RECOVERY LIGNIN AND ITS FOULING STUDY USING NANOFILTRATION

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RECOVERY LIGNIN AND ITS FOULING STUDY USING NANOFILTRATION

by

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ANIS FARHAIN BINTI ISMAIL

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LIST OF SYMBOL

	Symbol	Unit
A	Absorbance	-
a	Area of membrane	m^2
b	Path length of cell holder	m
Cf	Absorbance of feed	-
Cp	Absorbance of permeate	-
e	Molar extinction coefficient	L/mol.cm
J	Flux	$mL/min.m^2$
T	Time taken	min
V	Volume of solution	mL

LIST OF ABBREVIATIONS

H_2O	Water
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
ppm	Parts per million
Ra	Adsorption, biofouling
Rpb	Pore plugging
Rc	Cake layer
Rm	Membrane resistance
RO	Reverse Osmosis
SDI	Silt density index
SEM	Scanning Electron Microscopy
TMP	Transmembrane pressure
UF	Ultrafiltration
UV	Ultraviolet

PEMULIHAN LIGNIN DAN KAJIAN TENTANG PENCEMARANNYA MENGGUNAKAN KAEDAH PENAPISAN NANO

ABSTRAK

Pemulihan lignin adalah penting kerana ia mempunyai banyak aplikasi dan teknologi membran yang telah dibuat kajian sebagai asas penyelesaian pemulihan inovatif. Pemulihan lignin telah dikaji dengan menggunakan penapisan nano dan komersial membran dari Dow digunakan. Beberapa faktor telah digunakan untuk menganalisis penapisan lignin iaitu tekanan, kepekatan lignin dan nilai pH. Penolakan lignin meningkat apabila tekanan suapan meningkat. Penolakan tertinggi adalah 99.49% berlaku pada tekanan suapan 6 bar. Kepekatan lignin telah diubah kepada 10 mg/L, 100 mg/L dan 1000 mg/L untuk menyiasat berhubung lignin penolakan. Penolakan paling lignin berlaku semasa penapisan 10 ppm larutan lignin yang merupakan 70.09%. Pemulihan lignin juga dikaji pada pH yang berbeza seperti asid (pH 4), neutral (pH 7) dan asas (pH 9). Sifat-sifat fizikokimia lignin pada nilai pH yang berbeza juga dikaji. Toleransi pH pada pelbagai jenis membran boleh berbeza-beza secara meluas. Membran prestasi lignin penolakan bergantung kepada nilai pH. Semasa penapisan pada pH 9, penolakan itu adalah yang tertinggi iaitu 99,47%. Membran yang telah dicemari telah disiasat sepanjang kajian ini. Membran yang tercemar memberi kesan terhadap kecekapan penolakan lignin.

RECOVERY LIGNIN AND ITS FOULING STUDY USING NANOFILTRATION

ABSTRACT

The recovery of lignin is particularly important because it has many applications and membrane technology has been investigated as the basis of innovative recovery solutions. The lignin recovery was studied by using nanofiltration and commercialized Dow membrane is used. A few parameter were used to analyze the lignin filtration which were feed pressure, lignin concentration and pH values of lignin solution. The rejection of lignin increased as the feed pressure increased. The highest rejection was 99.49% occurred at feed pressure of 6 bar. The concentration of lignin were varied to 10 mg/L, 100 mg/L and 1000 mg/L to investigate the relation to lignin rejection. The lowest rejection of lignin occurred during filtration of 10 ppm of lignin solution which was 70.09%. Recovery of lignin also studied at different pH which were acid (pH 4), neutral (pH 7) and base (pH 9). The physicochemical properties of lignin at different pH value also studied. The pH tolerance of various types of membranes can vary widely. Membrane lignin rejection performance depends on pH value. During filtration at pH 9, the rejection was the highest which was 99.47%. The fouling of membrane has been investigated throughout the study. The membrane fouling give effect to the efficiency of lignin rejection.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Lignin is a vital factor in the metabolism of the growing plant and as a structural component of the nature plant cell wall. It is a valuable humus in the soil after digested by fungi or bacteria (Harkin, 1969). However, in the pulp mill, lignin is a bothersome wood constituent that must be removed from his chips before a good grade of paper can be made. Lignin is one of the valuable compound in black liquor. Black liquor from the pulp and paper industry contains hundreds of different compounds and several high-value organic chemicals are formed during alkaline pulping. Recovery of lignin is considered important as it has many applications in many industries such as fine chemicals and pharmaceutical. Wood components such as lignin and hemicellulose are extracted from the pulping liquor and used in high-value-added chemicals (Fargues, 1996; van Heiningen, 2006; Wising, 2006). In addition to being used as a biofuel (Axelsson, 2006; Olsson, 2006), lignin can be used as binder, dispersant or emulsifier (Gargulak, 2000)

Currently, membrane technology has been investigated as the basis of innovative recovery solutions. By using membrane, concentration of lignin and purity of recovered lignin can be increased. However, the complexity of lignin structure poses a very serious fouling problem on the membrane surface. Hence, it is very important that the physicochemical properties of both the membrane and lignin should be studied in detail manner.

For this research, membrane filtration such as nanofiltration used to lignin recovery. Commercialized membrane which is NF270 from Dow are used throughout this study. Lignin, alkali is also used in this study which act as feed. Operating parameters were studied which were pressure, concentration and pH value. These parameters are important in this study as it easy to adjust with suitable conditions.

