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Morphological and Mechanical Characterization of Ag Nanospecies Decorated Electrospun Membrane for Water Purification

by

Kshitij Thapa

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The undersigned certify that they have read, and recommended to the Institute of Engineering for acceptance, the thesis defense entitled "**Morphological and Mechanical Characterization of Ag Nanospecies Decorated Electrospun Membrane for Water Purification"** submitted by Kshitij Thapa, 076/MSMSE/009 in partial fulfillment of the requirements for the degree of Masters in Materials Science and Engineering.

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Abstract

Membrane development includes a wide array of technological fields, which includes design of process and product, various fields of engineering such as materials engineering, chemical engineering, and also interaction phenomena. Progress in membrane technology can help resolve most worldwide problems related to water, healthcare, energy, air, and consequently global warming. 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. The low cost and ease of fabrication of nanofibers with different functionalities make electrospinning superior to other techniques. Using this process, one can easily incorporate nanoparticles of metal and metal oxide through nanofibers to get composite nanomaterials for different 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 PAN shows amphiphilic, photocatalytic, and antibacterial characteristics. The fibers also show good mechanical properties for its serviceability. 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; AgBr loaded PAN fiber

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List of Acronyms and Abbreviations

$AgNO_3$	Silver Nitrate
Ag	Silver
Mg/L	milligrams/litre
PAN	Polyacrylonitrile
DMF	N, N-Dimethlformamide
CTAB	Hexadecyltrimethylammonium bromide
Ag-Br	Silver Bromide
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
2D	Two Dimensional
3D	Three Dimensional
SB ($NaBH_4$)	Sodium Borohydride
wt.%	Weight percentage
KV	Kilovolt
Rpm	Rotations per minute
Ag/PAN	Silver doped PAN fibers
AgBr/PAN	Silver bromide doped PAN fibers
MB	Methyl Blue Trihydrate
CTAB-PAN	Hexadecyltrimethylammonium bromide doped Polyacrylonitrile
UV	Ultraviolet
TEM	Transmission Electron Microscopy
ATCC	American Type Culture Collection

Chapter 1: Introduction

1.1 Background

Water is an essential 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, i.e., the release of oily wastewater into the water resources, mainly in the production industries such as the petrochemical industry, food and textile processing, crude oil production, etc. The environmental guidelines state that the concentration of oil and grease in the water released from industries should be in the limit of 10–15 mg/L. (Su, et al., 2012)

The main effects of water pollution on humans are that it causes the loss of lives and causes illness among the people who drink the contaminated water. Waterborne pathogens and the toxins released into the water resources adversely affect the health conditions of humans. In the environment, the living organisms that interact with the toxins and chemicals contaminated water get affected, and as a result, the chain of interaction occurs between the organisms, which in turn causes the various ecosystems to get affected. (Denchak, 2018)

Due to rapid industrialization and increasing energy demand, there is a common use of oils and industrial solvents for the production of various materials needed for our daily needs. To meet the energy requirements, fossil fuels are predominantly used as they are a cheaper source than other energy sources, and these fuels are required to be transported to various parts of the globe through sea routes. There are numerous cases of oil spills and other accidents that occur during transportation and the discharge of industrial waste. 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. Water can be purified naturally if it is allowed ample time to settle down or dilute the pollutants. This scenario is not possible due to the quantity of pollutants being produced. Filtration is an important step that we must take 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. (Obaid, et al., 2014)

1.2 Silver Nitrate and silver nanoparticles

$AgNO_3$ silver nitrate is an antiseptic inorganic compound composed of Ag^+ ions and NO_3^- ions. It is the most commonly used compound for the formation of Ag nanoparticles. It appears as a colourless or white crystalline solid. This compound turns black when exposed to either light or any organic material. $AgNO_3$ in its solid form has a trigonal planar arrangement and is used as a precursor to form other silver-containing compounds. (National Center for Biotechnology Information, 2022)

Silver has antibacterial properties as they prevent the growing of gram-negative and gram-positive bacteria along with some species of fungi. Silver nanoparticles are commonly formed with the reduction of silver salt ($AgNO_3$) along with a reducing agent by dissolving it in water. Different stabilising and capping chemicals may be used to prevent the accumulation of silver nanoparticles to increase its effectiveness. Silver nanoparticles have been used in domestic water filters and their possible expansion in various applications is being studied. (World Health Organization, 2018)

1.3 Polyacrylonitrile (PAN)

PAN is a synthetic resin which is formed from the polymerization of acrylonitrile, which is a derivative of the acrylic resins. It is a linear polymer with the molecular formula $(C_3H_3N)_n$. It does not melt under normal conditions as it is a thermoplastic, but the molecular structure degrades when the temperature reaches above 300 °C, before its melting point. The polymer is made from the hazardous monomer acrylonitrile and the bonding between the C-N nitrile groups in the polymer makes it hazardless. It is used to produce different products and is used as a precursor for the manufacture of high quality carbon fibers. (Qin, 2016)

PAN resists most organic solvents and is dissolved in special solvents to create the fibers. These fibers are soft and flexible and can be used as a substitute for wool as the properties of these fibers closely resemble each other. The fabricated synthetic fibers can be produced and sold at a fraction of the cost of natural fiber and offer resistance to sunlight, mildew, and moths. These fibers are used in apparel and can also be used as precursors for graphene and carbon fibers. Commercial production of PAN started in 1940 by the DuPont Company. (Britannica, 2014)

1.4 N, N-Dimethlformamide (DMF)

DMF ($HCON(CH_3)_2$) is a member of the family of formamides in which the methyl groups replace the amino hydrogens. It is one of the most common solvents used for chemical reactions. It is a polar aprotic hydrophilic solvent with a high boiling point. It is mostly used by industries as a solvent for the production of acrylic films, fibers, and surface coatings. It is an odourless, colourless liquid and is easily available on the market for the synthesis of polymers. (National Center for Biotechnology Information, 2022)

DMF has multiple roles, being a solvent of peptide bonds, a catalyst for synthesis of halides, a reagent of important chemical reactions, i.e., Friedel–Craft's reaction, Vilsmeier–Haack reaction, either electrophilic or nucleophilic agent, or as a stabiliser for reactions. DMF is used as a reducing agent for the reduction of silver nitrate into its nanoparticles. (Heravi, et al., 2018)

1.5 Hexadecyltrimethylammonium bromide (CTAB)

CTAB ($[(C_{16}H_{33})N(CH_3)_3]Br$) is an antiseptic and surfactant with antibacterial, antifungal, and antiviral properties. Its cation is an effective antiseptic agent against fungi and bacteria, which is used for selective cosmetics and the synthesis of gold nanoparticles and silica nanoparticles. It has a long chain of carbon along with an ammonium head group and three methyl groups, which lowers the liquid's surface tension and can be used for the removal of heavy metal ions. Since it can also remove heavy metal ions, it can remove various toxins from waste. (Elfeky, et al., 2017)

CTAB is amphiphilic in nature, which makes it able to modify the surface properties, which makes it suitable for detergency, wettability, and emulsion stabilization. If the concentration of the chemical exceeds the (CMC) critical micelle concentration of the liquid, then the molecules assemble by itself to form micelles, which in turn reduces the interfacial tension (IFT) to the minimum value. (Schramm, et al., 2003) CTAB is also used in combination with nanoparticles to reduce the IFT of the liquid. A specified concentration of CTAB and the nanoparticles creates a synergistic effect which can effectively reduce the IFT. (Saien & Gorji, 2017) CTAB would interact with the Ag nanoparticles to create Ag-Br composite which would be used to improve the surfactant and antiseptic properties.

1.6 Gram Positive, Gram negative bacteria and Fungi

The bacteria are differentiated on the basis of gram staining. Gram-positive bacteria are those bacteria on which there is a distinct purple appearance after gram staining with a thick layer of peptidoglycan and absence of lipid membrane. Gram negative bacteria are those bacteria on which after gram staining there is a pale reddish colour with a thin layer of peptidoglycan and presence of an outer lipid membrane. A common type of fungi is Candida albicans, which can be found in human gut flora. It can be found in commensal form, but a variety of conditions can cause it to be pathogenic.

Common types of gram-positive bacteria are Staphylococcus aureus (S. aureus), which is present on the human body's skin and doesn't cause disease on itself, but when it enters the human body through cuts or contact with mucous membrane, then it causes diseases and infections. A common type of gram-negative bacteria is Escherichia coli (E. coli), which produces enzymes that cause numerous diseases. There are many types of E. coli which may cause respiratory tract infections, diarrhea, pneumonia, urinary tract infections, etc. (Steward, 2019)

1.7 Problem statement

Pollution of water resources means that people will have fewer options for safe drinking water. It is one of the emerging problems in the world today and many people have been affected by water-borne diseases. Bacteria in water can cause severe illness and even death. Due to its antimicrobial properties, silver nanoparticles have been used for various purposes in the medical field. Silver compounds and their nanoparticles are toxic to microorganisms, which include many species of bacteria. It is essential that there be an efficient and effective synthesis of silver nanoparticles due to its extended application in the medical field and to its environmental and health concerns. (Prabhu & Poulose, 2012)

A huge amount of oil is released into the water and marine system every year from agricultural waste, industries, sewage, etc., and this causes a serious threat to the marine ecosystem due to light and oxygen deprivation and chemical toxicity. Cleanup of insoluble and soluble solvents from the water system has been one of the major problems that the entire world is facing. There has been ongoing research on the use of nanotechnology to carry out the separation of water and oil as these substances have a large active surface

area, have improved functionalities, and also have nano-scale dispersion. Research and techniques have been developed for water and oil separation with the use of foams, activated carbon, metal fine mesh, fibers, and textile substrates. (Gore, et al., 2019)

To carry out proper water separation on a nano scale, the materials should have high superwettability properties. The material must be able to have high absorption performance towards either water and/or oil. This high abdosprtion performance depends on the surface characteristics such as oleophobicity/superhydrophobicity (water/oil contact angle > 150°), oleophilicity/superhydrophilicity (water/oil contact angle 0°), and surface roughness at nano scale. Many techniques have been developed, such as electrospinning, layer assembly, air floatation, etc., due to the simplistic fabrication process of these methods. (Zhou, et al., 2013)

1.8 Research objectives

General Objective

- To develop a polyacrylonitrile (PAN) electrospun nanofiber decorated with Ag nanospecies capable of oil water separation and water purification.

Specific Objective

- To carry post electrospinning modification of PAN Nanofibers as amphiphilic membrane and hydrophobic membrane.
- To determine the maximum concentration of CTAB in polymer solution to obtain the best composite membrane for Ag-species decorated membrane.
- To carry the morphological and mechanical analysis of pristine and composite PAN membrane.

