

DECLARATION

I, _____ hereby declare that this work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree. I further declare that all cited sources are acknowledged by list of bibliography.

Signed.....

Date.....

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DEDICATION

This study is dedicated to:

- My parents (deceased) Lenka and Maletuka Mosia
- My brother (deceased) Tshidiso Mofokeng
- My Uncle (deceased) Mahlomola Mofokeng
- My baby girl (deceased) Katileho Malefe

I know you are still smiling down on me from heaven. Thank you.

ABSTRACT

There is huge concern in the mining and industries to manage wastewater prior to discharge into the environment. It is generally cheaper and cost reducing for industries to treat its own wastewater before discharging to the local authority sewer. Dense Media Separation (DMS) Powders Company produces milled and atoms ferro-silicon by pyro-metallurgical process. DMS Powders uses municipal water for all processes taking place in the plants. The water used during the processes of milled and atom ferrosilicon powder is discharged into the environment without being treated. By treating this process wastewater before discharging will result in reducing the water consumption by recycling and the penalty costs for polluting the environment.

The primary objective of this study is to find suitable method for treatment of DMS Powders' process water using selected membrane processes. Membrane processes are better choice compared to traditional physical/chemical treatment processes, due to their advantages of approving water quality, no phase change, no chemical addition and simple operation. Two commercial membranes namely; NF-, and SW30HR are used in the treatment of DMS Powders process water. These membranes were purchased from (Dow/Filmtec) Manufacturing Company (Pty) situated in South Africa.

Membranes were characterised by Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Fourie Transform Infrared (FTIR) instruments. For synthetic water three membranes (NF- , NF90, and SW30HR) are investigated for the study. The fluxibility indicated that NF- membrane has higher flux compared to NF90 and SW30HR membranes. All the three membranes were very good in terms of rejection on single salts. Fouling was studied on DMS Powders process water. Concentration polarization was formed on NF- and SW30HR membranes for M8A, M8B and M9 process water.

Investigations on selected membranes conclude that NF- membrane will be the suitable membrane for treatment of DMS Powders process water because of its high fluxibility and rejection. Discharged effluent of DMS Powders could comply with the legislature and environmental pollution could be minimised. The study revealed that fouling does occur during treatment of process water. SW30HR showed that M9 Plant had more fouling for M9 samples than other Plants (M8A and M8B). It was because of higher concentrations in suspended solids.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

MF	Microfiltration
NF	Nanofiltration
RO	Reverse Osmosis
UF	Ultrafiltration
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infrared
ICP	Inductively Coupled Plasma
TGA	Thermo Gravimetric Analysis
SEM	Scanning Electron Microscopy
FeSi	Ferrosilicon

Symbols

MWCO	Molecular weight cut-off	(Dalton)
C_f	Feed concentration	(ppm)
C_r	Retentate concentration	(ppm)
C_p	Permeate concentration	(ppm)
J_w	Clean water flux	($L.m^{-2}.hr^{-1}$)
ΔP	Pressure difference	(bar)
η	Viscosity	(Pa.S)
t	Time	(hr)
ε	Porosity	(-)
$\Delta \pi$	Osmotic pressure difference	(bar)
R	Retention coefficient	(-)
τ	Tortuosity	(-)
T	Temperature	(°C or K)

CHAPTER 1

OVERVIEW

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1. INTRODUCTION

The planet is faced with the necessity increase in water consumption to meet future agricultural demands while balancing social and environmental impacts associated (Chapagain and Orr, 2009). All over the world there's a serious pollution caused by coking water, especially in China, where coal is one of the main energy source for the iron and steel industry (Jin *et al.*, 2013). Water quality is deteriorated by the development of industrial parks in China which increased demands of freshwater (Tong *et al.*, 2013). Associated environmental impacts might overweigh the credits from avoided water production and wastewater discharge due to the important evaluation needed to improve water quality for reuse purposes (Mo and Zhang, 2012).

Industries use huge quantities of water during their manufacturing cycles and thus produce amounts of waste water, which pollute the environment (Szafnicki *et al.*, 1998). Pollution from industrial discharge can produce high levels of suspended solids that can subsequently contaminate sediments within the surface water system (Mulligan *et al.*, 2009). For an example, it is reported by Windom *et al.* that an average of approximately 40, 62, 80 and 92% of Cu, Cd, Zn and Pb respectively are carried by suspended solids in US east coast rivers (Windom *et al.*, 1991). Industries have adopted programs aiming at the minimization of water consumption due to the cost of water increase and the high cost of effluent treatment (Guelli *et al.*, 2006). Consequently, downstream use of the treated water is limited, and the highly visible nature of the pollution source often gives rise to the public concern (Jirankoval *et al.*, 2007).

The requirement for water in South Africa is influenced by many factors such as climate change, economic growth and standards of living (Adewumi, 2010). Groundwater resources are quite limited; maintaining their quality and using them sustainability is a key issue (Van Heerden, Blignault and Horridge, 2008). However, with water shortage in South Africa, water pollution is a cosmopolitan problem that needs urgent attention and prevention (Barnhoorn and van Vuren, 2004).

South Africa is lacking adequate sanitation, waste disposal and access to portable water due to large proportion resulted in increasing population, urbanization and

industrialization (Drechsel, Graefe and Cofie, 2006). When pharmaceuticals undergo different types of transformation phases. Thus exposes human health at risk via drinking water (Kumar, Chang and Xagorarakis, 2010). In rural communities, human health risks are caused by lack of service in untreated river water, these health risks include infectious diseases, acute or chronic chemical toxicity and carcinogenicity (Genthe *et al.*, 2013). In several countries the major contamination in ground water is chromium (Cr) occurring in two different oxidation states (chromium III and VI) (Kelepertzis, 2014).

Nowadays, the dairy industries are considered to be the largest source of polluting the environment with the food processing wastewater discharge (Tocchi *et al.*, 2012). Therefore, dairy wastewater special treatment is required to meet effluent discharged standards and to reduce the risks of environmental problems such as eutrophication in rivers, lakes and coastal waters. Surface water pollution is one of the most widespread environmental issues during the 21st century (Perrin *et al.*, 2014). In the near future, important challenges concerning both cost management and fulfilment of environmental regulations will be confronted (Liukkonen, Laakso and Hiltunen, 2013). Easier achievement for controlling treatment plant result in better understanding of both treated and untreated effluent (Qin, Gao and Chen, 2012).

Water is used for various applications during processes taking place in the industry and its quality changes due to introduction of contaminants (Banaei *et al.*, 2013). Paper industry is the second largest sector demanding water use and facing challenges of maintaining the current standards related to the quantity and quality of discharged wastewater (Fontanier *et al.*, 2005). Huge amount of textile industry effluent is generated in the various processes and varies extensively in terms of composition due to the impurities in fibre and chemicals used (Khandegar and Van Saroha, 2013). During manufacturing of various chemical fertilizers, effluent pond receives water from different processes in the plant and before this water can be released to the environment, it must be treated to remove phosphoric acid and other impurities (Mohammed *et al.*, 2014). The rate of water pollution is increased by increasing industrialization and rapid urbanization (Qasim and Mane, 2013). Water quality improvement for all purposes could easily be met by using membrane techniques (Vera, 2000).

Today membrane technology utilization is considered to be the best available technologies in many industrial processes and waste management applications (Cui, 2010). Membrane filtration technology using reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) membranes were used recently as a technology available (Watabane and Kimura, 2011). Membranes are semi – permeable which allows separation of mixture to be achieved by rejection of one component (retentate) and passing of the other components through the membrane (permeate) (Mauguin, 2005). The concentrations in the retentate are normally higher or double than that in feed water (Ayala, Smith and El-Din, 2009). Membranes are classified according to their pore size, size of particles and molecules retained (Li *et al.*, 2008). Molecular separation membranes can play an important role in the applications of wet bio – based fuel and (petro) chemical industry (Agirre *et al.*, 2014). Membrane distillation (MD) plays a crucial role in desalination and purification technologies, and have attractive features compared to other technologies (Tijing *et al.*, 2014).

During membrane filtration, particles and organic compounds in water can foul the membrane and reduce membrane flux (Dias, Oliveira and Semmens, 2010). Deposited solids that accumulate on the surface of the membrane, changes its structure and porosity by forming a cake layer (Xu, Chellam and Clifford, 2004). In this study membranes technology are selected for effluent treatment because of their low cost, clean and easy to operate, offering appreciable energy savings and produce high quality products. Most advisable membranes are polymers with combinations of high permeability and high selectivity properties (Geise, Paul and Freeman, 2014). A suitable membrane process for the treatment of Dense Medium Separation (DMS) Powders industry will be evaluated. Therefore, effluent will be treated to meet the legislations standards prior to discharge into the environment.

1.1. Objectives of study

Purification of water at DMS Powders operating plants is prioritized through sedimentation and membrane processes. The recovery of species such as

suspended solids and metal ions is also considered for recycling and reclamation in this study. The objectives are:

- ❖ To characterize selected membranes
- ❖ To determine the suitable method for water treatment at DMS Powders
- ❖ To quantify DMS Powders permeate water for suitability of recycling
- ❖ To study the rejection of the membranes on DMS Powders process water

1.2. Scope of the study

The research is more relevant to the treatment of DMS Powders process water. The content of the work is as follows:

Chapter 2 is a discussion about DMS Powders product which is ferrosilicon, treatment of selected elements with their physical and chemical properties and lastly membrane technology existence.

In Chapter 3 the discussion is based on materials and analytical instrumentations used.

The results of membrane characterization flux and rejection of salts on different membranes and surface chemistry are described in full details in Chapter 4.

Chapter 5 is a conclusion on results obtained and recommendation for future work.

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CHAPTER 2

LITERATURE SURVEY

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2. INTRODUCTION

In this Chapter, global water scarcities are discussed. The impacts on health and industrial pollution for international and national water are also discussed. Brief description of industrial process water at Dense Medium Separation (DMS) Powders is given too. The history of membrane technology processes and fouling is also mentioned.

2.1 Water scarcity

Over the last 50 years a rapid population growth and urbanization have tripled global water withdrawals and it is predicted that by 2030 almost half of humanity will face water scarcity (Stoker and Rothfeder, 2014). Water scarcity is defined as the point at which aggregate impact of all users impinges on the supply or quality of water under prevailing institutional arrangements to the extent that the demand by all sectors, including the environment, cannot be fully satisfied (scarcity, 2006). In the near future increasing demand brought by the economic development and population growth will face even more challenges (Hu and Cheng, 2013). Many countries are pressurised on irrigation systems as main consumptive user, because of the growing water scarcity (Malano, Burton and Makin, 2004). In the field of hydrology and water resources water scarcity assessment became a hot topic whereby water is the basic natural resources for the development of human society, as well as for survival of ecosystem (Oki and Kaneo, 2006; Vorosmarty *et al.*, 2010).

Climate change and regional water crises are fuelled interest on the growth of water consumption in urban and peri-urban areas (Otero *et al.*, 2011). Basic social services such as safe clean water and adequate sanitation in urban areas are strained because of increasing urbanisation throughout the world (Srinivas, 2009). Out of 10 million, 1.5 million diarrheal disease counts globally for children under the age of five who died needlessly each year (UNICEF/WHO, 2009). It is identified by two European studies that the pressure loss in drinking water systems is a significant risk factor for sporadic diarrhoeal disease (Hunter *et al.*, 2005). Over the past 15 years,

some 33% of waterborne outbreaks could be explained on problems in distribution (Nygard *et al.*, 2007; Risebro *et al.*, 2007).

2.1.1 International water scarcity

Over the past several decades in China, surface water and ground water are widely polluted by industrial and municipal wastewaters, household wastes and agricultural activities (Liu and Diamond, 2005). Pollutant discharges are extremely increased and caused widespread water pollution because of the fast industrial growth and rapid urban expansion (Huang, *et al.*, 2013; Hu & Cheng, 2013). In the water scarcity assessment water quality or water pollution is rarely regarded as an important factor (Oki and Kaneo, 2006; Vorosmarty *et al.*, 2010).

Fresh water scarcity in WANA (West Asia & North Africa) countries is reaching alarming levels. By 2025 water supply is expected to fall to less than 700 cubic meters, at the current moment WANA countries is less than 1500 cubic meters, much below the world average of about 7000 cubic meters (El Kharraz *et al.*, 2012). The quality of surface water is threaten by a variety of pollutants which lead to serious health risks and might be a contributing factor to the high mortality rate of 8.5% of all deaths due to diarrhoea in Southeast Asia (Wilbers *et al.*, 2014).

2.1.2 National water scarcity

In regions like southern Africa the problem of water scarcity is worse; of which Zimbabwe is part that still under development (Swatuk, 2008). In favour of the low-density areas in Bulawayo city, unfortunately the water distribution policy is skewed exposing poorer households to greater environmental health problems due to poor sanitation practices (Nyembe *et al.*, 2010). Rivers, streams and lakes are used routinely for human leisure interests and are all important sources of drinking water (Arvanitidou *et al.*, 1995).

In South Africa, 3.7 million have no access to any form of water supply infrastructure and an additional 5.4 million people who have some access are brought up to a basic level of services (Social Cluster, 2006). For South Africa to meet the Millennium Development Goals of halving by 2015, it can use an alternative of domestic rainwater harvesting (DRWH) (Kahinda, Taigbenu and Boroto, 2007). In most of the provinces in South Africa, the poor have no infrastructure and water services are quite poor (DWAF, 2006). Consumption of water used is restricted including significant depletion of aquatic ecosystem due to severe impacts of the pollution in the river system (Makinde, Moitsheki and Tau, 2007).

