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Enhancement of Mixed Matrix Ultrafiltration Polyethersulfone Membrane Incorporated with Iron Oxide Nanoparticle for Humic Acid Removal.

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DECLARATION

I declare that this thesis entitled "Enhancement of Mixed Matrix Ultrafiltration Polyethersulfone Membrane Incorporated with Iron Oxide Nanoparticle for Humic Acid Removal" is the results of my own research except as cited in the references.

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ENHANCEMENT OF MIXED MATRIX ULTRAFILTRATION POLYETHERSULFONE MEMBRANE INCORPORATED WITH IRON OXIDE NANOPARTICLE FOR HUMIC ACID REMOVAL

ABSTRACT

The Dry-Wet Phase inversion method was used to prepare the Polyether-sulfone Mixed Matrix Membrane (PES-MMM). Different concentrations of Iron Oxide Nanoparticles (IONPs) were added to the casting solution M2, M3, M4, and M5. In this study, the effects of IONPs on the morphology, performance, hydrophilicity, and anti-fouling of the fabricated PES-IONPs-MMM were analyzed. Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), contact angle, porosity, water content and pure water flux (PWF) measurements were used to characterize the physical and chemical properties of the fabricated PES-IONPs-MMM membranes. Among to this membrane, the hydrophilicity of the PES-IONPs-MMM (M5) surface was enhanced due to the increase in membrane surface water affinity. Also, the porosity of PES-IONPs-MMM (M5) has increased from 75.77% to 86.94%. The anti-fouling performance of the membrane fouled by Humic Acid (HA) solution was analyzed by measuring the fouling resistance parameters. The Relative Flux Reduction (RFR) of the PES MMM (M5) membrane has decreased from 23.30% to 19.34 while the Flux Recovery Ratio (FRR) has been increased from 61.88% to 79.33%.

ABSTRAK

Kaedah penyongsangan Fasa Kering-Basah digunakan untuk menyediakan Membran Matriks Campuran Polieter-sulfon (PES-MMM). Kepekatan Nanozarah Besi Oksida (IONP) yang berbeza telah ditambah kepada larutan tuangan M2, M3, M4, dan M5. Dalam kajian ini, kesan IONP pada morfologi, prestasi, hidrofilik, dan anti-kotoran PES-IONPs-MMM yang direka telah dianalisis. Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), sudut sentuhan, keliangan, kandungan air dan ukuran fluks air tulen (PWF) telah digunakan untuk mencirikan sifat fizikal dan kimia membran PES-IONPs-MMM yang direka. . Hidrofilisiti permukaan PES-IONPs-MMM (M5) telah dipertingkatkan disebabkan oleh peningkatan dalam pertalian air permukaan membran. Juga, keliangan PES-IONPs-MMM (M5) telah meningkat daripada 75.77% kepada 86.94%. Prestasi anti-kotoran membran yang dikotori oleh larutan Asid Humik (HA) telah dianalisis dengan mengukur parameter rintangan pengotoran. Pengurangan Fluks Relatif (RFR) membran PES MMM (M5) telah menurun daripada 23.30% kepada 19.34 manakala Nisbah Pemulihan Fluks (FRR) telah dinaikkan daripada 61.88% kepada 79.33%.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Humic substances (HS) played a crucial role in agriculture industry such as soil fertility and plant nutrients. Humic acid (HA) was humic substances which existed naturally after the decomposition of plant and animals. This organic acid was active in binding ions and organic molecules to form different complexes. This organic matter was the major foulant that adversely affected the system productivity over time. The occurrence of natural organic matter in water and soil was an important concern to ecosystem. Humic substances brought many functions as part of the life cycle through the soil and water and back to plants. According to World Health Organization (WHO), the concentration of HA in potable water should be limited to less than 100 ppm (Teow, 2016).

Untreated water containing HA that being released to the household or industry may harmed living organisms. The presence of HA in aqueous solutions was not directly toxic but has undesirable effects on the taste, odor and appearance to raw water and could lead to organic disinfectant by-products (DBPs), which were undesired and hazardous products in water treatment after disinfection (Maghsoodloo, Noroozi, Haghi, & Sorial, 2011; Tung, Xu, Zhang, Zhou, & Wu, 2019).

In the recent years, membrane separation technology had been chosen for HA removal due to its simple and cost effective method. Furthermore, membrane technology also reduced the usage of chemicals such as coagulants and flocculants as well as better for the environment. Clearly, these technologies offered a simple, ease of operation, low maintenance process and ability to meet various separation demands.

Membrane technology also known to be able to reduce the utilization of conventional wastewater treatment that consumed high cost due to the use of many processes including coagulation and flocculation. There were several types of membrane technology including microfiltration (MF), ultrafiltration (Al Harby et al.), nanofiltration (NF) and reverse osmosis (RO). Each of this membrane technology had different separation capacity prior to their pore size. For MF, the driven pressure of this type of membrane used in the range of micrometre which were down until 0.1µm and consumed operational pressure below 1 bar. UF otherwise used in the range of nanometer from 2 nm up to 100 nm with the pressure requirement from 1 to 6 bar. NF was the membrane process that operated for micrometre range from 1 nm and consumed pressures down 5 to 15 bars. Lastly, RO, it was a membrane process that were operated at pressure of 20 bar in the nonappearance of osmotic pressure. However, the pressures of 40 to 60 bar were required in desalination of seawater (Obotey Ezugbe & Rathilal, 2020)

Surprisingly, there was yet to be a particular investigation for aquaculture effluent waste removal employing membrane separation UF. Thus, the goal of this study was to develop a well-formulated membrane technology capable of tackling and removing a large proportion of humic acid removal. As a result, the current study was investigated the iron oxide nanoparticles blended into a PES matrix membrane to remove humic acid with minimal fouling. This method was produced by producing nanoparticles with the goal of producing conjugate chemicals inorganic compounds such as IO. The addition of IO nanoparticle with PES in matrix membrane had established mixed matrix membrane (MMM) as an effective technological strategy for humic acid removal elimination in this study environment.

Due to their high efficiency at separating different materials, low energy requirement, and simplicity of operation, membrane technologies are the subject of substantial research for wastewater treatment. (RO), (MF), (Al Harby et al.), (NF), and other types of membrane technology are becoming more and common in the scientific and technological communities. While NF, UF, and MF were designed to reject materials, RO, on the other hand, lacked well defined pores. Hancock (2016) states that, as shown in Figure 1.1 and Table 1.1, the tiniest monovalent ions can be removed by a RO membrane, NF membranes can remove most organic molecules and divalent ions, UF can reject big particles and may be able to remove some viruses, and MF can remove all bacteria.

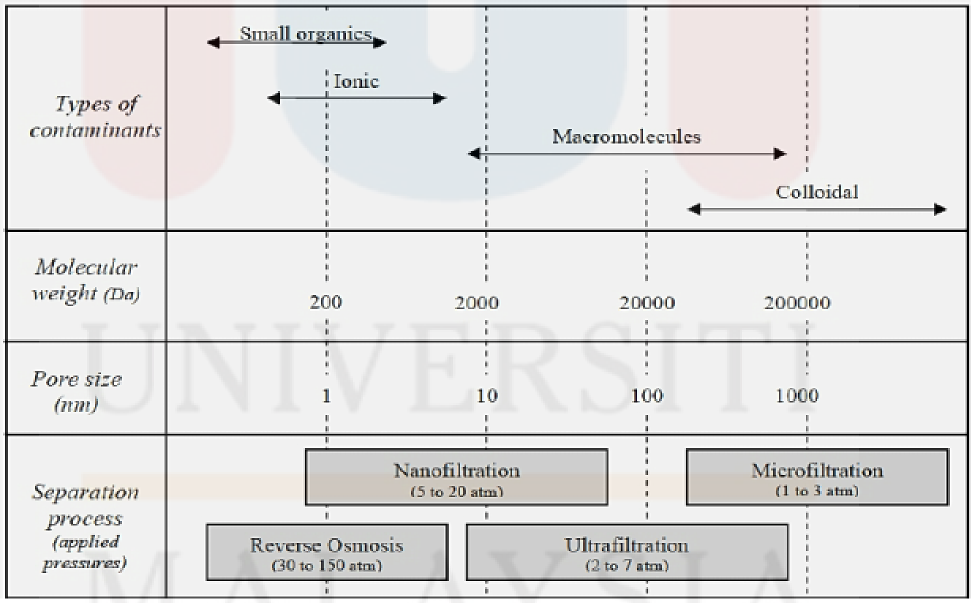


Figure 1.1: The filtration spectrum of membranes.

(Sources: Giwa & Ogunribido, 2012)

Table 1.1: Summary of membrane processes with description.

(Source: Luis, 2018)

Membrane Process	Description
MF	Pressure-driven membrane process in which membranes were used in micrometer range, down to 0.1 μm and required pressures below 1 bar.
UF	Pressure-driven membrane process in which membranes were used in nanometer range, down to 2 nm to 100 nm and required pressures below 1 to 6 bar.
NF	Pressure-driven membrane process in which membranes were used in micrometer range, down to 1 nm and required pressures below 5 to 15 bar.
RO	Pressure-driven membrane process in which membranes were dense and operated at pressures of 20 bar or even below, in the absence of osmotic pressure. Pressures of 40 to 60 bar were needed in seawater desalination. Higher pressures go up to 100 bar in high pressure reverse osmosis.

Based on the **Table 1.1**, it shown that UF had the best potential for HA removal among other processes due to increased productivity and lower pressure required than the others.

Consequently, the limits of UF have pushed researchers to narrow their attention and overcome the issues. Several studies on UF modification by blending (Yan, Li, & Xiang, 2005) and coating (Zhou, Zheng, Wang, Zhang, & Han, 2012) have been reported to develop hydrophilic membrane with high flux, anti-fouling, and antimicrobial properties. In the future, the complex interaction of nanoparticles (NPs) with membrane technology was establish mixed matrix membrane (MMM) as efficient technologies for aquaculture wastewater treatment.