1.2 Problem statement

Numerous applications of membrane processes are feasible in pulp mills. The challenges inherent in these applications vary. High pH and high temperature call for ceramic membranes when treating spent pulping liquors, whereas low cost membranes are needed when treating dilute process streams in mechanical pulp mills. However, no commercial membrane installations exist to date for the recovery of hemicelluloses and lignin in kraft and mechanical pulp mills especially by using nanofiltration. Nonetheless, recovery of lignin from kraft black liquor, and galactoglucomannan from thermomechanical pulp mill wastewater are current hot topics (Jonsson, 2016). Hence. In this studies commercial membrane from Dow was used. Greatest challenge during membrane filtration was flux decline, it was difficult to prevent due to wide molecular weight distribution of lignin molecules.

1.3 Research objectives

The main objectives of this study are:

i) To recover and concentrate the lignin from the solution at different pressure and concentration.

ii) To characterize the physicochemical properties of lignin and membrane at different pH value and their separation efficiency.

iii) To evaluate the fouling propensity of lignin on the nanofiltration membrane.

1.4 Scope of study

In this work, the alkaline lignin powered was used to study the lignin recovery by nanofiltration. The NF270 membrane was used throughout the study. A few parameters were studied to relate its effect toward lignin recovery using nanofiltration which were pressure, concentration and pH value. The pressure were varied from 2 bar to 6 bar and concentration of lignin also varied which were 10 ppm, 100 ppm and 1000 ppm.

Lignin separation also were tested with different solution pH which were pH 4, pH 7 and pH 9. All these three parameter were analysed to find their relation to lignin separation. Besides, NF270 was also characterized in terms of surface morphology from top surface layers and cross section of the membranes.

1.5 Organization of thesis

The following are the contents for each chapter in this study:

Chapter 1 introduces the lignin separation from black liquor in industries, problem statement, research objectives and organization of thesis.

Chapter 2 discusses the literature review of this study which includes introduction of black liquor and lignin, lignin purification, membrane technologies and membrane fouling.

Chapter 3 covers the materials and details of methodology. It discusses on the description of equipment and materials used, experimental procedure and description of parameters affecting the lignin separation process.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the effect of different parameters on lignin separation.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Black liquor

Black liquor is a thick, dark liquid that is a by-product of the process that transforms wood into pulp, which is the dried to make paper. Black liquor contains the bulk of the energy content of wood. It is used as fuel at papermaking facilities to generate electricity as well as heat needed to remove the water from pulp to make paper. Below are typical composition of black liquor (Wallberg, et al., 2003):

Table 2.1: Composition of black liquor

Component	**Variation Range**
Dry weight	(12-18) wt%
Polyaromatic components	(30-45) wt%
Saccharinic acid	(25-35) wt%
Formic acid	(0-10) wt%
Acetic acid	(0-10) wt%
Extractives	(3-5) wt%
Methanol	1 wt%
Inorganic elements (mainly sodium)	(17-20) wt%
Lignin	**(45-65) g/L**

2.2 Lignin

One of the main ingredients in black liquor is lignin, which is the material in trees that binds wood fibers together and make them rigid. Lignin which must be removed from wood fibers to create paper. Lignin is the major non-cellulosic constituent of wood. It is complex, amorphous highly crosslinked polyphenolic. Wood components such as lignin and hemicellulose are extracted from the pulping liquor and used in high-value-added chemicals (Fargues, 1996; van Heiningen, 2006; Wising, 2006). In addition to being used as a biofuel (Axelsson, 2006; Olsson, 2006), lignin can be used as binder, dispersant or emulsifier (Gargulak, 2000). Furthermore, lignin also used in phenolic resins (Danielson, 1998; Sarkar S. and Adhikari, 2000), as a precursor for carbon fibres (Kubo, 2005) and as a wet strength additive to kraft liner (Antonsso, 2008).

The exact composition varies according to the pulping method and the properties of the wood. Elementary analysis shows that lignin from black liquor has higher carbon content than other types of lignin, probably due to dehydration during pulping process (El Mansouri & Salvadó, 2006). The number of phenolic hydroxyl groups is an important property that determines the reactivity of lignin.

2.3 Lignin Purification

A few methods have been developed to recover lignin from solution and the current solution involves a combination of precipitation and membrane filtration, such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). Firstly, chemicals such as carbon dioxide, sulfuric acid or chlorine dioxide is added to reduce the solubility of lignin. Then, membrane filtration was used to separate the precipitated lignin. Greatest challenge during filtration was flux decline, it was difficult to prevent due to wide molecular weight distribution of lignin molecules.

Below is the summary of different strategies in which membrane fractionation can be used for the treatment of waste liquor from the pulp and paper industry.

Figure 2.1 above shows that during the pulping process, the raw material is separated into cellulose and lignin. The pulp can be treated by membrane filtration to isolate lignin molecules. The remaining solution can be recycled to the paper production. Additionally, the waste liquor from the paper mill can be treated by membrane filtration to isolate the containing lignin. The remaining solution can be recycled for energy generation.

