# MODIFICATION OF PVDF MEMBRANE USING LIGNIN AND CALCIUM CARBONATE FOR OILY WATER SEPARATION TO BE USED IN WATER DISPENSER

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**by**

**DINESVARAN S/O RAJESVERAN**

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**for the degree of**
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## LIST OF ABBREVIATIONS

| | |
|---|---|
| PVDF-Lig | PVDF coated with lignin |
| PVDF-Lig-CC | PVDF coated with lignin and loaded with $CaCO_3$ |
| PVDF-Lig-CCR | PVDF coated with lignin with $CaCO_3$ removal |
| EDTA-disodium | Ethylenediaminetetraacetic acid disodium salt dihydrate |
| CC | Calcium carbonate |
| CCR | Calcium carbonate removal |
| Lig | Lignin |
| APM | Airborne particulate matter |
| PVDF | Polyvinylidene fluoride |
| BL | Bilayer |
| PSf | Polysulfone |
| PVC | Polyvinyl chloride |
| SKL | Sulfonated kraft lignin |
| LCN | Lignin cellulose nanofibril |
| LS | Lignosulfone |
| LbL | Layer by layer |
| PVA-co-PE | Hierarchical poly (vinyl alcohol-co-ethylene) |
| PAN | Polyacrylonitrile |
| PET | Polyethylene terephthalate |
| CTA | Cellulose triacetate |
| CA | Cellulose acetate |
| PMMA | Poly (methyl methacrylate) |
| PANI | Polyaniline |
| PU | Polyurethane |
| BSA | Bovine serum albumin |
| NaCI | Sodium chloride |
| $MgSO_4$ | Magnesium sulphate |
| $MgCI_2$ | Magnesium chloride |
| CS | Chitosan |
| NPs | Nanoparticles |
| $TiO_2$ | Titanium oxide |

| | |
|---|---|
| PVA | Polyvinyl alcohol |
| DNDs | Detonation nanodiamonds |
| NSCS | N-succinyl chitosan |
| TLFCHs | Tendril-like functional carbon helices |
| CB | Cibacron Blue F3G-A |
| HA | Humic acid |
| BB41 | Basic Blue 41 |

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# PENGUBAHSUAIAN MEMBRAN PVDF MENGGUNAKAN LIGNIN DAN KALSIUM KARBONAT UNTUK PEMISAHAN AIR BERMINYAK UNTUK DIGUNAKAN DALAM DISPENSER AIR

## ABSTRAK

Lignin adalah biopolymer kedua paling banyak di dunia dan sumber struktur aromatik yang terdiri daripada banyak kumpulan hidrofilik. Lignin mempunyai keupayaan untuk digunakan sebagai penggalak hidrofilik dalam fabrikasi membran kerana ianya yang dapat meningkatkan ciri-ciri hidrofilik dan antikulat membran hidrofobik. Dalam kerja ini, lignin diperkenalkan dan disalut pada kedua-dua polivinylidene fluorida, PVDF dan PVDF dengan $CaCO_3$ memuatkan untuk penapisan air berminyak. PVDF dan PVDF dengan 3 wt% $CaCO_3$ membran direndam dalam 0.75 g larutan lignin yang mengandungi natrium klorida, NaOH dan air suling. PVDF yang asli dan membran disalut lignin dapat dicirikan dengan spektroskopi inframerah fourier transformasi (FTIR), dan mikroskop elektron imbasan (SEM) untuk perbandingan. Sudut hubungan bawah air dinamik digunakan untuk memeriksa sifat hidrofilik membran yang diubahsuai. Kebolehtelapan air tulen yang tinggi dalam penyingkiran bermula dari PVDF_lignin_$CaCO_3$ (PVDF-Lig-CCR), diikuti oleh PVDF_lignin_$CaCO_3$ (PVDF-Lig-CC), PVDF dan PVDF_lignin asli (PVDF-Lig). Penggunaan larutan 0.2 M EDTA-disodium dapat menyingkirkan kalsium karbonat di mana keliangan membran yang diubahsuai menunjukkan penurunan. Membran lignin bersalut PVDF mempamerkan sifat antifouling dengan penolakan minyak sehingga 99.36% manakala membran PVDF yang asli hanya menolak 87.50%. Kehadiran lignin pada membran PVDF menunjukkan prestasi antifouling yang terbaik walaupun ia mempunyai kebolehtelapan air berminyak yang lebih rendah tetapi stabil.

# MODIFICATION OF PVDF MEMBRANE USING LIGNIN AND CALCIUM CARBONATE FOR OILY WATER SEPARATION TO BE USED IN WATER DISPENSER

## ABSTRACT

Lignin is the world's second most abundant biopolymer and source of aromatic structures which consist of plenty of hydrophilic groups. Lignin have the ability to be used as a hydrophilic promoter in membrane fabrication due to its property which able to improve the hydrophilicity and antifouling properties of hydrophobic membranes. In this work, lignin was introduced and coated on both polyvinylidene fluoride, PVDF and PVDF with $CaCO_3$ loading for oily water separation. PVDF and PVDF with 3 wt% $CaCO_3$ loading membranes were immersed in 0.75 g of the lignin solution containing sodium chloride, NaOH and distilled water. The pristine PVDF and lignin coated membranes were characterized with Fourier-transform infrared (FTIR) spectroscopy, and scanning electron microscope (SEM) for comparison. The dynamic underwater contact angle was used to examine the hydrophilic properties of the modifed membranes. The pure water permeability was greatest in PVDF_lignin_$CaCO_3$ removal (PVDF-Lig-CCR), followed by PVDF_lignin_$CaCO_3$ (PVDF-Lig-CC), pristine PVDF and PVDF_lignin (PVDF-Lig). The usage of 0.2 M EDTA-disodium solution able to remove the calcium carbonate as the porosity of the modified membrane is reduced. The PVDF-coated lignin membrane exhibits antifouling properties with oil rejection up to 99.36% while the pristine PVDF membrane only rejected 87.50%. The presence of lignin as a hydrophilic promoter coated on PVDF membrane showed a good antifouling performance although it has lower but stable oily water permeability.