2.2 Industrial water

Industrial processing water requires different qualities of water for numerous applications taking place (Quevedo *et al.*, 2012). Water management plays an important role in sustainability of the natural environment and for industrial activities in mining regions (Uca Avci *et al.*, 2014). Environmental problems such as air and water pollution are caused by uncontrolled released and discharged by industries and it is a setback for economical and urban development's (Bougherira *et al.*, 2014). The treatment and discharge of industrial wastewater is currently a huge concern since polluted wastewater is release in large volumes (Efligenir *et al.*, 2014).

There are many technologies available for wastewater treatment (Fu and Wang, 2011; Series and Brillas, 2012), namely: coagulation-flocculation (Chang and Wang, 2007), precipitation (Shpiner, Vathi and Stucky, 2009), oxidation (Oller, Malato and Sanchez-Perez, 2011) and sorption (Wang, Lin and Juang, 2003). Amongst them all, pressure-driven membrane processes, demonstrated a great potential for the decontamination of aqueous solutions (Gherasim and Mikulasek, 2014; Murthy and Chaudhari, 2009; Narbaitz *et al.*, 2013). Pressure-driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), which have different applications. In all different types of membrane filtration processes, reverse osmosis and nanofiltration membrane technologies can be used to remove metallic ions directly without the need of secondary chemicals (Maher, Sadeghi and Moheb, 2014).

2.3 Dense Medium Separation (DMS) Powders process water

DMS Powders uses municipal water for all processes taking place in the plants. There are two plants at DMS Powders, namely: granulation plant (it is where milled ferrosilicon is produced) and an atomization plant (whereby atom ferrosilicon is produced). The water enters the granulation plant through underground pipes into the granulation tank which has a water capacity of 65 000 L. At the bottom of the granulation tank there are nozzles and jet pumps which separates Ferrosilicon (FeSi) solids from water, then the water is pumped with a pressure of 8 bar to the cooling water tank with a capacity of 8 000 L. This water still contains lighter solids (carbon as impurity), therefore it is pumped to the cyclone stack, which is used to separate lighter impurities from water. The water from cyclone stack is pumped into the storage water tank that has a capacity of 80 000 L. Not all the solids have been removed; water in storage tank is still contaminated by granulation process. Some 40 000 L of this water is pumped back into the granulation tank for reuse and other 40 000 L is pumped into the atomization plant. After the atomization process, the water is pumped back into the water storage tank. Atomization plant uses very high sensitive system of high pressure (3000 bar) pumps and these pumps need specific criteria to be met. These criteria are as follows:

- The sizing of the solids entering the HP pumps must not exceed 2 μm
- The solids concentration of the water entering the HP pumps must not exceed 100 ppm

The membrane technology will fit in the **project scope** illustrated in diagram (Figure 2.1). The membrane technology will be treating the water from the granulation tank before entering the highly sensitive high pressure pumps through the atomization plant. After atomization process the water will be pumped to the Atomization tank. When the Atomization tank is overflowing, the water will be discharged to the waste water cleaning tank then to Amcor dam. Before the water can be discharged it should comply with the legislature set by General – Special Effluent Standards Annexure (2009). Table 2.1 shows the special and general standard of which discharged wastewater should be met.

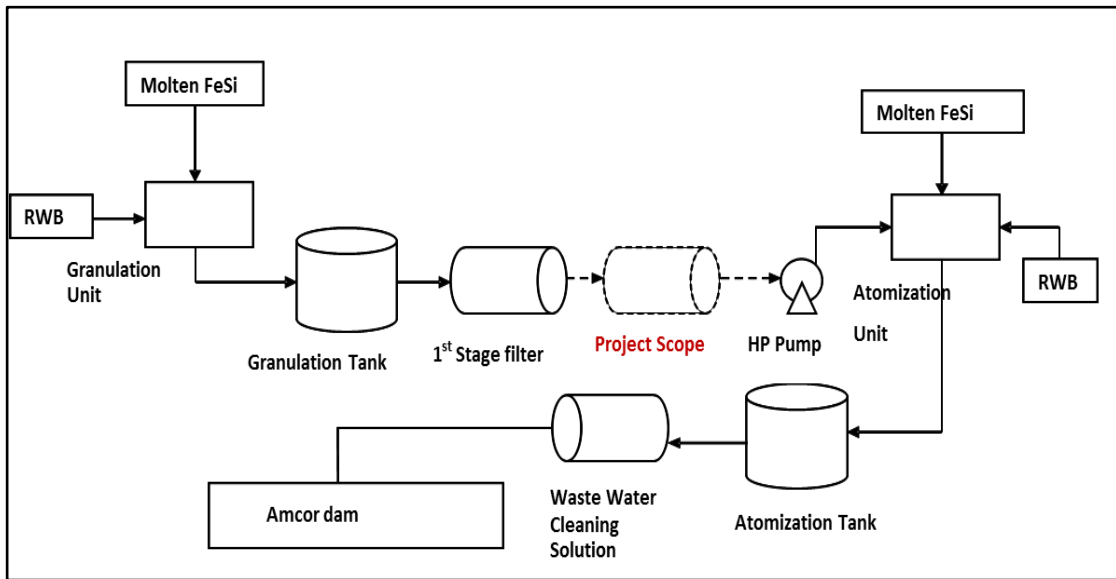


Figure 2.1 Layout of proposed water filtering solution for DMS Powders

Table 2.1 Special and general standards

Constituent	Maximum concentration in ppm
Iron (Fe)	0.3
Manganese (Mn)	0.4
Chemical Oxygen Demand (COD)	75
Copper (Cu)	1.0
Chromium (Cr)	0.5
Sodium (Na)	90
Phenolic compounds (Phenol)	0.1
Suspended Solids (SS)	25

- pH is between 5.5 and 9.5

- Conductivity does not exceed 250 milli-Siemens per metre (determined at 25° C)
- Temperature shall be a maximum of 35° C

2.4 Health risks caused by heavy metals in water

Iron is a metal in the first transition series on periodic table, with symbol Fe and atomic number 26. It occurs naturally in water in soluble form Fe (II) or Fe(OH)⁺ or complexed form like the ferric iron or bacterial form (Chaturvedi and Pragnesh, 2012). Removal of iron or impurities in solutions for many industrial situations is problematic; it mainly involve taste, visual effects, and clogging (Gosh, Solanki and Purkait, 2008). Energy dispersive X-ray (EDX) analysis revealed that iron is an important element for the growth of *anammox* bacteria (Liu and Horn, 2012). Fortunately for human health, the intake for iron has positive effects in moderate doses and is an essential nutrient (Chaturvedi and Pragnesh, 2012).

Manganese is an important trace element with symbol Mn and atomic number 25. It is found as a free element in nature (often in combination with iron), and in many minerals. Removal of manganese from wastewater depends on: the concentration and speciation encountered in the effluent; the volume of wastewater to be treated and economical aspects (Silva *et al.*, 2010). Nowadays, in all over the world, a huge number of water resources are being affected by Mn concentration that exceed 400 µg L⁻¹ such as Greece, Japan or Australia, among others (Frisbie *et al.*, 2012). From the toxicological point of view, manganese exposure on human beings affects nervous system functions and may even cause manganism (Alvarez-Bastida *et al.*, 2013).

Copper is an essential trace metal with symbol Cu and atomic number 29. It is used as a catalytic co-factor for many enzymes and is an important oligo-element in the food and water ingested by humans (Fraga, 2005). Naturally, the water with higher concentrations of heavy metals may be corrosive or aggressive and are very harmful when discharged without treatment (Bandita *et al.*, 2013). The main courses of heavy metal pollution in the environment are mining/smelting and the tailings generally containing higher concentration of heavy metals (Zhuhong, Quyi and Xin,

2013). Heavy metals tends to accumulate in living organisms because are not biodegradable causing several health effect. Copper in water may have severe effect in the brain and liver of people with Wilson's disease (Bojic, Bojic and Andjelkovic., 2009).

Among the trace chemical components present in natural water, chromium is one of the most important heavy metal ions with a symbol Cr and atomic number 24 (Sulistyo *et al.*, 2014). In recent year's chromium in water have received more attention because of its contamination generated from different industries such as metal finishing, pigment manufacture, electroplating and leather tanning (Salah *et al.*, 2012). Chromium dissolved in natural waters is primarily present in two oxidation states, (i.e. Cr (III) and Cr (VI)). Chromium (III) is essential for glucose, cholesterol and fatty acids metabolism, while chromium (VI) is highly toxic and possibly carcinogenic if inhaled or ingested (Effie *et al.*, 2013).

Removal of these mentioned heavy metals from water is very important in order to protect water supplies and human health. The most common simplest technique is precipitation followed by filtration (Chen *et al.*, 2009). Other methods are ion exchange and water softening for removal of iron (Vaaramaa and Lehto, 2003). In the last few decades, among these methods, membrane technology is introduced as environment protecting method for the heavy metals recovery (Csefalvay, Pauer and Mizsey, 2009). Application of the membrane processes was certainly determined by the physic-chemical properties of wastewater (Baker, 2004). Today membrane processes are used in wide range of applications in many industries and municipalities.

2.5 Membrane technology processes

In the recent decades, membrane technology has gained ground to classic separation process in wastewater reclamation and reuse (Ochondo-Pulido, Victor-Ortega and Martinez-Ferez, 2015). Membrane processes are better choice as compared to traditional physical/chemical treatment processes, due to their advantages of approving water quality, no phase change, no chemical addition and simple operation (Lain-Chuen, Dyi-Hwa and He-Yin, 2007). Membrane technology

applications are mostly favoured polymeric membranes because of their low cost and ease to operate (Sriharsha, Ramgopal and Mihir, 2014). Petersen, (1993) discovered a significant progress of the thin film composite (TFC) membrane. TFC consists of an ultra-thin barrier layer which determines the membrane separation efficiencies (Jegal, Min and Lee, 2002; Misdan, Lau and Ismail, 2012; Ahmad and Ooi, 2005). Influencing barrier layer properties, namely, surface charge, surface morphology, hydrophilicity, chemical functionality, and pore size are affecting the interaction between water and solutes (Childress and Elimelech, 2000; Kosutic, Kastelan-Kunst and Kunst, 2000; Mi *et al.*, 2006; Van der Bruggen *et al.*, 2004).

A membrane is a filtration process which selectively divides a feed stream into two phases (permeate and retentate). Permeate is the concentration that passes through the membrane and its lower than the feed. The retentate is the concentration rejected by the membrane and it is higher than the feed. Membranes can be thick or thin, homogeneous or heterogeneous, hydrophilic or hydrophobic. The main advantage of these processes is that they involve no chemical agents. They provide high quality treated water with low turbidity while the cost is low and they are easy to operate (Juang, Chen and Chen, 2008). For a separation process to be achieved, energy is needed. This energy input called the driving force can be any of the following (Mulder, 1997):

- Pressure gradient (ΔP),
- Concentration gradient (ΔC)
- Temperature gradient (ΔT), or
- Electrical potential gradient (ΔE)

2.5.1 Pressure driven processes

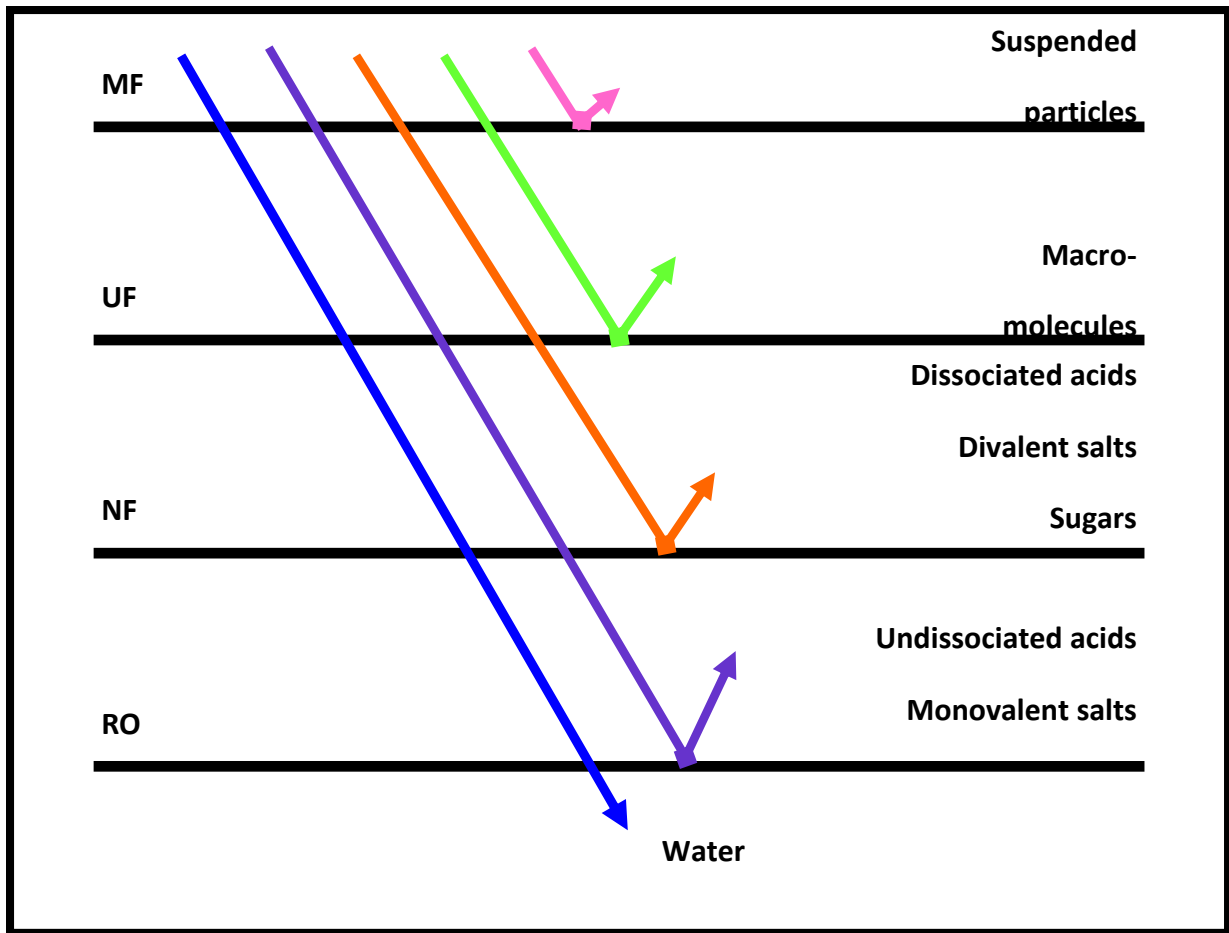


Figure 2. 2 Pressure driven membrane process

Figure 2.2, shows four [microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)] pressure driven membrane processes which have different applications.