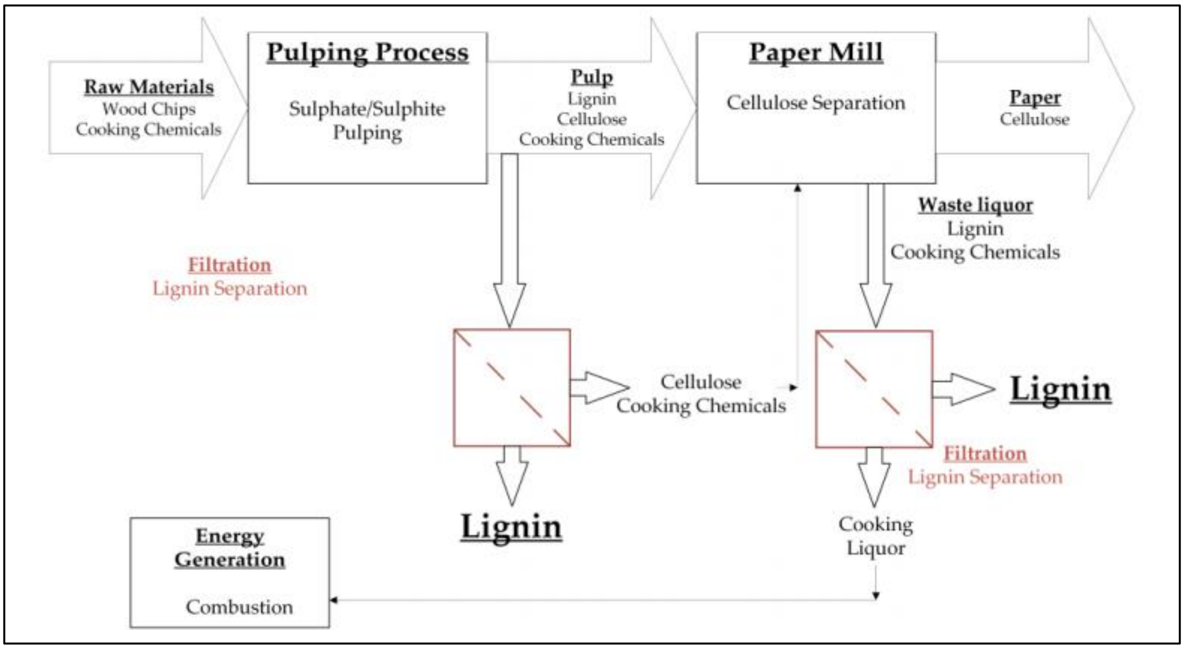


Figure 2.1: Summary of membrane fractionation

2.4 Membrane Technologies for Treatment of Black Liquor

Various studies have been carried out to investigate the ability of membranes to recover lignin precipitated from the black liquor as this technology is one of the methods to achieve efficient lignin recovery. Generally, ceramic membranes are ideal for the treatment of black liquors due to their ability to tolerate extreme pH values. Among the first studies using membrane filtration, the authors investigated the chemical reactivity of lignin as co-polymer in production of plastics as well as separation of high molecular weight lignin using 10 kDa polysulfolane membrane (Olivares, et al., 1988). This process able to increase lignin concentration in the retentate by ~174% and found out that purified lignin performed better as a co-polymer than chemically modified lignin.

Later studies compared diafiltration and acid precipitation for black liquor recovery (Uloth & Wearing, 1989). This study used a plate-and-frame module and polymer membranes with molecular weight cut-off (MWCO) varies from 6 to 50 kDa. The authors concluded that membrane with higher MWCO increase purity of recovered lignin whereas membrane with low MWCO are better for concentrating lignin. The ability of UF and selective precipitation was compared on further study to complete the fractionation of the lignin resulting from the black liquor of the pulping process (Toledano, et al., 2010). It was found that the precipitation as well as UF with ceramic membranes are effective techniques on fractionate lignin from black liquor.

The ultrafiltrated lignin fractions obtained from industrial black liquor also studied as the stabilizers of liquid-liquid and solid-liquid interfaces (Padilla, et al., 2002). Higher surface activity occurred due to increase of the molecular weight of the lignin fractions. Additionally, only high molecular weight fraction of lignin has measurable impact on viscosity of bentonite-lignin solution. The behaviour of fractionated and ultrafiltrated black liquor was further studied based on the glass transition temperature and chemical compositions. The study were carried out with aluminium oxide, titanium oxide and regenerated cellulose membranes. The increasing molecular weight of the lignin resulted in an increasing entanglement and rigidity of lignin molecule. This study showed that UF of black liquor allows the selective extraction of lignin fractions with particular thermo-mechanical properties.

Satyanarayana et al. (2000) investigated the impact of process and membrane parameters such as MWCO, Reynolds number, TMP and feed concentration by using various cellulose acetate UF and NF membranes (Satyanarayana, et al., 2000). Based on this study, it showed that higher MWCO increases the flux but reduces the lignin retention efficiency and there was relationship between Reynolds number and the flux. A higher Reynolds number cause slower layer formation and facilitated backward diffusion. The study also found that lignin retention increased with higher Reynolds numbers and approach asymptotically to maximum value.

Based on the findings of Wallberg et al. (2003) (Wallberg, et al., 2003), ultrafiltration of kraft black liquor by using aluminium oxide/titanium oxide membrane was studied. The lignin retention was depending on the feed temperature. At higher temperature, the retention declined due to the lignin become more soluble but, for the inorganic components, the retention varied depending on their valency. The result also showed that at 90°C, lignin retention was 90%, concentration also increased from 56 to 160 g/L.

Other studies used ceramic UF membranes with MWCO values 5 and 15 kDa were carried out. The black liquor has been separated at temperature exceeding 100°C (Wallberg & Jönsson, 2006). This study proved that in order to prevent membrane bursting, the maximum rate of temperature change should be 2-3 °C/min. Black liquor also has been separated in other study by using ceramic UF and NF membranes with MWCO values of 1, 5 and 15 kDa to extract small fraction of lignin in highly pure form (Keyoumu, et al., 2004). From this study, it was reported that different flux behaviours was observed for black liquor obtained from hardwood and softwood where lower flux was achieved in hardwood liquor due to the higher average molecular weight of the lignin fraction.

