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Analysis of Morphological properties of Ag_3PO_4 embedded Polyacrylonitrile electrospun membrane for waste-water treatment

by

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The undersigned certify that they have read, and recommended to the Institute of Engineering for acceptance, a thesis entitled "***Analysis of Morphological properties of Ag_3PO_4 embedded Polyacrylonitrile electrospun membrane for waste-water treatment***" submitted by Mr. Sugandha Shrestha (PUL-076-MSMSE-015) in partial fulfilment of the requirements for the degree of Master of Science Engineering in Material Science and Engineering.

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ABSTRACT

Electrospinning is a straightforward, inexpensive and quick method for the fabrication of nanofibres and nanofibre-based materials. In this work, electrospun polyacrylonitrile (PAN) nanofibres embedded with silver phosphate (Ag_3PO_4) have been fabricated. Electrospun PAN nanofibres were surface modified with hydrazine to form amidoxime groups —C(CN_2=NOH) for effective anchoring of silver ions, which is then converted to silver phosphate through chemical methods. The composite fibres that were produced in this way were evaluated using a Scanning electron microscope(SEM), Fourier transform infrared (FTIR), Ultraviolet-visible(UV-vis) and X-ray Powder Diffraction(XRD). Photocatalytic behaviour and antibacterial testing were done on the composite and analyzed. According to experimental findings, composite nanofibres made by reacting functionalized PAN nanofibres with 0.02 M concentration solutions of silver nitrate and disodium hydrogen phosphate are found to be more effective in the photo-degradation of dyes when exposed to visible light and for antibacterial activity, PAN nanofibres fabricated by utilization of 0.05 M concentration solutions was found to be the most effective.

Keywords: Electrospinning PAN nanofibre, Ag_3PO_4/PAN composite, Photodegradation, Antibacterial

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LIST OF ACRONYMS AND ABBREVIATIONS

SEM	:	Scanning Electron Microscope
XRD	:	X-Ray diffraction
FTIR	:	Fourier Transform Infra-Red
UV	:	Ultra-Violet
AOPAN	:	Amid-Oxime Polyacrylonitrile
PAN	:	Polyacrylonitrile
DMF	:	N,N-DiMethyl Formamide
MB	:	Methylene Blue
EDS	:	Energy Dispersive Spectroscopy

CHAPTER ONE

INTRODUCTION

1.1. Background

Water is one of the most essential resources on the planet. The component itself is the source of life and one of the most essential material resources for human survival and development. Water is a naturally occurring substance on our planet, and it is crucial for humans and other living things to have access to it in its purest form because life as we know it would be impossible without it. Natural and man-made activities with rising urbanization and industrialization have polluted and degraded water resources. Water pollution has become a severe environmental problem as well as a threat to human existence.

Water covers about 71% of the earth's surface (Shiklomanov, 2019), but freshwater resources which can directly be utilized by human beings include rivers, fresh-water lakes, shallow groundwater only compromise 0.03% of the total water content of our planet (Hernández-Chover et al., 2020). Excessive growth of our ever-increasing population has put forward a grim forecast of the global water demand to increase by 55% in 2050, whereas the global water deficit is estimated to be 40% in 2030 (Pavon, 2019). As per a study in 2019, approximately 2 to 4 billion people in Asia, the Middle East, Africa, and South America either do not have access to clean drinking water at home or experience water scarcity at least once every year (Pavon, 2019).

Water for aquatic creatures, drinking, sanitation, agriculture, and industrial use frequently includes a small amount of suspended organic and inorganic particles and a considerable range of microorganisms, including bacteria, algae, viruses, protozoans, and even higher species. Water gets polluted as the concentration of these substances increases. Several poisons and illnesses affect the water, even in low amounts. Overall, natural water and oceans get polluted by oil, dyes, silt, clay, animal excrement, minerals, and other impurities.

All these factors make it critical for every individual and government to recognize the significance of preventing water pollution. Water pollution may alter ecosystems and harm plants and animals. The reason for groundwater contamination is a lack of environmental awareness. Water pollution has also increased the risk of cancer, respiratory and skin problems, cognitive impairment, and heart disease. Water supplies can get contaminated with bacteria, protozoa, and viruses, resulting in diseases such as schistosomiasis and cholera. Humans are especially sensitive to this form of pollution in locations with insufficient water purification systems. In actuality, water pollution results in the contamination of water sources with contaminants that render the water unfit for swimming, cleaning, cooking, and other purposes. Innovative methods are needed to restore water resources to their original state due to pollutants, including chemicals, debris, bacteria, and parasites. Water is eventually contaminated by all types of pollution. Lakes and seas become contaminated by air pollution. Land contamination may contaminate an underground stream, a river, and the ocean. As a result, even trash thrown on an empty lot might eventually contaminate a water supply.

Over time, the leading causes of waste-water quality deterioration have been anthropogenic activities, population growth, climate change, and industrial expansion (Zhang et al., 2019). Industrialization and increasing human activities such as metal plating, fertilizers, insecticides, pesticides, tanneries, mining, paper manufacturing, and battery production, as well as many inorganic and organic pollutants released into our resources, are continuously endangering the resource as well as the ecological environment that thousands of living beings depend upon. Organic or inorganic pollutants in waste-water must be removed/degraded. To reduce pollution and unfavourable environmental effects, preserve the ecosystem, and adhere to legal water management rules, it is now necessary to apply an acceptable waste-water treatment technology (Hernández-Chover et al., 2020).

Emergent pollutants in waste-water worldwide have high chemical stability, low biodegradability, and water solubility and are mostly defiant against usually utilized waste-water treatment processes. These effluents as well as pollutants are found to be challenging to remove and either require the use of sophisticated and costly technologies or methods

that are not quite as effective. These problems hence point towards the requirement of processes or materials that would help provide a cost-effective and efficient water purification.

Figure 1.1 Industrial waste from textile factories in Africa (Ravi, 2021)

Coagulation and flocculation are two conventional techniques for waste-water treatment. There is no universal flocculent, and inorganic flocculants can create enormous amounts of sludge (Kimura et al., 2013). The hazardous byproducts restrict the effectiveness of precipitation procedures (Fu and Wang, 2011). Treatments based on ion exchange are highly beneficial for selective metal recovery at elevated concentrations ($>$100 mg per litre) (Kurniawan et al., 2006). Adsorption techniques have historically been the most affordable way to remove pollutants from waste-water; however, to obtain high efficiency, pre-treatment of the sorbent is typically necessary (Owlad et al., 2008). The previously mentioned methods are used to reduce the number of contaminants in waste-water to the minimal levels permitted by regulation. However, these processes do not produce clean water that is suitable for drinking (Zinicovscaia and Cepoi, 2016). A different approach is to use electrochemical techniques, which operate on the idea that metal ions deposit on a positive electrode surface and then recover in their elemental form (Brillas and Sirés, 2012; Fu and Wang, 2011). Despite having a wide range of applications in industries, many physico-chemical techniques possess drawbacks. Some

of these methods cause secondary water contamination, while others are ineffective or non-profitable at greater concentrations (Zinicovscaia and Cepoi, 2016). Consequently, designing low-cost but effective, all-encompassing yet environmentally friendly, picky, and scalable waste-water treatment technologies is extremely difficult.