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Water is indeed important to human beings to sustain their life and it can be used for various applications. The availability of the clean water produced is the important factor that needs to be highlighted. As the demand for water and the world population rises, it is predicted that the chances for the water to get contaminated are higher which indirectly could result in a more serious environmental problem. It has been highlighted the estimation the human population will rise by about 9 billion by the year 2050 (Ray et al., 2016). To compensate for the rise in population, adequate clean drinking water must be supplied consistently. But, it has become the most critical problem mankind needs to be highlighted (Parekh et al., 2018). It is proven by a study conducted by Bombe (2020), the demand for water and wastewater treatment is projected to rise to $211.3 billion by 2025 at a CAGR of 6.5% from 2019 to 2025 due to the factors such as clean water and new water resources global demand, population growth, environmental concern, etc.

Water pollution has turned into a global issue due to the rapid growth of industries, unplanned urbanization, and agricultural development as well. Among diverse types of contaminants in water, oil is recognized as one of the largest pollutants which is accumulated by the discharge of oily wastewater from everyday household activities, as well as industrial discharge including petrochemical, food, and oil & gas refineries. These oily wastewaters predominantly contain finely dispersed and highly stable oil-in-water emulsion droplets. Based on the statistics by World Health Organization (WHO), almost 785 million people gave concern about the quality of drinking water but 2 million people prone to use contaminated drinking water

(Organization, 2018). Drinking water sources could be one of the factors that cause such problems. As shown in Figure 1.1 in Bangladesh, almost 70 million population were affected by consuming water from groundwater sources. This is due to arsenic levels (pollutants) exceed the WHO recommended standard of 10µg/L. This pollutant also has affected almost 140 million people in 70 countries. Meanwhile, in France, it is discovered that 3 million population were drinking affected water and 97% of groundwater samples do not meet the WHO standards (Programme, 2017).

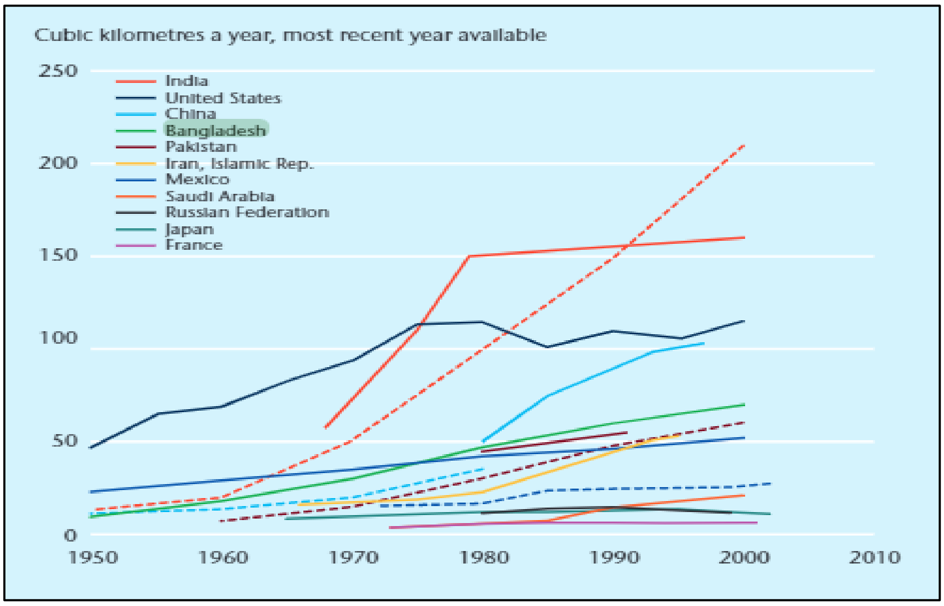


Figure 1.1 Usage of groundwater in some countries (Programme, 2017).

Physically accessible, acceptable, safe, and continuous clean drinking water are therefore very important criteria to be focused on. For that, Sustainable Development Goal target 6.1(SDG) which seeks to secure safe and affordable drinking water for all has been implemented to track down the drinking water from an improved water source. WHO also has produced series of water quality guidelines based on managing risk to provide proper clean water to all the premises (Organization, 2019).

According to Vatanpour et al. (2020), various water treatment techniques such as adsorption, absorption, coagulation, and membrane processes that can be used to treat the water are reported. Each of the methods holds, its advantages and disadvantages but it needs further optimization to improve the efficiency in removing the pollutants. In 2019, membrane separation held the biggest share of the entire water and wastewater treatment technologies market (Wood, 2019). Ding et al. (2016) reported that membranes have a wide range of applications including the production of high-quality water and the removal of toxic components from industrial effluents. It is classified as one of the physicochemical purification technologies available for filtering out contaminants.