The fractionation of black liquor was compared by using variety of membranes made from different materials which were cellulose acetate, aluminium oxide, polyaryl ether ketone, polyacrylonitrile and polyethersulfone. The percentage of lignin was summarized based on Table 2.2 below (Liu, et al., 2004):

Table 2.2: Percentage of lignin

Molecular Weight in kDa	**Percentage Abundance**
>60	61.8
60-30	21.8
30-10	1.2
10-6	1.8
6-3	2.4
<3	1.0

Black liquor from the alkaline pulping of the *Micanthus sinensis* were subjected to few stages of ultrafiltration, by using ceramic membranes of different cut-offs. All different permeates obtained was characterized and analysed for its pulping efficiency and ultrafiltration processes (A. Toledano, 2010). Lignin was extracted by acid precipitation and their chemical structure and thermal behaviour were analysed. This research also has classified common operating conditions for different membrane separation processes.

Table 2.3: Common operating condition for membrane separation

Process	Membrane type and pore size	Membrane material	Driving force (bar)	Applications
MF	Symmetric microporous (0.1 - 10 μm)	Ceramics, metal oxides, graphite, polymers	1 – 5	Sterile filtration, clarification
UF	Asymmetric microporous (1 – 10 nm)	Ceramics, polysulfone, polypropylene, nylon 6, PVC	1 – 10	Separation of macromolecular solutions
NF	Thin-film membranes	Cellulosic acetate and aromatic polyamide	10 – 30	Removal of hardness and desalting
RO	Asymmetric skin-type (0.5 – 1.5 nm)	Polymers, cellulosic acetate, aromatic polyamide	Up to 200	Separation of salts and microsolutes from solutions

Lignin also can be separate from kraft black liquor by tangential ultrafiltration (Orlando J. Rojas, 2006). The aim of this research was to determine the retention of kraft black liquor lignin and correlate this to the functional group distribution of the emerging fractions during UF. The performance of commercial membranes was evaluated with different cut-offs which were 150 kDa, 50 kDa, 5 kDa and 1 kDa. Retention and flux of each membrane was measured and systematic investigation of the lignin molecular weight (via gel permeation chromatography) and main functional groups (via nuclear magnetic resonance spectroscopy) was studied in lignin for various UF streams.

This research conclude that molecular weight of retentate and filtrate correlate with membrane MWCO. Lignin streams are characterized by reduced aliphatic OH concentration as membrane MWCO is reduced and an increased content in carboxylic groups. A few changes obtained in terms of concentration of condensed and non-condensed phenolic OH when undergo separation of membranes with different MWCO. Figure 2.2 below show the system for UF of lignin solutions with tubular membranes used in this research (Orlando J. Rojas, 2006).

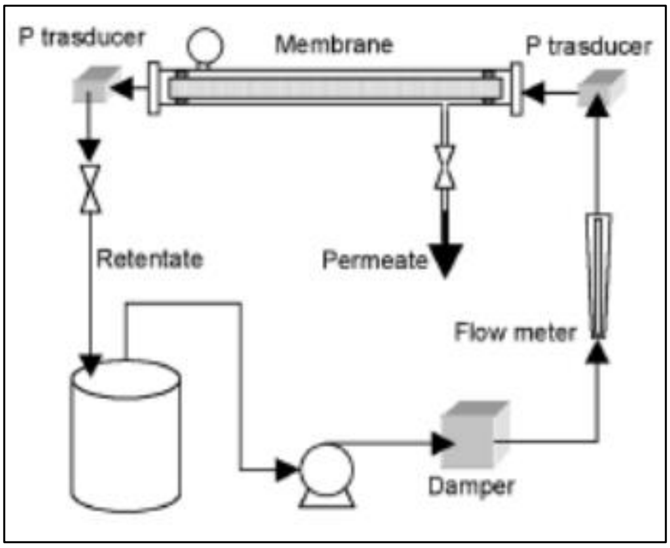


Figure 2.2: Ultrafiltration with tubular membranes

Furthermore, research on lignin separation from softwood black liquor by membrane filtration (A. Arkell, 2014). Ceramic and polymeric NF membrane were used to separate lignin from black liquor. To separate hemicellulose from lignin, UF was tested as a form of pre-treatment. Due to this, the flux drastically increased in NF. The ceramic membrane exhibit higher flux and lower lignin retention than polymeric membranes. From this research, it can conclude that lignin and hemicellulose can be efficiently separated from softwood black liquor by NF, with or without prior UF pre-treatment.

2.5 Membrane Fouling

Fouling of membranes causes a higher energy use, a higher cleaning frequency and a shorter life span of the membrane. Filtration of black liquor is exposed to fouling and this became an important cost factor in the context of industrial-scale processes as the pressure will increased at certain point where it is no longer economical.

One of the way to reduce the rate of fouling and prolong the life of membranes was to use effective cleaning strategies. Another way is to predict fouling by using Silt Density Index (SDI) of feed water. When the high value of SDI is obtained, it can conclude that feed water consist high amount of membrane plugging matter. Figure 2.3 below shown different type of resistance that may occur on the membrane.