2.5.1.1 Microfiltration (MF)

Different kinds of physicochemical and biochemical processes are widely using the pressure driven membrane processes such as microfiltration (MF) and ultrafiltration (UF) for the separation of solids from liquids (Dizge *et al.*, 2011). Pressure driven flow through a microporous membrane for separation and recovery of micron or sub-micron sized particles from fluids is indicated by the term microfiltration (MF)

(Kulkarni, Funk and Li, 1992). MF membrane consists of three regions: (1) a large pore region ($0.45\mu\text{m}$) as a pre-filter for capturing larger particles, (2) a nonwoven scrim used as a mechanical support and to facilitate manufacturing, and (3) a small-pore region ($0.1\mu\text{m}$) to provide the retention of small contaminants (Huang *et al.*, 2013). The pore sizes are respectively, according to the manufacturer.

2.5.1.2 Ultrafiltration (UF)

Various industrial processes mainly uses ultrafiltration (UF) membranes to remove suspended nanoparticulates, bacteria, macromolecules, etc. (Shannon *et al.*, 2008; Zhao, Zhu and Xu, 2007). Polymer ultrafiltration membrane with pore size ranging from 2-100 nm have an asymmetrically porous structure composed of a thin nanoporous selective active layer and a thick macroporous supporting layer (Wang *et al.*, 2014). For improving the fouling resistance of ultrafiltration membrane, the active layer tends to be more hydrophilic than the supporting layer. Characterisation of ultrafiltration membranes is based on nominal molecular weight cut-off, which is typically defined as the molecular weight of a solute that consists of a rejection of 90% (Zeman and Zydney, 1996; van Reis and Zydney, 2007; Zydney, 2011).

2.5.1.3 Nanofiltration (NF)

Nanofiltration is a pressure-driven separation process having separation characteristics between ultrafiltration and reverse osmosis membrane. It is a best alternative due to higher fluxes when compared to reverse osmosis (RO). NF is widely used in water softening application, as well as for pretreatment for RO (Mohammad *et al.*, 2007). Nanofiltration is a three-layer polysulfone based membrane with a polypiperazine or polyamide top layer (Luo and Wan, 2011). It involves separation of monovalent and divalent salts, or organic solutes with molecular weight in the range $200\text{--}1000\text{ g.mol}^{-1}$ (Vandezande, Gevers and Vankelecom, 2008) and a molecular size of about 1 nm. In nanofiltration membranes, surface charge formation is relevant in determining rejection properties in the case of electrolyte solutions (Bruni and Bandini, 2008).

2.5.1.4 Reverse osmosis (RO)

Reverse osmosis (RO) is a water purification technology that can provide high quality permeate and have many applications in potable water (Walha *et al.*, 2007; Aboabboud and Elmasallati, 2007; Venkatesan *et al.*, 2011) and wastewater treatment (Lu, Fan and Roddick, 2013). Aromatic polyamide (PA) membrane is widely accepted in RO membranes due to its excellent separation performances in terms of water flux and salt rejection (Cadotte, 1981; Baker, 2004). Transport mechanism in RO membranes occurs through the interactions with the membrane not by sieving only (Baker, 2004). RO membrane technology is a reference process increasingly used in seawater desalination (Fan *et al.*, 1968; Saltonstall, 1976; Kimuru and Nomura, 1981), ultrapure water production, wastewater treatment and reuse (Service, 2006; Li and Wang, 2010; Elimelech and Phillip, 2011; Shannon *et al.*, 2008). Therefore, RO membranes technology complies mostly with the rules and regulation of public health and environmental protection (Ochondo-Pulido, Victor-Ortega and Martinez-Ferez, 2015).

2.5.2 Nanofiltration Characterization

The electric charge of a NF membrane plays an important role in the charge separation during a filtration process due to the formation of electrical double-layer that are comparable or bigger than the pore size (Kotrappanavar *et al.*, 2011). Although it is established that the skin layer of polyamide membranes have bipolar (positive and negative surface group) charge distribution, no theoretical investigations are reported yet in the membrane technology (Zhu, Szymczyk and Balannec, 2011). The morphology and performance of membranes are strongly depended on the thermodynamics as well as kinetics of the phase inversion process (Barth *et al.*, 2000).

In each of the pressure-driven processes there are advantages and disadvantages. The membrane advantages are summarised as follows (Mulder, Thelon and Maaskant, 1997):

- Separation process can be carried out continuously
- Energy consumption can be operated out at low levels
- Separation can be carried out under mild conditions
- Additives are not required
- Up-scaling is easy

The membrane disadvantages are summarised as follows:

- Concentration polarisation or membrane fouling accumulation
- Short lifetimes
- Low selectivity or flux

2.5.3 Theory of Equations

The membranes are characterised in terms of pure water permeability and rejection of solutes. The law describe by Darcy for water flux through a membrane is shown in Equation 2.1):

$$J_W = A_W \cdot (\Delta P - \sigma \Delta \pi) \quad \text{(Equation 2. 1)}$$

Where A_W is the water permeability ($L \cdot m^{-2} \cdot h^{-1}$), which can be determined experimentally from the plot of J_W versus ΔP (shown in Equation 2.2), ΔP is the change in trans-membrane pressure (bar) an $\Delta \pi$ is the change in osmotic pressure. This implies that if the feed and the retentate contain pure water, i.e. change in osmotic pressure across the membrane become zero, therefore (Equation 2.1), will be reduced:

$$J_W = A_W \cdot \Delta P \quad \text{(Equation 2. 2)}$$

An alternative approach for expressing water flux through membrane is by using Hagen-Pouseuille (Mulder, 1997) (Equation 2.3):

$$J_W = \frac{\varepsilon r^2}{8 \eta \cdot \tau} \cdot \frac{\Delta P}{\Delta x} \quad \text{(Equation 2. 3)}$$

Where Δx , is the thickness of the membrane (m) and η is the viscosity of water (Pa.S). If both Darcy and Hagen–Poisseuille (Equation 2.2 and 2.3) are combined, quantification of water permeability becomes (Equation 2.4)

$$A_w = \frac{\varepsilon}{\tau} \cdot \frac{r^2}{8\eta\Delta x} \quad \text{(Equation 2. 4)}$$

Where ε is the porosity, which can approximately reveal how many pores can be found in a medium, and τ is the membrane tortuosity. In (Equation 2.5), for the cylindrical pores perpendicular to the membrane surface, $\tau = 1$ (Mulder, 1997). Therefore, when it is approximated that:

$$\varepsilon = \frac{1}{\tau} \quad \text{(Equation 2. 5)}$$

When combining (Equation 2.4 and 2.5) the following (Equation 2.6) is obtained:

$$\varepsilon r^2 = 8\eta\Delta x.A_w \quad \text{(Equation 2. 6)}$$

Retention (R), which is a measure for the rejecting ability of a membrane for a solute, can be expressed by Equation 2.7. Where C_p and C_f are permeate and feed concentration (ppm) respectively.

$$R = 1 - \frac{C_p}{C_f} \quad \text{(Equation 2. 7)}$$

2.6 Membrane fouling

Membrane fouling is defined as pore plugging and external pore blocking, resulting from deposition of particles and colloids on the membrane surface and precipitation

of smaller dissolved materials within the membrane pores and on the membrane surface (Pontie *et al.*, 2005). Foulants build-up on the membrane surface are known as concentration polarization (Lain-Chuen, Dyi-Hwa and He-Yin, 2007). The extent of fouling is strongly dependant on the types of membrane process and feed employed (Tarazaga, Compelerrors and Padilla, 2006). Membrane fouling and chemical cleaning compromised the quality of treated water and also increased the operational costs (Van der Bruggen, Manttari and Nystrom, 2008). Performance of membrane filtration and fouling factors depends on several factors that are listed in Table 2.2 (Hwang and Huang, 2009).

Table 2. 2 Fouling mechanism

Various Factors	Examples
Biological polymers	Proteins, carbohydrates, nuclei acids, etc.
Membrane characteristics	Morphology, membrane pore size, zeta potential, hydrophilic affinity, etc.
Bio-macromolecular characteristics	Molecular weight of biopolymers, zeta potential, configuration, etc.
Operating conditions of system	Filtration pressure, cross flow velocity, soluble microbial products (SMP) concentration, etc.

Plans to reduce fouling include pre-treatment of feed, optimization of operating conditions/protocols (Gao *et al.*, 2011; van der Waals, Stevanovic and Racz, 1989), and modification of the membrane surface (Rana and Matsuura, 2010; Nabe, Staude and Belfort, 1997; Reddy *et al.*, 2003). Fouling is classified into five types, for characterization depending on the process involved in their formation which are biological, corrosion, particulate, chemical reaction, and crystallization (Characklis, 1990; Epstein, 1981).

Industrial facilities should minimize the discharges into the environment with the purpose of keeping cooling system in optimal condition by using antifouling treatment

(Rubio *et al.*, 2014). Chemicals such as chlorine, chlorine dioxide, peracetic acid and quaternary ammonium (Cristiani, 2005), advanced oxidation process (Lakretz *et al.*, 2011), non-chemical treatments as UV radiation (Lopez-Galindo, Casanueva and Nebot, 2010; Cloete, L. and Brozel, 1998), ultrasound (Bott and Tianqing, 2004) and electric pulses (Cho, Lane and Kim, 2005) were studied as antifouling treatments.

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CHAPTER 3

EXPERIMENTAL METHODS

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3. INTRODUCTION

In this chapter the experimental approach for the flux studies and rejection of salts and effluents are discussed. Various materials and chemicals used in this study are also listed. Dead-end unit (bench-scale operation) set up, experimental procedure and analytical instrumentations utilised for the study are discussed. Scanning Electron Microscopy (SEM) which is employed for membranes surface morphology is also discussed.

3.1 Materials

3.1.1 Preparation of selected polymer membranes

Three commercial membranes namely; NF-, NF90 and SW30HR are used in the investigation. These membranes are purchased from (Dow/Filmtec) Manufacturing Company (Pty) situated in South Africa. The specifications of the membranes obtained from the supplier are given in Table 3.1.

Table 3. 1 Membrane characteristics as specified by the supplier.

MEMBRANE	NF-	SW30HR
Supplier	Dow / Filmtec	Dow/Filmtec
Material	Polypiperazine	Polyamide
Membrane type	FS	FS
Max. Operating temp (°C)	45	45
pH range	3-10	2-11
MWCO (Da)	150	100

MWCO = Molecular Weight Cut Off, FS = Flat Sheet, Da = Dalton

Based on the manufacturers' data sheet, NF- (polypiperazine- amide) having MWCO of 150 Da, is able to reject organics while permeating monovalent salts. This FS membrane is normally used in different applications including industrial and research academic institutions for acid processing, antifreeze and metal recovery.

SW30HR acts as a barrier to all dissolved salts and inorganic molecules, as well as organic molecules having MWCO over 100 Da. Water molecules, on the other hand, pass freely through the membrane creating a purified product stream. Rejection of dissolved salts is typically 95% to greater than 99%.

3.1.2 Polymer membrane preparation for dead-end unit operations

A blade was used to cut the polymer membranes into required sized disk area. The diameter of the disk membranes had an active area of $6,36 \times 10^{-4} \text{ m}^2$. The disk membranes were kept wet in deionised water for 24 hrs duration before use. This was to allow swelling of the inner surface material (porous support layer), pore size flexibility and easy permeation. Only one piece of membrane was used for each solution per operation on the experiments to be studied. Figure 3.1 shows preparation of membrane for dead-end unit.