Due to the advantages, polymers have become the primary materials in membrane technology. For the treatment process, various membrane materials such as polyethersulfone (PES), polysulfone (PSf), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyvinyl chloride (PVC), and cellulose acetate (CA) have been employed. The main disadvantage of this membrane in separation is membrane fouling and expensive cost. If foulant accumulates on the membrane, it will compromise separation performance and efficiency due to the deposition of unwanted molecules on the membrane's surface which will result in deterioration, a loss in a lifetime, and limits the membrane productivity (Gebreslase, 2018). Hence, to reduce the membrane fouling and reduce the cost, several techniques were developed such as surface modification of membranes, blending of membranes, and embedding of inorganic nanoparticles into polymer matrices which reduces membrane fouling and increase its permeability (Colburn et al., 2019, Shamaei et al., 2020a, Ding et al., 2016, Vilakati et al., 2015, Yong et al., 2019).

Recently, the use of lignin in membrane performance has been highlighted, and it has generated attention in a variety of fields, including wastewater treatment, desalination, and so on. Lignin is the component of lignocellulosic biomass which has a composition of 10-25 wt% lignin. The rests are cellulose and hemicellulose which have a composition of 35-55 wt% and 20-40 wt% respectively as shown in Figure 1.2. Based on Merriam-Webster (2020), lignin is an amorphous polymer linked to cellulose that gives stiffness and forms the woody cell walls of plants. It able to cementing material between them when combined with cellulose. . It is proven by Annunziata (2019) that lignin is very important in the formation of cell walls in wood and it can be categorized under a class of complex aromatic polymers. Yong et al. (2019) claimed that lignin is one of the most abundant natural polymers in biomass. According to Gong et al. (2016) and Santos et al. (2017), lignin has numerous functional groups including phenolic hydroxy, alcohol hydroxy, carbonyl, methoxyl, and carboxyl groups which give lignin strong hydrophilicity properties. Due to its hydrophilic properties, lignin is therefore highly used in membrane modification to solve the membrane fouling and increase its permeability. It is reported that different types of lignin derivatives have been used to improvise the membrane performances to increase its efficiency via modification methods (Vilakati et al., 2015, Shamaei et al., 2020a, Shamaei et al., 2020b, Ding et al., 2016, Yong et al., 2019). In addition, the properties of lignin, such as its polyanionic structure and lack of toxicity, make it an ideal component for modifying the bulk and surface properties of membranes.

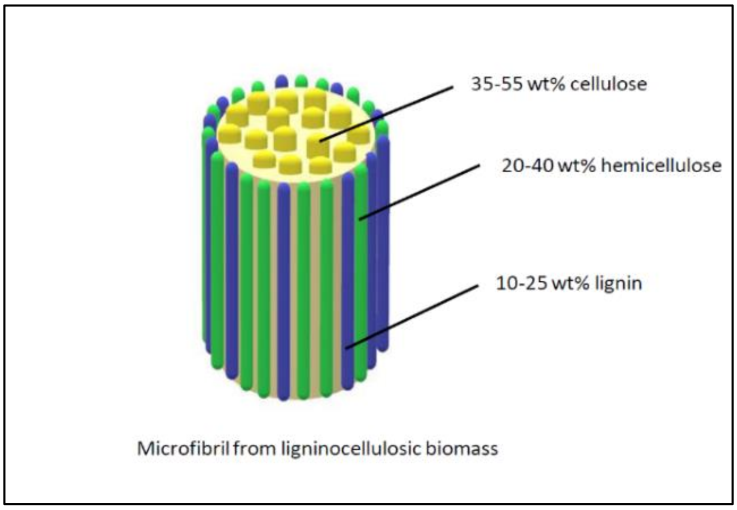


Figure 1.2 Lignocellulosic biomass configuration (drawn using Paint 3D application)

## 1.2 Problem Statement

Same characteristics as PVC exhibit in PVDF membrane including low cost, availability, good stability at high temperature. PVDF itself able to dissolve in various organic solvents and it can form a film. These characteristics make the PVC and PVDF be used as membrane precursors (Aji et al., 2020). But due to the PVDF membrane itself is hydrophobic, it leads to membrane fouling which eventually causes reduction of the permeation flux, the inefficiency of the system, and an increase in the membrane washing expenses. Therefore, modifications on the PVDF membrane were developed to solve the hydrophobic properties of PVDF via various modification techniques (Vatanpour et al., 2020, Aji et al., 2020, Jalal Sadiq et al., 2020, Ahmad et al., 2021, Ghazanfari et al., 2017, Haghighat et al., 2020, Yong et al., 2019). Similarly, all the reported articles highlighted that for drinking water or wastewater treatment, hydrophilic membrane will be the best choice instead of hydrophobic membrane due to high tolerance to provide better performances compared to hydrophobic membrane.

Lignin because of its unique properties such as hydrophilic, polyanionic structure, and nontoxicity. Therefore, it can be used as an additive to modify and improve the membrane. As reported, the blending method (Ding et al., 2016, Vilakati et al., 2015, Yong et al., 2019, Shamaei et al., 2020a, Esmaeili et al., 2018) and coating method (Shamaei et al., 2020b, Gu et al., 2019) are the most widely applied techniques to fabricate the membrane using different types of lignin. But, the lignin coating on the membrane often leads to a reduction in pore size which affects the porosity as well. To my best knowledge, the addition of hydrophilic agent such as lignin together with nanoparticles in membrane fabrication is never studied and new research will be viable to explore the membrane performance more. Only researches on calcium carbonate loading on polymeric membrane have been widely studied (Melbiah et al., 2017, Saki and Uzal, 2018). But, the PVDF membrane coated with lignin and calcium carbonate loading to be used in water dispensers for oil-water filtration has not been studied yet. Therefore, this study aims to fabricate PVDF and PVDF with calcium carbonate loading and both of them will be modified using lignin as a hydrophilic agent. The membrane characterization will be studied using FTIR and SEM. Furthermore, water contact angle, flux rejection, porosity, and pure water permeability will be studied to determine the increase in pore size and the anti-fouling propensity of the modified membrane.

