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Production of High Performance Membrane from Polyvinylidene Fluoride Nanofibers for Industrial Applications

A Thesis

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2023 A.D

1444 A.H

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿يَرْفَعُ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا
تَعْمَلُونَ خَبِيرٌ﴾

صدق الله العظيم

[سورة المجادلة: الآية 11]

Supervisor`s Certification

We certify that this thesis entitled (**Production of High Performance Membrane from Polyvinylidene Fluoride Nanofibers for Industrial Applications**) was prepared by (Wissam Mohammed Mustfa) under our supervision at Babylon University / College of Materials Engineering / Department of polymer and petrochemical industries , in Partial Fulfillment of the requirements for the Master Degree in Materials Engineering / Polymer.

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Date: / / 2023

Dedication

To "my dear wife"

You have been my source of inspiration, support, and guidance. You have taught me to be unique, determined, to believe in myself, and to always persevere. I am truly thankful and honored to have you as my eternal love.

Wissam



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Abstract

Iraq is considered one of the important oil countries in the world, and it is known that the oil industry is accompanied by products that have harmful environmental effects, and among these pollutants is produced water (PW). Produced water is considered one of the causes of pollution because it contains dangerous pollutants of organic and inorganic materials, so attention is required to treat this water before it is discharged to avoid environmental damage and seek to exploit part of the large quantities resulting from this water and try to invest it in purposes irrigation, and among the methods used in treating this type of water is the separation technique that is based on filtering. In ultrafiltration (UF) applications, it is very important to use Polyacrylonitrile (PAN) and poly (vinylidene fluoride) (PVDF) nanofiber membranes.

In this study, membrane nanofibers made of pure PAN, PVDF: PAN blends, and pure PVDF (M1, M2, M3, M4, M5 and M6) with different contents of PVDF: PAN in each blend as follows (0:100), (20:80), (40:60), (60:40), (80:20), (100:0) respectively, were produced by the electrospinning technique.

After finding the best mixing ratio (60:40) of the six manufactured membranes above in terms of permeability and recovery rate of flow and pollutants, work was focused on developing this ratio using nanomaterial particles and special chemical reactions in order to obtain the best working performance of the manufactured membrane, so three other membranes were produced (M7, M8, M9) with different contents of (PVDF: PAN: TiPP), (PVDF: AOPAN), (PVDF: AOPAN: TiPP) , respectively. The M9 (PVDF: AOPAN: TiPP) membrane showed the best performance through the results obtained during the application procedure using produced water filtration.

The prepared membranes were characterized by field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), contact angle measurements, X-ray diffraction (XRD), differential scanning calorimetry-thermogravimetric analysis (DSC-TGA). In terms of the physical properties, the viscosity of the membranes rises with rising PVDF content in the mixtures compared with the viscosity of the pure polymer solutions, this led to increases in nanofiber diameter, pore size, and porosity by 261.664%, 875.107%, and 114.41%, respectively, when the content of PVDF increased from 20% (M2) to 80% (M5); this was also accompanied by an increase in the surface wettability of the membrane depending on its contact angle. In addition, the thermal properties and crystallinity of PAN improved after increasing the PVDF content from 20% (M2) to 60% (M4). Moreover, the filtration efficiency of the membranes was measured to determine the percent reduction in pure water flux, reduction in mean depth (RMD) before and after using dry milk protein, the flux recovery ratio and porosity, giving values of 15.68%, 82.51%, 84.32%, and 67.79%, respectively, for the M4 membrane. On the other hand, the modify of PAN to AOPAN lead to decreased the contact angle and produced nanofiber surface more hydrophilicity specially at M9 (PVDF: AOPAN:TiPP) in spite of high nanofiber diameter according to high viscosity. The specifications of the developed composite membrane (M9) are characterized by a large pore size despite the significant increase in the diameter of the fiber, but at the same time the fibers have a high density, as well as its enjoyment of a low contact angle compared to the M4 membrane. While M9 has 91.79 % flux recovery ratio, therefore used M9 and M4 membranes were used for the purpose of treating product water (PW) associated with crude oil during extraction operations, and the results of the developed composite membrane (M9) were better results for removal the water pollutants compared with the results of M4.

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List Of Abbreviations

Abbreviation	Meaning
ACE	Acetone
AOPAN	Amidoxime-modified Polyacrylonitrile
ASTM	American Society for Testing Materials
AFM	Atomic Force Microscopy
C.O.D	Chemical oxygen demand
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetric
EC	Electrical conductivity
ENMs	Electrospun Nano-fibrous membranes
FRR	Flux recovery ratio
FT-NIR	Fourier Transform Near-Infrared Spectroscopy
FE-SEM	Field- Emission Scanning Electron Microscopy
NMs	Nanomaterials
Na ₂ CO ₃	Sodium carbonate
NH ₂ OH•HCl	Hydroxylamine Hydrochloride
KOH	Potassium Hydroxide
Pw	Permeability of pure water
P.W	Produced water
PAN	Poly acrylonitrile
RO	Reverse osmoses
Rt	Total fouling ratio
Sr	Solute rejection
TiPP	Titanium(IV) isopropoxide
TiO ₂	Titanium dioxide
TSS	Total suspended solid
Ultrafiltration	Ultrafiltration
UF	UF
UV	Ultraviolet-visible spectrophotometer
XRD	X-Ray Diffraction

List of Symbols

Abbreviation	Meaning	Unit
A	Surface area of membrane	m ²
C	Concentration	%
Ec	Electrical conductivity	μs/m
η	Viscosity	Pa·s
γ	Surface tension	N/m
J _{w1}	Pure water flux before used dry milk protein	L/m ² h
J _{w2}	Pure water flux after used dry milk protein	L/m ² h
ΔP	Operating pressure drop	Atm
P _w	Permeability of pure water	L/m ² .h. atm
Δt	Time of permeation	Hour
ε	Porosity	%
ρ _w	Water density	g/cm ³
I	Membrane thickness	M
MW	Molecular Weight	g/mole
r	Pore radius of membrane	M
V	volume of permeate	Liter

Chapter one
Introduction

1.1 Introduction

Many techniques and methods that aim to treat water and remove its pollutants are physical (including sedimentation, filtration, and centrifugation), biological, chemical and distillation methods [1-3]. Therefore, ultrafiltration technology (UF) is one of the most important applications to purify drinking water. Despite the many methods used to improve filtration efficiency, UF technology has attracted great interest among researchers because of its great importance in terms of economics and reliability because it utilizes new and highly effective polymeric membranes [4]. This nonwoven material has a porous structure. Porosity has a distinctive role and is considered to be one of the main parameters in the work of membranes; thus, focusing on porosity is necessary. It is possible to say that membrane porosity represents the ratio of the volume of the voids in the filter media to the total volume of the filter [5]. The relationship between porosity and fallow volume and their effect on the efficiency of the membrane used in the ultrafiltration process should also be noted, the porosity of the membrane determines the permeability, while the fallow size of the membrane determines the selectivity of particles and pollutants [6]. In all practical applications of membranes, everyone seeks to achieve the best output from the membrane work by making the permeability as high as possible with a high rejection rate at the same time, and this is considered an ideal condition that cannot be achieved in practice [7]. Among all the currently known materials, polymeric materials are most commonly used in the preparation of solutions for the production of membranes, due to their low cost, mechanical properties and the formation of nanofiber membranes, in addition to the appropriate flexibility that distinguishes these materials [8].

Poly (vinylidene fluoride) PVDF is considered an important polymer that has attracted attention, and there has been much research on this polymer because of its properties. PVDF is a thermoplastic, semicrystalline polymer with a degree of crystallinity that varies in the range of 35-70% [9]. As a result of its high thermal stability, good chemical resistance, giving it other applications, including in water treatment, gas separation, pollutant removal, and bioethanol recovery [10]. In addition, PVDF is used for microporous membranes due to its specific filtration properties [11]. However, there are some disadvantages that appear with this polymer, including its low permeability and fouling due to its hydrophobicity and therefore high operating costs, which limits its use [12,13]. Many researchers have shown that it is possible to address the problem of membrane fouling by increasing the hydrophilicity and pore walls of the membranes [14,15]. Therefore, to improve the antifouling property of ultrafiltration membranes, many methods have been used to modify membrane surfaces using hydrophilic additives, including blending, coating, absorption, and chemical grafting [14,16,17]. Blending has the best chance to be a unique method with a relatively low cost and easy operation in addition to being an environmentally friendly for manufacturing [18]. In addition, membranes with high efficiency in terms of their ability to flux pure water, high surface wettability, and better antifouling properties have been obtained [19]. PAN is one of the most prominent hydrophilic additives that has been combined with PVDF to manufacture blended nanofibers, as it was found that virgin PVDF membranes have a much higher roughness than virgin PAN membranes; thus, PVDF membranes are more prone to fouling due to their hydrophobicity and surface roughness [20], which is caused by their good adhesion to attract protein [21].

There are also some chemical treatments available for polymeric solutions, through which the performance of electrospun nanofibers can be improved in terms of rejecting pollutants and the ability to adsorb some heavy metal ions [22-25].

In order to test the quality of electrospun nanofibers and ensure their efficiency during work, their tolerance to working conditions, and the length of their life cycle, protein solutions can be used, such as milk, which contains protein as an essential part of its composition [26].

In general, membranes made from nanofibers have the ability to retain proteins and prevent them from crossing, membranes are also suitable for stable emulsions, especially water-soluble waste [27-28].

1.2 Aim of this Thesis

The primary aim of this thesis is to prepare and characterize a high-performance polymeric membrane used for filtration purposes, by following objectives as follows:

- 1- Preparing and characterizing the nanofiber membrane fabricated from a blend of (PVDF/PAN) solutions for the purpose of obtaining the best mixing ratio based on flux recovery ratio, rejected fouling and other physical properties
- 2- Adding TiPP to the best blend in addition to developing this blend through the reaction of hydroxylamine hydrochloride with PAN and in the presence of sodium carbonate to produce a blend of nanofibers from PVDF/AOPAN .
- 3- Performing a filtration process to test the efficiency of the fabrication membrane in terms of flux recovery ratio, rejected fouling and protein rejection .
- 4- The modified composite membrane is used in the application of removing pollutants and some metal ions from the water produced associated with oil extraction operations, in order to benefit from that water for irrigation purposes after treatment.

Chapter Two

Theoretical Part & Literature Review



2.1 Introduction

The term of Nanomaterials (NMs) is a common term and circulated not only in the academic, industrial and commercial aspects, but also during our daily lives, so it is necessary to understand this term and identify its most prominent characteristics and types.

To explain the term nanomaterials, the prefix for this word, which is “Nano”, means “dwarf”, derived from the Greek language [29] and these materials have been identified within the International Organization for Standardization (ISO) as materials that have an external dimension measured on the nanoscale [30]

Nanomaterials are pave the way for exploring new materials or improving the properties of existing materials, and thus provide materials with better qualities than traditional materials [31], they exist in different forms, including in one dimension, such as membranes and nano-coatings, and sometimes they are found in two-dimensional or three-dimensional forms, such as tubes and nanowires [32], As they are different in shape and size, NMs can also differ in composition. Some of them contain organic particles and others contain inorganic particles. They can also be found in the form of single particles, agglomerates, powders, or within a matrix, or with colloids and emulsions, or coated as in fluorides [33]. So that new materials are obtained with the required properties and according to the need by controlling the method of distribution, geometry, and manufacturing conditions [34]. Due to the distinctive properties of these materials (NMs), they can be invested in the field of water treatment and improving environmental conditions, where nanomaterials can move to the soil and perform their function for the characteristics of each type of these materials, these materials can act

as surfactants when added to liquids. In addition to addressing the problem of pollutants through adsorption of some harmful organic and inorganic substances suspended in water [35]. Nanomaterials can be used in separation and adsorption processes to get rid of pollutants, toxic substances, metals and dangerous elements [36]. Traditional water treatment methods such as (sedimentation, filtration, etc.) are sometimes insufficient to completely purify water and get rid of all pollutants and types of bacteria, so nanomaterials and their unique properties can be used to successfully complete this process [37].

2.2 Types of nanomaterials

For more details about nanomaterials and to understand them more broadly and accurately, it is necessary to know their types, as there are several classifications, including:

2.2.1. Based on their composition

They are classified into four categories as follows [38-44] :

2.2.1.1 Carbon-based nanomaterials

2.2.1.2 Organic-based nanomaterials

2.2.1.3 Inorganic-based nanomaterials

2.2.1.4 Composite-based nanomaterials

2.2.2 Based on their dimensions

Nanomaterials classified according to their dimensions into four types [45,46]:-

2.2.2.1 Zero-dimensional NMs (0-D)

2.2.2.2 One dimensional NMs (1-D)

2.2.2.3 Two dimensional NMs (2-D)

2.2.2.4 Three dimensional or bulk NMs (3-D)

2.3 Nanomaterials Synthesis Methods

The field of manufacturing nanomaterials is a modern and wide field, especially since there is a lot of new research and ongoing studies that work to exploit these materials, develop them and expand their manufacturing processes to obtain materials at the lowest cost and with unique characteristics [47]. In the field of preparing or manufacturing nanomaterials, there are two common synthesis approaches of nanomaterials, which are top down approach and bottom up approach, as shown in the figure below:-

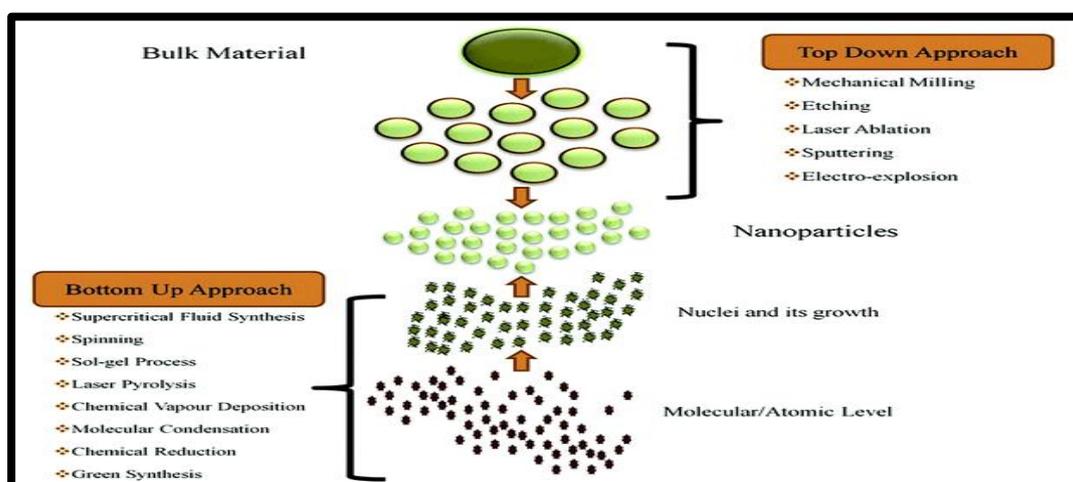


Figure (2.1) Methods for synthesis of nanomaterials [48]

2.4 Nanofibers Fabrication Techniques

To obtain nanofibers, several methods are available to manufacture them, but there are several factors that control the selection of the desired technology. Among these factors are alignment, cost, quantity required, and the material used in manufacturing. nanofibers are considered a class of nanomaterials that have wide uses and applications, the value of these fibers and their uses are increasing as a result of the diversity of the materials used in their manufacture, in addition to the multiplicity of methods of their production and the ease of their manufacture, the nanofibers can also be used as nanomaterials to reinforcement or enhance the polymer matrix [49,50], researchers have developed several techniques for manufacturing nanofibers, including: electrospinning, template-assisted synthesis, melt-blowing, force-spinning and flash-spinning, chemical vapor deposition, and physical vapor deposition [51].

2.4.1 Drawing Technique [52-54]

2.4.2 Phase separation Technique [55-57]

2.4.3 Template synthesis Technique [58]

2.4.4 Self-assembly Technique [59-61]

2.4.5 Electrospinning Technique

It is an electrical and mechanical technique that requires high voltages to produce nanofibers. This method is considered an extension of the electrospraying method. The history of this technique dates back to 1902 when Morton and Cooley independently invented two methods capable of dispersing liquids using electrostatic forces [62].

It is a well-known and common method that uses electrostatic forces and that these forces that affect the polymer solution (or solutions of composite materials) facilitate the spinning of nanofibers [63].

This technique is not without limitations, as it is known that the traditional electrospinning during the manufacturing process produces a single jet stream that exits from the Taylor cone, so the fiber productivity is low, as the amount of polymer produced ranges from (0.01-0.3) g/h.[64]. After that, the studies continued and the researchers focused on finding a solution to this limitation, where they found a way to improve productivity further through the use of multiple jet streams that produce a larger amount and thus increase the amount of production compared to the technology that consists of one nozzle [65,66]. The electrospinning method provides properties that cannot be provided or may be difficult to provide using other techniques such as the ability to orient the fibers and control their morphology [67]. Nanofibers are characterized by structures with distinctive characteristics, these properties developed their performance and efficiency in a way that made them superior to fibers manufactured by other traditional methods, as these fibers were characterized by good mechanical behavior and high surface area in addition to their functional ability, high porosity, all these developments contributed to the expansion of their fields of use, Thus, It has a major

role in the field of water treatment of all kinds, as the membranes enjoyed many advantages, as they overcame some of the problems that were facing membranes that were manufactured by other traditional methods, and among these advantages are the low cost, low energy consumption, and the ability to be recycled [68,69].

In order to understand the principle of electrospinning, in the figure no. (2.9) where the spherical droplet coming out of the polymer solution or any other solution that has a high molecular weight is under the influence of two forces, the first is an electrostatic force which is an external force trying to deform the spherical droplet, while the force The second is the surface tension force, which is considered a defense force trying to maintain the shape of the spherical droplet. While the two forces are in balance as in equation No. (2-1):-

$$\frac{1}{8p\epsilon_0} \frac{Q^2}{R^2} = 8p\sigma_s R \dots\dots\dots(2-1)$$

Where: **Q** is the charge on the droplet surface, **R** is the radius of droplet, **ε₀** is the vacuum permeability, and **σ_s** is the surface tension coefficient.

From the above equation, it can be seen that by increasing the electric field, the charge (Q) increases until it reaches a critical point where the electrostatic force becomes greater than the surface tension force. The occurrence of entanglement in the chains of the polymer solution, and this entanglement leads to access to a stable formation nanofibers as shown in the below figure (2.9) [60].

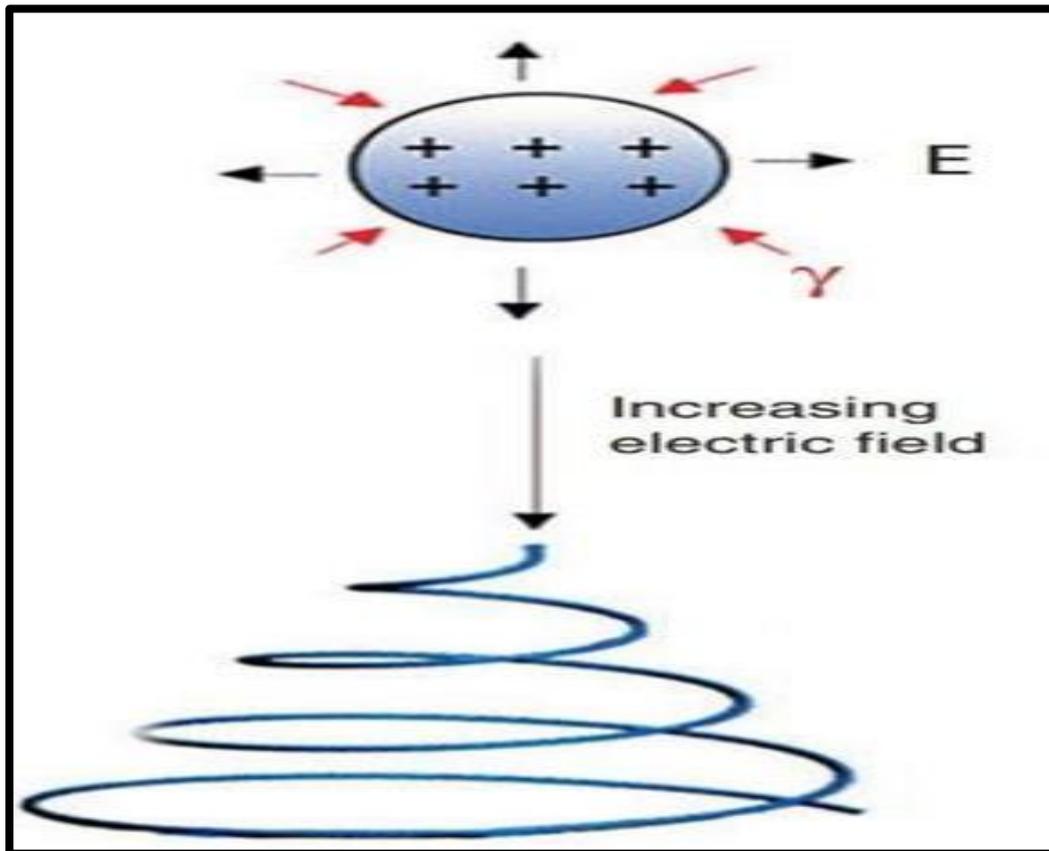


Figure (2.2) Principle of electrospinning [70].

(When the electrostatic repulsion forces are greater than the surface tension forces, then the spherical droplet will fragment into fibers)

2.5 Antifouling polymers:

The accumulation of pollutants on membranes made of electrospun nanofibers is considered one of the most important factors that reduce the life and efficiency of the membrane [71]. The adhesion of pollutants to the surface of the membrane leads to a decrease in permeability in addition to an increase in the required pressures and thus a higher cost. Therefore, it has become necessary to think about finding ways to avoid the effects of fouling accumulation, where the important role of anti-fouling polymers has emerged, examples of which include: zwitterionic polymers [72], poly(vinylpyrrolidone) [73], polypeptides [74] :-

2.5.1 Hydrophilic Polymer

This type of polymer interacts with water through hydrogen bonds. The most common and widely used polymer in water treatment applications to prevent fouling and reduce surface contamination is polyacrylates, poly(ethylene glycol) (PEG) [75-77].

2.5.2 Zwitterionic Polymer

Hydrophilic polymers: This type of polymer interacts with water through ionic bonds, and has gained great popularity recently, especially in membrane-based separation processes, as a result of its good properties in terms of rejecting pollutants and the hydrophilic surface. [78].

2.6 Electrospinning set-ups in the laboratory

The setup on a laboratory scale consists of four basic components of the electrospinning process as shown in Figure (2.10), including : a high-voltage AC or DC power source, a syringe pump, a nozzle, and a collector of various shapes, after applying the electrostatic force produced by the high voltage on the solution, as this solution is extruded through the needle at a controlled rate, and at a certain range of electric voltages, a drop of the solution will come out that forms on the tip of the needle and is subject to the applied electric field, as a result of the accumulation of charges on the droplet and its discharge, which results in a conical shape called a Taylor cone[79].