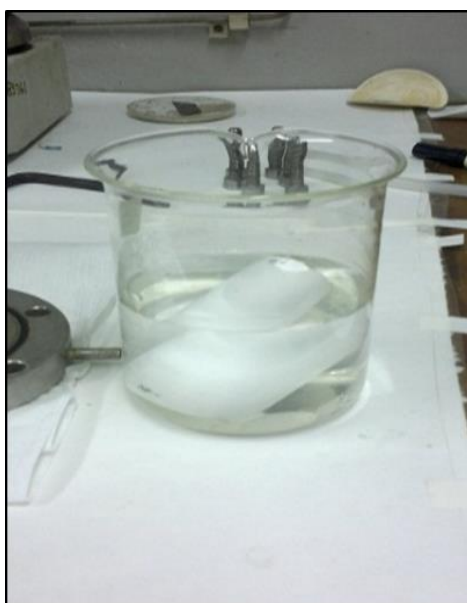


Figure 3.1 Preparation of membrane disks for dead-end unit operation

3.1.3 Chemicals used

Various inorganic salts were used for the current study and include; $\text{NaCl}_{(s)}$, $\text{MgCl}_{2(s)}$, $\text{Na}_2\text{SO}_{4(s)}$ and MgSO_4 . Solution mixtures were treated for single, binary and

quaternary salts for testing the behaviour of the selected membranes. Chemicals used and their suppliers are listed in Table 3.2.

Table 3. 2 Chemicals used in the study

CHEMICALS	SUPPLIER	PURITY (%)	MW (g.mol ⁻¹)
NaCl	Saarchem	99.5	58.4
Na ₂ SO ₄	Saarchem	97.0	119.1
MgCl ₂	Merck	99.5	95.2
MgSO ₄	LABCHEM	99.	120.4
H ₂ SO ₄	Glassworld	99.9	98.0

3.2 Analytical instrumentation

Spectroscopy technique was used for quantification of cations. The solutions were analysed during filtration (sample feed, permeate and retentate) processes using Inductive Coupled Plasma (ICP) instrument. The analyses were performed at Metalloys laboratory in Meyerton. SEM instrumentation analyses were outsourced from Sasol Technology (Sastech) division based in Sasolburg. For membrane characterization and properties, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared (FTIR) spectrophotometer instruments were used at Vaal University of Technology in Vanderbijlpark.

3.2.1 Scanning Electron Microscopy (SEM)

A Zeiss ULTRA 55 FEGSEM was used. The instrument uses a field emission tungsten hairpin filament with a ZrO reserve, as an electron source. Elemental analyses for SEM were performed. SEM allows a clear view of an overall membranes structure as a top surface, cross-section and bottom surface. Micrographs for the pore sizes, the pore size distribution and surface porosity can

also be observed. This instrument was also employed for characterising selected membranes investigated on the study. A narrow beam of electrons applied to hit the membrane sample was about 1- 25 kV of kinetic energy. The primary high energy electrons called incident electrons are reflected whereas secondary (low energy) are not reflected. Therefore, membrane images will be clearly viewed as micrographs. This principle is mainly applied for images visualisation (Mulder, 1996).

3.2.2 Thermo Gravimetric Analysis and Differential Thermal Analysis

Thermal analysis techniques are used to measure physical property of a substance or its reaction products as a function of time. STA 6000, simultaneous thermal analyser from PerkinElmer was used to measure thermogravimetric analysis (TGA) as well as differential thermal analysis (DTA). In a thermogravimetric analysis (TGA) the mass of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample increased (usually linearly with time). In DTA a sample was run under nitrogen, from 30 to 90 °C at a heating rate of 10 °C.min⁻¹. Then the difference in the heat flow between the sample and the reference was measured. Determination of the glass transition temperature T_g is one of the most important application of DTA (Skoog, Holler and Crouch, 2007). The mass loss is calculated as:

$$\text{Mass loss \%} = M_f - M_i$$

3.2.3 Fourier Transform Infrared (FTIR) spectrometer

The surface chemical functionality of the selected membranes was obtained with 400 FT-IR / FT-NIR spectrometer from Perkin Elmer. Clean dry membrane pieces were mounted on the ATR germanium crystal and 128 infrared scans were performed at a resolution of 4 cm⁻¹ at an incident angle of 45°. The IR penetration depth for this incident angle is 0.1 – 1 µm. A baseline was obtained initially without the sample on the crystal, and was subtracted for each membrane sample.

3.2.4 Inductively Coupled Plasma (ICP)

Optical Emission Spectrometer (OES) (Optima 5300DV) Perkin Elmer was employed for quantifying cations through their varying oxidation states (Na^+ and Mg^{2+}). This method uses inert gas (argon) plasma formed by the absorption of radio-frequency radiation to atomize and excite a sample for atomic emission spectroscopy. Plasma is a conducting gaseous mixture containing a significant concentration of cations and electrons. The nebulizer constantly introduces the sample in the form of a fine spray of droplets, called aerosol. An aerosol sample was introduced into the ICP by argon flowing at about $1 \text{ L}\cdot\text{min}^{-1}$ through the central quartz tube. With such continuous sample introduction into plasma, a steady-state population of atoms, molecules and ions were produced (Skoog *et al.*, 2004).

3.3 Dead – End Unit

Permeation and retention studies were performed on 1 L capacity bench-scale dead-end unit which is illustrated in Figure 3.2 Dead-end unit used for filtration. The unit has a top opening to allow solution through (feed inlet) and a magnetic stirrer (field) inside. The stainless steel unit is equipped with a circular flat sheet cell and is of two halves fastened together to tighten the bolts, and a porous support to allow permeation. The unit can be operated at pressure ranging from 5 to 20 bars for selected membranes processes. Nitrogen gas (N_2) was preferably used as the driving force throughout the study. Feed solutions were constantly stirred at 500 rpm to homogenize the samples (Modise, 2002).

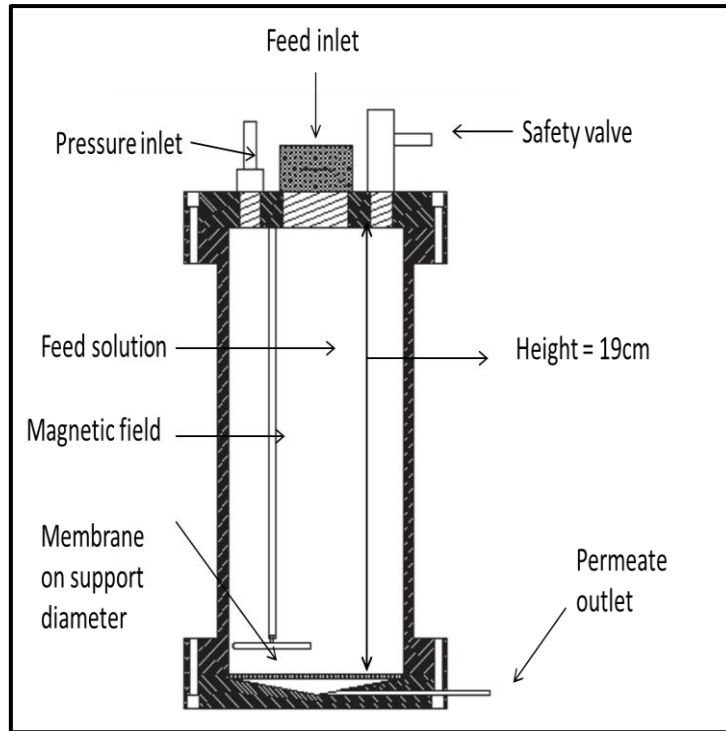


Figure 3.2 Dead-end unit used for filtration

3.4 Experimental and Methodology

3.4.1 Permeability studies

Flat sheets membranes were characterized in terms of water permeability, solute permeation and rejection of salt ions. Firstly, clean water permeability was investigated for all three membranes (pore size evolution), followed by rejection behaviour of charged solutes (NaCl , MgCl , Na_2SO_4 and MgSO_4) ions. For clean water experiment, permeate flux which is the volumetric rate of flow through unit membrane area, can be expressed by Equation 3.1 (Friel, 2003).

$$J_w = \frac{V}{S \cdot t} \quad \text{(Equation 3. 1)}$$

Where V is volume flux (l), while S is the surface area of the membrane (m^2) and t is the time (hr^{-1}) of permeation through the membrane.

Retention (R), which is a measure for the rejecting ability of a membrane for a solute, can be expressed by Equation 3.2.

$$R = 1 - \frac{C_p}{C_f} \quad \text{(Equation 3. 2)}$$

Where C_p and C_f are permeate and feed concentration (ppm) respectively. Retention of cation species are given and discussed under results and discussion.

3.4.2 Preparation and filtration of synthetic inorganic salts

Synthetic wastewater sample solutions of inorganic salts ($\text{NaCl}_{(s)}$, $\text{MgCl}_{(s)}$, $\text{Na}_2\text{SO}_{4(s)}$ and $\text{MgSO}_{4(s)}$) mixtures of concentrations 5, 10, 15 and 20 ppm, were prepared. These inorganic salts were weighed with the use of electronic weighing balance (SCALTEC, maximum of 200 g) apparatus and dissolved into a 1 L volumetric flask using deionized water. All salts were prepared as 1000 ppm (stock) solutions. Commercial atomic absorption (AA) standard solutions with a concentration 1000 ppm (99,9% purity), were used to prepare samples standards solutions.

Solution mixture of sodium chloride, magnesium chloride, sodium sulphate and magnesium sulphate with concentration of 5, 10, 15 and 20 ppm were operated at a pressure of 5, 10, 15 and 20 bar for single salts. For binary and quaternary salts solution mixture for four different salts with concentration of 20 ppm were operated at a pressure of 20 bar only, the reason being that single salt studies showed that the membranes were not active at low concentrations (5 – 15 ppm) and at low pressure of 5 – 15 bar. Both permeate and retentate were collected, flux and rejection measurements of sodium and magnesium solution mixture were evaluated regarding the behaviour obtained on the selected membranes

3.4.3 Rejection studies

Rejection measurements of sodium and magnesium solution mixture were evaluated on single, binary and quaternary salts regarding the behaviour obtained on the selected membranes.

3.5 Sampling and treatment of DMS process water

DMS process water was monitored for a period of two years (December 2011 – December 2013), checking routine analyses without being treated. Three different sampling points were available for sampling DMS process water, namely: M8A, M8B and M9. Process water was each sampled with three sample containers of 1 L. Each sample container was labelled as follows:

- Name of sampling point
- Sampling date
- Name of membrane going to be used for filtration

Before sampling, the taps were allowed to run for 5 minutes and then the plastic sampling containers were rinsed three times together with their lids to avoid contamination from the site (DMS). Samples were kept at a low temperature (4 °C) inside a cooler bag filled with ices cubes and transported from Meyerton DMS Powder plant to Vaal University of Technology in Vanderbijlpark for filtration on selected membrane processes.

3.5.1 Filtration and rejection of DMS process water

The membranes (NF- and SW30HR) were used during filtration of DMS process water, with a bench top scale (dead end filtration unit) operated at 20 bar for all experiments. New piece of membrane disks were used for each investigation. Both permeate and retentate were collected for quantification using ICP instrument. Flux

and rejection measurements were done to evaluate the performance on these selected membranes.

3.6 Fouling studies

Lastly, the quaternary salts (solution mixture of NaCl, MgCl₂, Na₂SO₄ and MgSO₄) experiment was prolonged for two hours duration at a pressure of 20bar to get a clear view of fouling on the selected membranes. Both permeate and retentate were collected, flux and rejection measurements of Na and Mg solution mixture were evaluated for foulants obtained on the membranes. Process water experiments from DMS Powders were also prolonged for eight hours to collect a 500 ml permeate for further analyses. Flux and rejection measurements were also evaluated regarding fouling on selected membranes.

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CHAPTER 4

RESULTS AND DISCUSSION

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4. INTRODUCTION

Chapter 4 is divided into two sections. In Section A the membrane characterisation by SEM, TGA, and FTIR instruments is discussed. Analysis of synthetic water whereby the flow and rejection is monitored for each selected membranes is given in Section A. In Section B the DMS Powders process water effluent is treated with selected membranes and comparison on which one will be the best for treatment of process water effluent on DMS Powders. The study is concluded by fouling studies of the process water effluent during membrane process treatment.

