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Fabrication and Characterization of Mixed Matrix Ultrafiltration Membrane Incorporated with Alumina Oxide Nanoparticle for Humic Acid Removal

NUR SAIDATUL ATHIRAH BINTI MD ZAIYADI

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DECLARATION

I declare that this thesis entitled Fabrication and Characterization of Mixed Matrix Ultrafiltration Membrane Incorporated with Alumina Oxide Nanoparticle for humic acid removal is the results of my own research except as cited in the references.

Signature : ____________________________

Student's Name : ____________________________

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Supervisor's Name : ____________________________

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ABSTRACT

This research aims to develop and analyze the properties of mixed matrix ultrafiltration membranes combined with aluminum oxide nanoparticles for the purpose of humic acid removal. This membrane was developed by integrating polyethylene sulfone (PES) as the main polymer, with the addition of aluminum oxide nanoparticles (Al_2O_3NPs) as a biopolymer.

The main objective of this ultrafiltration membrane is to improve the separation efficiency and resistance to organic pollution in humic acid. The membrane manufacturing process involves the preparation of a PES solution that has been doped with a predetermined weight percentage of PES and Al_2O_3NPs. Several membrane compositions have been developed to investigate the effect of varying Al_2O_3NPs content on membrane performance. The optimal thickness of the flat membrane is achieved through the dry phase drying method.

The physical and chemical properties of the membrane have been thoroughly studied. Membrane hydrophobicity was determined through contact angle measurements, while hydrodynamic parameters such as separation ability and membrane filtration ability were evaluated. Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out to explore the chemical structure of the membrane and the interaction between PES and Al_2O_3NPs.

The conclusion of this study is expected to provide a comprehensive understanding of the potential application of mixed matrix ultrafiltration membranes with Al_2O_3NPs in improving separation efficiency and membrane resistance to water pollution. Implications of this technology for water pollution treatment, especially for humic acid treatment.

Keywords: Mixed matrix membrane, Ultrafiltration, Aluminum oxide nanoparticles, Humic acid removal, Membrane properties.

ABSTRAK

Penyelidikan ini bertujuan untuk membangunkan dan menganalisis sifat-sifat membran ultraturasan matriks campuran yang digabungkan dengan nanopartikel aluminium oksida untuk tujuan penyingkiran asid humik. Membran ini dibangunkan dengan mengintegrasikan PES sebagai polimer utama, dengan penambahan nanopartikel aluminium oksida Al_2O_3NPs sebagai biopolimer.

Objektif utama membran ultrafiltrasi ini adalah untuk meningkatkan kecekapan pemisahan dan ketahanan terhadap pencemaran organik dalam asid humik. Proses pembuatan membran melibatkan penyediaan larutan PES yang telah didop dengan peratusan berat PES dan Al_2O_3NPs yang telah ditetapkan. Beberapa komposisi membran telah dibangunkan untuk menyiasat kesan kandungan Al_2O_3NPs yang berbeza-beza terhadap prestasi membran. Ketebalan optimum membran rata dicapai melalui kaedah pengeringan fasa kering.

Sifat fizikal dan kimia membran telah dikaji dengan teliti. Hidrofobisiti membran ditentukan melalui pengukuran sudut sentuhan, manakala parameter hidrodinamik seperti keupayaan pemisahan dan keupayaan penapisan membran dinilai. Analisis Fourier Transform Infrared Spectroscopy (FTIR) telah dijalankan untuk meneroka struktur kimia membran dan interaksi antara PES dan Al_2O_3NPs.

Kesimpulan kajian ini diharapkan dapat memberikan pemahaman yang menyeluruh tentang potensi aplikasi membran ultraturasan matriks campuran dengan Al_2O_3NPs dalam meningkatkan kecekapan pemisahan dan rintangan membran terhadap pencemaran air. Implikasi teknologi ini untuk rawatan pencemaran air, terutamanya untuk rawatan asid humik.

Kata kunci: Membran matriks campuran, Ultrafiltrasi, Nanopartikel oksida aluminium, Penyingkiran asid humik, Sifat membran.

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LIST OF ABBREVIATIONS

HA	Humic Acid
UF	Ultrafiltration
Al_2O_3NPs	Alumina Oxide Nanoparticles
g	Gram
WHO	World Health Organization
ppm	Parts Per Million
DBP	Disinfection By-Products
MF	Microfiltration
RO	Reverse Osmosis
PES	Polyethersulfone
MMM	Mixed Matrix Membrane
HS	Humic Substances
NOM	Natural Organic Matter
DMAc	Dimethylacetamide
FA	Fulvic Acid
FTIR	Fourier Transform Infrared Spectroscopy
L	Liter
RFR	Relative Flux Reduction
FR	Flux Recovery
Rm	Intrinsic Resistance
Rf	Fouling Resistance
Rr	Reversible Adsorption Resistance
Rir	Irreversible Adsorption Resistance
PWF	Pure Water Flux
JWF	Initial Pure Water Flux
JHA	HA Permeate Flux
JWF2	Final Pure Water Flux
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared
NPs	Nanoparticles

LIST OF SYMBOLS

mg/L	Miligram per Litre
℃	Degree Celsius
µm	Micrometre
nm	Nanometre
^{o}	Angle
g/cm^3	Gram per Cubic Centimetre
cm^{-1}	Reciprocal Centimetre
m^2	Square Metre
L/m^2 .h	Litre per square metre timeL/m2
m^3 /s	Cubic metre per second
µ	mean
Pa·s	Pascal-second
cm^3	Cubic centimeter
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 Research Background

Fabrication and characterization of mixed matrix ultrafiltration (UF) membranes, in combination with Al_2O_3NPs, for the purpose of humic acid (HA) removal encompasses several significant factors. Humic acid, a naturally occurring component of humic substances, is generated through the decomposition of plant and animal materials. Its presence is well-known for its impact on soil fertility and plant development. (Pettit, 2004). However, untreated water discharged into household or industrial settings containing humic acid can lead to numerous issues. The World Health Organization (WHO) recommends a safe concentration limit of less than 100 ppm of humic acid in potable water (Sajjadi et al., 2015). While humic acid may not be directly toxic, its presence can negatively affect the taste, smell, and appearance of raw water, and potentially contribute to the formation of organic disinfection by-products (DBP), which are harmful substances generated during the water treatment process after disinfection

To overcome this challenge, membrane filtration technology, especially UF, has been identified as a potential method to remove humic acids and treat water.. UF technology involves the use of separate membranes to separate suspended particles, organic debris and pollutants from the air, achieving high separation efficiency (Bodzek, 2019). Various types of membrane technologies, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are now increasingly popular among the scientific and technological communities (Yang et al., 2019).

Based on the findings of Figures 1.1 and 1.2, membrane technology encompasses four unique processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF, which employs membranes with larger pore sizes ranging from 0.1 μm to 1 μm, operates under low pressure, typically below 1 bar, and is effective in removing large particles like bacteria from a liquid. UF, in contrast, utilizes membranes with smaller pore sizes ranging from 2 nm to 100 nm and requires higher pressure, around 1 to 6 bar, making it an efficient method for separating large proteins, biomedical contaminants, and viruses from liquids (Hampu et al., 2020). NF uses membranes with even smaller pores, approximately 1 nm to 10 nm, and works at higher pressures of around 5 to 15 bar, making it effective for separating divalent ions, organic molecules, and compounds that dissolve in the air. Lastly, RO involves the use of a dense membrane without well-defined pores and requires very high pressure, ranging from 20 to 100 bar, making it highly proficient in separating small molecules, monovalent ions, and compounds from air, especially for sea air desalination (Anis et al., 2019).

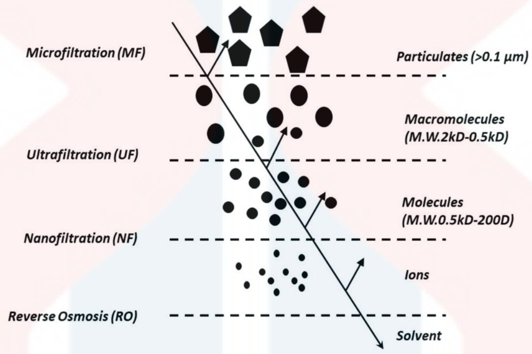

Figure 1.1: Membrane process Characteristics

Source: (Charcosset, 2016)

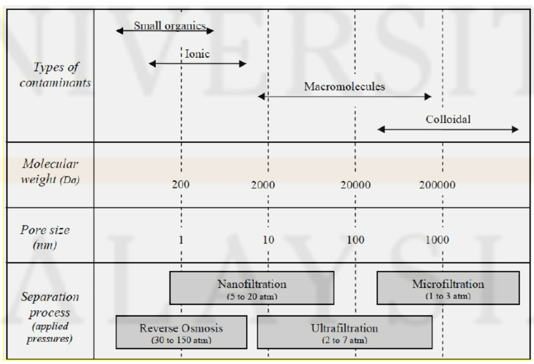

Figure 1.2: The filtration spectrum of membranes

Source: (Giwa & Ogunribido, 2012; Ibrahim et al., 2013)

Each of these four membrane processes provides varying solutions for liquid separation, depending on the specific separation requirements, the size of the particles or molecules to be filtered, and the desired efficiency for the particular application (Strathmann, 1981). Continued development in this field is improving the efficiency and performance of liquid filtration processes. The utilization of ultrafiltration (UF) has gained prominence in the treatment of wastewate,, owing to its capacity to remove significant quantities of solids and dissolved organic matter (Villacorte et al., 2015). However, UF has its limitations, such as impurities and a decrease in flux over time, which have prompted researchers to explore modifications to enhance its efficiency. In this regard, the incorporation of alumina nanoparticles into polyethersulfone (PES) matrix membranes was studied to improve their performance (Gohari & Abu-Zahra, 2018).