1.2. Nanomembranes for water treatment

The potential for using membranes and nanotechnology for water purification is enormous. The features of nanomembranes, such as re-usability, fouling, and hydrophilicity, indicate it becoming a viable alternative to currently available conventional techniques for water purification. Affordable capital cost, low energy consumption, and high efficiency for effluents of lower concentrations are also good advantages that point to why nanomembrane technology has benefits compared to conventional water treatment processes. Nanomaterials also can be physically altered and have a high porosity for application in water purification. Research in this field hence may aid in the conservation of ocean ecosystems as well as the reduction of water pollution hazards, agricultural waste removal from bodies of water and industrial waste separation, which affect the ecosystems of all water creatures.

1.3. Silver nanoparticles and silver phosphate

Silver has antibacterial properties as they obstruct the growth 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 from increasing their effectiveness. Silver nanoparticles have been used in domestic water filters, and their possible expansion in various applications is being studied (Organization, 2018).

Silver phosphate is a light-sensitive substance employed in emulsion form in photography. It serves as a bactericide, astringent, etc., in medicine and as a catalyst in various processes. Silver phosphate (Ag_3PO_4) has been thought to be a potential high-efficiency semiconductor compoung in research sectors. It has been claimed that Ag_3PO_4 has

more vigorous photo-catalytic activity in visible light than many other photo-catalysts described in recent literature, which has sparked a lot of interest. However, because of the enormous surface-to-volume ratio, nano-structural Ag_3PO_4 forms lumps in powder form, resulting in a loss in effective surface area and, as a result, photo-catalytic efficacy.

1.4. Polyacrylonitrile (PAN)

PAN is a synthetic resin formed from the polymerization of acrylonitrile, a derivative of 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 as a precursor for manufacturing high-quality carbon fibres (Qin, 2016).

PAN resists most organic solvents and is dissolved in special solvents to create the fibres. These fibres are soft and flexible and can be used as a substitute for wool as the properties of these fibres closely resemble each other. The fabricated synthetic fibres can be produced and sold at a fraction of the cost of natural fibre and offer resistance to sunlight, mildew, and moths. These fibres are used in apparel and can also be precursors for graphene and carbon fibres. Commercial production of PAN started in 1940 by the DuPont Company (Britannica, 2022).

1.5. Gram Positive and Gram negative bacteria

The bacteria are differentiated based on 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 the absence of a 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 the presence of an outer lipid membrane. 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. Many types of E. coli may cause respiratory tract infections, diarrhoea, pneumonia, urinary tract infections, et cetera (Steward, 2019).

1.6. Problem Statement

To utilize a convenient process to produce a cost-effective surface oximated Ag_3PO_4/PAN composite membrane for the purpose of waste-water treatment which could very well degrade dyes and possess anti-bacterial properties. The research and this thesis are aimed to support finding and investigate methods/materials to improve water treatment methods to improve human health and also help to reduce the harm that could befall aquatic creatures that live in the ocean as well as freshwater bodies. The thesis will work towards understanding and testing the material comprehensively to find out the surface morphology and characterization of the material by testing the composite by Scanning electron microscope(SEM), Fourier transform infrared (FTIR), Ultraviolet-visible(UV-vis) spectroscopy and X-ray Powder Diffraction(XRD). Testing will also be done to check the ability of the nanomembrane to separate organic contaminants and check the composite's bacteriostatic capability and photocatalytic degradation capability under visible light, long wavelength and short wavelength.

1.7. Objective

1.7.1. General objective

- The general objective of this research work is the surface functionalization of Polyacrylonitrile (PAN) to make a stable nanofibre for the purpose of water treatment

1.7.2. Specific objectives

- To fabricate polyacrylonitrile(PAN) nanofibres by electrospinning

- To fabricate Ag_3PO_4/PAN nanofibrous membrane by treatment of hydrazine followed by Ag^+ adsorption and chemical treatment
- To carry the morphological analysis of pristine and composite PAN membrane
- Testing of the nano membrane's efficiency in photodegradation and bactericidal activity

1.8. Report outline

The report consists of the following chapters: Chapter 1 - The introduction gives details about the background of why the research is being carried out, the problem statement, the objectives that the research is trying to fulfil, and the study's limitations.

Chapter 2 - Literature Review details the relevant literature 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 tests carried out and observations from those tests with the necessary data and figures.

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

CHAPTER TWO

LITERATURE REVIEW

2.1. Silver based photocatalysts and Silver Phosphate

Silver-based photo-catalysts with significant charge separation capacity under visible light have increased interest in recent years (Wang et al., 2014). Because of its visible light sensitivity to photo-degradation of organic contaminants (Yi et al., 2010) and bacterio-static capability (Liu et al., 2012), silver phosphate (Ag_3PO_4) has been thought to be a semiconductor compound with a potential of significant efficiency in research sectors. It has been claimed that Ag_3PO_4 has more vigorous photo-catalytic activity in visible light than many other photo-catalysts described in recent literature, which has sparked a lot of interest. However, because of the substantial surface-to-volume ratio, nano-structural Ag_3PO_4 forms lumps in powder form, resulting in a loss in effective surface area and, as a result, photo-catalytic efficacy.

As a result, most efforts have concentrated on the production of inorganic/Ag_3PO_4 hetero-structures by random incorporation of Ag_3PO_4 with different semiconductor materials, such as with cerenium dioxide (Ag_3PO_4/CeO_2) (Yang et al., 2014), titanium dioxide (Ag_3PO_4/TiO_2) (Yao et al., 2012), zinc oxide (Ag_3PO_4-ZnO) (Dong et al., 2014), bismuth Phosphate ($BiPO_4/Ag_3PO_4$) (Li et al., 2013), ferric oxide (Fe_3O_4/Ag_3PO_4) (Li and Mao, 2012), silver halides (AgX/Ag_3PO_4) (Bi et al., 2011), and so on. However, the formation of organic/Ag_3PO_4 composites, combined with polymer nanofibres in a well-defined way, has received little attention. In this context, combining nano-structural Ag_3PO_4 with polymer nanofibres might be a pivotal approach to maintain or enhance their photo-chemical reactivity and open up new applications.

2.2. Electrospinning and Fabrication of Ag_3PO_4/PAN nanofibres

According to many research papers, using polymeric nanofibres as templates or co-catalysts might deliver remarkable qualities to nanoparticles in comparison to their bulk counterparts (Dong et al., 2007; Gole and Murphy, 2005). Polymeric nanofibres are ar-

ranged in a matrix form which prevents inorganic nanoparticles from forming agglomerates and regulates particle size in such composites, making separating the utilized composite nanofibres easier. Polymeric nanofibres are in matrix form, shielding the inorganic nanoparticles from forming agglomerates, managing the distribution and size of the particles, and making the used composite nanofibres separation process easier (Panthi et al., 2015a; Lu et al., 2005). As a result, selecting an appropriate polymer is critical for manufacturing composite nanofibres. To date, various types of polymer composite nanofibres have been formed by integrating nano-structural semiconductors in/on various polymer nanofibres via electrospinning, followed by other strategies such as solvo-thermal (Panthi et al., 2013a), direct dispersion (Panthi et al., 2014), solid-gas reaction (Wang et al., 2013), sol-gel (Panthi et al., 2013b), and so on. However, only a few reports have been published on synthesising composite nanofibres of silver phosphates by surface modification of electrospun nanofibres (Panthi et al., 2017).

