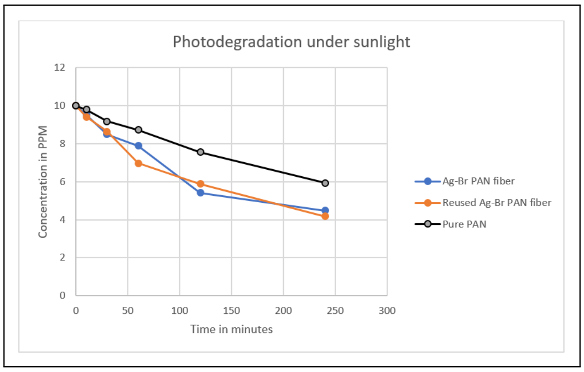

Figure 12: Graph between concentration in ppm vs time

3.6 Antibacterial Test

The positive control produced the zone of inhibition of 9mm. The zone of inhibition test of the modified Ag-Br PAN membrane and the 1% CTAB-PAN membrane shows that they have a good effect on bacterial growth and fungi growth. The zone of inhibition for the 1% CTAB-PAN membrane ranges from 6-8 mm and the zone of inhibition for the Ag-Br PAN membrane ranges from 3-5 mm for the gram-positive bacteria, gram-negative bacteria, and fungi [10] [Figure 10].

Table 2: Zone of Inhibition for the prepared samples

Sample	1% CTAB-PAN	AgBr PAN
Bacillus subtilis	6,7,7 (mm)	4,4,4 (mm)
Escherichia coli	7,7,8 (mm)	4,4,4 (mm)
Candida albicans	7,7,7 (mm)	5,5,3 (mm)

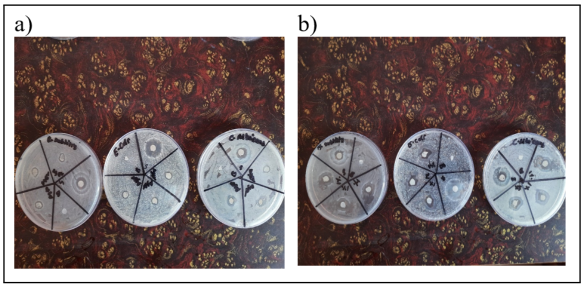

Figure 13: antibacterial test with a) AgBr PAN fiber and b)1% CTAB-PAN as sample

3.7 Filtration Test

The experiment was carried out on 2D AgBr PAN membrane [11]. The samples of size 6cm X 6cm were used for the experiment. Equal volume of cooking oil and distilled water was used to carry out the experiment. The oil was separated and settled at the top while the distilled water stayed on the bottom of the flask. The flow rate was calculated to be 0.01363 ml/sec [Figure 11].

Figure 14: Filtration test setup

3.8 Mechanical strength Test

The stress vs strain graph was plotted between the pristine PAN and its composite fibers with drum rotation speed maintained at 500rpm. From the diagram, it is easy to notice that the Young's Modulus and Tensile Strength of the composite fibers is maximum at 1% CTAB-PAN fibers. The breaking point of the pure PAN is maximum and it decreases with increase in the percentage of CTAB. There is a drastic decrease in the Young's Modulus and Tensile Strength for the 0.5% and 2% fibers. This may be due to better alignment and less formation of beads in the fibers.

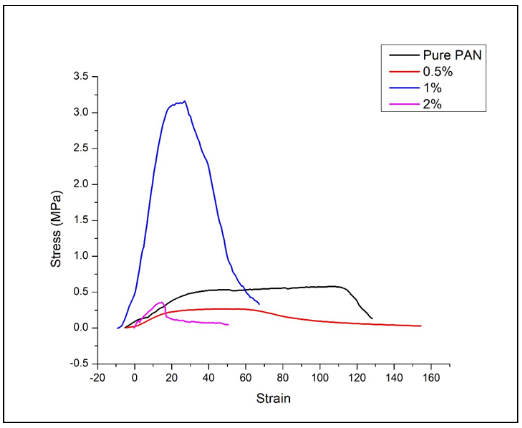

Figure 15: Stress vs. Strain graph of pristine PAN and composite fibers

Table 3: Comparison of tensile properties of the composite fibers

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Breaking Point
Pure PAN	0.01408	0.58037	110.42
0.5% CTAB-PAN	0.00827	0.26126	61.43
1% CTAB-PAN	0.1206	3.1602	28.79
2% CTAB-PAN	0.03216	0.3546	15.35

4. Conclusion

The development of AgBr with CTAB and polymer solution prior to electrospinning can produce CTAB-PAN fibers which can be converted into AgBr PAN fibers. The as-formed composite membrane is amphiphilic, photocatalytic and antibacterial in nature. The composite nanofiber also has good morphology. By designing a dual membrane using these two different membranes, a promising filter media can be introduced to remove bacteria, dyes, and oil from contaminated water.

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