The greater the strength of the electric field, the charges will increase on the edges of the polymer drop until the applied electric force overcomes the surface tension of the solution, which leads to the expansion and elongation of the polymer as a result of the mechanical force [80].

Then, after the process of stretching and pulling the fibers, the process of solidification of the solution occurs, the evaporation of the solvents, and the fibers are directed towards the collector, which carries an opposite charge to the charge of the solution [81].

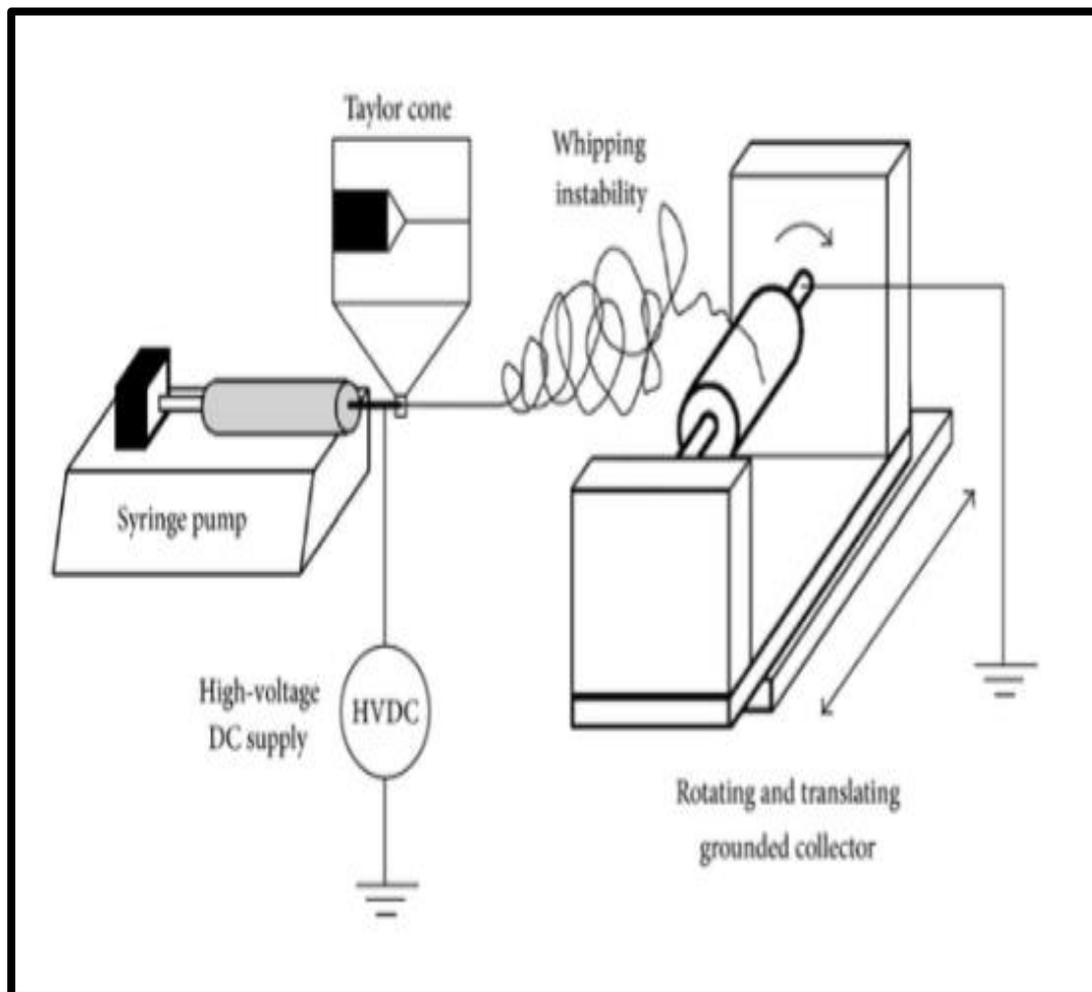


Figure (2.3) Traditional electrospinning setup [82]

2.7 Parameters affecting the Electrospinning process:

There are many factors and parameters that directly or indirectly affect the electrospinning process, as the shape and morphology of the fibers produced in this way can be controlled by understanding this information and the effect of each of them [61,83]

2.7.1 Polymer solution parameters: These parameters include the following :-

2.7.1.1 Effect of Molecular Weight and Viscosity

It is one of the most important factors affecting the electrospinning process. It is known that low molecular weight is undesirable in the electrospinning process because it leads to the formation of smaller droplets [70] and an increase in the molecular weight lead to an increase in the diameter of the produced fibers[84]. Also, the amount of cross-linked chains in the polymer solution has an effect on the viscosity of the solution [85].

2.7.1.2 The Effect of Surface Tension

The surface tension of the solution is one of the factors that greatly affect the electrospinning process, and thus its effect on the production of fibers, by reducing the surface tension, the electrospinning process can produce nanofibers without beads, and in the case of increasing the surface tension, droplets are produced, not nanofibers, because the high tension causes inactivity, On the other hand, the solvents that are among the components of the polymer solution also have an effect on the surface tension [86].

2.7.1.3 The Effect of Dielectric Constant

The dielectric constant of solvents can be defined as a measure of their polarity. It was found that in the case of solutions that suffer from a high dielectric constant, it is possible to add some solvents to them such as (DMF), where these solvents act as agents to improve the shape of the resulting fibers [87], and solvents that have A high dielectric constant can be used to improve the electrospinnability of the solution, where the dielectric constant has a direct or indirect effect on the diameter of the nanofibers manufactured by the electrospinning method, as it reduces the diameter of the fibers and reduces the formation of grain so(beads) in the resulting fibers [88,89].

2.7.1.4 Electrical Conductivity of Solution

The electrical conductivity of the solution is one of the factors that improve the nanofibers produced by electrospinning. As the conductivity increases, the efficiency of the electrospinning process increases and small and soft nanofibers are produced. Therefore, the increase in conductivity is considered one of the factors affecting positively. Therefore, the conductivity of the solution is sometimes improved by adding ions or salts [90]. Also, improving the electrical conductivity of the solution is considered an economic advantage because it reduces the voltage required for the electrospinning process [91].

2.7.1.5 Effect of Concentration

The concentration of the solution is among the most important factors affecting the electrospinning process because it affects at the same time several properties of the produced nanofibers, including (fiber diameter, beads formation). The higher the concentration lead to the greater the diameter. On the other hand, the high concentrations of the polymer

solution limit the formation of Beads, where it was found that high concentrations work to homogenize the solution and thus produce more homogeneous fibers [92-94].

2.7.2 Processing conditions (setup parameters)

2.7.2.1 The effect of applied voltage

The applied voltage is an effective factor in the electrospinning process, where there are negative effects resulting from the increase or decrease from the limit decided to perform the process, the increase in the applied voltage leads to an effect on the length of the fiber, the length of the fiber decreases with the increase in the applied voltage in addition to that the increase in the applied voltage also affects the structure Nanofibers because they affect the initial shape of the drop coming out of the solution [95,96]). Several researchers also found that the diameter of the nanofibers decreases and beads are formed as a result of the increase in the amount of this factor [91,96].

2.7.2.2 Effect of Needle Diameter

The smaller the diameter of the needle used in the electrospinning device, this will lead to the fact that the spherical droplet that comes out of the head of the needle will have a smaller size, and therefore it has a high surface tension, and this means that it requires a greater electrostatic force in order to overcome the surface tension force, which means that more time is available for this drop to move and reach to the collector , thus producing fibers with a small diameter and few beads [98].

2.7.2.3 Effect of a Flow rate of solution

It is considered one of the factors with a high influence in the electrospinning process, as it affects the transfer of the solution from the

needle to the collector, and this stage is considered important in the production of fibers. Increasing the speed of transmission of the solution and its components during jetting will lead to a decrease in the charge density and the formation of beads with the increase in the diameter of the fibers. Therefore, it is considered The formation of large diameter fibers with beads on them is the result of increased flow rate [96,99,100].

2.7.2.4 Effect of a Tip-to-collector Distance

The greater the distance between these two parts of the electrospinning device, this will lead to an increase in the curvature of the polymer solution at a jet from the needle nozzle heading to the collector, where the less the distance between the tip of the needle and the collector, this will lead to an increase in the diameter of the nanofibers in the electrospinning process [101].

2.7.3 Ambient conditions:

include humidity, pressure, air velocity in the chamber, and type of atmosphere

2.7.3.1 The effect of a humidity

The conditions of the surrounding environment are among the factors affecting the electrospinning process. When the process is performed in a humid environment, water vapor in the atmosphere may condense on the surface of nanofibers, which in turn affects the morphology of these fibers [102,103]

Increasing the humidity leads to an increase in the diameter of the fibers and thus an increase in the thickness of the membrane, in addition to that increasing it affects the surface morphology of the nanofibers [104].

2.7.3.2 The effect of a temperature

The temperature has a wide impact on the electrospinning process, as the temperature increases, several changes will occur in the polymer solution in addition to its internal components, as some solvents may evaporate as a result of the high temperature, which affects the properties of the resulting fibers, so the porosity increases when the solvent evaporates as a result of the heat [105]. Also, a decrease in the viscosity of the solution occurs when the temperature is increased, and it leads to the production of regular nanofibers [106].

Table (2.1) is a summary of the most important factors affecting the electrospinning process [107]:-

Table (2.1) The most important parameters affecting electrospinning [107]

Solution Properties	Symbol	Effect on morphology and structure	Effects on diameter
Concentration	$C \uparrow$	Increasing concentration leads to increase in fiber diameter.	Nanofiber diameter \uparrow
Viscosity	$\eta \uparrow$	Increasing viscosity leads to thicker nanofibers without beads, but too high viscosity causes generation of beads.	Nanofiber diameter \uparrow
Solution Electrical conductivity	$\sigma \uparrow$	Increasing conductivity leads to thinner nanofibers.	Nanofiber diameter \downarrow
Surface tension	γ	No conclusive correlation has been established between the surface tension and the nanofiber morphology.	-
Molecular weight of polymer	$M_r \uparrow$	Increasing polymer molecular weight leads to formation of a nanofiber with fewer beads.	-
Volatility of solvent	A_{solvent}	Higher volatility requires higher flow rate and leads to formation of a nanofiber with fewer beads.	-
Solution relative Volatility	A	Porous microstructure appears because of higher volatility.	-
Dielectric constant	ϵ	Sufficient dielectric constant of the solvent is needed for successful electrospinning.	-
Flow rate	$Q \uparrow$	Higher flow rate results in thicker nanofibers. Too high flow rate causes the generation of beads.	Nanofiber diameter \uparrow
Applied voltage	$V \uparrow$	Higher applied voltage leads to thinner nanofibers.	Nanofiber diameter \downarrow
Needle diameter	D	Minimum is required to get smoother nanofibers	Nanofiber diameter \downarrow
Needle tip to collector distance	$D \uparrow$	Beaded morphology occurs when the distance is too short and the electric field is too strong.	Nanofiber diameter \downarrow
Geometry of collector	-	Metal collectors with conductive frame or rotating drum are preferred	-
Relative humidity	Ψ	Porous microstructure appears due to evaporation-cooling effects. Lower humidity enables higher flow rate and the generation of beads is reduced.	-
Temperature	$T \uparrow$	Higher temperature leads to thinner nanofibers.	Nanofiber diameter \downarrow

2.8 Polyvinylidene Fluoride (PVDF)

This polymer is considered one of the family of fluoropolymers, and it is preferred because of its many distinctive properties, the most prominent of which are thermal stability, mechanical strength, and good process ability, in addition to its chemical resistance to several materials, including organic solvents, bases, acids, oils, and fats [108] Table 2.2, which shows the physical and mechanical properties of this type of polymer. The other name for this polymer is poly (1, 1-difluoroethylene) and it consists of the repeating unit (CH₂-CF₂). Through the free radical polymerization of 1,1-difluoroethylene (CH₂=CF₂) which occurs at a temperature between 10-150 degrees Celsius and a pressure ranging between 10-300 atmospheric pressure, PVDF is manufactured through this process , as shown in Figure (2-11) below [109] :

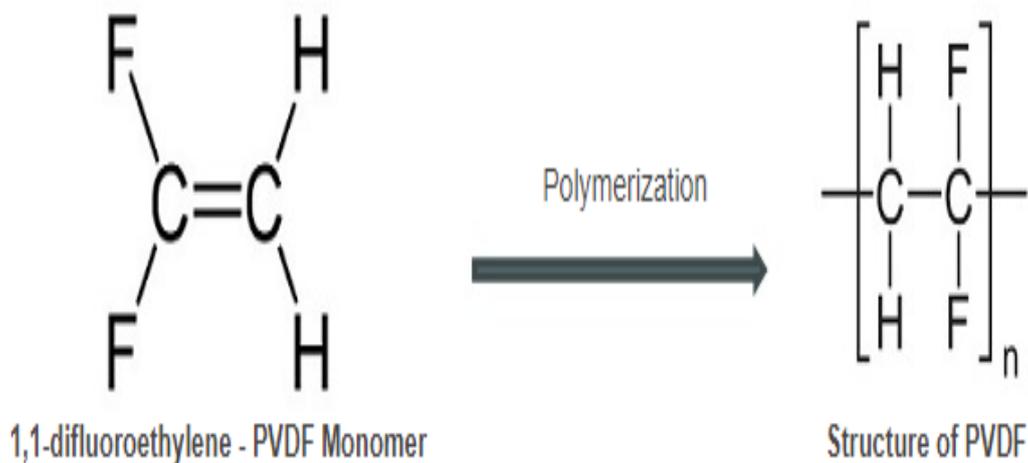


Figure (2.4) Free radical polymerization of the PVDF [109,177]

Table 2.2 the mechanical and physical properties of PVDF [109,110].

Property (Standard)	Data
Color	Colorless opaque resin
Density (g/cm ³)	1.78
Melting point, °C, ASTM D-3418	177
Glass transition temperature, °C	-35
Tensile stress at 23°C, MPa, ASTM D-638	35-55
Elongation at 23°C, %, ASTM D-638	25-500
Young's modulus at 23°C, MPa, ASTM D-638	1340-2000
Processing temp. range, °C	200-300
Dielectric strength, kV/mm, ASTM D-149	260-950

2.9 Polyacrylonitrile (PAN)

This type of polymer has a variety of uses, and among its most prominent uses is its role in the manufacture of membranes because of its good resistance to solvents, in addition to its distinctive structure and the ability of this polymer to change this structure under the influence of heat [111,112]. PAN is a kind of polymer that has several names, including polyvinyl cyanide and Creslan61, which is a semi-crystalline polymer of organic resins. This type of polymer is distinguished by having a very important functional group called the nitrile group, this group is used for interactions and is the cause of attraction interactions between molecules [113].

One of the methods by which PAN granules or powder is produced is the acrylonitrile monomer polymerization method [114], as shown in figure No. 2.12

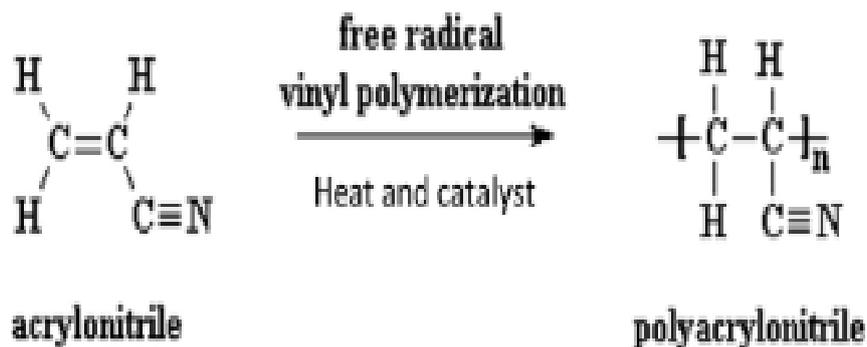


Figure (2.5) Polymerization of acrylonitrile to PAN [114]

Table (2.3) the mechanical and physical properties of Polyacrylonitrile [115]:

Property	Data
Glass transition temperature , °C	100
Decomposition temperature, °C	175
Melting temperature, °C	317
Amorphous density at 25°C , g/cm ³	1.184
Molecular weight for repeat unit , g/mol	53.06
Operating temperature (continuous) , °C	130 (Max)

2.10 N,N-dimethylformamide (DMF)

DMF with purity (99.5%). DMF is a colorless liquid organic substance. It is more than just a solvent, as this solvent is a unique chemical. In addition to being an effective solvent, it can be used in other cases in the form of a stabilizer, catalyst, or reagent .

Table (2.4) Properties of DMF [178]

Property	Data
Formula	C ₃ H ₇ NO
Molecular weight , g/mol	73.09
Boiling point , °C	153
Melting point , °C	-60.48
Density , (g/mL)	0.9445
Flash point , °C	58

2.11 Acetone (ACE)

Acetone is a colorless, flammable, volatile liquid and is one of the simplest ketones [179]. Some properties of ACE as shown in Table (2-5) below

Table 2.5 Properties of ACE [179]

Property	Data
Formula	C ₃ H ₆ O
Molecular weight , g/mol	58.079
Boiling point , °C	56.05
Melting point , °C	-94.7
Density , (g/mL)	0.7845
Flash point , °C	-20

2.12 Titanium (IV) isopropoxide (TiPP)

Titanium (IV) isopropoxide, It is considered one of the metal alkoxides that are liquid under ambient conditions with a structure formula as shown in figure below

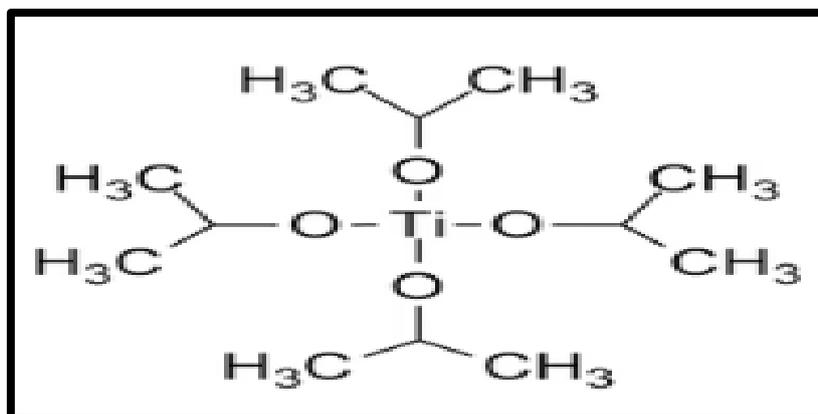


Figure 2.6 structure formula of TiPP [180]

, (TiPP) is a long-term thermal stability precursor, which is one of the precursors of TiO₂ [180]. The table below shows some attributes of TiPP

Table 2.6 Properties of TiPP

Property	Data
Formula	C ₁₂ H ₂₈ O ₄ Ti
Molar mass, g/mol	284.219
Boiling point, °C	232
Melting point, °C	17-20
Density, (g/cm ³)	0.96

2.13 Sodium carbonate (Na_2CO_3)

Sodium carbonate or washing soda (among its other names) in its natural state, it is an odorless, white powder, purchased from Thomas Baker Chemicals Private Ltd, Mumbai, India. Article No. 143359 and CAS.no.[947-19-8].

Table 2.7 physical properties of sodium carbonate and its hydrates [181,182]

Property	Anhydrous	Monohydrate	Heptahydrate	Decahydrate
Formula	Na_2CO_3	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$
Molecular weight, g/mol	105.99	124.00	232.10	286.14
Density at 20 °C, g/cm ³	2.533	2.25	1.51	1.469
Heat of fusion, J/g	316	-	-	-
Specific heat capacity at 25 °C, J g ⁻¹ K ⁻¹	1.043	1.265	1.864	1.877
Melting point, °C	851	105 ^a	35.37 ^b	32.0

2.14 Electrospun nanofiber applications

The nanofibers produced by the electrospinning method have distinctive and unique properties, due to the advantages that the method has that are not available in other manufacturing methods, the most important of these advantages: It is considered a scalable method, a method with an automated path that does not require a lot of labor and therefore has a low cost [116]. Some researches that dealt with the study of techniques used in the manufacture of nanomaterials to take full advantage of them recommended the use of membranes made of nanofibers produced by the method of electrospinning with the use of fluorinated polymers and hydrocarbons because of their water-repellent properties [117]. Therefore among all available products and materials, nanofiber electrospinning products made of polymeric materials are considered to be the best and most widely, as they are involved in a wide range of applications and in various fields, including energy, health and environment [118]. Due to the wide applications of nanofibers produced by the electrospinning method as shown in Figure. (2.13), our study focused on the environmental field and how to treat water pollution (produced water) by using one of the techniques of the pressure-driven membrane processes, which is the ultrafiltration technique.

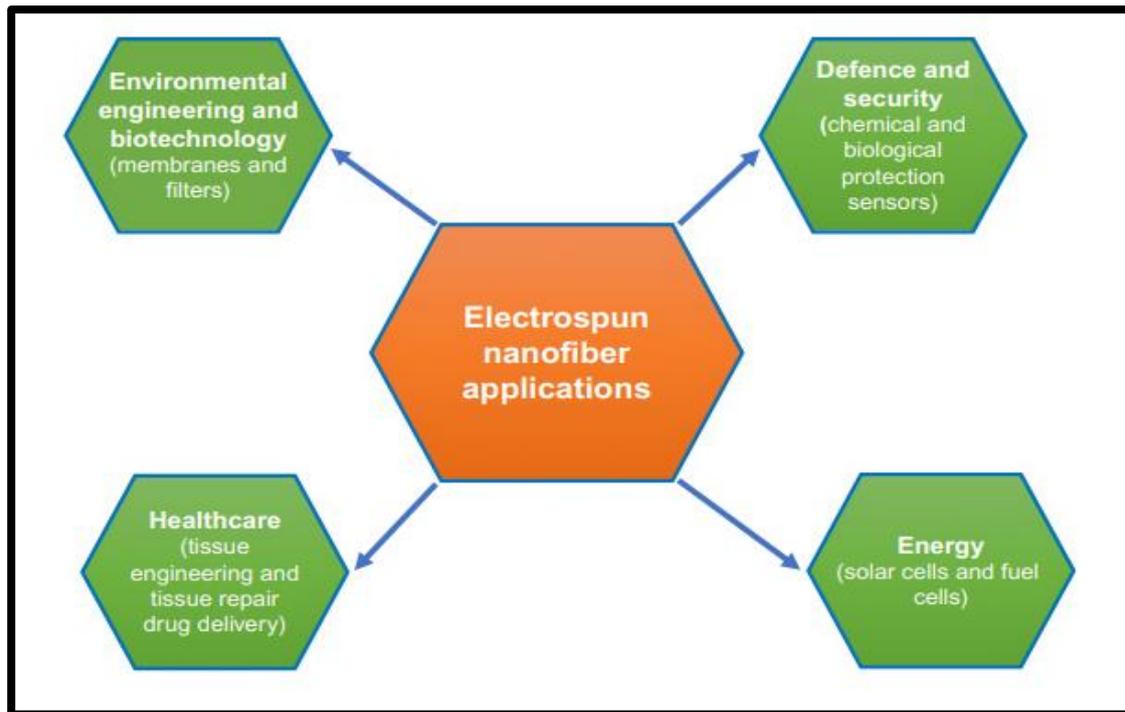


Figure (2.7) Application areas for electrospun nanofibers [119].