By varying the process/material conditions, electrospinning is an easy, adaptable, and cost-effective approach for producing a sheet of nanofibres (diameter: 50-1000 nm or higher) with diverse functions. Thus, these nanofibres have a uniform diameter, higher specific surface area, extraordinarily long length, and a higher proportion (length to diameter) (Wang et al., 2013). Using these benefits, several electrospun nanofibres with varying compositions have been created using the electrospinning technology; polymeric nanofibres (Choi et al., 2008), metallic nanofibres (Barakat et al., 2009), ceramic nanofibres (Panthi et al., 2013c), and composite nanofibre (Panthi et al., 2014, 2013b) with potential uses in a range of fields. Furthermore, the morphological structure of electrospun nanofibres is affected by electrospinning parameters such as polymer molecular weight, flow rate, the concentration of polymer in solution, distance from tip to the collector, applied electric voltage, and so on (Yu et al., 2014). We know that the PAN nanofibre diameter can be increased with the increase of polymer concentration, whereas fibre alignment can be increased by increasing the electric field above 10kV. It is also known that the increase in collector rotation speed helps to increase the fibre's alignment and durability.

The following properties of PAN mentioned below have further supported why we se-

lected the material for the use of the material as a nanomembrane for the purpose of water treatment

- Adding nanoparticles in PAN alters the arrangement of the nanofibres, changing the centralization of polymer, which can, in turn, influence the mechanical, synthetic, and electrical properties (Villarreal-Gómez et al., 2021)
- Expanding the polymer concentration builds the elasticity of the nanofibres i.e. increased tensile strength, and adding nanoparticles can differently affect it
- PAN polymer, when heated above 180°C discharges energy and transforms into a rigid unbending structure which is called cyclization
- PAN fibre can keep up with its structure above 1000°C assuming sluggish heating is applied, and the intensity of heat energy delivered is taken out to create carbon fibres
- PAN polymer possesses environmental stability, high processability, and low density, allowing it to be readily removed from the solution after usage (Yu et al., 2014).

2.3. Research gap

The research in this document presents a successful attempt to fabricate Ag_3PO_4/PAN composite nanofibres using a simple electrospinning process, followed by surface modification using aqueous hydrazine solution on PAN nanofibres. $-C \equiv N$ groups of PAN were changed to $C(NH_2)$=NOH groups during this treatment, which was exploited for secure attachment of Ag^+ ions and successive development of Ag_3PO_4 nanoparticles. PAN polymer was chosen for this investigation owing to the presence of $-C \equiv N$ groups, which may be transformed into —$C(CN_2$=NOH) groups, i.e. amidoxime groups from the reaction with hydrazine for the suitable incorporation of nanoparticles to nanofibre surface. Furthermore, PAN polymer possesses numerous properties like structural stability, low density, and ease of manufacture, allowing it to be readily removed from the solution after usage. Silver doping in PAN nanofibres approach of water treatment has been approached in this thesis as the doping process can further advance the antimicrobial properties and increase the fibre diameter. $AgNO_3$ has been uti-

lized as it is commonly used for forming Ag nanoparticles which can be easily reduced by refluxing, chemical reduction, heating and UV treatment. The research looks into how different process parameters can turn polyacrylonitrile's charge to be electronegative by using hydrazine and how it affects the immobilization of silver phosphate on the PAN nanofibre. In this research, after successfully creating an electronegative PAN nanomembrane by use of hydrazine, different concentrations of silver nitrate and disodium hydrogen phosphate treatment was done for successful immobilization of silver phosphate on the PAN surface. It also studied the characterization of the membrane and how well the silver phosphate embedded on the PAN nanofibre surface helps to improve the photocatalytic and anti-bacterial properties of different concentrations of composite fibres. The photocatalytic activity of composite nanofibres was examined using visible light photo-degradation of methylene blue (MB). MB is a cationic dye composed of the heterocyclic aromatic chemical molecule di-methyl amino-phenothiazinium chloride. It is commonly found in waste-water containing dyes which is released from numerous industries related to textile processing, dyeing, feather processing, and so on. Due to its excellent stability and anti-biodegradable characteristics, it is difficult to disintegrate using traditional methods. Similarly, the eradication of Escherichia coli and Bacillus subtilis germs was investigated. There has been very little research on creating an electronegative fibre membrane using solutions such as hydroxylamine for the successful immobilization of silver phosphate, but there is no research regarding the use of hydrazine hydrate, which has similar characteristics to hydroxylamine. We tried embedding the PAN membrane with silver phosphate, known for its good photocatalytic and antibacterial properties as silver phosphate as nanoparticles agglomerate and have lower efficiency. The research also aims to evaluate the appropriate concentration of compounds to form silver phosphate in the nanomembrane that would yield the best morphological characteristics for real-life use cases for water treatment.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1. Research Steps

Figure 3.1 shows the step-wise detailed procedure to fabricate the composite, whereas Figure 3.2 shows step-wise research methodologies used in the study