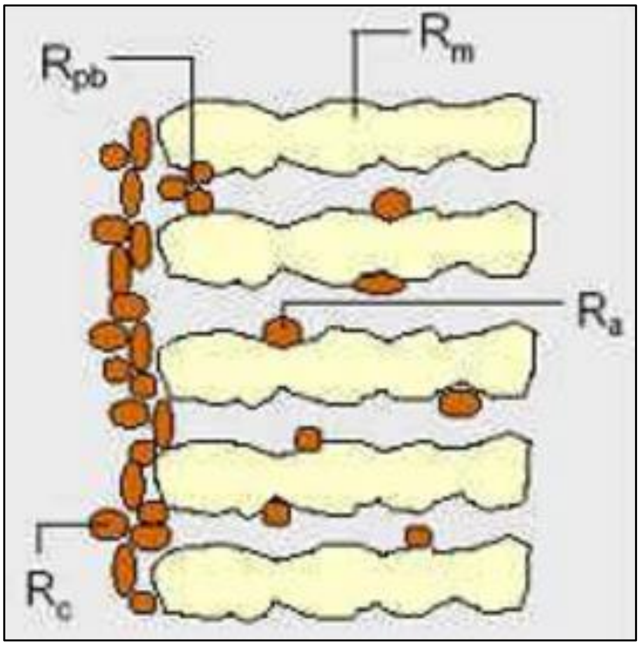


Figure 2.3: Different type of resistance occur on membrane

$$R_{total} = R_m + R_C + R_{pb} + R_a \quad (2.1)$$

Where,

R_m = membrane resistance

R_a = adsorption, biofouling

R_{pb} = pore plugging

R_c = cake layer

Chemical cleaning strategies for ceramic membranes for their treatment of spent sulphite liquor was proposed by Ebrahimi et al. (2015) (Ebrahimi, et al., 2015). During their studies, to decrease fouling, a back flush at certain pressure also shown. However, they concluded that cleaning was more efficient when there was a longer interval between flushes.

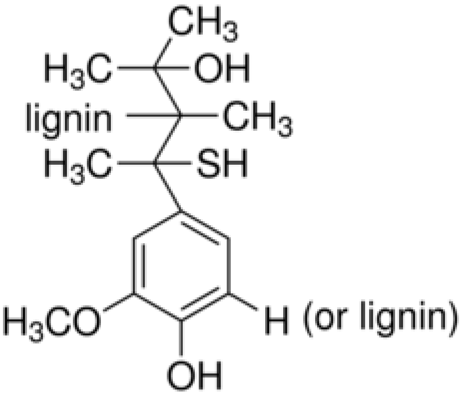
CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In this study, alkaline lignin powdered is used for the preparation of lignin solution which is alkaline treated. The properties of lignin are summarized in Table 3.1 below.

Table 3.1: Lignin properties

Properties	
Chemical Name	Lignin, Alkali
Chemical Structure	
CAS No	8068-05-1
Molecular Formula	$C_{30}H_{25}CIN_6$
Molecular Weight	505.01
Melting Point	257°C
Solubility	H_2O; soluble

Commercialized membrane (NF270) from Dow is used in this experiments. NF270 is a hydrophilic membrane with high multivalent retention and permeability. The membrane can withstand wide pH range of chemical. NF270 also has high removal of organics with excellent hardness retention. During pre-treatment, deionized water and ethanol solution (30% of ethanol) are used to soak the membrane. Operating limits for this type of membrane are shown in Table 3.2.

Table 3.2: Operating limits of membrane

Membrane type	**Polyamide thin-film composite**
Maximum operating temperature	45°C
Maximum operating pressure	41 bar
Maximum pressure drop	
- Tape wrapped	- 0.9 bar
- Fiberglassed	- 1.0 bar
pH range (continuous operation)	2 – 11
Maximum feed silt density index	SDI 5
Free chlorine tolerance	< 0.1 ppm

3.2 Research Methodology

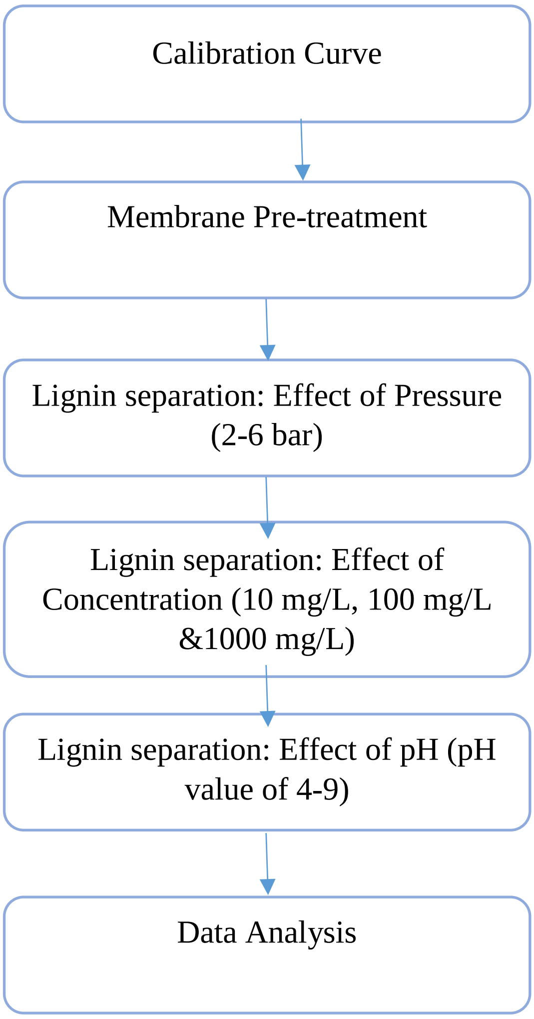


Figure 3.1: Flow chart of research methodology

Figure 3.1 shows the overall process for this research study. The calibration curve of lignin concentration and UV light absorption was constructed. This can be done by using UV-Vis spectrophotometer at UV length of 279 nm. The membrane needs to undergo pre-treatment before use to separate the lignin. Then, the effect of pressure was studied by varying the pressure during the filtration process at 2 bar, 3 bar, 4 bar, 5 bar and 6 bar. Next, concentration of lignin solution was varied for 10 mg/L, 100 mg/L and 1000 mg/L. After that, the effect of pH value (pH 4 to pH 9) of lignin solution. Lastly, all the data collected were analysed and calculated based on given equation.

