

SYNTHESIS AND CHARACTERIZATION NANOFIBERS MEMBRANE BY ELECTROSPINNING FOR ADSORPTION OF METHYLENE BLUE

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Penelitian Kolaborasi Internasional

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SYNTHESIS AND CHARACTERIZATION NANOFIBERS MEMBRANE BY ELECTROSPINNING FOR ADSORPTION OF METHYLENE BLUE

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AKHMAD ARIF JUNAIDI

FOREWORD

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Authors

ABSTRACT

Methylene blue is a cation dyestuff that is often used in the textile industry, and is susceptible to being discharged into water because, this compound is only used about 5% while the remaining 95% will be disposed of as waste. The method of handling waste that is often done is to use a membrane. One of the superior polymers used as membranes is PVDF which is thermoplastic (strong) but has a lack of rejection which is less than the maximum which is usually caused by pore size that is too small so that it can easily be blocked (fouling). To overcome this, bentonite is added to the PVDF membrane in hopes of increasing rejection. Bentonite is then dispersed into a PVDF membrane that is made by phase reversal. PVDF membranes and PVDF-Bentonite composite membranes have been successfully made with porous, hydrophobic characterization, and by adding bentonites to the polymer will reduce the contact angle. PVDF-Bentonite composite membrane was successfully made with a thickness between 0.05-0.08 mm and an average pore size below 2 μm so that it is classified as an ultrafiltration membrane. After testing the separation ability of the PVDF-Bentonite composite membrane against the sample solution, it is known that the membrane rejection coefficient under optimum conditions is at 1 bar pressure and pH 5 with a rejection coefficient value of 82.65% and permeability of 19.197 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. An increase in the rejection coefficient and permeability of the modified membrane where under the same conditions the usual ultrafiltration PVDF membrane has a rejection

coefficient of 76.45% and permeability of $8.921 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

Keyword : *nanofibers, bentonite, PVDF, methylene blue*

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CHAPTER I

INTRODUCTION

I.1. Background

Currently, the need for clean water is a big problem in various countries, including in Indonesia, this is due to polluted waters. The existence of industries with poor waste treatment and disposal systems is the cause of pollution. One of them is textile waste that is not treated and disposed of directly into the waters, whereas this textile waste is dominated by organic pollutants which are carcinogenic and difficult to degrade naturally. The processing of textile waste has been carried out by various methods, both simple and sophisticated methods. For example, waste treatment by adding certain

chemicals such as coagulant and chlorination processes, the process is able to overcome or treat existing waste but also creates new problems, namely increased operational costs due to the use of a lot of chemicals and continuously and the process produces residues in very large quantities. big too, so that over time it will develop into a source of new pollutants that are also dangerous for environmental sustainability, another way is a biological processing process that involves a bioremediation process, but it still has many shortcomings due to lack of flexibility, not maximally taking all contaminants of dye waste[1].

Various methods are used to overcome these problems, including the method of adsorption, photoelectrodegradation and membrane technology. The adsorption method is often constrained by the need for large enough adsorbents and the constraints on disposal after use, while photoelectrodegradation requires considerable energy consumption. The adsorption method has also been carried out, this method is very good for waste treatment but has a weakness, namely the ability to be reused (regeneration) is very low, so that it will result in the use of very high costs[2]. Based on the weaknesses of the above method, a method of treating waste using membrane technology was developed. Membrane technology is known as a clean and

environmentally friendly technology. The factors that encourage the use of membranes in water treatment are regulations on the treatment and supply of clean water, the increasing need for clean water, commercialization of membrane technology due to its application in the wider community, and operational costs that can be maximally suppressed with more optimal membrane manufacturing innovations [3]. The process of treating sewage using membranes has several advantages, namely that it can be said to be relatively simple, it does not use chemicals for processing, it can be applied to a larger processing scale. These advantages are the basis for the use of membrane technology for processing waste in the textile industry.

To reduce the cost of using the membrane, regeneration can be done on the membrane so that it can be used repeatedly, namely by cleaning the membrane regularly. Meanwhile, to overcome the main weakness of membrane technology, was fouling[4], it is done by selecting the appropriate filtration process according to the characteristics of textile wastewater, or by improving the membrane material used so as to minimize fouling. As in this study, improvements were made to the material properties of the membrane by adding bentonite, with the hope that it would be able to reduce fouling and increase the performance of the membrane.

Membrane technology is quite promising and water treatment using this membrane is growing rapidly because it has advantages including that it can take place in soft conditions, it is easy to scale, the energy consumption is relatively lower and the process can be carried out in a sustainable manner. Currently, the use of membrane materials and their modifications is being developed to produce superior performance. There are several types of membrane manufacturing techniques, including printing, phase inversion, stretching, and etching, resulting in membranes with different characteristics. One of the membrane manufacturing techniques that has recently attracted attention is the nanofiber membrane that has recently received special attention because of its wide potential use in various fields.

The electrospinning method is a simple way to form nanoscale fibers[5]. Since 1980 and especially in recent years nanofiber has been a promising material because it has several advantages, namely its surface area on the nm^2 scale, superior mechanical performance such as stiffness and tensile strength[6], high porosity, small pore size, light weight, high permeability. Nanofibers have a specific surface area and high porosity[7]. This property is what causes nanofibers to be widely used as adsorbents to remove heavy metal ions[8]. Nanofibers can be

applied in various applications such as wastewater treatment, food processing, pharmaceutical products[9], biomedical and membrane applications[10]. Nanofiber performance improvement is carried out through the addition of other materials (composites) or functionalization[11]. One of the promising organic polymers is polyvinylidene fluoride (PVDF) which is thermoplastic, hydrophobic and has good mechanical stability[12]. Various modifications to the PVDF were carried out to overcome the weaknesses of the PVDF membrane by mixing porous or hisdrophilic materials to improve membrane performance[4,13,14]. Some of the inorganic materials added as fillers are CuO and CaCO₃[15], ZnO[14], TiO₂[16], ZrO[17] and Mg(OH)₂[4].

Another promising material is bentonite, which is a natural mineral that has a negative charge and is abundant in Indonesia[18]. Research on bentonite as a membrane filler has been carried out and has been able to increase the mechanical properties and thermal properties of membranes. PVDF membrane modification with the addition of clay can increase the resistance of the membrane to surface abrasion[19], improve membrane mechanical properties, provide better performance[20], increase the polarity of the membrane surface and also

increase the selectivity of the membrane in the separation of dyes.

This research will develop the manufacture of PVDF nanofiber[21,22] material modified with bentonite prepared by electrospinning. The addition of bentonite to the PVDF nanofibers is expected to increase the hydrophilicity properties and increase the adsorption capacity of the nanofibers, especially against cationic dyes, namely methylene blue. This research is expected to produce a combination of new PVDF-Bentonite nanofibers membrane that provide better performance for dye adsorption in polluted waters.

I.2. The Problem of Research

- 1 How the optimum condition for synthesis of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning
- 2 How the characteristics of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning
- 3 How the performance of PVDF and PVDF-Bentonite nanofiber membrane on methylene blue absorption.

I.3. The Aim of Reserach

In general this research aims to synthesize new materials, PVDF and PVDF-Bentonite nanofiber membranes prepared by electrospinning to improve their performance for adsorption of blue methylene

Purpose specifically:

- determine the optimum condition for synthesis of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning
- determine the characteristics of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning
- determine the performance of PVDF and PVDF-Bentonite nanofiber membrane on methylene blue adsorpstiom

CHAPTER II

LITERATURE REVIEW

II.1 Dye Pollution

Pollution or pollution is defined as changes in the characteristics of air, water, and soil unwanted physical, chemical or biological that can endanger health, survival life, as well as human activities or living things others. Meanwhile, according to [23], pollution or pollution is referred to as changes in abiotic factors due to natural and caused by human activities that have exceeded the limit tolerance threshold of the biotic ecosystem. Nowadays, Rapid population growth is also driving high human needs that must be met. Pattern human life that tends to be more consumptive is a fundamental factor in the occurrence of pollution). Pollution or pollution arises

because of the presence of pollutants in an ecosystem. Pollution or pollution arises because of the presence of pollutants in an ecosystem. On Basically, ecosystems naturally have ability to neutralize pollutants present in an ecosystem so that the balance and natural harmony can be maintained. nature naturally have microorganisms as decomposers. However, if contaminants or pollutants cannot be neutralized or repaired by nature (non-recycle or non-renewable or non-degradable), then the pollutant will cause pollution or pollution. Thus, pollution can be said to occur when the amount of pollutant exceed or exceed the carrying capacity environment[24].

Contaminants that are slowly degradable Polutans, specially non-degradable ones, can harmful to the environment. Therefore, it is necessary to prevent its existence to enter the environment of water, soil, as well as air. as well as pollutant dyes. Dyes are organic compounds which absorb light in the visible region regions). The main characteristics of dyes include: the presence of a chromogen-chromophore conjugate system (electron acceptor), electron resonance (delocalization electrons of the benzene, naphthalene, or aromatic rings anthracene by binding to a chromophore (such as an azo . group) (-N=N-), carbonyl (=C=O), -CH=) group on the bond double conjugated links. System

The conjugation plays a role in the absorption of electromagnetic radiation that produces color. Existence functional groups such as amine (-NH₂), hydroxyl (-OH), carboxyl (-COOH), etc. are known as auxochromes, which are electron-donor-ionizable, can increase the solubility of dyes in water and increase the binding capacity of the dye to a material[25]

Dyes based on their properties are divided into substances anionic, cationic, and non-ionic colors. Whereas Based on their chemical structure, dyes can be classified into several groups, including: azo, nitro, indigo, anthraquinone, nitrate, and so on [26]. As for based on the color index data, the azo dyes used has a chromophore -N=N- is a class of substances the color with the largest number and widely used in various textile industries. However, the majority of substances Azo group colors are reactive and toxic..

According to [27], annually, there are more than 7 million tons of dyes synthetic dyes produced by various industry, and more than 10,000 kinds of dyes are produced for industrial use. Industrial activity that produce pollutant dyes causing increased accumulation of pollutants in water bodies cause various environmental problems. Synthetic dyestuffs are very difficult to degrade and is

very stable because it has a molecule of aromatic with a complex structure [28].

Accumulation of dye pollutants such as congo red in the aquatic environment even in large quantities a little can cause obstruction of penetration by sunlight to the water, thus interfering with the process photosynthesis and respiration in plants and affect the existing ecosystem order [29]. Meanwhile, according to [23], coloring products and various by-products contained in waste water or dust produced in industries such as the textile industry, can have serious health effects long term and damage to various vital organs (brain, heart, liver, and kidneys) and in the system human immune, reproductive, and respiratory systems. Exposure to dye pollutants directly through inhalation can cause respiratory problems such as: asthma, allergies, nausea, eye and skin irritation, and dermatitis. Meanwhile, exposure to dye pollutants directly through the food chain, can causes tuberculosis, gene mutations, cancer, and heart

II.2. Methylene Blue

Dyes are chemical compounds that can be bonded to a surface or fiber to reveal color. Dyes are widely used in various textile, paper, plastic, leather, cosmetic and pharmaceutical industries. The general grouping of dyes based on their chemical structure are: azo, anthraquinone, indigo, nitroso, nitro and triarylmethane. In addition, dyes can also be grouped based on their particle charge when dissolved in an aqueous solvent, the classifications are cationic (base dyestuffs), anionic (acidic, reactive and direct dyes) and neutral (dispersion dyes).

Dyes have high color intensity and clear appearance even at low concentrations. Dyes can affect the photosynthetic activity of aquatic biota because of the reduced intensity of light that can penetrate into the water and can also be toxic to some aquatic biota. Dyes are also carcinogenic and mutagenic to various types of organisms in the waters as well as humans. Methylene blue ($C_{16}H_{18}N_3SCl$, Mr = 319.852 g/mol) is a thiazine cationic dye (base dye) with very strong adsorption power. This compound is in the form of dark green crystals and when dissolved in water will produce a blue solution. In general, methylene blue is used in wool dyeing, paint production, textiles, paper, office equipment, cosmetics and in the field of microbiology). The use of methylene blue can cause

several effects, such as irritation of the digestive tract if swallowed, causing cyanosis if inhaled, and irritation of the skin if touched by the skin. The molecular structure of methylene blue can be seen in Figure II.1 below:

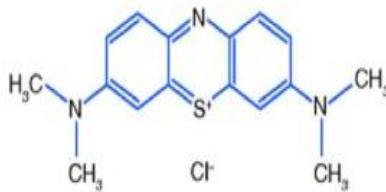


Figure II.1. Molecular Structure of Methylene Blue

II.3 Poliviniliden Fluoride

Polyvinylidene Fluoride (PVDF) has been used in many applications that use harsh chemicals (harsh chemical) since 1964 due to the chemical nature of the PVDF polymer which is inert (very stable), making it difficult for chemical reactions to occur. The difficulty of chemical reactions using PVDF polymer is what is able to increase the life time of the membrane with this material from PVDF longer than some other polymer materials. PVDF can be used for applications that require purity, strength, resistance to solvents, acids, and heat.