1.9 Report Outline

The report consists of the following chapters:

Chapter 1 - Introduction gives details about the background of why the research is being carried out, the problem statement, objectives that the research is trying to fulfill, and limitation of the study.

Chapter 2 - Literature Review gives details about the relevant literature done for conducting the research and analysis of the thesis.

Chapter 3 - Material and Methodology gives details of the experiments done for the study. It also includes the characterization techniques used to define the material.

Chapter 4 - Result and Discussion discusses the different tests carried out and observations from those tests with the necessary data and figures.

Chapter 5 - Conclusion and Recommendation discusses the summary of the research based on the results with the necessary recommendations and future work.

Chapter 2: Literature Review

2.1 Electrospinning of PAN nanofibers

Electrospinning is the process of producing nanofibers by charging the polymer solution under a high voltage electric field through a spinneret to form a fiber or filament through solidification. Many advancements have been made in the electrospinning process, which has been used for the continuous production of fibers on a micro and nano-scale. The fibers made with the electrospinning process have numerous applications due to their unique properties, which include filtration, drug release, wound dressing, tissue engineering, etc. The basic components of the process include a high-voltage system, spinneret, and collector. Changing various parameters determines the properties of the created fibers. (Akdere & Schneiders, 2021)

As the solution is applied with electric field, the surface on the droplet of the solution becomes electrically charged and it starts to flow from the droplet as the surface starts to deform due to the applied field. This phenomenon is known as Taylor cone. From the cone, the jet elongates, solvent tries to form thin fibers which gets deposited on the collector. There is common assumption that when the critical potential φ_0* is reached and increasing it any further destroys the equilibrium, Taylor cone is formed having a half angle of 49.3°. (Yarin, et al., 2001)

The fibers are created by mixing nanomaterials with polymers to produce scaffolding. The nanoparticles are aligned with the created fibers, which reduces the overall Gibbs Free Energy. This is a major advantage in creating fibers, and the electrospinning process also does not need any functionalization, i.e., it only requires solvent to dissolve the polymer and carry out dispersion of the nanoparticles. The parameters that affect the electrospinning process are flowrate and viscosity of solution, polymer concentration in the solution, applied electric field intensity, air humidity, and the work distance from the jet to the collector. (Varghese, et al., 2019)

Changing the working distance, concentration, and applied electric field intensity can improve the alignment of the fibers and improve the overall properties of the materials. The nanofibers are found to be aligned with the length of the fiber as long as the width of the gap but with decreased density. The change in concentration results in the best

alignment of nanofibers for 10–15 wt.% concentration. The fibers begin to form at 8.5KV, but a continuous jet could not be maintained with a width of 3 cm and a concentration of 15% wt. Electrospinning from above 10KV resulted in an increase in alignment but decreased when voltage increased from 11KV. The research shows that the best combination of adjustments in parameters can form the best aligned nanofibers. (Jalili, et al., 2006)

PAN nanofibers can be electrospun by the function of electric field, polymer concentration, and solution flow rate in dimethylformamide. The research discusses the increase in the fiber diameter with the increase in polymer concentration from 30nm to 3.0μm. The flow rate also increases the fiber diameter and decreases with working distance, but the fiber is not affected by the change in electric field at the given working distance. Beads were formed for fibers below 350nm, but the fibers were found to be beaded above this value. (Wang & Kumar, 2006)

2.2 Filtration Medium

Filtration is an important process to remove pollutants and particulates from processes. There are various types of filtration methods employed, which are mechanical, biological, and chemical filtration. The medium of filtration may be made from various substances to form a membrane layer or using natural materials such as sand, gravel, clay, etc. Recent studies have been carried out on nanofiber filtration as it has numerous advantages over other forms of filtration, which include small pore size, low basic weight, high permeability, high specific surface area, and interconnectivity. This also helps to incorporate nanomaterials, which can be used to perform nano-scale functions and have high efficiency. These nanofiber materials can be used for air filtration, water filtration, antimicrobial filtration, desalination, metal ion filtration, catalytic filtration, and oil/water separation. (Qin & Subianto, 2017)

It is important to know that water filtration must be able to get rid of contaminants and impurities even in particulate form. The use of conventional fibers such as melt-blown fibers and spun-bonded fibers is inefficient in the filtration of the ultrafine particles found in water or air due to the micro-sized fiber diameter of the particles, large porous size, etc. The introduction of nanoparticles into the fibers of the filter membrane can improve the

hierarchical structure and the filtration properties. The nanoparticles can increase the surface roughness and the area roughness of the fibers, making them suitable for removing particulates. (Su, et al., 2017)

Wastewater in industries can be treated using membrane filtration. The membrane can be built from various materials such as polyurethane (PU), polyvinyl acetate (PVAc), polyacrylonitrile (PAN), etc. The most common material used to develop membranes for the filtration process is polyacrylonitrile. The filtration process is mostly affected by the pore size, fiber diameter, and morphology, which affect the thermo-mechanical properties and capillary flow porometry of the created nanofibers. (Al-Attabi, et al., 2017)

2.3 Ag nanoparticles grown on PAN Nanofiber

Ag/PAN composite nanofibers are found to be an effective antibacterial material as they are found to be durable and slowly release Ag ions into the surface. This slow release helps to provide strong antibacterial activity against the gram-positive and gram-negative microorganisms. $AgNO_3$ is reduced to form Ag nanoparticles which get embedded into the PAN matrix, and electrospinning helps to form smooth and continuous nanofibers. (Shi, et al., 2011)

With the help of a chelating effect, Ag nanoparticles were found to be uniform in size on the surface of the PAN fiber, which prevents the Ag nanoparticles from aggregation and allows catalytic recycling. The catalytic performance of the composite nanofiber was observed, and other tests showed that there was interaction between the Ag ions and the PAN surface and the ions were distributed uniformly. (Zhang, et al., 2010)

The Ag/PAN composite nanofibers have excellent filtration and antimicrobial properties as the silver nanoparticles help in bacterial reduction. The nanoparticles have a larger surface area, which contributes to an increase in antimicrobial efficiency. The high porosity and small pores of the nanofibers help to carry out filtration of the microbial particles with higher efficiency than that of gauze masks, and the decoration of silver nanoparticles on the surface of the fibers has high bacterial reduction rates. The research discusses the antimicrobial properties and filtration properties of the Ag/PAN fiber with amino-terminated hyperbranched polymer and determined it to be 99.9% and 99.96% effective

against S. aureus and E. coli, and 99.9% effective for removing smaller particles ranging from 0.1 μm~0.7 μm. (Yao, et al., 2016)

2.4 AgBr as photocatalyst in visible light

AgBr has been comprehensively studied for its photocatalytic activity. There is a problem with AgBr as it forms Ag ions during the photocatalytic process, which reduces the photocatalytic activity. (AgBr-MT) The research shows that melt-treated AgBr fabricated under a bromine atmosphere could be a possible solution to this problem as the research shows an improvement in photocatalytic activity and self-recovery of AgBr due to the reduction of unstable Ag ions at the top and edge sites by the melt process and surface reconstruction under bromine gas. (Duan, et al., 2021)

AgBr and Ag/AgBr suffer from constant formation of Ag^0 which causes the degradation. A theoretical survey was carried out to investigate the optical properties and electronic states of the Ag on AgBr surface using density functional survey. The adsorption of Ag on the AgBr surface allows visible adsorption and enhances the adsorbed surface. The changes in the adsorption spectrum is due to the formation of energy gap region for the AgBr. As a result, the Ag^0 reduces the AgBr photolysis and enhances the stability. (Chi, et al., 2014)

The research investigates the photocatalytic activity of AgBr by preparing AgBr(N_2) with solid($AgNO_3$)– solid(KBr) reaction. The photoactivity is lowered due to the formation of Ag ions when left cooled under natural air. There was linear increase of photoactivity in AgBr(N_2) and AgBr with the increase in irradiation time irrespective of the Ag crystalline formation suggesting that Ag formed from the process's behavior could be different from the latent image of photographic process. (Kobayashi, et al., 2013)

2.5 Post Processing

Post processing of fibers is the process of improving the hierarchical properties of the created fibers by changing their characteristics and achieving the required functions and properties. Modifications to the fibers can be physical, chemical, or physico-chemical, whichever suits the fibers best. The modifications that can be made physically to the fibers are heating, leaching, heating and stretching, surface adsorption, ultrasound treatment, UV treatment, plasma treatment, etc. The modifications that can be made chemically to the fibers are surface hydrolysis, deposition of minerals, and chemical crosslinking. The

modifications that can be made physico-chemically are carbonization in a reducing atmosphere, sintering in an oxidising atmosphere, plasma treatment with surface grafting, or surface anchoring. All of these methods of modification are based on scientific recognition. (Kowalczyk, 2020)

After the electrospinning process is carried out, the fibers created have less mechanical integrity and require post-processing to improve their strength. Tests are carried out on the post-treated fiber by either using a single fiber or deriving specimens from the membrane. The morphology of the fiber must be considered for post treatment as there should be minimal losses in fiber morphology while enhancing the required properties. (Nauman, et al., 2021)

Due to the manufacturing restrictions on the preparation of the material, its utility becomes limited. Post processing is a very important process to improve the orientation of molecules and mechanical properties of the nanofibers. FTIR and XRD of the post-drawn fibers indicate that the fibers are organised into kinked chain segments in hexagonal structures which are at right angles to the fiber axis. This increased the fiber's Young's modulus by 100% and its ultimate tensile strength by 500%. (Brennan, et al., 2019)

The bioactivity of the Ag nanoparticles differs according to the doping of Ag ions onto the electrospun nanofibers. Different methods are used to incorporate the Ag nanoparticles onto the electrospun nanofibers and are checked to determine the most efficient route. The efficiency of the methods is determined by discussing the antimicrobial activity of the fibers and the limits of the methods used. The effective methods that were determined by the research on incorporating the Ag nanoparticles were ultraviolet irradiation and direct blending as these methods produced efficient results and their simple execution. (Villarreal-Gómez, et al., 2021)

$AgNO_3$ is commonly used for the formation of Ag nanoparticles as it is reduced by various methods. The research utilises three methods for the reduction, which are: refluxing the solution; using a reducing agent such as sodium borohydride; and heating the prepared composite nanofibers. The characterization of the fibers showed that Ag particles were distributed in the fibers homogeneously and that the composite fibers had strong antimicrobial properties. (Mahapatra, et al., 2012)