SECTION A: LABORATORY STUDIES

4.1 Membrane surface morphology with SEM and EDX

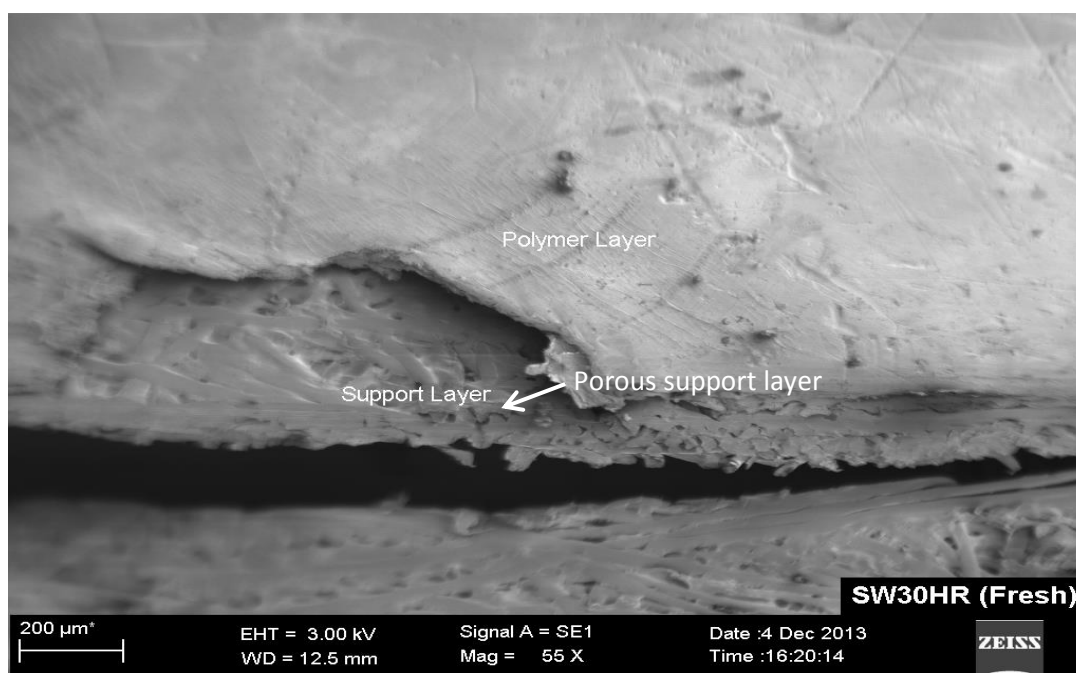


Figure 4.1 Cross sectional view of SW30HR (fresh) membrane

Membranes images of SW30HR (fresh), NF- (fresh), and NF90 (fresh) are captured by SEM and EDX to provide information on membrane's surface morphology. Figure 4.1 shows smooth surface layer and cross-section of SW30HR membrane indicating three distinct layers, namely; top polymer layer (1), porous support (2) and

non-woven layer (3). The most important layer during membrane separation process is the top layer. This is where charge density is and rejections are taking place. Such charge density as a result of the functional groups on the polymer and can either be of negative or positive tendencies. Porous support and non-woven layer allow permeation during membrane processes (Bandini, *et al.*, 2005). These layers were also observed in NF- membrane (see Appendix A).

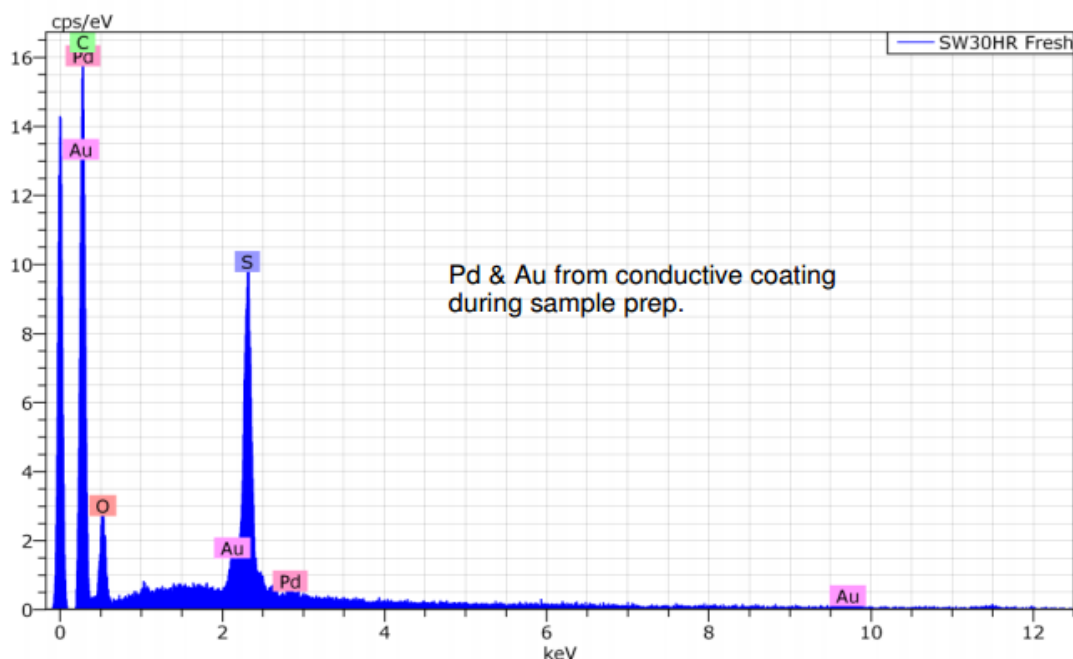


Figure 4.2 EDX Analyses of SW30HR (fresh) membrane

Figure 4.2 showed that during sample preparation Pd and Au were used as conductive coating. EDX analyses indicate that a polymer of SW30HR membrane consists of sulphur and oxygen. This will further be investigated during the study. EDX analyses were also observed on NF- polymer (see Appendix B).

4.2 TGA and DTA Analysis

The Molar mass is calculated as:

$$\text{Mass loss (\%)} = M_f - M_i$$

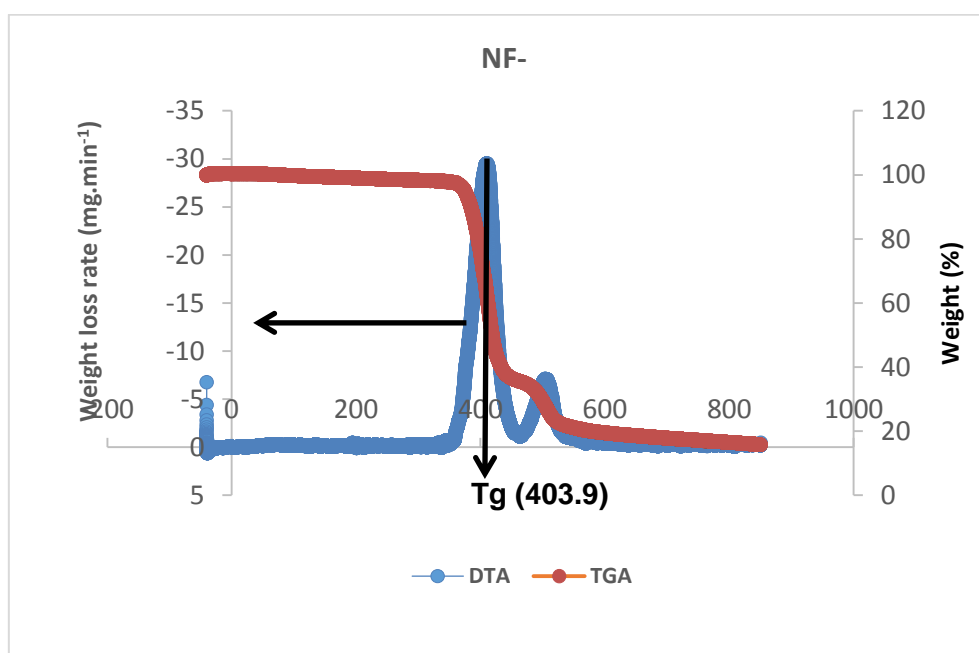


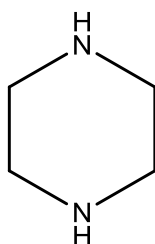
Figure 4.3 DTA and TGA graphs for NF- membrane polymer

Figure 4.3 shows the TGA curve and DTA peaks on NF- membrane. TGA curve shows two decomposition steps. NF- membrane polymer was stable up to 340 °C. The first decomposition step was observed in the range of 340 °C to 440 °C, resulting in a mass loss of 60.0%, suggesting to a loss of a polymer layer. The second decomposition was observed in the range of 470°C to 550°C, with a mass loss of 14.0%, suggesting to a loss of a support layer. For SW30HR the curve and the peaks were almost similar. First decomposition step was observed at 383 °C to 490 °C, resulting in a mass loss of 57.8%. Second decomposition was observed at 511 °C to 594 °C, resulting in mass loss of 5.1%, followed by a complete decomposition. DTA showed the curves of decomposition temperatures, phase transition and glass transition (Tg). The glass transition temperature Tg was the most important application of DTA. For NF- Tg was 403.9, this was where the polymer

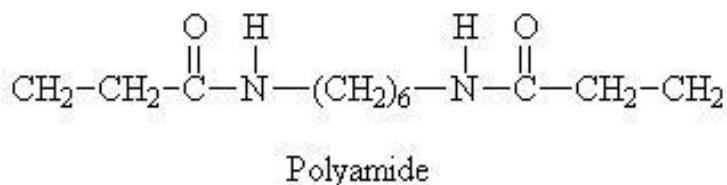
changed from a glass to a rubber. For SW30HR TGA and DTA analyses refer to Appendix C.

4.3 Polymer membrane functional group study by FTIR

Scheme 4.1 and 4.2 showed the chemical structures of piperazine and polyamide



Scheme 4.1 Chemical structure of Piperazine



Scheme 4.2 Chemical structure of Polyamide

The aim of employing FTIR is to identify the functional groups in chemical structure of polymeric species present in the NF and RO membranes used. The FTIR spectra of the membranes used in this study are illustrated in Figure 4.4. The results show that SW30HR fit the characteristics of fully aromatic polyamide, while NF- has characteristics of semi-aromatic polypiperazine amide.

The primary amines contain N-H bonds. These are assigned between 3100 and 3500 cm^{-1} . The saturated hydrocarbon C-H stretching absorptions all occur below

3000 cm^{-1} . The position of the C=C stretching frequency does vary slightly as a function of orientation around the double bond in aromatic rings. An amide medium N-H is assigned between 1590 and 1650 cm^{-1} , for aromatic rings. The C-H out-of-plane bending is typically the most informative relative to the location and spatial geometry of the double bond, where terminal and medial double bond may be clearly differentiated. C-N is assigned to a medium amine between 1000 and 1245 cm^{-1} .

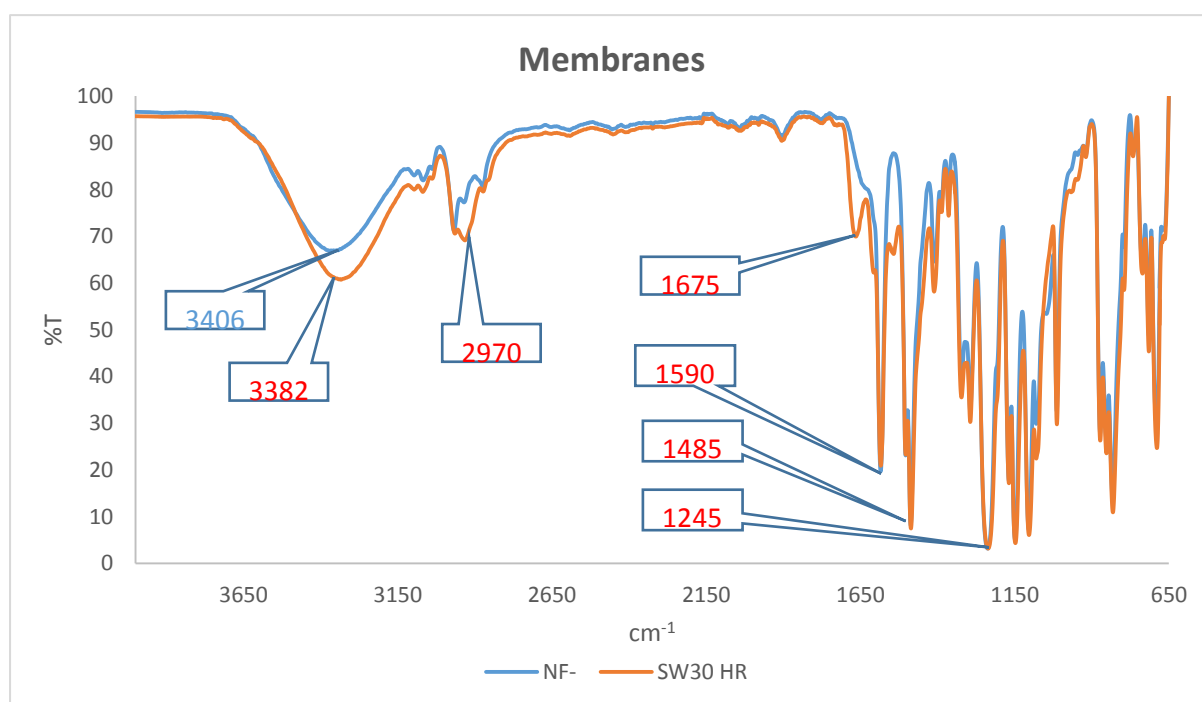


Figure 4.4 FTIR spectra on NF- and SW30HR membranes

The fully aromatic SW30HR membrane in Figure 4.4 is assigned to all the peaks appearing in the spectrum, which proves that it's a polyamide membrane. For NF- membrane, there is a slightly difference of two peaks assigned between 2850 – 3000 cm^{-1} and 1630–1680 cm^{-1} , when compared to SW30HR membrane. The assumption can be made that NF- membrane is a polypiperazine amide membrane.

Table 4.1 shows the origin and assignment of the peaks with their wave numbers in cm^{-1} .

Table 4. 1 Functional groups frequency and assignment

Origin	Group Frequency Wave number (cm ⁻¹)	Assignment
N-H	3300 – 3400	Amines – wk – N-H
C-H	2850 – 3000	Methyl – asym / sym – C-H stretch
C=C	1630 – 1680	Alkenyl – var – C=C stretch
N-H	1590 – 1650	Amide – med – N-H
C-H	1445 – 1485	Methylene – C-H bend
C-N	1000 – 1245	Amine – med - C-N

4.4 Clean water permeability

Pure water (deionised) permeability is determined on the three selected membranes from the plot of flux (L.m⁻².hr⁻¹) vs. pressure (bar) as shown in Figure 4.5.