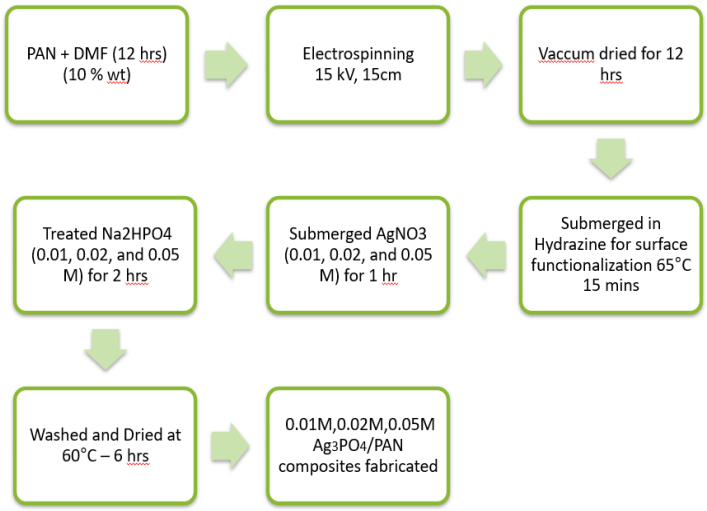

Figure 3.1 Step wise preparation of Ag_3PO_4/PAN composites

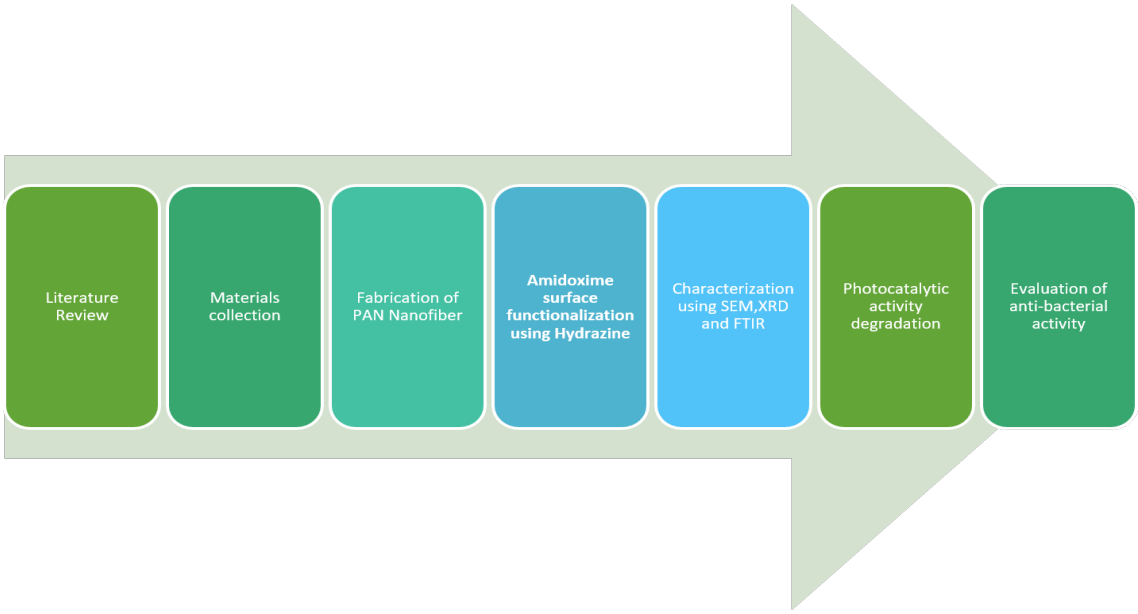

Figure 3.2 Preparation of Ag_3PO_4/PAN composites

3.1.1. Literature Review

A great deal of research was done on previous works that had been done. A literature review was carried out using the world wide web, books, journals, and previously published research papers. The literature review in question dealt with water filtration and oil-water separation using nanomembranes. Additionally, it implied research into the existing literature on photo-catalysts and antibacterial nanofibrous materials as well as an examination of the production of Polyacrylonitrile (PAN) embellished with an electrospun nanofibre made of an Ag nano species. A review of previous studies on hydrophobic compact membranes and photo-catalytic amphiphilic membranes, as well as previous studies on the mechanical and morphological structure and properties of nanomembranes, were carefully investigated as an additional aid to this research.

3.1.2. Materials

In the research conducted, the following materials were used: Polyacrylonitrile (PAN, d:1.184 g/ml at 25°C, MW: 150,000, Sigma Aldrich Chemistry), 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), disodium hydrogen ortho-phosphate (Na_2HPO_4, MW: 141.96 g/mol, Central Drug House, New Delhi) and Hydrazine Hydrate (80% Extra pure H_6N_2O, LOBA Chemie). Required solutions were prepared by utilization of double distilled water.

3.1.3. Electrospun PAN nanofibre fabrication and amidoxime surface functionalization using hydrazine

PAN powder was dissolved in the DMF solution using a magnetic stirrer by constant stirring for 12 hours, maintaining room temperature conditions to create a PAN solution (10 weight %), which was filled into a 10 ml plastic syringe with a metallic needle attachment and then it was connected to a high voltage power source that could generate DC voltages between 0 and 30 kV. The applied voltage for the electrospinning process was 15 kV. The growing nanofibres were gathered on aluminium foil-wrapped spinning drum collectors that were situated 15 cm from the needle tip. The entire electrospinning

procedure was carried out at an ambient temperature and atmospheric pressure. The electrospun PAN nanofibres were vacuum-dried for 12 hours to get rid of the remaining solvent. Electrospun PAN nanofibres were submerged in a 50 ml (1M) aqueous solution of aqueous hydrazine solution at 65°C for 15 minutes for surface functionalization with amidoxime groups as per earlier research that showed conversion % and softness of nanofibre mat were adequate for experimental work (Panthi et al., 2017). After that, the surface functionalized PAN nanofibres which contained amidoxime groups, were washed to stop the further reaction with distilled water and then dried at 45°C for 6 hours. Electrospinning was conducted at the laboratory setup available at the Nano Laboratory of IOE Pulchowk Campus.

Figure 3.3 Electrospinning process

The following formula was used to compute the conversion of PAN's nitrile groups into amidoxime groups (Lin et al., 1993)

$$C_n = \frac{W_1 - W_0}{W_O} X \frac{M_0}{M_1} x100$$

where C_n represents the ratio of Polyacrylonitrile to amidoxime groups. The initial weight of the Polyacrylonitrile nanofibre membrane is W_0, the modified weight is W_1, and the molecular weights of the hydrazine and acrylonitrile monomer, respectively, are M_0 and M_1.

3.1.4. Ag_3PO_4 /PAN composite nanofibres fabrication

To facilitate the coordination of positive silver ions with amidoxime groups, modified PAN nanofibres which were surface functionalized, were submerged in $AgNO_3$ solution of varying concentrations (0.01, 0.02, and 0.05 M) at 27°C for an hour. The positive silver ions coordinated nanofibres were then treated for 2 hours at 25°C with Na_2HPO_4 solutions analogous to 0.01, 0.02, and 0.05 M concentrations, respectively. Positive silver ions coupled with amidoxime groups mix with Phosphate(PO_4^{3-}) ions on the surface of PAN nanofibres during this treatment to create Ag_3PO_4 nanoparticles. The treated nanofibres were then thoroughly washed with distilled water before drying at 65°C for 6 hours. Figure 3.4 shows a schematic depiction of the manufacturing of all Ag_3PO_4/PAN composite nanofibres.

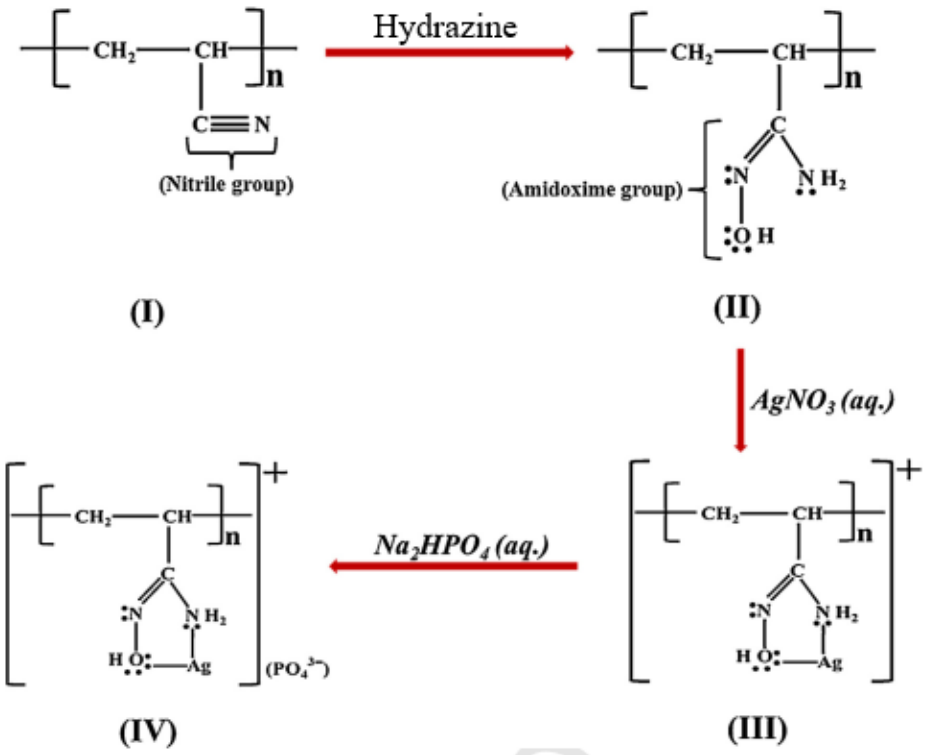

Figure 3.4 Schematic illustration for surface modification of electrospun PAN nanofibres with amidoxime groups (I–II) and preparation of Ag_3PO_4/PAN composite nanofibres (II–III) (Panthi et al., 2017).