## 1.3 Objectives

i. To study the surface modification of PVDF membrane coated with lignin and calcium carbonate loading.

ii. To study the effects of lignin and calcium carbonate on porosity and other properties.

iii. To study the effects of EDTA-disodium in removing the calcium carbonate from the modified membrane.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Lignin has been used to modify the membrane as summarized in Table 2.1. The modification must fulfill a variety of requirements, including producing an antifouling membrane, narrowing the membrane's pore distribution, and increasing or decreasing the membrane roughness. Different approaches to modify the polymer membrane have been reported including blending method, layer by layer assembly, photo-irradiation, surface plasma irradiation, and so on. But the most common method used is blending and coating methods.

## 2.2 Lignin modification methods and their performances

### 2.2.1 Blending method

The most commonly used method to modify the polymer membrane is by blending method as shown in Figure 2.1. Blending involves the direct mixing of lignin into a dope solution containing polymer, solvent, and other non-solvent additives. PES dope solution blended with sulfonated kraft lignin (SKL) was precipitated using water as a non-solvent bath (Shamaei et al., 2020a). The PES membrane blended with 3wt% of SKL showed excellent properties when compared with the virgin membrane and it is a hydrophilic membrane as well. The membrane permeability of the modified membrane is increased to 68.6 $L/m^2h.psi$ by increasing the SKL concentration. The modified membrane exhibited antifouling properties although the rejection rate is slightly reduced to 56.1%. The virgin membrane is hydrophobic which increase the contact angle and it is not suitable for oily water separation.

Similar case is proven by Ding et al. (2016) PES membrane was further blended with lignin–cellulose nanofibril (LCN). The membrane dope solution was prepared by dissolving 18 wt% of PES and 0.3 wt% PVP in LCN colloidal suspension resulted from acidification with 20 wt% sulphuric acids. Membrane permeability is not studied but the fabricated membrane showed an increase in LCN content from 0 wt% to 1.2 wt% causes the permeate flux to increase from 322.8 L/m$^2$h to 692.3 L/m$^2$h. As a result, the contact angle was reduced which indicate that the membrane is highly hydrophilic to oily water filtration. The modified membrane showed a lower contact angle due to the presence of polar functional groups in LCN which interact with water by hydrogen bonds. The virgin membrane has high contact angle which increases the chances of foulant to accumulate on membrane.

Differently, Esmaeili et al. (2018) dissolved the lignin in a mixture of NMP and DMF before preparing the PES solution for membrane casting. Lignin is extracted from ionic liquid, deep eutectic solvents (DES) is used and the modified membrane with 1 wt% DES-lignin showed a higher permeability of 96.9 L/m$^2$h.bar compared to the neat PES membrane. It also observed that by increasing the lignin concentration, the permeability was increased and the water contact angle was reduced. This indicated that the membrane produced becomes more hydrophilic due to the presence of functional groups in lignin. According to Gong et al. (2016) and Santos et al. (2017), lignin has functional groups such as phenolic hydroxy, alcohol hydroxy, carbonyl, methoxyl, and carboxyl group which gives strong hydrophilicity properties. A similar technique was adopted by Vilakati et al. (2015). PSf membrane with 0.5 wt% lignin achieved a rejection of 94% which able to filter the oily water after 120 min of immersion when comparing with PSf membrane with 0.125 wt% lignin and neat PSf membrane.

Meanwhile, Yong et al. (2019) adopted the blending technique to fabricate PVC membrane incorporated with lignin, PEG 400, and DMAc. The effect of lignin on membrane hydrophilicity and fouling resistance was investigated using different lignin content. The modified membrane shows an increment in pore size from 19.7 nm to 25.5 nm when lignin content was increased from 0 to 50 wt%. According to Gallego Ocampo et al. (2016), Membranes with a larger pore size are more prone to fouling by allowing more oil to be in permeate site and have a lower permeate flux drop. These phenomena are complicated by the trade-off principle, which states that higher water permeability often leads to decreased selectivity since larger species have higher permeability than smaller ones. Adversely, the permeate flux also rejection rate are increase as well as the lignin content is increased.

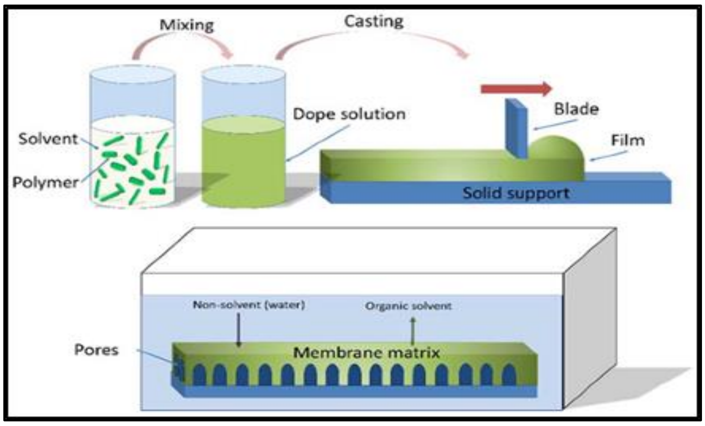


Figure 2.1 Preparation to modify the membrane (Hamzah and Leo, 2016)