2.6 Fabrication of 3D membrane material

Electrospun nanofibers are densely packed fibers in a 2D array, and this restricts the electrospun fibers in tissue regeneration. The development of a facile post-electrospinning method was carried out to overcome the problem of compactness and make the nanofibers into 3D scaffolds. The process was that the nanofibrous mat was submerged in an SB (sodium borohydride) solution, which filled the the mat structure's interconnected pores. Hydrolysis takes place to produce hydrogen gas, which forms clusters in the nanofibers. The clusters formed minimise the free energy and reorganise the nanofibers into a macroporous, low-density, multi-layered spongy 3D scaffold. The solvent of SB (methanol or water) plays an essential role in the post-electrospinning process. (Joshi, et al., 2015)

A gas foaming technique can also be used to create the 3D nanofibrous membrane from a 2D membrane. The paper discusses the fabrication of nylon-6 by the electrospinning technique to create an air-freshening spongy material. The electrospun material created from the N6 pellets dissolved in acetic acid and formic acid (1:4 w/w) was soaked in SB solution, which acted as a gas foaming reagent. Different concentrations of SB solution were used along with time varied to create the 3D fibrous membrane. (Mulmi & Pant, 2018)

2.7 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

SEM is the process of identifying the surface topography and structure of the sample by focusing the electron beam on the surface of the sample so that the image could be formed by the interaction of the electron to produce various signals. TEMs are microscopes that use electron beam particles to help the visualisation of samples and produce a magnified image. The principles of particle and wave optics of electrons produce the image from the samples. The formation of the images into the samples is produced by the beam's interaction with the surface particles, which are either elastic or inelastic interactions. These interactions determine the image that we see of the specimen that we are observing. (Zhou, et al., 2006) (Kohl & Reimer, 2008)

A tungsten filament cathode-equipped electron gun emits an electron beam thermionically in a conventional SEM. One or two condenser lenses focus the electron beam (energy range

of 0.2 keV to 40 keV) to a spot with a diameter of between 0.4 nm to 5 nm. In the electron column, the beam travels via pairs of deflector plates that bend the beam in the x and y axes such that the scan produced over a rectangular area is in a raster pattern. The primary electron beam's interactions with the specimen result in repeated random scattering and absorption, which causes the electrons to lose energy. The sample and the electron beam transfer energy, which results in the production of electromagnetic radiation, high-energy and secondary electrons, all of which can be sensed by specialized detectors. Images illustrating the distribution of specimen current can also be produced by detecting the beam current. As a result of the computer's video memory being synced with the beam position on the specimen, the image that is produced is a distribution map of the strength of the signal being emitted from the scanned area. (Egerton, 2005)

2.8 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique for obtaining the infrared spectrum of emission, absorption, and photoconductivity of solids, liquids, and gases by translating the raw data from the interferogram into actual process using Fourier transform. This technique is used to determine the compounds that are present in the sample. It is very useful for carrying out the nanoparticle's surface characterization. The chemical composition of the nanoparticles can be identified easily, as can the surface reactivity of the sites. The spectrum generated from the Fourier transform contains absorption peaks which relate to the vibration frequencies between the nanoparticles and atomic bonds. The peaks in the spectrum show the material's nature. (Torres-Rivero, et al., 2021)

This method shines a multi-frequency beam of light at the sample instead of a monochromatic beam, and then evaluates how much the sample absorbs the beam. The beam is then modified to contain a different frequency combination in order to generate a second data point. This process is swiftly repeated many times during a brief period of time. Then, the data generated by the computer calculates the absorption at each wavelength by working backward from the data.(Griffiths, et al., 2007)

2.9 X-ray Powder Diffraction (XRD)

XRD is used for the identification of the phase of a crystalline material. It is mostly used for the characterization of carbon materials. It gives important data points about the lattice

constants and crystallisation size. The XRD patterns can be analysed with the round robin test, which is done by various laboratories in Japan to correctly analyse the diffraction patterns. The diffraction peaks 002, 004, 110, 112, and 006 lines, which were computed by automatic diffractometers, determine the X-ray parameters to help compare data easily. Pulverization and sieving are used to reduce sample size to less than 100 m. Diffraction profiles must be measured and their intensity must be corrected with the help of an internal standard of silicon to avoid shifting. The full width of the diffraction is determined at half maximum intensity and then the accuracy of the values is determined. (Iwashita, 2016)

2.10 Tensile Strength Measurement

The tensile strength of fibers is important as it helps the fibers stay durable when they are used for a variety of applications. The conditions for the tensile properties measurement of plastic or polymer films or sheets less than 1 mm thick are carried out as per ISO 527-3:2018. The research talks about using an Instron 5943 tensile testing machine for measurement. The sample sizes of 100x10mm were prepared and measured five times for measurement accuracy. Two groups of samples were divided for sample measurement; samples were cut parallel and perpendicular to the formation of the fiber. The results show that drum rotation speed is an important factor for tensile strength as the fibers were found to have more durability with an increase in drum speed. (Pham Le, et al., 2021)

Varying the rotational speed can affect the tensile strength of the fibers. In the research, the rotation speed of the collector was varied from 500rpm to 2500rpm with the increment of 500rpm. It was found that even though the diameter of the fibers decreased from 313 ± 52 to 229 ± 47 nm with the increased collection speed, the overall mechanical properties improved such as the tensile strength and Young's modulus for the polyvinyl chloride nanofiber mats. (Pham Le, et al., 2021)

2.11 Contact angle

It is the angle made between the solid surface and the liquid vapour interface. This angle determines whether the material is hydrophobic, hydrophilic, superhydrophobic, superhydrophillic, oleophobic, oleophilic, etc. Surface roughness greatly affects the contact angle and wettability of the surface. The impact of roughness depends on whether the droplet fills in surface ridges or leaves air gaps between it and the surface. Control of

the wetting contact angle can be attained with the accumulation or combination of many organic and inorganic molecules on the surface. (Förch, et al., 2009)

2.12 Antibacterial and antifungal test

There are numerous methods to screen and evaluate antimicrobial activity. The most common methods are broth or agar dilution, well diffusion, and disk-diffusion. Each method has its own advantages and limitations. (Balouiri, et al., 2016) Kirby-Bauer testing is the most common form of antibacterial test where the bacteria is grown overnight in a growth medium such as agar, and antibiotic wafer discs are added to it. The clear medium over the discs indicates that the antibiotic is acting against bacteria and fungi. The diffusion of antibiotics over the area decreases with increasing distance, and the clear area over the discs is known as the zone of inhibition. The size of the zone shows the potential microbial inhibition capacity of the antimicrobial agent. (Reynolds, 2021)

To carry out the Kirby-Bauer test, a homogeneous coating of a pure bacterial culture that has been calibrated for turbidity and suspended in saline is swabbed onto an agar plate. On top of the agar, a filter paper disk is subsequently applied that has been treated with the extract. The contents of the disk diffuse into the agar from the treated filter paper. The diffusion of antibiotics over the area decreases with increasing distance, which is maximum at the discs. No colonies will form if the antibiotic concentration is greater than or equal to the effective concentration. Greater zones of inhibition typically correspond to decreased minimum inhibitory concentrations (MICs) of antibiotic or extract for that particular bacterial strain. For larger molecules of antibiotics and hydrophobic nature of the extracts, the case doesn’t stand as the diffusion process is slow in the agar. (Hudzicki, 2009)

2.13 Research Gap

The research looks into how different process parameters affect the creation of nanonet structures from a PAN solution that contains cation surfactants (addition of CTAB and meltblown). In comparison to electrospun PAN fibers, the CTAB-PAN fibers displayed an increased thermal and mechanical performance. The research evaluated the pore size distribution and filter effectiveness of PAN nanofiber webs and CTAB-PAN nanofiber using meltblown. (Kang, et al., 2021)

There has been few research on embedding Ag nanoparticles on the CTAB loaded PAN fibers which would create AgBr nanoparticles. Numerous research indicates the presence of Ag nanoparticles on PAN fibers and their characteristics and properties were studied. In this research, the Ag nanoparticles are reacted with the CTAB present in the PAN fibers to create AgBr nanoparticles which is known to be a good photocatalytic and antibacterial agent. The development of the AgBr PAN composite nanofibers would be carried out and its morphological and mechanical properties would be evaluated. The research would also aim to evaluate the best concentration of CTAB in fiber that would yield the best mechanical properties and the morphological characteristics.

Chapter 3: Research Methodology

3.1 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 used as received. Additional chemicals such as Methyl Blue Trihydrate (MB, MW: 373.90 g/mol, assay>=99%, Himedia Laboratories Pvt. Ltd.) were used for various tests including testing the photocatalytic action of the nanofibers and formation of AgBr.

3.2 Fabrication of composite electrospun mats

Electrospinning was conducted at the laboratory setup available at the Nano Laboratory of IOE Pulchowk Campus. 10% by weight PAN were dissolved in DMF solution and prepared using magnetic stirrer until the particles were dissolved. This step was followed by the addition of different amounts of CTAB to the solution (0.5%, 1%, and 2%) by weight with respect to the solution and stirred until the particles were dissolved. The solution was kept in the ultrasonic cleaning machine for the particles to disperse properly for 1 hour, maintaining a bath temperature of 20°C. The solution was then immediately carried out for electrospinning in a closed chamber for 4 hours at the following parameters. Applied voltage of 15KV, 25cm distance from the tip to the collector, 1.5 ml/hr flow rate, temperature maintained at room conditions, with drum rotation speed maintained at 500rpm. The prepared mat was then vacuum dried for 24 hours to remove the DMF from the surface of the developed nanofibers.