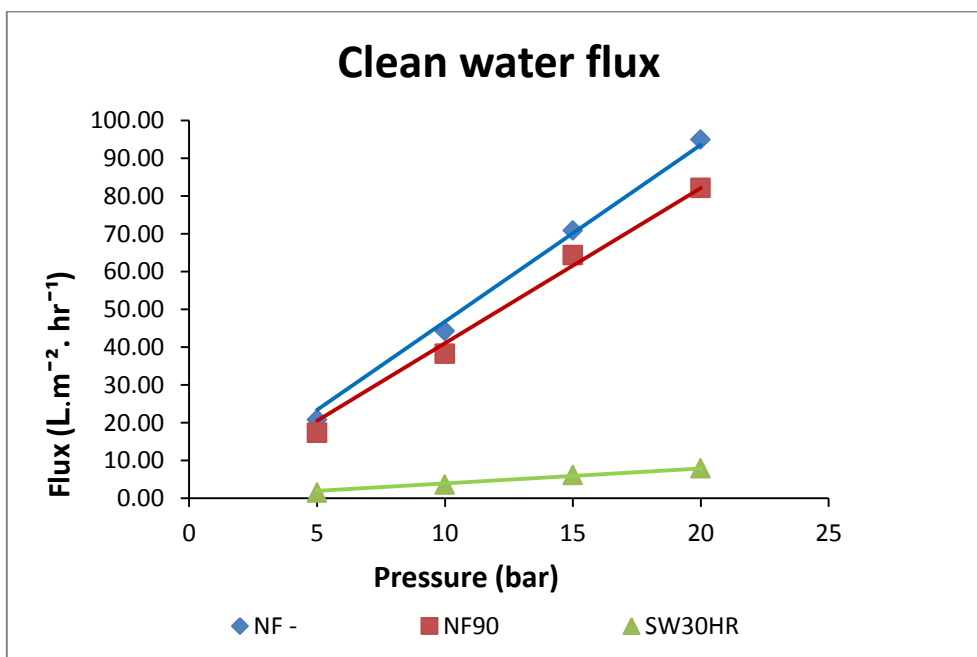


Figure 4.5 Flux through various membranes

Since molecular weight and charge or concentration polarization have effect on permeability, deionized water is used for flux studies in membrane characterization. The water flux (J_w) through the membranes is calculated by using Darcy's law [$J_w = A_w \cdot (\Delta P - \Delta \pi)$], where A_w is the water permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{hr}^{-1} \cdot \text{bar}^{-1}$). In this way the permeability of the membrane is determined with subsequent determination of the pore size.

NF⁻ was found to have the highest flux of $95.0 \text{ L} \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$ at 20 bar. This suggests that the membrane showed larger pore size distribution when compared to NF90 ($82.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$), and SW30HR ($8.0 \text{ L} \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$). The fluxibility was expressed in decreasing order as $\text{NF}^- > \text{NF90} > \text{SW30HR}$. It was consequently assumed that the pore sizes will follow the same trend.

Table 4.2 was a summary of clean water flexibility of the polymer membranes. NF- was of nanofiltration in nature where SW30HR showed the reverse osmosis (RO) tendencies. NF90 was also more of RO than nanofiltration but may have the tendency of nanofiltration.

Table 4.2 Clean water fluxibility on selected membranes

Membrane	$A_w (\text{L} \cdot \text{m}^{-2} \cdot \text{hr}^{-1} \cdot \text{bar}^{-1})$
NF-	4.68
NF90	3.34
SW30HR	0.39

4.5 Determination of single salt flux

Permeability of ions was performed during the investigation of flux measurements for single salts (NaCl , MgCl_2 , Na_2SO_4 and MgSO_4).

Figure 4. 6, Figure 4.7,

Figure 4. 8 and

Figure 4.9 show selected membranes tested for different salts for 20 ppm concentration at 20 bar during fluxibility measurements.

4.5.1 NaCl Salt Flux

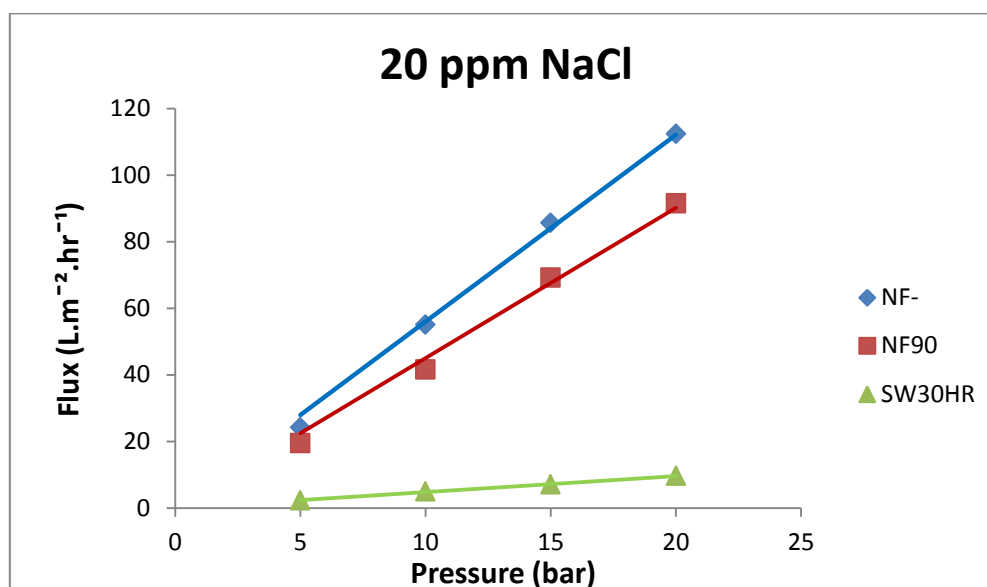


Figure 4. 6 NaCl flux on selected membranes

For NaCl flux with a concentration of 20 ppm on selected membranes, NF- has the highest fluxibility ($5.61 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$) amongst the other membranes. Followed by NF90 with a fluxibility of $4.51 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$ and SW30HR showed the lowest fluxibility of $0.48 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$ (illustrated in Table 4.3). The decreasing order of the flux was the same as the clean water flux ($\text{NF}^- > \text{NF90} > \text{SW30HR}$). The behavior was because of the pore size of the membranes, as it was mentioned in Figure 4.5 that NF- showed a large pore size distribution in comparison to other membranes.

4.5.2 MgCl₂ Salt Flux

NF- showed higher fluxibility ($4.57 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$) for 20 ppm MgCl₂ at 20 bar as compared to other two membranes, followed by NF90 with a fluxibility of $4.23 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$ and lastly SW30HR showed a fluxibility of $0.43 \text{ L.m}^{-2}.\text{hr}^{-1}.\text{bar}^{-1}$. The

behaviour of these selected membranes on MgCl_2 flux was similar to clean water flux in terms of the flux trend ($\text{NF}^- > \text{NF90} > \text{SW30HR}$).

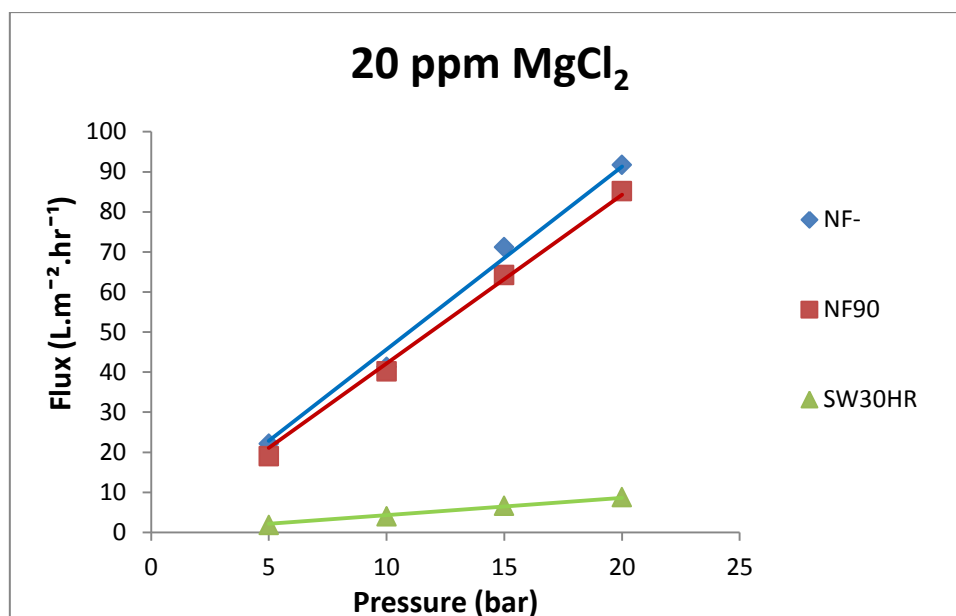


Figure 4.7 MgCl_2 flux on selected membranes

4.5.3 Na_2SO_4 Salt Flux

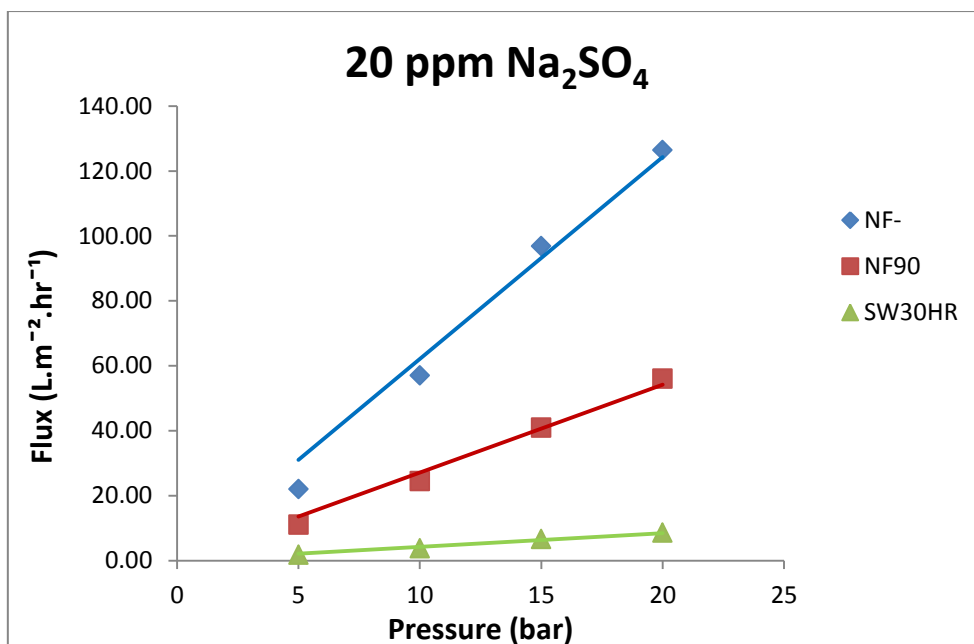


Figure 4. 8 Na₂SO₄ Flux on selected membranes

The fluxibility and the decreasing trend of 20 ppm Na₂SO₄ was the same as the NaCl and MgCl₂ flux, NF- with the highest flow of 6.21 L.m⁻².hr⁻¹.bar⁻¹, NF90 flux was 2.71 L.m⁻².hr⁻¹.bar⁻¹ and always the lowest flow of 0.42 L.m⁻².hr⁻¹.bar⁻¹ for SW30HR. NF- fluxibility of Na₂SO₄ was higher than that of NaCl and MgCl₂, this was because of the bigger SO₄²⁻ co-ion which was strongly pulled through the membrane surface. The membrane surface might be positively charged.

4.5.4 MgSO₄ Salt Flux

Even though the flow and the decreasing trend of MgSO₄ was the same as the above three salts (NaCl, MgCl₂ and Na₂SO₄) concentrations, NF- fluxibility was 3.98 L.m⁻².hr⁻¹.bar⁻¹ high but when compared with NF- flux of the above three salts concentrations it was the lowest (illustrated in the Table 4.3). This was similar for NF90 (1.78 L.m⁻².hr⁻¹.bar⁻¹) and SW30HR (0.32 L.m⁻².hr⁻¹. bar⁻¹), respectively these were caused by molecular weight as it was illustrated in Chapter 3, Table 3.1. The bigger the molecular weight, the lower the flux will be because of the porosity size on the membranes surface.

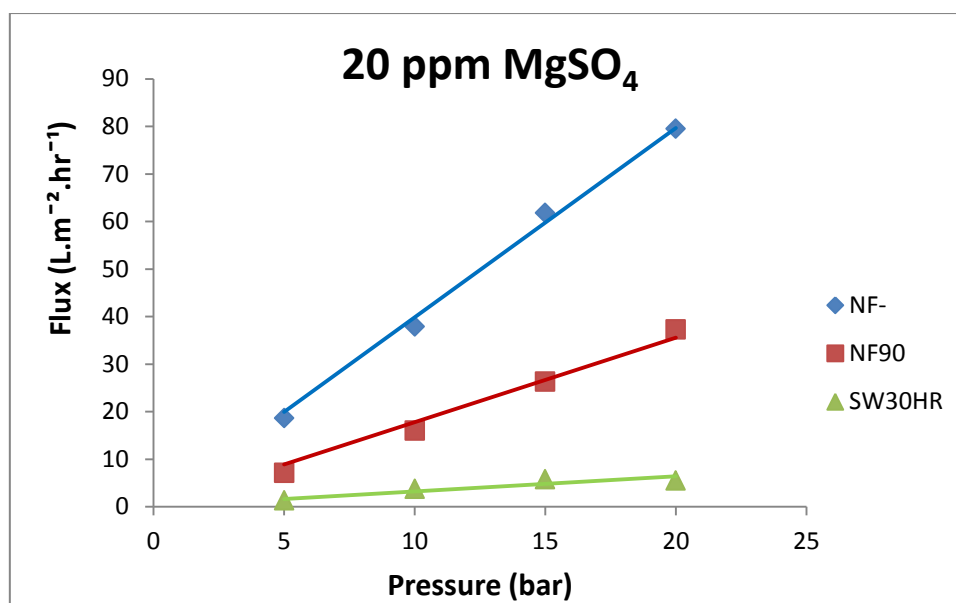


Figure 4.9 MgSO₄ flux on selected membranes

Table 4.3 Fluxibility measurements on different single salt at 20ppm

Membranes	NaCl (MW)	MgCl ₂ (MW)	Na ₂ SO ₄ (MW)	MgSO ₄ (MW)
NF-	5.61	4.57	6.21	3.98
NF90	4.51	4.23	2.71	1.78
SW30HR	0.48	0.43	0.42	0.32

The fluxibility measurements on NF- membrane for NaCl and Na₂SO₄ in the Table 4.3 showed that the charge density also plays a role.