1.2 Problem Statements

Water is a molecule formed by the covalent interaction of hydrogen and oxygen. It is a crucial liquid for practically all species, from the tiniest bacterium to people, and serves various functions and purposes. Ironically, despite increasing economic and human population expansion, the quality of pure water continues to deteriorate. Human routines that use water for industrial reasons such as food processing, chemical processing, cosmetics, and many others (Pabbati et al., 2021). Water pollution caused by humans is referred to as wastewater. Physical, chemical, and biological contaminants are commonly found in wastewater.

The presence of HA in water forms carcinogenic DBPs suchas halogenated organics which direct exposure can cause cancers, miscarriages and nervous system complications without an appropriate treatment process (Hamid et al., 2011). Humic substances were divided into three main types which are HA, fulvic acids (FA) and humin (Susic, 2016). Generally, HA were used in agricultural industry to enhance plant growth also act as soil bactericidal and plant fungicidal. However, HA chelate heavy-metals and bound toxic chemicals to form toxic metal complexes. The process of HA removal from wastewater had remained a challenge and important process in future.

Removal of HA from aqueous solution had been implemented for quite some time ago but most were utilizing removal method, such as filtration (Darwish, Al Abdulgader, AlRomaih, & Alalawi, 2019), flocculation (Rojas et al., 2011), oxidation (Tung et al., 2019), biological method (Yuan et al., 2019) and adsorption (Zhou, Zhou, Ma, & Xu, 2019). However, the drawback of the processes mentioned were high energy consumption with more than two steps of separation process, complex equipment and high usage amount of chemicals which increased the cost of operation and produced harmful substances. Hence, there had been a more promising techniques such as membrane technology.

The issue statement for HA in wastewater treated by UF membrane is to research the efficiency of UF membranes in removing suspended particles and organic matter from HA removal. Understanding the performance of UF membranes under various operating parameters such as flux, transmembrane pressure, and feed concentration, as well as assessing the implications of these conditions on the quality of the treated water, is required. Furthermore, the study will assess the economic feasibility of using UF membranes as a treatment method for HA removal in wastewater.

The capacity of membrane technology to remove micro-substances is gaining greater attention. UF, MF, NF, and RO are some of the most prevalent membrane technologies used to clean wastewater (RO). Because its working mechanism involves concentration polarisation and low pressure, UF was the major focus of this study due to its efficacy for their method of separation, which may minimise the cost of production compared to NF and RO.

Fouling is one of the major issues with UF membranes. The collection and agglomeration of micro-molecules, as well as bio fouling, will have a detrimental influence on the UF membrane's performance. As a result of this difficulty, more pressure must be applied, resulting in increased cost and energy usage. The fouling event is determined by membrane characteristics such as membrane pore size and hydrophobicity. As a result, modifications to the membrane must be made to offset this disadvantage.

In the context of this work, the combination of PES with IONPs to create an appropriate PES-IONPs-MMM to remove HA. IO is an inorganic substance. Iron oxide nanoparticles (IONPs) contribute to the enhancement of mechanical properties in mixed matrix membranes (MMMs) through their reinforcing effect on the polymeric matrix. The incorporation of IONPs tends to promote a more interconnected and robust structure within the composite material. The nanoparticles act as effective fillers, distributing stress more uniformly throughout the membrane. This dispersion helps resist deformation and improves the overall tensile strength, modulus, and durability of the MMM. As a result, the membrane becomes more resistant to mechanical stress, providing greater stability and longevity in practical applications. The improved thermal stability of mixed matrix membranes containing iron oxide nanoparticles arises from the unique properties of these nanofillers. IONPs disperse within the polymeric matrix and act as thermal conductors, facilitating efficient heat dissipation. This characteristic helps prevent the degradation of the polymer matrix at elevated temperatures. Additionally, the presence of IONPs may contribute to the formation of a thermally stable network within the membrane, reinforcing its structure and preventing thermal-induced deterioration. As a result, the MMM exhibits greater resistance to thermal stress, making it suitable for applications in environments with varying temperatures. Iron oxide nanoparticles possess a high surface area due to their nanoscale dimensions and often high porosity. When incorporated into mixed matrix membranes, these nanoparticles significantly increase the overall surface area of the composite material. This enlarged surface area provides more active sites for interactions with gases, pollutants, or other target substances in applications such as gas separation or water purification. The enhanced surface area facilitates greater contact between the membrane and the surrounding environment, leading to improved performance and efficiency in adsorption or permeation processes. In this sense, the addition of IO as a new formulation in PES-IONPs-MMM should be capable of improving membrane characteristics that can increase HA removal.

Furthermore, despite the rapid growth of membrane technology, to the best of our knowledge, PES-IONPs-MMM has yet to be thoroughly investigated for HA removal, particularly to reduce fouling. The approach of employing PES-IONPs-MMM in UF for HA removal has yet to be tested. Thus, investigating the addition of IONPs in PES-MMM would be intriguing for crucial features such as membrane antifouling. The hydrophilicity, fouling resistance of membrane after incorporation addition of IONPs in PES MMM for HA removal can be further evaluated during this study.

1.3 Objectives

The main objectives of this research are:

1. To determine the physical and chemical properties of PES-MMM ultrafiltration membrane incorporated with IONPs for HA removal.
2. To study the performance of fabricated PES-IONPs-MMM based on permeation and HA rejection analysis using dead end filtration.
3. To evaluate the fouling mechanism of the fabricated PES-IONPs-MMM after HA removal.

1.4 Scope of Study

In this study, PES-IONPs-MMM UF membranes were carried out by dry-wet phase inversion technique. IONPs were added in the dope solution at different composition to minimize agglomerations and improve the properties of the membranes. The fabricated PES-IONPs-MMM were characterized in term of surface morphology, hydrophilicity and surface functional group using scanning electron microscope (SEM), contact angle, and Fourier-transform infrared spectroscopy (FTIR). Next, the scope of this study was also to determine the efficiency of fabricated PES-IONPs-MMM for the removal of HA. Dead-end configuration was used to study the performance evaluation of fabricated PES-IONPs-MMM for HA flux, HA rejection and water flux. Also, fouling evaluation and mechanism of fabricated PES-IONPs-MMM were investigated. The data were analysed and used to calculate the flux recovery ration (FRR) for fouling resistance evaluation.

1.6 Significant of Study

Following the advancement of technology, various disciplines of technology, including membrane technology, continue to evolve and be updated. In this study, membrane technology was used as a physical instrument with excellent efficacy in rejecting certain undesired products. Because of its excellent performance and cheap manufacturing cost, membrane technology is the subject of several studies. This study has a few implications. This research and findings might help us better understand the importance of IONPs in the membrane. This is because IONPs has gained popularity due to its versatility in a variety of applications, including HA removal. As a result of this research, we will have a better grasp of IONPs chemical properties in terms of its potential to minimise fouling and increase the hydrophilicity of membrane UF. Furthermore, IONPs used in this study to improve the performance of the membrane on HA removal and antifouling properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Humic Substances

The humic substances (HS) were natural organic matters (NOM) which existed abundantly in untreated waters such as rivers. HS was classified into three main categories which are FA, HA and humins according to their solubility. The elemental composition of humic materials was approximately 40–60% carbon, 30–50% oxygen, 4–5% hydrogen, 1–4% nitrogen, 1–2% sulfur and 0–0.3% phosphorus (Sutzkover-Gutman, Hasson, & Semiat, 2010). HS were negatively charged at pH of natural waters.

Compared to the HS found in natural waters which was dominated by FA, the Aldrich HA was considered to have larger molecular sizes and higher aromatic and metal contents (Taniguchi, Kilduff, & Belfort, 2003). In other words, the commercial HA possess higher rejection than natural water where permeation fluxes were lower.

A class of naturally occurring organic chemicals known as Humic Substances (HS) are present in peat, coal, and other sedimentary settings as well as in soil. They are created by the breakdown of plant and animal matter and are made up of a complex mixture of substances, such as Fulvic Acids (FA), Humic Acids (HA), and humins. Also, it considered to be a significant part of the biosphere as a structurally defined element of soil organic matter because they control several physical and chemical processes in soil. They help to give surface soils their brown colour. HS are crucial for plant development, soil fertility, and water purification. Additionally, they are employed in water purification to eliminate pollutants and in agriculture as a soil amendment (Kumar Gautam et al., 2021). In Table 2.1 below, the HS compounds’ elemental composition is tabulated.

Table 2.1: Elemental composition in HS.

Source: (Fernando Mahler et al., 2021)

	Carbon	**Oxygen**	**Hydrogen**	**Nitrogen**	**Sulfur**
Fulvic Acid	35.1-75.7%	55.8%	0.4-7.9%	0.5-8.2%	0.1-55.8%
Humic Acid	37.2-75.8%	7.9-56.6%	1.6-11.7%	0.5-10.5%	0.1-8.3%
Humin	48.3-61.6%	28.8-45.1%	7.3-14.2%	2.9-6%	0.1-0.9%

2.1.1 Humic Acid

The humic acid (HA) endowed with aromatic and aliphatic characteristic which contributed to surface charge and reactivity mainly by the phenolic and the carboxyclic groups (Sutzkover- 12 Gutman et al., 2010). As reported in the literature of Sutzkover-Gutman et al (2010), the variability of naturally occurring humic substances was responsible for membrane fouling due to the presence of divalent ions which can seriously affects the charge of membrane surface.

HA contained several functional groups such as carboxylic acid, phenolic hydroxyl and alcoholic hydroxyl with average composition value shown in Table 2.3. From Table 2.3, HA contained the most carboxylic acid group which gave the ability to form complexes with metal ion. The metal complexes contaminated the water reservoirs, but HA contributed to metal inactivation which was possible to reduce the toxicity and corrected the water quality standards (Moiseenko et al., 2012).

Table 2.3: Average composition of functional groups in HA.