Al_2O_3NPs were chosen due to their potential to enhance membrane properties such as hydrophilicity, anti-fouling properties, and mechanical strength (Sherugar et al., 2021). The goal is to create a MMM capable of efficiently removing humic acids with minimal fouling. This study aims to address environmental concerns related to the presence of humic acids by using membrane technology, specifically UF, and improving its effectiveness through the integration of Al_2O_3NPs into MMM (Khan et al., 2023).

1.2 Problem Statement

The treatment of humic acid wastewater presents notable environmental challenges owing to the intricate composition of contaminants found in the effluent. (Tom et al., 2021). In the context of humic acid, conventional treatment methods often fall short in effectively removing pollutants, leading to the discharge of wastewater with adverse effects on aquatic ecosystems. (Akpor et al., 2014). The presence of suspended solids, organic matter, and nutrients in humic acid wastewater necessitates innovative and efficient treatment approaches (Turcios & Papenbrock, 2014).

Ultrafiltration (UF) membranes have emerged as a promising tool for wastewater treatment, offering the potential to address the challenges associated with humic acid removal(Goh et al., 2022) . However, membrane fouling remains a critical issue that hinders the performance of UF membranes in humic acid removal. Fouling, caused by the deposition of organic and inorganic substances on the membrane surface, results in a reduction of the permeate flux, an increase in operating costs, and the need for frequent maintenance (Ahmad et al., 2022).

To improve the performance of UF membranes in treating humic acid,, we propose the incorporation of Al_2O_3NPs into the MMM (Siddique et al., 2021). Al2O3 NPs, with their unique properties, are expected to improve the hydrophilicity, mechanical strength, and anti-fouling characteristics of the membrane (Jhaveri & Murthy, 2016). However, challenges related to achieving optimal dispersion, compatibility with the polymer matrix, and maintaining membrane integrity need addressing.

This study aims to fabricate and characterize a PES-MMM-Al_2O_3NPs membrane for HA removal. The research aims to address problems such as membrane fouling to reduce fouling issues related to UF membranes in humic acid removal, focusing on the development of antifouling properties (Al-Timimi et al., 2023). In addition, optimal Al_2O_3NPs dispersion can also overcome the challenges associated with achieving a uniform dispersion of Al_2O_3NPs in the polymer matrix, ensuring improved performance and stability (Mallakpour et al., 2021). The study will also examine the compatibility of Al_2O_3NPs with the polymer matrix, aiming to maintain the structural stability and mechanical strength of the membrane while enhancing the separation efficiency. Finally, the HA removal efficiency is the overall value of PES-MMM-Al_2O_3NPs performance designed in terms of pollutant removal efficiency, permeate flux, and durability in realistic HA conditions (Farid et al., 2022).

1.3 Objectives

In this research, there are several objectives which need to be achieved. The objectives are:

i. To fabricate and characterize the physical and chemical properties of PES-MMM-Al_2O_3NPs ultrafiltration membrane for HA removal.

ii. To study the performance of fabricated PES-MMM-Al_2O_3NPs ultrafiltration membrane for HA removal

iii. To evaluate the fouling mechanism of the fabricated PES-MMM-Al_2O_3NPs ultrafiltration membrane for HA removal.

1.4 Scope of Study

This research study is primarily focused on the fabrication and characterization of PES-MMM-Al_2O_3NPs for removing HA. The study aims to utilize advanced techniques, particularly investigating the dry-wet phase inversion method, coupled with the integration of Al_2O_3NPs to improve membrane properties and dispersion characteristics. To achieve the desired results, different formulations of PES and Al_2O_3NPs was systematically prepared. The fabricated PES-MMM-Al_2O_3NPs The membranes underwent comprehensive characterization using advanced tools such as Fourier Transform Infrared Spectroscopy (FTIR) to analyze surface morphology, porosity, hydrophilicity, and structural integrity. The study also aims to evaluate the performance of the PES-MMM-Al_2O_3NPs in HA removal using dead-end ultrafiltration configurations to assess flux, rejection efficiency, and fouling mechanisms. Through the development of an efficient membrane for sustainable and effective HA removal, this study aims to offer valuable insights into the advantages of incorporating Al_2O_3NPs into the membrane matrix, in addition to addressing fabrication techniques.

1.5 Significant of Study

The significance of this study is its valuable contribution to the advancement of membrane technology for humic acid removal. By integrating Al_2O_3NPs into MMUFMs, a novel approach with transformative potential has emerged. The utilization of membrane technology not only provides superior efficiency but also offers a cost-effective alternative to traditional treatment methods. The study's outcomes reveal a better understanding of the synergistic effect between Al_2O_3NPs and the MMM, leading to improved performance and properties. The innovative membrane technology is poised to enhance humic acid removal, thereby satisfying commercial, industrial, and environmental requirements. Additionally, the research provides insights into fouling mechanisms, enabling the formulation of NPs that enhance membrane longevity and separation efficiency. The broader impact of this study includes societal benefits such as environmental conservation, sustainable practices in HA management, and intellectual innovation capable of shaping a more resilient and eco-friendly world. Overall, this research significantly contributes to the development of effective and sustainable wastewater treatment techniques, which hold far-reaching positive implications for the global community and the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Alumina oxide

Alumina oxide nanoparticles (Al_2O_3NPs) have become important in various scientific and industrial applications due to their unique properties, including high surface area, excellent mechanical strength, chemical stability and attractive structural formula. The Figure 2.1 shows the structural formula of Al_2O_3NPs .

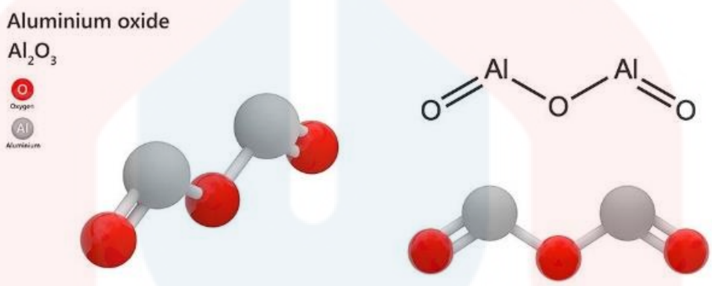

Figure 2.1: The structural formula of Al_2O_3NPs

Source: (Edger, 2013)

In the field of membrane technology, the integration of Al_2O_3NPs has shown great potential to improve membrane performance, especially in water treatment applications (Gudkov et al., 2022). The water-attracting property of Al_2O_3NPs is an important characteristic that influences its interaction with water molecules. (Rezvani et al., 2019). The intrinsic hydrophilicity of Al_2O_3NPs confers advantages in membrane applications, augmenting water permeability and mitigating fouling issues inherent in filtration processes. Furthermore, the catalytic attributes of Al_2O_3NPs are pivotal in degrading humic acids, thereby enhancing their efficacy in eliminating waterborne pollutants. (Khan et al., 2021).

There are various methods to integrate Al_2O_3NPs into different polymer matrices., such as polyethersulfone (PES), polyvinylidene fluoride (PVDF), and polysulfone, in membrane fabrication. The choice of polymer matrix and integration method has a significant impact on the structural and functional properties of the membrane (Dechnik et al., 2017). Methods including phase inversion, mixing, and electrospinning have been employed to ensure a uniform dispersion of Al_2O_3NPs within the membrane matrix.(Khraisheh et al., 2021).

Incorporating Al_2O_3NPs nanoparticles into membranes offers promising advancements in membrane technology, particularly in water treatment. This innovative approach extends across diverse fields, including water purification (Khulbe & Matsuura, 2021). Particularly in water treatment, membranes infused with Al_2O_3NPs demonstrate heightened efficacy in rejecting various contaminants like heavy metals, dyes, and bacteria. This underscores the considerable potential of Al_2O_3NPs in mitigating pivotal challenges encountered in water and wastewater treatment. The incorporation of Al2O3 nanoparticles into membranes represents a promising avenue for advancing membrane technology, particularly in the realm of water treatment. (Yee et al., 2014). The versatility of Al_2O_3NPs, coupled with their compatibility with different polymer matrices, opens the way to tailor membranes with better selectivity, permeability, and antifouling properties. As research in this field develops, further exploration of fabrication techniques and comprehensive characterization will undoubtedly contribute to the continued advancement of membrane-based technologies for water treatment (Saleem et al., 2020).

2.2 Membrane technology

Membrane technology has emerged as a promising solution for humic acid removal, providing an efficient separation process without relying on extensive chemical treatment (Goh et al., 2022). HA containing wastewater poses unique challenges due to its complex pollutant composition, making the ability of membrane technology to selectively filter pollutants invaluable (Ahmad et al., 2022). This technology utilizes a semi-permeable barrier that allows the passage of water molecules while restricting the movement of unwanted material based on size, making it an ideal candidate to address the specific needs of humic acid-containing effluents. UF membranes, with defined pore sizes and molecular weight cut-offs, have undergone extensive study for the removal of contaminants such as suspended solids, organic matter, and pathogens from wastewater (Cifuentes-Cabezas et al., 2021). The literature highlights the advantages of UF in terms of providing a physical barrier to pollutants, which results in improved water quality. However, membrane fouling remains a constant challenge in UF applications (Mohammad et al., 2012). Humic acid wastewater contains various particles such as algae, bacteria, and organic debris, leading to fouling challenges that may impact membrane performance over time. (Ahmad et al., 2022).