2.14.1 Water Treatment by using Nanofibrous Filtration Media

The water used in this application is called “produced water”.

It can be defined as one of the types of polluted industrial water that is extracted as a by-product during the extraction of crude oil or gas, and this water is considered polluted and toxic and leads to great risks to the environment because of its components that include many heavy metals, oil impurities, high total solids and hydrocarbons in addition to chemical oxygen demand [120,121]. It is well known that the oil and gas extraction processes are processes that consume water, but they are also a source of water production, as these processes are accompanied by large quantities of water [122].

The oil industry is considered an industry in continuous development and a large expansion because of its profitable economic return, but on the other hand, this industry is considered one of the most prominent sources

of pollution that exist on the earth, because of the pollutants left behind by this industry in very large quantities, as the amount of process water, which is the water resulting from operations refining of crude oil may sometimes reach an amount approximately 1.6 times more than the amount of crude oil, and in general there are multiple and complex methods used in treating the produced water associated with oil extraction operations, including (membrane technologies, adsorption, coagulation, advanced oxidation, photocatalytic degradation, etc.) These operations can overlap with each other in order to achieve the desired goal of processing operations [123-125].

Membrane technologies are considered one of the technologies suitable for working within the fields of bioseparation in addition to wastewater treatment applications, provided that pre-treatment is carried out on them first, and many studies have shown the suitability and effectiveness of using microfiltration and ultrafiltration technology in the pre-treatment of produced water, while the rest of the technologies are used filtration in the treatment of other types of water with less salinity [126-130].

Due to the seriousness and toxicity of the produced water and its great impact on the environment, its discharge without treatment has become a dangerous environmental problem that everyone must work to avoid and treat, so the produced water and / or waste water of the petroleum industry are treated through three basic stages, as shown in the figure (2.14), [126,131]

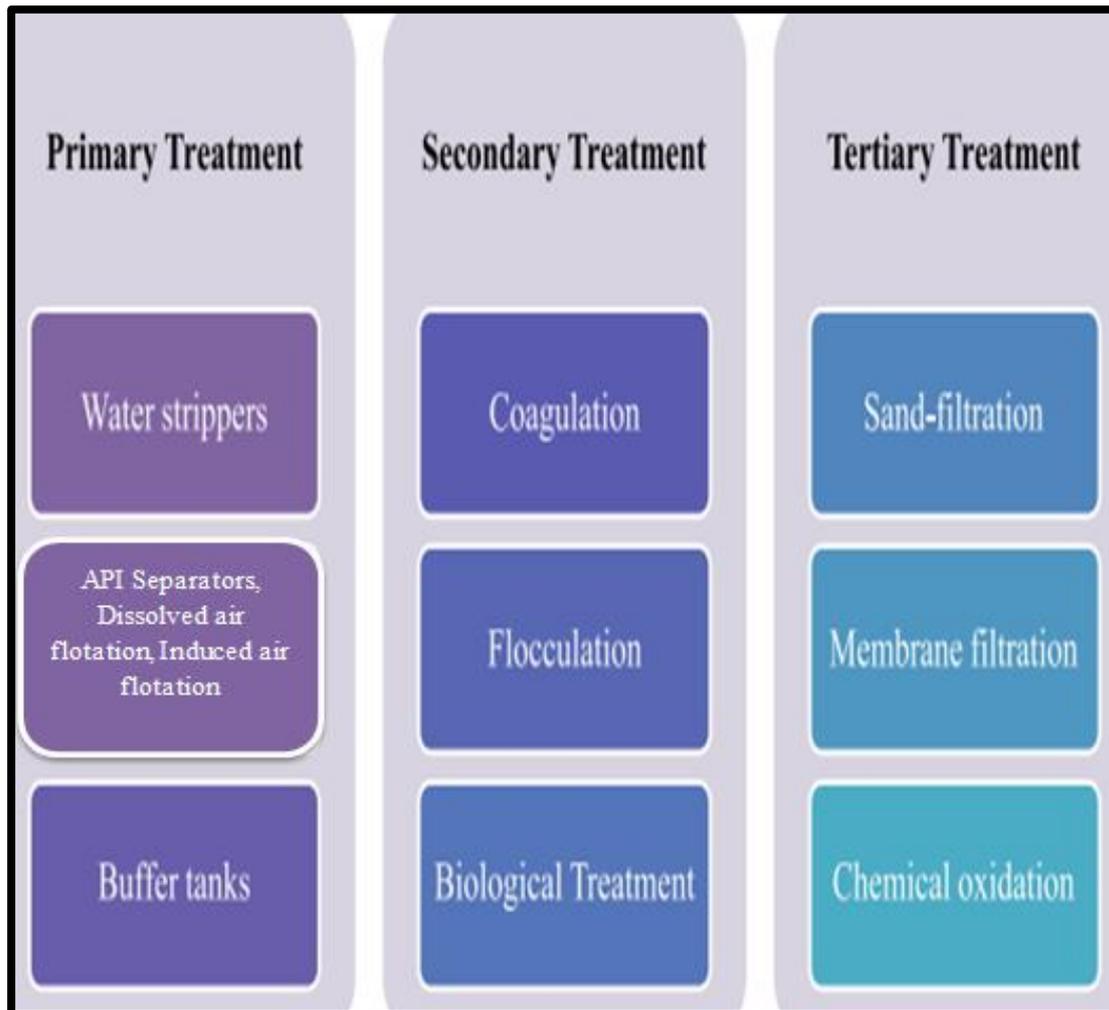


Figure (2.8) Petroleum operations wastewater treatment [132].

2.15 Filtration Process

It is one of the common methods in the treatment of liquids or air, where the filtration process takes place through the passage of the feed stream or air through a porous medium that acts as a barrier that prevents the passage of unwanted materials with specific sizes depending on the size of the pores in the porous medium or barrier [133,134] .

The principle of filtration is based on the physical properties of the filter medium and the substances to be removed. The filter medium has pores or openings of specific sizes that allow the fluid to pass through while trapping particles or contaminants larger than the pore size. The principle

of filtration can also involve mechanisms such as adsorption, where certain substances adhere to the surface of the filter medium, or sieving, where particles are physically blocked based on their size [135-137].

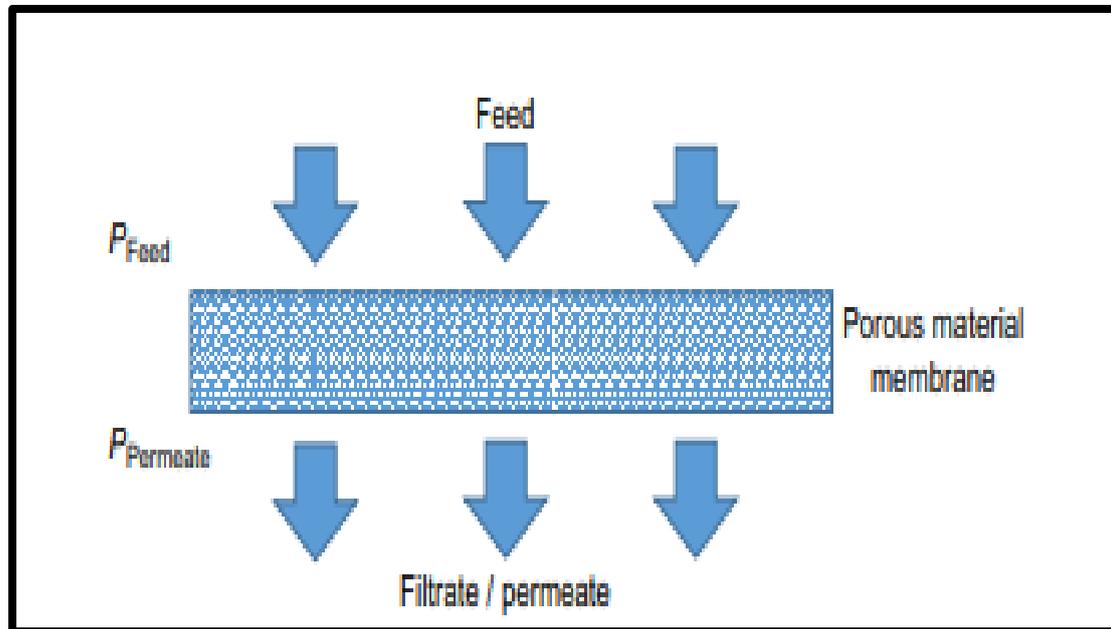


Figure (2.9) General Principle of The Filtration Process Through Porous Media , When $P_{Feed} > P_{Permeate}$, The flow will occur through the porous medium [137].

2.15.1 Types of filtration:

Based on the particle sequestration site the filtration is divided into two main parts as shown in the figure (2.16) [138,139]:-

a- Particles are separated outside the surface of the porous medium (surface filtration).

b- Particles are separated inside the surface of the porous medium (depth filtration).

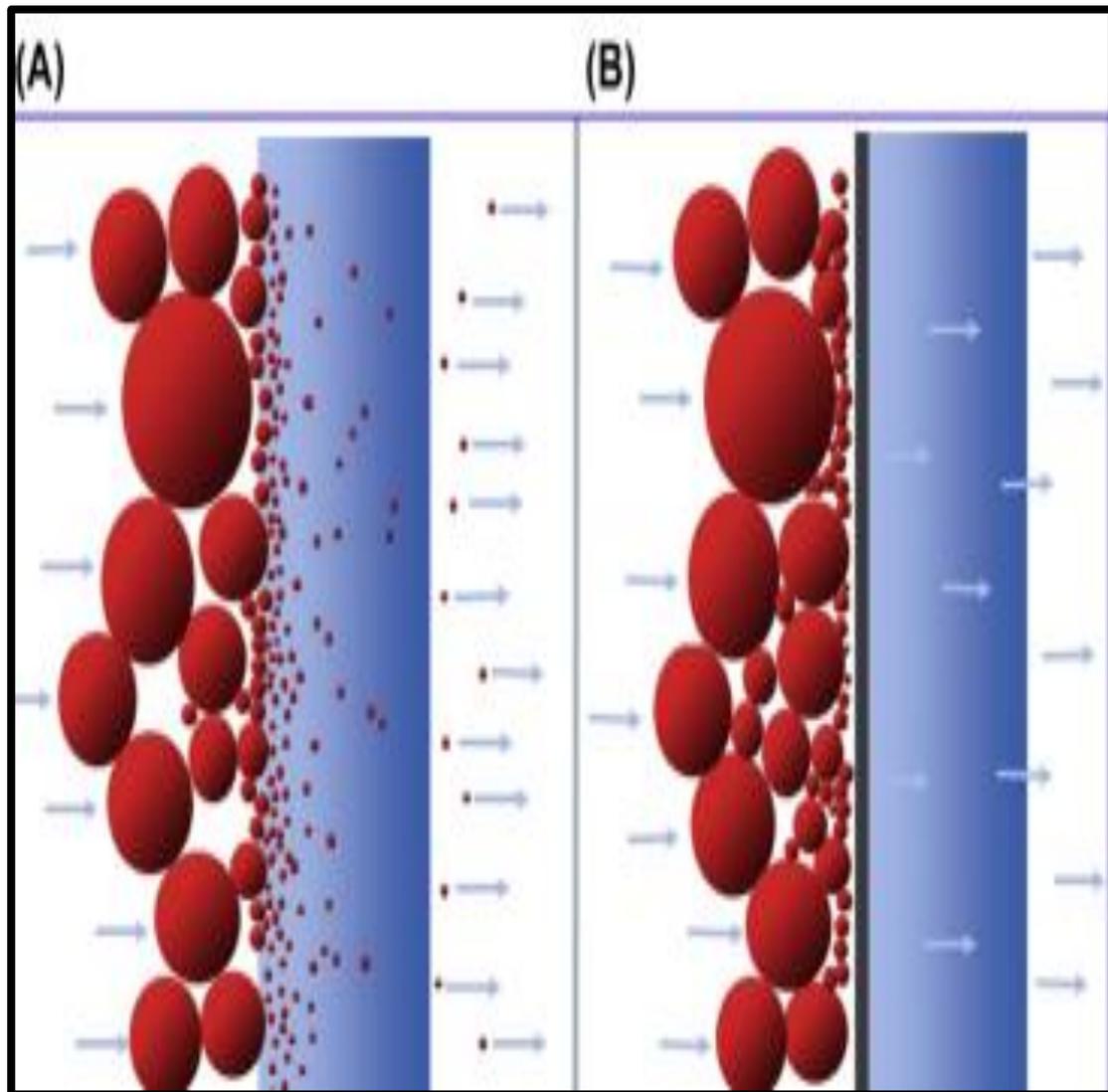


Figure (2.10) (A) depth filtration and (B) surface filtration [138,139]

2.16 Pressure-Driven Membrane Processes

Membrane technology is considered one of the modern technologies that differ from the rest of the well-known technologies such as adsorption, flotation, coagulation, ion exchange and other technologies. Recently, this technology has been used in industrial pollution control and treatment operations due to its unique characteristics, including ease of operation, high efficiency during work and the small area that you occupy on the site [140-144].

Table.(2.8) Pressure-Driven membrane processes and their characteristics [129].

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Permeability (L/h.m ² .bar)	> 1,000	10 - 1,000	1.5 - 30	0.05 - 1.5
Pressure (bar)	0.1-2	0.1 - 5	3 - 20	5 - 120
Pore size (nm)	100-10000	2 - 100	0.5 - 2	< 0.5
Rejection :				
•Monovalent ions	-	-	-	+
•Multivalent ions	-	-/+	+	+
•Small organic compounds	-	-	-/+	+
•Macromolecules	-	+	+	+
•Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving Charge effects	Solution Diffusion
Applications	Clarification; pretreatment; removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

Separation processes based on the use of pressure as a driving force are characterized by their high efficiency and ease, in addition to their low cost. Therefore, they are the most widely used and widespread among

other separation processes that depend on concentration or electric potential difference as a driving force [146].

2.17 Types of Pressure-Drop Membrane Processes

These Processes can be generally classified into four types, as follows in Table.(2.4) [145]:-

2.17.1 Microfiltration (MF)

It is one of the Pressure-Driven Membrane Processes where the membrane is used to separate suspended solid particles or molecules, and it is one of the separation techniques that use membranes. It is involved in many fields, the most important of which is the field of wastewater treatment or industrial water. Through this technology, pollutants (particles and molecules) are separated whose diameters range from (0.1-10) μm , sieving is the separation mechanism, and this technique does not need high pressures, as it works under very low pressures ranging between (0.1-2 bar) [147-149].

2.17.2 Ultrafiltration (UF)

It is one of the Pressure-Driven Membrane Processes, which mainly uses the membrane in the separation process. This membrane is an asymmetric porous medium that contains pores with sizes ranging from (2 - 100) nm as shown in the table (2.8). This process is based on sieving as separation mechanism. When the contaminated liquid passes through In the membrane, macromolecular , suspended solids, bacteria and colloid in the solution will be intercepted and separated by the porous membrane [150-152].

2.17.3 Nanofiltration (NF)

Is another pressure-driven membrane separation process that mainly uses the membrane in the separation process, as this membrane contains pores of smaller sizes than (MF, UF) ranging from (0.5 - 2) nm as shown in the table (2.8). Nanofiltration rejects particles of smaller sizes than in each of (UF, MF) where it works to separate mono- cations and divalent cations in addition to removing bacteria and viruses, while (MF,UF) removes soluble pieces in a feed stream Thus, these two processes are used to provide pre-treatment for the RO, NF) processes [153-156].

2.17.4 Reverse Osmoses (RO)

It is the most efficient method among all pressure-based membrane processes, as when the feed stream passes through the porous membrane that has an average pore size smaller than 1 nanometer, most of the pollutants, including salts and heavy metals, will be separated from the solution and retained by the membrane. Therefore, this process is considered good in terms of efficiency, but at the same time expensive because it requires high pressure rates compared to other methods [157-160].

2.18 Adsorption

It is a superficial process during which ions, atoms, or molecules in a liquid or gas adhere to or accumulate on the interface of a material that separates two phases [161] as in Figure (2.17) .

Adhesion occurs as a result of two forces from interactions that exist between adsorbent and adsorbate: Physical forces (van der Waals or hydrogen bonding) and the other forces are chemical bonds (covalent bonding) [162-163].

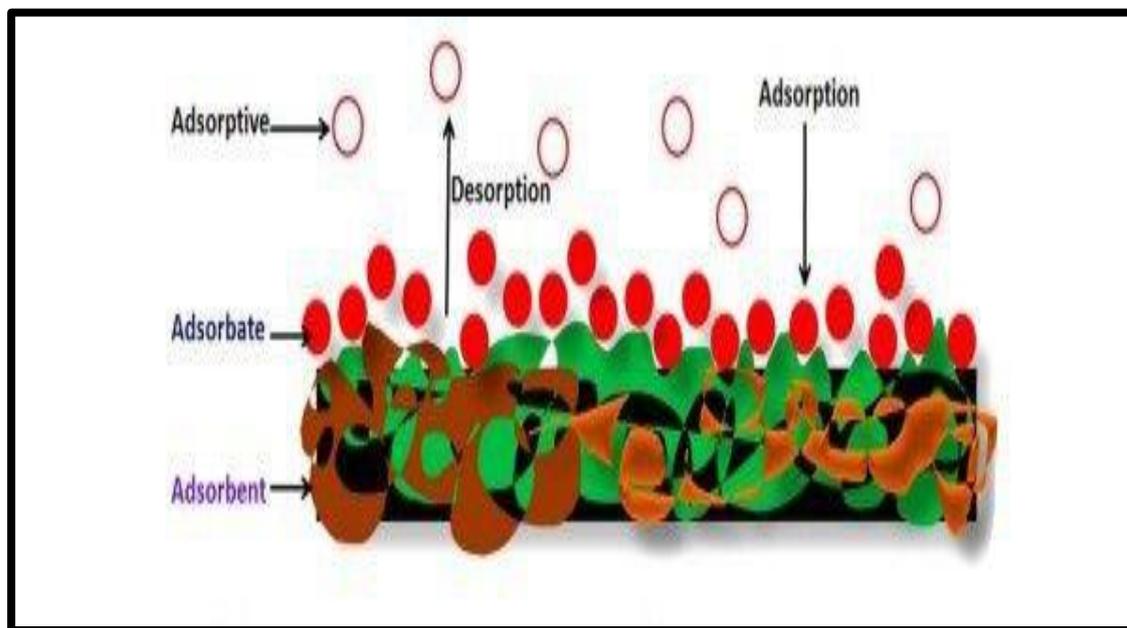


Figure (2.11) General mechanism for the adsorption [161]

Recently, this method has been used in several fields, including environmental protection, pollutant treatment, and heavy metal removal from industrial water , Despite the simplicity of this method, it has proven its effectiveness and its high ability to adsorb liquid pollutants, and the adsorption efficiency increases with the increase in the surface area of the interface [164]

Among the nanomaterials that have the ability to adsorb organic and inorganic pollutants are carbon nanomaterials, polymers, metal oxides, silica and other adsorbent materials. The adsorption efficiency of nanofibers can be improved by adding nanoparticles of materials that are characterized by their ability to adsorb pollutants, as the electrospinning process helps in the spread of these particles and distributes them properly, which limits their accumulation, which is one of the most important problems of nanoparticles [165,166].

2.19 Literatures Review

In the context of the included filtration process, which is done by using nanofibers manufactured by the electrospinning method of a polymeric solution consisting of the best mixing ratio of (PVDF / PAN), literature review can help researchers identify the latest techniques, materials, and applications.

Some recent studies in the field of electrospinning include:

In the year 2006, Gopal, Renuga, et. al, in their study, they discussed the importance of developing a fiber membrane prepared from electrospun nanofibers and its potential for use in liquid separation and particle removal applications. Polyvinylidene fluoride copolymer was chosen due to its unique properties.

These fabricated membranes were then characterized and showed similar porosity and flow characteristics to those of microfiltration. These manufactured membranes were used to separate polystyrene particles with sizes (1.5 and 10 μm), and the membranes succeeded in rejecting the particles by 90%. Finally, after knowing the morphological and operational characteristics of these fibers, they indicated that the electrospun nanofibers prepared from PVDF solution can be used as membranes for water treatment before applying the reverse osmosis treatment, or they can be used as filters before the ultrafiltration or nanofiltration process in order to reduce pollution and maintain the rate of the flow [167]

In the year 2016, Faisal A. AlMarzooq et. al, Their study focused on porous membranes in terms of the importance of characterizing structural membrane parameters such as surface roughness, pore size, , pore density

and pore geometry and distribution, as there is a close relationship between these parameters with the performance and evaluation of membranes. Their study included a method for measuring these structural parameters of the membrane by evaluating the analysis of scanning electron microscope (SEM) images of three different types of porous membranes: Polyvinylidene fluoride, polycarbonate, and polytetrafluoroethylene membranes. The result was that SEM microscopic image analysis is an effective method for characterizing membranes, and determining both surface pores, their total size, and pore geometry and distribution [175].

In the year 2017, Yalcinkaya, F., et. al, these researchers focused their studies on preparing electrospun composite membranes for use in treating oily wastewater. Despite the properties of the resulting fibers, they were require modification and improvement of the properties of both permeability and resistance to pollution. Therefore, the surface of the resulting fibers was treated by using microwave plasma treatment using Argon (Ar)gas and a second treatment included chemical modification using sodium hydroxide. The fibers produced showed good permeability and pollution resistance properties, except for the weakness of the membrane during the cleaning process.

the results of this study showed that the resulting membranes possess hydrophilic and oil-loving properties in addition to enhancing the permeability properties. The treatment methods used in this study, which included plasma treatment and the chemical method in addition to grafting with the TiO₂ functional group on the surface of the membrane, were considered sufficient methods for producing PVDF/PVDF , treated PAN suitable for use in oily wastewater separation and treatment techniques [170]

In the year 2017, Anvari, Arezou, et. al, they prepared ultrafiltration membranes from a blend of PVDF/PAN and studied the effect of mixing ratios on both the morphology and the anti-polluting behavior of these prepared membranes. The performance of the membranes was also evaluated using one of the filtration methods of pure water and bovine serum albumin (BSA). Result they reached is that the hydrophilicity increases with an increase in the ratio of PAN in the solution & the lowest percentage of rejection of the bovine occurs with the lowest percentage of addition of PAN , which is 10%, that the increase in PAN reduces the angle of contact and increases the adhesion action and reduces the equilibrium water content, but the percentage of PAN polymer if exceeds 10%, it does not give any noticeable improvement. The percentage of 10% increases the percentage of Pure Water flux and the percentage of BSA decreases. By increasing PAN , the porosity and hydrophilicity will increase, thus increasing the flow of pure water, retention of PBC, and increased protein retention (meaning high fluid permeability, retention and prevention of protein passage [171]).