### 2.2.2 Coating method

The coating is one of the simplest methods of membrane modification. Shamaei et al. (2020a) studied layer by layer assembly method. PES membrane was coated with poly (diallyl dimethylammonium chloride) (pDAC) as polyanion and lignin as polycation as shown in Figure 2.2. The pDAC solution was poured over the PES membrane and allowed to stay for 1 h before immersed in deionized water for 20 min. The anionic lignin was then poured over the pDAC-coated substrate and allowed to stay for 1 h again to form the first bilayer. The fabricated membrane of PES-3BL with 2wt% lignin and 2wt% pDAC attained because the water contact angle is reduced to 22.6±0.5º, the anti-fouling performance is reduced and it provide a better result to filter the oily water. The permeability decreases from 3.8 L/m²h.psi to 1.6 L/m²h.psi as the number of coating bilayer increase to 3 layers. Based on water contact angle, the hydrophilic membrane which have lower contact angle tend to provide anti-fouling performances and it is highly suitable for oily water separation.

Meanwhile, in a study by Gu et al. (2019), the PSf membrane was coated with polyethyleneimine (PEI) as polycation and lignosulfonate (LS) as polyanion. As the number of bilayers increases, the contact angle reduces to 44.1º. The coated membrane exhibited a smooth surface. In addition, the coated membrane showed improvement in terms of hydrophilicity which could inhibit the foulant adsorption. However, the multiple-layer coatings caused a reduction in permeability. The modifications allow lignin to be applied homogeneously to the entire membrane structure but the incompatibility of hydrophilic lignin derivatives with hydrophobic polymers makes modified membranes with controlled pore size and desirable mechanical stability problematic.

It can be concluded that the hydrophilic membrane is more suitable for oily water separation compared to hydrophobic. For that, membrane which have less contact angle and which provide better separation efficiency should be used.

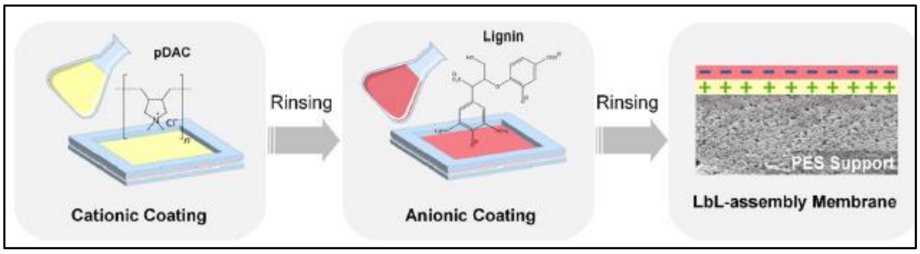


Figure 2.2 Layer by layer assembly for membrane modification (Shamaei et al., 2020b).

Table 2.1 Lignin derivatives with different modification methods.

| Methods | Membrane | Lignin | Techniques | Permeability | Average pore size (nm) | Rejection (%) | Water contact angle (º) | Ref |
|---|---|---|---|---|---|---|---|---|
| **Blending** | PES | 3 wt% SKL | Immersion precipitation | 68.6 L/m²h.bar | 34.9 | 56.1 | - | (Shamaei et al., 2020a) |
| | | 1.2 wt% LCN | Immersion precipitation | - | - | 94.0 | 42.0 | (Ding et al., 2016) |
| | | 1wt% DES-Lignin | Phase inversion | 96.9 L/m²h.bar | - | 86.6 | 45.6±1.2 | (Esmaeili et al., 2018) |
| | PSf | 0.5 wt% LS | Phase inversion | - | - | 94.0 | - | (Vilakati et al., 2015) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | PVC | 0.5 wt % Lignin | Phase inversion | - | 25.5 | 97.4 | 41.5 | (Yong et al., 2019) |
| **Coating** | PES-3BL | SKL | LbL assembly | 1.6 L/m$^2$h.psi | - | 90.0 | 22.6±0.5 | (Shamaei et al., 2020b) |
| | PSf-5BL | LS | LbL deposition | - | - | - | 44.1 | (Gu et al., 2019) |

## 2.3 Effect of nanoparticles towards membrane performances

Nanofillers or nanoparticles (NPs) are the types of particles whose application depends on the materials and fields. It is called nanoparticles because the particles are in the three-digit range of nanometer from 1 nm to 1 μm. Recently, the incorporation of NPs into polymeric membranes has become an area of intense research in recent years. This is due to the addition of NPs causes the nanocomposite membrane to exhibit positive performances in terms of permeability, selectivity, strength, and hydrophilicity. Different types of nanoparticles exist such as metal/metal oxides based, carbon-based, and other nanoparticles.

There are different types of metal/metal oxides-based NPs that are available such as copper, zinc, alumina, metal-organic frameworks, and zinc oxides which are being incorporated in the membrane to provide a better membrane performance, especially in water treatment. All the research emphasizes the lower cost of NPS. Hence, zinc oxide (ZnO) could be a good option. The addition of ZnO increases the surface-to-volume ratio and making it an alternative potential framework that could meet the need for a reliable and low-cost gadget.