The molecular structure of PVDF is not symmetrical with the formula $\text{CH}_2 - \text{CF}_2$. The structural formula is as shown in Figure II.2 below:

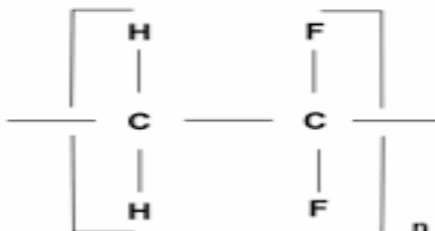


Figure II.2 Molecular Structure of PVDF

General properties of PVDF are as shown in Table II.1 below

Table II.1. General properties of PVDF

Properties	Value
Form	White Powder
Solubility	Insoluble in Water
<i>Elongation</i>	12 – 600 %
Tensile Strength	21,0 – 57,0 MPa
Modulus of elasticity	1380 – 55.200 MPa
Glass transition temperatur (Tg)	-60 – -20 °C
Melting Temperature (MT)	141 – 178°C

The properties of PVDF that support PVDF as a membrane material are as follows:

1. Crystalline Properties

PVDF has semicrystalline properties, the crystallinity is able to control the variable molecular weight, molecular weight distribution, polymerization method, temperature, and cooling rate.

2. Thermal Stability

Stability comes from the fluorine atom which has a high electronegativity and the C-F bond has a high dissociation energy

3. Chemical Resistance

In general, PVDF has stable resistance to many chemicals

4. Wide pH Range

PVDF can be used in a wide pH range so it does not require a certain pH in its use.

From the description above, it is explained that PVDF is quite superior as a polymer starting from its crystalline properties, thermal stability, chemical resistance, and can be used in a fairly wide pH range. The advantages of PVDF will be very beneficial in applications that require membrane materials with non-reactive properties. The application of PVDF membranes can be used as a polymer membrane material for water treatment, for the separation of ethanol and water[30], to protect paper relics from environmental damage[31], and others

II.4. Bentonite

Bentonite is a type of clay which found in nature which has a basic color depending on the type of fragment and the amount of mineral, ranging from brownish white, greenish or reddish.

Bentonite crystals have a plate like shape and structure

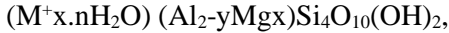
the lattice is like pyrophyllite with a negative charge at each layer unit. Cations that are around deposits of bentonite will partially fill the load the negative and the cations can be exchanged for other cations. Bentonite is light, soft, easy to absorb water, easy to be broken, with a specific gravity of about 2.4-2.8 g/mL and can function as an ion exchanger

According to [32], bentonite is a term for hydrated clay in colloidal form consisting mostly of clay minerals montmorillonite. Besides montmorillonite, bentonite contains a small amount of other mineral ingredients such as illite, kaolinite, halloysite, quartz, calcite and pyrite. The table below shows the chemical composition of montmorillonite mineral. Chemically, the mineral montmorillonite is described as hydrous aluminum silicate which contains small amounts of alkali and alkaline earth metals. Chemical structure of minerals montmorillonite in general can be written:

- a. Cation group A, consisting of Al^{+3} , Fe^{+3} , Cr^{+3} , Mn^{+3} present in an octahedral structure.
- b. Group B cations, consisting of Al^{+3} , Sr^{+4} are present in tetrahedral structure.
- c. The group C cation ($O_{10}(OH,F)$) consists of oxygen and hydroxyl.
- d. Group D cations consist of a type of cation that can be exchanged for other cations and is a

5. cations adsorbed on the surface

The molecular formula for montmorillonite is usually written as



where M^+ are Na^+ , K^+ , Mg^{2+} , or Ca^{2+}

Structurally, the mineral montmorillonite is composed of two basic building blocks, namely the octahedral layer aluminum and silica tetrahedral layers. In unit cell single montmorillonite contains two layers silica tetrahedral and in between are layers of octahedral aluminum [33].

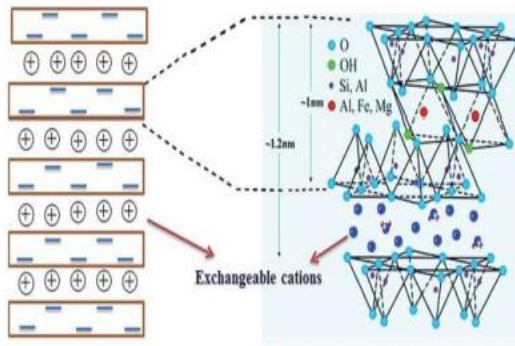


Figure II.3. Montmorillonite structures

Montmorillonite consists of thin platelets with thickness is less than 1 nm. Each octahedral layer aluminum is linked together by oxygen and sandwiched between the silicon tetrahedral layers. Layers connected together by the Van der Waals force which worked and formed as a pile of plates[34]. For each Al atom present in the central layer in a bonded octahedral structure with 2 hydroxyl groups and 4 oxygen atoms. Silicon atoms that form a tetrahedral structure with oxygen present below and above the layer Al atoms.

The cations in bentonite can be exchanged with other cations where these cations will bond to the clay surface electrostatic, this is due to the presence of a negative charge on the bentonite surface. The montmorillonite has adsorption capacity approx. 70 meq/100 g with a surface area of 700-800 m²/g[35].

Cation exchange is also affected by substitution isomorphic in which high valence cations undergo substitution with a low-valent cation originating from the outside (if the cation radius is not too high) different). Generally, isomorphic substitution occurs in octahedral layer where one out of every six cations Al³⁺ is replaced by the cation Mg²⁺. While on the layer tetrahedral, Al³⁺ cation replaces 15% of Si⁴⁺ cations[35].

Bentonite based on material composition, chemical properties and its physics (pH, deposition time, strength expand, base exchange capacity, and so on). divided into two types, namely Na-bentonite (sodium bentonite-swelling bentonite) and Ca-bentonite (calcium bentonite-nonswelling bentonite)[36]. Na-bentonite (sodium bentonite-swelling bentonite) also referred to as Wyoming-type bentonite. The structure of Na bentonite contains more Na^+ ions than Mg^{2+} and Ca^{2+} ions. Na-bentonite is a type of bentonite which has the ability to expand (swelling).

When immersed in water, Na-bentonite can have swelling power up to eight times and able to be dispersed in water for some time. Na-bentonite colored cream (cream) or white in dry conditions, and looks shiny when exposed to the sun and also in wet conditions. In addition, the mineral Na-bentonite has several characteristics, including having a pH of suspension colloidal value of 8.5-9.5 (base), the ratio of lime and high soda, Na^+ ions occupy the position ion exchange, and cannot be activated.

Generally, Na-bentonite is used as a plug leaks in dams, internal mixing materials manufacture of paints, raw materials in pharmaceuticals, sludge drilling, as well as molding sand adhesives in industry metal casting[36].

In contrast to Na-bentonite, Ca-bentonite (calcium bentonite- nonswelling bentonite) is a type of bentonite that does not have the ability to expand (swelling). Ca-bentonite (calcium bentonite – nonswelling bentonite) can also be referred to as Mg-bentonite.

Ca-bentonite structure contains more content of calcium (K_2O) and magnesium (MgO) compared to the sodium content. When dispersed into water, Ca-bentonite will settle quickly This is due to the nature of Ca-bentonite which slightly absorbs water.

However, Ca-bentonite has good properties as suction naturally or after activation. Ca bentonite also has rapid slaking properties, is blue in color, gray, red, brown, and yellow in dry conditions.

In addition, the mineral Ca-bentonite has several characteristics Also, some of them have the pH of their colloidal suspensions of 4-7 (acid), the ratio of sodium and calcium low, as well as more magnesium and calcium ions occupy many ion exchange positions. Generally, Ca bentonite is used as a bleach in oil Silica, alumina, and other bentonite content such as Fe, Mg, Ca, Na, Ti, and K make bentonite too can be used as adsorbent. However, bentonite less stable when used as an absorbent

This is due to the nature of easy to absorb water in bentonite.

So that the application of bentonite as an adsorbent will maximum if modified first. Activation bentonite using acid can increase bentonite clay adsorption ability. Process activation of bentonite will make mineral acid dissolves and reacts to the components such as Mg salt, Ca salt, and tar which can close the pores on the adsorbent, so that it can be obtained bentonite with a larger active site. Other than that, bentonite surface with high acidity too improve adsorption ability when compared bentonite adsorption ability before activation

II.5. Membrane

Membrane comes from the Latin, namely membrana which means pieces of cloth, paper skin. The membrane is a selective barrier between two phases which has the ability to remove one component of the feed mixture better than the other components, so that separation can be achieved[3]. The separation process on the membrane can occur because of the selectivity of the membrane, namely the ability to separate a particle from the mixture because the particle size is larger than the membrane pore [37]. The scheme of the separation process on the membrane can be seen in Figure 2.4 below:

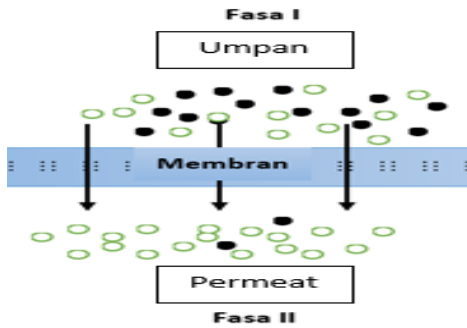


Figure II.4. Schematic of the Separation process on membrane

The fouling process can cause the feed flow through the membrane to decrease, causing a decrease in membrane performance.

During the separation process, the membrane may experience fouling. Fouling is a blockage in the membrane that occurs due to the accumulation of particles, colloids, macromolecules, and salts on the surface and inside the pore walls of the membrane [37].

II.6. Membrane Classification

The separation process that occurs on the membrane in general is a filtration process, but if we look in more detail the separation process on the membrane is one of the filtration methods that applies flow distribution between feed and permeate. In fact, there are many principles that can be applied in separating the two streams. This separation principle is one of the factors in classifying the types of membranes [38].

II.5.1. Membrane Classification based on Structure

The first classification discussed is the classification based on the structure of the membrane, namely:

1. Porous Membranes: membranes that have pores and their separation is based on differences in particle size; and membrane pore size.

Example :

- a. Microfiltration is like passing water, retaining microbes
 - b. Ultrafiltration is like retaining mineral salts
2. Non-porous membrane: a membrane that has no pores with the principle of separation based on differences in solubility and diffusion ability.

Example :

- a. gas permeation;
- b. Pervaporation;

c. Dialysis.

The working principle of this porous membrane is based on the difference in the size of the particles to be separated (water and oil) with the membrane particles. Porous membranes are divided into two types, namely symmetric membranes and asymmetric membranes which are described as follows:

1. Symmetrical membrane:

a membrane that has a homogeneous structure and pore size with a thickness of 10-200 m.

2. Asymmetric membrane:

a membrane that has a heterogeneous structure and pore size between the top and bottom, usually the top has a smaller pore size than the bottom of the membrane. The choice of membrane pore type can be adjusted to the application that will be used using the membrane, so for water and oil separation applications use an asymmetric membrane. Asymmetric membranes will combine the high selectivity of a dense membrane and a high permeation rate [37].

II.5.2 Membrane Classification based on Function

Classification of membranes based on various membrane functions.

Table II.2 Principle of Separation of Microfiltration Membranes and Ultrafiltration Membranes

The Difference	Microfiltration Membrane	Ultrafiltration Membrane
Structure	Porous membrane Asymmetric	Porous membrane Asymmetric
Thickness	10 – 150 μm	\approx 150 μm
Pore size	0,05 – 10 μm	\approx 1 – 100 nm
Push Strength	pressure < 2 bar	pressure 1 – 10 bar
Separation principle	<i>Sieving mechanism</i>	<i>Sieving mechanism</i>
Membrane Material	Polymer, ceramic Analytic application, sterilization, water purification, bioreactor membrane, waste treatment,	Polymer, ceramic Dairy production, food, metallurgy, textile, pharmaceutical, automotive, waste treatment
Main application		
Process Membrane	Phase 1: cair Phase 2: cair	Phase 1: cair Phase 2: cair

It can be seen that the classification of membranes based on their function for the separation of water and oil is on microfiltration membranes and ultrafiltration membranes. The classification of membranes that will be used in this study is based on the principle of particle size, where the types of microfiltration and ultrafiltration membranes can separate particles with a size of 0.1 – 10 microns. Furthermore, from these two membranes will be selected according to their nature to get better performance. The explanation in the classification of microfiltration and ultrafiltration membranes can be presented in Table II.2

Table II.2 above describes the principle of separation of microfiltration membranes and ultrafiltration membranes, it can be seen that the two classifications of membranes are equally applicable in the treatment of waste containing oil. However, the top layer of the ultrafiltration membrane is denser than the microfiltration membrane, because the pore size of the ultrafiltration membrane is smaller and the surface porosity is lower

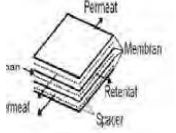
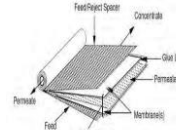
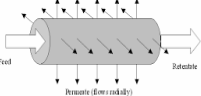
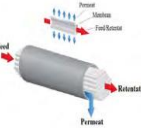
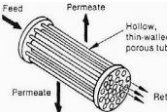
The denser top layer of the membrane will result in a higher hydrodynamic resistance of the ultrafiltration membrane than the microfiltration membrane. This condition will minimize the tendency for blockages to

occur and increase the membrane life time in the analysis (Baker, 2012). Therefore, in this study an ultrafiltration membrane will be used for maximum results.