2.3 Mixed Matrix Membrane (MMM)

Mixed Matrix Membrane (MMM) has emerged as a promising approach in the field of membrane technology, offering unique properties that significantly increase its effectiveness in wastewater treatment applications (Qadir et al., 2017). Figure 2.2 shows a simplified representation diagram for a mixed matrix membrane with high CO2/H2 selectivity.

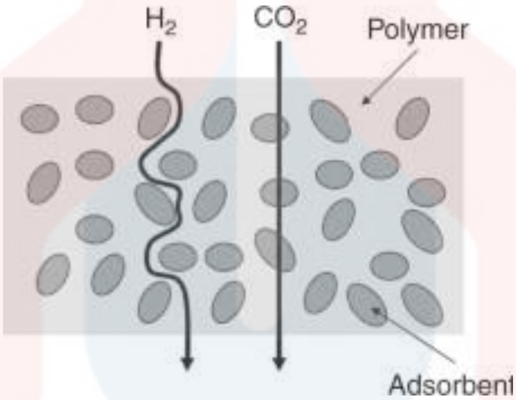

Figure 2.2: Simplified representation for mixed-matrix membrane to have high CO2/H2 selectivity.

Source: (Goh et al., 2011)

Through the incorporation of various additives into the polymer matrix, these membranes address specific challenges associated with traditional polymer membranes. In wastewater treatment, MMM plays a crucial role in enhancing the separation efficiency and fouling resistance of the membrane (Qadir et al., 2017). Incorporation of inorganic nanoparticles, particularly alumina oxide nanoparticles, into a polymer matrix, particularly PES (García-Ivars et al., 2019).The inclusion of Al_2O_3NPs increases the hydrophilicity of the membrane surface, reducing fouling issues and promoting water diffusion.

Nanoparticle selection is a crucial consideration in MMM, with researchers investigating various materials based on their unique qualities The inclusion of nanoparticles not only enhances the hydrophilicity of the membrane but also provides antimicrobial and antifouling properties, particularly relevant in humic acid removal, where fouling and the presence of organic matter pose significant challenges. MMM has demonstrated superior performance compared to traditional polymer membranes, with the incorporation of nanoparticles resulting in enhanced permeability, selectivity, and fouling resistance (Qadir et al., 2017). MMM is a valuable asset in addressing the complex composition of wastewater streams, offering versatility in tailoring for specific contaminants and applications. As wastewater treatment technology advances, MMM stands as a promising channel for innovation. Optimization of MMM composition is a method of fabrication and long-term performance will contribute to its wider use in sustainable and efficient wastewater treatment processes (Lu et al., 2017). The exploration of Mixed Matrix Membranes (MMM) in the context of humic acid treatment opens the way to designing membranes that can withstand the challenges posed by diverse water sources.

2.4 Polyethersulfone (PES)

Polyethersulfone (PES) has indeed received significant attention in membrane technology due to its extraordinary chemical and physical properties (Kallem et al., 2021). As a basic material in membrane fabrication, PES has exhibited versatility in various applications, especially in wastewater treatment. However, the hydrophobicity inherent in PES has posed challenges regarding fouling and permeability issues. Therefore researchers have explored strategies to improve hydrophilicity and overall performance (Otitoju et al., 2018). The PES structural formula is not presented in Figure 2.3, the diagram illustrates various aspects related to membrane fabrication, morphology, or performance enhancement techniques. This visual representation serves to clarify key concepts and methodologies related to the development and optimization of PES-based membranes.

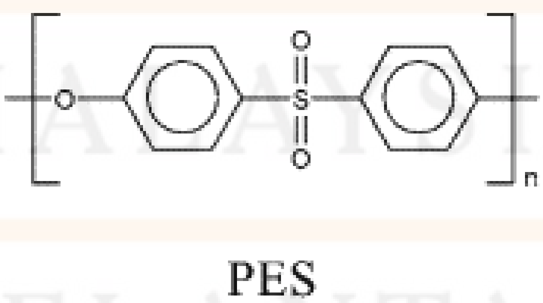

Figure 2.3: The structural formula of non-functional PES

Source: (El-Hibri & Axelrad, 2016)

The challenge posed by the hydrophobic nature of PES has been addressed through modifications aimed at improving its hydrophilic and antifouling properties. For example, carboxylation, where a carboxyl group replaces a hydrogen atom in an aromatic ring, has been investigated to improve the hydrophilic and antifouling properties of PES membranes. Carboxylated PES membranes have shown improved antifouling properties, making them more efficient for water treatment (Heidari et al., 2021).

In humic acid removal, PES-based membranes can address environmental challenges. Given the presence of contaminants such as humic acid, PES-based MMM , which incorporate additives such as alumina oxide nanoparticles, can improve membrane properties. (İlyasoglu et al., 2022). Al_2O_3NPs contribute to both enhanced hydrophilicity and antifouling properties, making them useful in addressing critical issues in humic acid removal.

The use of PES-based membranes underscores the importance of tailoring membrane materials to specific application requirements. As the focus shifts towards increasing hydrophilicity and fouling resistance, PES remains an essential component in the pursuit of efficient and sustainable membrane technologies for wastewater treatment (Bóna et al., 2023). The exploration of PES modifications and their integration into mixed matrix systems presents new avenues to address challenges in various water treatment scenarios.

2.5 Humic Acid

Humic matter (HS), especially humic acid (HA), is an important component of natural organic matter (NOM) in untreated waters. HS is classified into fulvic acid (FA), humic acid (HA), and humin based on solubility. Figure 2.4 shows the structural formula of HA:

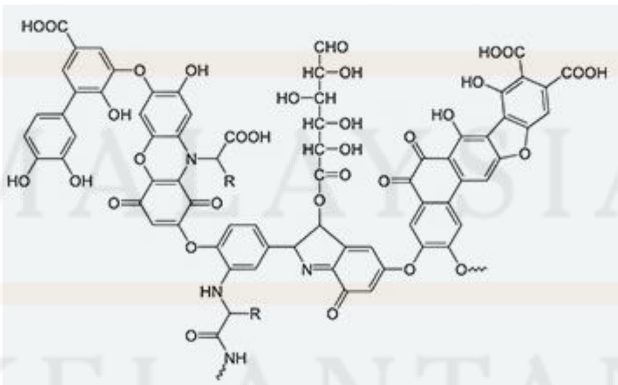

Figure 2.4: The structural formula of humic acid (HA)

Source: (Robertson, 1996)

They are characterized by a composition of about 40-60% carbon, 30-50% oxygen, 4-5% hydrogen, 1-4% nitrogen, 1-2% sulfur, and 0-0.3% phosphorus (Gaffney et al., 1996). HA, in particular, has aromatic and aliphatic features, contributing to surface charge and reactivity through phenolic and carboxylic groups. The variability of naturally occurring humic substances, as well as the presence of divalent ions, can cause membrane fouling. The structure of HA contains functional groups such as carboxylic acid, phenolic hydroxyl, and alcohol hydroxyl. Carboxylic acid groups, in particular, are prevalent in HA, allowing it to form complexes with metal ions. These metal complexes can affect water quality, but HA contributes to the deactivation of metals, reducing toxicity and improving water quality standards. HA is insoluble at acidic pH values below 2 and soluble at higher pH values. Its chemical structure is dominated by phenol groups and long carboxylic fatty acids, making it hydrophobic (Yang & Antonietti, 2020). HA has positive and negative effects on water quality, such as increased acidity, formation of metal complexes, and darkening of water color. Membrane technology is used to remove HA from water, ensuring compliance with drinking water quality standards and guidelines (Alzahrani & Mohammad, 2014).

CHAPTER 3

MATERIALS AND METHOD

3.1 Materials and Chemicals

3.1.1 Chemicals

Chemicals and reagents required for membrane fabrication, characterization and membrane performance testing have been outlined in detail by function in Table 3.1.

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

NO.	Chemical / Reagent	Purpose	Manufacturer
1	Humic Acid (HA)	Sample solution	Sigma-Aldrich
2	Polyethersulfone (PES)	Membrane polymer	BASF
3	Alumina oxide nanoparticles (Al_2O_3NPs)	Biopolymer	Sigma- Aldrich
5	Acetic Acid	CS solvent	Wego Chemical Group
6	Nitrogen gas	Compress dope solution	Well gas (Malaysia)
7	Dimethylaceta mide(DMAc)	Solvent	Sigma-Aldrich (USA)
8	Ethanol	Co-solvent for membrane wetting	Merck
10	Deionized water PVD	Clean the membrane	Synergy, Milipore, USA
11	Distilled water	Coagulation bath	UMK laboratory

3.1.2 Equipment

Each equipment had the specific function with the method of usage. Therefore, proper utilization of equipment with high care to achieve maximum performance. The equipment involve were outlined in details with its function in Table 3.2.

Table 3.2: List of Equipment used and its functions.

No	Equipment	Purpose
1.	Glass plate/cover	Slows down solvent evaporation, allowing for the formation of a film with uniform thickness without curling.
2.	Magnetic Stirrer	Establishes a rotating magnetic field to enable the immersed stir bar to spin very quickly.
3.	Electronic balance	Quickly and precisely measures the mass of a substance.
4.	Casting knife	Restrains coating with a wide range of film widths.
5.	Plastic Basin	Immerses the polymer cast film-coated glass plate in a non-solvent solution for a coagulation bath.
6.	Stopwatch	Measures the amount of time elapsed from a particular time.
7.	Thermometer	Measures the temperature of the solution.
8.	Membrane casting machine	Produces flat sheet polymeric membranes by coating a thin film of polymer solution.
9.	Oven	Dries the sample and evaporates solvents.
10.	Contact angle goniometer	Measures the contact angles of the membranes.
11.	Fourier transform infrared. spectroscopy (FTIR)	Uses infrared light to identify the presence of certain functional groups, side chains, and cross-links.
12.	Dead-end stirred cell filtration	Batch process for the filtration system to test the performance of the membrane.