Figure 1 Electrospinning process

3.3 Post Treatment Process

3.3.1 Ag deposition on PAN/ CTAB composite nanofibers

For silver deposition, PAN/ CTAB composite nanofibers were made into sizes (4 cm × 4 cm) and were placed into 25 ml of 1×10^{-3} N $AgNO_3$ solution. The fiber mats were then kept in the solution for 24 hours. After washing the prepared mats with distilled water, the mats were vacuum dried for 24 hours at room temperature.

a) b)

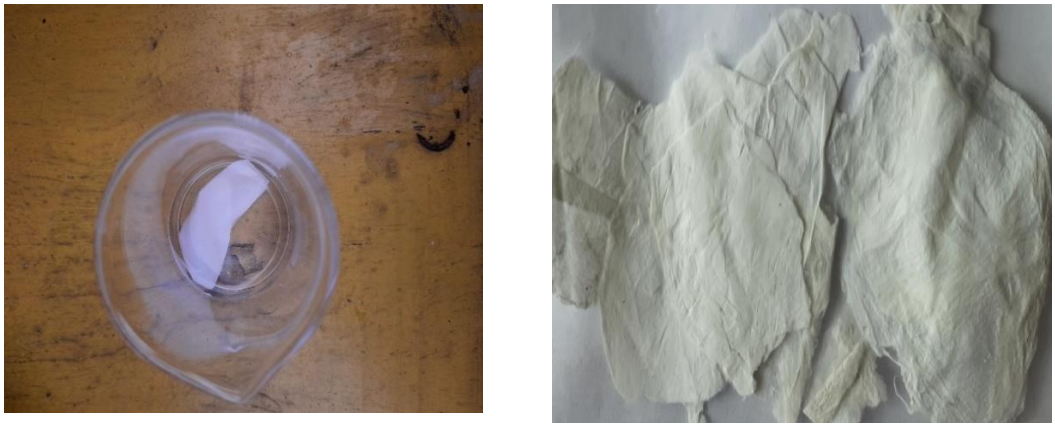


Figure 2 a) Preparation of CTAB-PAN fiber in $AgNO_3$ Solution and b) Developed AgBr PAN fibers

3.3.2 Development of 3D structure of PAN fiber

For the silver deposition and formation of the 3D structure, the pristine PAN nanofibers were made into sizes (5cm × 5cm) and were placed in 1×10^{-3} N $AgNO_3$ solution. 1 N concentration of Sodium Borohydride (SB, $NaBH_4$) was made and equal parts of the solution were added to the beaker containing $AgNO_3$ solution and the PAN nanofiber. The beaker was covered in aluminium foil to contain the gas formed and placed in a shaker set at medium speed to allow the solution to stir continuously. The PAN mat was kept in the solution until there was a noticeable colour change (a light brownish color). The 3D PAN mat was separated from the solution and washed with distilled water. After washing, the 3D PAN mat was dried in an oven for 24 hours at 30◦C.

a) PAN fiber in $AgNO_3$ and $NaBH_4$ solution *b) 3D membrane left for washing and drying*

Figure 3 Preparation of Ag NPs loaded 3D PAN nanofibrous membrane

3.4 Characterization of the electrospun membrane

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 PAN fibers was further evaluated by using SEM-EDS mapping and X-ray diffraction (Rigaku X-ray diffractometer, Japan). The antibacterial test was carried out using zone inhibition method for different membranes towards gram-negative, gram-positive bacteria and fungi. Triplicate samples of the developed membrane of CTAB-PAN

fibers and silver-coated AgBr PAN fibers were used with the PAN membrane used as a negative control and Kanamycin Antibiotic as a positive control for evaluation. The mechanical properties of the composite fibers were determined by tensile strength measurement test (Instron 5943 tensile testing machine).

3.5 Photocatalytic activity measurements

The photocatalytic properties of the AgBr 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 100ml borosilicate beakers under direct sunlight and under UV irradiation light at 365nm. The experiments were carried out in the natural environment in the sunlight and inside the UV chamber. For the degradation experiments, 20ml of MB dye (10ppm concentration) was reacted with the Ag doped AgBr PAN fiber mats under the given conditions. The samples for the activity measurement were taken at regular intervals, taking 2 ml of dye at a time, and the dye concentration of the dipped mats were measured by noting down its absorbance at 665 nm with a UV–visible spectrophotometer (HP 8453 UV–vis spectroscopy system, Germany). The methods of data recording and calculation of the Methylene Blue concentration in ppm are carried out following our previous study. (Pant, et al., 2011)

Figure 4 Photocatalytic degradation of MB under sunlight and under UV at 365nm

3.6 Antibacterial Test

Bacillus subtilis (Gram-positive), *Escherichia coli* (Gram negative), and *Candida albicans* (fungi) were used to analyze the antibacterial property of the 1% CTAB-PAN fiber and

silver coated 1% AgBr PAN fiber. The Kirby-Bauer test, which is also known as the Zone of Inhibition test, was used for characterization of the microbiological properties of the developed composite fibers. The test was conducted as per the "Performance Standards for Antimicrobial Susceptibility Testing".

The model organisms were *Bacillus subtilis* ATCC 6051, *Escherichia coli* ATC 8739, and *Candida albicans* ATC 2091. For the positive control, 5 µl of prepared 5 mg/ml Kanamycin Antibiotic was used. For negative control, pure PAN fiber was used and the samples of 1% CTAB-PAN fiber and AgBr PAN fiber were triplicated as shown in the following figure. All the similar procedure was followed for the prepared samples.

a) b)

Figure 5 antibacterial test with a) AgBr composite fiber and b)1% CTAB as sample

The following table shows the zone of inhibition formed for the prepared samples.

Table 1 Zone of Inhibition for the prepared samples.

Zone of Inhibition for control = 9mm		
	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)

3.7 Filtration Property Testing

To test the filtration property of the developed fibers, the water sample containing oil and water was taken. The sample water was filtered through the AgBr decorated PAN fiber as per the setup shown in the figure.

Figure 6 Filtration setup of water and oil sample

The methodology is shown in flowchart as per the figures below:

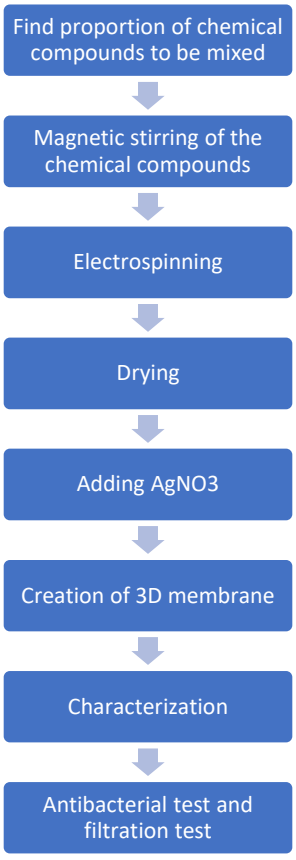


Figure 7 Methodology

Chapter 4: Result and Discussion

4.1 Analysis of fiber under the optical microscope

The fibers with CTAB concentration of 0.5%, 1%, and 2% were developed. The first inspection of the developed fibers was examined under the optical microscope at 4x and 10x magnification. The magnified image of the pristine mat showed that there were no suspended PAN particles and the PAN fibers are compact structure. The magnified PAN mat were shown below. [Figure 8] For the 3D PAN structure, the fibers are seen to be loosely packed due to the hydrolysis action. [Figure 11]

a) b)

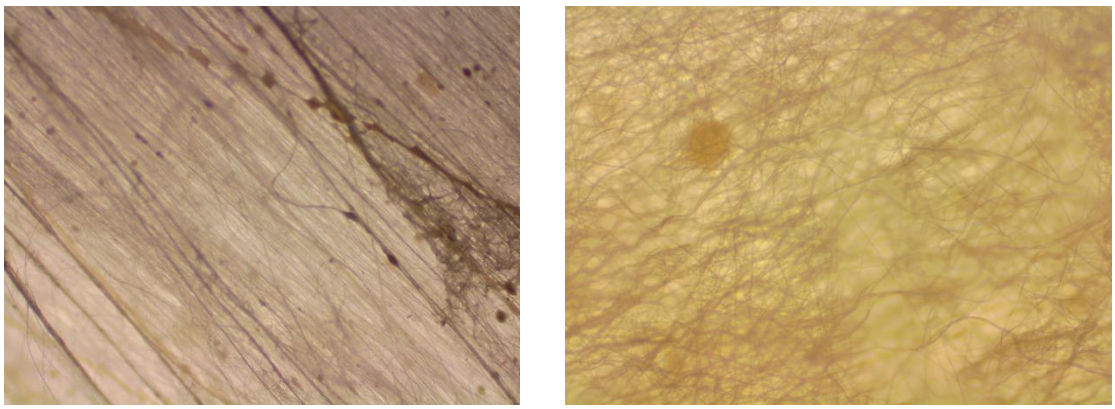


Figure 8 Optical image of pristine PAN fiber under a) 4x and b) 10x zoom

The magnified image of the CTAB-PAN fiber with various concentration ranging from 0.5%, 1%, and 2% showed that the 1% PAN fiber mat had great morphology. The fibers alignment increases as the concentration of CTAB in the fibers increases. The development of large beads in the fibers also increases with the CTAB concentration so the 1% PAN fiber has the best morphology. The figures of the CTAB doped PAN fiber with varying concentration are shown below [Figure 9]

a) b) c)

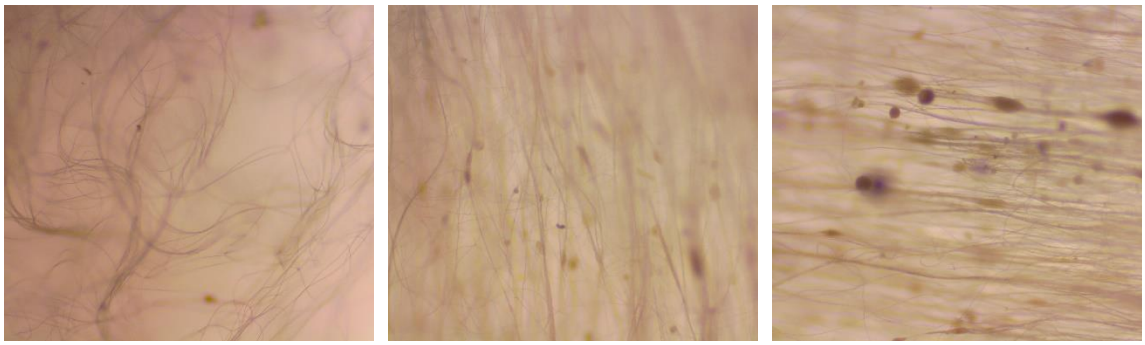
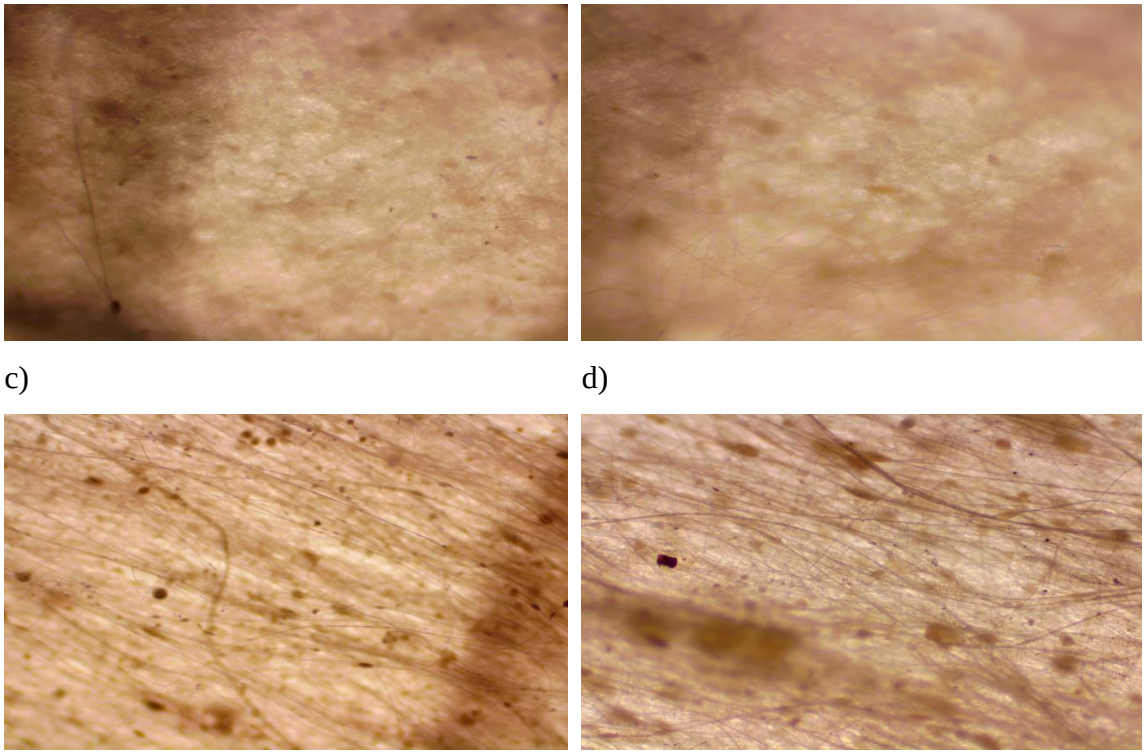