II.5.3 Membrane Classification based on Module

The third classification is the classification of membranes based on the module or the shape of the membrane. Several types of membrane modules can be seen in Table II.3 below:

Table II.3 Several types of membrane modules

No	Membrane Classification	Types of Membrane Module	Picture
1	Membrane Flat Form wide and have cross section great star	<p><i>Plate and frame</i></p> <p>a. <i>Packing density:</i> 100-400 m²/m³</p> <p>b. Used for electrolysis, RO, and ultrafiltration</p> <p><i>Spiral wound</i></p> <p>a. <i>Packing density:</i> 300-1000 m²/m³</p> <p>b. used for separation, especially preventing bacteria from growing</p>	 
	Membrane tubular The shape in accordance with the place printing membrane	<p><i>Tubular</i></p> <p>a. Diameter: > 5 mm</p> <p>b. <i>Packing density:</i> < 300 m²/m³</p> <p>c used for ultrafiltration, but relative high cost</p> <p><i>Capiler</i></p> <p>a. Diameter: 0,5-5 mm</p> <p>b. <i>Packing density:</i> 600-1200 m²/m³</p> <p>Udes for ultrafoltration and microfiltration</p> <p>Serat berongga</p> <p>a. Diameter: < 0,5 mm</p> <p>b. <i>Packing density:</i> < 30.000 m2/m3</p> <p>c used for gas separation and ultrafiltration.</p>	  

The membrane module described above can be used according to the application.

II.5.4 Membrane Classification based on Source Material

The next classification of membranes based on source of materials is shown in Table II.4 below:

Table II.4 Classification of Membranes Based on source of materials

No	Membrane classification	Description	example
1	Anorganic Membrane	Made of inorganic materials	ceramic, glass, dan metal
2	Polymer Membrane	Made of polymer	cellulose acetate, Polyvinilidine flouride, dan polysulfone.
3	Biological membrane	Made from living things	Lipids

Table II.4 above describes the classification of membranes based on the material of origin which is divided into inorganic membranes, polymeric membranes, and biological membranes. Furthermore, a

literature study was carried out to find out from the references of previous studies that had been carried out on several membrane materials with the best performance results in water and oil separation applications.

II.5.5 Membrane Classification based on pore size

Based on the pore size, membranes can be divided into:

1. Microfiltration

Microfiltration is a filtration process that uses a porous membrane to separate suspended particles with diameters ranging from 0.1-10 μm . This type of membrane has a pore size of 0.05-10 μm , mostly made of some kind of polymer or ceramic, has a thickness of 10-150 μm and generally only survives at a pressure of < 2 bar. A large-scale application of microfiltration membranes is to treat microorganisms in drinking water. There are two types of flow in the membrane, namely dead-end and cross-flow. Both types of flow have their own advantages and disadvantages depending on their use. Membranes with dead-end models are usually applied for sterile filtration/sterilization of food or beverage products.

2. Ultrafiltration

The pore size of the ultrafiltration membrane ranges from 0.05 - 1 μm with a thickness of about 150 μm and can work at a pressure of 10 bar. Ultrafiltration membranes can be made using polymers such as polysulfone (PS) and polyacrylonitrile (PAN) or ceramics such as zirconium oxide and aluminum dioxide[39]. The separation process in the ultrafiltration membrane occurs due to hydrostatic pressure which forces the liquid to penetrate the semipermeable membrane which causes the solvent and suspended solids to be retained but water and solvent pass[37].

Ultrafiltration membranes can be used following a dead-end or cross-flow model as in microfiltration membranes. The separation ability of ultrafiltration membranes is strongly influenced by the size and shape of the pores. The use of ultrafiltration membranes can be applied to the separation of suspended particles and macromolecules. The pores in the ultrafiltration membrane are smaller than the pores in bacteria and yeast cells, so ultrafiltration is able to provide rejection of up to 100% of the microbes dissolved in the feed[40].

3. Nanofiltration

Nanofiltration membranes are membranes with pore sizes < 2 m. This membrane is usually often applied to surface water and groundwater which has smaller suspended solids and can work from 10 bar to 25 bar pressure. Nanofiltration can also be used to filter natural organic substances and synthetic dyes as well as for softening. Softening is a process carried out to separate polyvalent cations [38].

4. Reverse Osmosis

When a solvent (eg water) flows from a more dilute solution across a semipermeable membrane to a more concentrated solution, equilibrium in the system will then be reached when the concentrations in both solutions are equal. The difference in pressure between a solution with a high concentration and a solution with a low concentration is called the osmotic pressure. Reverse osmosis occurs when a solution with a higher concentration is subjected to greater pressure than the solution with a lower concentration, resulting in the movement of particles from a concentrated solution to a more dilute solution.

Reverse osmosis is a filtering method that can separate many types of large molecules and ions from solution[37]. Asymmetric or composite membranes can be used as reverse osmosis with the characteristics

of having a pore size of < 2 nm, working at a pressure of 15-25 bar on brackish water samples while for seawater purification this membrane can work at a pressure of 40-80 bar[39].

II.7. Membrane Composition Materials

Membrane materials used in water treatment have the following characteristics:

1. Hydrophilic, ie materials that can interact attractively with water
2. Water permeability, the material must be able to pass water
3. Selectivity, in addition to the ability to pass through the membrane, must also have selective properties, especially in separating water from its impurities.
4. Having anti-bacterial properties, the need for drinking water with high purity is one of the criteria for quality water. To produce quality water, the problem is usually the level of bacteria that will grow, especially in membranes that tend to be static. So the membrane itself must have the property of being able to kill bacteria attached to the surface of the separating membrane
5. Has strong mechanical resistance properties. In water treatment with membranes, a sufficiently high

operating pressure is required to pass the desired particles through the pores of the membrane.

The membrane constituent material itself can be derived from a variety of materials such as polymers, metals, ceramics and others.

Polymer membranes are often used for water treatment because polymers have various properties and characteristics as shown in table 2.1. Other polymers used as membranes are membranes of Polyalcohol (PA), Polyvinyl alcohol (PVA) Cellulose Acetate (CA), polyacrylonitrile (PAN).

Table II.5. Types of polymers and their properties in the manufacture of membranes

POLYMER	CHARACTERISTICS
Polysulfone	Hydrofobic
	Hydrogen Bond
	Easy Fouling
Polyethersulfone	Less hydrophobic
	Hidrogen bond with water
	Can reject proteins and polysaccharides
Fluoropolymer cmposite	Veryhydrophobic
	Not easy to fouling

Membranes made of PAN, PA, PVA, CA tend to be hydrophilic, usually this type of membrane will be prone to fouling. Meanwhile, hydrophobic membranes tend to be strong and not prone to fouling.

To overcome this problem, the polymer is mixed with other materials or commonly referred to as composites.

II.8. Membrane Characterization Parameters

Characterization is carried out to determine the physical properties of the resulting membrane so that it can be used as desired. This characterization includes contact angle, mechanical properties (tensile test), FTIR, porosity test, membrane morphology test (SEM-EDX) flux and rejection to determine the performance results.

2.8.1 Contact Angle

If a liquid or gas is exposed to a solid, it will come into contact with one another. The size to determine how much contact power a liquid has with a solid is described by the contact angle. The contact angle describes the interaction between the liquid and the solid surface which can be seen through the shape of the fluid on the solid surface. One of the tools used to determine this contact

angle is the contact angle goniometer. The scheme of the contact angle is as follows:



Figure II.5. Liquid droplet profile on the surface

The magnitude of the contact angle is used to determine how much a liquid wets the surface of a solid object. If the contact angle is large ($> 90^\circ$), then the wetting that occurs is not good. Meanwhile, if the contact angle is small ($< 90^\circ$), then wetting occurs very well. Wetting is said to be perfect if the value of the contact angle is very small (0°)

2.8.2. *Tensile Test*

This tensile test is a test of the mechanical properties of the membrane that shows a measure of the strength of a material, which includes stress and strain. To determine

the mechanical strength of the membrane, it can be calculated using the formula:

Stress

Stress (σ) is defined as the magnitude of the force (F) divided by the cross-sectional area (A). According to the following formula:

$$\sigma = F/A \dots\dots\dots(2.1)$$

Strain

Strain (ϵ) is defined as the relative change in the shape of a material subjected to stress. Strain due to tension in the material is defined as the increase in length (l) to the initial length (l_0) according to the following formula:

$$\epsilon = (\Delta l)/l_0 \dots\dots\dots(2.2)$$

2.8.3 FTIR (Fourier Transform Infra Red)

IR spectroscopy is used for structure determination with important information about the functional groups of a molecule. Determination of this structure is done by looking at the plot of the IR spectrum detected by the FTIR device which states the amount of IR radiation that is transmitted through the sample as a function of frequency or wave number.

2.8.4 Membrane Porosity Test

The membrane porosity test is carried out to determine the amount of substances or components that can be absorbed by the membrane. The porosity test is usually carried out on water, so it can be seen how much water is absorbed by the membrane. The trick is to soak the membrane in water for 24 hours at room temperature, then the membrane is weighed. After that, the membrane was dried in an oven at 60°C for 48 hours until it was completely dry and then weighed again. The magnitude of the porosity can be calculated using the following formula

$$\% \text{ Porosity} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\% \dots\dots\dots(2.3)$$

2.8.5 Membrane morphology

The characterization of the membrane morphology test using SEM was carried out with the aim of knowing the surface structure and cross-section of a membrane using an electron microscope.

The working principle of SEM is that a primary electron beam is fired into a membrane sample, then the sample is reflected or emitted, which is called a secondary electron. Non-conductive membranes must be coated with a

conductive coating to prevent damage from prolonged exposure to electrons.

2.8.6 Flux and Rejection

Several factors that can affect the performance and effectiveness of the membrane include: permeability, selectivity, structure and morphology of the membrane. In determining the performance of the membrane, the permeability is represented by the flux value. Flux is the amount of feed that can pass through the membrane at any given time. Meanwhile, permeability describes a measure of the velocity of a particle when it penetrates the membrane. Several factors that affect permeability are pore size, number of pores, operating pressure and membrane thickness. The flux value can be determined based on Equation 2.4 (Mulder, 1992).

$$J_w = \frac{\Delta V}{A \cdot t} \dots \dots \dots (2.4)$$

With, J_w is flux (L/m²h), V is volume of permeate displaced (L), A is effective membrane surface area (m²), t is time during permeate storage (hours)

The performance of the membrane is also determined based on the selectivity of the membrane, namely the ability of a membrane to be able to pass species and retain

certain species. Selectivity in membrane measurement is seen through the determination of the rejection coefficient which is determined based on the concentration of solutes that do not penetrate the membrane. Membrane selectivity can be influenced by pore size and the size of a species (Scott et al., 1996). The value of the rejection coefficient can be determined based on Equation 2.5.

$$\%R=(C_u-C_p)/C_u \times 100\% \dots\dots\dots (2.5)$$

With %R is rejection coefficient, Cu is feed concentration (ppm), Cp is concentration of permeate (ppm)

II.9. Membrane Synthesis Technigue

In this study, membranes were made using the phase reversal method, which is a process to control polymers from a solution phase to a solid. Generally, membranes that are printed using a phase reversal technique have an asymmetric structure and a larger pore size compared to membranes made by solvent evaporation.

The process of making membranes using a phase reversal technique consists of four steps, namely the manufacture

of a homogeneous printing solution (dope), dope solution printing, solvent evaporation and polymer deposition in non-solvent.

The following are several types of membrane manufacturing techniques and their advantages and disadvantages,

Tabel II.6 Membrane Manufacturing Technique

Manufacturing	strenght	weakness
Phase inversion Fabrication Methods Immersion precipitation Principle : Solution printed and put in coagulation bath	<ul style="list-style-type: none"> • Good particle size distribution • Thermodynamically stable • High Porosity • Additives improve mechanicals properties 	<ul style="list-style-type: none"> • if additives are added, the stability of the additive nanoparticles must be increased • tendency blockage still big enough.
Phase inversion Fabrication Methods <i>Thermally induced Phase Separation (TIPS)</i> Principle : Solution prints are cast at high temperatures and then colded	<ul style="list-style-type: none"> • distinctive spherical crystal structure • high porosity • distribution • good pore size, homogeneous and smaller • Clogging is reduced when additives are plentiful 	<ul style="list-style-type: none"> • The addition additives changes the structure • Relatively difficult choice of solvent • In the synthesis requires high temperatures

		<ul style="list-style-type: none"> • The cost of synthesis is relative high
<p>Sintering Principle : Pressure and thermal at high temperature until the particles appear porous</p>	<ul style="list-style-type: none"> • High stability • Inorganic and organic • Easy process • Low cost. 	<ul style="list-style-type: none"> • For manufacture of MF membranes • High temperature • Low porosity • Low solubility
Manufacturing	strenght	weakness
<p>Stretching Principle : Withdraw semicrystalline polymer in the direction of extrusion up to polymers parts parallel to the direction the extrusion and a pore is formed membrane</p>	<ul style="list-style-type: none"> • Porosity • Relative high membrane yiled. • Relative high mechanical strenght. 	<ul style="list-style-type: none"> • Semikrystalline • High crystallinity. • Low mechanical strenght. • Techniques must be combined • Must determine the direction of extrusion
<p>Track-etching Principle : polymer film shooting wth radiation particles high energy in the perpendicular direction to form a path. Then movie</p>	<ul style="list-style-type: none"> • Symmetrical porous membrane. • Shooting electrons can set • The membrane that can bi generated modified 	<ul style="list-style-type: none"> • Relative high cost because it uses high concentration of radiation particles • Relative long time synthesis

inserted in an acid or alkaline bath		<ul style="list-style-type: none"> • Relative low porosity properties
<p>Template leaching</p> <p>Principle : Removing one of the film components from a system to produce a membrane porous</p>	<ul style="list-style-type: none"> • Work specifically in the separation of compounds in porous solids • The membrane pore diameter is relative small 	<ul style="list-style-type: none"> • Membranes produced are many variations • Requires relatively large costs

The six PVDF membrane manufacturing techniques described in Table II.6, can be seen from the advantages and disadvantages they have, that the phase inversion PVDF membrane fabrication technique using the precipitation immersion method has advantages over other techniques. The advantage of this phase inversion is in accordance with the results of[41] which states that the phase inversion technique is widely used in the manufacture of PVDF membranes compared to other manufacturing techniques, because it is able to control the pore size of the membrane and the resulting performance is relatively good.