In the year 2017, Polisetti, V., & Ray, P, they prepared membranes from polymeric materials, namely (PAN, PVDF) by phase inversion method. Several types of membranes were prepared (Virgin PAN, Virgin PVDF, a mixture of both with different compositions). After characterized these membranes and studying their performance in terms of pure water flux and fouling characteristics, It was found that the relative percentages of (PAN, PVDF) have a significant impact on the properties of the Membranes, as there were hydrophilic properties for the blend films compared to the virgin PVDF membrane. Also, the PVDF membrane showed a higher surface roughness than the rest of the Membranes. With the increase of PAN content in the mixture, it was

noticed that there was an effect on the morphology of the blend, so the structure changed from macrovoid to a finger-shaped structure. Finally, the (PVDF: PAN 30:70) membrane showed the highest flow recovery rate among all the membranes with an acceptable mechanical strength [172].

In the year 2017, Ren, Jing, et. al, they used hydroxylamine hydrochloride in the presence of a small amount of inhibitor for the production of modified AOPAN nanofiber films, the purpose of adding the inhibitor is to prevent crosslinking of the manufactured solution and to ensure a smooth surface and a uniform amidoximation degree. After producing the AOPAN solution, they found that the films made from this solution had a high capacity to adsorb the following materials: Cu(II), Pb(II), and methyl orange (MO) after drying. They also noticed that the adsorption capacity doubled and reached more than 50% of what it was in the first adsorption, and this indicates the possibility and reusability of these films for water treatment [173].

In the year 2018, Sutton-Sharp, E., et. al, they conducted a comparison of the quality of work for ten membranes, these membranes treat the produced water, and through their performance and operating characteristics in addition to their structure, it is determined which of them is effective in terms of cost and the length of its life. During this comparison, several parameters were adopted to evaluate performance, including: rejection, permeability, fouling, and the life span. The test was conducted on product water extracted from a real oil field, and the test result was that all membranes removed 99% of the oil, compared to 80-85% for the known traditional techniques.

Although the results of the study gave preference to ceramic filtration media because of its strong structure, it also showed that polymeric membranes have many benefits, the most prominent of which is low cost, low weight and footprint [174].

In the year 2020, Mokhtari-Shourijeh, Zahra, et. al, during their study, they prepared composite nanofibers of (PVDF/PAN) that were characterized by being porous and capable of adsorption and could be used in industrial wastewater treatment to remove dyes from them. Thus, the possibility of performing the adsorption function efficiently. Where they were able to modify the surface of the nanofibers by adding nanomaterials of NaHCO₃ added to the electrospinning solution. Then, the nanofibers are immersed in a solution containing hydrochloric acid and distilled water (10% vol / vol HCl) until the nanofibers are washed and salts are extracted from them, thus increasing the porosity. These nanofibers porous aminated PAN/PVDF, which is characterized by its high porosity, has been successfully used to remove dyes from industrial wastewater [176].

In the year 2021, Mohammed, Y. A., et. al, through their study, which dealt with the preparation of compound solution of Polyvinylidene fluoride/amidoximized Polyacrylonitrile (PVDF/AOPAN) and after the electrospinning process of this solution, (KOH) was used to treat the electrospun nanofibers. After perform the structural and morphological characterization of the resulting fibers, the results showed that the resulting fibers have excellent adsorption capability for both nickel Ni(II) and lead Pb. (II). EDS analysis also confirmed the fact of this adsorption through the presence of metals.

The final results also showed that converting PAN to AOPAN improved its hydrophilicity, in addition to that the adsorbent material showed excellent regeneration effectiveness by using 0.5 M of hydrogen chloride (HCL). Finally, this study showed that PVDF/AOPAN is an effective adsorbent for removing Pb. (II), Cu(II), and Ni(II) removal [22].

In the year 2021, Mehta, Jigesh, et. al, they prepared ultrafiltration membranes from blend (PVDF-PAN) by phase inversion method, where different concentrations were used to prepare a mixture, where the concentrations of (PVDF, PAN and PVB) were 10-14%, 2-4% and 2%, Respectively, while preserving the concentrations of the total amount of the polymer content at concentrations of (12-16)%, the prepared films were modified and treated with a 2% of (NaOH) solution. The effect of increasing the concentration of the polymer on pore size and porosity, as it was found that the composite films had a separation efficiency of more than 99.8%, and the unmodified films showed a rejection of 99.8-95.4%. Finally, a good preparation of the membrane blend is suitable for use in wastewater treatment applications [177].

2.20 Summary of Literature Reviews

Below is a summary of some tips and scientific facts that were taken into account from previous studies compared to the most important things that were conducted during our study to modify and improve the properties required for nanofibers to achieve the main aim of this thesis, as follows:-

- Previous studies have indicated the importance of preparing nanofibers by preparing a blend of polymers in order to benefit from the common properties of the components of this blend, were most of these studies dealt with different percentages of the components that make up this blend, so we prepare a group of blends in different percentages to produce nanofibers membranes of and conducting physical and operational tests to find out and determine the best blend ratio .
- Published research and studies have shown an established and distinctive fact for nanofibers that are manufactured using the electrospinning method because of their distinctive properties, including ease of control. It is considered an inexpensive, economical method in addition to its availability in our university laboratories. Therefore, the electrospinning method was used to produce nanofibers in our study.
- Most previous studies used Bovine serum albumin, while in this study, dry milk protein was used as a substitute for Bovine serum albumin in conducting operational tests for the manufactured membranes to determine the extent of the ability of the manufactured membranes to trap the protein and not allow it to pass through them.
- The chemical and surface treatment methods for the produced membranes led to achieving distinctive results for the manufactured membranes, where the modification of PAN to AOPAN led to decreased the contact angle and produced nanofiber surface more hydrophilicity specifically at M9 (PVDF: AOPAN:TiPP) , M9 has 91.79% flux

recovery ratio, It is also characterized by a high ability to recover its effectiveness after cleaning ,therefore used M9 and M4 membranes were used for the purpose of treating product water (PW) associated with crude oil during extraction operations

Chapter Three
Experimental Part



3.1 Introduction

This chapter deals with the materials and devices used, the process of preparing solutions of all types, methods of fabrication nanofibers, in addition to methods of testing and operating the membranes that have been manufactured. Finally, this chapter includes the application in which the membrane is used.

3.2 Used Materials

3.2.1 Polyvinylidene fluoride (PVDF)

Polyvinylidene fluoride powder (PVDF with MW = 275000 gm./mol) was purchased from Sigma-Aldrich ,USA. With CAS.no.[24937-79-9]. PVDF is a semi-crystalline thermoplastic fluoropolymer, usually 50% - 70% crystalline .

3.2.2 Polyacrylonitrile (PAN)

PAN was used as a polymeric material in the form of white powder, with Molecular weight 150,000 g/mol, from Sigma-Aldrich, USA. With CAS.no.[25014-41-9] and the linear formula $(C_3H_3N)_n$.

3.2.3 N,N-dimethylformamide (DMF)

DMF with purity (99.5%) and CAS.no.[68-12-2] was purchased from Shanghai Chemical Reagents Co., Ltd, China with Formula C_3H_7NO , Molecular weight 73,09 g/mol .

3.2. 4 Acetone (ACE)

Acetone is a colorless, flammable, volatile liquid and is one of the simplest ketones [184]. It was purchased from Shanghai Chemical Reagents Co., Ltd, China , Formula C₃H₆O, Molecular weight 58.079 g/mol .

3.2.5 Dry Milk Protein

Dry milk powder was used as a basic material for the purpose of testing the performance of the manufactured membrane. This milk powder contains an amount of protein estimated at about 16 % or (24.1g /100g). Dry milk powder obtained from Nestlé Dubai Manufacturing L.L.C Dubai-UAE.

3.2. 6 Titanium (IV) isopropoxide (TiPP)

Titanium (IV) isopropoxide 97% , from Sigma-Aldrich, USA. With CAS.no.[546-68-9] and the linear formula Ti{OCH(CH₃)₂}₄ , with Molecular mass 284,219 g/mol .

3.2. 7 Sodium carbonate (Na₂CO₃)

Sodium carbonate or washing soda (among its other names) in its natural state, it is an odorless, white powder, purchased from Thomas Baker Chemicals Private Ltd, Mumbai, India. Article No. 143359 and CAS.no. [947-19-8] .with Molecular weight 105.99 g/mole, Melting point 851 °C.

3.2. 8 Hydroxylamine Hydrochloride

Hydroxylamine Hydrochloride (NH₂OH·HCl) was purchased from Sigma-Aldrich, USA. With CAS.no. 5470-11-1, with Molecular mass 69.49 g/mole, Melting point (155-157) °C .

3.3 Preparation of Solutions

The process of preparing solutions is considered an essential and important stage in the practical part of this study, and it required great time and attention. This process can be summarized in three parts , as follows:-

- Preparation of pure and blends polymers solutions.
- Preparation of the modified polymeric solution.
- Preparation of composite material solution.

3.3.1. Preparation of pure and blends polymers solutions

12% (w/w) of PVDF powder was dissolved in a mixture of a solvent consisting of (50% acetone/50% DMF). This dissolution took place at (30–45 °C) and in humidity not exceeding 43%, where a magnetic stirrer was used to mix the solution and sonicated for one hour until obtaining homogeneity, the purpose of using ultrasound is for the purpose of dispersing the solution and obtaining complete homogeneity of the resulting solution. 12% (w/w) of PAN powder was dissolved in a solvent (100% DMF),this dissolution also took place under the same conditions above, as it continued to use the magnetic stirrer at a temperature of (30-45 ° C) and in a humidity not exceeding 43% until a homogeneous solution was obtained .

After completing the preparation of pure polymer solutions, here at this stage the polymers are mixed with each other within different mixing ratios for the purpose of obtaining the best polymer blend solution after conducting laboratory tests in addition to physical tests that are conducted on nanofibers manufactured by electrospinning.

Then, Four types of blends of (PVDF: PAN) were prepared with a weight ratio of (20:80, 40:60, 60:40, 80:20). The polymeric blend solutions continue to be mixed according to the above ratios at 30-35°C for one hour to be ready for the electrospinning process, as shown in the Figure (3.1) which represents the stages of obtaining the best blending ratio.

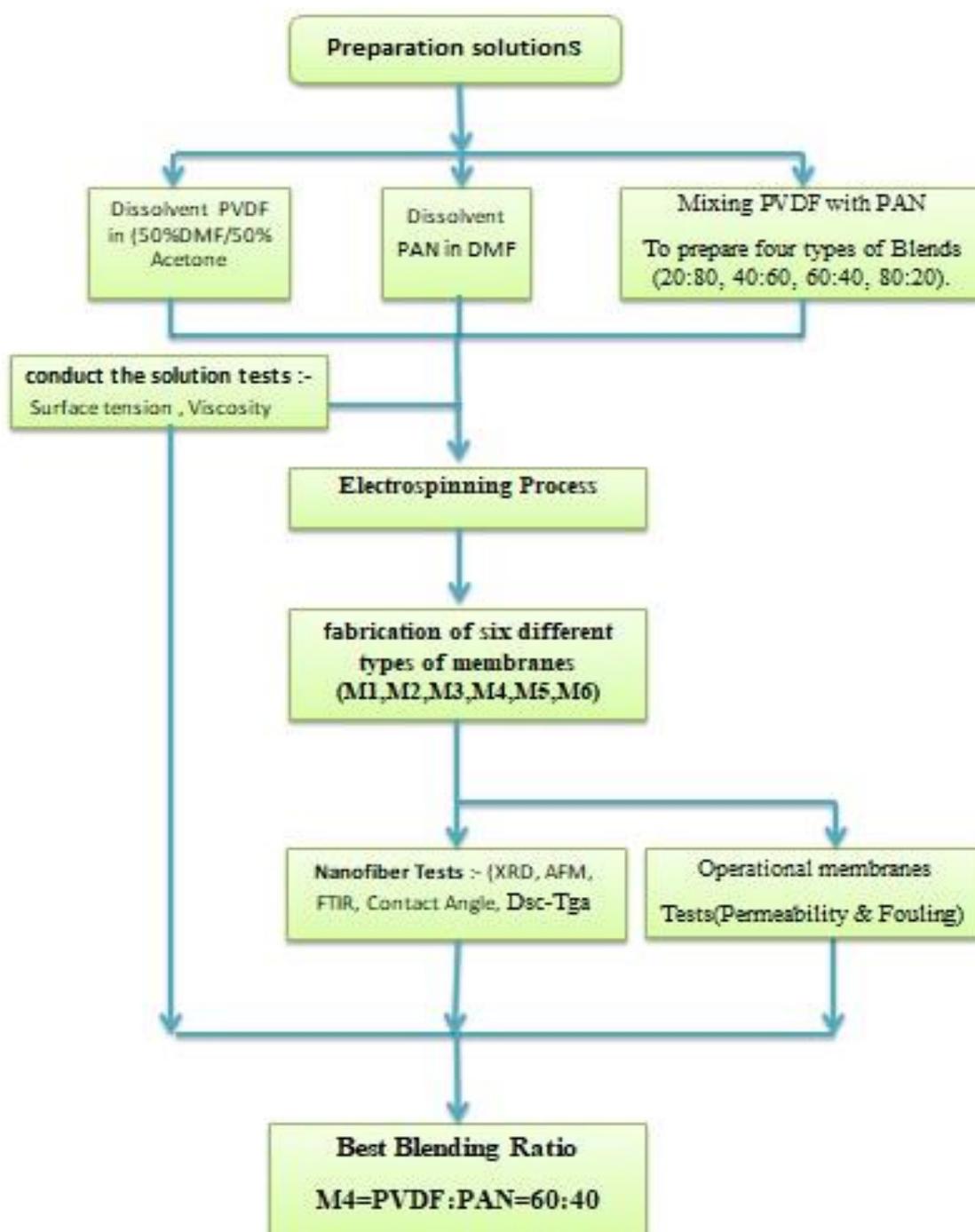


Figure. (3.1) Stages of Obtaining the Best Blending Ratio

3.3.2. Preparation of the modified polymeric solution

After obtaining the best Blend ratio of (PVDF / PAN), this ratio is modified by:-

- Adding 16% wt. from hydroxylamine hydrochloride (NH₂OH.HCL) of the weight of polymer in blend (60/40)
- Adding 12% wt. of sodium carbonate to the same blend solution . The reaction takes place at a temperature between (60 -70) ° C for a period of 3 hours, after the reaction is over and the solution is left to cool naturally, after which the solution is filtered and the insoluble substances are isolated, thus obtaining a new modified mixture called PVDF/AOPAN. The equation below in the figure (3.2) shows the nature of the reaction that occurs and how the new mixture (PVDF/AOPAN) is formed, which is an effective adsorbent for the absorption of metal ions [22] .

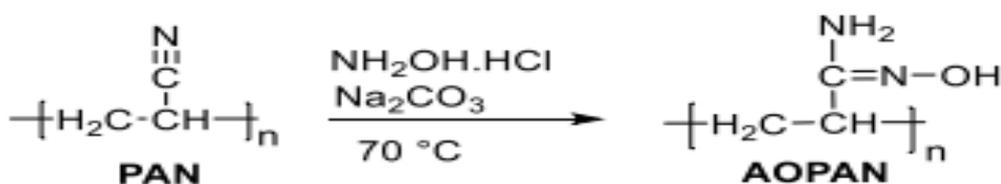


Figure (3.2) Reaction of hydroxylamine hydrochloride with Polyacrylonitrile [22]

3.3.3. Preparation of composite material solutions

After obtaining the best mixing ratio for film production, which represents (PVDF / PAN) (60/40), a composite polymeric material solution and a developed composite polymeric material solution are then prepared, and this is done by adding (TiPP) in two different ways, as follows:

The first method: dilution of TiPP by using ethanol in a mixing ratio (TTIP:Ethanol) 3:7 , then adding 5%wt. of diluted TiPP to a blend solution (PVDF/PAN) with continuous mixing using a magnetic stirrer until homogeneity is reached , the result is a composite polymer solution (PVDF: PAN: TiPP) 60:40:05

The second method : adding 5%wt. of diluted TiPP to the modified blend solution (PVDF/AOPAN) with continuous mixing using a magnetic stirrer until homogeneity is reached , the result is a reinforcement modified composite polymer solution (PVDF:AOPAN: TiPP) 60:40:05. As shown in figure (3.3), which represents both methods for obtaining composite materials solutions

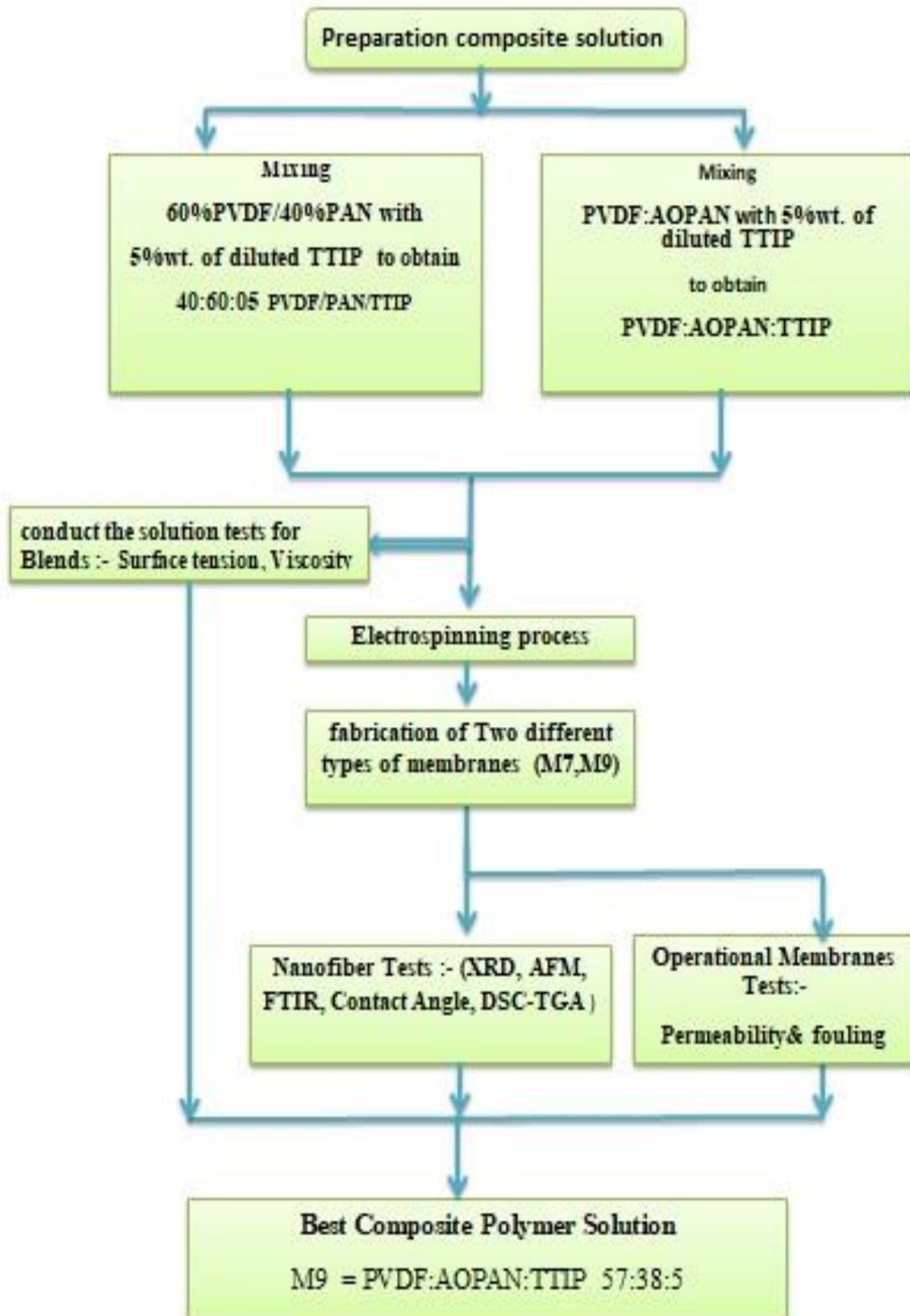


Figure (3.3) Best composite materials solutions

3.4 Electrospinning

The electrospinning device was used in the process of fabrication of Nano-Fibrous Membranes, where the polymeric solutions are placed in a syringe with a capacity was 1 ml, ending with a needle with an inner diameter of 0.63 mm, and placed in an MS-2200-Daiwha syringe infusion pump, with a feeding rate was 1 ml / hour, with an electric voltage of 20 kV, at rotation speed was 600 rpm and a distance between the needle and the rotating collector was 15 cm . The metal needle will connect to the positive power source while the collector will connect to the negative power source. As a result of the applied high voltage, a high external electric field will be generated between the two electrodes that can overcome the surface tension of the viscous polymer solution and push it to form a polymer jet , as shown in figure (3.4) which shows the shape of the electrospinning device.