(Source: Barlokova & Ilavsky, 2012)

Functional group	HA
-COOH	4.4
-OH	3.3
-OH (R)	1.9
= C = O	1.2
-O – CH_3	0.3

In addition, HA was insoluble at acidic pH values less than 2 and soluble at higher pH values. The chemical structure was dominated by phenol groups and long carboxylic fatty acids which was hydrophobic. The negative effect of HA on water quality such as acidity increased, formation of metal complexes and intensity of the colour of water such as HA was dark brown (Kanmaz, 2019). Due to these effect, the HA were removed in water by membrane technology in order to satisfy the quality of drinking water with indicators such as value stipulated for faecal coliforms on turbidity, pH and disinfection based on World Health Organization of Guidelines for Drinking-Water Quality (GDWQ) (Fewtrell & Bartram, 2001) and commercial use

2.2 Membrane Technology

In today's world, membrane technology is gaining popularity and is increasingly being utilised for a variety of treatment methods, including wastewater treatment. Because of their remarkable efficacy on rejecting tiny substances. Membrane is described as a unique, thin, semipermeable barrier that holds components while allowing others to pass through based on certain qualities. Membrane filtration techniques used to filter or eliminate undesirable macromolecules include reverse osmosis, microfiltration, ultrafiltration, and nanofiltration. Microfiltration (MF) membranes generally have pore diameters ranging from 1 m and are widely used to separate and distinguish microorganisms, large colloids, viruses, and cells in water. MF membranes have been investigated for a variety of water and wastewater matrices (Ouyang et al., 2019).

In this sense, a membrane is described as a selective barrier between two phases, with the term ‘selective' inherent to a membrane or a membrane process. In this study, ultrafiltration was used as one of the physical methods to eliminate HA. This type of membrane filtration is based on the use of porous membranes with IO ranging from 1 to 300 kDa, pore sizes ranging from 2-100nm, and trans membrane pressures ranging from 2 to 4 bars.

2.3 Polyethersulfone

Many membrane materials are frequently utilised in today's world, including polypropylene, polysulfone, polyethylene, PES, and PVDF. The primary emphasis of this research is polyethersulfone polymer. Polyethersulfone is commonly employed as a key based membrane because to its superior chemical and physical properties, which make it appropriate for usage as a filtering membrane-based material.

However, this polymer has its own disadvantage, which is its hydrophobicity. This negative attribute is not beneficial for wastewater treatment since hydrophobicity can lead to reduced membrane permeability and, as a result, greater fouling events. Referring to (Ladewig & Al-Shaeli, 2017) The hydrophilicity of PES can be enhanced via carboxylation, in which the carboxyl group replaces the aromatic ring's hydrogen atom. Figure 2.4 shows PES contains ether and sulfone groups in repeating units.

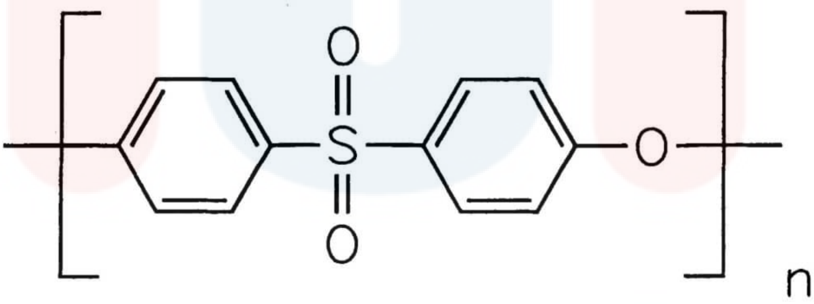


Figure 2.4: Chemical formula of non-functional PES polymer.

(Maximous et al., 2009)

2.4 Hydrophilicity Enhancement Properties of PES

The casting solution’s IONPs additions enhanced membrane performance. Increases in PES hydrophilicity could be achieved through blending, graft polymerization, and surface chemical modification, among other techniques (Liu et al., 2019).

Gao et al., 2021 claims that the assembly of IONPs improved the hydrophilic stability of the membrane. The contact angle demonstrated how the membrane’s hydrophilicity was enhanced by the addition of IONPs. Additionally, the modified membrane had a greater pure water flux recovery ratio (>79%) than the pure PES membrane (61%). In other words, the addition of the IONPs might enhance the permeability performance of the PES membrane. The mixing adjustment preserves the PES’s physical and mechanical characteristics while simultaneously enhancing its hydrophilic qualities, water permeability, and fouling resistance. It is a quick and easy method to increase the hydrophilicity of PES membrane (Liu et al., 2019).

Graft polymerization is yet another technique. By attaching monomers to the side of an existing polymer backbone, a polymer chain is created. In situ graft polymerization and live polymerization are the two main varieties of graft polymerization. In situ graft polymerization involves combining the monomers and the seed polymer in a reactor. In the meantime, living polymerization include the seed polymer is modified with a functional group to enable the controlled addition of monomers to the developing chain. Graft polymerization can be used to produce a range of polymer materials with special qualities, like increased toughness, strength, and thermal stability. Also, higher water flux can be achieved because the presence of hydrophilic chains on the membrane surface makes it easier to reduce the interfacial tension with water. Additionally, the antifouling resistance improves with increased membrane hydrophilicity (Pinem et al., 2019).

2.5 Polyethersulfone Mixed Matrix Membrane

Polyethersulfone (PES) mixed matrix membranes (MMMs) with IONPs have been studied for a variety of applications, including water, wastewater treatment and HA removal. IONPs have been utilized as fillers in PES membranes to improve its permeability, selectivity, and fouling resistance.

PES mixed matrix membranes with IONPs have been demonstrated to be successful in removing HA in the wastewater. For example, Ebrahimi et al. (2018) studied the effectiveness of PES MMM with IO in the treatment of synthetic wastewater containing nitrogen and phosphorus. The researchers discovered that PES MMM containing IO exhibited higher flux rates and lower fouling rates than PES membranes without IO. The study also discovered that PES MMM with iron oxide had greater nitrogen and phosphorus removal effectiveness than PES membranes without IO.

The effectiveness of PES MMM with IONPs in the treatment of HA removal in another investigation. The researchers discovered that PES MMM containing IO exhibited higher flux rates and lower fouling rates than PES membranes without IO. The researchers also discovered that PES MMM containing iron oxide had higher removal effectiveness for suspended particles, organic matter, nitrogen, and phosphorus than PES membranes without IO.

PES-MMM containing IONPs have demonstrated potential in enhancing membrane filtration performance in the treatment of HA removal. The use of IONPs as fillers in PES membranes can improve their permeability, selectivity, and fouling resistance, resulting in more effective and efficient in HA removal.

2.5 Iron Oxide Nanoparticles

IO or a metal oxide that comes with excellent antibacterial and physicochemical qualities (Moezzi et al., 2012). IO is commonly employed as to remove carbon-based photocatalyst pollutants and toxins from the air and water (Xu et al., 2012). Because of the utilization of IO nanomaterials has received much attention due to their unique properties such as extremely small size, high surface-are-to-volume ration, surface modifiability, excellent magnetic properties, and great biocompatibility (Xu et al., 2012). As a result, IONPs is one of magnetic that have been synthesized by energy milling, ultrasonic impregnation and using Tridax procumbens leaf extract and IO also can be used in wastewater treatment for adsorb heavy metals compared to other metal oxides, silver exhibits higher toxicity to microorganisms while it shows lower toxicity to mammalian cells (V, 2018). Along with their best optical properties, IONPs dispersion is also lively for HA removal. The applications for IONPs are for adsorption capacity which also have high surface areas and can adsorb various substances onto their surfaces. This property makes them useful in HA removal applications for removing contaminants such as heavy metals, organic pollutants, and phosphate through adsorption onto their surfaces. Addition of IONPs can help to improve PES membrane for contaminant removal.

2.5.1 PES Membrane Incorporated with IONPs

In **Table 2.4**, it shows the summary of the PES incorporated with IO based on its performance evaluation which are its permeability of membrane were produced that can proved its hydrophilicity, the static contact angle, and the performance of its pure water flux.

Table 2.4: PES membrane incorporated with IO.

PES Wt.%	Additives Wt.%	Types of Filtrations	Properties	Performance Evaluation	Ref.
18	IO (0.1-2.0) CA (2)	UF	The contact angle achieved in this work for 2.0 wt.% of IO exhibited 39.87°	Permeability produced using 2.0 wt.% in hydrophilicity of the membrane the permeability and the hydraulic resistance.	(Evangeline et al., 2019)
26	PVP (0.5) DMF (36.23) NMP (36.23) IO (1.04)	UF		Pure PES ENMs showed a small reduction in oil rejection (2.6-6.6%) when compared to other ENMs (87.16-91.15%). Excellent water flux recovery (79.50%) when tested with synthetic oil solution (12,000 ppm).	(Al-Husaini et al., 2019)

Based on the Table 2.5, the application of different type of polymers in the fabrication of UF exhibit excellent performance in the permeability of membrane were produced that can proved its hydrophilicity, the static contact angle, and the performance of its pure water flux. In contrast, although PES, PVP, DMF, NMP, CA and IO are commonly applied as base polymer in the fabrication of UF membrane, PES membranes have high mechanical strength and chemical resistance, while PVP has the good performance in membrane. The performance of IONPs in membranes, IONPs can exhibit antifouling properties when incorporated into membranes (Altalhi & Mazumder, 2023). The presence of IONPs can create a hydrophilic surface that reduces fouling by repelling foulants such as proteins, organic matter, and colloidal particles. This can lead to improved membrane performance and reduced fouling rates (Nawi et al., 2022).

CHAPTER 3

MATERIALS AND METHOD

3.1 Materials

The chemicals and reagents that are will be required for fabrication of PES were shown in Table 3.1.

Table 3.1: List of chemicals and reagents along with their functions.

No	Chemical / Reagent	Purpose	Manufacturer
1	Humic Acid	Sample solution	Sigma-Aldrich
2	Polyethersulfone (PES)	Membrane polymer	BASF
3	Iron oxide	Inorganic NPs	The Chemours Company
4	Acetic Acid	CS solvent	Wego Chemical Group
5	Nitrogen gas	Compress dope solution	Well gas (Malaysia)
6	N-N-dimethylacetamide (DMAc)	Solvent	Sigma-Aldrich (USA)
7	NaOH	pH adjuster	Merck
8	Deionized water	Clean the membrane	Synergy, Milipore, USA
9	PVD		

10	Distilled water	Coagulation bath	UMK laboratory

3.2 Equipment

Equipment that was uses had specific function with the method of usage. Therefore, a proper utilization of equipment applies to achieve maxmum performance. The equipment involves was outlines in detail with its function in Table 3.2.