One of the most commonly used phase inversion techniques is immersion precipitation. The results of the membrane performance obtained are superior in terms of relatively low cost, easy to modify with other additives,

and do not require high temperatures in the manufacture of membranes. Thus, in this study using membrane manufacturing techniques. Phase inversion PVDF using the precipitation immersion method.

II.10 Nanofibers

Nanofibers are defined as fibers having a diameter between 100 nm to 1 μm [42]. The characteristics of nanofibers are that they have small pores, high porosity[43], are biodegradable and have a large surface area to volume ratio[44]. Nanofibers have very distinctive properties, very strong, large surface to volume ratio, and porous. The nature of the nanofiber is that its surface is more flexible and has high mechanical strength / properties. These properties make nanofibers a very promising material for use in various industrial fields, such as the composite, automotive, pulp and paper, electronics, textiles, optics, agriculture, cosmetics, health, medicine, sports and pharmaceutical industries.

II.11 Nanofiber synthesis methods

There are several techniques to synthesis nanofibers. These techniques include, phase separation, bicomponent extrusion template synthesis, drawing, meltblowing, electrospinning and centrifugal spinning.

a. *Bicomponent extrusion*

Bicomponent fibers can be defined as extruding two polymers together in the same fiber from the same spinneret. In bicomponent extrusion two polymers are delivered to a simple spinneret hole, split by a blade edge or septum, which feeds the two segments into side by side arrangements

b. *Phase Separation*

In phase separation, a polymer is initially blended with a solvent before suffering gelation. The major mechanism in this system is the separation of phases owing to physical inconsistency. The solvent phase is then extracted, leaving the other residual phase. A detailed method for poly(L-lactic) acid (PLLA) nanofibrous producing in a five main steps, polymer dissolution, gelation, solvent extraction, freezing and freeze-drying[45]

c. *Template Synthesis*

Template synthesis is another commonly used approach mostly to produce inorganic nanofibers e.g. carbon nanotubes and nanofibers or conductive polyaniline (PANI), polypyrrole (PPy) etc. Template synthesis involves the use of a template or mold to get a preferred material or structure. Thus the casting technique and DNA replication can be believed as

template-based synthesis. The template mentions to a metal oxide membrane with nano-scale diameter thickness pores. By the use of water pressure along with the porous membrane control causes extrusion of the polymer which, by contacting with a solidifying solution, provides a nanofibers whose diameters are managed by the pores.

d. *Drawing*

The drawing process can be characterized as dry spinning at a molecular level. The process can only be applied to viscoelastic materials that can experience a high degree of deformations, but remaining sufficiently solid to hold up the developed stress during pulling. A typical drawing method requires a SiO₂ surface; a micropipette and a micromanipulator to produce nanofibers. However, this process produced nanofibers in a laboratory-scale one by one which prevents it from being scaled up to industrial level

e. *Meltblown technology*

Meltblown technology involves a single step production of fibers by a polymer melt extruding through an orifice die and drawing down the extrudate with a hot air, usually at similar temperature as the molten polymer. The air exerts the drag force to

attenuate the melt extrudate into fibers, which are then gathered in the form of a nonwoven mat

f. *Electrospinning*

Electrospinning is a famous procedure for the electrostatic production of polymer nanofibers. Formhals published the first patent for preparing artificial threads by electrospinning in 1934. Electrospinning is a smart method to attain nanofibers as it is simple to use and it produces non-woven mats with a wonderful volume/area ratio

Electrospinning is definitely the preferred method for nanofibers fabrication; nevertheless it faces some drawbacks for instance high electric field necessities, solutions with superior dielectric properties, low production rate, high production cost and many other safety correlated topics, electrospinning could not be suitable for mass production of certain materials

g. *Centrifugal spinning*

Centrifugal spinning, or Forcespinning, is a recently developed nanofiber forming method and it draws extensive interest mainly due to its high production rate, which is 500 times faster than traditional electrospinning. Rather than using electrostatic force, centrifugal spinning

develops centrifugal force to realize the high-rate production of nanofibers.

II.12. Synthesis Nanofibers membrane by electrospinning

The electrospinning method is a method that uses electrostatic forces to form fibers. This method is relatively easy and simple to form nano-sized fibers[46]. The electrospinning device consists of several parts, the capillary tube, a high voltage source that is positively and negatively charged, and a fiber collector. A syringe/injector is used to push fluid into the capillaries. A tension source is placed on the syringe and fiber collector. Several parameters that need to be considered in order to form nanofibers are the concentration of polymer[47], amount of electric voltage applied[48], the distance between the tip of the needle and the collector[9,49], the flow rate of the liquid, the concentration of the polymer, and the molecular weight of the polymer [50].

Several parameters that need to be considered in order to form nanofibers are the magnitude of the applied voltage, the distance between the tip of the needle and the collector, the flow rate of the liquid, the concentration of

the polymer, and the molecular weight of the polymer[50].

a. Electrical voltage

The magnitude of the electric voltage affects the morphology and diameter of the fibers formed. If the voltage is less, then the electrostatic force is also weak so that the fiber beam has not yet been formed, or even if it can form, the fiber is cut off, and beads appear. If the voltage is too large, the electrostatic force is also large so that the diameter of the resulting fiber is also large[48].

The strength of the electric field applied to the solution can produce fiber diameters from a few microns to tens of nanometers. Suboptimal field strength can cause poor fiber yield or even failure in fiber formation. The electric field strength for certain polymers/solvent systems that is too weak or too strong will lead to the formation of fibers with beads. In general, an increase in the use of a higher electrical voltage will cause a faster spinning process rate because the rate of polymer coming out of the capillary tip will increase. The effect of increasing the applied voltage can be seen in Figure II.6.

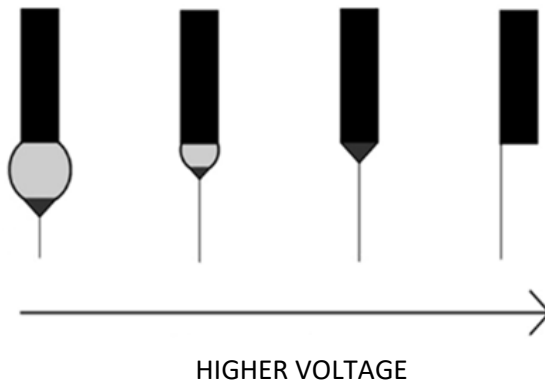


Figure II.6 Effect of voltage variation on fiber formation [50]

Figure II.6 explains that the applied stress affects the formation of the Taylor cone. When the applied voltage is relatively low, a hanging drop (pictured in light gray) will be seen forming at the tip of the capillary. A Taylor cone (pictured in dark gray) then forms at the tip of the droplet. However, as the applied voltage increases (moves from left to right), the droplet volume decreases until a Taylor cone forms at the tip of the capillary. An increase in the applied tension will result in a less good fiber. The strength of the electric voltage given must be really optimal. An

electric voltage that is too low or too high will produce nanofibers with beads[50].

b. Distance from the tip of the needle to the collector

If the distance is too narrow then the drying is not perfect, so the resulting fiber contains a lot of beads. If the distance is wide enough then the drying will be perfect so that the resulting fiber becomes smooth (Doshi and Reneker, 1995). Distance also affects the shape and diameter of the obtained fibers[9].

c. Flow Rate

A low flow rate is highly recommended in this process, because at low flow rates, the polymer solution has sufficient time for polarization to occur which will then form fine fibers with small diameters [51], while too high flow rates result in fibers that have beads because there is not enough time for the solvent to evaporate before reaching the collector [9].

d. Solution Concentration and Viscosity

In order to form fibers, it is necessary to have sufficient concentration of polymer solution so that inter-chain entanglements are formed. In addition, the polymer concentration is affected by the viscosity and surface tension of the solution. According to[43], the concentration characteristic of the polymer solution is

directly proportional to the viscosity of the solution, which has the greatest influence on the size and morphology of the nanofibers. If the polymer concentration is too low, nanofibers will form in the form of round spots or beads on the surface and droplets due to too low a viscosity. This may also be due to some solvents reaching the collector and causing the fibers to become wet thereby forming junctions and spheres. The solution viscosity increases significantly, resulting in a more uniform fiber. However, if the solution is too thick, the electrospinning process is impossible because of a blockage at the tip of the needle (the solvent evaporates faster).

The diameter of the nanofiber is also affected by the concentration of the polymer solution. Too high a viscosity of the solution results in thicker fibers. Solutions with higher conductivity or charge density generally help to produce a more uniform fiber. The conductivity can be increased by the addition of salt (will not stay in the final product), alcohol, or surfactant.

e. **Polymer Molecular Weight**

Polymer molecular weight that is too low tends to form granules because the polymer chain entanglement is not enough to form fibers. If the molecular weight of the polymer is too large, it tends to form large diameter fibers in the form of ribbons[47].

Another advantage of this technique is that it can produce fairly long (continuous) nanofibers. Some commercial uses/applications of electrospinning fibers include:

1. Fiber reinforcement in composite materials.
2. Non-wetting surface coating on ordinary textiles.
3. Support for very thin polymer separation membranes.
4. Application of insecticides on plants.
5. Routes for the production of non-woven fabrics.
6. Wound dressing materials (Deitzel et al., 2001)

II.13. Previous research Studies

The processing of textile waste has been carried out by various methods, both simple and sophisticated methods. For example, waste treatment by adding certain chemicals such as coagulant and chlorination processes, the process is able to overcome or treat existing waste but also creates new problems, namely increased operational costs due to the use of a lot of

chemicals and continuously and the process produces residues in very large quantities. big too, so that over time it will develop into a source of new pollutants that are also dangerous for environmental sustainability, another way is a biological processing process that involves a bioremediation process, but it still has many shortcomings due to lack of flexibility, not maximally taking all contaminants of dye waste[1].

The adsorption method has also been carried out, this method is very good for waste treatment but has a weakness, namely the ability to be reused (regeneration) is very low, so that it will result in the use of very high costs[2]. Based on the weaknesses of the above method, a method of treating waste using membrane technology was developed. Membrane technology is known as a clean and environmentally friendly technology. The factors that encourage the use of membranes in water treatment are regulations on the treatment and supply of clean water, the increasing need for clean water, commercialization of membrane technology due to its application in the wider community, and operational costs that can be maximally suppressed with more optimal membrane manufacturing innovations [3]. The process of treating sewage using membranes has several

advantages, namely that it can be said to be relatively simple, it does not use chemicals for processing, it can be applied to a larger processing scale.

These advantages are the basis for the use of membrane technology for processing waste in the textile industry. To reduce the cost of using the membrane, regeneration can be done on the membrane so that it can be used repeatedly, namely by cleaning the membrane regularly. Meanwhile, to overcome the main weakness of membrane technology, was fouling[4], it is done by selecting the appropriate filtration process according to the characteristics of textile wastewater, or by improving the membrane material used so as to minimize fouling. As in this study, improvements were made to the material properties of the membrane by adding bentonite, with the hope that it would be able to reduce fouling and increase the performance of the membrane.

PVDF membrane modification with the addition of clay can increase the resistance of the membrane to surface abrasion[19], improve membrane mechanical properties, provide better performance[20], increase the polarity of the membrane surface and also increase

the selectivity of the membrane in the separation of dyes.

CHAPTER III

RESEARCH METHODS

III.1 Tools and Materials

III.1.1. Tools

The equipment used in this study were beaker, 10 mL volumetric pipette, analytical balance, dropper pipette, stirring rod, glass plate, black duct tape, coagulant bath, magnetic stirrer, stirrer, membrane reactor, pH meter, ruler, scissors, stopwatch and instruments such as UV-Vis Spectrophotometer, FTIR, SEM, tensile test equipment, membrane reactor.

III.1.2. Materials

The materials used in this research are Co polymer Polyviniliden Fluoride (PVDF), Bentonite 4A, Dimethyl Acetamide (DMAc), Methylene Blue, Aquademineral.