3.2 Method

3.2.1 Preparation of Membrane

The manufacturing process of PES, UF membranes incorporated with Al_2O_3NPs for HA removal follows a systematic process outlined below:

Table 3.3: Membrane and formulation composition

Label of the membrane	**UF Membrane**	**PES wt.%**	**DMAc wt.%**	Al_2O_3NPs **wt.%**
M1	PES Membrane	17.0	83.0	-
M2	PES Membrane + Al_2O_3NPs	16.0	82.5	1.5
M3	PES Membrane + Al_2O_3NPs	16.0	82.0	2.0
M4	PES Membrane + Al_2O_3NPs	16.0	81.7	2.3
M5	PES Membrane + Al_2O_3NPs	16.0	81.5	2.5

The fabrication process used a dry-wet phase inversion technique. Before the fabrication process, PES undergoes drying at 80 °C for 20 hours. The casting solution was prepared by stirring PES with DMAc solvent for 12 h at 70 °C. After 20 minutes of degassing, the solution was spread on a glass plate using a casting knife with a thickness of 250 µm. The resulting polymer cast film is then immersed in distilled water for solvent and non-solvent exchange procedures. Membrane curing takes place at room temperature for one day, in line with the methodology established by (Celik et al., 2011).

The fabrication process UF PES membranes combined with Al_2O_3NPs involves a series of careful steps to ensure successful nanoparticle integration for enhanced membrane properties. The membranes, denoted as M2, M3, M4, and M5 in Table 3.3, were prepared using the dry-wet phase inversion technique. For membranes incorporating Al2O3NPs (M2 to

M5), precise concentrations DMAc were dispersed into the casting solution. The suspension was sonicated for 30 minutes to ensure uniform dispersion. Afterwards, the casting solution was degassed for 20 minutes to remove air bubbles. The solution was also spread evenly on a glass plate using a casting knife with a thickness of 250 µm.

3.2.2 Characterization of Fabricated Mixed Matrix Membrane

The systematic and detailed fabrication and characterization of mixed matrix ultrafiltration membranes incorporated with Al_2O_3NPs for HA removal is a complex process. The fabrication process involves careful selection and blending of materials, with PES chosen as the membrane polymer, and Al_2O_3NPs added to improve membrane performance. The dry-wet phase inversion method is used to create membranes with the desired characteristics for efficient wastewater treatment. To begin the fabrication process, a doping solution containing PES, alumina nanoparticles, and N-N-dimethylacetamide (DMAc) solvent is prepared (Dorosti et al., 2011). Each membrane labeled M1 to M5 has a specific composition, with the concentration of Al_2O_3NPs varying for optimization. Before the formation of the membrane, PES undergoes a drying process to ensure that the conditions are suitable.

The dry-wet phase inversion method starts with casting the solution onto a glass plate using a casting knife, forming a polymer cast film. The film is then immersed in distilled water, initiating the solvent and non-solvent exchange process. The cured membrane is left to dry at room temperature for a day, creating a structure suitable for ultrafiltration. Characterization of these mixed matrix membranes is crucial in evaluating their suitability for humic acid removal. Physical and chemical characterization methods provide a comprehensive understanding of the structural and functional properties of the membranes. These methods are selected based on their accuracy, efficiency, and non-destructive nature to ensure preservation of the or Iginla membrane properties.

3.2.3 Physical Characteristic

The physical characterization of the produced PES MMM necessitates several essential techniques to assess surface morphology, pore characteristics, and hydrophilicity. These techniques include Scanning Electron Microscopy (SEM), Contact Angle (CA), and Porosity measurements.

3.2.3.1 Contact Angle (CA)

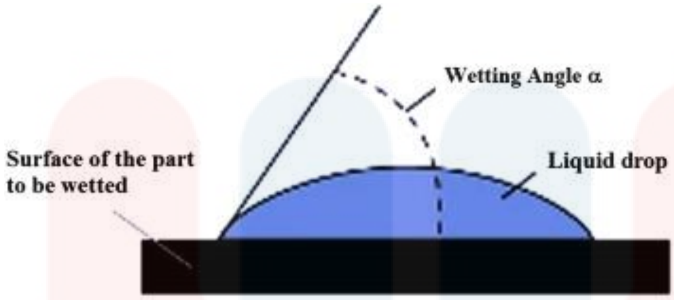

Figure 3.1: Contact Angle Measurement Techniques for Nanomaterials

Source: (Chapter, 2017)

Hydrophilicity of the artificial Mixed Matrix Ultrafiltration Membrane (MMM) incorporated with Al_2O_3NPs for humic acid removal can be evaluated using the contact angle (CA) method. This critical characterization technique provides insight into the interactions between membrane surfaces and water, which influence membrane performance in treating humic acid-contaminated wastewater. To carry out the CA evaluation, the membrane sample was placed on a glass slide, ensuring that the upper surface was facing up. A water droplet is carefully deposited onto the dry membrane surface, and the contact angle between the droplet and the substrate is measured using a contact angle goniometer. A sessile drop technique was used, and a CAM 200 contact angle meter was used for accurate measurements at room temperature. Following the deposition of water droplets, digital images were captured, and contact angle readings were obtained using the image analysis software "DROP" (Lamour et al., 2010). The process is taken from 3 different locations on the membrane surface. Average contact angle values and corresponding standard deviations were calculated, ensuring a comprehensive assessment of the hydrophilic nature of MMM.

3.2.3.3 porosity

The assessment of porosity is a crucial aspect of characterizing the fabricated mixed matrix ultrafiltration membranes. To determine porosity, the dry weight of the membrane is initially measured. Subsequently, the membrane is wetted and immersed in deionized water (DI) for a duration of 24 hours. After this soaking period, excess moisture on the membrane surface is carefully removed using filter paper, and the wet membrane's weight is recorded. The next step involves drying the wet membrane in an oven set at 25 degrees Celsius for a duration of 10 hours. The dry weight of the membrane is then measured. The porosity (ε) is calculated using the formula:

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

Where ε was the membrane porosity, Ww was the wet membrane weight (g), Wd was the dry membrane weight (g), dw was the pure water density (1.0 g/cm3) and dp was the polymer density (1.37 g/cm3) (Che Miur et al., 2022).

3.2.3.4 Mean porosity

The mean pore (Rm)of the membrane is a critical parameter that reflects the size of the pores within the ultrafiltration membrane. The determination of mean pore size involves utilizing the Guereout-Elford-Ferry equation, expressed as follows:

$$rm = \sqrt{\frac{(2.9-1.75\,Porosity)8\eta lQ}{Porosity\ x\ A\ x\ \Delta P}} \qquad \text{Equation 3.2}$$

Where η was the water viscosity (8.9 × 10−4 Pa.s), l was the membrane thickness (m), Q was the PWF (m3 /s), A was the area (m2) and ΔP was the operating pressure (1 bar) (Sharma et al., 2019).

3.2.3.3 Water Content

Following a 24-hour soak in water, the membranes' water content was assessed, and their weight was documented before being blotted using blotting paper. After being subjected to a vacuum drier at 75°C for 48 hours, the dry weights of the previously wet membranes were obtained. The percentage of water content (WC) was then calculated utilizing the following equation:

$$WC = \frac{(Wwet - Wdry)}{Wwet}x100 \qquad \text{Equation 3.3}$$

Where Wwet and Wdry are the membrabe’s wet and dry weights, respectively.

3.2.4 Chemical Characteristic

Chemical Properties can provide insight into the structure, composition, and potential applications of membranes such as FTIR Analysis (Fourier Transform Infrared Spectroscopy) is a powerful tool in membrane research, offering valuable insight into the structural and chemical properties of membranes.

3.2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.3 shows an instrument based on FTIR infrared spectroscopy Fourier. FTIR was used to gain insight into the chemical composition and molecular structure of the membrane. FTIR analysis focuses on studying changes in chemical bonds and identifying specific functional groups present on the membrane surface.

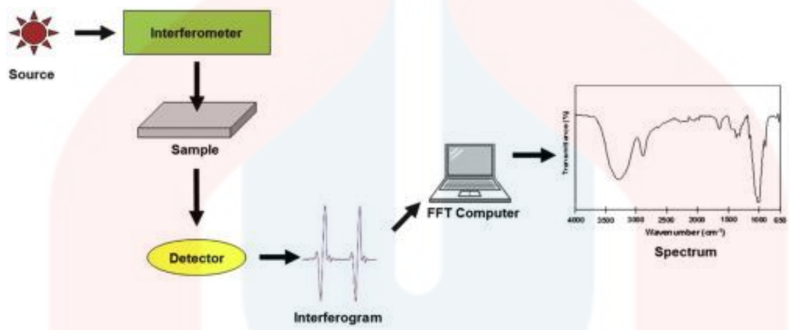

Figure 3.3: The instruments based on infrared spectroscopy.