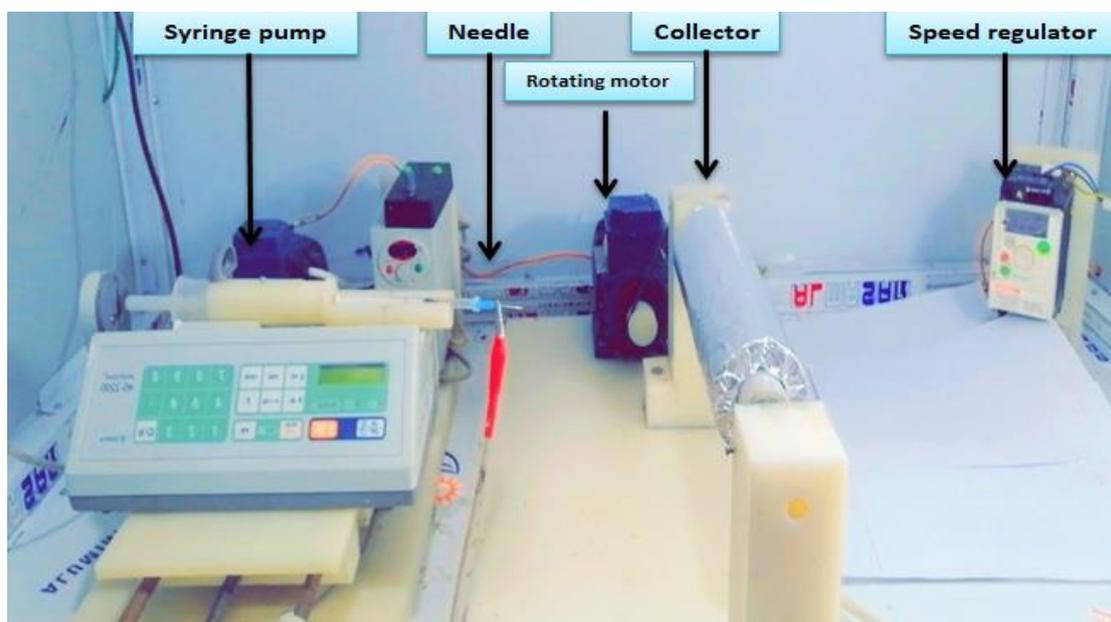


Figure (3.4) Electrospinning device

Here, in this method, pre-perforated aluminum foil will be used, which will be wrapped around the rotating collector in the device. At the end of the process, membranes of nanofibers will be produced stable over the perforated aluminum foil. The purpose of this procedure is to facilitate the use of these membranes later in the filtration process. As shown in the figure 3.5 which shows the shapes of nanofiber membranes that have been produced . In addition to the table (3.6) that shows codes and compositions of these membranes

Table 3.1 Codes and Compositions of Membranes

Membrane code	PVDF: PAN: TTIP(w/w)
M1	00:100:00
M2	20:80:00
M3	40:60:00
M4	60:40:00
M5	80:20:00
M6	100:00:00
M7	57:38:5
M8	PVDF:AOPAN:TTIP 60:40:00
M9	PVDF:AOPAN:TTIP 57:38:5

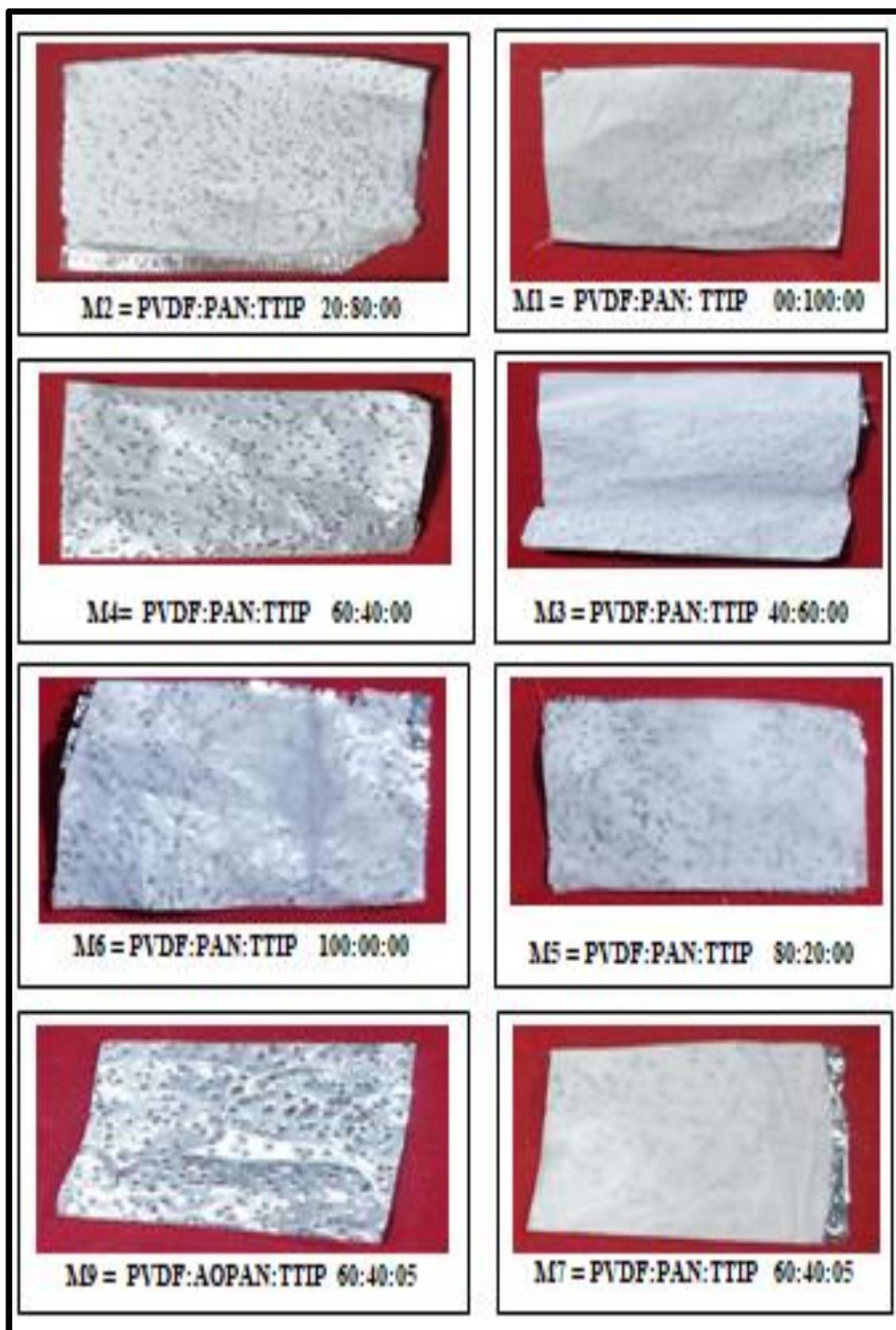


Figure (3.5) The shape of Nanofiber Membranes produced by Electrospinning

3.5 FILTRATION

The device used in the filtration process, as shown in Figure (3.9), consists of the following parts:

- Small pump of Taiwanese origin (Maximum Output Pressure 125 PSI), Voltage/Amps: 24V DC/0.23 A).
- Two pressure gauges (Pressure Gauge 150 psi)
- The membrane cell, which is a basin with dimensions of 3 cm (25 x 8 x 8) made of stainless steel (type 304). The membrane cell consists of three channels, nanofiber membranes are placed inside these channels.
- Polymeric connecting valves and pipes that withstand high pressures (Maximum pressure 300 psi).
- A cylindrical tank with a diameter of (20) and a height of (30 cm) to carry the solution required to be filtered.
- An aluminum box with dimensions of 3 cm (110 x 40 x 40) in which the above components are installed.

The nanofiber membranes are installed inside the membrane cell, then we provide the device with the electricity source and operate it, and after the device is set up within the required pressure limits until the device is stable within this pressure, then the time periods are recorded and the quantities of the filtered solution are measured.

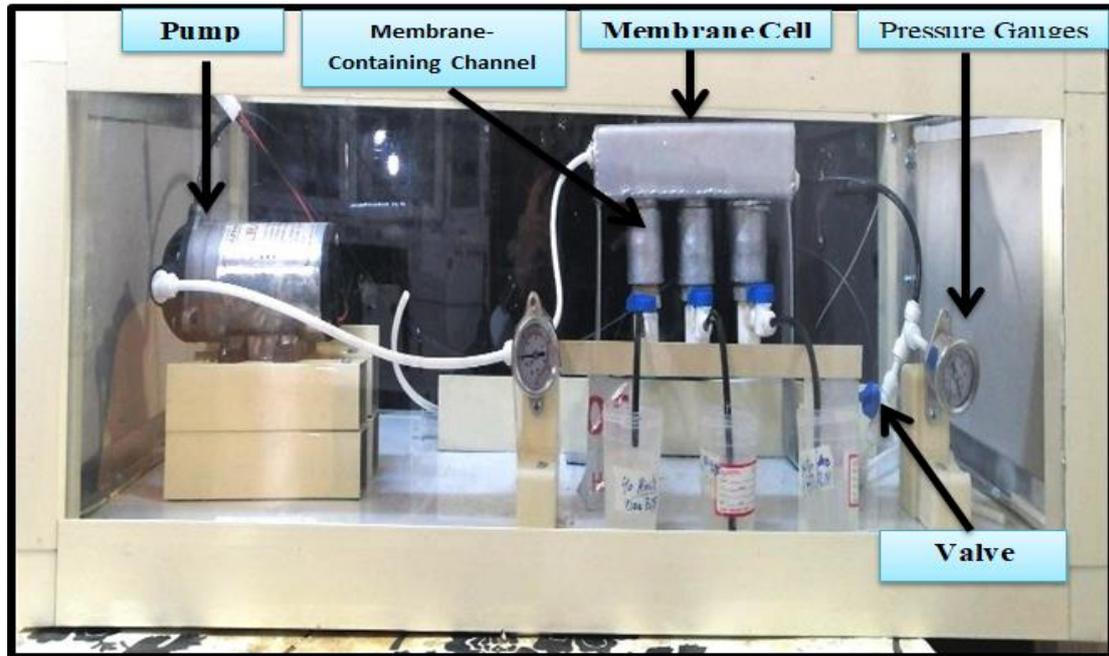


Figure (3.6) Filtration Device

3.6 Tests

3.6.1. Surface Tension test

By using the device TEN202 (JZYW-200B) SURFACE INTERFACIAL TENSIOMETER available in the materials engineering laboratories of the University of Babylon / Iraq, the surface tension of all solutions used in this study was measured, according to ISO 1409, using a platinum ring, it is immersed in the solution in a cylindrical petri dish, and then slowly the ring is pulled up across the surface. We note that when the ring is pulled up, part of the solution sticks to the ring in the upper surface area of the liquid, and therefore the device will measure the surface tension of the solution in (mN/m) unit. The figure (3.7) below shows the shape of the device TEN202(JZYW-200AL)



Figure (3.7) TEN202 (JZYW-200AL)

3.6.2 Viscosity test

Brookfield DV-III Ultra Rheometer available in the laboratories of the College of Materials Engineering at the University of Babylon / Iraq, according to ASTM D7395, where this device was used to measure viscosity and shear rate in units of (mPa.S), (s^{-1}) respectively. In addition to finding the relationship between shear stress and shear rate. The figure (3.8) below shows the shape of the device.



Figure (3.8) Brookfield DV-III Ultra Rheometer

3.6.3 X-ray diffraction (XRD) test

Due to the importance of the crystalline properties, as they are considered among the most important properties that determine the efficiency of the produced nanofibers, an X-ray diffraction test must be performed to identify and evaluate these properties. Device (D8 Bruker, Germany) shown in Figure (3.9) was used to determine the crystalline properties, which include crystallinity rate and crystalline size. This test was performed in Iran by CAC Laboratories.



Figure (3.9) XRD (D8 Bruker, Germany)

3.6.4 Field-Emission Scanning Electron Microscopy (FE-SEM):

By using field-emission scanning electron microscopy (FE-SEM) (MIRA3 TESCAN- FRANCE) according to ASTM E2809-22 , shown in Figure.(3.10) ,the topography and the morphologies of nanofibers , which are the basis for the manufactured Membranes, was investigated and characterized. A well-defined characterization of size, diameter and shape of the manufactured nanofibers and the extent of good specifications of these fibers are the main factor that determines the efficiency of the membranes and the extent of their effectiveness in industrial applications. This test was performed in Iran by CAC Laboratories.

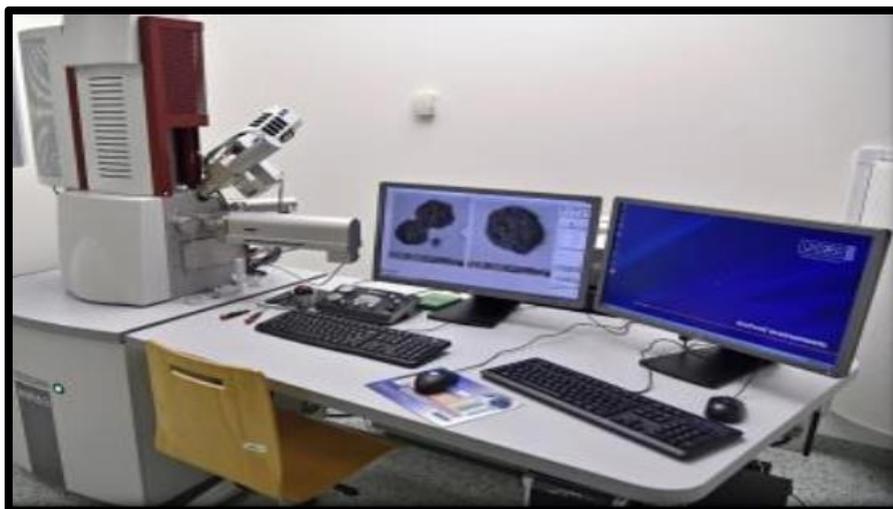


Figure (3.10) Field emission scanning electron microscopy (FE-SEM)

3.6.5 Fourier Transform Infrared Spectroscopy (FTIR)

In order to know the interactions that occur between the polymer blend in addition to determining the functional groups present in the material and analyzing the chemical composition of the nanofibers, used the Fourier-transform infrared spectrophotometer (FT-IR) (Spectrum two, PerkinElmer, USA), according to ASTM E168, shown in Figure.(3.11).

This test is a common analytical method for analyzing the chemical composition of materials and providing valuable information on the efficiency of nanofibers. This test was performed in Iran by CAC Laboratories.



Figure (3.11) (FT-IR) device

3.6.6 Thickness Test

By using a coating thickness gauge of the type (TT260, TIME GROUP Inc) as in Figure (3.12) available in the laboratories of the College of Materials Engineering at the University of Babylon / Iraq, several readings were taken from different places for a small piece taken from the manufactured membrane. This piece represents a sample with dimensions of (2cm*2cm) and by taking an average of these readings, the approximate value of the used membrane thickness was obtained.



Figure (3.12) coating thickness gauge device

3.6.7 Atomic Force Microscopy (AFM) Test

The surface topography of pure and blends membranes nanofibers measured by atomic force microscopy (Naio AFM 2022, Nanosurf AG, Switzerland) as in Figure (3.13) and roughness surface properties were measured by Mountains SPIP® Academic 9.3.10249 software.

Through the high-resolution imaging technique provided by this test, we were able to test the nanofiber membranes and know their properties with a very high accuracy. This test was performed in Iran by CAC Laboratories.

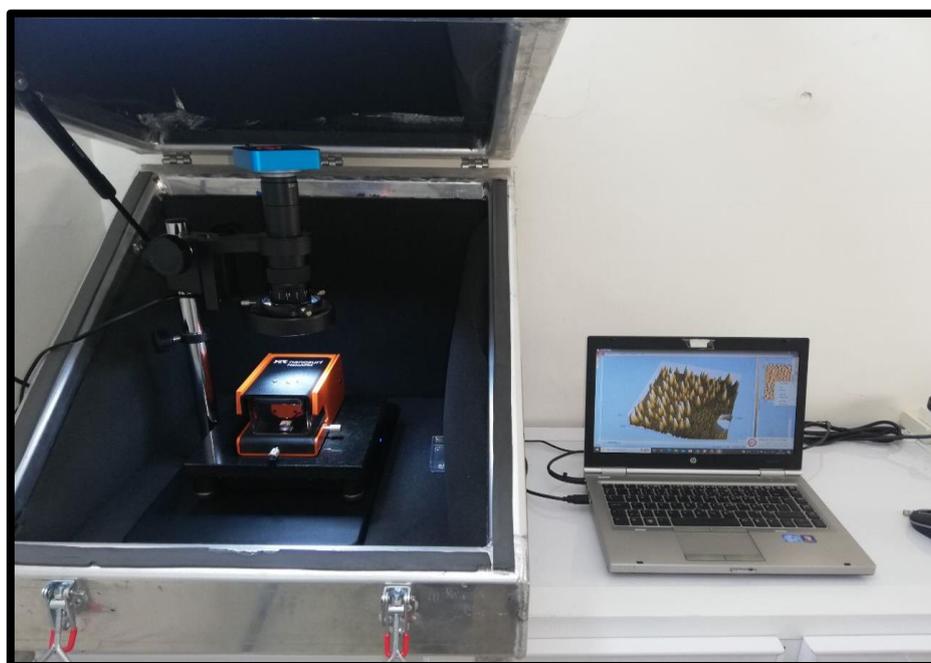


Figure (3.13) Atomic Force Microscopy

3.6.8 Differential Scanning Calorimetry-Thermogravimetric Analysis

Differential scanning calorimetry-thermogravimetric analysis (DSC-TGA, SDT Q600 V20.9 Build 20), the average error of thermal effects was $\pm 3\%$ and Netzsch melting enthalpy was calculated using the Proteus program, as in Figure (3.14). The DSC-TGA technique is a powerful tool for studying the thermal properties of materials, TGA

(Thermogravimetric Analysis) can be used to study its thermal stability and decomposition temperature of a sample, whereas DSC (Differential Scanning Calorimetry) can be used to study the glass transition temperature and melting point

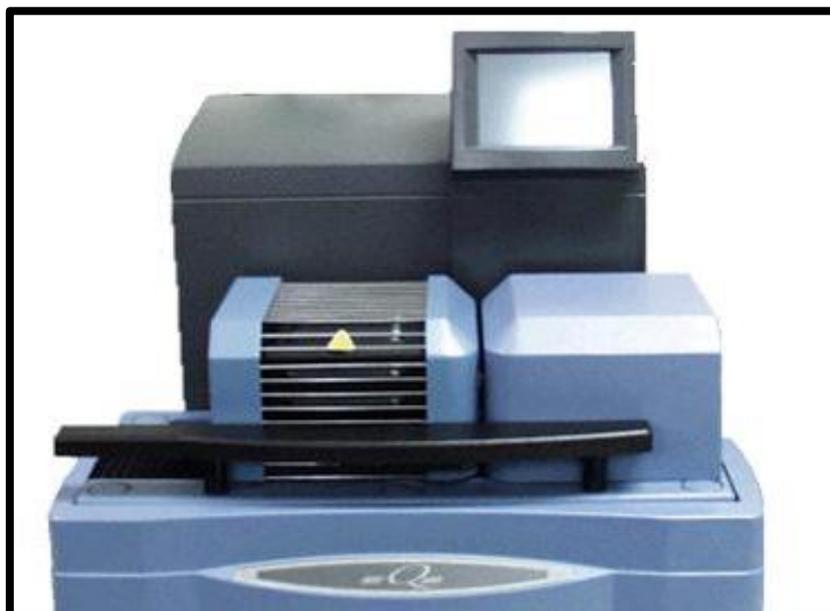


Figure (3.14) (DSC –TGA) MODEL SDT Q600

3.6.9. UV-Visible Spectrophotometer

By a UV-Visible spectrophotometer (UV-1800 Shimadzu-Japan) as in Figure (3.15), available in the laboratories of the Faculty of Materials Engineering at the University of Babylon / Iraq, which was used to determine the light absorption of the sample. Through this device, the optical absorption spectra of the solutions were measured.

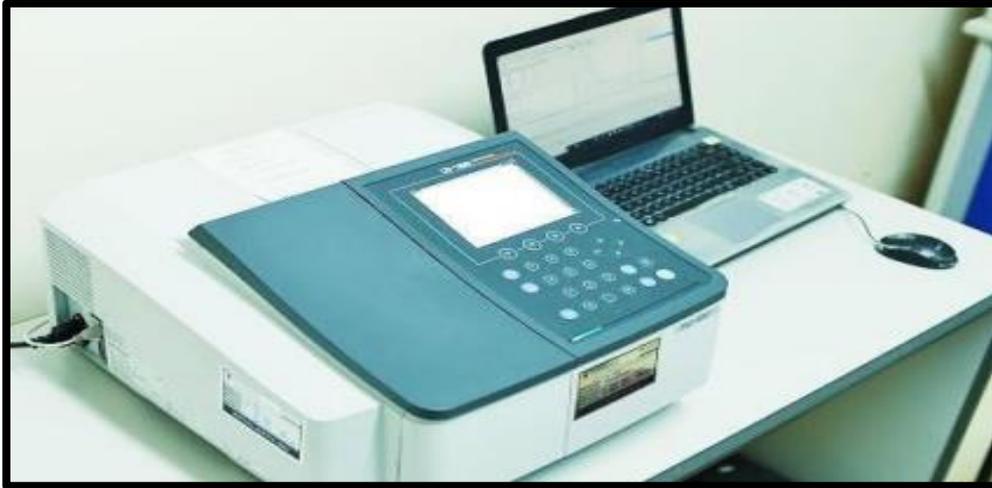


Figure (3.15) UV-1800 Shimadzu-Japa

3.6.10. HACH DR2800 Spectrophotometer

Using the HACH DR2800 Spectrophotometer of Indian origin and located in the laboratories of the Al-Muaymira sewage station in Babil province, the concentrations in the produced water samples were tested.



Figure (3.16) HACH DR2800 Spectrophotometer

3.7 Test and Evaluation of Nano-Fibrous Membranes

In order to achieve the desired goal of this study, which includes the production of high-performance membranes, attention and focus must be paid to the subject of testing and evaluation. the Figure (3.17), represents the types of tests used in the evaluation :-

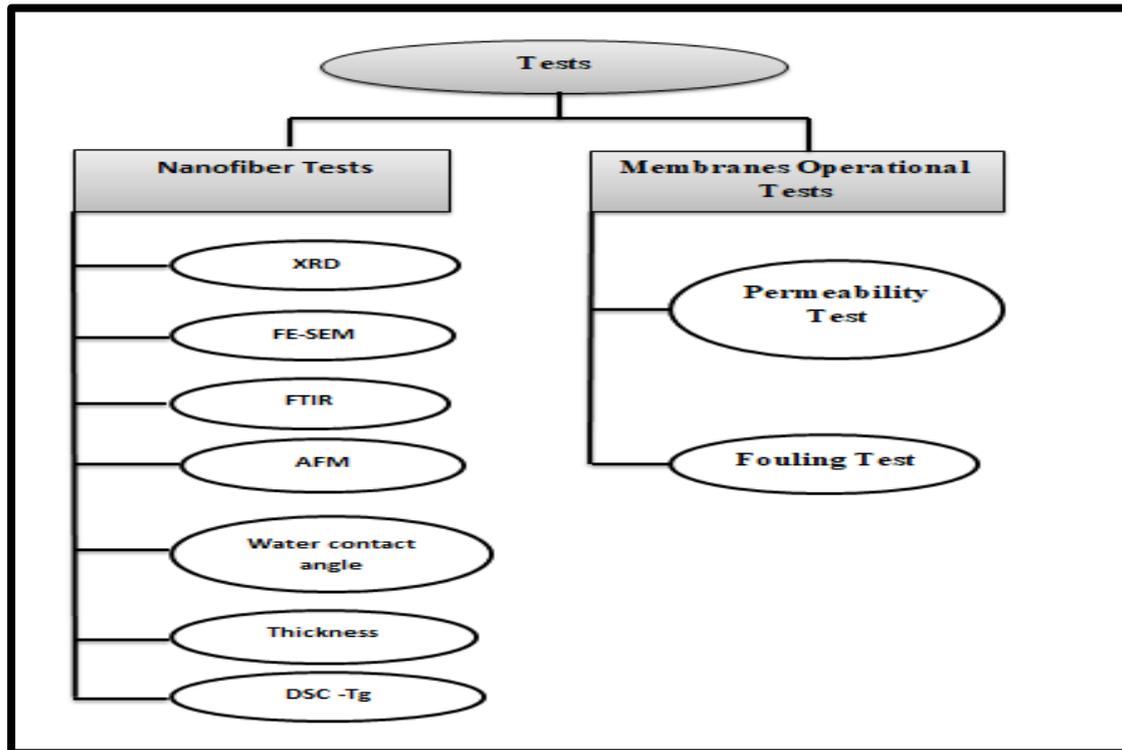


Figure (3.17) types of tests used in the evaluation

3.7.1 Nanofiber Tests

These tests include each of (XRD, FE-SEM, FTIR, AFM, Water contact angle, Thickness, DSC-TGA), which was previously discussed in this chapter under Paragraph No. (3.6).