III.2. Research Methodology

This research consists of several stages, synthesis, characterization and application:

III.2.1. Synthesis of PVDF and PVDF-Bentonite nanofibers membranes

The synthesis nanofibers is carried out using electrospinning equipment. The initial stage of the process is that the PVDF solution is inserted into a 5 mL syringe. The solution contained in the syringe must not contain air bubbles, this will affect the fibers that will be produced. Then the solution is pumped through a silicone hose with a diameter of 0.6 mm and a syringe with a diameter of 0.70 x 38 mm into the spinneret. The metal tip of the spinneret is connected to the positive pole of the high voltage current source by tightening the thread found on the spinneret support. The aluminum foil sheet is placed on top of the negative pole as a nanofiber collector which is formed during the electrospinning process.

The electrospinning process is carried out at room temperature and lasts 3-4 hours until a nanofiber layer is formed on the aluminum foil. The observations made on the electrospinning parameters that affect the formation of nanofibers include polymer concentration, electric voltage, spinneret tip distance to collector and flow velocity. Optimization variations of PVDF nanofiber synthesis by electrospinning are listed in Table III.1

Table III.1. Optimization parameters for PVDF nanofibers membrane synthesis

Parameters	Variation
Solution concentration (% w/v)	15, 17,5, 20, 22,5
Power supply voltage (kV)	17, 18, 19, 20
Spinneret tip distance to collector (cm)	11,13, 15 dan 18
Flow rate (mL/menit)	0,001; 0,004; 0,008, 0,01

The synthesis of the PVDF-Bentonite nanofiber membrane, variations in the addition of bentonite were carried out, namely 5, 10 and 20% (w/v). The electrospinning technique is presented in Figure III. 1

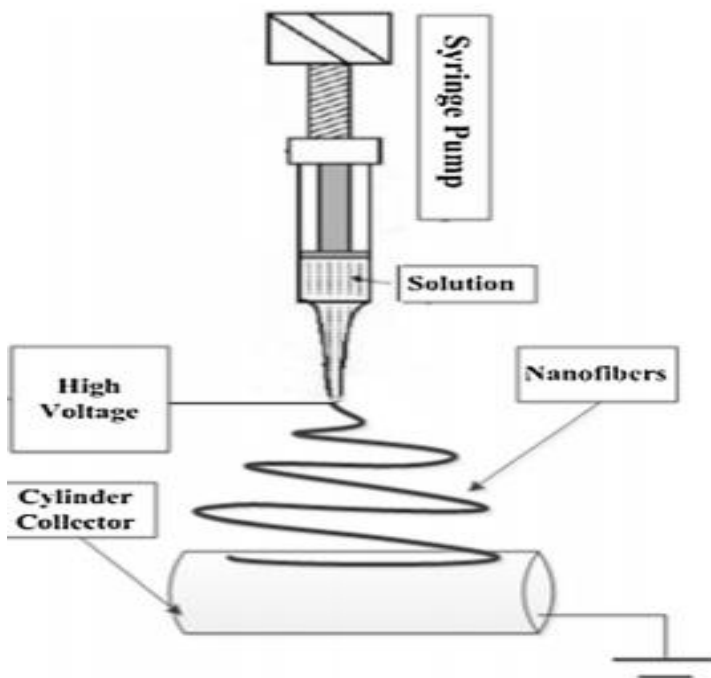


Figure III.1. Schematic of the electrospinning process[7]

III.2.2 Characterization of PVDF and PVDF-Bentonite nanofiber membranes

- Optical Microscope

Observations using an optical microscope were carried out in order to determine the morphology of the fibers formed immediately before further analysis. A small number of fibers formed by the electrospinning process were accommodated on an objective glass and observed with an optical microscope (Eclipse E400, Nikon) at 400x magnification.

- Characterization of the hydrophilicity of the nanofibers

The hydrophilicity properties of the nanofibers were analyzed by measuring the contact angle of the nanofibers to water. The method used is the method of measuring water droplets on the surface of the nanofiber. The contact angle is measured manually based on the DSA (Drop Shape Analysis) method by observing the sessile drop using a camera. The contact angle of the water droplets was measured using a fitting using ImageJ software in the contact angle plugin mode. Each sample was measured 3 times with different nanofiber positions.

- Characterization of nanofibers morphology
The surface morphology, cross-section, and distribution of bentonite in the nanofiber were characterized using a Scanning Electron Microscope (SEM). The characterization of the elemental composition of the nanofibers was carried out using Energy Dispersive X-Ray Spectroscopy (EDX).

- Characterization of functional groups or interactions of PVDF and Bentonite
Analysis to determine the presence of typical functional groups contained in PVDF and PVDF-Bentonite nanofibers membranes used Fourier Transform Infrared Spectroscopy (FTIR).

- Structural characterization
The solid structure of PVDF and PVDF-Bentonite nanofibers membranes was determined using X-Ray Diffraction Miniflex Rigaku with λ source Cu K α .

- Characterization Porosity
The method used to perform the membrane porosity test is by immersing the membrane in

water for 24 hours at room temperature, then the membrane is weighed. After that the membrane was dried in a vacuum oven at 60°C for 48 hours until it was completely dry and then reinstalled. The amount of membrane porosity can be calculated using the following equation:

$$\% \text{ Porosity} = ((W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}) \times 100\% \dots\dots(\text{III.1})$$

- Characterization of Thermal Properties

Analysis of the thermal properties of Bentonite, PVDF and PVDF-Bentonite nanofiber membranes were determined using DTA/TGA.

III.2.3. Applications of PVDF and PVDF-Bentonite nanofiber membranes for methylene blue adsorption

- Membrane permeability value

The permeability of the membrane to water is tested by placing a printed membrane sheet on top of the support in a series of membrane cells as shown in Figure III.2.

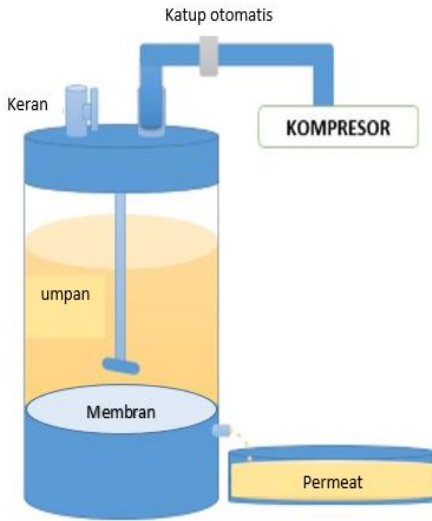


Figure III.2 Schematic of the membrane reactor

Then the feed solution containing aquademineral is put into the feed tank through the water inlet valve and stirred with a magnetic stirrer. The reactor is pressurized at 2 bar and left for 1 hour until compacting occurs. The pressure in the isolated reactor is then slowly lowered over a range of 0.5 bar. At each pressure drop, permeate storage is carried out and the time is calculated using a stopwatch. The flux value can then be determined based on the following equation

$$J_w = \Delta V / Axt \dots\dots\dots(III.2)$$

Where J_w is the flux (L / m²h), ΔV is the volume of permeate removed (L), A is the effective membrane surface area (m²), and t is the time during permeate storage (hours)

- Determination of the value of the rejection coefficient

The membrane rejection coefficient of the sample solution which had previously been pH adjusted using a pH meter at pH 3, 4, 5 and 6, was tested by placing a printed membrane sheet on top of the support in a series of membrane cells as shown in Figure 3.1. Then the feed solution is put into the feed tank through the water inlet valve and stirred with a magnetic stirrer. The reactor is pressurized at 2 bar and left for 1 hour until compacting occurs. The pressure in the isolated reactor is then slowly lowered over a range of 0.5 bar. At each pressure drop, permeate storage is carried out and the time is calculated using a stopwatch. The collected permeate is then measured for concentration using a UV-Vis

spectrophotometer. The rejection coefficient is then determined using the following equation:

$$\% R = (C_u - C_p) / C_u \times 100\% \dots\dots\dots(III.3)$$

Where % R is the rejection coefficient, the feed concentration C_u (ppm), and the permeate concentration C_p (ppm).

CHAPTER IV

RESULT AND DISCUSSION

In this chapter, we will discuss the synthesis of PVDF nanofiber membranes, PVDF-bentonite nanofibers, characterization including FTIR, SEM mapping EDX, tensile strength, and their application to the treatment of dye waste methylene blue.

IV.1. Synthesis PVDF nanofibers membran

The synthesis of PVDF nanofibers, PVDF-Bentonite nanofiber composites was carried out using the electrospinning method, by charging the polymer solution which was then dropped from the spinneret to

the collector[50]. The polymer solution expelled from the needle tip forms nanofibers continuously due to an electric force (high voltage potential of the polymer solution) which overcomes or opposes the surface tension. The best way to get uniformity and fine fibers is to make nanofibers using a variety of parameters until the optimum conditions are obtained[49].

The concentration characteristics of the polymer solution are directly proportional to the viscosity of the solution, which has the greatest influence on the morphology and size of the nanofiber diameter (Lin et al., 2004). In this study, PVDF solutions were made with concentrations of 15; 17.5; 20 and 22.5% (w/v). Electrospinning nanofibers were observed using an optical microscope (Figure IV.1). These results indicate that there are morphological differences of the formed nanofibers. If the polymer concentration is too low, nanofibers will form such as round stains and droplets on the surface of the nanofiber. This is due to some of the solvent reaches the collector and causes the nanofibers to get wet, forming junctions and beads (Fig. IV.1(a)). At a concentration of 17.5% (w/v) nanofibers were formed (Figure IV.1 (b)), but still had many beads and small droplets. The beads formed on the nanofibers are caused by the influence of the surface tension of the solution. When the surface tension dominates the Coulomb force the electric field in the

radiating solution (jet) so that the jet is not sufficiently stretched by the electric field. In addition, the solvent in the jet is not sufficiently evaporated because of the large number so that the resulting nanofiber is in the form of beads.

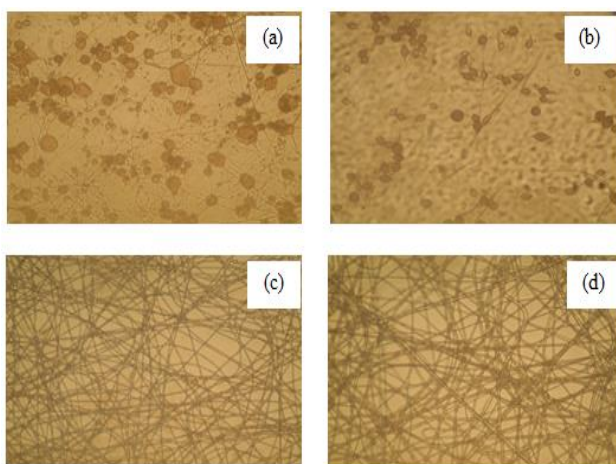


Figure IV.1 PVDF nanofiber optical microscopy images at various concentrations (% w/v), 15(a), 17.5(b), 20 (c) 22.5% (d)

At 20% (w/v) PVDF polymer formed nanofiber (Figure IV.1 (c)), where the electric field strength exceeds the surface tension of the solution. The higher the viscosity and charge density of a solution, the surface tension decreases so that the jet is stretched enough by the

electric field. The amount of solvent in the jet solution is small and sufficiently evaporated so that the resulting nanofiber is better and more continuous. Increasing the viscosity of the solution affects the increase in resistance to jet breaking. If the solution used is too thick, the electrospinning process cannot be carried out because there is a blockage at the needle tip (the solvent evaporates faster).

Electrical voltage is a very important component in the electrospinning process to produce nanofibers[48,50]. An electric field must be strong enough to overcome the surface tension during the electrospinning process. At low voltage, the resulting fiber is in the form of round or beaded spots, while at high voltage it causes emission from the surface of the solution at the end of the spinneret to the collector to produce uniform and continuous fibers. Various voltage variations are used to produce different morphological shapes of nanofibers as shown in Figure IV.2.

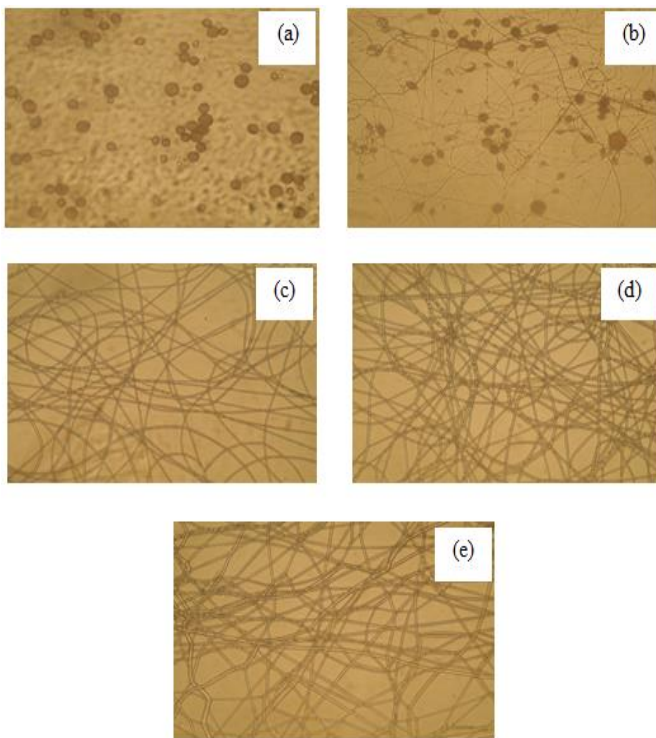


Figure IV.2 PVDF nanofiber optical microscopy images at various applied voltages (kV), 17(a), 18(b), 19(c), 20(d) and 21(e).