Figure 9 Optical image of a) 0.5% CTAB-PAN fiber, b) 1% CTAB-PAN fiber and c) 2 % CTAB-PAN fiber under 10x zoom

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. Visible inspection of fiber shows the color of Ag decorated mat changes to yellowish for the 3D PAN membrane. The magnified image of the Ag decorated 3D PAN membrane and 1% CTAB-PAN fiber membrane. [Figure 10 c) and d)]

a) b)



c) d)

e) f)

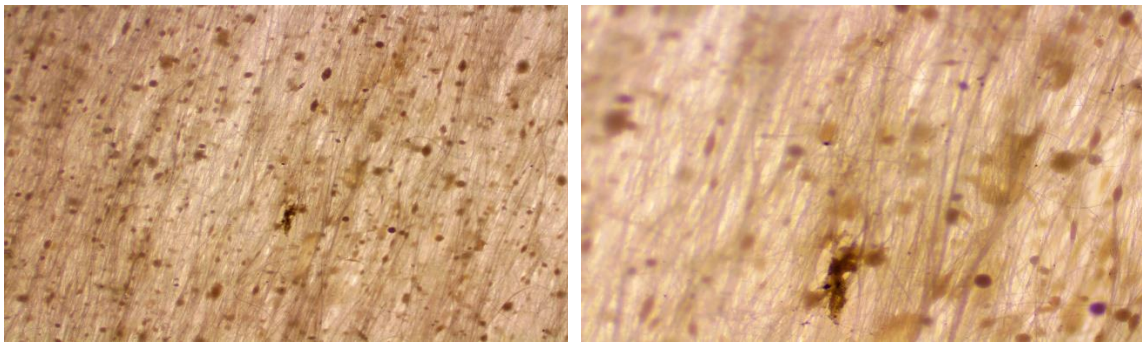


Figure 10 Optical image of AgBr PAN membrane under 4x and 10x zoom for a) b) 0.5%, c) d) 1% and e) f) 2%

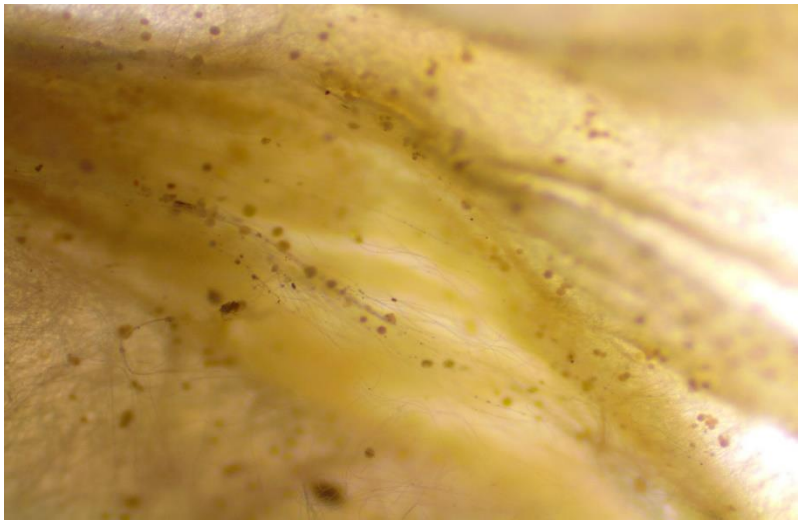


Figure 11 3D Ag PAN membrane under 4x zoom

4.2 Membrane Morphology

The FE-SEM images of the pristine PAN mat, CTAB doped PAN mat, and the AgBr PAN mat after under different magnifications are shown in the figure. 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. The length of the fiber from the FE-SEM images was measured using ImageJ.JS online software. For the pristine PAN mat, the diameter of the fiber was determined to be 150.736 nm. [Figure 12] For the CTAB doped PAN mat, the diameter of the 0.5% CTAB-PAN fiber was determined to be 162.53

nm [Figure 13], 1% CTAB-PAN fiber was determined to be 145.149 nm [Figure 14], and 2% CTAB-PAN fiber was determined to be 139.335 nm. [Figure 15] For the AgBr PAN mat, the diameter of the fiber was determined to be 141.057 nm. [Figure 16]

a) b)

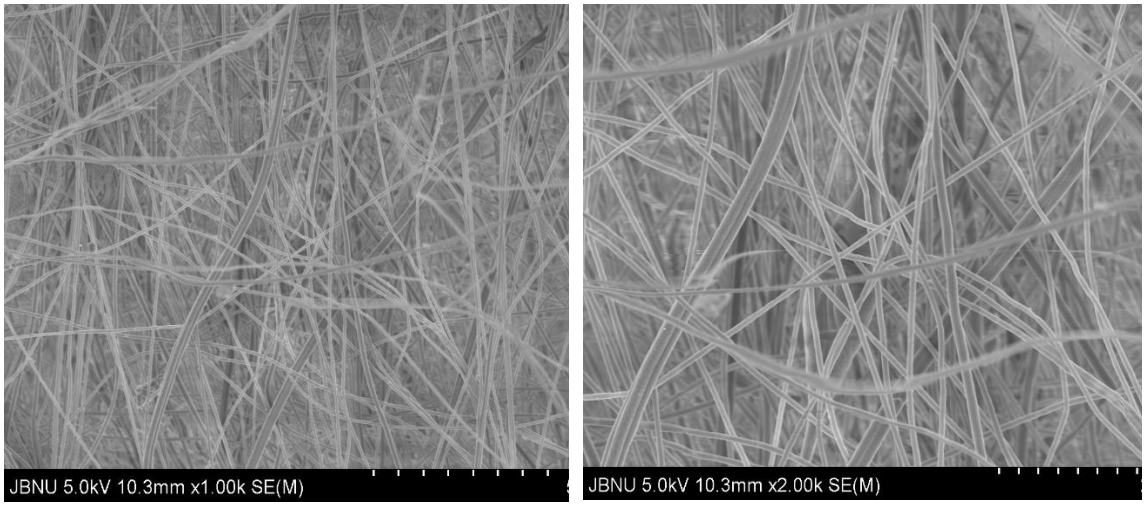


Figure 12 FE-SEM images of PAN mat under a) 1K and b) 2K magnification

a) b)

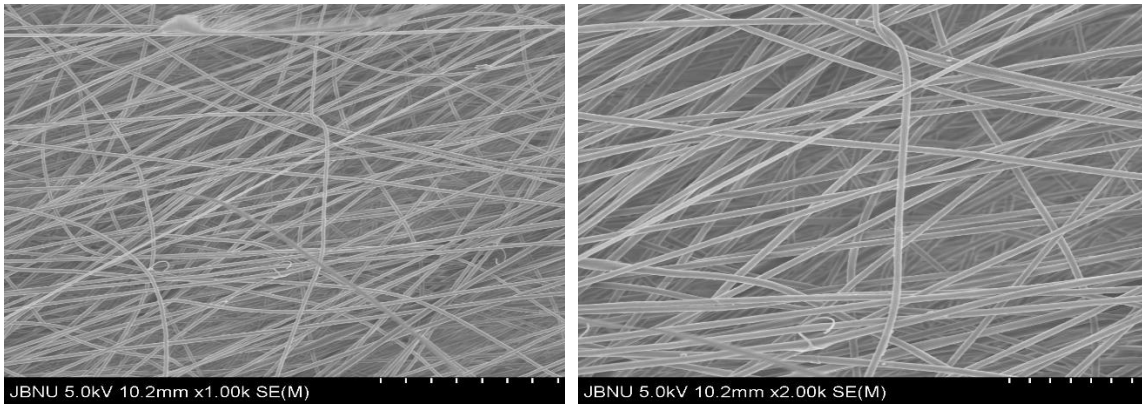


Figure 13 FE-SEM images of 0.5% CTAB-PAN mat under a) 1K, and b) 2K magnification

a) b)

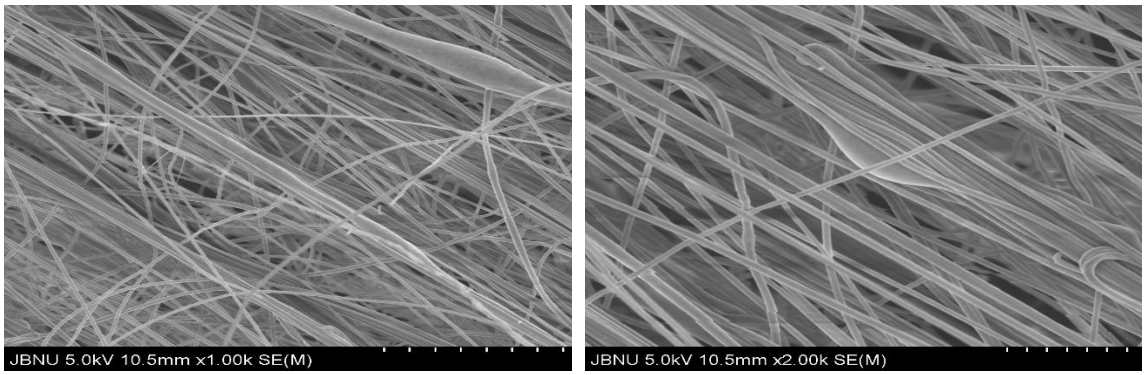


Figure 14 FE-SEM images of 1% CTAB-PAN mat under a) 1K, and b) 2K magnification

a) b)