3.3 Calibration Curve

According to Beer’s Law, under ideal conditions, a substance’s concentration and its absorbance are directly proportional: a high-concentration solution absorbs more light, and solution of lower concentration absorbs less light. Since concentration and absorbance are proportional, Beer’s Law makes it possible to determine an unknown absorbance of lignin after determining the concentration.

The concentration were varied from 1 ppm to 100 ppm at wavelength of 279 nm. Lignin contains phenolic groups that absorbs light. The lignin concentration can be determined by measuring light absorption at 279 nm. The UV light was measured using UV-Vis spectrophotometer (UVmini-1240). All the sample collected were tested with the UV-Vis spectrophotometer to get value of absorbance at certain wavelength.

3.4 Membrane Pre-treatment

The membranes were first soaked in the deionized water for 10 minutes. After that, it was soaked in the ethanol solution (30% ethanol and 70% deionized water) and left for 24 hours. After 24 hours, the membranes were soaked again in deionized water for 10 minutes before being used in the experiment.

3.5 Pure Water Permeability

The pure permeability, also known as the pure water flux is defined as the volume of water that passes through a membrane per unit time, per unit area and per unit of transmembrane pressure. This method is to indicate the effort required to generate permeate for a membrane and to compare initial performance of a membrane.

Firstly NF270 was compressed at 7 bar using deionized water for about 30 minutes prior to the permeation test. After compression, the pressure was released until it reaches 2 bar. First 5 mL of permeate was discarded to remove the entrapped water. Then, the time were taken for the subsequent permeate to reach 1 mL and repeated three time to get average. The steps were repeated for 3 bar, 4 bar, 5 bar and 6 bar. After that, the valve for gas tank was closed and the gas were released.

3.6 Lignin separation: Effect of Pressure

The permeation and rejection test were carried out using high pressure dead end filtration cell as shown in Figure 3.2.

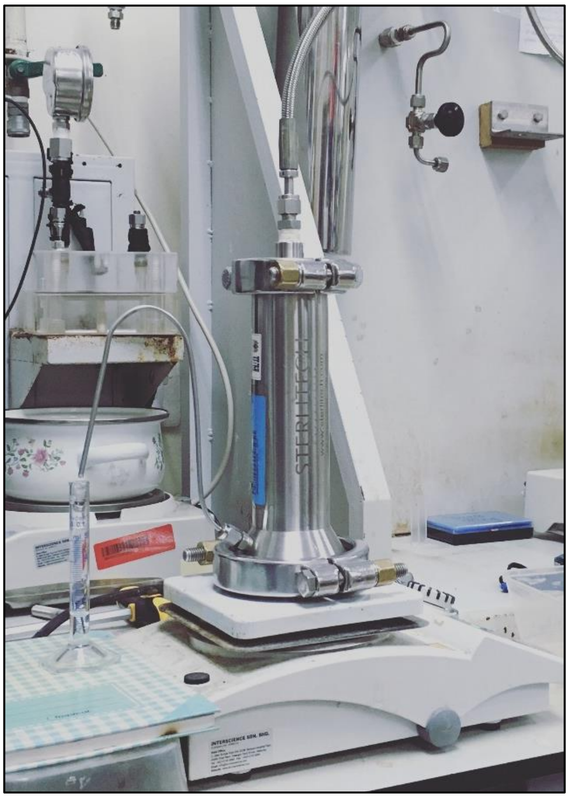


Figure 3.2: Dead end filtration unit

The water was replaced with the 100 ppm lignin solution and the permeate data was collected again under the same pressure as for the pure water. Time were taken for the permeate to reach 1 mL and another 5 mL collected for rejection determination. The collected permeate were tested at wavelength of 279 nm using UV-Vis spectrophotometer.

All the values of absorbance were used to calculate the percentage of rejection by using equation 3.1:

$$Rejection = 1 - \frac{C_p}{C_f} \tag{3.1}$$

Where,

C_p = Absorbance of permeate

C_f = Absorbance of feed

The flux for water and membrane were calculated by using equation 3.2 below:

$$Flux, J = \frac{V}{t \times a} \qquad (3.2)$$

Where,

V = Volume of lignin, L

T = time taken, hr

a = Area of membrane, m^2

3.6 Lignin separation: Effect of Concentration

In studying the effect of concentration, similar method to Section 3.5 was repeated except that the concentrations were varied to 10 mg/L, 100 mg/L and 1000 mg/L. The operating pressures were repeated for 3 bar, 4 bar, 5 bar and 6 bar. The permeate was collected and the samples were subjected to UV-Vis spectroscopy measurement to determine the rejection.

3.7 Lignin separation: Effect of pH

The lignin solution of 100 ppm was tested at different pH value which were pH 4, pH 7 and pH 9. The same method as in Section 3.5 were also used to study the effect of pH value on the membrane permeability and rejection efficiency of lignin on the membrane. The membrane was subjected to operating pressure of 7 bar.

3.8 Membrane characterization: Morphology of NF270

For scanning electron microscopy (SEM), membranes samples were dried in room temperature and cryogenically broken in liquid nitrogen. Then, the obtained cross-sections were gold coated in vacuum conditions at 17Kv. The cross sections, top and bottom surfaces of the membranes were characterized by SEM (TM3000 SEM).

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the experimental results and discussion consisting of four main sections. The first section discusses on the effect of pressure on lignin separation by using different pressure. The second and third section discuss on the effect of concentration and pH on lignin separation by nanofiltration (NF) respectively. The fourth section review the effect of membrane fouling towards lignin separation.

4.1 Effect of pressure

Figure 4.1 shows the pure water flux and lignin permeation at different operating pressure. From this figure, the flux are increased linearly with pressure but the lignin permeate shown was lower than pure water flux. This is due to the concentration polarization of the membrane where it is a phenomenon in which the composition at the feed-membrane interface differs from the composition in the bulk of the feed mixture (Wijmans, 2000).