For clarity, different samples in this report were referred to as PAN for pure Electrospun PAN nanofibres, AOPAN for surface functionalized Electrospun PAN nanofibres with

amidoxime groups, and the samples were referenced as composite-1, composite-2, and composite-3 were obtained by treating AOPAN varying concentration of $AgNO_3$ and Na_2HPO_4 in aqueous solutions, respectively.

3.1.5. Characterization

The structural surface characterization of PAN, AOPAN, and composites were examined using a scanning electron microscope (SEM). Composites have been named composite 1, composite 2, and composite 3 or 0.01 M, 0.02 M and 0.05 M to indicate the composite made from the treatment of 0.01 M,0.02 M and 0.05 M silver nitrate and disodium hydrogen ortho-phosphate respectively. The surface morphology of the PAN, AOPAN and the developed composites were also evaluated using X-ray diffraction, which was used to determine the phase of the materials, and it's the crystalline structure of the nanoparticles using Cu Ka (l = 1.540 Å) radiation at Bragg angles which ranged from 10°- 80°. To analyze the surface functionalization and bonding topologies of polymer with nanoparticles, Fourier transform infrared (FTIR) spectroscopy was used. A UV-vis spectrophotometer was used to measure the UV-vis diffusive reflectance spectra of the composites.

3.1.6. Photo-catalytic activity investigation

Investigating the photocatalytic activity of various composite nanofibres included the degradation of MB dye solution (25 ml, 10 ppm concentration) degrade in a straightforward photochemical reactor. Each composite nanofibres was of the same size, 4 cm x 4 cm. The solution was agitated magnetically for 10 minutes in the dark before being exposed to radiation to create an equilibrium between dye and photocatalyst. In this experiment, the composites immersed in MB dye solution were directed towards a natural atmospheric environment on a sunny day in September between 10 AM to 1 PM. Aliquots were obtained at 10-minute intervals, and a UV-vis spectrophotometer was used to quantify the dye solution's concentration spectrophotometrically by recording the absorbance at 663nm.

3.1.7. Evaluation of antibacterial activity

Growth inhibition and disc diffusion susceptibility experiment were used to evaluate the antibacterial efficacy of composite nanofibres bought from the American Type Culture Collection (ATCC) against Gram-negative (E. coli ATCC8739) and Gram-positive (B. subtilis ATCC6051) as-fabricated were examined in this investigation. Using the disk diffusion assay on LB agar plates and 37°C incubation temperature, the antibacterial activity of composite nanofibres was evaluated against E. coli and B. subtilis. An LB agar plate with $1.5x10^6$ colony forming units (CFU/ml) of bacteria was utilized for the lawn culture. In 5 mm diameter disks, pure PAN and triplicated samples of Ag_3PO_4/PAN composite nanofibres were cut and placed. Then, using a sterile cotton swab, each bacterium was lawn grown on the LB agar plate. To achieve a bacterial accumulation of about $1.5x10^6$ CFU/ml for the growth inhibition investigations, 100 ml of a Tryptic Soy Broth solution was used to grow the bacteria. The mixture was incubated at 37°C for 12 hours while being shaken constantly. The bacteria were re-suspended and then diluted up to the concentration of 10^{-7} times after being washed and centrifuged. The diluted cell solutions were cultured for 12 hours, maintaining the temperature at 37°C on a Tryptic Soy Broth solution in the dark before the composite nanofibres exposed the bacteria in daylight. The cells, Pure PAN and Ag_3PO_4/PAN composite nanofibres (5 x 3 cm in area), were inserted into the solution for the antibacterial testing and left there for 5 hours during the day.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Membrane morphology of PAN, AOPAN, and Ag_3PO_4/PAN composites

SEM was used to describe the surface morphology and elemental makeup of PAN, AOPAN, and composite nanofibres. Due to bending instability and spinning jet, all formulations have uninterrupted nanofibres with random orientation, as illustrated in the images below (Figure 4.1,Figure 4.2,Figure 4.3,Figure 4.4,and Figure 4.5).

All samples under magnification presented uninterrupted bead-free nanofibre with random orientation, which could have emerged due to the bending instability accompanied by the spinning jet. Electrospun polyacrylonitride membrane looks fluffy and consists of nanofibres with a diameter of 218nm (Figure 4.1). After the treatment of the fibre with hydrazine for 15 minutes at 65°C, the morphology of the resulting nanofibres (AOPAN) was not damaged (Figure 4.2); however, the average diameter was found to be increased to 299nm. The increase in the average diameter of AOPAN is attributed to the hydrophilic nature of hydrazine hydrate. This could be due to the PAN nanofibres getting inflated by water due to the conversion of the nitrile groups into the amidoxime groups.

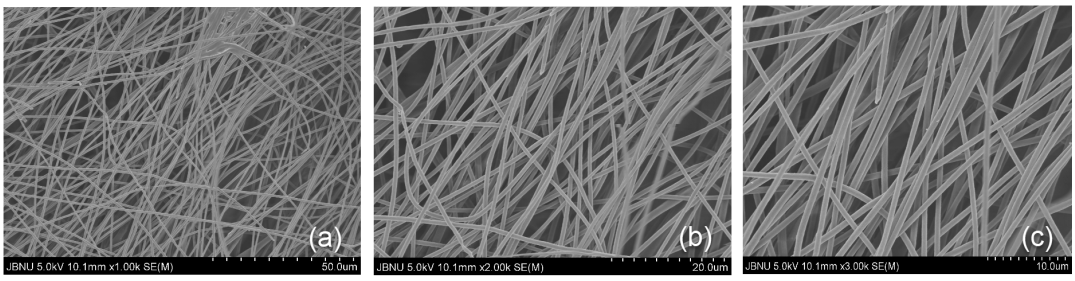

Figure 4.1 SEM images of Pure PAN mat under (a) 1000X (b) 2000X and (c) 5000X magnification

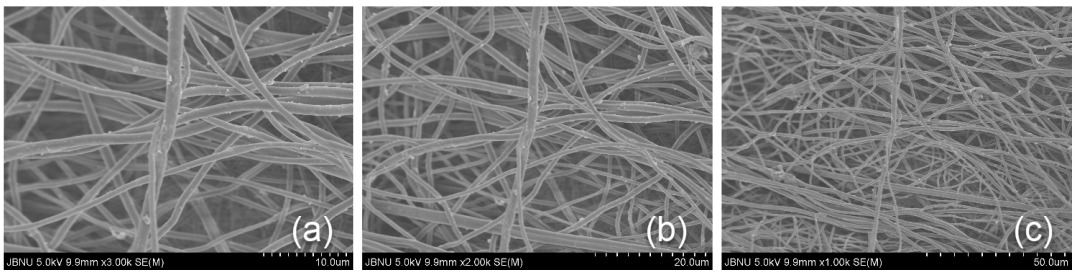

Figure 4.2 SEM images of AOPAN mat under (a) 1000X (b) 2000X and (c) 5000X magnification

After growing silver phosphate nanoparticles on the surface of AOPAN nanofibres, the composites' surface is no longer smooth. As shown in figure(Figure 4.3), composite-1 displayed heterostructures, where silver phosphate secondary nanoparticles have an average size of 66.56 nm and were found to be distributed uniformly across the surface of AOPAN nanofibres without substantial aggregation. But with an increase in reactant concentrations, the average size of the particles was found to be increased to 114nm in composite-2(Figure 4.4) whereas the average size of the particles increased dramatically in composite-3 to 440nm(Figure 4.5). Hence, measurement of the nanoparticles in the high magnification images of the composite nanofibres showed growth in the size of the particles, which in turn showed the concentration of the reactants increasing, which will decrease the exposure levels of nanoparticles.