If the applied voltage is low, resulting in nanofiber with poor morphology, not uniform, there are many droplets and beads. This is due to the difference in tensile strength (stretching) of the polymer solution jet from the applied

electrical voltage. At low voltage, the tensile strength of the polymer jet decreases, so that the beads are not sufficiently stretched to become nanofibers. When the voltage is increased, the amount of stretch of the polymer solution jet also increases so that the spherical beads in the nanofiber gaps will be pulled into a straight shape so that the resulting nanofiber looks more uniform.

Flow rate is the amount of solution flowing at a certain rate per unit time. In Figure IV.3 there are differences in the morphology of the nanofibers produced due to the difference in the given flow rate[9]. When the given flow rate is small, the number of droplets contained at the tip of the needle decreases, so that the number of charge polarizations on the surface is also small. At the same electrical voltage, the droplets at the tip of the needle are sufficiently pulled towards the collector to form nanofibers as shown in Figure IV.7 (a). As the flow rate is increased, the number of droplets at the needle tip increases and the charge polarization on the surface increases as well. At the voltage At the same time, the droplets will be drawn towards the collector to form nanofibers, but only part of it is drawn. This is due to the large number of surface charge polarizations on the needle tip drop, the voltage is not enough to attract all the charges on the drop so that some of it does not stretch to form nanofibers (Figure IV.7 (b)).

Dalton et al., (2005) have reported that lower flow rates produce uniform nanofibers with smaller diameters, whereas high flow rates produce nanofibers that have beads because there is not enough time for the solvent to evaporate before reaching the collector. The distance between the needle tip to the collector also affects the shape and diameter of the nanofiber that will be produced. The distance between the needle tip and the collector (the distance between the two electrodes) must be appropriate to allow the solvent to dry before reaching the collector[47,51].

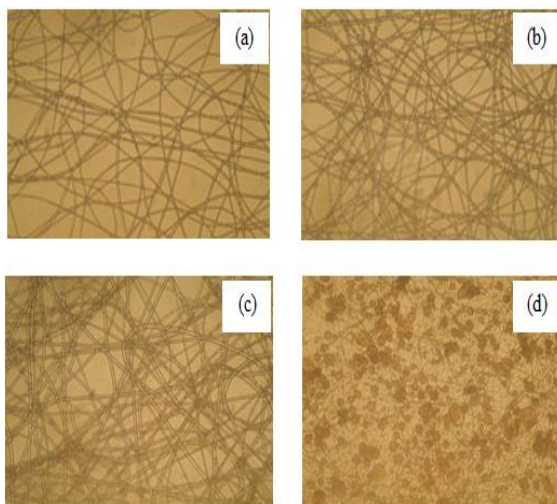


Figure IV.3 PVDF nanofiber optical microscopy images with various flow rates (mL/h), 0.01 (a), 0.04 (b), 0.08 (c), and 0.1 (d).

The difference in the distance between the tip of the needle and the collector affects the distance of the polymer solution jet and the strength of the electric field so as to produce different morphological shapes of nanofibers. Various variations of needle tip distance to collector shown in Figure IV.4. When the distance is decreased, the travel time of the polymer solution also decreases, so that the electric field strength increases to form straight and continuous nanofibers (Figure IV.4(a)).

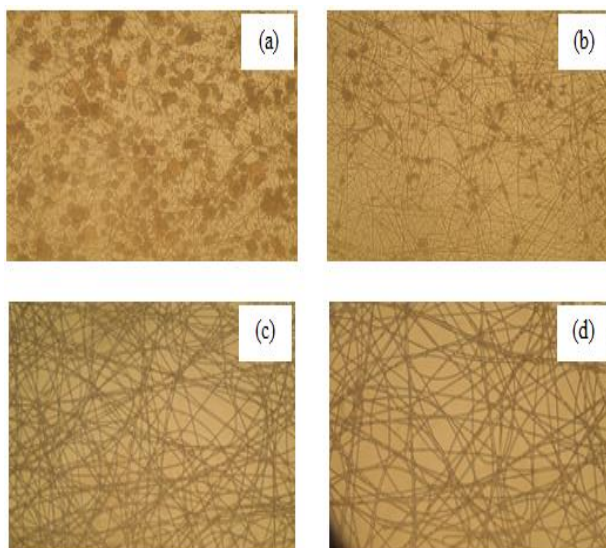


Figure IV.4. PVDF nanofiber optical microscopy images at various spinneret and collector tip distances (cm), 11 (a), 13 (b), 15 (c), and 17 (d).

When the distance between the needle tip to the collector is increased, the travel time of the polymer solution to the collector increases, so that the nanofibers formed are not as straight as they are twisted. This is because the stretching power of the polymer solution is reduced but the solvent in the polymer solution is sufficiently evaporated when it reaches the collector, so that the nanofibers are fairly uniform, without beads and are continuous (Figure IV.8 (b)).

IV.2. Characterization

The membrane characterization includes contact angle, tensile test, FTIR, porosity test and SEM test.

IV.2.1. Characterization of functional groups by FTIR

FTIR analysis of PVDF and PVDF-Bentonite nanofibers membranes aims to determine the functional groups contained therein. The spectrum is recorded from the wave number 4000-400 cm^{-1} .

From the picture above, some typical peaks of PVDF can be seen. The presence of saturated C-F bonds was indicated by the absorption at wave numbers 1010.70 cm^{-1} , 1033.85 cm^{-1} and 1089.78 cm^{-1} . The absorption peaks at wave numbers 792 cm^{-1} and 839 cm^{-1} indicate the presence of swing vibrations from CH_2 .

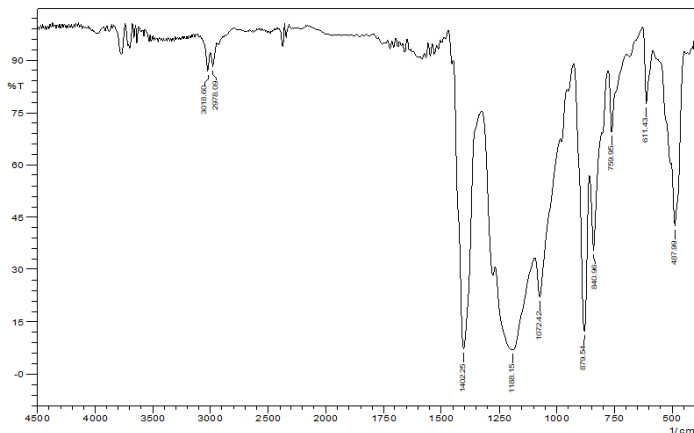


Figure IV.5 FTIR spectra of PVDF nanofibers

The presence of CF_3 bonds is indicated by the appearance of peaks at wave numbers 756.10 cm^{-1} , 1261.45 cm^{-1} and 1330.88 cm^{-1} . While the absorption at wave number $3200\text{-}2800 \text{ cm}^{-1}$ shows the C-H stretch region

Table IV.1 Spectrum Analysis of PVDF nanofiber membrane

Wave number (cm^{-1})	Functional Group
1010,70	C-F saturated
1089,78	C-F saturated
1033,83	C-F saturated
792	CH_2
839	CH_2
756,1	CF_3
1261,45	CF_3
1330,88	CF_3

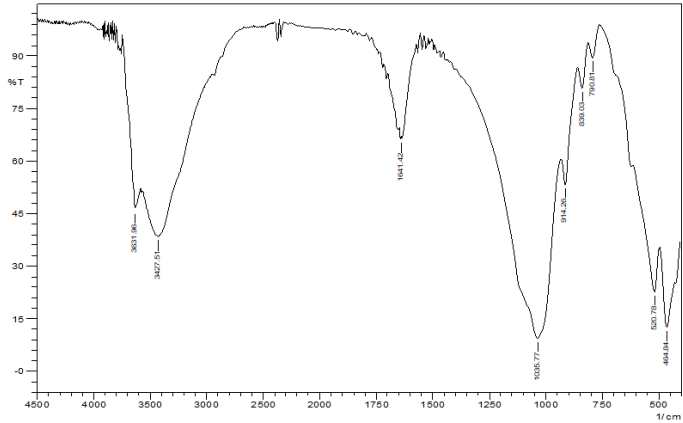


Figure IV.6 FTIR spectra of bentonite

Table IV.2 Spectrum analysis of Bentonite

Wave number (cm ⁻¹)	Functional Group
3631.96	stretching O-H
3427.51	Stretching O-H (H-O-H)
1641.42	bending O-H
1035.77	Si-O-Si
914.26	Al-OH-Al
790.81	Al-O-Al
464.84	Si-O

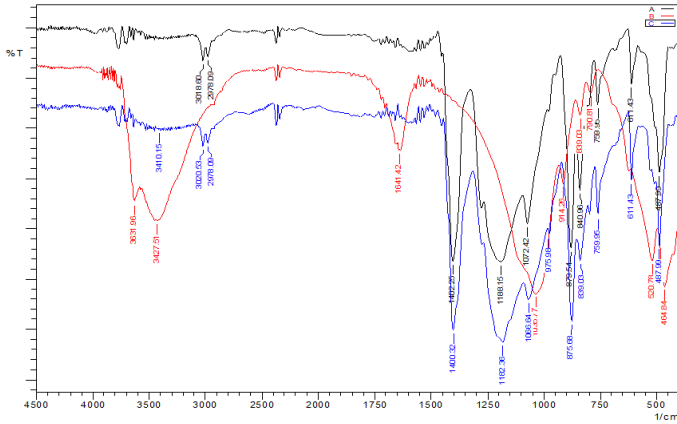


Figure IV.7 FTIR spectra of PVDF nanofibers(A), Bentonite(B) and PVDF-bentonite nanofibers(C)

Table IV.3 Spectrum Analysis of PVDF-Bentonite nanofiber membrane

Wave number (cm ⁻¹)	Functional Group
3500 - 3400	stretching O-H
3200-2800	stretching C-H
1600	bending O-H
1400 – 1200	C-F
1090 - 1040	Si-O-Si , Al-O-Al
1400	C-N
1200	CF ₃
1100 - 1200	C=C
800	C-H
760	Si-O

with the appearance of a peak at wave number 1090-1040 cm^{-1} which indicates the presence of Si-O-Si and Al-O-Al groups, and a peak at 760 indicates a Si-O group, it can be concluded that the bentonite has been successfully added to the nanofibers membrane.

IV.2.2. Surface morphological and elemental characteristics with SEM-EDX

Scanning Electron Microscope (SEM) was used to see the morphology of the PVDF nanofibers membrane and the distribution of bentonite particles in the PVDF-bentonite nanofibers membrane. As shown in Figure IV.8

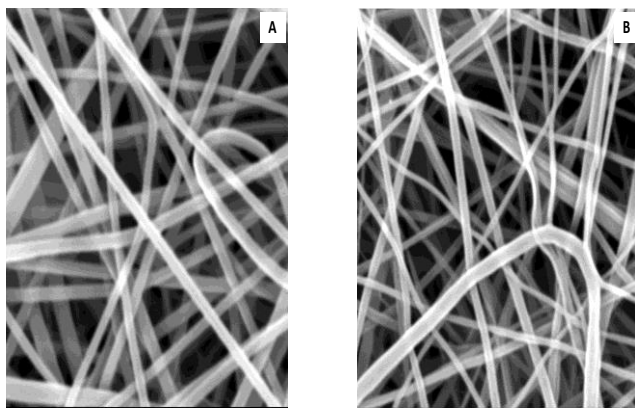


Figure IV.8. SEM image of PVDF(A) and PVDF-bentonite (B) nanofibers membrane

In Figure IV.8 it can be seen that there is a difference in the diameter of the PVDF nanofiber with the diameter of the PVDF-Bentonite nanofiber. The diameter distribution of the nanofibers is shown in Figure IV.7. The average diameter of PVDF nanofibers is around 396.5 nm while the average diameter of PVDF-Bentonite nanofibers is around 470,5 nm. These results indicate that the diameter of the PVDF nanofibers decreased with the addition of bentonite. Bentonite is an ionic polyelectrolyte, causing a higher charge density on the jet surface (taylor cone) which is emitted during the electrospinning process.