Source: (Griffiths, 1983)

FTIR measurements were carried out using a state-of-the-art instrument, the FTIR Nicolet Nexus 670, equipped with the smart accessory OMNI-sample attenuated total reflection (ATR). The ATR configuration, coupled with a diamond crystal operating at an incident angle of 45^{o}, ensures accurate and reliable data acquisition. The instrument covers a wide wavenumber range from 4000 to 425 cm^{-1}. For each of the five membrane samples, FTIR spectra were recorded as an average of 32 scans to increase the signal-to-noise ratio and reliability of the data. The spectral resolution is set at 4 cm^{-1}, providing a detailed view of the molecular vibrations and chemical bonds in the membrane material. The obtained FTIR spectra were then analyzed to interpret the various peaks corresponding to specific functional groups. Different vibrational modes, such as stretching and bending, have been identified, contributing to the characterization of the chemical properties of the membrane. The data obtained allows to understand the unique fingerprint of the molecular structure of the membrane, it can explain the chemical characteristics of the membrane. FTIR helps in overall evaluation and improvement of membrane properties.

3.2.5 Performance Studies of Fabricated Polyethersulfone Mixed Matrix Membrane

3.2.5.1 Preparation and Analysis of Humic Acid Feed Solution

In the investigation of the Polyethersulfone (PES) mixed matrix membrane performance, the Humic Acid (HA) solution served as the feed solution, facilitating the assessment of the membrane's capability to reject HA while maintaining high flux. To prepare the HA solution, 0.05 g of artificial HA was dispersed in 1 L of Deionized (DI) water. As the molecular weight of the artificial HA ranged between 20,000 to 50,000 Da, no pre-treatment was necessary. To ensure homogeneity, the HA solution underwent an hour of sonication. Next, the pH of the HA solution was adjusted to 7.70 using a pH bench, with the aid of 1 M of Hydrochloric Acid (HCl) and 1 M of Sodium Hydroxide (NaOH). Moreover, the HA solution's concentration was standardized at 50 mg/L and maintained through UV spectrophotometer readings at 254 nm (Liao et al., 2001). This meticulous preparation ensured a controlled and consistent feed solution, vital to the subsequent performance studies of the UF membrane.

3.2.5.2 Membrane Permeation Test for Humic Acid removal

Performance evaluation of Polyethersulfone (PES) membranes focused on parameters such as Pure Water Flux (PWF), Humic Acid (HA) flux and HA rejection. The setup of the membrane permeation test was to clarify the effectiveness of the PES membrane in removing HA. In this configuration, compressed nitrogen air was introduced into the dead cell. The applied pressure from the nitrogen gas serves the dual purpose of filtering HA molecules and inducing diffusive flow (Cheshomi et al., 2018). Permeation flow is calculated using an electronic weighing balance, This weighing balance is seamlessly integrated with a computer through a specialized software known as "Win-CT." The use of compressed nitrogen air, coupled with accurate electronic measurements, allows precise monitoring of the diffusion flow, facilitating a comprehensive analysis of the performance of PES membranes in HA removal. This setup ensures reliable data acquisition and direct transmission to a computer for further analysis and interpretation.

In the initial phase of ultrafiltration (UF), the new membrane experiences pressure, resulting in a decrease in flux without fouling. To ensure consistent performance, all new membranes were subjected to pure water filtration until a steady state was reached before performance evaluation began. Throughout the UF process, the PES-MMM-Al_2O_3NPs receives a continuous supply of nitrogen gas. Humic Acid (HA) flux was measured systematically by weighing the permeate from the membrane bioreactor at regular time intervals. Calculation of Pure Water Flux (PWF) is carried out using Equation 3.4:

$$J\mathcal{w}\mathcal{F} = \frac{V}{Amt} \qquad \text{Equation 3.4}$$

Where JwF was the pure water flux (L/m2 .h), V was the permeate volume (L), Am was the effective filtration area (m2) and t was the measurement time (h) (Che Miur et al., 2022).

After the completion of pure water filtration, the HA solution was introduced at a pressure of 2 bar for one hour. The concentration of HA before filtration and the permeate concentration after the experiment were measured. At various time intervals, the HA flux was determined using Equation 3.5. A digital weighing balance, integrated with a computer through a data weighing system, facilitates accurate and efficient data acquisition.

$$\text{JHA} = \frac{V}{Amt} \qquad \text{Equation 3.5}$$

Where JHA was the HA flux (L/m2 .h), V was the permeate volume (L), Am was the effective filtration area (m2) and t was the measurement time (h) (Che Miur et al., 2022).

3.2.6 Fouling Resistance Evaluation

The evaluation of fouling resistance involved the calculation of relative flux reduction (RFR), flux recovery, and the application of Darcy's law for comprehensive analysis (Nimmo et al., 1987).

The RFR is calculated using Equation 3.6:

$$\text{RFR}(\%) = 1 - \frac{\text{JTS}}{\text{JWF}} \times 100\% \qquad \text{Equation 3.6}$$

Where RFR was relative flux reduction, JTS was tested solution (HA solution) permeate flux (L/m2 .h) and JWF was the initial water flux.

After washing the membrane with distilled water for 15 minutes, flux recovery (FR) was calculated (Luo & Wang, 2022) using Equation 3.7:

$$FR\ (\%) = \frac{JWF2}{JWF} \times 100\% \qquad \text{Equation 3.7}$$

Where $JWF2$ was the PWF after washing step (L/m2 .h).

In previous research, Darcy's law was widely used to calculate the fouling resistance for filtration (Chen et al., 2016). Therefore, the Darcy's law was shown in Equation 3.8:

$$JWF = \frac{TMP}{\mu \sum R} = \frac{TMP}{\mu Rt} \qquad \text{Equation 3.8}$$

Where TMP was the transmembrane pressure (Pa), μ was the permeate viscosity (Pa·s) and $\sum R$ will remained the same with Rt which is total resistance (cm-1).

The total resistance indicated here include the intrinsic membrane resistance and fouling resistance (Rf) (Córdova et al., 2016). For Rm, it was calculated using the Equation 3.9:

$$Rm = \frac{TMP}{\mu J\ WF} \qquad \text{Equation 3.9}$$

The total resistance were assumed as the sum of intrinsic membrane resistance, Rm and fouling resistance, Rf caused by reversible, Rr and irreversible, Rir adsorption on pore (Ahmad et al., 2018). These resistances were calculated by obtaining the result data from experiment using the Equations 3.10 - 3.13:

$$Rt = Rm + Rf = Rm + Rr + Rir \qquad \text{Equations 3.10}$$

$$Rt = \frac{TMP}{\mu Jts} - Rm \qquad \text{Equations 3.11}$$

$$Rir = \frac{TMP}{\mu Jwf2} - Rm \qquad \text{Equations 3.12}$$

$$Rr = Rf - Rir \qquad \text{Equations 3.13}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chemical Characteristics

4.1.1 ATR-FTIR Analysis

ATR-FTIR spectroscopic studies were carried out in nanoparticle membranes between wavelengths between 4000 cm-1 to 500 cm-1. The FTIR spectra of M1 and M5 are shown in figure 4.1 and figure 4.2:

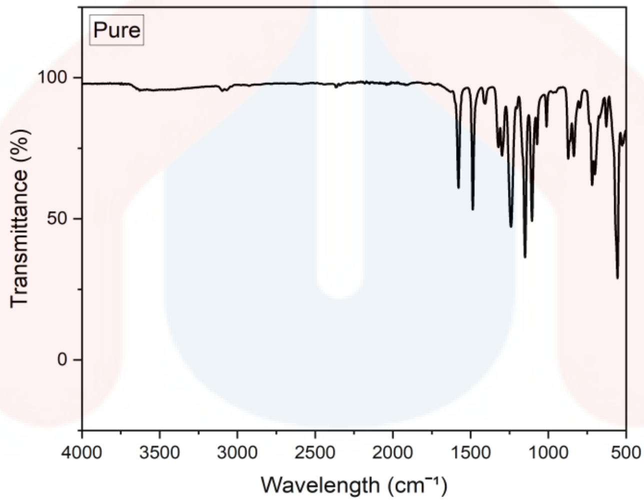

Figure 4.1: ATR-FTIR spectrum of pure membrane

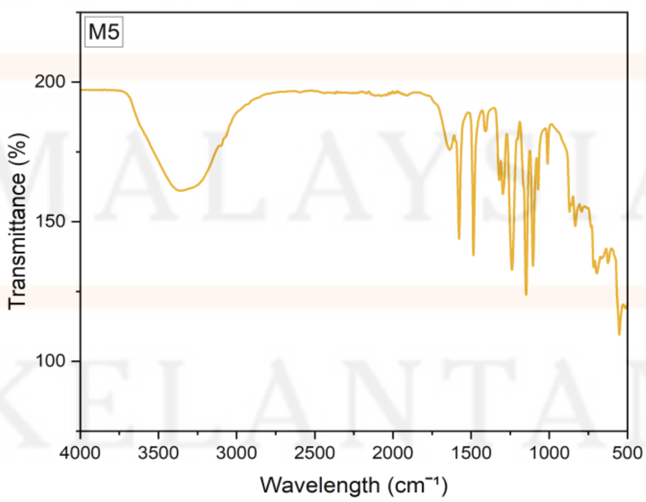

Figure 4.2: ATR-FTIR spectrum of membrane with Alumina Oxide Nanoparticle

FTIR ability to analyze unique vibrational frequencies is used in identifying surface functional groups, demonstrating its analytical prowess (He et al., 2017). Through this method, a comprehensive analysis of the chemical composition of the membrane can be carried out. By carefully examining these spectra, it becomes possible to gather important information about any changes made during the fabrication process and also to determine whether bonding occurs between the polymer matrix and the alumina nanoparticles based on the observed spectral peaks that indicate the occurrence of interactions. In addition, specific indicators such as hydroxyl (-OH), carbonyl (C=O) among others create a clear change in the FTIR spectral signal when introducing alumina oxide nanoparticles- further reinforcing the successful integration into the membrane structure with better properties associated with establishment & response (Faure & Lafond, 1995).