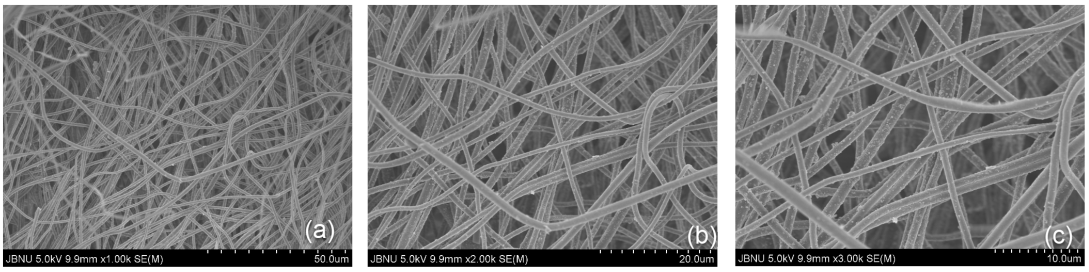

Figure 4.3 SEM images of 0.01 M - composite-1 mat under (a) 1000X (b) 2000X and (c) 5000X magnification

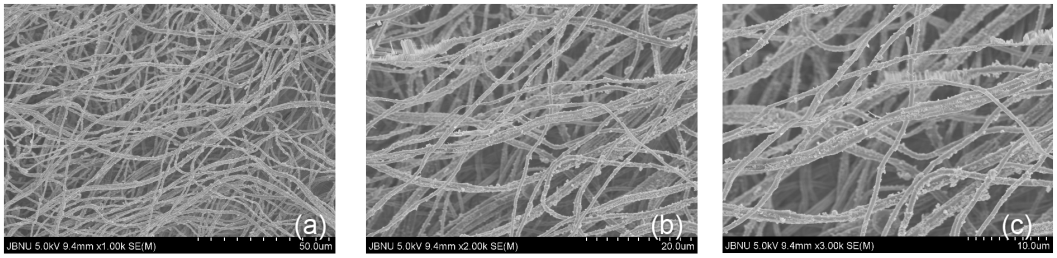

Figure 4.4 SEM images of 0.02 M - composite-2 mat under (a) 1000X (b) 2000X and (c) 5000X magnification

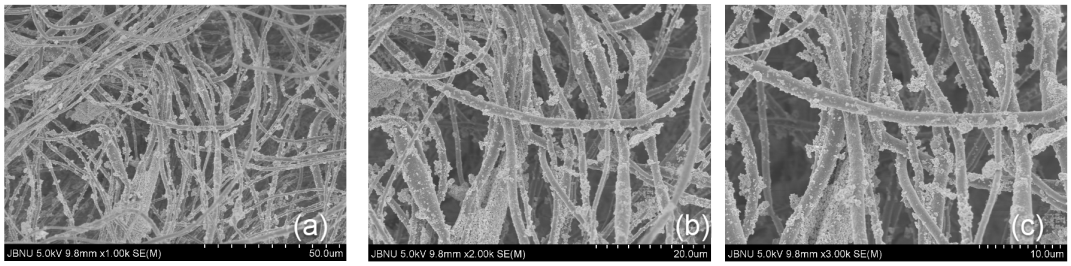

Figure 4.5 SEM images of 0.05 M - composite-3 mat under (a) 1000X (b) 2000X and (c) 5000X magnification

4.2. Analysis of functional groups present in the Ag_3PO_4/PAN composites

The FTIR analysis of the samples was done at the Instrument Section in the Department of Plant Resources, Thapathali, Kathmandu. FTIR was done to confirm if amidoxime groups were present in the three composites PAN fibre. Figure 4.6 shows the FTIR spectra of various samples. The FTIR spectrum of Ag_3PO_4 embedded composites reveals absorption bands centred at approximately 550 and 1075 cm^{-1} that ought to be attributed to the oscillation of molecules of PO_4^{3-} (Panthi et al., 2017; Miller et al., 2001). The stretching oscillation of doubly bonded oxygen (P=O) (Moustafa and El-Egili, 1998; Liang et al., 2012) in the composites could explain another strong band at 1400 cm^{-1}. Other absorption bands centred at about 1625 cm^{-1} and 3100 cm^{-1} were attributed to the stretching oscillation of H-O-H and the bending vibration of O-H of physically absorbed di-hydrogen monoxide molecules (Huang and Zhu, 2007), respectively. The FTIR spectra of pure PAN in Figure 4.6 revealed a distinctive absorption band at about 2245 cm^{-1} that was allocated to nitrile groups ($-C \equiv N$) (Panthi et al.,

2015b), the intensity of which was significantly reduced after treatment with hydrazine in AOPAN. This reduction in intensity was caused primarily by the partial conversion of PAN's nitrile group to amidoxime groups (-C(NH2)=NOH) during the surface modification with hydrazine.

Furthermore, AOPAN nanofibres exhibited correlative amidoxime bands at approximately 1075, 1643, and 31-3650 cm^{-1}, which were ascribed to the stretching vibrations of N-O, ($-C \equiv N$), and N-H/O-H, respectively. As a result of these findings, it is possible to conclude that the nitrile groups of PAN were moderately converted to amidoxime groups by administrating them with hydrazine. These bands were also observed in all composite nanofibres (Figure 4.6). Notably, absorption bands corresponding to PO_4^{3-} and P=O were also noticed in the FTIR spectra of all composite nanofibres (Figure 4.6), indicating that Ag_3PO_4 nanoparticles were successfully grown on AOPAN nanofibres via the formation of coordinate bonds between positive silver ions and amidoxime groups, as shown in Figure 4.6.