Table 3.2: List of equipment used and its functions.

No	Equipment	Purpose
1	Glass plate/cover	To sluggish the evaporation of solvent, permitting for a film with a uniform thickness without curling
2	Magnetic Stirrer	To establish rotating magnetic field to allow the immersed stir bar to spin very quickly
3	Electronic balance	To quantity speedily and precisely the mass of a ingredient
4	Casting knife	To restrain coating with extensive range of film widths
5	Plastic Basin	To immerse the polymer cast film coated glass plate in a non-solvent solution for coagulation bath
6	Stopwatch	To measure the amount of time elapsed from a particular time
7	Thermometer	To measure the temperature of the solution
8	Sonicator	To apply sound energy to agitate particles in solution which can use to mix solution, speed the dissolution and remove dissolved gas from liquids.
9	Membrane casting machine	To produce flat sheet polymeric membranes by coating a thin film of polymer solution
10	Oven	To dry up the sample and evaporating
11	Dead end stirred cell	Batch process for filtration system to test the performance of membrane
12	Scanning electron microscope (SEM)	To produce images of the membrane samples by scanning the surface with a focused bean of electrons which yield various. signals to obtain information about the surface composition

13	Contact angle goniometer	To measure the contact angles of the membranes
14	Fourier transform infrared. spectroscopy (FTIR)	Used infrared light to identify the presence of certain functional. groups, side chains and cross-links

3.3 Membrane Preparation

Table 3.1 states the fabrication of PES-MMM in this study. Where M1 was a control parameter, which was solely pes without addition of IONPs which was the purposes to observe the capability of PES for HA removal. M2 until M5 were the fabrication of PES-MMM that were incorporates with different concentration of IONPs. Table 3.3 presents the summarizes membranes and the compositions of dope solutions.

Table 3.3: Membrane and formulation composition.

Label of the membrane	UF Membrane	PES wt.%	DMAc wt.%	CS-IO HNPs wt.%
M1	PES Membrane	17.0	83.0	-
M2	PES + IONPs	16.0	82.5	1.5
M3	PES + IONPs	16.0	82.0	2.0
M4	PES + IONPs	16.0	81.7	2.3
M5	PES + IONPs	16.0	81.5	2.5

The dry-wet method approach was used to construct the PES-IONPs-MMM membranes for UF. Before fabrication of membrane was formed, the PES was dry at 80 °C for 20 hours. Initially, the pure PES casting solution was created by continuously agitating it with the solvent DMAc for 12 hours at 70 °C. For around 20 minutes, the solution was degassed. Following that, the casting solution was distributed over a glass plate using a casting knife with a thickness of 250 µm (Celik et al., 2011).

3.4 Characterization of Fabricated Mixed Matrix Membrane

In the context of this study, membrane characterisation holds important key aspect to identify the many properties of membrane that provide detail information of the membrane nature. Membrane characterization undergone by pervious research can be divided into physical and chemical characterization. Membrane characterization should exhibit the accurate and keep the originality of studied membranes properties, for sure the characterization method should be not consuming high period to conduct and does not disturb or destroy membranes.

3.4.1 Physical Characterization

In this study, physical characterizations were performed to explore the surface morphology, and other physical features of the membrane. Contact angle, and membrane porosity are among the characterization.

3.4.1.1 Scanning Electron Microscopic (SEM)

The first physical characterization that was examined in this investigation is by using SEM. SEM was used to analyse and assess the surface morphology and surface structure. To conduct SEM in this study, the membrane was sliced into tiny pieces and immersed in nitrogen liquid for around one minute. The membrane is then broken, and a vertical double-sided carbon adhesive foil is attached as a sample container.

3.4.1.2 Contact Angle (CA)

The hydrophilicity of the membrane was used to determined using the contact angle method. The membrane samples were placed on a glass slide for this examination. The double-sided tape was used to ensure that the membrane faces upright. Using instruments known as motor powered micro syringes, water droplets was be put on the surface of a dry membrane. The pictures captured by the camera was analysed using imaging software called DROP to determine the contact angle for the membrane. The measurements were performed ten times to ensure that the data obtained are accurate.

3.4.1.2 Porosity

The dry weight of the membrane was used to assess its porosity. To begin the porosity test, the membrane was wetted and immersed in DI for about 24 hours. After 24 hours, the extra moisture from the membrane was cleaned away using filter paper, and the membrane's weight will be to measure. The membrane was next being dried in an oven at 25 degrees Celsius for 10 hours. The mathematical formula was used to compute the dry weight (Vatanpour et al., 2012).

$$\varepsilon(\%) = \frac{Ww - Wd}{(Ww - Wd)/\alpha w + Wd/\alpha\rho} \times 100\% \qquad Equation\ 3.1$$

Where Ww was the wet membrane weight (g), Wd was the dry membrane weight (g), dw was the pure water density (1.0 g/cm^3), and dp was the polymer density (1.37 g/cm^3).

3.4.1.3 Water Content

The membranes were weighed before being wiped with filter paper after being soaked in water for 24 hours to determine their water content. The wet membrane was dries for 48 hours at 75 °C in oven to get their dry weights. The percentages of water content were calculated using the calculation shown below (Abedini et al., 2011):

$$WC = \frac{(Wwet - Wdry)}{Wwet}\ x\ 100\% \qquad Equation\ 3.2$$

3.4.2 Chemical characterization

Chemical characteristic emphasis on membrane composition and structure.

3.4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was utilized in this investigation to determine the functional group present in the membrane. This procedure was aid in understanding the surface chemistry of the produced membrane, as well as a better understanding of chemical bonding and molecular changes in the membrane. The surface chemistry of the synthesized membranes was determined using FTIR spectroscopy to examine the changes in chemical bonding of the molecules. With the use of the JASCO FTIR-4100, FTIR spectra with wave numbers ranging from 4000 cm^{-1} to 500 cm^{-1} .were obtained.

3.5 Performance Evaluation of the Fabricated PES-IONPs for HA Removal

3.5.1 Preparation and Analysis of Humic Acid Feed Solution

HA solution was used as the feed solution which is used to study the performance of UF membrane in term of HA rejection and flux. HA solution was prepared by dispersing 0.05 g of HA in 1 L of DI water. Therefore, no pre-treatment needed because it was artificial HA with molecular weight ranging from 20,000 to 50,000 Da. The HA solution was sonicated for an hour for homogenous solution. The pH of HA was adjusted to 7.70 by pH bench with the aid of 1 M of HCl and 1 M of NaOH. In addition, the concentration of HA solution was fixed at 50 mg/L by using UV spectrophotometer at wavelength of 254 nm.

3.5.2 Membrane Permeation Test for HA Removal

The performance of PES membrane was investigated based on PWF, HA flux and HA rejection. The set-up configuration of the membrane permeation test was illustrated in Figure 3.1. The compressed nitrogen air was supplied into the dead-end cell. The pressure of nitrogen gas filtered out the HA molecules and induce permeate flow. The permeate flow was measured by the electronic weighing balance. The electronic weighing balance was connected to the computer through a software recognized as ‘’Win-CT’’. It was very easy to use which data was transmitted and generated from the balance directly into the computer.

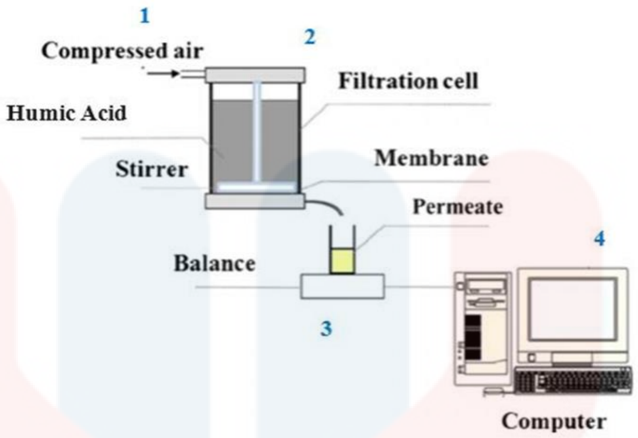


Figure 3.1: Dead-end filtration schematic diagram.

(**Source:** (Zhu et al., 2015))

3.5.3 Fouling Resistance

First, the new membrane was applied with pressure during the UF which caused the flux decline without any fouling. Therefore, all new membranes were filtered with pure water until achieving the steady state before evaluating the performance. The PES-IONPs-MMM was continuously supply with nitrogen gas. The HA flux was measured by weighing the permeate of membrane bioreactor on the weighing balance at interval time. The PWF was calculated quantitatively by using the Equation 3.3 (Bahmani et al., 2017; Zhu et al., 2015):-

$$J_{WF} = \frac{V}{A_m t} \qquad Equation\ 3.3$$

Where J_{WF} was the pure water flux (L/m^2 .h), V was the permeate volume (L), A_m was the effective filtration area (m^2) and t was the measurement time (h).

After the pure water filtration, HA solution was carried on at a pressure of 2 bar for an hour. The concentration of HA before filtration and permeate after the experiment was measured. At different interval of time, the HA flux was calculated by using Equation 3.4 (Bahmani et al., 2017). The digital weighing balance was connected to the computer through data weight system.

$$J_{HA} = \frac{V}{A_m t} \qquad Equation\ 3.4$$

Where J_{HA} was the HA flux (L/m^2 .h), V was the permeate volume (L), A_m was the effective filtration area (m$^{2)}$ and t was the measurement time (h).

3.7 Determination of Fouling Mechanism

The fouling resistance was investigated and determined using relative flux reduction (RFR) and Equation 3.5 (Ayyaru & Ahn, 2017)

$$RFR(\%) = 1\text{-}\frac{JTS}{JWF}) \times 100\% \qquad \text{Equation 3.5}$$

Where RFR was the relative flux decrease, JTS was the permeate flux (L/m^2.h) of the tested solution (Humic Acid), and JWF was the starting water flux.