Furthermore, the use of FTIR spectroscopy supports the confirmation of the existence of alumina nanoparticles as shown by graph M5 and ensures their successful integration into the membrane matrix. This is an important component in understanding how these particles increase their effectiveness, especially for removing humic acids (Dablemont et al., 2008). By identifying the exclusive peak related to alumina oxide, accurate measurement of the nanoparticle concentration in the membrane material can be achieved while providing insight into the possible formation of functional groups that promote interactions between those groups and humic acid molecules. This interaction plays an important role in achieving higher rejection rates with superior performance results (Han et al., 2013). Therefore, any change or increase observed in a particular peak associated with HA interaction can be directly related to the overall effectiveness when extracting humic acid from the feed solution.

4.2 Physical Characteristics

4.2.1 Physical image of membranes

The figure 4,3 shows the physical image of the pure membrane and the addition of nanoparticles

Figure 4.3: Physical image of membranes.

The color analysis conducted on the mixed ultrafiltration membranes infused with Alumina Oxide Nanoparticles revealed numerous significant findings. Membrane M1, composed of pure polyethylene sulfone (PES) without any added nanoparticles, retained the characteristic white color of PES. Similarly, M2 to M5, which incorporated Al2O3 NPs, did not exhibit any significant color changes. This analysis suggests that the inclusion of Alumina Oxide Nanoparticles in the membrane does not result in any noticeable visual impact on the membrane's overall color. The white Al_2O_3NPs combined with white PES, resulting in the membrane's color remaining unchanged. Furthermore, the findings indicate the effectiveness of the membrane production process in preserving the original color of PES and the nanoparticles utilized. The conclusions drawn from this color analysis provide a clearer understanding of the visual properties of the membrane and the interactions between the materials involved in membrane formation and the incorporated nanoparticles.

4.2.2 Contact Angle

The contact angle analysis of fabricated membrane is shown in Figure 4.4 The membrane contact angle plays a vital role in determining the hydrophilicity and separation efficiency of mixed matrix ultrafiltration membranes that integrate Al2O3 NPs

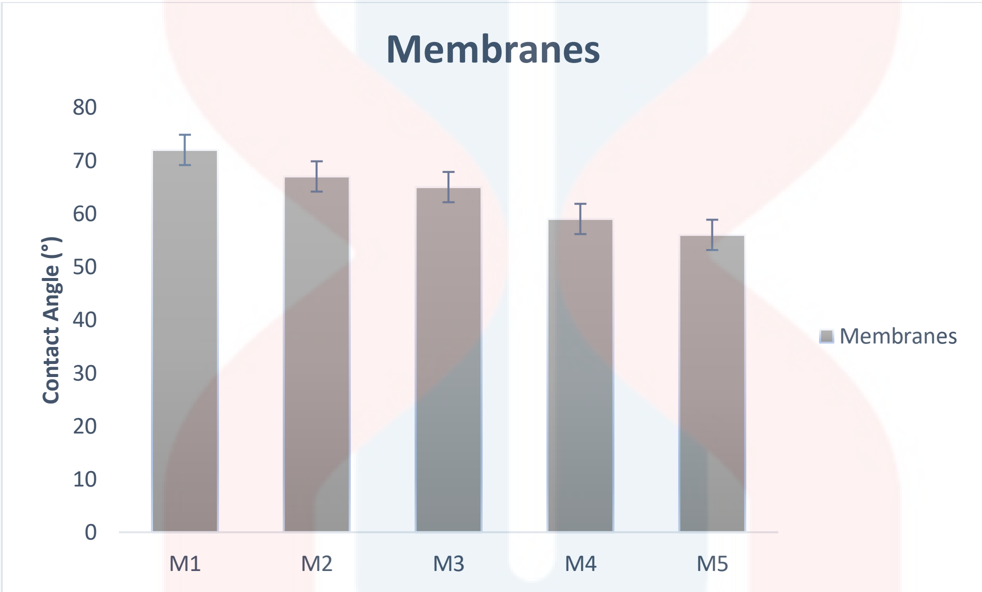

Figure 4.4: The contact angle of the fabricated membranes.

The findings of this study show that the pure PES membrane (M1) achieved the highest contact angle of 72°, indicating a greater level of hydrophobicity. However, the addition of Al_2O_3NPs resulted in a decrease in the contact angle across all membranes (M2 to M5), suggesting an increase in hydrophilic properties. The reduction in contact angle from M2 to M5, along with an increase in the weight of Al_2O_3NPs, indicates an enhanced interaction of the membrane with air. Among all the membranes tested, M5 exhibited the highest hydrophilicity, with a contact angle of 56°, indicating that the incorporation of Al_2O_3NPs at 2.5% by weight had a significant hydrophilic effect. This improved hydrophilicity can offer benefits in water filtration applications, where wettability of the membrane by water can increase solute content and, consequently, improve filtration efficiency. Overall, the results suggest that Al_2O_3NPs play a positive role in enhancing the hydrophilic properties of ultrafiltration membranes, which is critical for water treatment and membrane filtration applications.

4.3 Performance Study

4.3.1 Membrane Porosity and Water Content

Membranes	Porosity (%)	Water Content (%)
M1	58.59	30.23
M2	64.43	32.64
M3	70.81	39.57
M4	69.89	38.89
M5	68.24	36.79

Table 4.1: Overall membrane porosity and water content Membrane

Table 4.1 presents comprehensive data on membrane porosity and water content. The integration of Al_2O_3NPs into MMM has induced notable structural alterations, consequently influencing their performance. The porosity value reflects the volume of interconnected voids and channels in each membrane structure. Based on those values, M3 has the highest porosity of 70.81%, followed by M4 with a porosity of 69.89%. M5 has a porosity of 68.24%, M2 has a porosity of 64.43%, and M1, a pure PES membrane, has the lowest porosity of 58.59%. Higher porosity is generally associated with increased water permeability and filtration efficiency, and trends in porosity values are consistent with the incorporation of Al_2O_3NPs in mixed matrix membranes. M3 stands out with the highest porosity at 70.81%, indicating a significant void volume in the membrane structure. M4 follows closely with a porosity of 69.98%, while M5 and M2 exhibit porosity values of 68.24% and 64.43% respectively. The variation in porosity values reflects the effect of incorporating Al_2O_3NPs into the MMM (Hashemi et al., 2023). The interaction between the polymer matrix and nanoparticles during the membrane formation process creates a more porous and interconnected network, which can increase water permeability and filtration efficiency(Saleem et al., 2020). These structural modifications have potential benefits for applications in ultrafiltration processes, emphasizing the importance of understanding and controlling membrane porosity for improved performance.

Whereas, by calculating the water content and porosity of each membrane, we can get an idea of its structural properties. The pure PES membrane, M1, has a relatively low water content of about 30.23% and a lower porosity of about 58.59%. M2 exhibits a linear relationship between water content (32.64%) and porosity (64.43%). M3 has the highest combination with a water content of around 39.57% and a porosity of around 70.81%, showing an exceptional ability to absorb water. M4 (38.89%) and M5 (36.79%) exhibit increased water content in line with their respective porosity. Introducing Al_2O_3NPs in the MMM consistently contributes to increased hydrophilicity and the formation of larger pore structures. This result aligns with the findings of(Kumar et al., 2016) and (Talavari et al., 2020), who suggested that nanoparticles have the potential to enhance membrane morphology, consequently increasing water content (Rastgar et al., 2017).

4.3.2 The rejection percentages

Membranes	Initial pure water flux (JWF) (L/m_2h)	HA permeate flux (JHA) (L/m_2h)	initial pure water flux (JWF_2) (L/m2 .h)	Rejection (%)
M1	46.09	35.15	36.81	75.5
M2	73.38	49.38	44.37	82.3
M3	98.58	57.21	46.56	90.2
M4	96.09	67.23	61.72	84.6
M5	191.63	86.30	81.34	82.9

Table 4.1: The initial pure water flux, HA permeate flux and final pure water flux of the membranes

The table 4.1 highlights the membrane rejection percentage from M1 to M5, which is a critical factor in evaluating the effectiveness of Humic Acid (HA) removal during the ultrafiltration process. A discussion of the rejection percentage offers insight into the effect of membrane composition, particularly variations in Polyethersulfone (PES), and the addition of Al2O3 nanoparticles on membrane performance. M1, a pure membrane composed of 17.0% PES and 83.0% Dimethylacetamide (DMAc), showed a rejection percentage of 75.5%. Despite the modest rejection, these results indicate that the natural properties of PES contribute to some degree of HA removal. The rejection efficiency can be attributed to the size exclusion effect and the interaction between HA molecules and the PES membrane material. On the other hand, the rejection percentage increased significantly in membranes M2 to M5, which featured a mixture of Al_2O_3NPs in each membrane while maintaining a consistent composition of PES and DMAc. The weight percentage of Al_2O_3NPs increased in

M2 to M5, thereby increasing the rejection percentage. M2, with 1.5% Al_2O_3NPs, showed a rejection increase of 82.3%. These results show the positive influence of Al_2O_3NPs on the rejection ability of the membrane. Nanoparticles likely contribute to the creation of a more selective membrane structure, increasing rejection without significantly affecting flux. The trend of increasing rejection percentage continued with M3, M4 and M5, peaking at 90.2% for M3. This progressive increase in rejection indicates that the presence of Al_2O_3NPs increases the membrane's ability to repel HA molecules, possibly by creating a more tortuous path or promoting interactions that prevent their passage through the membrane (Liao et al., 2018).