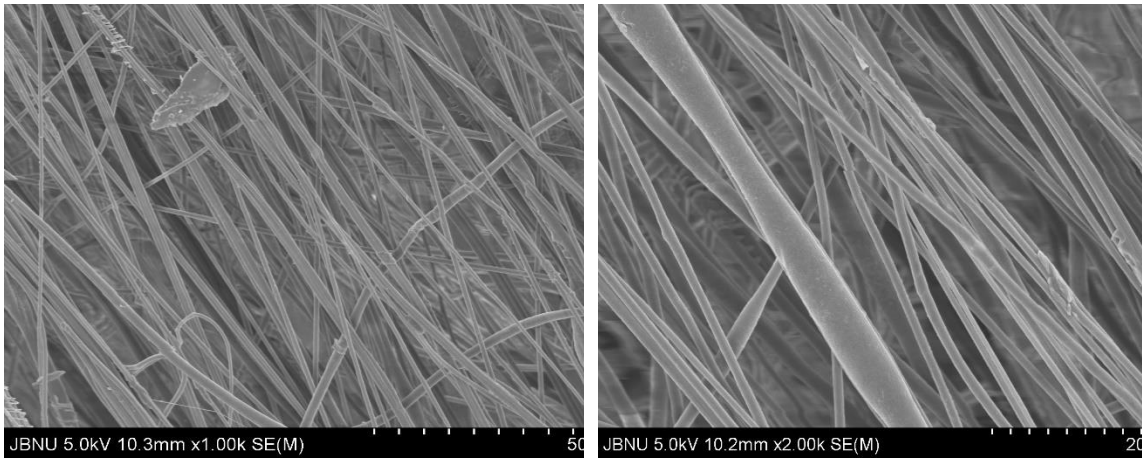


Figure 15 FE-SEM images of 2% CTAB-PAN mat under a) 1K, and b) 2K magnification

a) b)

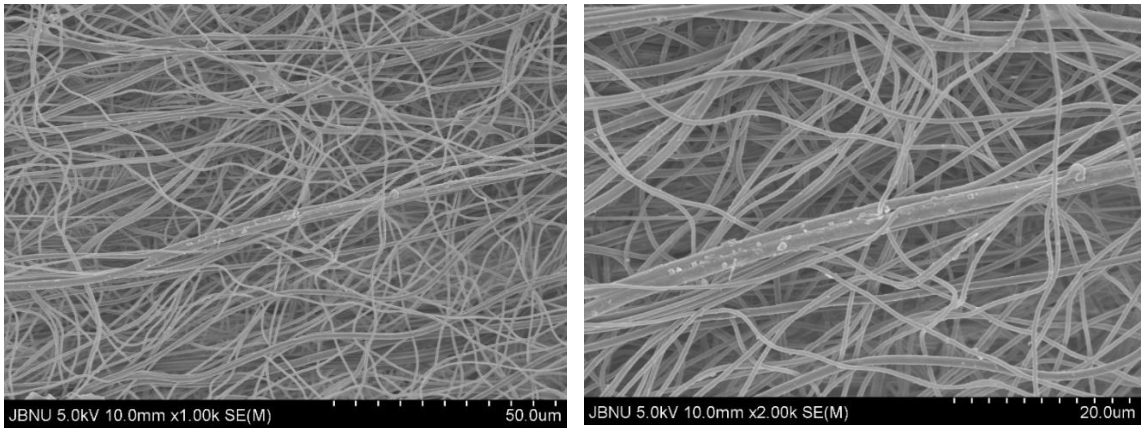
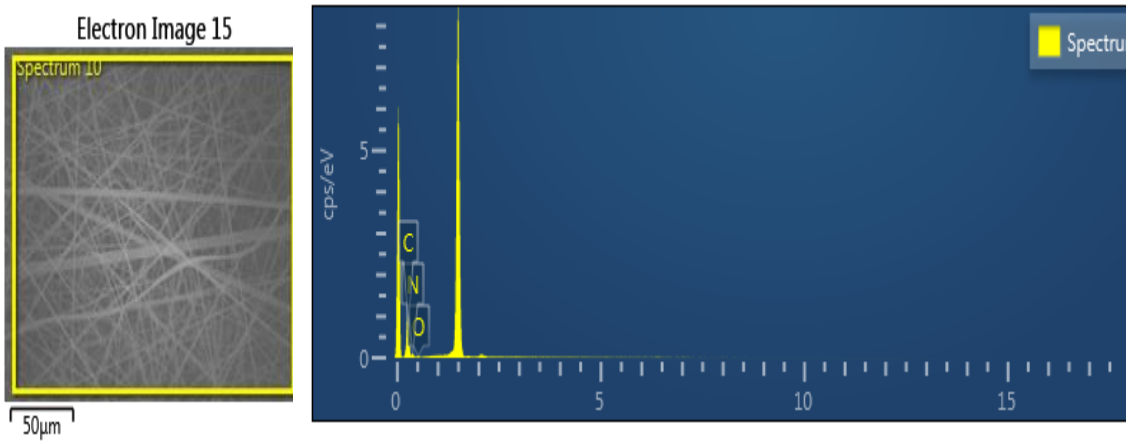


Figure 16 FE-SEM images of AgBr PAN mat under a)1K and b)2K magnification

The EDX results of the fiber are also shown in the following figures and tables below. These results help to determine if any foreign elements are present in the sample along with the homogeneity of the sample and the elemental distribution. The results of the table are on the basis of percentage by weight and atomic weight. From Table 3, we can confirm that CTAB particles has been embedded onto the PAN matrix. In Table 4, we can also confirm the formation of AgBr on the composite PAN fibers which shows the values of the element on the spectrum.

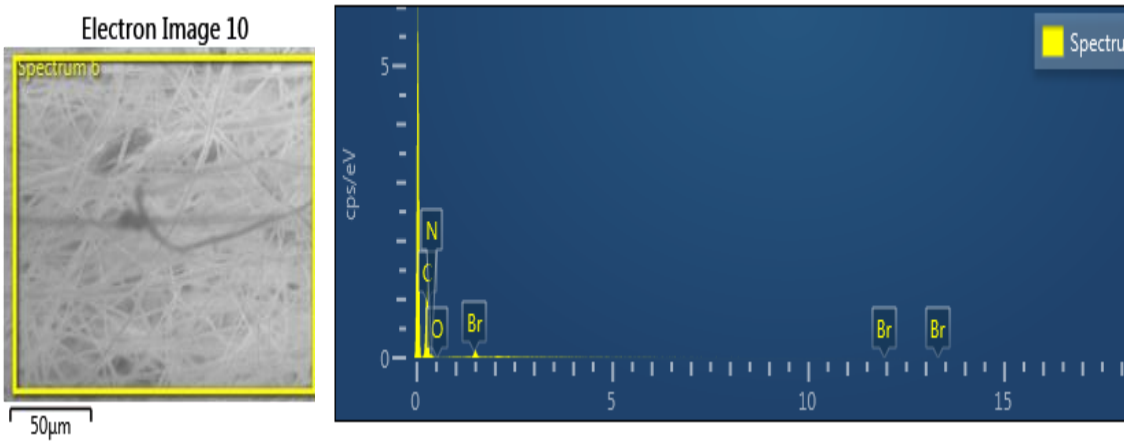
Table 2 EDX of PAN fiber



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt % Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.80	0.00799	54.70	2.22	58.98	C Vit	Yes	
N	K series	0.49	0.00086	37.80	2.40	34.95	BN	Yes	

O	K series	0.05	0.00017	7.50	1.26	6.07	SiO2	Yes	
Total:				100.00		100.00			

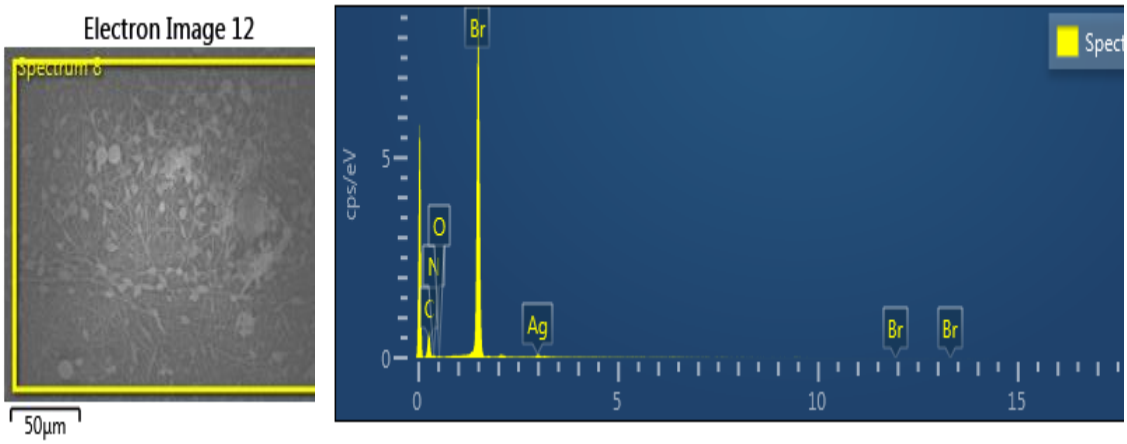
Table 3 EDX of CTAB-PAN fiber



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt % Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.95	0.00948	67.46	2.20	73.88	C Vit	Yes	
N	K series	0.32	0.00057	25.72	2.35	24.16	BN	Yes	
O	K series	0.01	0.00004	1.27	0.57	1.05	SiO2	Yes	

Br	L series	0.11	0.00103	5.54	0.38	0.91	KBr	Yes	
Total:				100.00		100.00			

Table 4 EDX of AgBr PAN fiber



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	0.51	0.00514	34.83	0.68	77.73	C Vit	Yes	
N	K series	0.00	0.00000	0.00	0.00	0.00	BN	Yes	
O	K series	0.03	0.00009	0.41	0.13	0.68	SiO2	Yes	

Br	L series	7.51	0.06725	63.22	0.67	21.20	KBr	Yes	
Ag	L series	0.13	0.00135	1.54	0.14	0.38	Ag	Yes	
Total:				100.00		100.00			