The constructed membrane was cleaned out with distilled water for roughly 15 minutes, and filtering was resuming with pure water input into the feed tank. Along with *Equation 3.6*, the second period of PWF computation was utilised to estimate the flux recovery of the membrane (Vatanpour et al., 2012).

$$FRR(\%) = \frac{JWF2}{JWF} \times 100\% \qquad Equation\ 3.6$$

The total resistance mentioned here included intrinsic membrane resistance and fouling resistance (Rf). Equation 3.7 was used to compute Rm quantitatively (Ahmad et al., 2018).

$$R_m = \frac{TMP}{uJWF} \qquad Equation\ 3.7$$

The total resistance was calculated as the sum of intrinsic membrane resistance, Rm, and fouling resistance, Rf owing to reversible, Rr, and irreversible, Rir pore adsorption. These resistances were computed using the experimental results and Equation 3.8 (Ahmad et al., 2018).

$$R_t = R_m + R_f + R_r + R_{ir} \qquad Equation\ 3.8$$

$$R_f = \frac{TMP}{uJ\mathrm{T}S} - R_m \qquad Equation\ 3.9$$

$$R_{ir} = \frac{TMP}{uJWF2} - R_m \qquad Equation\ 3.10$$

$$R_r = R_f - R_{ir} \qquad Equation\ 3.11$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Chemical Characteristics

4.1.1 ATR-FTIR Analysis

ATR-FTIR spectroscopy studies were carried out in nanoparticles membranes between wavelengths ranging from 4000 cm^{-1} to 500 cm^{-1}. The FTIR spectra of pure membrane without IO nanoparticles were shown in Figure 4.

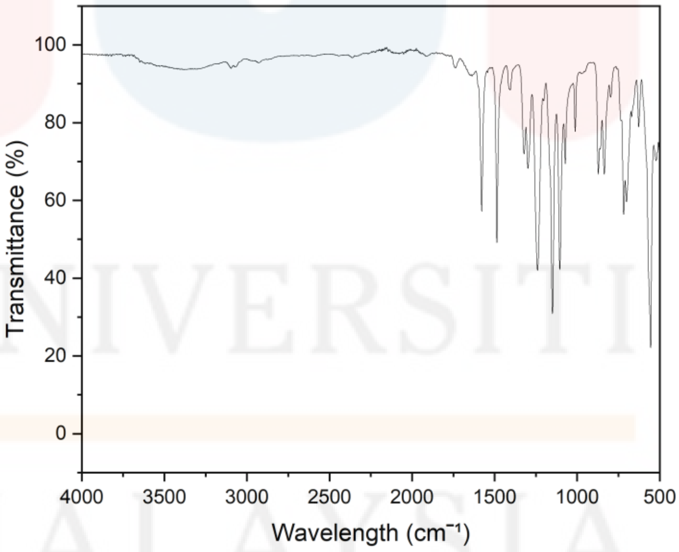


Figure 4: The pure PES membrane's FTIR spectroscopy.

Based on the spectra, the pure membrane does not reveal any significant peak because it does not contain IONPs. The absorption peak at below 1600 cm^{-1} was attributed to the stretching vibration of the C=C (carbon-carbon double bond) of benzene ring. However, it does not reveal any significant peak above 2000 cm^{-1}.

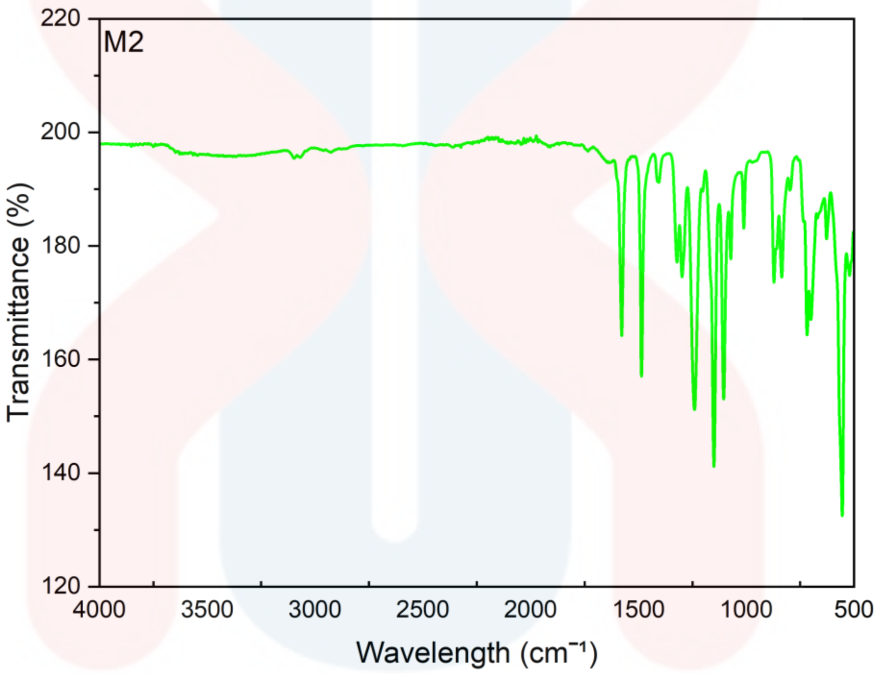


Figure 5: The ATR-FTIR spectroscopy of M2 with IONPs

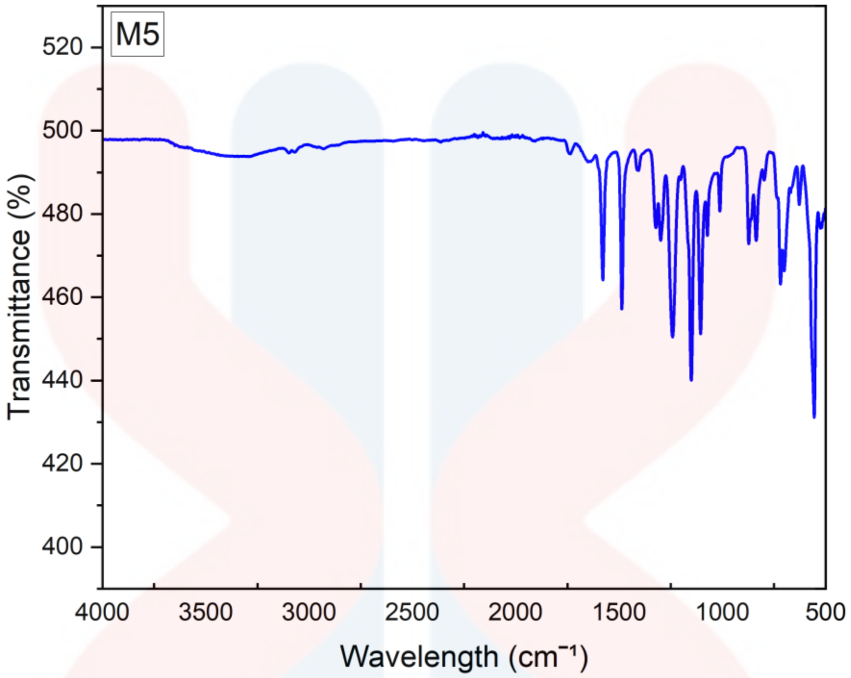


Figure 6: The ATR-FTIR spectroscopy of M5 with IONPs.

As seen in Figure 4.2 and Figure 4.3, the transmission FTIR spectra below 1000 cm^{-1} were ignored because of their over saturated absorption. However, the region around $1450cm^{-1}$ corresponds to being presence the from 1300 cm−1 to 1500 cm−1 correspond to being presence of the organic compound containing carbon-hydrogen (C-H) bonds. The broad span from 1500 cm^{-1} to 3000 cm−1 correspond to the presence of alkane groups that containing the C-H stretching vibrations of the polymer. On the other hand, the peak at 3200 cm^{-1} to 3600 cm^{-1} may have been caused by the hydroxyl groups in PES mixed with IO nanoparticles. The peak of the Fe-O stretching in iron oxide nanoparticles where determine around 500 cm^{-1} to 700 cm^{-1} is represented by this peak.

4.2 Physical Characteristics

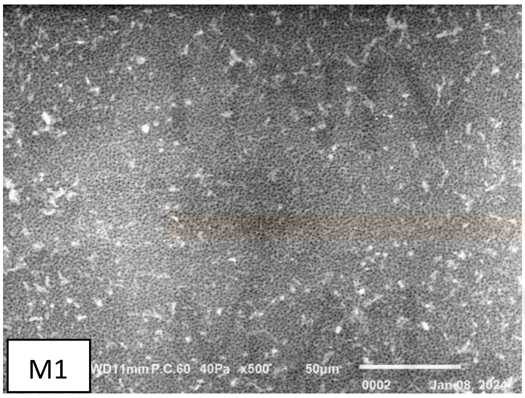
The physical images of the fabricated membranes are displayed in Figure 7. Based on the Figure 7, the combination of polymer PES with the bioactive polymer IO nanoparticles have contributed to dark colour and light dark colour because of PES was white in flakes form and bioactive polymer IO nanoparticles were dark in powder form. M1 was contained only pure polymer PES, M2 was contained polymer PES and 1.5% wt IO nanoparticles, while M3, M4, and M5 were contained polymer PES with addition of bioactive polymer IO nanoparticles with different formulations.

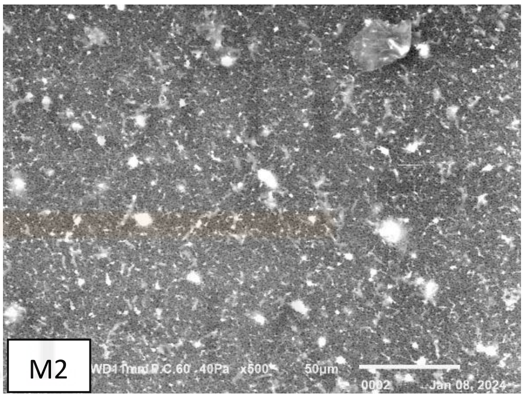
Figure 7: Physical image of membranes.

Due to the membrane's upper layer having the most interaction with the distilled water during the phase inversion process, the hydrophilic of bioactive polymer IONPs would migrate to the top layer of the membrane, putting together a composite membrane (Abdallah et al., 2015). However, due to bioactive polymer IONPs have contribute to any colour, it remains white, dark, and light dark colour.