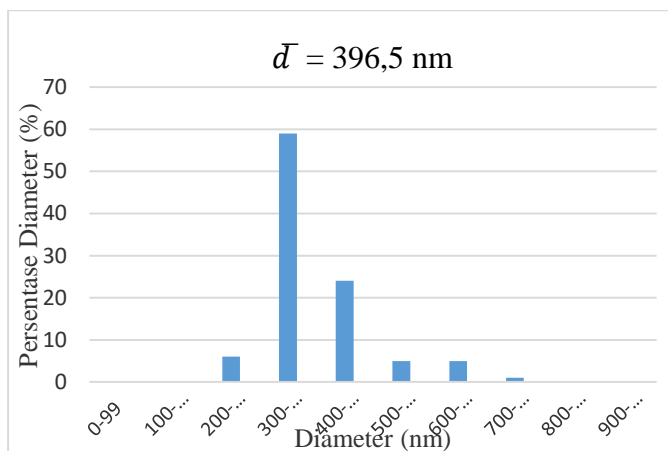


Figure IV.9. Diameter distribution PVDF naofiber

As the charge carried by the jet (beam) increases, the elongation (elongation) force becomes higher in the jet under an electric field. It is known that the overall tension in the nanofiber depends on the repulsion force of the excess charge on the beam (taylor cone). Thus, as the charge density increases, the nanofiber diameter becomes smaller

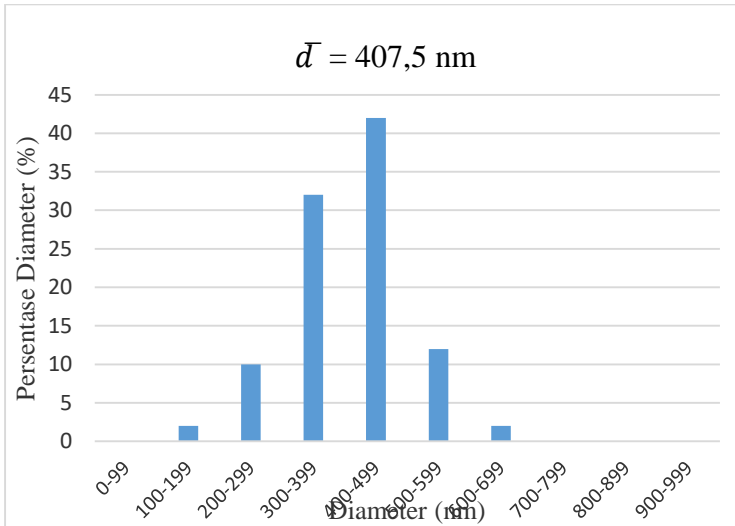


Figure IV.10. Diameter distribution PVDF-bentonite (1%) nanofibers membrane

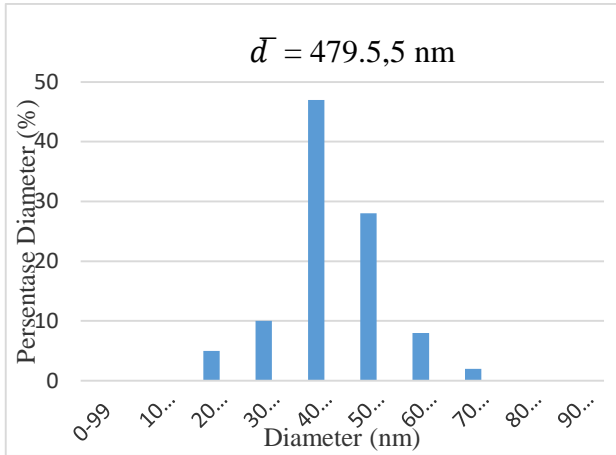


Figure IV.11. Diameter distribution PVDF-bentonite (2,5%) nanofibers membrane

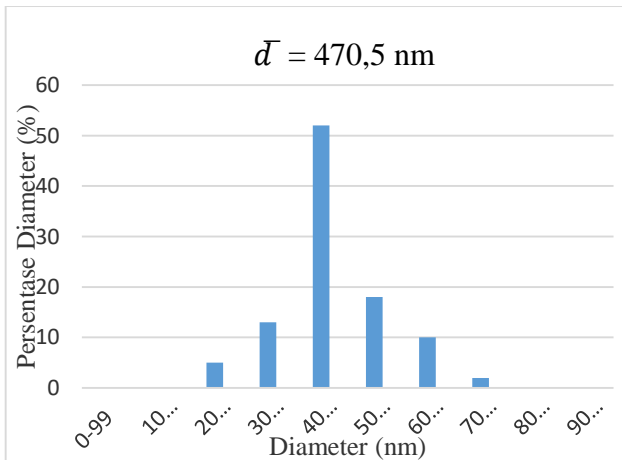


Figure IV.12. Diameter distribution PVDF-bentonite (5%) nanofibers membrane

EDX SEM test was also conducted to determine the composition of the constituents of each membrane. To further ensure the presence of zeolite in the membrane, EDX mapping was carried out.

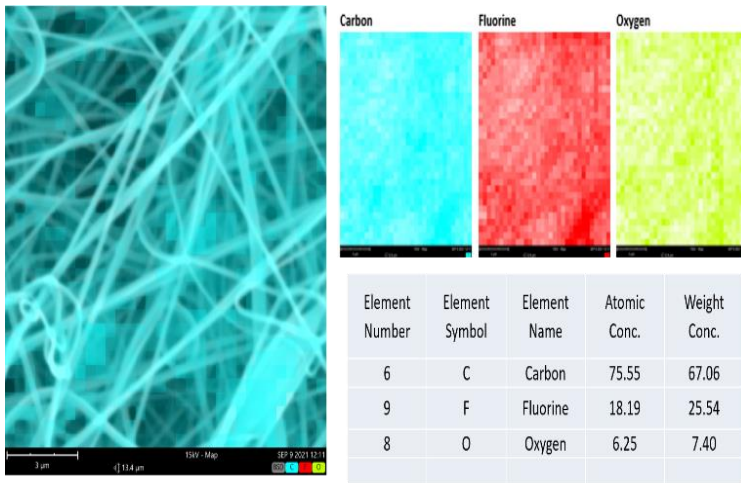


Figure IV.13. Mapping EDX of PVDF(A) nanofibers membrane

From the results of the EDX mapping, it is known that the constituent elements of PVDF nanofibers are C indicated by light blue, F indicated by red and O indicated by green.

And to prove the presence of bentonite in PVDF-Bentonite nanofibers, EDX mapping was carried out,

and from the Figure IV.14 it can be seen that in addition to the C, F and O elements which signify PVDF, there are also Al and Si elements which represent bentonite. Al is indicated by a yellow color, while Si is indicated by an orange color.

From this data it can be concluded that bentonite has been successfully added to the PVDF-bentonite nanofiber

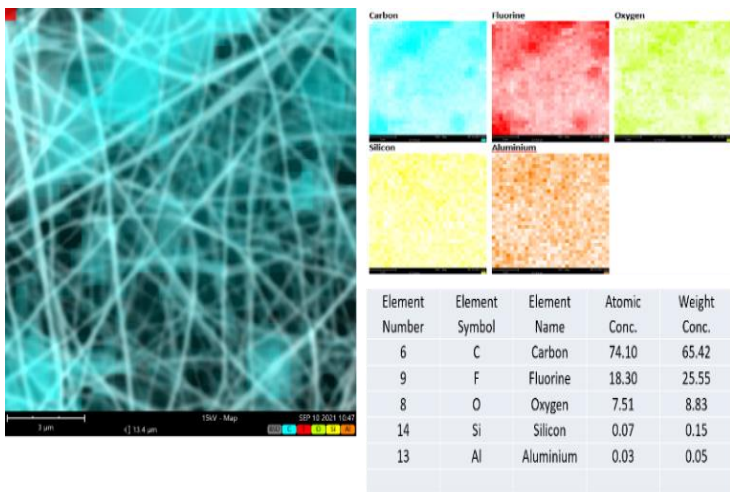


Figure IV.14. Mapping EDX of PVDF-bentonite (5%) nanofibers membrane

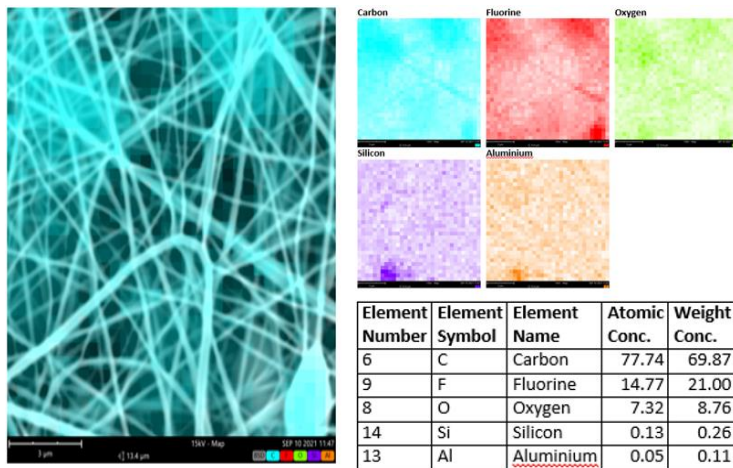


Figure IV.15. Mapping EDX of PVDF-bentonite (10%) nanofibers membrane

IV.2.3. Characterization of the hydrophilicity of nanofiber

The membrane analyzed for its properties against water through the contact angle. The contact angle was measured manually using the DSA (Drop Shape Analysis) method by observing the sessile drop using a camera. From the image recorded on the camera, the angle of contact with the fitting is calculated using ImageJ software. A small contact angle ($<90^\circ$) indicates a high level of wettability (the membrane is hydrophilic), while a large contact

angle ($>90^\circ$) indicates a low level of wettability (the membrane is hydrophobic)[52]. The profile of the water droplets on the membrane is as shown in Figure IV.16.

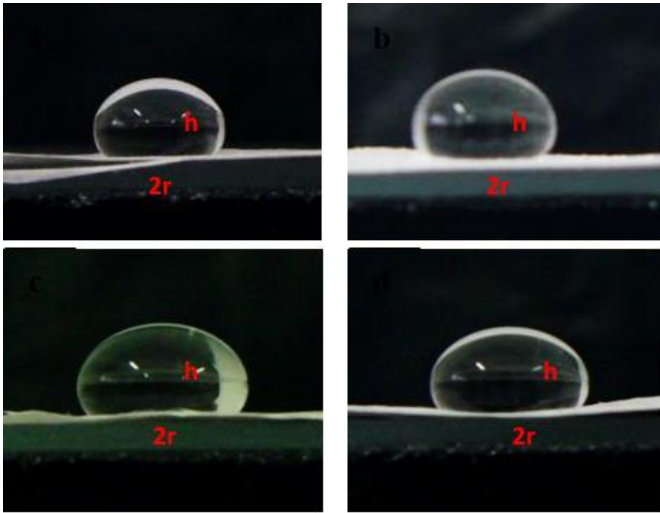


Figure IV.16. Contact Angle of water on PVDF (a) PVDF-Bentonite 1% (b) PVDF-Bentonite 2,5% (c) PVDF-Bentonite 5% (d) nanofiber membranes

Table IV.4 shows a decrease in the value of the contact angle along with the addition of composites. The addition of the bentonite 2,5% composite matrix gave a decrease in the value of the contact angle as much as 10.67° while the addition of the bentonite 1%

composite matrix gave a smaller decrease in the contact angle value of 3.28°, then the the addition of the bentonite 5% composite matrix gave a greater decrease in the value of the contact angle, which was as much as 11.78°.

Table IV.4. Nanofiber membrane contact angle

Nanofibers membrane	Contact angle (°)
PVDF	111,62
PVDF Bentonite 1%	108,34
PVDF Bentonite 2,5%	100,95
PVDF Bentonite 5%	99,84

overall the contact angle for the nanofiber membrane shows a value above 90° which indicates a low level of membrane wetness and indicates that the membrane is hydrophobic. When the contact angle is greater than 90° it generally means that the liquid minimizes contact with the surface so as to form compact droplets. The shape of a liquid droplet is determined by the surface tension of the liquid. In a pure liquid, a large number of molecules are attracted in all directions with the same force as their neighboring molecules, so that the net force is zero, this attractive force is called surface tension. However, the molecules on the surface have no

neighboring molecules to provide a balanced net force. Instead, they are pulled inward by neighboring molecules creating an internal pressure that will affect the shape of the liquid droplet. For membranes with hydrophobic properties, the cohesive forces (liquid-liquid) is stronger than the adhesion force (solid-liquid interaction) so that it will create a droplet character with an angle of $> 90^\circ$, the greater the value of the contact angle indicates that the surface tension is increasing and the surface energy is decreasing because the adhesion force is getting weaker.

Table IV.4 has shown that with the addition of bentonite there will be a decrease in the value of the contact angle which indicates a decrease in surface tension and an increase in surface energy, this is influenced by the presence of surface roughness due to the addition of composites.