The reason being that the molecular weight of Na₂SO₄ (119 g.mol⁻¹) was higher than that of NaCl (58.44 g.mol⁻¹), instead of NaCl fluxibility (5.6 L.m⁻².hr⁻¹.bar⁻¹) being higher than Na₂SO₄ (6.2 L.m⁻².hr⁻¹.bar⁻¹) was the other way around. The assumption was NF- membrane could be a positive membrane, but this will be further concluded by rejection measurements.

4.6 Polymer membrane rejection of single salts: The effect of molecular charges

The rejection behaviour of charged solute (NaCl, MgCl₂, Na₂SO₄ and MgSO₄) as single salt on three selected membrane was evaluated at a concentration of 20 ppm each with varying pressure (5 to 20 bar). Rejection was calculated as follows:

$$R = 1 - \frac{C_p}{C_f}$$

4.6.1 Rejection of NaCl (Na⁺)

20 ppm NaCl (as Na⁺) concentration with varying pressure of 5 to 20 bar are highly rejected on all membranes (NF- , NF90, and SW30HR) as shown in Figure 4.10. NF90 showed the highest rejection of 98.0%, SW30HR was 95.0% and with NF- showing 80.0% rejection. NF90 and SW30HR membranes had higher rejection than NF- because of the pore size on the membrane surface and again the higher the flux, the lower the rejection.

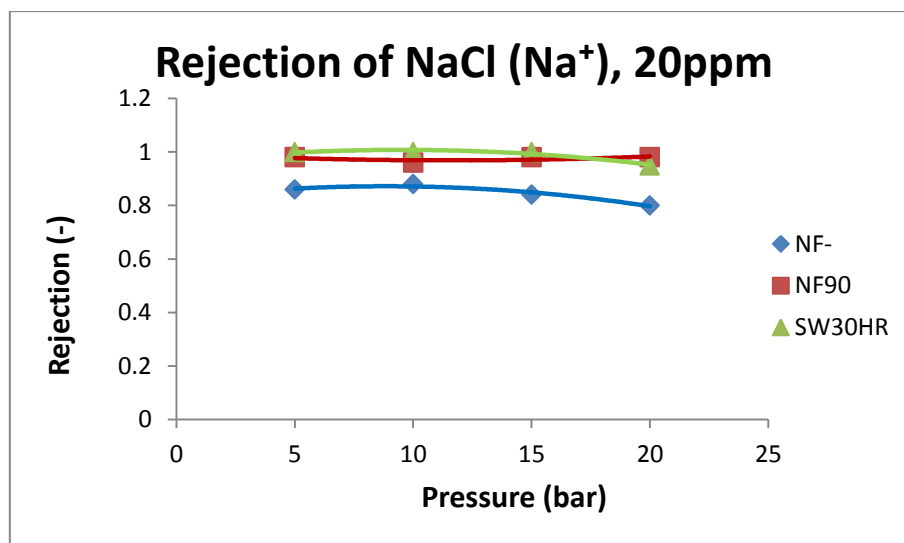


Figure 4.10 Plot of rejection vs pressure of NaCl

4.6.2 Rejection of MgCl_2 (Mg^{2+})

In Figure 4.11, MgCl_2 (as Mg^{2+}) at a concentration of 20 ppm with varying pressure of 5 to 20 bar was also highly rejected by NF-, NF90 and SW30HR membranes. This could be because of the Mg^{2+} divalent nature and size.

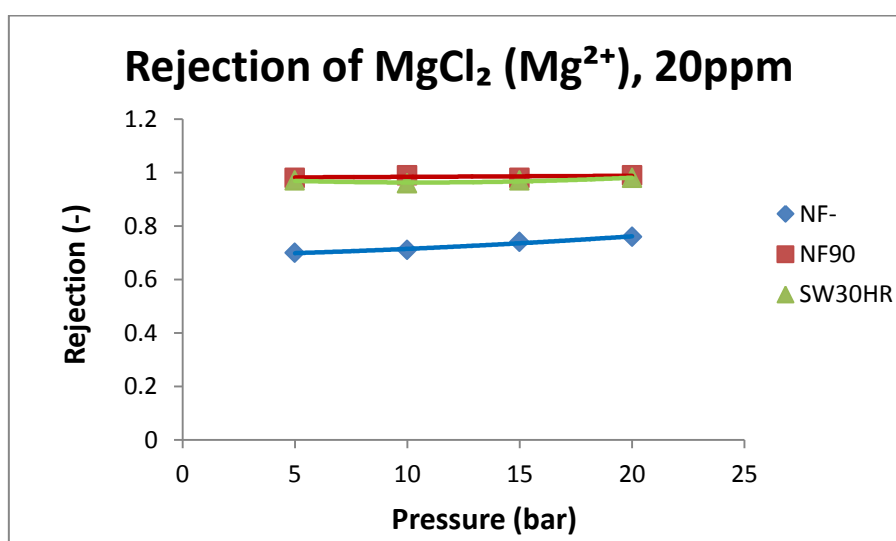


Figure 4.11 Plot of rejection vs pressure of MgCl_2

4.6.3 Rejection of Na_2SO_4 (Na^+)

For 20 ppm Na_2SO_4 concentration as Na^+ shown in Figure 4.12, all the membranes (NF-, NF90 and SW30HR) performed the same with good rejection at 20 bar. This could be because of the Na^+ monovalent nature and size.

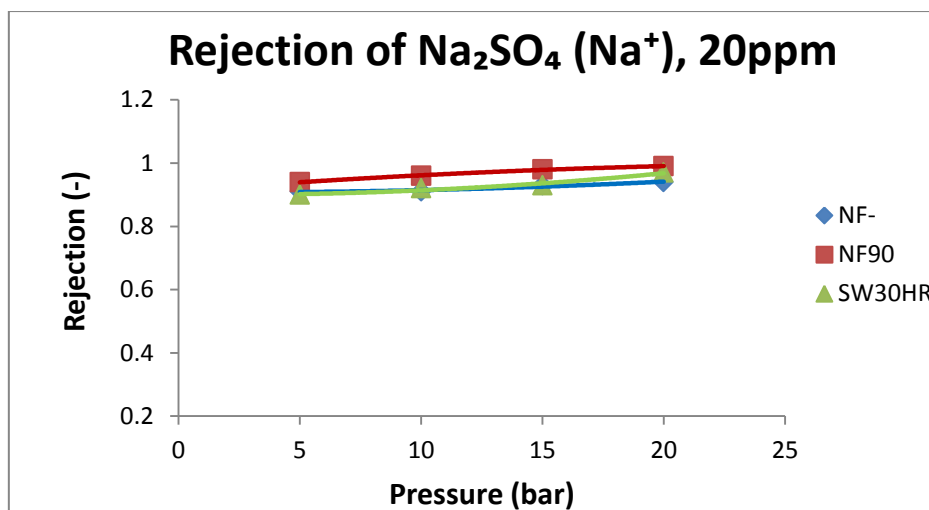


Figure 4.12 Plot of rejection vs pressure of Na₂SO₄

4.6.4 Rejection of MgSO₄ (Mg²⁺)

Rejection on MgSO₄ as Mg²⁺ at 20 ppm concentration with varying pressure of 5 to 20 bar in Figure 4.13, NF90 and SW30HR membranes performed excellent with 100% rejection. NF- membrane rejected only 66.0%. This could be because of the bigger SO₄²⁻ co-ion with the high electronegativity and larger molecular size.

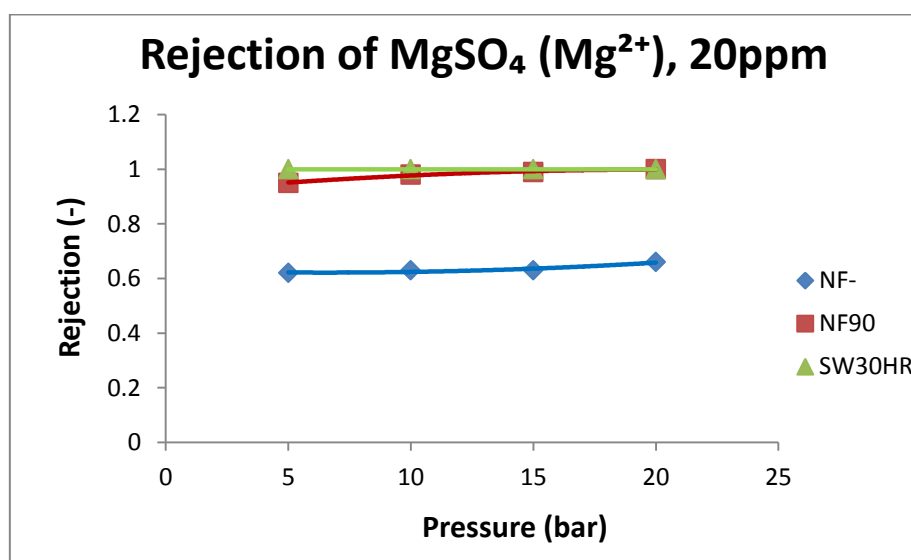


Figure 4.13 Plot of rejection vs pressure of MgSO₄

Table 4. 4 Measurement of single salt rejection

All the three membranes were very good in terms of rejection. MgSO_4 salt was 100% rejected on NF90 and SW30HR membranes (Table 4. 4).

Membranes	NaCl	MgCl_2	Na_2SO_4	MgSO_4
NF-	80.0%	76.0%	94.0%	66.0%
NF90	98.0%	99.0%	99.0%	100%
SW30HR	95.0%	98.0%	97.0%	100%

4.7 Determination of binary salt system

NF90 membrane was eliminated from binary salt system and through all the investigations following.

4.7.1 Effect of NaCl / MgCl_2 system on flux

Figure 4.14 showed single and binary salt flux on NaCl / MgCl_2 system using Nf- and SW30HR membranes. The flux was low on binary salts as compared to single salts and this was caused by the big molecular weight which struggles to pass through the pores of the membrane unlike in single salts.

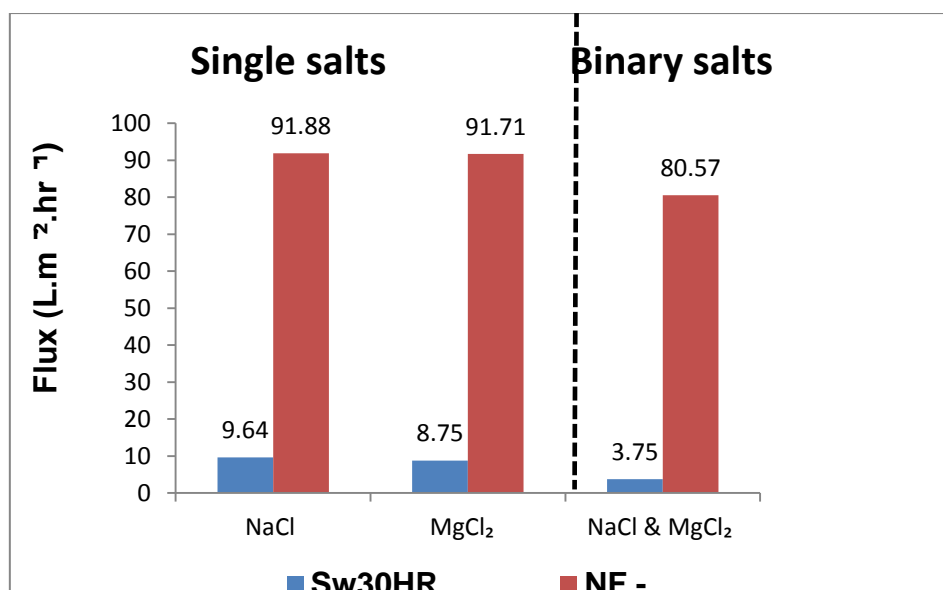


Figure 4.14 Single vs Binary salts (NaCl / MgCl₂) system

4.7.2 Effect of NaCl / Na₂SO₄ system on flux

The flux for binary salts (showed in Figure 4.15) on NaCl / Na₂SO₄ system was lower than in single salts, which was expected from the membranes. It was not easy for binary salts to pass through the membrane pores like in single salts and was because of their bigger molecular weight as they (Na⁺/Na⁺) struggle to pass through the pores.