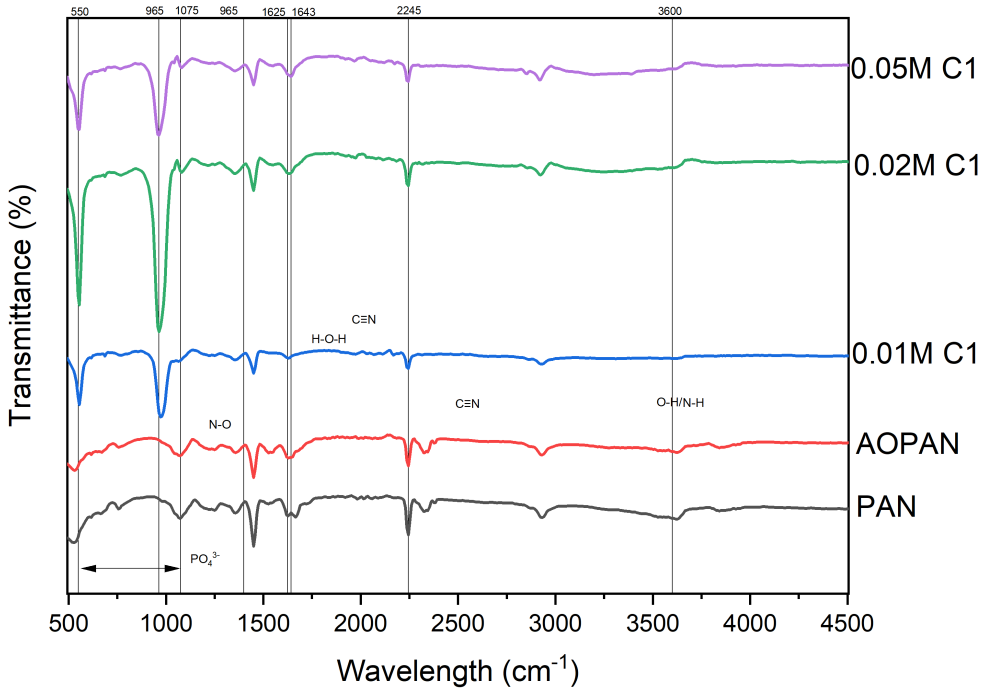

Figure 4.6 FTIR Spectra of PAN,AOPAN and Ag_3PO4/PAN composite of different concentrations i.e. 0.01 M,0.02 M and 0.05 M

4.3. Analysis of Diffraction peaks of the Ag_3PO_4/PAN composites

The XRD analysis of the samples was done at the Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur. XRD analysis was carried out to examine the crystalline structures of the three different prepared composite nanofibres, PAN fibre and AOPAN fibre (Figure 4.7). The sharp diffraction peaks of all three composites at 38.17°, 44.3°, 64.4°and 77.5°corresponds to the plane of silver crystals (1 1 1), (2 0 0), (2 2 0) respectively confirms the presence of silver nanoparticles in the composite ((Jemal et al., 2017)). The strong peak centred at about 17°and an ample non-crystalline peak at 20–24°in the composite nanofibres were assigned to the (1 0 0) and (1 1 0) crystallographic planes of PAN polymer, respectively (Li et al., 2012). Notably, the intensity of Ag_3PO_4 diffraction peaks was diminished in composite nanofibres compared to the pure Ag_3PO_4 powder (comparison with respect to (Panthi et al., 2017)), which should be ascribed to the low content of Ag_3PO_4. Furthermore, no peaks for any other impurities were observed. These findings revealed that PAN and Ag3PO4 nanoparticles with high crystallinity and purity made up all of the composite nanofibres.

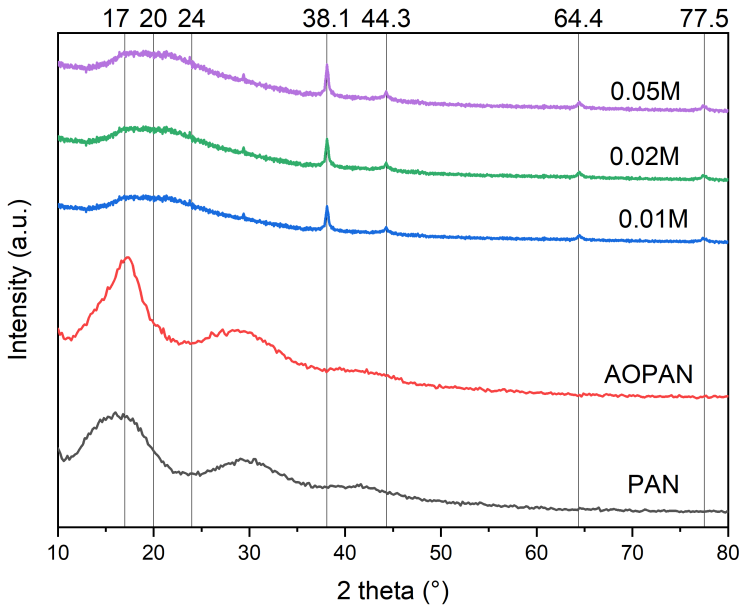

Figure 4.7 XRD Spectra of PAN,AOPAN and Ag_3PO4/PAN composite of different concentrations i.e. 0.01 M,0.02 M and 0.05 M

4.4. Analysis of photocatalytic behavior of the Ag_3PO_4/PAN composites

The catalytic activities of a photocatalyst can be investigated once the optical absorption behaviour is analyzed, as it acts as a critical factor in determining whether a catalyst can work under visible light or not. Therefore, UV-vis diffusive reflectance spectra of all three composites were observed keeping PAN fibre as a reference. The UV-vis diffusive reflectance spectra results are shown in figure Figure 4.8, which show sharp fundamental absorption edges at around 520nm and an uninterrupted strong absorption in the range of 520-700nm for all Ag_3PO4/PAN composite nanofibres which is in agreement with the results of a previous report (Panthi et al., 2017). These results show that it can be degraded in sunlight.

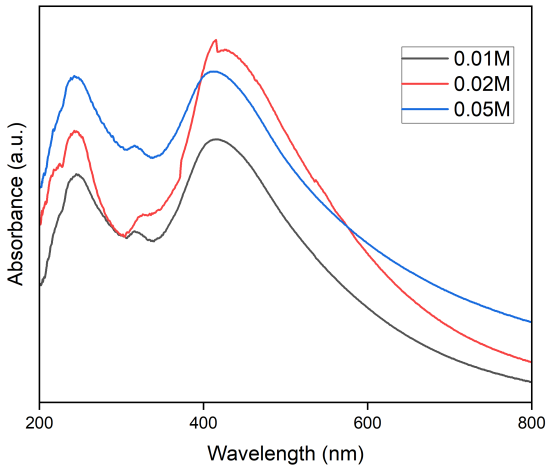

Figure 4.8 UV-vis diffusive reflectance spectra of Ag_3PO4/PAN composite of different concentrations i.e. 0.01 M,0.02 M and 0.05 M

The photocatalytic activity of the as-prepared samples was evaluated by photodegradation of MB dye solution under visible light irradiation in sunlight on a sunny day in September. The degradation is represented as the variation of (C_t/C_0%) with irradiation time, where C_0 and C_t are the concentration of dye solution at an initial time and time t, respectively. For comparison, the performance of pure PAN was also presented. As shown in figure (Figure 4.9, complete degradation of MB dye solution was obtained in 60 min in the case of composite 2 while composite 1 and 3 could degrade about 86%

and 84 % respectively within one hour.

The concentration of MB dye solution can only be slightly decreased by pure PAN nanofibres because of its slight absorption property (Panthi et al., 2017).