3.7.2 Membranes Operational Tests

These tests are considered a very important part of the membrane filtration system in order to ensure that the system works efficiently and effectively and to maintain the continuity of this efficiency for the longest

possible period ,the membrane operational tests performed include the following:-

3.7.2.A. Permeability Test

Permeability and pollutant rejection are among the most important parameters used to determine the membranes performance. Ultrafiltration (UF) was used for PVDF: PAN membranes where partial permeability occurs during the separation process. Constant operating parameters were used as room temperature, specified period of time (20 minutes), operating membrane pressure of 30 Psi, and $(25 * 10^{-5} \text{ m}^2)$ a membrane area, pure water flux before used dry milk protein (J_{w1}) was calculated by using Eq. (3-1) [184]:

$$J_{w1} = \frac{V}{A.t} \quad (3-1)$$

Here (J_{w1}) is Pure water flux before used dry milk protein (L/m²h), **V** the volume permeate (L), **A** is the membrane area (m²) and **t** is the time (h). In order to calculate the amount of rejected protein dry milk (DM) and to know the fouling behavior of the membranes, a protein solution (500 ppm) in pure water under an operating pressure of 30 Psi was used.

The separation efficiency of the membrane nanofibers can be found through the permeability of pure water and the use of dry milk protein, according to the Eq. (3-2) [185]:

$$P_w = \frac{V}{A * \Delta t * \Delta P} \quad (3-2)$$

Where, **P_w** is permeability of pure water (L/m².h. atm), **V** is the volume of permeate (L), **A** is surface area of membrane (m²), **Δt** is time of permeation (h), and **ΔP** is the operating pressure drop (atm). The protein

solution was passed through the membrane continuously for 5 hours, during this period the amount of water permeable was collected for every 30 minutes. The purpose of this is to analyze the incoming and permeable protein solution by Shimadzu UV-Vis spectrophotometer with a wavelength of 280 nm to find the concentration value of the protein solution and applied the Eq.(3-3) to calculate the protein rejection [184]:

$$SR\% = 1 - \frac{C_p}{C_f} * 100 \quad (3-3)$$

Where the % **SR** is the percentage of solute rejection, and **C_f** and **C_p** are concentrations of dry milk in feed and permeate, respectively.

3.6.2.B. Fouling Test

The rejected dry milk protein remaining in the membrane resulting from the passage of the protein solution through the membrane, where the membrane is cleaned by using Citric Acid (C₆H₈O₇) at a concentration of 2% under 30 Psi pressure for 30 minutes. Pure water is passed again under the same conditions to calculate pure water flux after used dry milk protein (**J_{w2}**). The flow recovery ratio (FRR) and the total fouling ratio (Rt) can be found, through which the fouling characteristics of the membrane can be evaluated [184].

$$FRR\% = \frac{J_{w2}}{J_{w1}} * 100 \quad (3-4)$$

Since FRR: flux recovery ratio, J_{w1}- initial pure water flux, J_{w2} -pure water flux after fouled [186].

$$Rt\% = 1 - \frac{J_p}{J_{w1}} * 100 \quad (3-5)$$

where R_t is Total fouling ratio, J_p is fouled flux

After completing the tests for each of the permeability and pollution and obtaining the values of each of them, then the values of each of the Porosity and Average Pore Size are found as shown below :

- Porosity and Average Pore Size :-

The porosity of membrane was done by using **dry-wet method** . This is done by immersing the membrane samples in pure water for 24 h, after which these samples are wiped with tissue paper and then weighed the mass (g) of membrane at equilibrium with pure water (W_{wet}). The samples are entered into a vacuum oven at a temperature of 70 °C for a period of 4 hours until a constant mass (g) is obtained, which is the dry mass (W_{dry}). The porosity (%) of membrane was limited according to the following relation [185]:

$$\varepsilon = \frac{W_{wet} - W_{dry}}{V \rho_w} \times 100\% \quad (3-6)$$

Where, ε is the porosity (%), V is the membrane volume (cm^3), ρ_w is the water density (1 g/cm^3). On the other hand, the average pore radius of membrane was calculated by using the Guerout-Elford-Ferry relation [190]:

$$r = \sqrt{\frac{(2.9 - 1.75\varepsilon) * 8\eta IQ}{\varepsilon * A * \Delta P}} \quad (3-7)$$

Where, r is the pore radius of membrane (m), η is the water viscosity at 25 °C, I is the membrane thickness (m), Q is the permeate water volume per time (m^3/s), A is the area of membrane (m^2), ΔP operating pressure (Pa).

3.8 APPLICATION

The produced water (PW) is the salty water that comes out to the surface during oil and gas production processes and is also called formation water, salinity is a characteristic that distinguishes the produced water, and salinity means the concentration of salt in the water and is referred to as TDS. Produced water considered one of the causes of pollution because it contains dangerous pollutants of organic and inorganic materials, so attention is required to treat this water before it is discharged to avoid environmental damage, and among the methods used in treating this type of water is the separation technique that based on filtering [186]. The produced water has many different chemical and physical properties. These properties differ according to the geographical location of the field, its formation, and the type of hydrocarbon product [187,188].

Ultrafiltration (UF) is one of the well-known and common filtration methods (MF, NF, RO), compared to these common methods, ultrafiltration is the most effective method for treating produced water due to its ability to remove oils at a high rate and does not require chemical additives nor the use of high pressures and thus low energy costs in addition to that it does not need a wide area to work [189].

Filtering the produced water is the application used in this thesis to test the manufactured membranes and find out the extent of their success and efficiency. Samples of the produced water were brought from one of the evaporation basins located in the Halfaya oil field (Halfaya oil field - Al-Kahla'a area - Amarah city - Missan province) and preliminary tests were conducted on the samples before filtration in the laboratories of Al-Qasim University the Al-Muaymira sewage station (Hilla city - Babil province - Iraq) .

Chapter four

Results and Discussion



4.1. Viscosity and contact angle

Viscosity is one of the main parameters influencing the properties of nanofiber membranes, such as the fiber diameter, porosity, and pore size of the membrane fibers, especially when blending polymers such as PVDF and PAN [195,196]. Increasing the content of PVDF in the PVDF: PAN solutions led to an increase in the blend solution viscosity. Since the viscosity of pure PVDF is higher than that of pure PAN, a decrease in the homogeneity of the polymer solutions occurs with increasing PVDF content in the mixture. These results agree with those of a previous study [190].

The highest value of viscosity was observed with the M4 and M5 membranes when increased the PVDF contents from 20% to 80 % in PVDF: PAN, while increased the viscosity when modify the PAN to AOPAN in PVDF: AOPAN and after adding the 5wt.% from TiPP to PVDF : AOPAN :TiPP. Figure (4.1) shows the viscosity and water contact angles of pure PVDF, pure PAN, and different PVDF: PAN blends as a function of the PVDF content in the membrane. To endow the films with better properties and performance, it is necessary to determine whether the films are hydrophobic or hydrophilic. An increase in surface wettability is an indication of a decrease in the contact angle on the film surface. Many research studies have focused on the contact angles of PVDF films as well as pure PAN. An increase in the contact angle depends on increases in the PAN concentrations of the polymeric solutions [193]. In addition, the surface of the PAN membrane was more hydrophilic than the surface of the PVDF membrane, and the contact angles of the blended membranes were less than the contact angles of the pure membranes. Thus, the blended membranes had a more hydrophilic surface than the surfaces of the pure polymer membranes. The surfaces of

membranes M3 and M4 displayed the best hydrophilicity .On the other hand, the modify of PAN to AOPAN lead to decreased the contact angle and produced nanofiber surface more hydrophilicity specially at M9 (PVDF: AOPAN: TiPP) in spite of high nanofiber diameter, this result agree with previous study [194] .

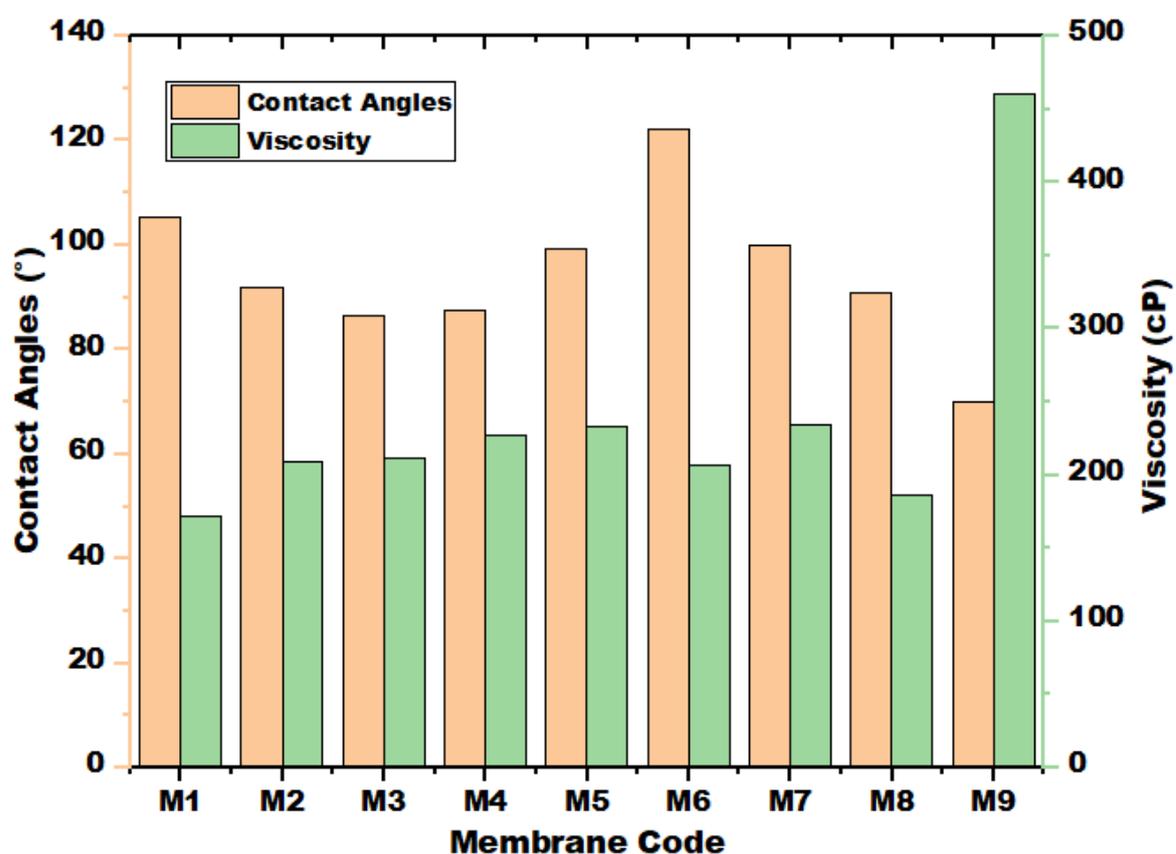


Figure (4.1) Viscosity and water contact angles of the pure PVDF, pure PAN, different PVDF: PAN, modify bend, and composite blends membranes as a function of the PVDF content sorted according to membrane code

4.2. Morphological Properties

To evaluate the properties of the electrospun membranes, the microscale test was performed on the produced membrane samples on single fibers because of the difficulty and high cost of this type of assessment [192]. Field emission scanning electron microscopy (FE-SEM) was used to observe the upper surface at a certain magnification to determine the morphological properties of the membranes, such as diameter (nm), pore size (μm^3), and porosity (%), which were measured by Image J software. The porosity of the membranes can be calculated by comparing the average pore volume with volume from the FE-SEM image using the following equation [195]:

$$\Phi = \frac{V_p}{V_{\text{total}}} * 100 \quad (4-1)$$

where Φ is porosity, V_p is volume pore, and V_{total} is volume total.

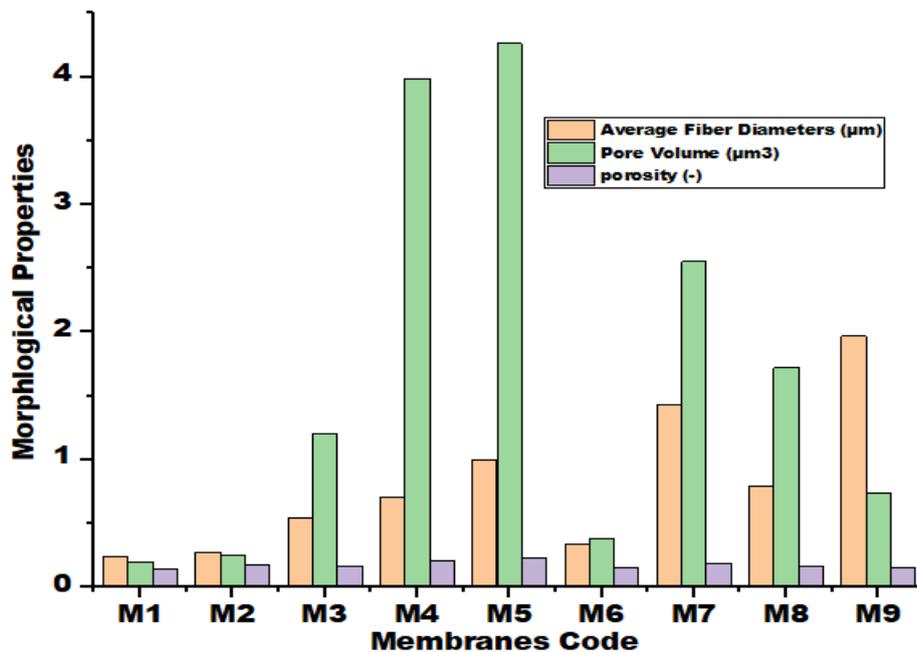


Figure 4. 2 Average nanofiber diameters, pore volumes, porosity of the pure and blended, modify bend , and composite blends membranes as a function of PVDF content in the PVDF: PAN nanofibers.

According to previous studies, there is a direct relationship between the diameter of the fibers and the porosity and diameter of the pores, the porosity increases with an increase in the fiber diameter, or increasing the diameter of the fiber increases the size of the pores [196].

Figure (4.2) shows the average nanofiber diameters and pore volumes of the pure and blended membranes as a function of PVDF content in PVDF: PAN nanofibers M1, M2, M3, M4, M5, M7, M8, and M9. The viscosity results clearly show that the viscosity of polymeric solutions rises with an increase in PVDF content for membranes M1 to M6, and increased after modified the PAN to AOPAN by reaction with hydroxylamine hydrochloride and after adding the 5 wt.% of Tipp since there is a direct relationship between viscosity and fiber diameter [197], significant increases in the diameter, pore size, and porosity from 0.275 ± 0.075 to 0.996 ± 0.044 μm , 0.248 ± 0.00416 to 4.261 ± 1.068 μm^3 , and 0.165 ± 0.036 to 0.224 ± 0.07 (261.664%, 875.107%, and 35.75%), respectively, were observed when the content of PVDF increased from 20% (M2) to 80% (M5) as a result of the increased solidification rate with increasing PVDF content.

While Figure (4.3) show the 10 μm scale bar of the FE-SEM images for pure PAN , modify PVDF: AOPAN , and composites blends nanofibers as PVDF: PAN: TiPP and PVDF: AOPAN: TiPP, the FE-SEM image increased the nanofiber diameters after modified blend (60:40 PVDF: PAN to 60:40 PVDF: AOPAN) and after added the 5 wt.% of TiPP to blend and modify blend at M7 and M9 , after modified the PAN to AOPAN by reaction with hydroxylamine hydrochloride and after adding the 5 wt.% of TiPP since there is a direct relationship between viscosity and fiber diameter [31], significant increases in the diameter as shown in figure (4.2), from 0.704 ± 0.075 to 0.976 ± 0.044 μm and decreased the pore size, and porosity from 3.987 ± 0.11416 to 1.721 ± 0.068 μm^3 , and 0.21 ± 0.036 to 0.168 ± 0.07 respectively .

FE-SEM images show an increase in the diameter of the nanofibers, in addition to an increase in the density of the fibers, especially when adding Titanium isopropoxide (TiPP) to the blend, as well as an intertwining of the nanofibers, and their formation resembles a necklace when developing the blend, which leads to filling voids and a decline in pore size, and porosity, in spite of the significant increase in fiber diameter :

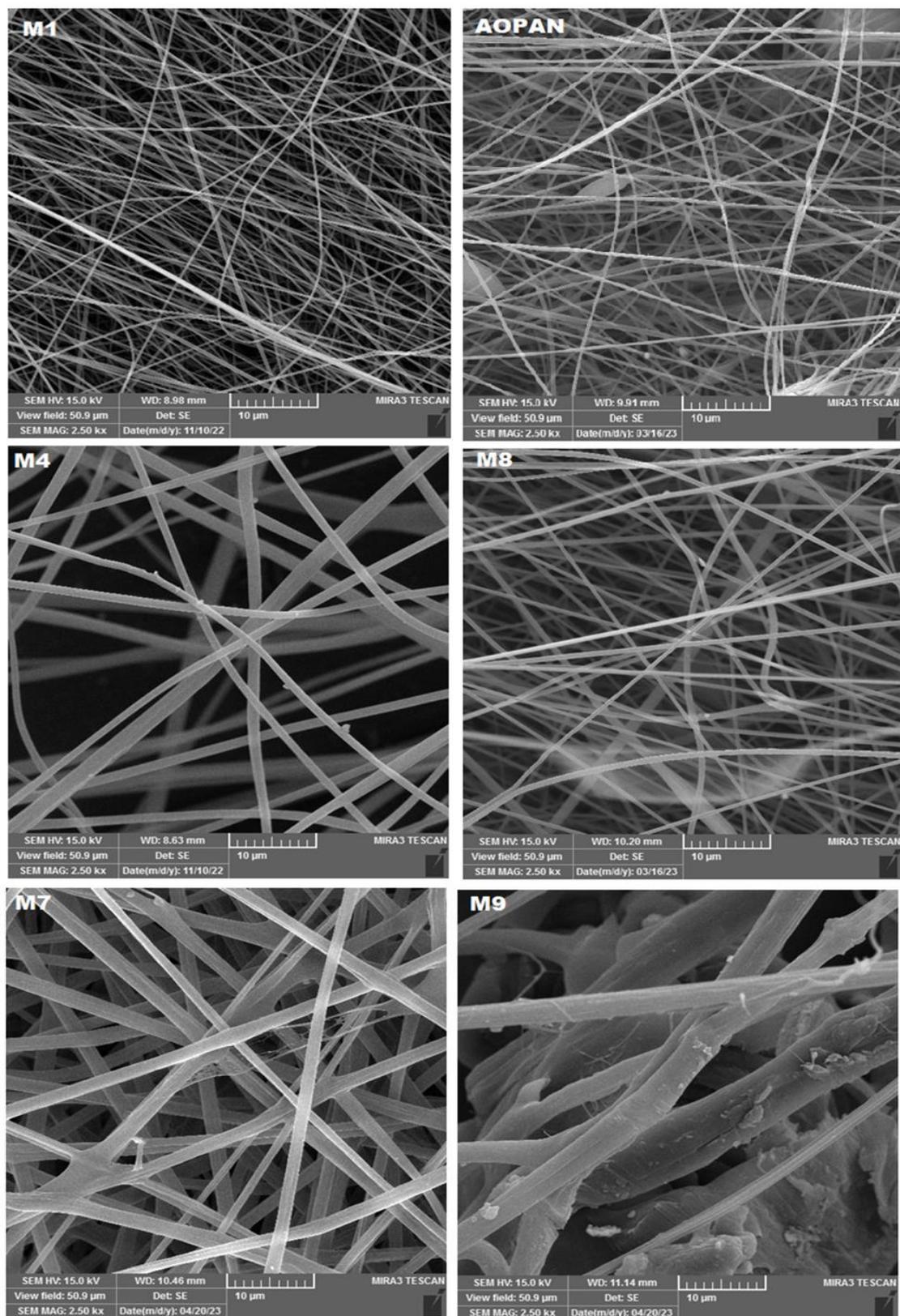


Figure 4.3 show the 10 μm scale bar of the FE-SEM images for pure PAN (M1), modify PVDF: AOPAN (M8), and composites blends nanofibers as PVDF: PAN: TiPP (M7) and PVDF: AOPAN: TiPP (M8) respectively.

On the other hand, from the FE-SEM images at the 2 and 20 μm scale and energy dispersive X-ray spectroscopy (EDX) analysis for M1, M4, M8, M7, and M9. It is possible to display the atomic results of nitrogen, carbon, oxygen and fluorine, where the full nitrogen is from PAN at M1 and the full fluorine is from the PVDF polymer at M6.

These results also confirmed that the atomic percentage of fluorine increased with the addition of PVDF to the blend, as shown in Figure (4.4). Additionally, membrane M4 contains both of the weight and the atomic percentages of nitrogen and fluorine in PAN and PVDF, respectively. On the other hand, after adding the titanium isopropoxide (TiPP) to 60:40 PVDF: PAN at M7, the composite nanofibers contained the nitrogen, carbon, oxygen, fluorine, and titanium, while the after modify and added the titanium isopropoxide (TiPP) to the PVDF: PAN to PVDF: AOPAN: TiPP at M9, the composite modify blend contains the nitrogen, carbon, oxygen, fluorine, titanium, and chlorine .