The higher the concentration of bentonite added, the more hydrophilic the nanofiber surface will be. This is also confirmed by the data on free energy of surface hydration of nanofibers ($-\Delta G_{SW}$) which increases with increasing zeolite concentration. The increase in the value of $-\Delta G_{SW}$ indicates that the surface of the nanofibers is easier to interact with water. The relationship between hydrophilicity, hydration free

energy and the addition of zeolite can be seen in Figure IV.17 as follow

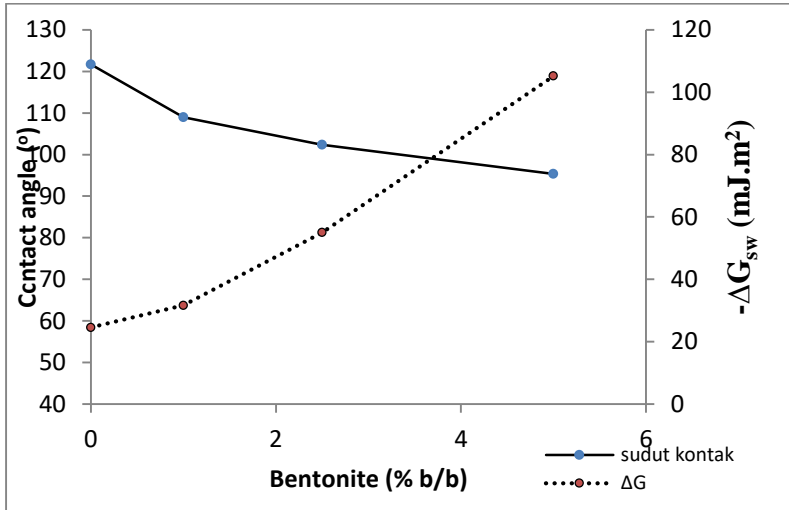


Figure IV.17 Contact angle and surface hydration free energy of PMMA nanofibers and PMMA-Zeolite composite nanofibers

IV.2.4. Spreading Time Analysis

The spreading time measurement is carried out to determine the time required for the liquid to completely wet the membrane (totally wetting). The length of time it takes for the liquid to wet the

membrane depends on the pore density and the nature of the membrane itself. Changes in the value of the contact angle and the time required for the liquid to wet the nanofiber membrane are shown by the following data

Table IV.5 PVDF nanofiber membrane spreading time

Time (minutes)	Contact Angle (°)
0	111.62
30	108.34
60	103.61
90	100.70
120	99.89
150	95.47
180	88.80
210	78.59
240	67.48
270	52.82
300	33.74
330	0,00

Table IV.6 PVDF-Bentonite 1% nanofiber membrane spreading time

Time (minutes)	Contact Angle (°)
0	115.65
30	111.44
60	108.85
90	106.55
120	102.10
150	99.69
180	90.09
210	88.24
240	77.64
270	70.05
300	57.32
330	0

Table IV.7 PVDF-Bentonite 2.5% nanofiber membrane spreading time

Time (minutes)	Contact Angle (°)
0	100.95
30	99.84
60	97.70
90	94.05
120	91.42
150	88.42
180	84.51
210	79.19
240	74.81
270	66.69
300	60.47
330	46.51
360	38.50
390	28.37
410	0

Table IV.8 PVDF-Bentonite 5% nanofiber membrane spreading time

Time (minutes)	Contact Angle (°)
0	102.38
30	101.81
60	99.75
90	97.27
120	96.23
150	93.17
180	89.91
210	86.46
240	81.95
270	77.27
300	70.07
330	58.10
360	51.73
390	40.93
410	29.58
422	20.27

From the data obtained, then a graph is made of the relationship between the value of the contact angle and the time required for the liquid to completely wet the membrane. The relationship between contact angle and wetting time is presented in the following Figure.

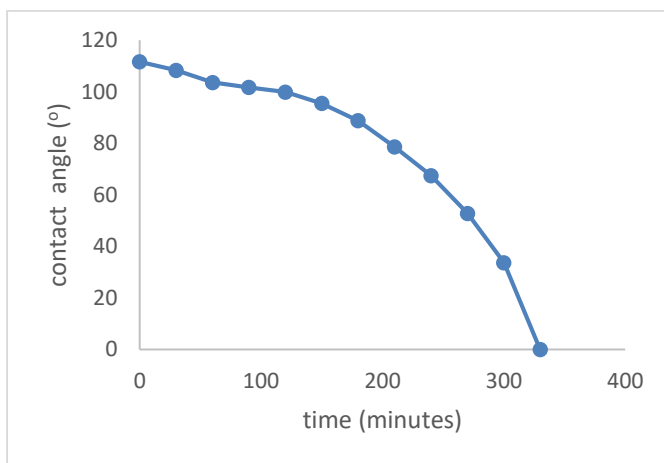


Figure IV.18. Relationship between wetting time and membrane contact angle value 24% PVDF nanofiber

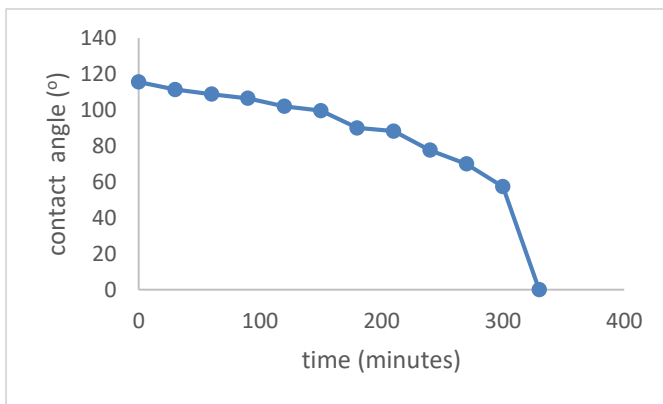


Figure IV.19. Relationship between wetting time and membrane contact angle value 24% PVDF bentonite 1% nanofiber

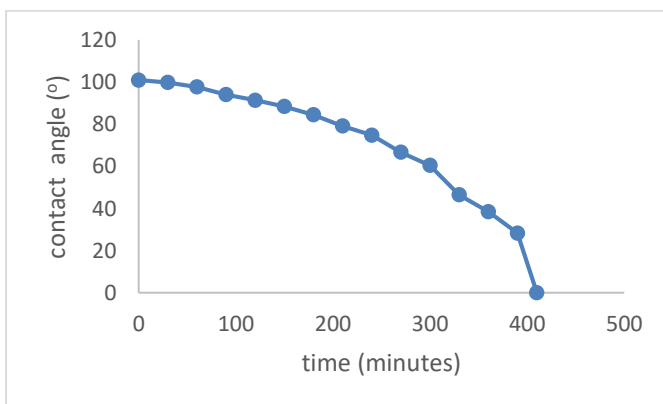


Figure IV.20. Relationship between wetting time and membrane contact angle value 24% PVDF bentonite 2.5% nanofiber

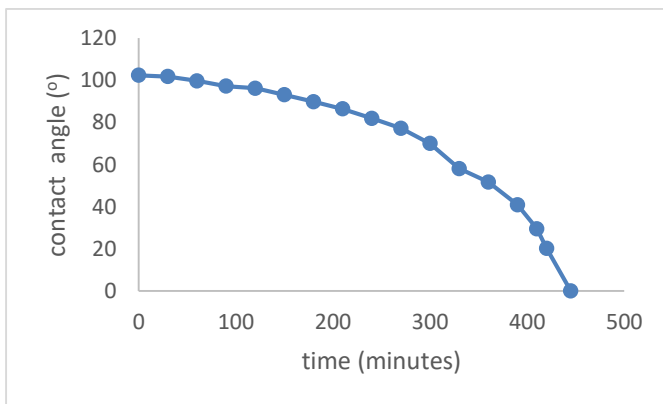


Figure IV.21. Relationship between wetting time and membrane contact angle value 24% PVDF bentonite 5% nanofiber

From the data and graphs shown respectively by Tables IV.5-IV.8 and Figure IV.18-IV.21, it shows that the addition of nanosilica does not change the wetting time, the addition of bentonite can provide a longer wetting time. This happens because the addition of nanocomposites will affect the porosity of the nanofiber membrane, as evidenced by the change in the time required for droplets to wet the membrane. This change in porosity will affect the migratory capacity of lithium ions in the battery, but this needs to be confirmed further by measuring the porosity of the membrane

IV.2.5. XRD Analysis

The diffraction peaks of the copolymer PVDF nanofibers are shown in Figure IV.22

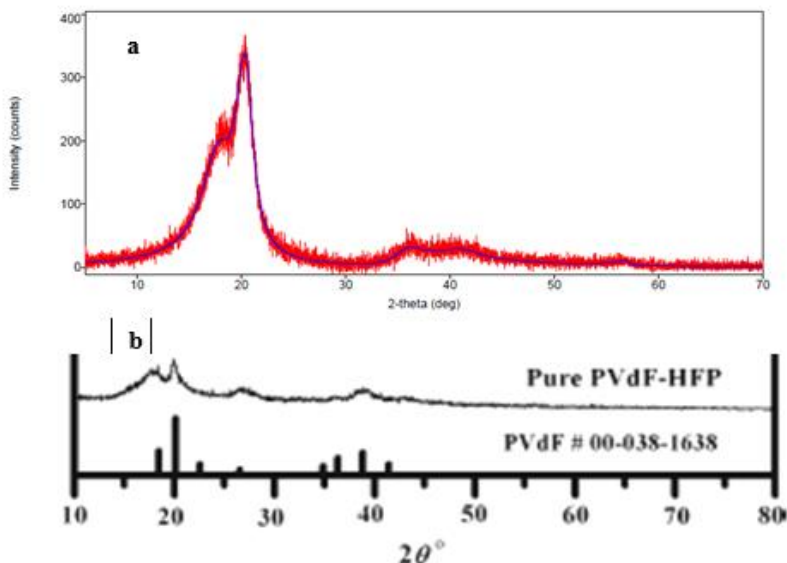


Figure IV.22 Diffraction pattern of PVDF nanofiber (a), PVDF diffraction pattern of HFP copolymer and standard PVDF based on JCPDS # 00-038-1638 (b)

Figure 4.22.a. has shown a pattern that is in accordance with the diffraction pattern of PVDF copolymer HFP results of Padmaraj et al. (2013) (figure 4.22.b) which has been adapted to the standard PVDF diffraction pattern based on the Joint Committee on Powder Diffraction Standards (JCPDS) # 00-038-1638. Padmaraj et al.

(2013) reported that the PVDF-HFP diffraction peaks appeared at around 18.5°, 20°, 26.6°, and 38.9°, in the XRD pattern of the PVDF nanofiber diffraction peaks appeared at 17.66°; 20.34°; 36.09° and 41.3°.

IV.2.6. Mechanical strength characterization

The tensile strength test carried out is obtained results that with the addition of zeolite will reduce the tensile strength. Strong drop tensile strength is due to the presence of bentonite, use of bentonite can be reduce the intermolecular forces, can interfere with intermolecular interactions so that can increase the mobility of the membrane chain, The addition of zeolite can increase flexibility membrane by interfering with interactions between adjacent molecules so that intermolecular forces of attraction reduce

Mechanical properties can be described through tensile test measurements. The mechanical strength of the membrane is expressed in Young's modulus, which is the ratio of stress to strain. The data for tensile test for the membranes can be seen in Table IV.9

Table IV.9. Tensile strength

Nanofiber membranes	Young's Modulus
PVDF	6.9784
PVDF bentonite 2.5%	13.9228
PVDF bentonite 5%	3.7286

IV.3. Application for adsorption methylene blue

Flux test is the ability of the membrane through the filtrate. Measurement of flux value and rejection in methylene blue waste treatment using nanofiber PVDH and PVDF bentonite membrane. The membrane is cut according to the size of the filtration membrane with 47 mm diameter, then the membrane is flowed into the distilled water first so that the pores stable membrane

Table IV.10. Flux of membrane

Nanofiber membranes	Flux (L/m ² .jam)
PVDF	48.53
PVDF bentonite 2.5%	70.64
PVDF bentonite 5%	52,58

Table 4.10 explains that the addition of bentonite will increase the flux, but with increasing a lot of addition of bentonite on the membrane value the resulting flux is

getting smaller. other than that the longer the filtration process makes the value flux is decreasing, it is indicates that fouling occurs on the membrane

The value of the rejection coefficient shows the selectivity membrane, the more the addition of bentonite the value of the rejection coefficient increases, so that the more selective the resulting membrane. On the addition of 10 grams of silica is obtained The coefficient is quite large, this is because that the addition of silica will open the pores membrane so that more molecules of a substance the color caught in the membrane because more and more cavities are formed makes the dye molecules easily pass through the membrane and the presence of bentonite which has a negative surface will be able to hold the blue metiken dye which is a cationic dye (positively charged) so that it can be retained in the membrane.

Table IV.11. Rejection Coefisien of membrane

Nanofiber membranes	Rejection Coefisien(%)
PVDF	42,1405
PVDF bentonite 2.5%	43,4477
PVDF bentonite 5%	25.6373

Then the filtration is carried out repeatedly with the aim of to determine the effectiveness and resistance membrane From the table IV.12 it is found that although the bentonite PVDF membrane has the same or slightly higher adsorption capacity for dyes, if the membrane is used repeatedly it will show better results

Table IV.12. Rejection Coefisien of membrane (repetition)

Nanofiber membranes	Rejection Coefisien(%)	
	1	2
PVDF	42,1405	7,172
PVDF bentonite 2.5%	43,4477	28,4150
PVDF bentonite 5%	25.6373	16,9771

CHAPTER V

CONCLUSSION AND SUGGESTION

V.1 Conclusion

1. To optimum condition for synthesis of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning was 20% (w/v) concentration, voltage 11,5 kV, flow rate is 0.08 mL/h and distance from nozzle tip to collector wa 13 cm.
2. PVDF and PVDF-bentonite nanofibers formed have uniform fibers with diameters around 400 nm, with the addition of bentonite will increase Young's modulus., increase the hydrophilicity properties so as to improve the performance of the membrane

3. The performance of PVDF nanofiber membranes to absorb methylene blue is 42.14%, while PVDF-bentonite nanofibers membranes are 43.45% with better repeatable membrane performance

V.2. Suggestion

This research is only limited investigation on the optimum condition for synthesis of PVDF and PVDF-Bentonite nanofiber membrane prepared by electrospinning and the characteristics performance of PVDF and PVDF-Bentonite nanofiber membrane on methylene blue absorption. The following are recommendations for future research on this field: firstly, the general understanding of synthesis by electrospinning with the variation distance from nozzle tip to collector. Secondly, the variation of concentration of Solution concentration.

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