4.3 FTIR analysis

The FTIR analysis of the samples was done at the Instrument Section in the Department of Plant Resources, Thapathali, Kathmandu and in the physics department at Amrit Science Campus, Lainchaur, Kathmandu. The 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-PAN and AgBr PAN fibers clearly shows that some functionalities are added after the formation of composite PAN membrane. 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. (Sigma Aldrich, n.d.) (Prakash, et al., 2013)

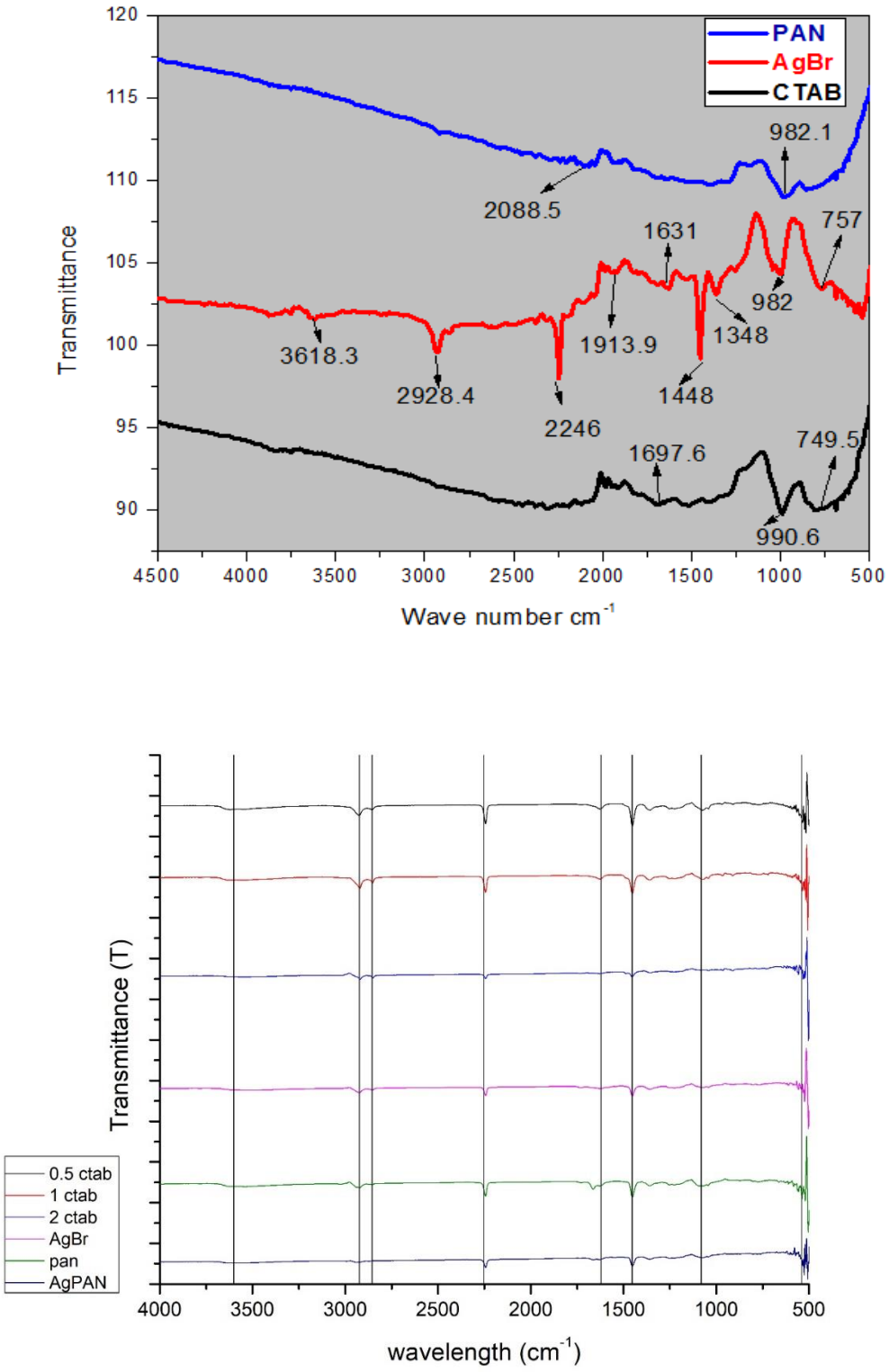


Figure 17 FTIR image of pristine PAN fiber, AgBr PAN fiber, Ag doped PAN fiber, 0.5%, 1% and 2% CTAB-PAN fiber

4.4 Contact Angle

The contact angle and surface energy measurements of the PAN fiber were carried out in the Applied Science Lab at Kathmandu University. The volume of microdrop used was 4-6 microlitres to carry out the experiment. The droplets formed on the surface need to be formed for at least 2 minutes for the measurement to take place. As per the table below, the contact angle was found to be 101.25 ± 0.39 which means that the surface of PAN fiber is hydrophobic. The same experiment could not be carried out for the AgBr PAN fiber as the water droplets were immediately absorbed by the surface of the composite fiber, making the surface hydrophilic.

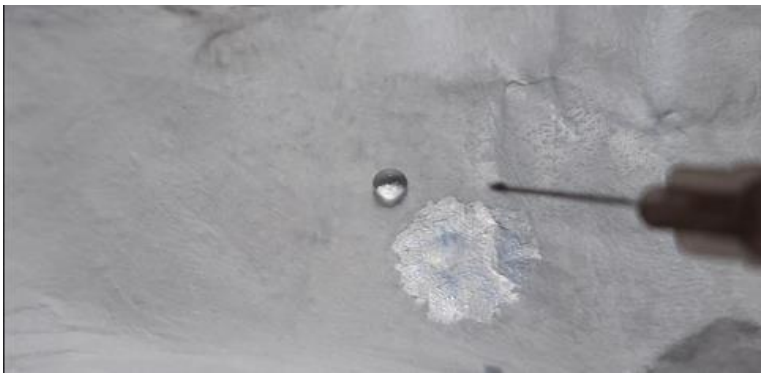
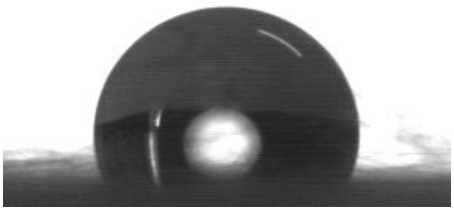


Figure 18 Formation of water droplet and absorption of oil droplet in Ag/PAN membrane



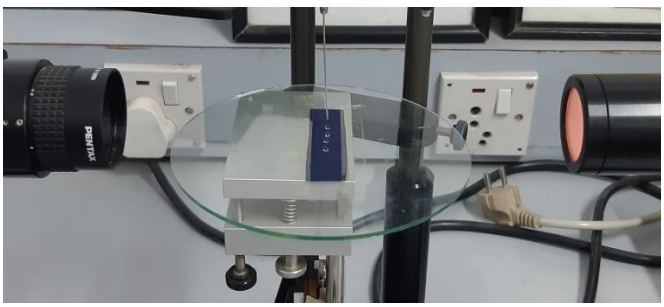


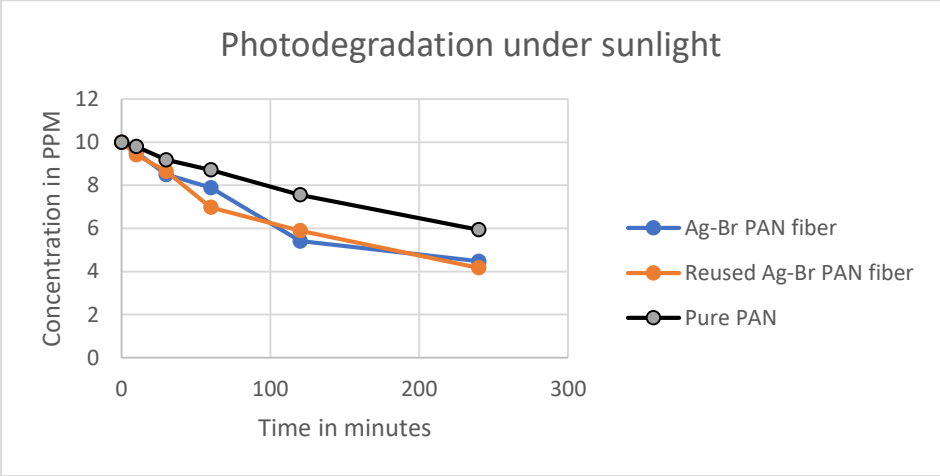
Figure 19 Contact angle measurement

Table 5 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

4.5 Photocatalytic activity measurement

The photocatalytic activity was measured for the Methyl Blue degradation at various intervals of time under UV light and sunlight by using the approximate amount of nanofiber mat. Methyl Blue degrades under direct sunlight or UV irradiation. The composite nanofiber prepared enhances the properties of the degradation due to the deposition of Ag nanoparticles. The sample was reused, and the photocatalytic action of the reused sample was also determined. The methods of testing the photocatalytic degradation activities were done as per the previous study. 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 for the degradation of dyes.



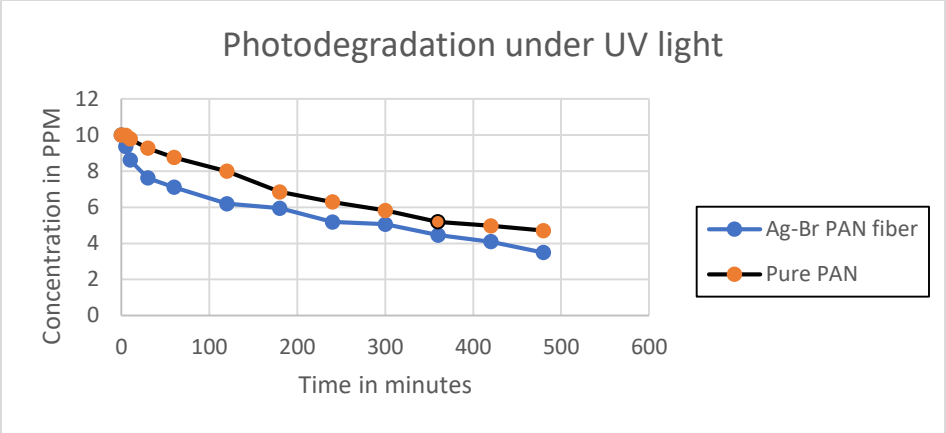


Figure 20 Graph between concentration in ppm vs time

4.6 Antibacterial test

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 6-8mm and the zone of inhibition for the AgBr PAN membrane ranges from 3-5mm for the *Bacillus subtilis*, *Escherichia coli*, and *Candida albicans*. There is less formation of Br ions in the AgBr PAN membrane as compared to 1% CTAB-PAN membrane which is found to be an excellent antibacterial agent.