In general, the cause of concentration polarization is the ability of a membrane to transport some species more readily than the others. The higher the concentration polarization caused additional resistance to flow due to the increased of osmotic pressure. Hence, the flux is much lower during lignin filtration since time is inversely proportional to the flux as shown in equation 3.2.

The linear line in the graph shows that the flux of membrane increased along with the pressure. The highest flux which was 1037.03 mL/min.m^2 was obtained at the 6 bar. The limiting flux was not reached with operating pressure below 7 bar.

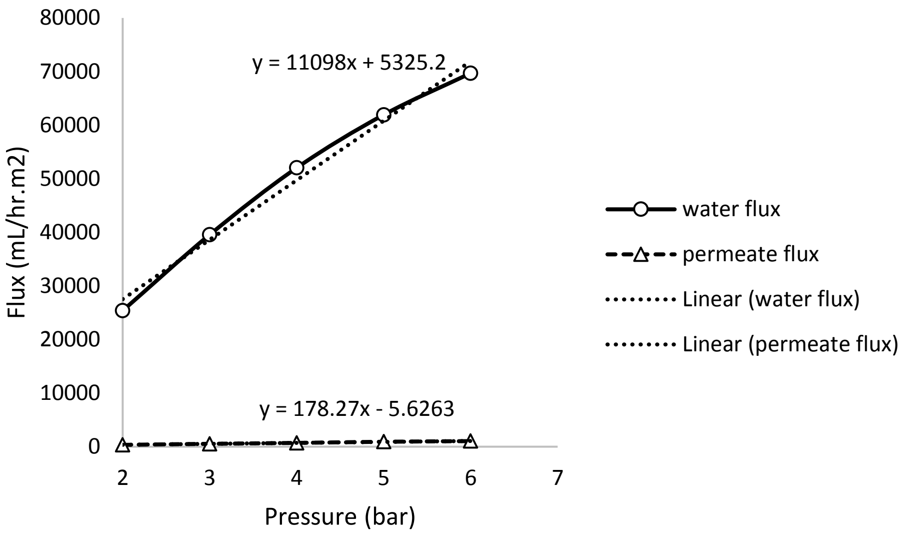


Figure 4.1: Effect of pressure on the flux of nanofiltration

From slope of both flux, the hydraulic resistance of the membrane, R_m and hydraulic resistance of gel layer can be calculated based on equation 3.3 and 3.4.

$$J = \frac{\Delta P}{\mu(R_m)} \tag{3.3}$$

$$J = \frac{\Delta P}{\mu(R_m + R_g)} \tag{3.4}$$

Where,

J = Flux

ΔP = Pressure

R_m = Hydraulic resistance of membrane

R_g = Hydraulic resistance of gel layer

The value for Rm is 9.01063×10^{-5} while for R_g is 0.005519362. At moderate to high concentration of lignin, the resistance of the gel layer is significantly greater than that of the membrane and flux becomes independent of membrane permeability. Under continuing pressure, R_g will increase as lignin accumulates at the membrane surface. Greater R_g reduce flux. Resistance will continue to grow until net transport of solute toward membrane equals back diffusion if solute toward the bulk solution caused by the pressure gradient. Any further increase in TMP will cause the gel layer to thicken and flux will remained unchanged (Warren L. McCabe, 1993).

The percentage of rejection of lignin by varying the pressure during lignin separation are given in Figure 4.2. The rejection of lignin were more than 99% for all values of pressure and slightly increased with increasing pressure. The highest rejection of lignin was seen at 6 bar which was 99.49%. This proved that the separation is based on the sieving mechanism whereby the size of the lignin is bigger than the membrane pore size.

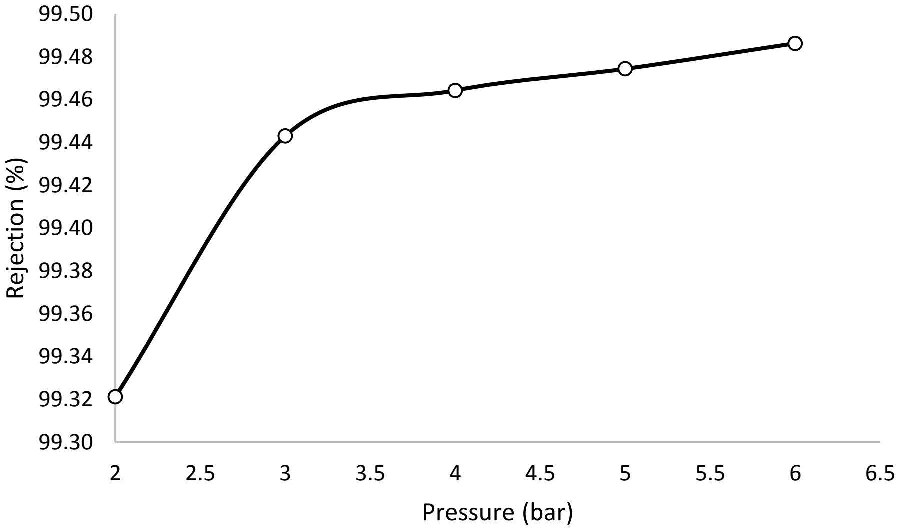


Figure 4.2: Rejection against pressure for 100 ppm

4.2 Effect of lignin concentration on nanofiltration

The Figure 4.3 below show the membrane flux for different concentrations. The trend for each concentration were almost the same for membrane flux. This showed that lignin has poor interaction with the membrane surface and contribute insignificant gel layer at the initial stage of the separation regardless of the operating pressure.