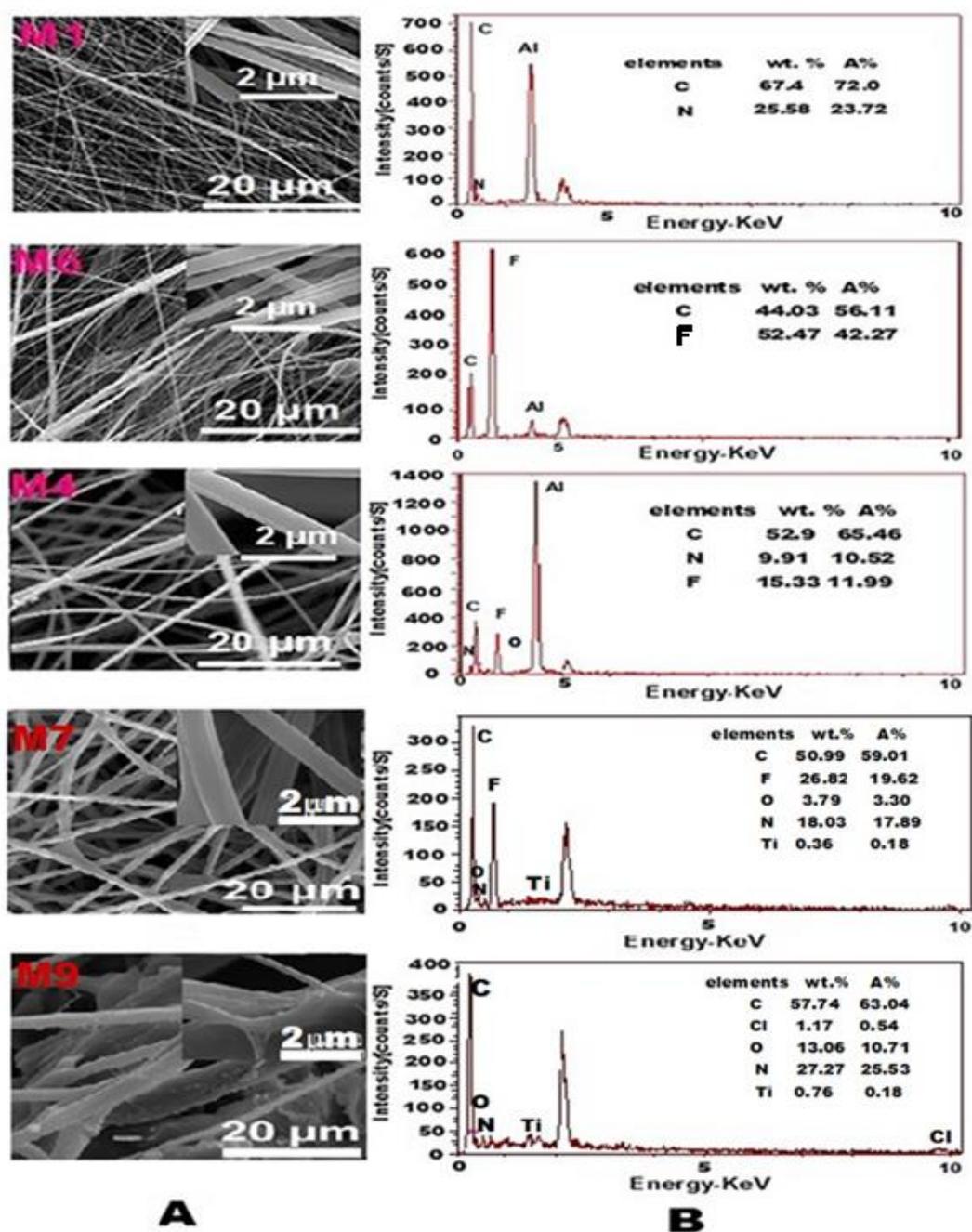


Figure 4. 4 (A) FE-SEM images (2 and 20 μm) and (B) energy dispersive X-ray spectroscopy (EDX) analysis of pure polymers at (M1 and M2) , blend polymers M4 , composite blend M7 , and modify composite blend M9 of the membrane nanofibers.

4.3. FTIR Analysis

Figure 4.5 shows the FTIR spectra of the samples in the range from 500 to 4000 cm^{-1} to determine the structural characterization of PAN, PVDF, and the PVDF/PAN blend. The FTIR spectrum of the PAN nanofibers showed peaks at approximately 2925 cm^{-1} , 2244 cm^{-1} , 1735 and 1,666 cm^{-1} , which were assigned to the stretching vibrations of CH_2 , $-\text{C}\equiv\text{N}$, $-\text{C}=\text{O}$, and $-\text{C}=\text{N}$ groups, respectively. The peaks at approximately 1460 and 1270 cm^{-1} represent the different vibrations of CH and C-O, and the peak at approximately 3618 cm^{-1} represents the C-H stretching band [198-200]. Additionally, the FTIR spectrum of pure the PVDF nanofibers presented peaks at approximately 487 and 531 cm^{-1} , representing the α -phase, and the peaks at approximately 838, 1184, and 1274 cm^{-1} correspond to the β -phase and the α -phase and β -phase indicate that the PVDF nanofibers are semicrystalline [201]. The characteristic peak is approximately 1,173 cm^{-1} is the symmetric stretching of the $-\text{CF}_2$ group, and the peak at 876 cm^{-1} is specific to the C-F stretching “vibration of the amorphous phase [202]. The spectral peaks at approximately 2240, 1735, and 1250 cm^{-1} are due to $-\text{C}\equiv\text{N}$, $-\text{C}=\text{O}$, and C-O in the PAN polymer, while the peaks at approximately 840 and 880 cm^{-1} denote the C-C-C and CF stretching vibrations of PVDF. In the blend, we noted that the nitrite group peak shifted from 2244 to 2240 cm^{-1} when the atomic % of fluorine increased in the PVDF: PAN blend. We also found new peaks at approximately 1182 and 1665 cm^{-1} , which were assigned to the stretching vibrations of C-N and C=N groups [204,206]. Other words, the FT-IR spectra of PVDF:AOPAN :TiPP apparent immersion a new peaks at 1043 and 1665 represented the stretching vibrations of N-O and C=N, but reducing in the absorption peaks in AOPAN spectra such as reduced the peak of $-\text{C}=\text{N}$ groups to 2242 cm^{-1} , the peak of CH stretching in CH,

CH₂ at 2936 and 2871 cm⁻¹, peak at 3359 related to hydroxyl groups peaks corresponding to Ti-O from 454 cm⁻¹, the absorption peaks as C=O stretching at 1735 and C=O groups in primary amines (NH₂) 1665 cm⁻¹ and shifting the symmetric stretching of the -CF₂ group of PVDF from 876 cm⁻¹ to 879 cm⁻¹ [22,206,207]

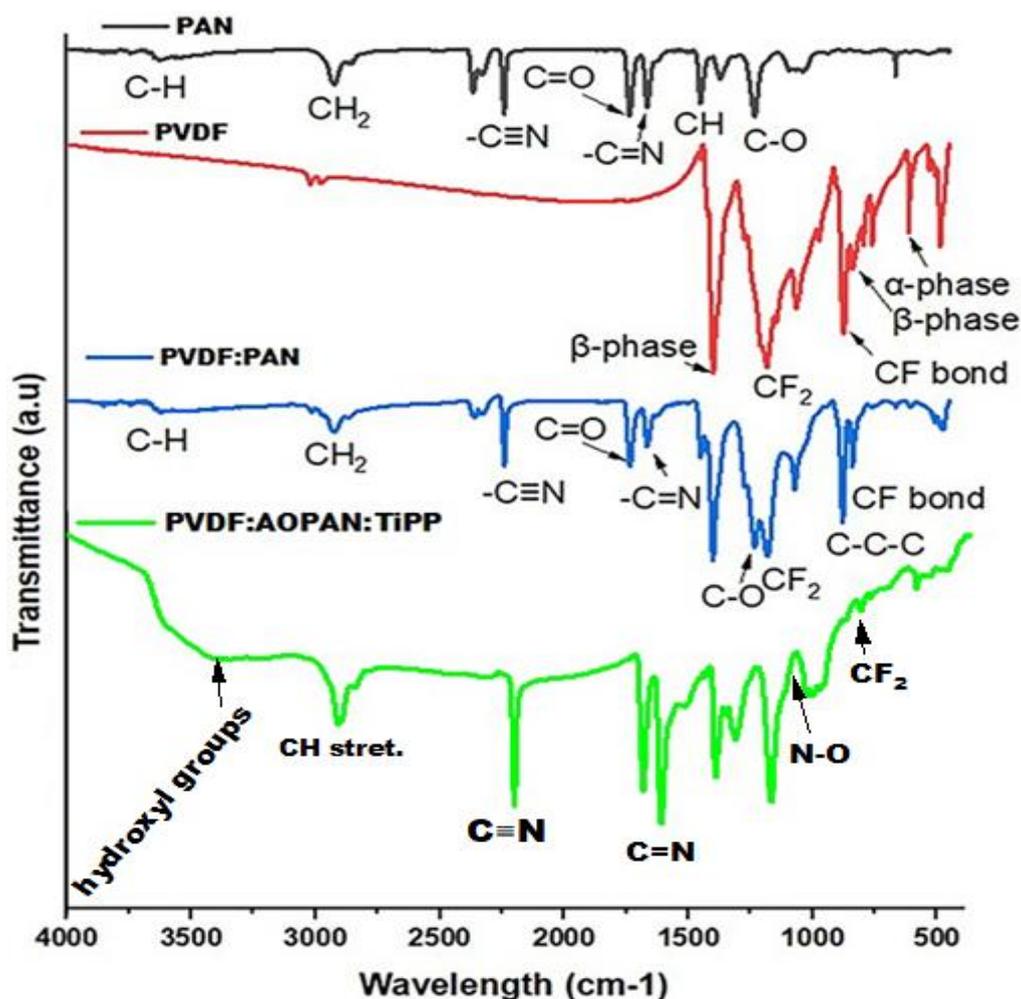


Figure 4.5 FTIR spectra of pure PAN and PVDF, PVDF/PAN, PVDF: AOPAN: TiPP composite blended nanofibers.

4.4. X-ray Diffraction (XRD) Analysis

X-rays are specialized for measuring crystalline properties such as crystallinity percentage and crystalline size. Figure 4.6 and Table 4.1 show the scattering of X-rays and crystalline properties such as average crystalline size and percent crystallinity for the manufactured membranes. All sample membranes for pure polymers and blend showed broad peaks at 2θ of 20.4533, 20.5024, and 17.8942 for M1, M4, and M6, respectively according to d-spacing 0.1186, 0.1516, and 0.1349 Å as shown in Table 4.2. The increasing of PVDF content caused an increase in the average crystalline size and percent crystallinity of the membrane compared with the crystalline properties of pure PAN. The best crystalline properties for the blended membranes were observed with M4. Increasing the content of PVDF in PVDF: PAN caused an increase in crystallinity because PVDF is semicrystalline and contains both the α -phase and β -phase, which enhanced the polarity of the electrons around the fluorine atom [201]. On the other hand, the samples of membrane after adding the titanium isopropoxide (TiPP) to PVDF: PAN caused the increment in the average crystalline size and percent crystallinity were 35.43 and 22.08% respectively. While the effect of addition the titanium isopropoxide (TiPP) to modified blend nanofibers membrane (PVDF: AOPAN) were 77.39 and 30.62% at M9 compared with these properties at M4. The chemical reaction between the hydroxylamine hydrochloride and PAN: DMF solution with present of sodium carbonate at 70 °C to produce the Amidoxime polyacrylonitrile (AOPAN) and immersion a new bands lead to stretch vibration of C–N, stretching vibrations of N–O, and C=N groups, which contribute to the success of the conversion of PAN to AOPAN, these results are agree with previous studied [208,209].

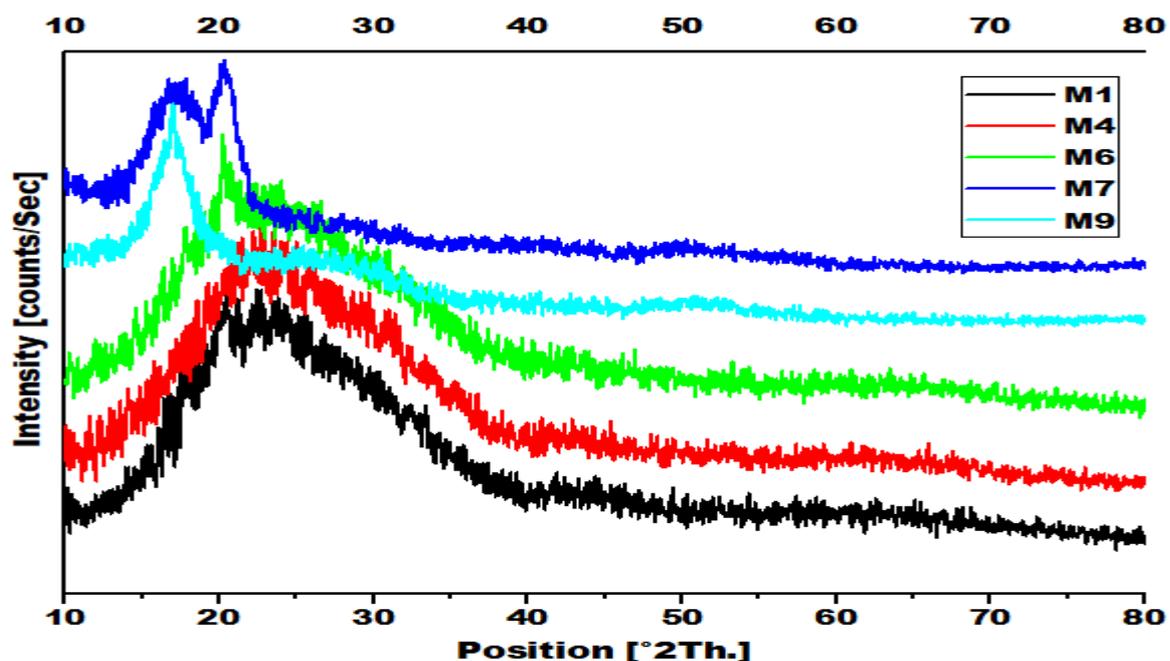


Figure 4. 6 XRD patterns of the membrane samples for pure polymers at (M1 and M6) , blend polymers at M4 , composite blend at M7 , and composite modify blend at M9 respectively .

Table (4.1) the crystalline properties of the membrane samples.

Membrane Code	Pos. [°2Th.]	d-spacing [Å]	Crystalite Size [nm]	Crystallinity [%]
M1	17.725	0.1186	21.76	21.74
M4	22.675	0.1516	35.43	22.08
	20.175	0.1349		
M6	24.025	0.1602	55.45	25.10
	16.725	0.1112		
	20.275	0.1355		
M7	50.275	0.3271	58.34	28.62
	16.975	0.1136		
	25.475	0.1698		
M9	44.275	0.2901	77.39	30.62

FWHM: Full width at half maximum

4.5. Thermal Properties

To characterize the membranes that were manufactured and to determine which has the best performance in terms of thermal properties, differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) was used over the heating range of 30.8 to 980.90 °C, as shown in figure (4.7). The exothermic DSC thermograms showed that the thermal behavior of the nanofibers changed in the membrane samples.

It was observed that increasing the content of PVDF in the PVDF/PAN nanofibers leads to an improvement in the thermal decomposition, as the temperature of decomposition increased from 323.28 to 486 °C for pure PAN [211] to pure PVDF, while the required heat capacity for fusion increased from 145.6 to 706.6 J/g for M1 to M5 since the thermal stability of PVDF is higher than that of PAN. In other words, the TGA thermographs showed that the decrement in weight loss was 18.4% when the PVDF content was increased from pure PAN (M1) to 60% (M4) [203,211].

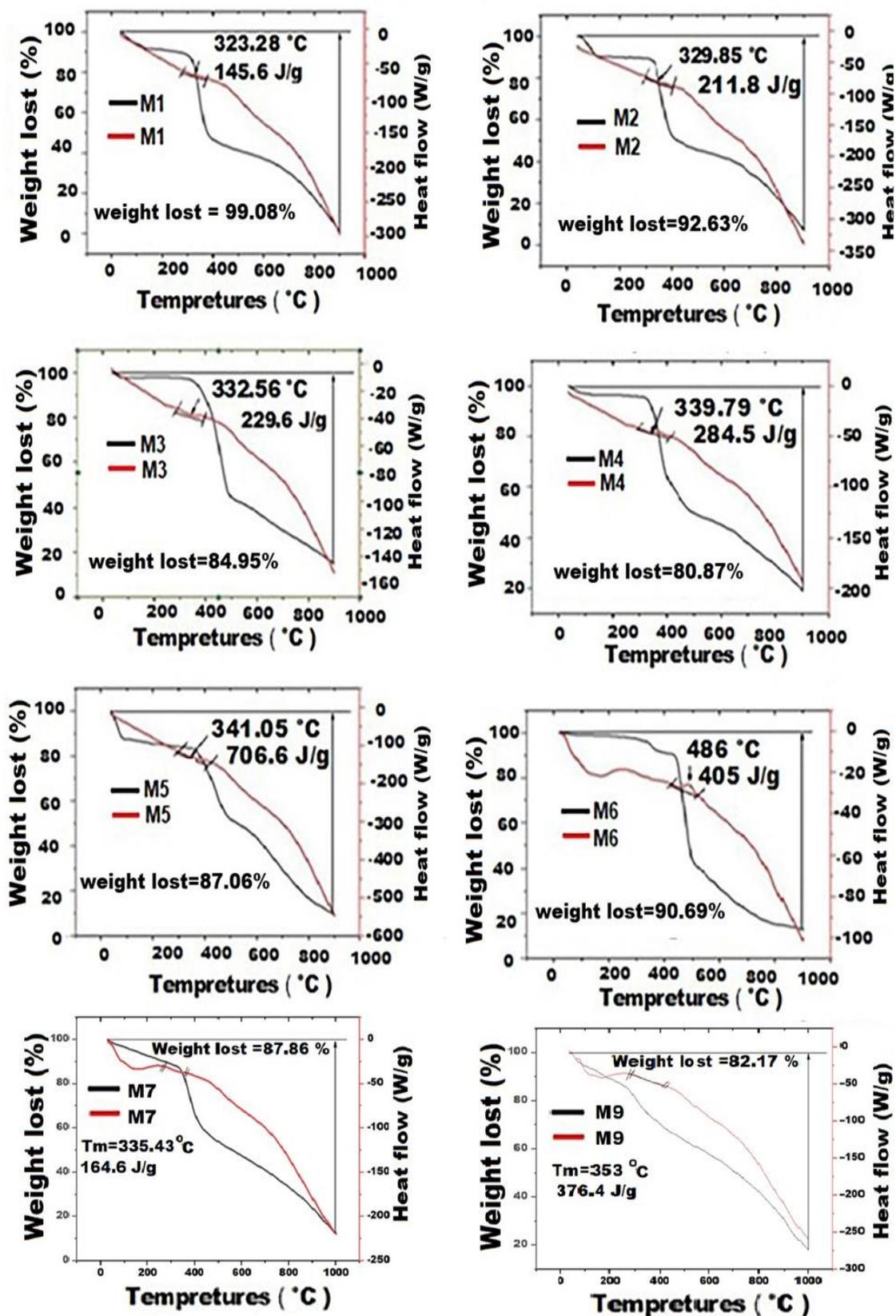


Fig. (4.7) DSC-TGA thermograph analysis of the pure and blended membrane samples

4.6. Effect of Dry Milk Protein on the Filtration Efficiency of the Membranes

4.6.1 Effect of Dry Milk Protein on Surface Topography

Surface roughness and mean pore depth are important parameters that were studied by AFM. Figure (4.8) shows the effect of dry milk protein on the surface topography via 2D and 3D AFM images of the pure and blended membrane nanofibers before and after dry milk protein was used.

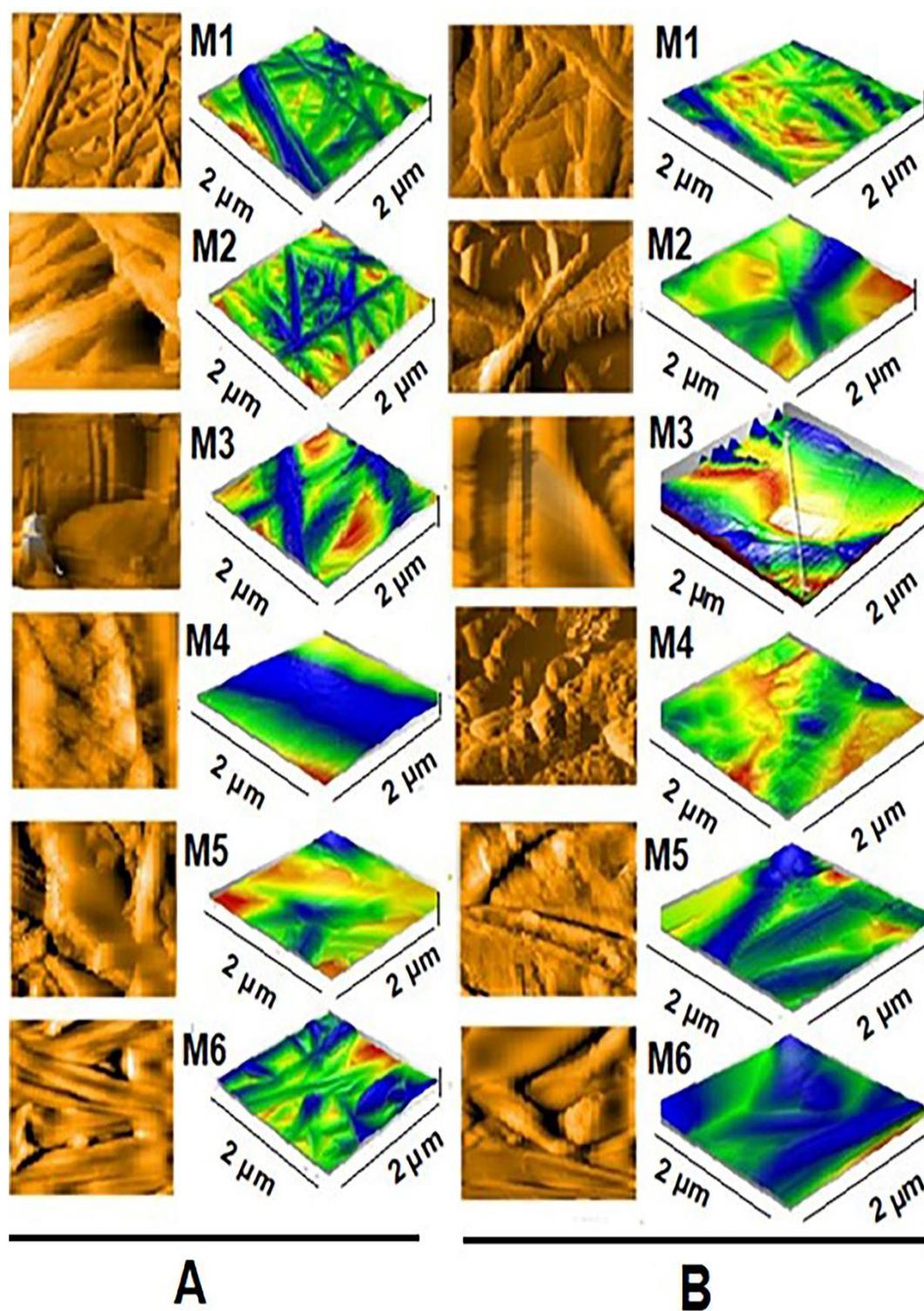


Fig. (4.8) The effect of protein (DM) on the surface topography of the pure and blended membrane nanofibers, (A): AFM images (2D and 3D) before using dry milk protein, (B): AFM images (2D and 3D) after using DM protein.