The addition of NPs caused an increment in the membrane porosity, permeability and it reduced the contact angle. This theory is proven by Kusworo et al. (2021) whereby PSf membrane incorporated by GO and ZnO nanoparticles showed an increment of porosity up to 83.00±1.18% compared with pristine PSf. This indicates that the addition of NPs on the modified membrane increases the void space in the membrane. Similarly, the water flux of the PSF/GO/ZnO membrane increased as well due to the higher availability of hydrophilic sites, which expedites the sorption ability of water. The contact angle of the PSF/GO/ZnO membrane reduced from 80º to 52º due to hydrophilic NPs.

Besides, the increment of NPs in membrane dope solution has shown a positive impact on membrane performance. However, beyond its limits of increment, the membrane showed slightly negative performance. Based on Ghoul et al. (2017), incorporation of ZnO nanoparticles into the polyamide membrane reduced the contact angle from 94.4º to 18.0º which proved the existence of hydrophilic NPs. The presence of ZnO enhanced the membrane hydrophilicity, which is highly favorable to the flux of water. At 0.007 g loading of ZnO, the membrane exhibited the highest water flux (48.46 L/m2.h). Beyond 0.007 g of ZnO, the water flux decreased due to the synergetic consequence of an accumulation of ZnO nanoparticles and reduced porosity. Almost similar findings are reported in Hou et al. (2014), Guo and Kim (2017), and Saki and Uzal (2018) using different types of polymeric membranes and nanoparticles. Although the different materials are used, still the performance of the membrane was almost similar. The result of their findings is depicted in Table 2.2 alongside other reporting results.

Table 2.2 Performances of membrane incorporated with nanoparticles for separation.

| Nanoparticles | Concentration (wt%) | Oil rejection (%) | Water flux (L/m$^2$.h.bar) | Porosity (%) | Change in water contact angle (°) | Ref |
|---|---|---|---|---|---|---|
| **Calcium carbonate, $CaCO_3$** | 0.75 | 98.0 | - | 85.8 | 76.2-20.0 | (Melbiah et al., 2017) |
| **Calcium carbonate, $CaCO_3$** | 10.00 | 92.0 | - | 70.0 | 92.0-84.0 | (Saki and Uzal, 2018) |
| **Titanium oxide, $TiO_2$** | 0.80 | - | - | 79.6 | 67.9-55.1 | (Guo and Kim, 2017) |
| **Zinc oxide, ZnO** | 0.70 | 99.0 | - | - | 94.4-28.0 | (Ghoul et al., 2017) |
| **Zeolitic imidazolate frameworks, ZIF-8** | 0.40 | 99.4 | 1.38 | - | 62.8-33.2 | (Aljundi, 2017) |
| **Zinc oxide dope with aluminium** | 0.50 | 98.0 | 2.06 | - | 74.0-13.0 | (Al-Hobaib et al., 2016) |

## 2.4 Effects of addition of EDTA solution on membrane performances

Ethylenediaminetetraacetic acid (EDTA) is an organic chelating agent that is widely used in printing, electroplating, and other industries due to its ability as a cleaning agent for membrane fouling (Kim and Baek, 2019). Based on Hao et al. (2011) and Al-Amoudi and Lovitt (2007), EDTA very useful in preventing fouling in the membrane due to its ability to sequester metal ions including calcium ions and iron (III) ions. Its two amino groups and four carboxyl groups can be used as the binding sites of metal ions as shown in Figure 2.3.

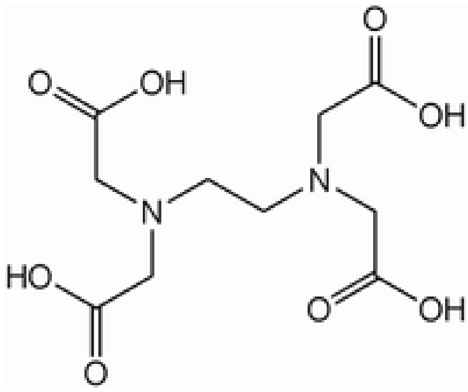


Figure 2.3 Chemical structure of ethylenediaminetetraacetic acid (EDTA)

Based on Hao et al. (2011), the effect of EDTA on the membrane was studied by comparing membranes fouled by different foulants, such as humic acid and calcium ion. The addition of EDTA on the membrane which fouled by both humic acid and calcium ions exhibited higher permeability compared with the membrane with an absence of EDTA. In addition, this membrane exhibited lower rejection which showed the decomposition of calcium ion-humic acid complex. Similar findings are reported in Roy et al. (2020), Zhang et al. (2018), and Li et al. (2017) whereby they proved that the permeability of the membrane with the presence of EDTA exhibited significant improvement in permeability compared to the membrane with an absence of EDTA.

Based on Moghadasi et al. (2007), few factors have affected the removal of foulants using EDTA solution such as pH, flow rates, temperature, and concentrations. The permeability recovery occurs rapidly when the flow rates, concentration, and temperature of the EDTA solution are increased and it enhanced the removal of scale or foulant. Within the pH range from 4.5 to 6.6, the pseudo-first-order rate constant decreased by a factor of three which indicates the formation of scale which affects the permeability and porosity as well.

## 2.5 Lignin potential and its performance

### 2.5.1 Lignin based absorbent

Besides the usage of lignin in membrane modification, lignin can be utilized as an adsorbent in the treatment of water and wastewater. Adsorption happens when a pollutant interacts physically or chemically with the surface of the adsorbent. Neutralization is governed by the interaction between the adsorbent and ions in wastewater whereby the oppositely charged will attract each other and neutralize. Chen et al. (2018a) had reviewed that the neutralization mechanism will result in complexation. Therefore, sedimentation or filtration is needed to remove it. The lignin-based adsorbent is mainly used in the removal of heavy metals from wastewater.