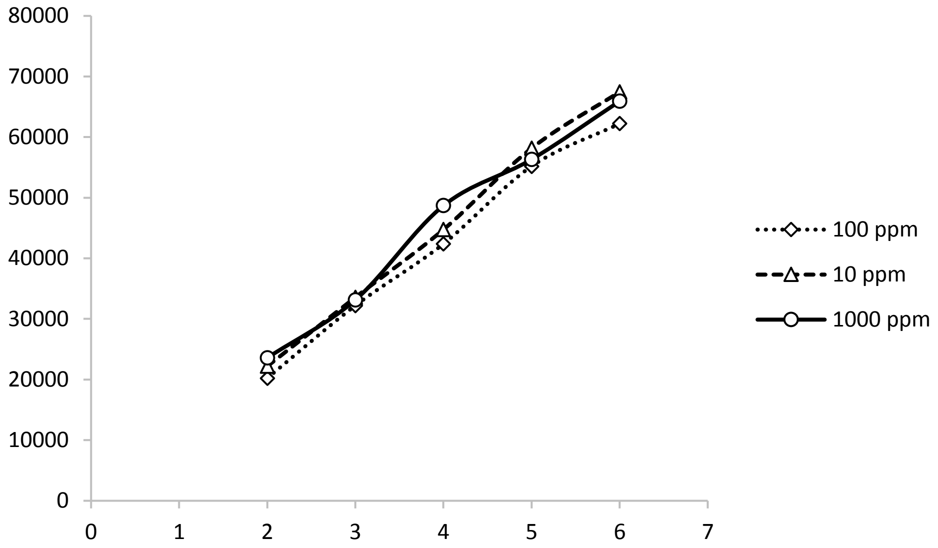


Figure 4.3: Flux against pressure for different concentration

However, it can be seen from Figure 4.4 that the membranes showed consistent rejection at low lignin content except at 5 bar due to some error during the first run.

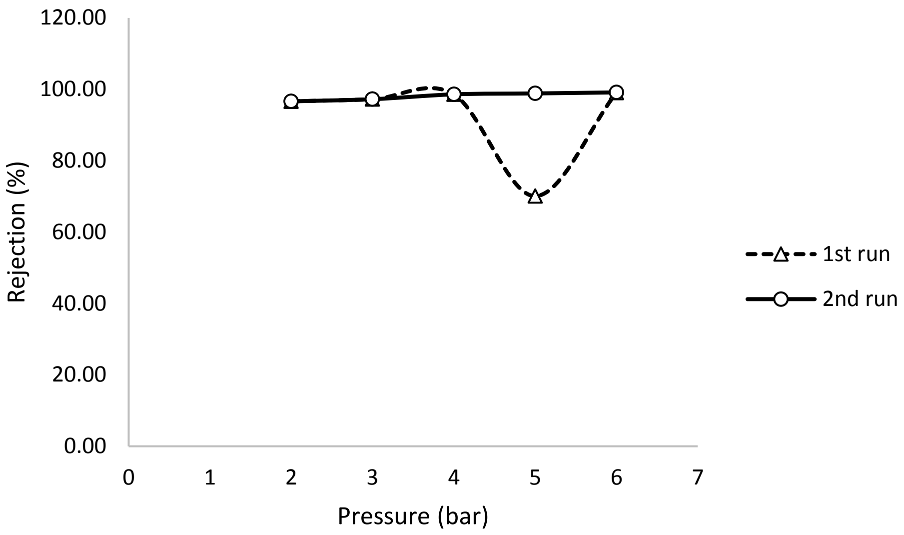


Figure 4.4: Rejection against pressure for 10 ppm of lignin solution

The rejection of lignin at concentration of 100 ppm and 1000 ppm were shown in Figure 4.5 and Figure 4.6. For both concentration, at 6 bar, the rejection obtained was the highest which were 99.49% and 99.45% respectively. The membranes showed increasing rejection at higher lignin content which means that lignin rejection is concentration dependent.

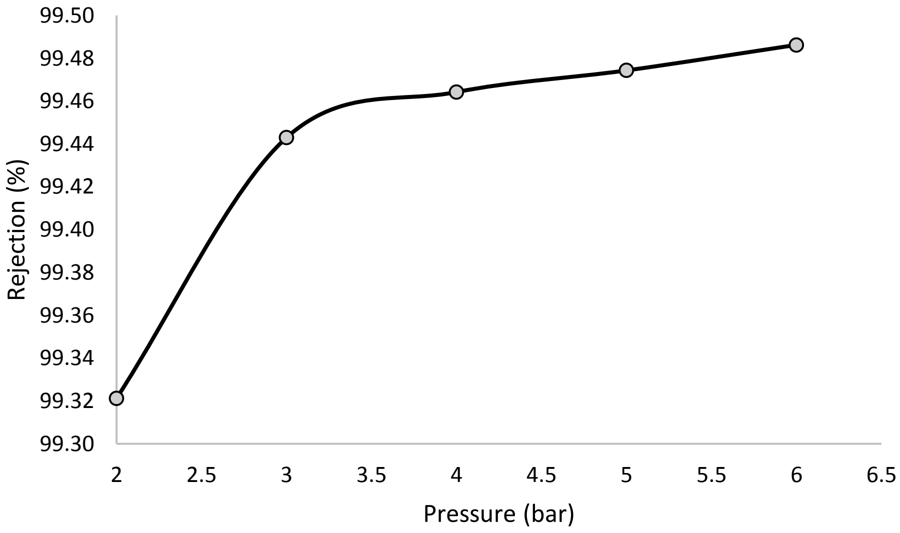


Figure 4.5: Rejection against pressure for 100 ppm of lignin solution