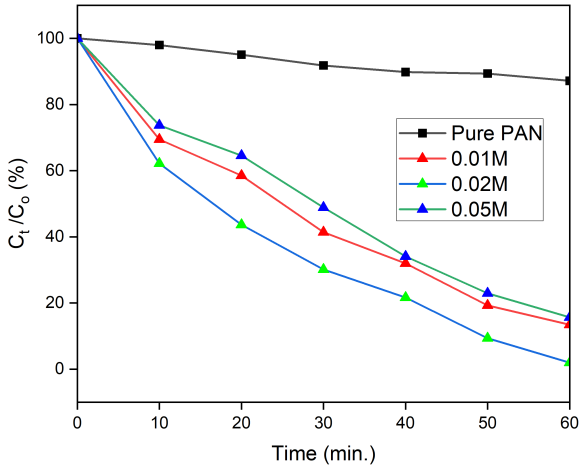

Figure 4.9 XRD Spectra of PAN,AOPAN and Ag_3PO4/PAN composite of different concentrations i.e. 0.01 M,0.02 M and 0.05 M

4.5. Analysis of Antibacterial Properties of the Ag_3PO_4/PAN composites

The antibacterial activity of composites against E. coli and B. subtilis was evaluated by measuring the width of inhibition zones. In the case of E. coli, the diameter of inhibition zones was found to be approximately 6 mm, 7mm, and 9 mm for composite-1, composite-2, and composite-3 nanofibres, respectively(Figure 4.10 a). Similarly, in the case of B. subtilis, the diameter of inhibition zones was about 6 mm, 6 mm, and 8 mm for composite 1, composite-2, and composite-3 nanofibres, respectively (Figure 4.10 b). As shown in the figure, composite-3 nanofibres had the lowest survival of both types of bacteria, while pure PAN nanofibres did not show any antibacterial activity. Therefore composite-3 nanofibres can offer great promise in their application in bactericidal activity. The results showed that composite-3 nanofibres exhibited better performances in both tests, offering great promise in bactericidal activity. Moreover, the higher bactericidal effect of composite nanofibres against E. coli in comparison to B. subtilis might be related to the cellular wall content differences between Gram-negative

and Gram-positive bacteria. Herein, we contend that the increased antimicrobial activity of composite-3 nanofibres than that of composite-1 and composite-2 nanofibres should be relative due to the high concentration of Ag_3PO_4 nanoparticles present in composite-3, while the lesser efficiency of composite-1 and composite-2 nanofibres should be attributed to the low content of Ag_3PO_4 present in the fiber with smaller particle size. Using a pure PAN nanofibre mat as a control revealed no zone of inhibition, showing that pure PAN lacked antibacterial action against Gram-negative and Gram-positive bacteria. Comparison with a similar composite of PAN with Ag_3PO_4 showed better antibacterial properties (Panthi et al., 2017) made through 0.02 M concentration of $AgNO_3$ and Na_2HPO_4 due to the higher surface area of Ag_3PO_4 present in the composite. Whereas our sample showed a 0.05 M concentration composite having better antibacterial properties. This could possibly mean that we could try higher concentrations formation of Ag_3PO_4 in the PAN fibre through the same process to improve the antibacterial activity of the material composite.

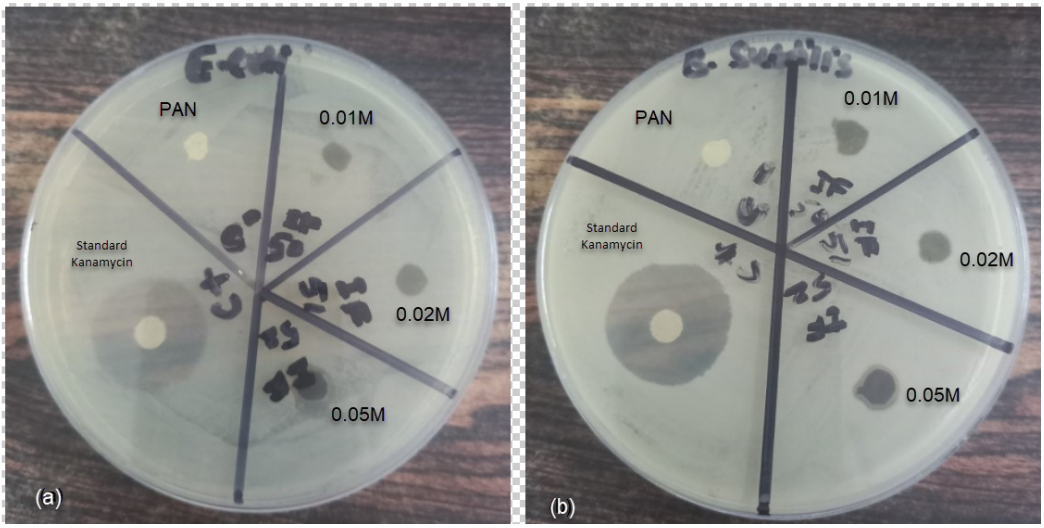

Figure 4.10 Zone of inhibition test on (a) E. coli and (b) B. subtilis

Ag_3PO_4/PAN composite nanofibres' potential photo-catalytic and antibacterial activity may be described in photo-generated reactive oxygen species (ROS). The minimal recombination of photo-generated holes and electrons is a critical factor in Ag_3PO_4's ability to attain excellent photo-catalytic efficiency. Being a semiconductor, Ag_3PO_4

may produce electron-hole pairs when exposed to visible light.

When Ag_3PO_4 is exposed to visible light, its valence band (VB) electrons are stimulated to move to the conduction band (CB), departing holes behind. As a result, excited electrons are absorbed by dissolved O_2 in solution to create O_2 radicals, which then react with H^+ ions to create H_2O_2 and produce OH radicals. On the other hand, photo-generated holes can also produce OH radicals when they interact with H_2O or OH ions. Ag_3PO_4's antibacterial action and the photo-degradation of MB are caused by the ROS (OH radicals) that will be subsequently produced.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

6.1. Conclusion

Using a straightforward and adaptable process, electrospun PAN nanofibres with embedded silver phosphate (Ag_3PO_4) nanoparticles were created. Electrospinning was then followed by chemically converting the nitrile groups of PAN into amidoxime groups by interacting with hydrazine for 15 minutes in an aqueous solution at 65°C. Through amidoxime functional groups, Ag^+ were coordinated on the surface of PAN nanofibres, and after reacting with ${PO_4}^{3-}$, Ag_3PO_4 nanoparticles were produced.

- Composite 2 showed greater photo-catalytic degradation capability, but the slow degradation process does not warranty real-life uses for this composite made through the process explained in the thesis.
- Composite 3 showed greater antibacterial properties with future research towards higher concentration attachment of Ag_3PO_4 nanoparticles on PAN could help produce better antibacterial materials for effective water treatment.
- The amalgamation of amidoxime functional groups with Ag_3PO_4 nanoparticles in the system was intended as a successful strategy for the proper attachment of nanoparticles to achieve enhanced performances.
- Therefore, Ag_3PO_4/PAN composite nanofibres could exhibit enhanced photo-catalytic and antibacterial efficacies.
- Overall, our experimental findings point to the potential of Ag_3PO_4/ PAN composite as a practical and affordable nanofibrous membrane, particularly useful in the field of water treatment.

6.2. Recommendations and Future works

We have the following recommendations for future work on the research subject

- PAN nanofibre charge can be changed to electronegative by utilizing other similar

compounds. In this thesis, hydrazine was used whereas Hydroxyleamine (Panthi et al., 2017) was used for proper attachment of Ag_3PO_4 on the fibre. Results between the two nanofibre composites were different and can show other properties.

- XPS analysis and TEM can be done for more detailed morphological analysis of the sample
- Increase in concentration showed increased antibacterial results, which could mean further research could be done for better results
- Contact angle analysis can be done to see the utilization of the nanomembrane for oil-water separation
- Mechanical testing and Thermal analysis(TGA and GSC tests) can be analyzed for further sustainability of the material in actual life use.

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