4.2.1 Determination of Surface Morphology Using Scanning Electron Microscopy (SEM)

To ascertain the impact of the concentration of IONPs on the membrane morphology, SEM images were captured. The SEM top surface morphology pictures of the membranes are shown in Figure 4.5. As shown in these pictures, higher IONPs composition caused more porous structures. It was affirmed by the porosity of the membrane increase. However, in some membranes it seems the black spot agglomerated. This might be due to do not used of the sonicator during the mixing of the dope solution. IONPs may not be thoroughly mixed into the casting solution as a result, and this could have an adverse effect on membrane qualities including hydrophilicity and surface roughness. Meanwhile, the white spot agglomerated on the casting membrane was indicated as the IO nanoparticles. It can be seemed clearly in the SEM micrograph of M2 that contained polymer PES with the addition of IONPs. However, because of the organic addictive, adding biopolymer cellulose to the casting solution appears to be able to inhibit the agglomeration of IONPs.





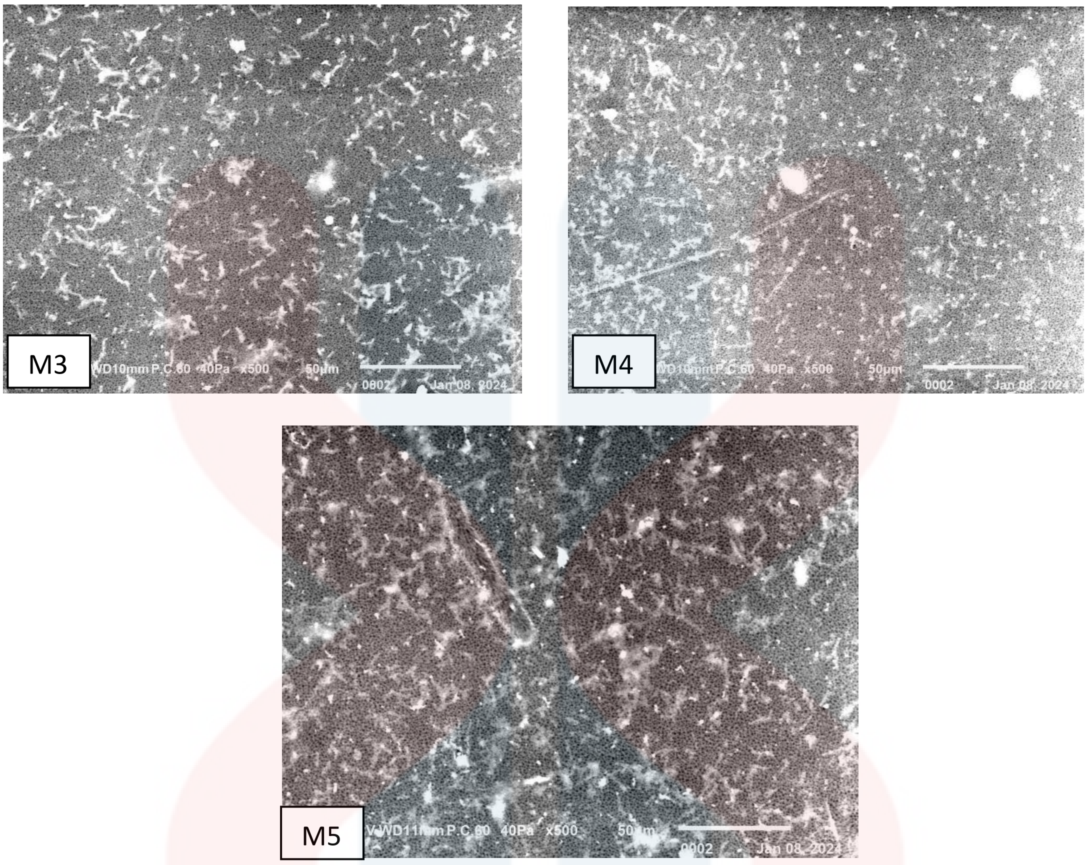


Figure 8: The SEM micrographs images of M1, M2, M3, M4, and M5 membrane of top surface at 500 X magnification.

Due to the limited flow-ability of PES and distilled water, phase inversion began when the cast film was submerged in the solution (Gohil & Choudhury, 2019).The development of the polymer phase's nuclei was triggered simultaneously by the flowability of the solvent DMAc and the distilled water. The nuclei phase is when a polymer starts to solidify or crystallize. The diffusional flow of DMAc from the cast film's surroundings continued because it was submerged for 24 hours. It causes the nuclei to keep growing until the membrane concentration increases and solidifies, a process known as de-mixing (Hołda & Vankelecom, 2015). Additionally, the membrane shape might be impacted by the rate of the de-mixing process. The slow rate of de-mixing process can lead to free growth of nuclei throughout the cast film. Consequently, the formation of porosity is suppressed (Figoli et al., 2016).

As a hydrophilic addictive, IONPs were added to increase the instability of de-mixing in distilled by forming a more dynamic and complicated system. This could enhance the membrane's efficacy in treating water (Li et al., 2009). As a result, the hydrophilic IONPs craving caused the structure to become more porous. However, the greater IONPs concentrations reveal an increase in the membrane's porosity.

As shown in Figure 8, M5 surface was relatively smoother than the others. It was clearly observed that the embedded of IONPs were not agglomerated but homogeneously dispersed in the membrane. When hydrophilic nanoparticles were added, the phase inversion process immediately caused the solvent and distilled water to separate, improving the membrane's porosity.

4.2.2 Contact Angle

The contact angle analysis of fabricated membrane is shown in **Figure 9**.

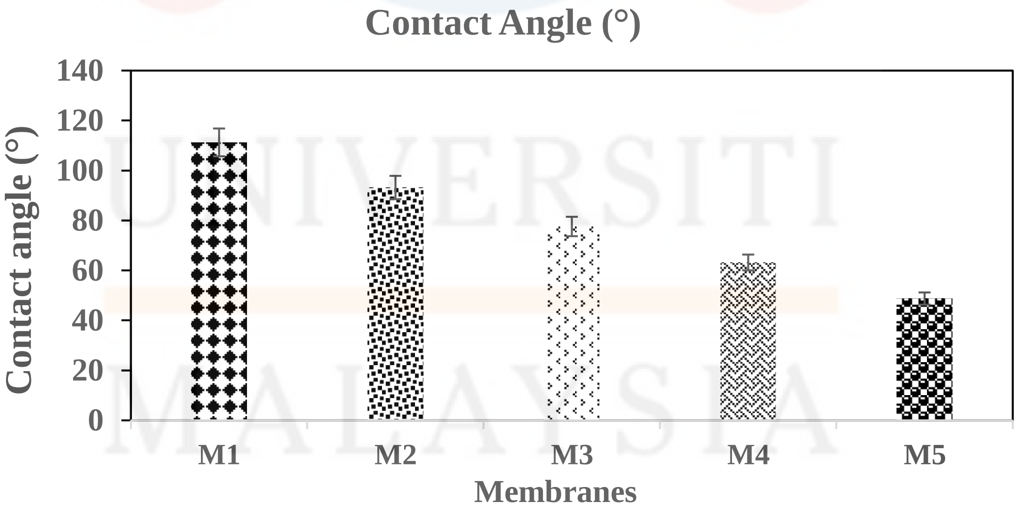


Figure 9: The contact angle of the fabricated membranes.

To assess the effect of IONPs on membrane hydrophilicity, the angle between a small droplet of water and the membrane surface was measured by a contact angle instrument. As clearly shown in Figure 9, the addition of the nanoparticles did improve the hydrophilicity of the membranes by decreasing the contact angle by approximately 15.6%, 14.4% and 13.45% for M3, M4 and M5 respectively. The highest contact angle of 111.25° was obtained by pure PES membrane, M1 which showed the lowest hydrophilicity while the lowest contact angle of 48.75° was obtained by M5 indicated the highest hydrophilicity. The presence of IONPs in M5 membranes had also improved the hydrophilicity due to the amine hydrophile groups and carboxyl groups of functionalized nanoparticles (Mak et al., 2011). It was observed in this study that the increase of hydrophilicity with addition functionalized nanoparticles. Incorporation of hydrophilic nanoparticles increases the water diffusion into the polymer matrix. This is due to the decrease of interface energy and the migration of nanoparticles to the top layer of membrane matrix during coagulation bath and therefore, alleviation of the surface contact angle (Rajesh, Ismail, & Mohan, 2012).

4.2.2 Porosity and Water Content

Table 5 showed the overall membrane porosity and water content of M1, M2, M3, M4, and M5.

Table 5: The overall membrane porosity and water content of M1, M2, M3, M4, and M5.

Membrane	Porosity (%)	Water Content (%)
M 1	75.77%	69.51%
M 2	76.30%	70.13%
M 3	79.67%	71.00%
M 4	83.17%	78.30%
M 5	86.94%	82.93%

The modification of the fabricated membrane was measured by calculating the membrane porosity based on Table 4.1 was used to determine the porosity of the membranes and estimate their free volume. According to Table 4.1 , the addition of the IONPs increased the membrane's overall porosity in the order of M5>M3>M3>M2, which resulted in a lower concentration of polymer at the interphase between the polymer solution and the distilled water during the phase inversion process. As a result, the membrane's permeability and porosity improved. According to Table 4.1's water content, all PES MMM had larger water contents than M1's pure PES membrane. IONPs improved the membrane's hydrophilicity, increasing its capacity to absorb water. The membranes' increased porosity boosts water absorption as well. The presence of IONPs in the casting solution encourages the growth of the upper layer's hydrophilicity, which results in a stronger water affinity (Mak et al., 2011). Based on the physical analysis, the results showed that PES MMM (M5) exhibited the most favourable membrane characteristics as compared to the pure-based PES membrane. Further investigation revealed that the increase in the wt.% of the IONPs during membrane fabrication resulted in an increased in the membrane's morphology, hydrophilicity, porosity, and water content. These findings suggest that the addition of IONPs into PES-MMM can enhance the performance and properties of the resulting membrane, thus demonstrating its potential for various application in separation processes.