Adsorption capacity is the main parameter that showed the ability of the lignin-type as a potential adsorbent in removing the heavy metals from wastewater as shown in Table 2.3. As reported by Li et al. (2015a) and Yang et al. (2013) using alkali lignin and lignin-melamine formaldehyde showed the highest adsorption capacity which is 120.0 mg/g and 142.3 mg/g as compared to other adsorbents. Both these adsorbents were prepared using different techniques as well. Alkali lignin prepared by Mannich reaction is used to graft the polyethyleneimine (PEI) on the lignin matrix followed by esterification to form a porous structure. While lignin-melamine formaldehyde prepared by aldol condensation reaction between phenolic hydroxyl of lignin and formyl of melamine-formaldehyde under acidic conditions followed by in-situ polymerization. It shows showed the highest adsorption, 142.3 mg/g for Cd (II) because of a large pore throat (HIPE 6 foam) prepared had foam with open-cell structure and maximum adsorption capacity of HIPE 6 is 73.2 mg/g. It contributed to powerful adsorption capacity.

Jin et al. (2017) claimed that the adsorption capacity of heavy metal ions is controlled by the chemical interaction between the adsorbent and the contaminant. In acidic conditions, strong electrostatic repulsion is formed. The LBA surface was surrounded and protonated by hydronium ions which will decrease the interaction between the adsorbent and heavy metals. In alkali conditions, the LBA surface contains the imino groups that will deprotonate and able to interact with heavy metals.

Besides lignin to be used as an adsorbent, it can be utilized in heavy metal and dye removal in membrane separation. Lignin membrane can work as an absorbing element to absorb the heavy metals and lignin adsorbents will adsorb the heavy metals onto it.

It can be deduced that the lignin has mutiple function and can be used as adsorbent as well besides for membrane modification. Besides, heavy metals being adsorbed from wastewater. It is believed that it can be used to adsorbed the oily water as well.

Table 2.3 Lignin-type adsorbent for removal of heavy metal.

| Lignin based adsorbent | Heavy metal | Adsorption capacity (mg/g) | Ref |
|---|---|---|---|
| Wheat straw lignin | Cu (II) | 35.0 | (Todorciuc et al., 2015) |
| Alkynylated lignin | Cd (II) | 87.4 | (Jin et al., 2017) |
| Alkali lignin | Pd (II) | 120.0 | (Li et al., 2015c) |
| Lignin-melamine formaldehyde | Cu (II)<br>Cd (II) | 73.2<br>142.3 | (Yang et al., 2013) |
| Kraft lignin | Cr (IV) | 33.3 | (Jin et al., 2014) |

### 2.5.2 Lignin based flocculant

Flocculation involves the aggregation of the colloidal particles aggregated through charge neutralization. Flocculant will neutralize the charged colloidal particles by reducing the repulsive force between the adjacent particles and it was aggregated by van der Waals force. Two types of flocculant can be found which are synthetic organic flocculant and biomass-based flocculant. Flocculant has widely used in wastewater treatment.

Lignin has the potential to be used as a flocculant to treat wastewater. It has been proven by a few studies as shown in Table 2.4. In preparation of alkali lignin by amination whereby amine group is introduced and impregnated with lignin-based cationic flocculant, showed better flocs behavior. The removal of humic acid was increased. Unfortunately, this study did not observe the parameter of dye removal rate (Li et al., 2015b).

Similarly, Zhang et al. (2013) showed grafting of alkali lignin with trimethyl quaternary ammonium salt with sodium alginate (2:1 mass ratio). The efficiency of flocculant was evaluated by methylene blue (MB) and acid black ATT. Both dyes were removed effectively (97.1% and 94.9%). From this study, the optimum pH for MB is 8. In alkaline conditions, the repulsion between MB and flocculant increases with increasing pH causes the flocculation performance to reduce. In acidic conditions, the flocculant enhanced the positive charge availability and the bridging ability of the flocculant.

Meanwhile, a study by Couch et al. (2016) showed that 76 wt% of pulp lignin was modified with nitric acid treatment. The modified lignin removed up to 77.0% of ethyl violet and 88.0% of basic blue. The sample pH and salt content affected the dye removal. A higher removal rate of 99.1% was observed using the kraft lignin by oxidation and sulfomethylation at pH 9 (He et al., 2016).

Besides lignin to be used as a flocculant, it can be utilized in heavy metal and dye removal in membrane separation. Lignin membrane can work as an absorbing element to absorb the heavy metals and lignin adsorbents will adsorb the heavy metals onto it. It can be deduced that the lignin can be used as adsorbent as well besides for membrane modification. Besides, dye being adsorbed from wastewater. It is believed that it can be used to adsorbed the oily water as well.