4.3.3 Humic Acid Flux

An ultrafiltration experiment was conducted to study the permeability of MMM with humic acid figure 4.5 shows Pure water flux while 4.6 shows humic acid flux

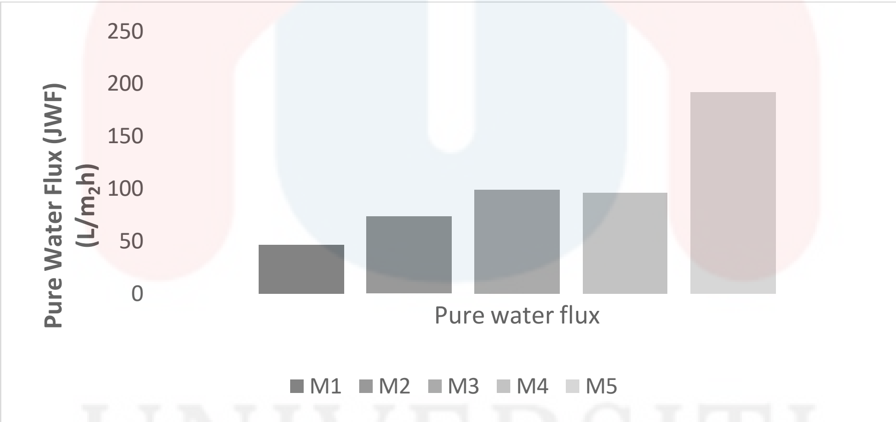

Figure 4.5: Pure water flux

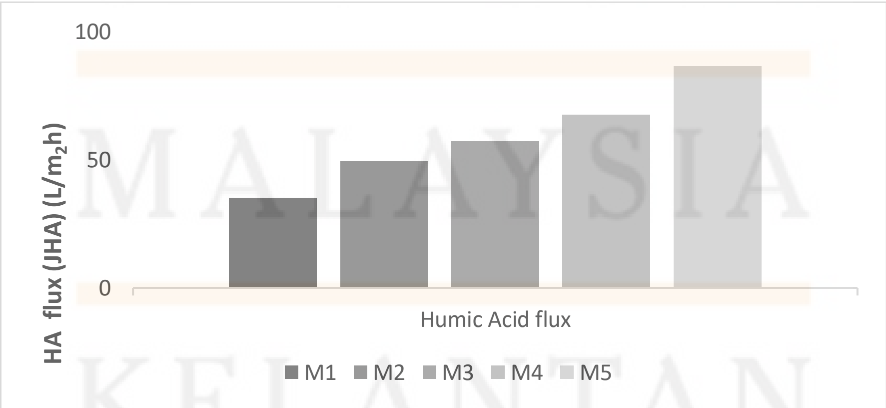

Figure 4.6: Humic Acid flux

Pure water flux (PWF) and humic acid (HA) are important parameters in evaluating membrane efficiency, selectivity, and overall suitability for water treatment applications (Najid et al., 2022). The fluctuations observed in the PWF profile indicate the membrane's hydraulic permeability and fouling resistance. The initial decrease in PWF is consistent with normal ultrafiltration behavior, due to the pressure exerted on the membrane. When the membrane reaches a steady state, a stable PWF suggests consistent and reliable performance throughout the filtration process. The introduction of nanoparticles, especially Al_2O_3NPs in specific membranes such as M2, M3, M4, and M5, introduced variations in PWF. Nanoparticles play an important role in changing membrane properties, affecting pore structure, hydrophilicity, and overall permeability. Membrane-specific variations in PWF patterns highlight the effects of nanoparticle composition and content on performance (Najid et al., 2022). HA flux profiles elucidate the efficiency of membranes in selectively adsorbing humic acids, a key factor in evaluating their organic matter removal capabilities. Membranes with a higher rejection percentage, exemplified by M3, showed a lower HA flux, indicating an effective removal of organic constituents. Time dynamics of HA flux filtration exhibit the temporal efficiency of membranes in rejecting humic acids (Tian et al., 2023). Membranes incorporating nanoparticles showed enhanced HA rejection, resulting in lower HA flux. This underlines the positive contribution of nanoparticles to the selectivity towards humic acid molecules. A membrane-specific response becomes evident in the observed variation in HA flux. Membranes with a higher rejection percentage effectively block the passage of humic acid molecules, emphasizing the importance of tailored membrane design for specific water treatment goals.

4.4 Fouling Study

4.4.1 Membrane Fouling Analysis

Fouling represents a major challenge in membrane-based water treatment systems, mainly due to the hydrophobic nature of typical membranes (El Batouti et al., 2021). In this study, we aim to address the fouling issue through the fabrication and characterization of a Mixed Matrix Ultrafiltration Membrane combined with Mixed Matrix Ultrafiltration Membrane for HA removal. The incorporation of Al_2O_3NPs into the polymer matrix of the membrane introduces a new approach to increase fouling resistance (Baniasadi et al., 2021).

Membranes with inherent hydrophobic properties are prone to fouling, leading to reduced efficiency, increased maintenance costs and decreased water flow. The introduction of hydrophilic Al_2O_3NPs aims to reduce this challenge. Evaluation of fouling resistance includes calculation of relative flux reduction (RFR), flux recovery, and application of Darcy's law for comprehensive analysis (Diez et al., 2014). RFR measures the reduction in flux due to fouling, while flux recovery measures the membrane's ability to regain its initial flux after washing. Darcy's law provides insight into overall fouling resistance (Gao et al., 2019).

The designed membrane shows better fouling resistance compared to normal membranes (McCloskey et al., 2012). The hydrophilic nature of Al_2O_3NPs contributes to the reduction of both reversible and irreversible fouling mechanisms. Reversible impurities, such as cake layer formation or concentration polarization, can be effectively reduced by physical washing methods (Goosen et al., 2005). Irreversible fouling, due to adsorption or pore clogging, is also minimized by the presence of hydrophilic nanoparticles. The normalized flux ratio was analyzed to measure the effect of Al_2O_3NPs on fouling resistance under varying HA concentrations (Zhou et al., 2019). The results show that Al_2O_3NPs -incorporated membranes exhibit enhanced fouling resistance, which is particularly noteworthy in scenarios involving lower HA concentrations. The relative flux reduction (RFR) was calculated quantitatively and the hydraulic cleaning properties of the membrane can be evaluated by the flux recovery ratio (FRR) as shown below Figure 4.7 for 30 minutes. To achieve the best performance, the membrane will show great antifouling properties with Low RFR and high FRR.

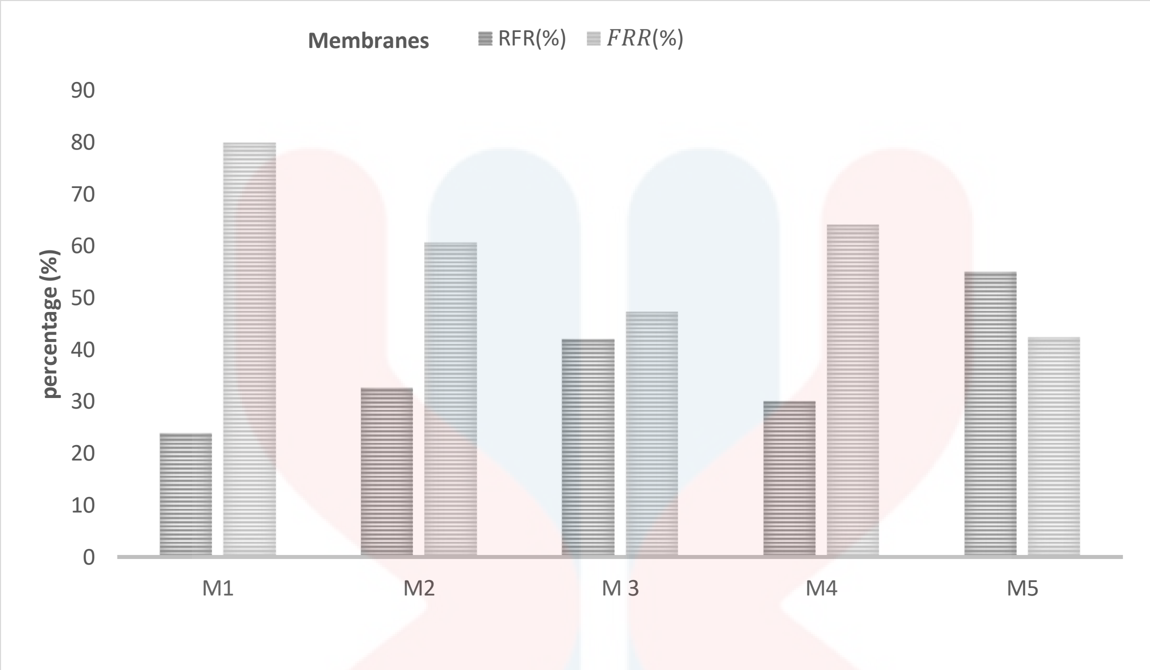

Figure 4.7: The Antifouling Parameter of the fabricated membranes

The evaluation of fouling resistance in membrane processes is crucial for assessing the performance and longevity of the membranes. In this study, two key parameters were employed to characterize fouling: relative flux reduction (RFR) and flux recovery (FR). These parameters provide insights into the fouling behavior and the effectiveness of membrane cleaning procedures. Relative flux reduction (RFR) was utilized to quantify the reduction in permeate flux over time due to fouling. RFR is calculated using the initial water flux (JWF) and the permeate flux during the testing solution (HA solution) (JTS). The calculated RFR values for membranes M1 to M5 ranged from 24.3% to 17.1%, indicating a decrease in water permeability as the filtration progressed. The higher RFR values suggest a greater decline in membrane performance due to fouling.