4.3 Performance Study

4.3.1 Pure Water Flux

The dead-end filtration tests were performed on all fabricated membrane at 50mg/L. The Pure Water Flux (PWF) test was performed on all the fabricated membranes at 250 mL of distilled water as shown in Figure 5. From Figure 5, it was observed that the PES MMM has a higher value in the PWF, rather than the pure PES membrane. The PWF of pure PES membrane, M1 had the lowest value of 45.43 L. m2 /h. Pure PES membrane, M1 had lowest permeability compared to those containing IONPs due to the relatively inherent hydrophobicity properties in the base PES membranes and a little bit of the pore formation on the membrane's surfaces (Sotto et al., 2011)

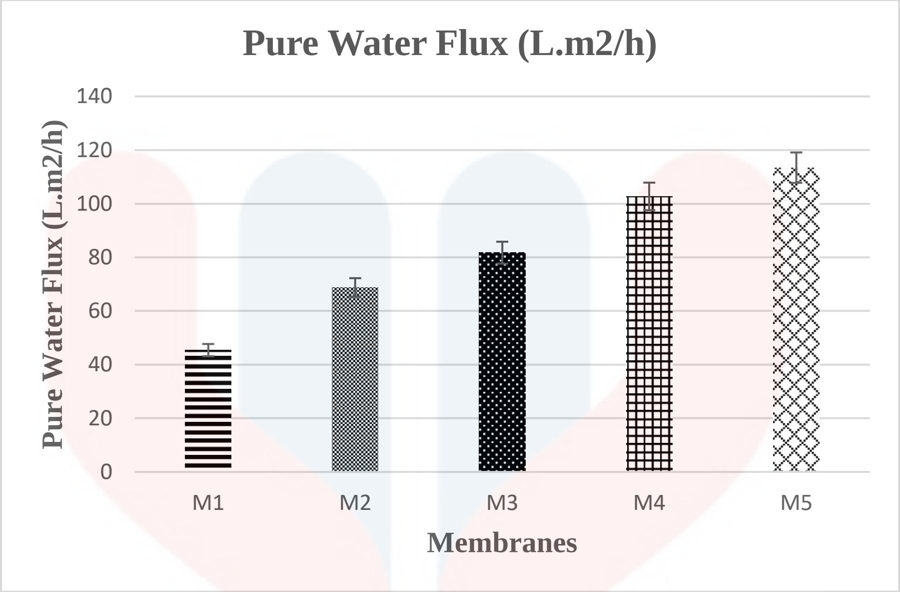


Figure 10: The Pure Water Flux of different membrane against filtration time (50mg/L).

The contact angle measurement demonstrated that the combined membrane's outstanding hydrophilicity was in good agreement with its high permeability (Figure 4.2.1). The contact angle reduction supported the PWF's improving trend. It is generally known that an increase in membrane hydrophilicity is directly correlated with an increase in water permeability. The membrane permeability may also be aided by the adsorption of water molecules within the membrane matrix. The maximum value of the water flux of 113.45 L. m2 /h belonged to the M5 membrane modified with IONPs. M5 obtained the highest flux due to the presence of pores on the membrane. Nevertheless, the other membrane with the addition of bioactive IO nanoparticles obtained a value of PWF of 68.81 L. m2 /h, 81.76 L. m2 /h, and 102.73 L. m2 /h belonged to the M2, M3, and M4 respectively.

In fact, the experimentally determined values of porosity, water content, and hydrophilicity on the manufactured membrane are in excellent agreement with the permeation potential of the membrane. The addition of IONPs improved porosity, hydrophilicity, and water content which led to enhance the water flux (Kumar & Ismail, 2015) . However, in some membrane, the permeability decrease might be attributable to the membrane's IO nanoparticles aggregation. It can block the passage of molecules through the membrane (Al Harby et al., 2022).

4.3.2 Humic Acid Removal

The permeability of various materials was examined through ultrafiltration studies the fabricated membrane with concentration 50 mg/L of HA. The Humic Acid Flux (Shoparwe et al.) is shown in Figure 4.8.

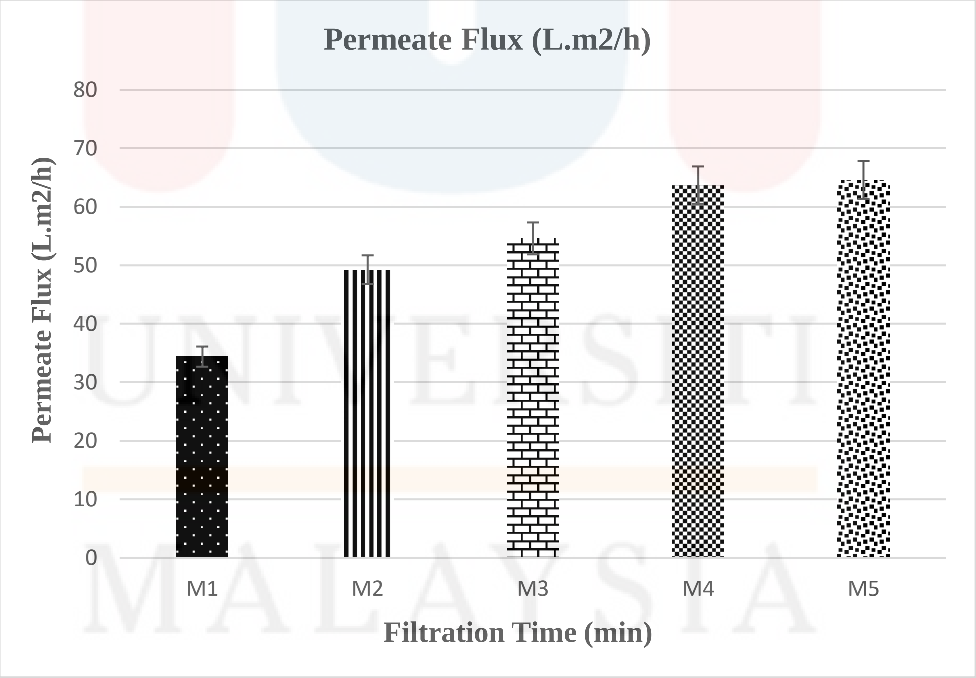


Figure 11: The permeate flux of different membrane against filtration time (50mg/L).

Figure 11 shown the measured permeated flux of HA were lower than of PWF due to the deposition of the feed on the membrane surface. At the same time, the HA molecules can be swept away from the membrane surface under stirred conditions (Marshall, 2018). The HAF for the pure PES membrane, M1 were 34.39 L. m2 /h. With the incorporation of bioactive polymer IO nanoparticles on the casting solution, the HA flux was increased substantially from 49.23 L. m2 /h, 54.59 L. m2 /h, 63.71 L. m2 /h, and 64.61 L. m2 /h for M2, M3, M4, and M5.

4.3.3 Humic Acid Rejection

The HA Rejection (Al Harby et al.) is shown in the Table 4.2. Table 4.2 presents the HAR of the fabricated membrane in filtering the HA solution.

Table 6: The initial pure water flux, HA permeate flux and final pure water flux of the membranes.

Membranes	**Initial Pure Water Flux (J_{WF}) (L.m^2/h)**	**Humic Acid Flux (Pabbati et al.) (L.m^2/h)**	**Final Pure Water Flux (J_{WF2}) (L.m^2/h)**	**Rejection (%)**
M1	**45.43**	**34.39**	**35.71**	**39.36**
M2	**68.81**	**49.23**	**51.53**	**68.77**
M3	**81.76**	**54.59**	**55.78**	**79.62**
M4	**102.73**	**63.71**	**64.29**	**86.53**
M5	**113.45**	**64.61**	**66.21**	**92.89**

Table 4.2 presents the results of the rejection performance of all the fabricated membrane. The rejection rate of all PES MMMs was found to be significantly higher than M1. However, the HAR of the membrane with the addition of the bioactive polymer IO nanoparticles, M5 exhibiting the highest rejection rate at 92.89%. This is attributed to the enhanced hydrophilicity and porosity of the membrane resulting from the presence of IO nanoparticles. Furthermore, the HAR of the M2, M3 and M4 were 68.77%, 79.62% and 86.53% respectively. The addition of IO nanoparticles had a significant influence on the

rejection performance of the fabricated membrane, as expected due to the similarity in operating pressure. However, the HAR of the M2 and M4 showed a lower rejection rate at 68.77% and 79.62% respectively. The results demonstrated the permeate flux decreased slightly after the first cycle, likely due to reversible fouling. Importantly, the permeate flux of M5 remained constant in subsequent cycles, indicating the membrane's good stability and integrity. Based on the analysis, PES MMM M5 was found to be the best-performing membrane among all others, with the highest rejection rate of 92.89% for HA rejection. These results demonstrated the potential of incorporating bioactive polymer IO nanoparticles in the fabrication of the PES MMMs for enhanced separation performances.

4.4 Fouling Study

4.4.1 Membrane Fouling Analysis

Fouling is one of the main disadvantage problems due to the potential of nonpolar molecules to bind to the membrane's hydrophobic surface (Nady et al., 2011) .There were many obstacles to the fouling activities, including decreased efficiency, high maintenance costs, and flux decline. To maintain their performance, hydrophobic membranes may need to be cleaned or replaced more frequently (Ahmad et al., 2015). The polymer matrix's ability to withstand membrane fouling is increased by the addition of IO nanoparticles. Compared to the pure PES membrane, M1, fouling of the IO nanoparticles entrapped membranes were dramatically reduced. The performance of the membrane in terms of fouling was examined while considering the various contributions of the membrane's resistance to water permeation, including reversible (Rr), irreversible (Rir), and total resistances (Rt) (Shoparwe et al., 2021).

Reversible or irreversible fouling mechanisms are both possible. The creation of the cake layer concentration polarization of foulants onto the membrane area, or both, are the main causes of reversible fouling. With the appropriate physical washing, such as backwashing or surface washing, it can be eliminated (Jepsen et al., 2019). On the other hand, irreversible fouling is brought on by pore obstruction or adsorption (Ouda et al., 2022)

The degree of reversible and irreversible fouling significantly decreased as the result of IO nanoparticles between the polymer matrix were responsible for mitigation of foulants. The hydrophilic membrane also improved the membrane permeation.