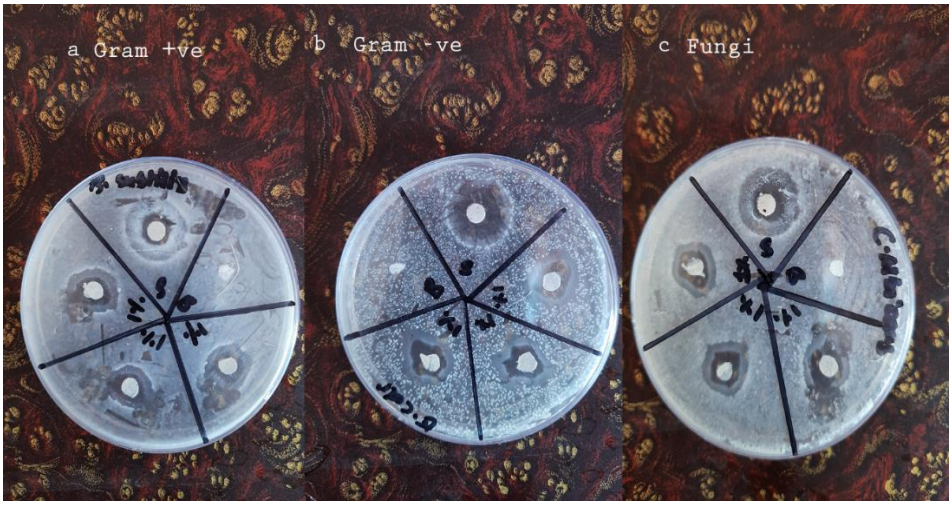


Figure 21 Zone of inhibition test for 1%CTAB-PAN fiber

Figure 22 Zone of inhibition test for Ag-Br PAN fiber

4.7 Filtration test

First, the filtration process was carried out for the doped 3D AgBr PAN membrane as per the setup for separation of water and oil. The 3D membrane was not an effective solution as the loose scaffold allowed the droplets of oil to pass through the filter membrane. After that, the experiment was carried out on doped 2D AgBr PAN membrane. The samples of size 6cmX6cm were used for the experiment. Equal volume of cooking oil and distilled water was used to carry out the test. 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 using the following table:

Table 6 Calculation of Flow Rate

S.N.	Volume(ml)	Time(sec)	Flow rate(ml/sec)
1	10	737	0.01356
2	12	871	0.01379
3	14	1032	0.01356

4.8 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 doped 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.

Table 7 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

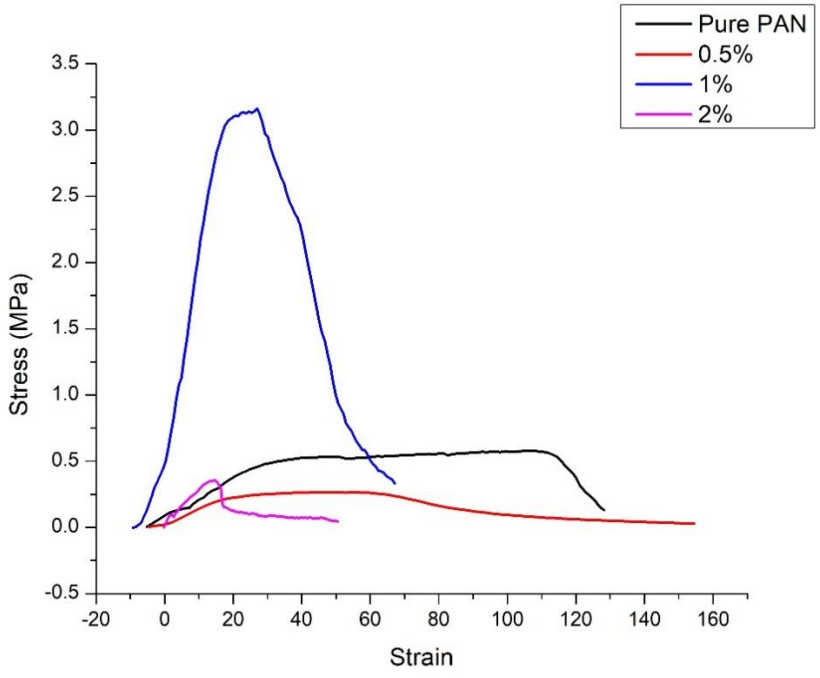


Figure 23 Stress vs. Strain graph of pristine PAN and composite fibers

4.9 XRD

XRD analysis was carried out to determine the crystalline structure of the synthesized composite. The XRD analysis shows the molecular and crystalline structure of the Ag decorated PAN membrane. The AgPAN showed a strong diffraction centered at 2θ angle of around 17◦ and weak diffraction centered at 2θ angle of around 31◦. These have been the characteristics reflections for the PAN hexagonal lattice. The peaks centered at around 17◦ and 31◦ correspond to the (110) and (200) planes. The broad peak of the Ag PAN fiber shows the amorphous nature while the sharp peaks of the CTAB-PAN fiber shows the crystalline nature of the particles formed on the fibers.

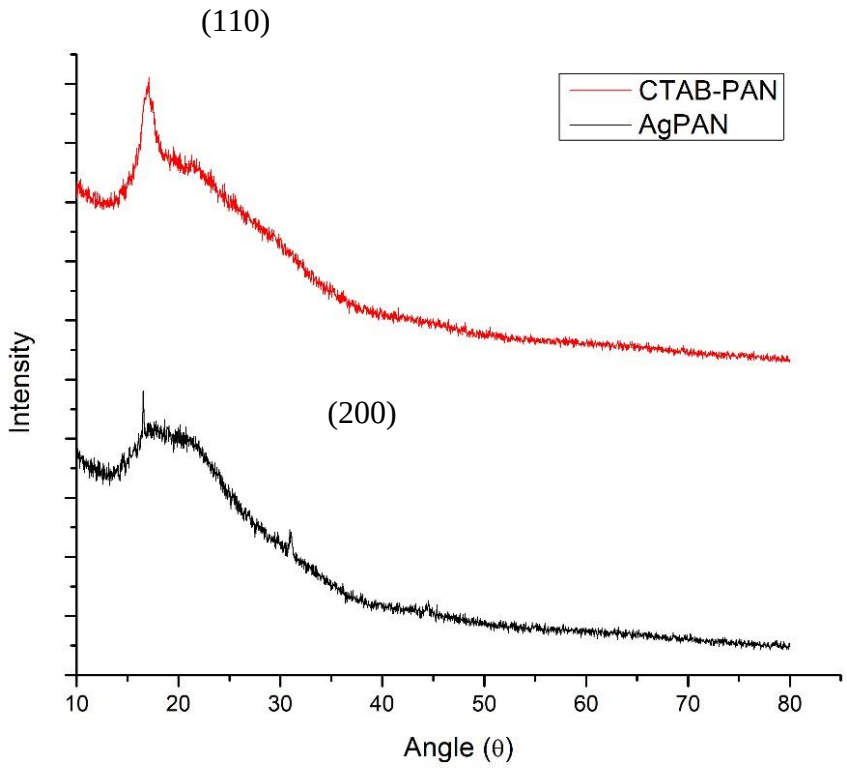


Figure 24 XRD Analysis

Chapter 5: Conclusion, Recommendation and Future Work

5.1 Results and Conclusion

The results of the tests can be summarized in the following points below:

- From the optical microscope, SEM and EDX mapping, we can conclude that the alignment of the fibers increases with the concentration of CTAB in the sample, but the bead formation also increases, so 1% CTAB was suited best for further application. There is also the formation of AgBr particles.
- From the FTIR analysis, there is shift in peaks and functionalities are added after the formation of composite PAN membrane embedded with AgBr nanoparticles.
- The contact angle was found to be 101.25 ± 0.39 which means that the surface of PAN fiber is hydrophobic in nature.
- The photocatalytic activity of the AgBr PAN fibers was measured for MB dye and reused again under sunlight and UV light, and it was found to be nearly of the same efficiency proving that the material can be reused again for the degradation of dyes.
- The zone of inhibition for the 1% CTAB-PAN membrane ranged from 6-8mm and the zone of inhibition for the AgBr PAN membrane ranged from 3-5mm, indicating that there is less formation of Br ions which is an excellent antibacterial agent. The effectiveness may decrease but it is still a good antibacterial agent.
- The 3D membrane was not an effective solution in filtration as the loose scaffold allowed the droplets of oil to pass through the filter membrane. For the 2D membrane, the oil was separated and settled at the top while the distilled water stayed on the bottom of the flask and the flow rate was calculated to be 0.01363 ml/sec.
- From the mechanical strength test, the Young's Modulus and Tensile Strength of the composite fibers was maximum at 1% CTAB doped PAN fibers at 0.1206 MPa and 3.1602 MPa. The breaking point of the pure PAN was maximum at 110.42 and it decreased with increase in the percentage of CTAB.
- The peaks centered at around 17 and 31 degrees correspond to the (110) and (200) planes for the XRD analysis.

In summary, the development of AgBr PAN fiber with polymer solution prior to electrospinning can produce CTAB loaded PAN fibers which can be converted into AgBr PAN fibers. The developed composite membrane is amphiphilic, photocatalytic and antibacterial in nature. The composite nanofiber also has good morphology and improved mechanical properties. The 3D scaffolding was also created with AgBr PAN membrane with $AgNO_3$ and $NaBH_4$ which was not effective in filtration. 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.

5.2 Recommendations and Future Work

It is recommended to develop thick 2D fiber bases to carry out the filtration process due to its compact nature. It is also recommended to study the use of the Ag decorated composite mat structure in medical and industrial applications. It is recommended to grow Ag nanoparticles in the dark for 24hrs for the even distribution of the nanoparticles on the fibers and to increase the surface area of the fibers. The study of the composite mat for air filtration could be an option for future research as the development of the 3D membrane could be an option.

The methods used in the thesis for the fabrication of the composite fibers is simple and effective while the materials that were used were non-hazardous which allows for further research work in many areas. The following may be carried out for further study on this area.

- Variation of proportion by weight of the composition of PAN and CTAB and compare for its effectiveness.
- Test the thermal properties of the fibers to determine its effectiveness against variation in temperature for industrial applications.
- Further study of photocatalytic degradation of other dyes under UV light.
- Health hazard evaluation of the composite fiber can be carried out.
- Improvement of mechanical properties by new mechanism can be explored.

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