The AFM images prove that there was a clear change in the topography of the membrane surface after using dry milk protein, as the gaps between the nanofibers were closed or reduced in size in most of the membranes with dissolved protein materials, especially membranes M3 and M4. Table 4.2 shows the surface roughness, mean pore depth, and percent reduction in mean pore depth of the pure and blended membranes before and after using dry milk protein. The root mean square (RMS) and the mean roughness (Sa) on the surfaces of the blended membranes were higher than those on the pure membranes because surface roughness depends on the increase in the diameter of the nanofiber [212]. Additionally, the RMS values for PAN and PVDF were 278.0 and 384.1 nm, respectively, while the RMS of M5 was 592.9 nm, and membranes with less surface roughness have better antifouling properties [213]. In addition, the highest percent reduction in mean depth (RMD) is desirable, as it indicates the ability of the membrane surface to reject protein materials and provide high filtration efficiency, and the RMD% of M3 and M4 were 75.17 and 82.51%, respectively.

Table (4.2) Surface roughness, mean pore depth, and percent reduction in mean pore depth before and after using dry milk protein for the pure and blended membranes.

Membrane Code	RMD (%)	A (nm)			B (nm)		
		RMS	Sa	MPD	RMS	Sa	MPD
M1	33.37	278.0	220.9	80.99	259.3	206.5	53.96
M2	67.19	303.2	237.0	318.1	515.1	412.8	116.1
M3	75.17	451.0	360.8	353.9	634.7	446.2	123.2
M4	82.51	435.2	334.2	397.6	843.8	613	69.53
M5	20.65	592.9	465.9	496.2	628.7	455.3	252.4
M6	29.88	384.1	299.4	192.4	635.3	443.7	134.9

A: Surface roughness and mean pore depth before using dry milk protein;

B: Surface roughness and mean pore depth after using dry milk protein.

RMD: Reduction in mean depth, RMS: Root mean square, Sa: Roughness average, MPD: Mean pore depth.

4.6.2 Dry Milk Protein Rejection and Membrane Permeability

To calculate the amount of rejected dry milk protein (DM) and to determine membrane contamination, six standard solutions of DM in RO water were generated at room temperature at concentrations of, 100, 200, 300, 400, 500, and 600 ppm to construct a calibration curve, as shown in Figure (4.9A). Linear fitting of the curve gave R^2 value of 0.9681, as shown in figure (4.9B). The DM concentration can be calculated using the following equation:

$$C(\text{ppm}) = \frac{\text{Absorbance}(\text{a.u.}) - 0.2455}{0.0048} \quad \dots (4-2)$$

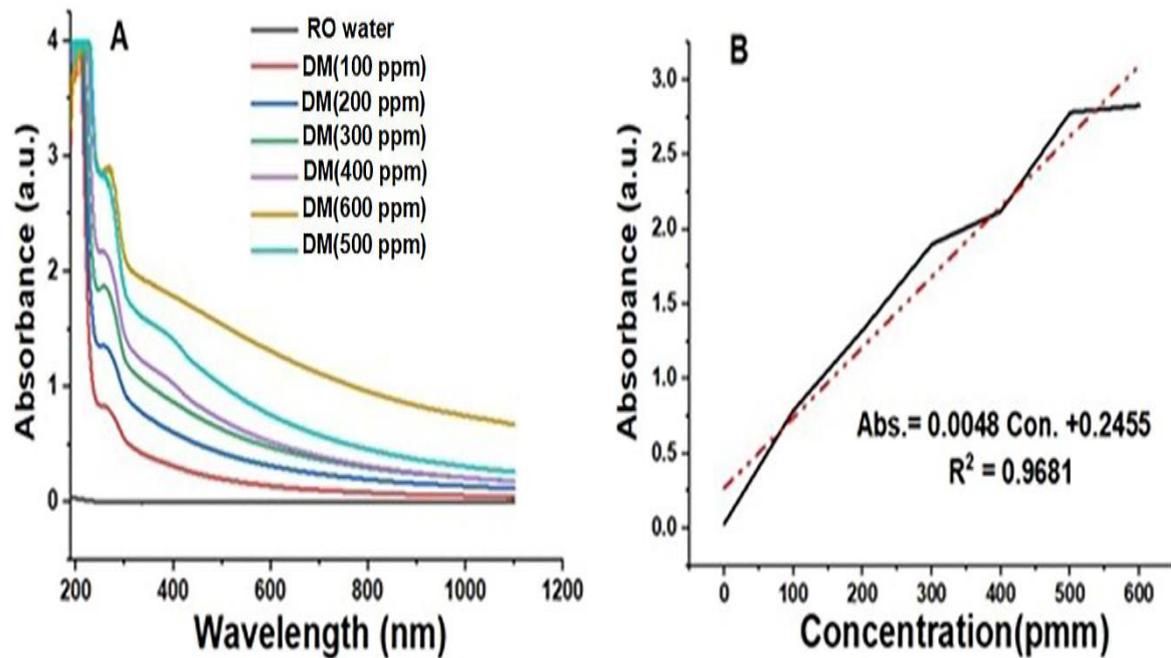


Fig. (4.9) (A): UV–VIS spectra and **(B):** calibration curve for the determination of DM concentration using standard samples in reverse osmosis water

Figure (4.10) The pure water flux before using dry milk protein (J_{w1}) and the pure water flux after using dry milk protein (J_{w2}) for the pure and blended membranes. According to the surface wettability results, the pure membranes made of both PAN and PVDF have high contact angles with water because both polymers had a relatively high concentration (12 wt.%). Since the contact angle increases with increasing concentration, the polymer blends have low contact angles compared to those of each polymer, and the surfaces of the membranes change from hydrophobic to hydrophilic between M3 and M4.

In addition to the EDX analysis, the atomic number of fluorine and the nitrile group were close between M4 and M3. Thus, M4 and M3 have the highest pure water flux before using dry milk protein as well as after, and these results prove the separation efficiency of these membranes. Therefore, blending PVDF with PAN led to an improvement in the flux of the membrane and the percentage of porosity [214]. On the other hand, after reinforcement of the blend nanofibers membrane at M4 (60:40 PVDF: PAN) with 5 wt.% of Tipp and reinforcement of the modify blend membrane at M9 (PVDF:AOPAN:TIPP) a perient high water flux with more wettability specially at M9 .

Table (4.3) The flux recovery ratio, solute rejection, total fouling ratio, and porosity of the membranes and their pore size before and after using dry milk protein.

Membrane Code	FRR (%)	Sr (%)	Rt (%)	Porosity (%)	A (µm)	B (µm)
M1	42.04	46.83	61.18	60.96	0.0245	0.0160
M2	67.28	39.33	60.35	62.41	0.0344	0.0240
M3	72.0	44.58	56.26	63.31	0.0300	0.0231
M4	84.32	44.63	51.53	67.79	0.0293	0.0269
M5	52.27	46.10	68.94	49.49	0.0473	0.0342
M6	50.64	36.33	70.88	58.12	0.0327	0.0233
M7	59.97	87.84	46.95	34.5	0.0420	0.0366
M8	53.0	88.4	65.96	28.9	0.0368	0.0347
M9	91.79	89.61	8.108	18.4	0.2355	0.2303

FRR: Flux Recovery Ratio; **Sr:** Solute Rejection; **Rt:**Total Fouling Ratio; **A:**Pore Size Before Dry Milk Protein Use; **B:**Pore Size After Dry Milk Protein Use

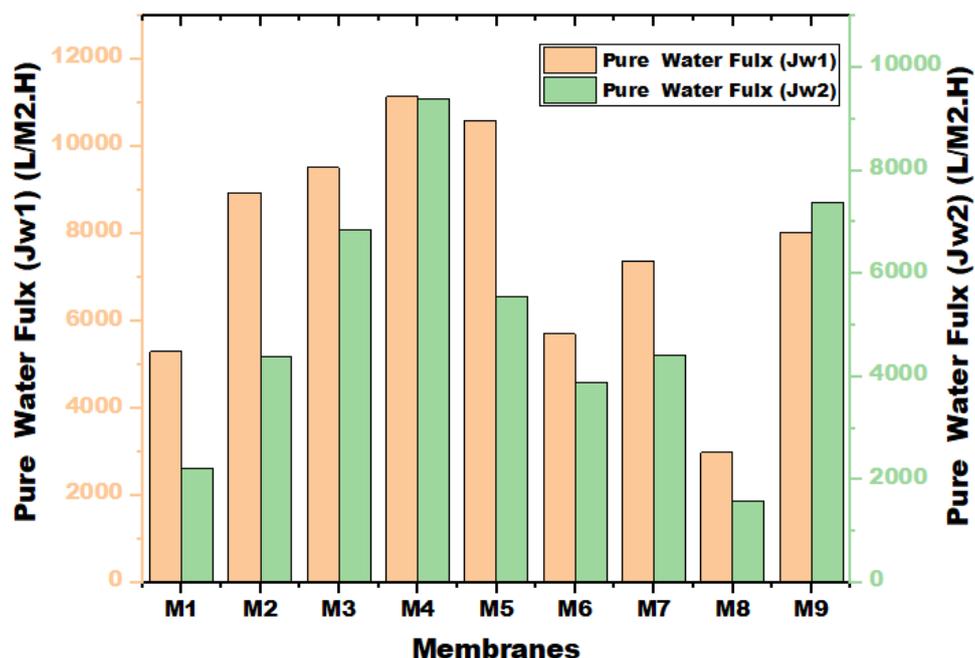


Fig. (4.10) Pure water flux before using dry milk protein (Jw1) and pure water flux after using dry milk protein (Jw2) for the pure and blended membranes.

In addition, Table 4.3 shows the results of the flux recovery ratio, solute rejection, total fouling ratio, and porosity assessments in addition to the pore size before and after using dry milk protein. M3 and M4 have the highest recovery ratios of 72 and 84.32% due to their high porosities of 63.31 and 67.79%, respectively. Additionally, there were small changes in their pore sizes after using dry milk protein, 28 and 15.68%, respectively. These results were accompanied by lower percentages of total fouling and dissolved material rejection than the sample with the highest percentage of total fouling (Pure PVDF) because the balance between the atomic and weight ratios of PAN and PVDF in the M3 and M4 blends limited the adhesion of protein material on the surface of the membrane and reduced the efficiency of the membrane in the filtration process [215]. Therefore, the decrease in flux led to an increase in the rejection of dissolved materials [216].

After one hour of DM application, the flux at M4 was 2,828 ($L/m^2.h.atm$), while the flux at M6 was 353 ($L/m^2.h.atm$), as shown in Figure (4.10). These results prove that the incorporation of PAN in the PVDF: PAN membranes not only increases the hydrophilicity and enhances the flux but also helps to enhance the return of the membranes to a higher flux [193]. Finally, a membrane that has good performance should have a good rejection ratio and suitable permeability [216]. After reinforcement of the blend nanofibers membrane at M4 (60:40 PVDF: PAN) with 5 wt.% of Tipp and reinforcement of the modify blend membrane at M9 (PVDF:AOPAN:TiPP) , we noted the highest flux recovery ratio and solute rejection at M9, because the nanofibers of this membrane had low contact angle and high water contents and permeability, in addition of this membrane had low pore size and porosity in spite of the large diameter of nanofibers. According to the above results the membranes M4 and M9 represented the best membranes filtrations efficiency.

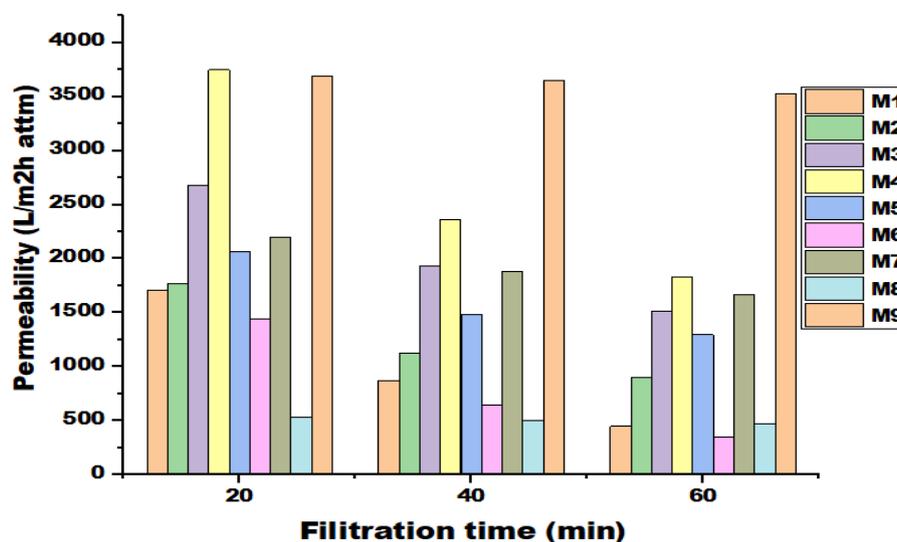


Fig. (4.11) Permeability as a function of filtration time for the pure and blend membranes.

4.7 Application

The work was carried out by using 10 liters of produced water associated with crude oil extraction operations in the Halfaya oil field in Maysan Province, southern Iraq. The filtration unit was operated for half an hour and 30 Psi operating pressure. Membranes (M4 and M9) were used, because they have the highest flux recovery ratio for the purpose of water treatment from the pollutants listed in the table (4.4), the result was that the membrane is the best as it works to purify the water from pollutants was M9. The normal range of pH for irrigation water is from 6.5 to 8.4 according to the standards of the Food and Agriculture Organization [217]. And the water sample used is within this range and has been reduced to a lower level by means of a membrane (M9). In addition, the pollutants such as NO₂ ions, total suspended solids (T.S.S), and Cyanide (CN) were reduced their concentrations with suitable concentration according to international Standards as (Law 93/1962: Law 93/1962 for Discharge of waste waters provided by food and agriculture organization (FAO), PML: Permissible Maximum Limit in wastewater, world health organization (**WHO**) [218,219]. On the other hand , the concentration rate of SO₄ ions was reduced to 337.4 ppm for the purpose of using it for irrigation purposes , this results was agree with pervious study [217] .

Table (4.4) shows the results of water treatment by blend membrane (M4) and composite modify blend membrane (M9).

No	Pollutants	A	B	C	D	Ref.
1	pH	6.69	6.34	6.18	6.5-8	[223]
2	T.S.S	54	54	29	25-150	[218,219]
3	Cl ⁻¹	135525	104967	103872	200-300	[220]
4	NO ₂	1.4	1.1	0.8	3	[218,219]
5	C.O.D	6975	5700	2900	120-1100	[219]
6	SO ₄	467.4	345.6	337.4	200-400	[220]
7	CN	0.4	0.044	0.025	0.2-2	[219]
8	Cr	0.3	0.3	0.25	5	[222]
9	Cu	4.3	4.3	3.35	40	[222]
10	EC (μS/cm)	3200	3000	2000	0-3000	[221]
11	T.D.S	315000	132370	123220	500-1500	[220]
12	Cd	1.91	1.67	1.62	1.476-2.236	[221]

A:Feed Water (ppm);B:Permeable water from M4 (ppm); C: Permeable Water from M9 (ppm); D: FAO/WHO irrigation standards

During the work on the treatment of the produced water, it is required that the focus be more on each of the salts and minerals, because their concentrations are high and harmful, and they have the characteristic of accumulation and accumulation in the long term, and they are not suitable for agricultural or irrigation works, unlike the other components that are represented by hydrocarbons, which are distinguished by their organic nature that allows them to biologically deteriorate in the soil [224].

Chapter five

Conclusions and Recommendations



5.1 Conclusions

The main problems that limit the efficiency of nanofiber membranes is the fouling that occurs after treatment with dissolved protein materials, as well as the concentration and quality of the fouling.

- In this study, dry milk was utilized, as it is the main source of protein materials. In addition, the incorporation of PAN nanofibers in the PVDF: PAN membranes improved the physical properties and filtration efficiency of PVDF nanofibers to improve the wettability of the membrane surfaces and convert them from hydrophobic to hydrophilic despite the increase in the viscosity of the blend.
- The blend PVDF with PAN led to increases in the diameters of the nanofibers, pore volume, porosity, and surface roughness compared with pure polymer nanofiber
- Converting polyacrylonitrile to amidoximized polyacrylonitrile after adding hydroxylamine hydrochloride led to obtaining nanofibers with a high ability to adsorb some heavy metal ions (CN, Cr, Cu, SO₄).
- The EDX test show the equilibrium state between the atomic number of fluorine and the atomic number of the nitrile group in PVDF and PAN, respectively at M4 .
- Blending PVDF with PAN enhanced the crystalline and thermal properties of PAN, in contrast to the clear increase in the flux recovery ratio and the pure water flux before and after using dry milk protein.
- M4 and M9 having a lower percentages of total fouling and rejection of dissolved materials compared with pure PVDF, which had the highest percentage of total fouling.

- The specifications of the developed composite membrane (M9) are characterized by a large pore size despite the significant increase in the diameter of the fiber, but at the same time the fibers have a high density, which reduces the size of the voids between them, as well as its enjoyment of a low contact angle compared to the M4 membrane.
- M9 also has a high water flux and a high flux recovery ratio.
- M9 and M4 membranes were used for the purpose of treating water produced during oil extraction operations, and the results of the developed composite membrane (M9) was better .

5.2 Recommendations

The researcher recommends using the results of this work for the purpose of using it in the following applications:

- The use of developed and composite membranes to remove heavy metal ions from industrial water such as copper, nickel and cadmium ions.
- The use of membranes in the fields of gas purification
- As an inhibitor for the occurrence of crosslink in AOPAN solution, potassium hydroxide (KOH) can be added instead of sodium carbonate, then after adding it to the solution, it is stirred continuously at a temperature of 70°C for two hours to obtain AOPAN..

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يعتبر العراق من الدول النفطية المهمة في العالم، ومن المعروف أن صناعة النفط تصاحبها منتجات ثانوية لها آثار بيئية ضارة، ومن بين هذه الملوثات هو الماء المنتج (PW). تعتبر المياه المنتجة أحد أسباب التلوث لاحتوائها على ملوثات خطيرة من مواد عضوية وغير عضوية لذا يجب الاهتمام بمعالجة هذه المياه قبل تصريفها لتجنب الأضرار البيئية والسعي لاستغلال جزء من الكميات الكبيرة الناتجة عن هذه المياه ومحاولة استثمارها لأغراض الري، ومن الطرق المستخدمة في معالجة هذا النوع من المياه، تقنية الفصل التي تعتمد على التصفية.

في تطبيقات الترشيح الفائق (UF)، من المهم جدًا استخدام أغشية ألياف نانوية بولي أكريلونيتريل (PAN) وبولي (فلوريد فينيلدين) (PVDF).

في هذه الدراسة، تم إنتاج ألياف نانوية غشائية مصنوعة من بوليمر البولي أكريلونيتريل النقي، بوليمر البولي (فلورايد فينيلدين) النقي، مزيج من كلا البوليمرين بواسطة تقنية الغزل الكهربائي وبمحتويات مختلفة من البولي (فلوريد فينيلدين) في كل مزيج للحصول على ستة أنواع من الأغشية وهي (M1, M2, M3, M4, M5, M6) وكما يلي (0:100), (20:80), (40:60), (60:40), (80:20), (100:0).

بعد إيجاد أفضل نسبة خلط للأغشية الستة المصنعة أعلاه من حيث النفاذية ومعدل استرجاع التدفق والملوثات، تم التركيز على تطوير هذه النسبة باستخدام جزيئات المواد النانوية والتفاعلات الكيميائية الخاصة من أجل الحصول على أفضل أداء عمل للغشاء المصنع، لذلك تم إنتاج ثلاثة أغشية أخرى (M7, M8, M9) بمحتويات مختلفة من (PVDF: PAN: TiPP), (PVDF: AOPAN), (PVDF: AOPAN: TiPP) على التوالي.

أظهر غشاء M9 أفضل أداء من خلال النتائج التي تم الحصول عليها أثناء إجراء التطبيق باستخدام تنقية المياه المنتجة.

تم تشخيص هذه الأغشية المحضرة وذلك عن طريق المسح المجهر الإلكتروني (FE-SEM)، الفحص المجهرى للقوة الذرية (AFM)، قياسات زاوية التلامس، حيود الأشعة السينية (XRD)، قياس المسعر التفاضلي - التحليل الحراري الوزني (DSC-TGA).

فيما يخص الخصائص الفيزيائية ، تم ملاحظة ان هناك ارتفاع في لزوجة الأغشية مع ارتفاع محتوى PVDF في المزيج مقارنة بلزوجة محاليل البوليمر النقية. هذه الزيادة في اللزوجة أدت إلى زيادة في قطر الألياف النانوية وحجم المسام والمسامية بنسبة (261.664) % و (875.107) % و (114.41) % على التوالي عندما زاد محتوى PVDF من 20% في الـ (M2) إلى 80% (M5) ؛ وقد ترافق ذلك أيضاً مع زيادة في قابلية الغشاء للبلل اعتماداً على زاوية التلامس الخاصة به. بالإضافة إلى ذلك ، تحسنت الخصائص الحرارية وبلورة PAN بعد زيادة محتوى PVDF من 20% (M2) إلى 60% (M4).

علاوة على ذلك ، تم قياس كفاءة الترشيح للأغشية لتحديد نسبة الانخفاض في جريان الماء النقي ، وانخفاض متوسط العمق (RMD) قبل وبعد استخدام بروتين الحليب الجاف ، ونسبة استرداد التدفق والمسامية ، بإعطاء قيم (15.68) % ، (82.51) % ، (84.32) % ، (67.79) % على التوالي للغشاء رقم M4

من ناحية أخرى ، فقد تم تعديل PAN والحصول على AOPAN حيث أدى ذلك إلى تقليل زاوية التلامس وأنتج سطح ألياف نانوية أكثر محبة للماء خاصة في الغشاء الذي يحمل الرمز (PVDF: AOPAN: Tipp) (M9) على الرغم من قطر الألياف النانوية المرتفع وفقاً للزوجة العالية.

بعد ان تم تصنيع الغشاء المركب المطور (M9) والذي تميز بـ حجم المسام بالرغم من الزيادة الكبيرة في قطر الألياف ولكن في نفس الوقت تتمتع الألياف بكثافة عالية ، فضلاً عن تمتعها بزاوية تلامس منخفضة مقارنة بغشاء M4. في حين أن غشاء M9 امتاز بأمتلاكه نسبة استرداد التدفق وصلت الى (91.79) % ، تم تطبيق واستخدام هذه الاغشية M9 و M4 المنتجة في مجال معالجة الماء المنتج (PW) وهو الماء الذي يخرج من باطن الارض ومصاحباً للنفط الخام خلال عمليات الاستخراج ، وكانت نتائج التي اظهرها الغشاء المركب المطور (M9) أفضل النتائج بالنسبة لإزالة ملوثات المياه مقارنة بنتائج M4.



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كلية هندسة المواد
قسم البوليمر والصناعات البتروكيمياوية

إنتاج غشاء عالي الأداء من الألياف النانوية لبولي فينيلدين فلورايد للتطبيقات الصناعية

رسالة

مقدمة إلى كلية هندسة المواد / جامعة بابل وهي جزء من متطلبات
نيل درجة الماجستير في هندسة المواد / البوليمر

من قبل الباحث

وسام محمد مصطفى محمد

(بكالوريوس هندسة المواد 2009)

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