The membrane was washed under running water for 15 minutes after dead-end cell filtration was finished to eliminate the loosely bound foulant from the membrane surface. The membranes were then measured as per normal for the initial JWF, JHA, and JWF2. Relative Flux Reduction (RFR) and Flux Recovery Ratio are the two primary metrics used to assess a membrane's anti-fouling capabilities (FRR). The hydraulic cleaning abilities of the membranes may be evaluated by the FRR, as illustrated in Figure 12 below. The RFR was quantitatively estimated. The best performance was provided by a membrane with a low RFR and high FRR because it has a high separation efficiency and a low fouling rate (Ouda et al., 2022).

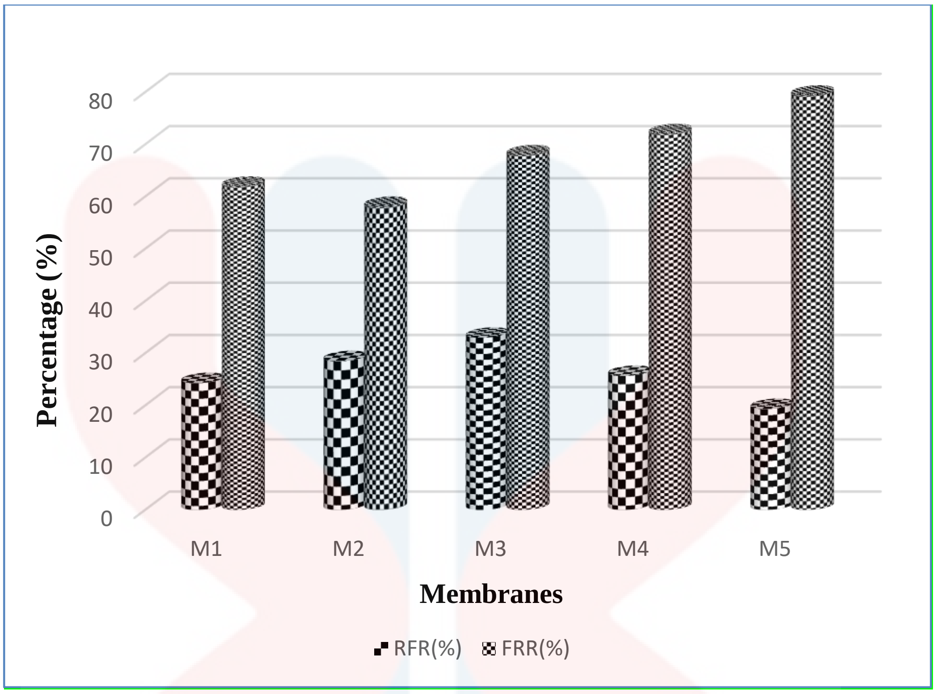


Figure 12: The Antifouling Parameter of the fabricated membranes.

The most popular method for examining a membrane's ability to reduce fouling is the FRR. This technique can demonstrate the irreversible fouling with the presence of adsorption of foulant on membrane surface. A high value of FRR indicated a strong resistance to membrane fouling and low value of RFR indicated the lower chance of membrane fouling. The FRR and the water fluxes varied due to different types of fouling mechanism (Shoparwe et al., 2021). Based on the Figure 4.9, the lowest RFR fallen into M5 which indicated lower chance of fouling. In other words, these three membranes had better antifouling ability compared to others. After membrane washing, the membrane permeability can be recovered through evaluating the cleaning efficiency by FRR value. M5 obtained the highest FRR value which implied high cleaning efficiency.

Basically, a high number of research and studies had been focused on the membrane modification to achieve the possible structure of antifouling property of membranes. Pure PES membrane, M1 seem to experience serious fouling activity due to the hydrophobic nature of HA which made it prone for HA fouling. All the PES MMM experience less severe fouling with higher reversible fouling. As shown in Figure 4.10, M5 membrane displayed the highest percentage of FRR and lowest percentage of RFR in removal of concentration of 50 mg/L of HA which confirmed the positive efficiency of the referred IO nanoparticles in the enhancement of the antifouling characteristic of PES MMM. This would reduce the cost in maintenance as well as sustainable filtration materials.

PES polymer was prone for HA adsorption due to the mutual interaction of natural hydrophobic characteristic. IO nanoparticles be able to adsorb HA via ligand interaction and electrostatic (Ebrahimi et al., 2012). At the same time, the adsorption mechanisms were not emphasized in this study. The filtration resistance of 50 mg/L of HA was shown in Figure 4.10.

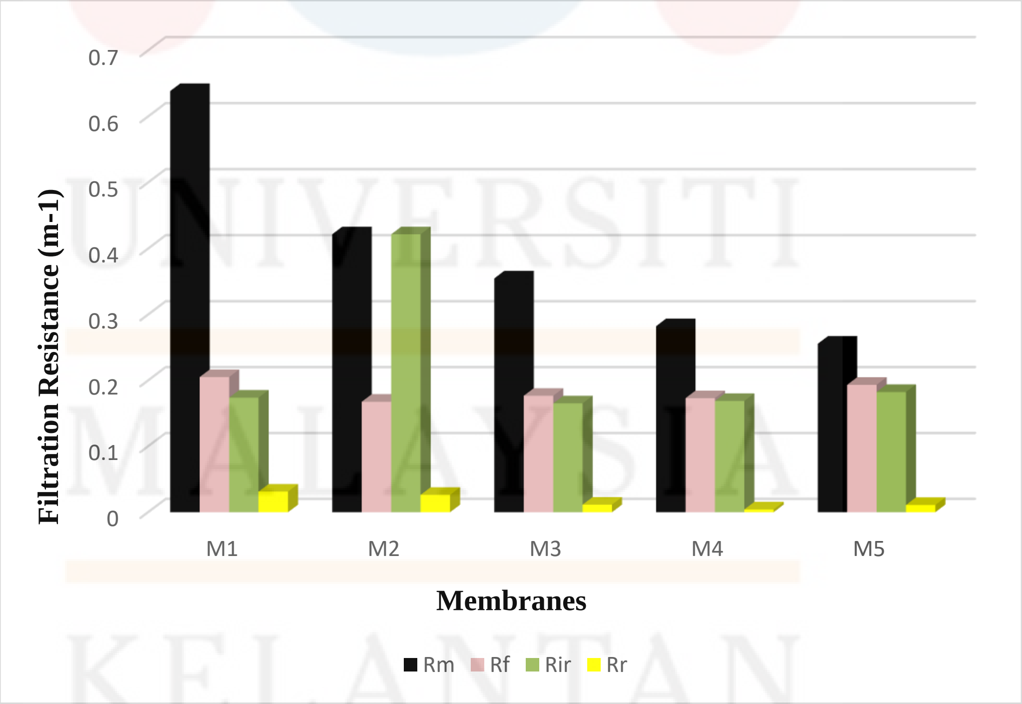


Figure 13: The Filtration Resistance of Different Membrane.

Generally, membrane fouling can be classified as hydraulically reversible and irreversible (Shoparwe et al., 2021). The reversible fouling resistance in fabricated membranes was presented in Figure 4.10. The result illustrated that the resistance factor in the modification membrane were lower than pure PES membrane. As describe above, the hydrophilic IO nanoparticles could immobilize water molecules in the vicinity of membranes when the hydrated layer hinder the HA molecules to form strong bonds that causes fouling on membrane surface. The sum up of Rr and Rir of the PES MMM were lower compared with pure PES membrane. The results showed that the ability of antifouling of pure PES membrane was significantly improved by the self-assembly of IO nanoparticles. In summary, the total filtration resistance of M3, M4, and M5 were improved ever since the surface properties of the membrane were modified.

All PES MMM has decreased fouling resistance, according to this investigation of the membrane filtration resistance. Among all PES MMM, M5 has the lowest Rir and highest Rr 18.242% and 1.09% respectively, making it the most antifouling membrane. Therefore, M5 demonstrated that the key properties of the innovative ultrafiltration PES MMM used in the current market were high reversible fouling, low irreversible fouling, and high rejection of waste.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study successfully achieved all of its objectives, with IONPs demonstrating good permeation performance and rejection of hazardous substances due to their increased hydrophilicity and porosity. M5 showed a considerable increase in HA rejection and reversible fouling and decrease in irreversible fouling of HA making M5 the anti-fouling material with the best performance. The IONPs used in this study had guaranteed functional groups and were shown to significantly improve the morphology, performance, and antifouling properties of the membranes. Overall, IONPs were found to be excellent antifouling membranes and show promise for new applications in membrane technology. In summary, the research conducted a thorough characterization IONPs and demonstrated their potential as materials for antifouling membranes. The study’s findings suggest that the use of these materials could significantly improve membrane performance and lead to new application in the field of membrane technology.

5.2 Recommendations

The following recommendations have been made for future work to achieve successful development:

1. Generally, almost everything in earth had microorganisms that could not be seen by naked eyes. These microorganisms may be beneficial or harmful to our living organisms as well as ecosystem. Therefore, it is very important to understand and identify the ways to reduce or inhibit the microbial activity. In future, antibacterial testing could be beneficial by identify the membrane antibacterial properties

which all membranes have different surface roughness, pore size and hydrophilicity. Generally, IONPs had been widely studied due to its antibacterial properties. Therefore, membrane incorporated IO could be used to identify the antibacterial effect and had been reported to inhibit the growth of bacteria. By applying the IONPs would seems to inhibit the bacterial activities.

2. The stability of IONPs could be another future research perspective. Although, IONPs had been carried out, but the slight agglomeration still existed. Therefore, future work on improving the dispersion of nanoparticles in the membrane such as utilization of in-situ method or photo-catalytic method of IONPs good performance.
3. The fabricated membrane could also be applied in crossflow filtration due to its several advantages in industry. The crossflow technology could improve the membrane lifespan as well as the continuous performance in a longer duration with lower maintenance and handling cost.
4. In future, the formulation of the membranes could be used to apply in the form of hollow fibre due to its high surface area as well as efficient removal of waste.
5. Lastly, the fabricated MMM should be used to perform real water waste from river sources through dead-end filtration so that performance evaluation could be comparable. It also able to prove the membrane real time application.

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