Table 2.4 Lignin-based flocculant in wastewater treatment.

| Lignin based flocculant | Modification | Dye removal rate (%) | Ref |
|---|---|---|---|
| **Alkali lignin** | Amination with epichlorohydrin, N, N-dimethylformamide, and ethylenediamine | - | (Li et al., 2015b) |
| **Alkali lignin** | Grafting trimethyl quaternary ammonium salt with sodium alginate | Methylene blue: 97.1<br>Acid Black: 94.9 | (Zhang et al., 2013) |
| **Pulp lignin (76 wt%)** | Nitric acid treatment | Ethyl violet: 77.0<br>Basic blue: 88.0 | (Couch et al., 2016) |
| **Kraft lignin** | Oxidation and sulfomethylation | Ethyl violet: 99.1 | (He et al., 2016) |

## 2.6 Modification of membrane using biopolymer

Recently, the application of biopolymer has been applied widely by scientists in various kinds of fields. Up to date, biopolymers such as alginate, cellulose, and chitin has been selected to fabricate to be used in wastewater treatment and the selection of biopolymers is mainly due to the attractive properties such as biocompatibility and hydrophilicity which makes them a potent candidate to improve membrane performance to efficiently cleanse water of harmful pollutants.

### 2.6.1 Cellulose-based membranes

Cellulose is a type of biopolymer that can be divided into few derivatives, cellulose nanoparticles (CNs), cellulose nanofibers (CNFs), and cellulose nanocrystals (CNCs). It has some distinguishing characteristics, including excellent strength, a high surface-area-to-volume ratio, and the ability to deliver high flux and rejection when combined with another polymeric membrane. Cellulose-based membrane and its parameters are tabulated in Table 2.5.

Based on the study conducted by He et al. (2015), salicylic acid (SA) was separated from an aqueous solution using cellulose acetate (CA) composite membrane. Using sulfonated polysulfone (SPS) as the polymer, DMSO as the solvent, and polyethylene glycol-4000 (PEG 4000) and ionic liquid 1-butyl-3-methylimidazolium chloride (BMIM-Cl) as the additives, the membrane was blended and changed using the phase inversion method. The modified membrane exhibited a lower contact angle which contributing to the hydrophilicity of the membrane. This is owing to the existence of a functional group in SPS, as well as hydrogen bond interactions. The modified CA membrane and neat CA membrane were evaluated with SA, phenol, and p-HB. Relatively, SA showed the highest selectivity coefficient than the phenol and p-HB.

Meanwhile, Li et al. (2015a) was studied the effect of BSA on the PVC-co-PE nanofibers blended with cellulose. The membrane was modified by extruding method and self-assembly. The modified PVC-co-PE/cellulose membrane exhibited a 100% flux recovery ratio during repeated filtration and fouling evaluation. The presence of large hydrophilicity of the cellulose layer in the modified membrane enhanced the anti-fouling properties. The PVC-co-PE/cellulose membrane (diameter 2-10nm) showed 97% rejection for BSA. Due to the large proportion of hydroxyl in the vinyl alcohol segment of PVA-co-PE, the hydrophilicity of the PVA-co-PE nanofibrous membrane is greater than the neat membrane. Due to the cellulose hydrophilic layer and hydroxyl in the vinyl alcohol segment of PVA-co-PE. The contact angle reduces to 9.4º.

Differently, in Rascón-Leon et al. (2018), CA/PANI membrane resulted in a higher contact angle, 59.6±0.7º in their study as compared to others. This could be due to only a single CA which possesses the hydrophilicity properties to cause the contact angle to be higher than the previous study. The modified membrane showed the highest selectivity towards silver recovery, 98%.

It can be deduced that biopolymer, cellulose have its unique property that can help and increase the efficiencies of membrane performances by apply them directly for certain application such as for water treatment and etc.

Table 2.5 Cellulose-based membrane and its parameters.

| Cellulose-based membrane | Contaminants | Pure water flux | Rejection (%) | Contact angle (º) | Ref |
|---|---|---|---|---|---|
| **PVA-co-PE/cellulose** | BSA | 30.0 L/m2.h at 0.2 MPa | 97.0 | 9.4 | (Li et al., 2015a) |
| **PAN/cellulose** | NaCI | 1.1±0.1 L/m2.h at 1 bar | 82±6 | 32.6±0.4 | (Livazovic et al., 2015) |
| **PET/CTA** | NaCI<br>MgSO4<br>MgCI2 | >4.0 L/m2.h at 0.2 MPa | >80.0 | 50.3 | (Chen et al., 2018b) |

| | | | | | |
|---|---|---|---|---|---|
| **CA/PMMA** | HA | 334.5 L/m2.h at 250 kPa | 99.9 | - | (Gebru and Das, 2018) |
| **CA/PANI** | Ag (II) | - | 98.0 | 59.6±0.7 | (Rascón-Leon et al., 2018) |
| **CA/CTA** | Mg (II)<br>Ca (II)<br>Hg (II)<br>Cu (II) | 6.4 L/m2.h | 99.9 | - | (Chen and Lee, 2019) |
| **CA/PVC** | NaCI | 40 L/m2.h at 40 bar | 99.9 | - | (El-Gendi et al., 2017) |
| **CA/PU** | Chromium (IV) | 13.9 L/m2.h at 0.4 MPa | 97.4 | 34.19 | (Riaz et al., 2016) |

### 2.6.2 Chitosan based membrane

Chitosan (CS) is another type of biopolymer that is commonly utilized to make adsorbents for heavy metal and dye removal. The significant amount of amino and hydroxyl groups in CS expands its potential as a heavy metal and dye adsorbent. The amino group serves as the reactive side for the adsorption process and surface modification. Chitosan-based membrane and its parameters are tabulated in Table 2.5

The heavy metal rejection properties were analyzed by Kumar et al. (2014) by using the modified membrane, polysulfone/N-succinyl chitosan (PSf/NSCS). The membranes, accompanied by immersion precipitation, were synthesized by blending.