Additionally, flux recovery (FR) was determined after washing the membranes with distilled water for 30 minutes. FR represents the ability of the membrane to regain its initial flux after cleaning. The calculated FR values for membranes M1 to M5 varied from approximately 79.8% to 42.4%. A higher FR indicates better membrane recovery after cleaning, reflecting the effectiveness of the cleaning process in removing fouling materials. The observed trends in RFR and FR highlight the impact of fouling on membrane performance and the importance of membrane cleaning. Membranes with higher RFR values experienced more substantial fouling, leading to a greater reduction in water permeability.

The subsequent FR values demonstrate the varying degrees of success in restoring membrane performance through cleaning procedures.

In conclusion, the analysis of RFR and FR provides valuable insights into fouling behavior and the effectiveness of cleaning strategies. Understanding these parameters is essential for optimizing membrane processes and ensuring the long-term efficiency of water treatment systems. Further investigations could explore additional factors influencing fouling and develop advanced cleaning methods to enhance membrane performance.

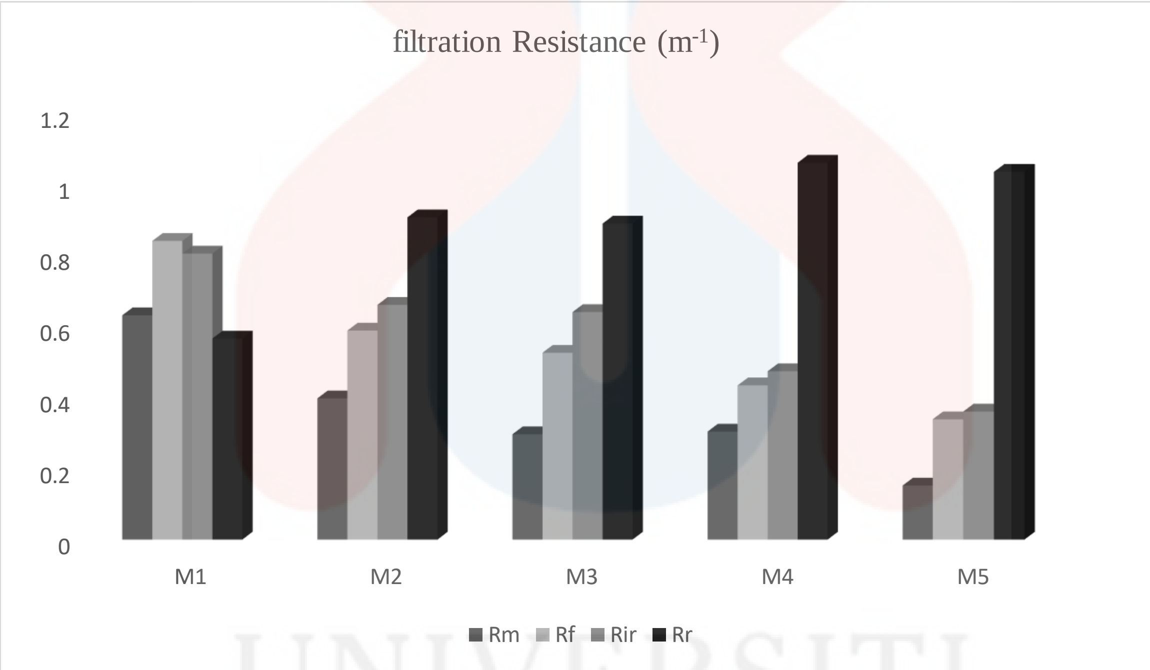

Figure 4.7: The filtration Resistance of Different Membrane

The Different Membrane Filtration Resistance values for each membrane (M1 to M5) provide a valuable insight into their filtration performance, especially in the context of humic acid removal. Understanding this resistance component is important to understand the membrane behavior during the filtration process and guide the discussion of its effectiveness in water treatment applications. Membrane M1 pure shows moderate intrinsic resistance (Rm), indicating a reasonable inherent resistance to water flow. Relatively high fouling resistance (Rf) indicates susceptibility to fouling, emphasizing the importance of an effective cleaning strategy. Both reversible and irreversible adsorption resistances (Rr and Rir) are important, further emphasizing the need for robust cleaning procedures. The M2 membrane exhibits lower intrinsic resistance and fouling compared to M1. Although both reversible and irreversible adsorption resistances are high, indicating potential fouling challenges, lower Rm and Rf values suggest better water flow characteristics. Membrane M3 shows the lowest intrinsic resistance (Rm) among membranes, indicating favorable water flow properties. Moderate fouling resistance (Rf) and significant reversible and irreversible adsorption resistance highlight the potential of M3 for water flow enhancement and pollution reduction. Whereas, the M4 membrane exhibits higher intrinsic resistance and fouling, indicating potential challenges in water flow and fouling management. The large reversible and irreversible adsorption resistance emphasizes the importance of effective cleaning procedures.

Finally, the M5 membrane stands out with the lowest intrinsic resistance and fouling, exhibiting excellent water flow characteristics and resistance to fouling. Both reversible and irreversible adsorption resistances are important, emphasizing the importance of cleaning strategies. The incorporation of alumina nanoparticles into the membrane, especially in M5, shows potential benefits for increased water flow and resistance to fouling. However, further investigation of the specific interactions between nanoparticles and membrane properties is required to optimize membrane design for efficient humic acid removal. These findings contribute to ongoing efforts to design membranes with better performance in water treatment applications.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In conclusion, the fabrication and characterization of mixed matrix ultrafiltration membranes combined with alumina oxide nanoparticles have resulted in significant progress in the field of humic acid (HA) removal. Through a careful fabrication process and careful characterization, the membrane has demonstrated enhanced capabilities in addressing the challenges associated with humic acid filtration. Incorporation of alumina oxide nanoparticles has been shown to play an important role in improving membrane performance, with significant results in rejection efficiency and antifouling properties. The addition of various concentrations of alumina oxide nanoparticles to the Polyethersulfone (PES) matrix was required for the successful fabrication of these mixed matrix membranes, denoted as M2 to M5. This deliberate modification results in membranes of various compositions, each with a different humic acid removal performance. The rejection percentage, which ranged from 82.3% to 90.2%, demonstrates the membrane's effectiveness in the selective removal of humic acid from water sources.

Additionally, membrane characterization revealed that the addition of alumina oxide nanoparticles improved permeation performance. The membrane has improved hydrophilicity, porosity, and pore size, which are all important factors in achieving efficient ultrafiltration. Furthermore, the membrane's antifouling properties have been significantly improved, ensuring consistent performance over long periods of operation. This research could be useful in water treatment processes where humic acid removal is a critical goal. This mixed matrix membrane's tailored design, combined with the synergistic effect of alumina oxide nanoparticles, positions it as a valuable asset in addressing water quality challenges. As the demand for effective and sustainable water treatment solutions grows, this membrane makes an important contribution to the field.

Finally, to investigate optimising nanoparticle concentration to achieve an optimal balance of rejection efficiency and diffusion performance. Furthermore, investigating the scalability and long-term durability of these membranes in real-world conditions is critical for their practical application in water treatment plants. Overall, the fabrication and characterization of a mixed matrix ultrafiltration membrane containing alumina oxide nanoparticles represents a promising step forward in the pursuit of effective humic acid removal for clean and safe water sources.

5.2 RECOMMENDATIONS

For future development, the following recommendations have been suggested for future work:

1. **Nanoparticle Loading Optimization:**

More research can be done to optimize the loading of alumina oxide nanoparticles in the membrane matrix. Understanding the effect of different nanoparticle concentrations on membrane performance, such as rejection efficiency and permeability, will provide valuable insight into achieving the ideal balance between enhanced humic acid removal and overall membrane integrity.

2. **Surface Modification of Nanoparticles:**

Surface modification of alumina oxide nanoparticles is being investigated to improve their compatibility with the polymer matrix. Functionalization of nanoparticles can improve their dispersion, adhesion and interaction with membrane materials, potentially leading to better performance and membrane lifetime.

3. **Long Term Stability Study:**

Long-term stability studies are needed to evaluate the durability and performance sustainability of the designed membrane over a long period of time. Under continuous operating conditions, investigating potential changes in membrane characteristics such as structure, rejection efficiency and permeability will provide a comprehensive understanding of their practical applicability.

4. **Assessment of Antifouling Properties:**

The antifouling properties of the membrane must be evaluated before it can be used in the field. Future research should include comprehensive studies on fouling mechanisms, cleaning strategies, and the development of fouling-resistant membranes. To reduce the effect of fouling, additional antifouling agents or surface modifications can be used.

5. **Real Water Testing:**

It is important to verify membrane performance under real world water conditions, especially with water samples containing humic acids from natural sources. Experiments with real water samples will provide a more accurate picture of the difficulties and complexities associated with humic acid removal in practical applications.

6. **Scaling and Industrial Applications:**

For potential commercialization, it is necessary to investigate the scalability of the fabrication process and evaluate the membrane performance on an industrial scale. Addressing issues such as large-scale production, cost-effectiveness, and compatibility with existing water treatment processes will be critical to the successful implementation of water treatment facilities.

7. **Comparison with Other Nano Materials:**

Other nanomaterials commonly used in mixed matrix membranes can be studied comparatively. Evaluating the performance of alumina oxide nanoparticles compared to other nanomaterials may reveal distinct advantages or synergistic effects, thereby contributing to the development of more efficient and versatile membranes.

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