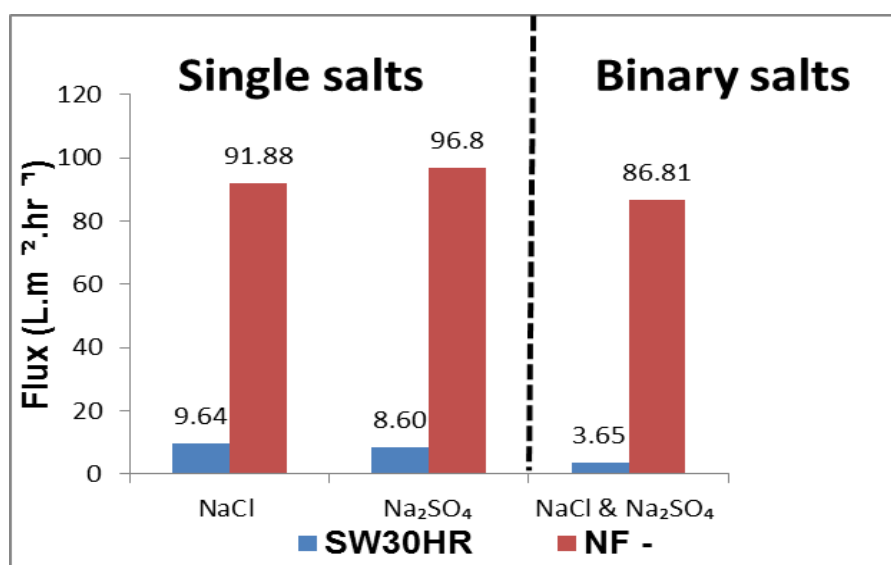


Figure 4.15 Single vs Binary salts (NaCl / Na₂SO₄) system

4.7.3 Effect of MgCl₂ / MgSO₄ system on flux

For both of the membranes (SW30HR and NF-) performance using binary salts system,

Figure 4.16 showed that the flux was higher than when compared with single salt on MgSO₄. This might be caused by the negative surface charge density on the membrane. For MgCl₂ single salt when compared with binary salt system the flux of Mg²⁺/Mg²⁺ was as expected for both membranes (SW30HR and NF-).

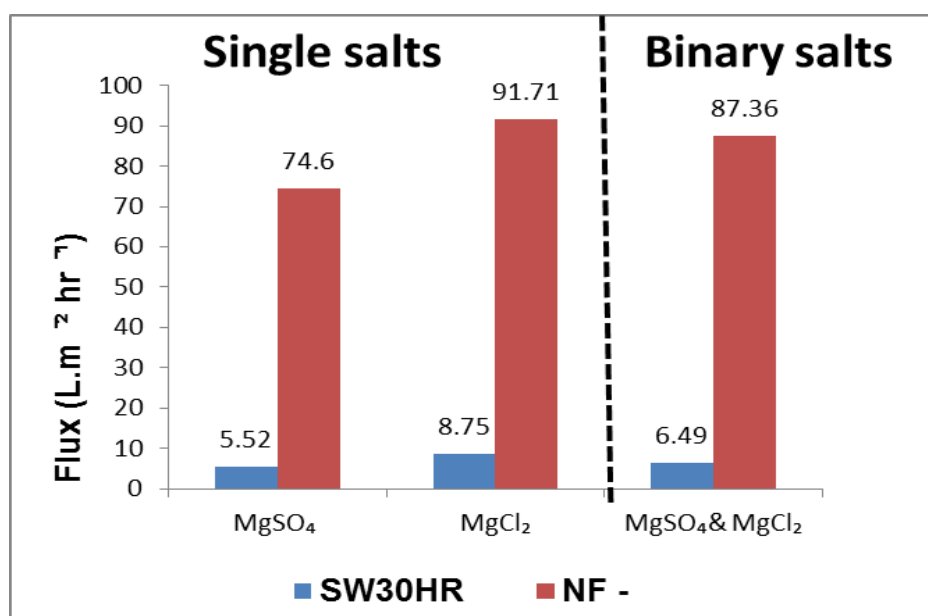


Figure 4.16 Single vs Binary salts (MgCl₂ / MgSO₄) system

4.7.4 Effect of MgSO₄ / Na₂SO₄ system on flux

Figure 4.17 showed a flux of single salts compared with binary salts on SW30HR and NF- membranes and the results were as expected that binary salts flux being lower than single salts.

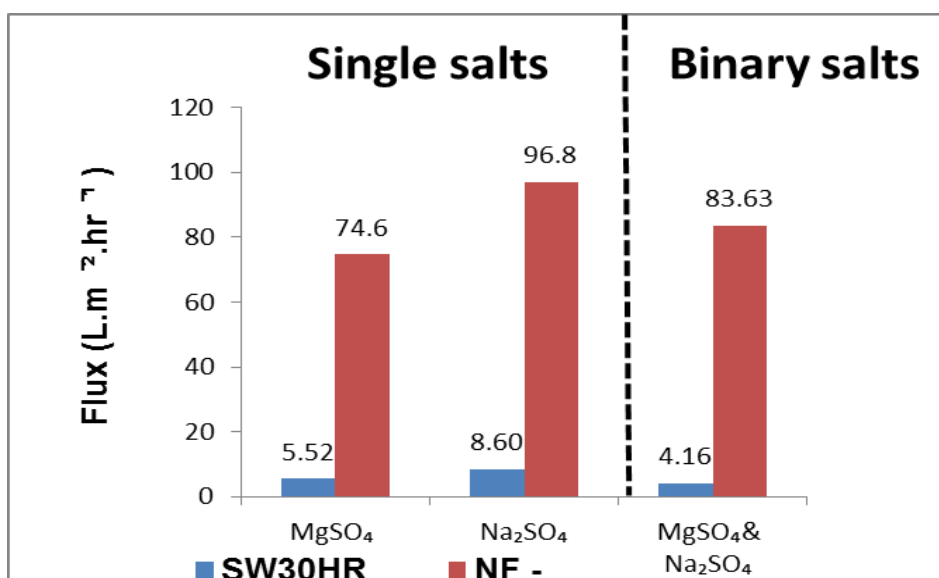


Figure 4.17 Single vs Binary salts (MgSO₄ / Na₂SO₄) system

NF- membrane flux on single salt (MgSO₄) behaves differently with a lower flux than in binary salts flux. This might be caused by the negative surface charge of the density as well.

4.8 Rejection of binary salt system

4.8.1 Rejection of NaCl as Na⁺ / MgCl₂ as Mg²⁺

Single salts were better rejected than when binary system as shown in Figure 4.18. SW30HR and NF- membranes highly rejected single salts than binary salts of NaCl as Na⁺ and MgCl₂ as Mg²⁺. Charge density played a big role on the membrane surface in both membranes. Both membranes still have good rejection of binary salts.

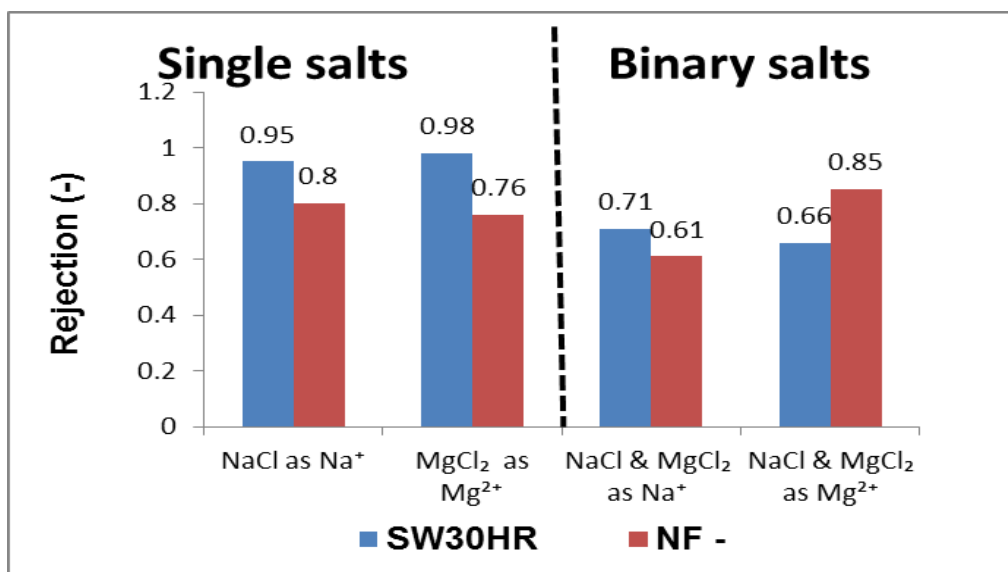


Figure 4.18 Rejection of single and binary salts ions (Na⁺ / Mg²⁺)

4.8.2 Rejection on NaCl and Na₂SO₄ as Na⁺

Figure 4.19 shows higher rejection of single salts than in binary salts, and SW30HR membranes rejecting better than NF- membrane. This is because SW30HR membrane is denser than NF- membrane. NaCl as Na⁺ on single salts rejection was the same as in binary salts on NF- membrane but for Na₂SO₄ as Na⁺ single salt rejection was better than in binary salts. This could be because of the bigger molecular size.

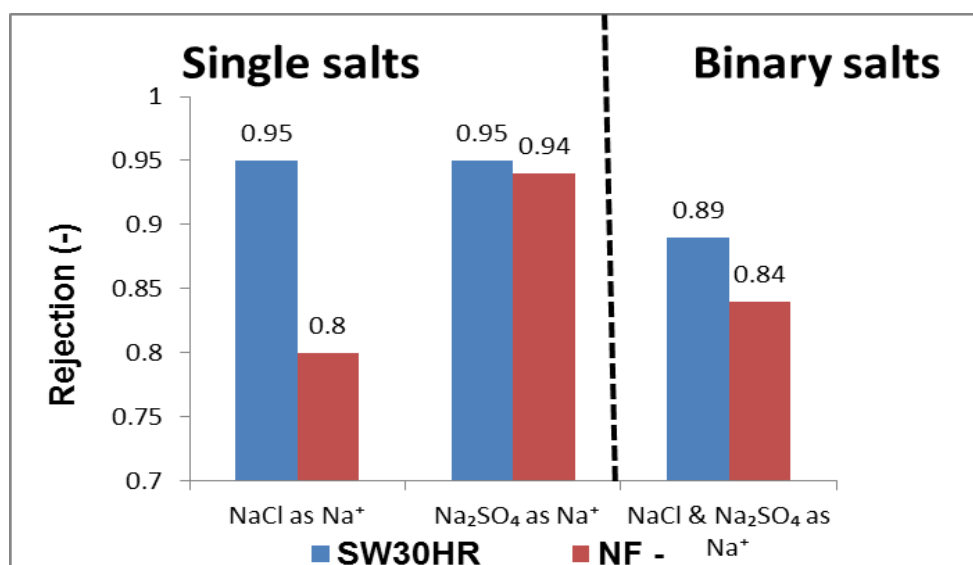


Figure 4.19 Rejection of single and binary salts ions (Na^+)

4.8.3 Rejection of MgCl_2 / MgSO_4 as Mg^{2+}

For single salts, SW30HR rejects better than NF- but of binary salts, NF- showed better rejection than SW30HR as illustrated in Figure 4.20. This was because of the dense SW30HR membrane and the charge density on the NF- membrane surface. MgSO_4 as Mg^{2+} of single salts did not go through the pores of SW30HR membrane at all, which means it was 100% rejected and MgCl_2 as Mg^{2+} was 98% rejected.

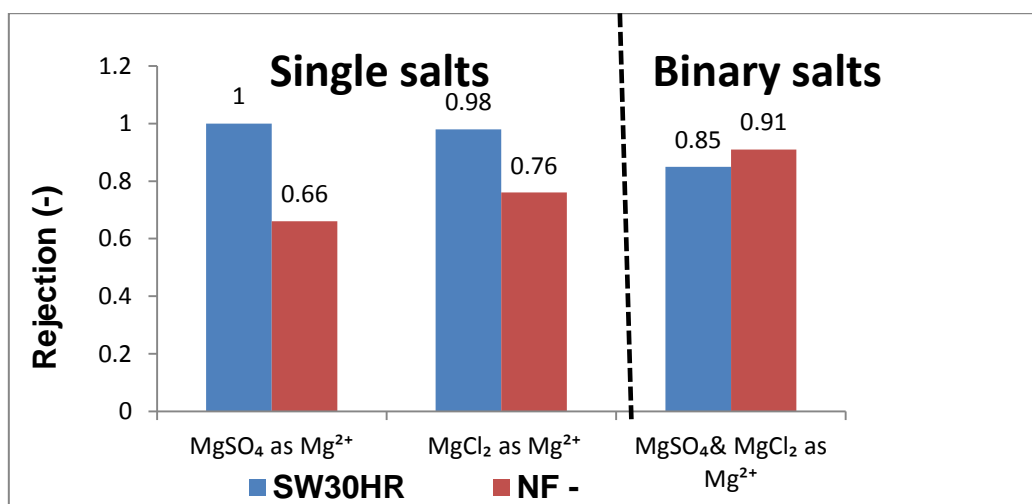


Figure 4.20 Rejection of single and binary salts ions (Mg^{2+})

4.8.4 Rejection of MgSO_4 as Mg^{2+} / Na_2SO_4 as Na^+

Single and binary salts in Figure 4.21, shows similar rejection of MgSO_4 and Na_2SO_4 concentrations in both SW30HR and NF- membranes, except for MgSO_4 as Mg^{2+} for single salt with 100% rejection on SW30HR membrane.

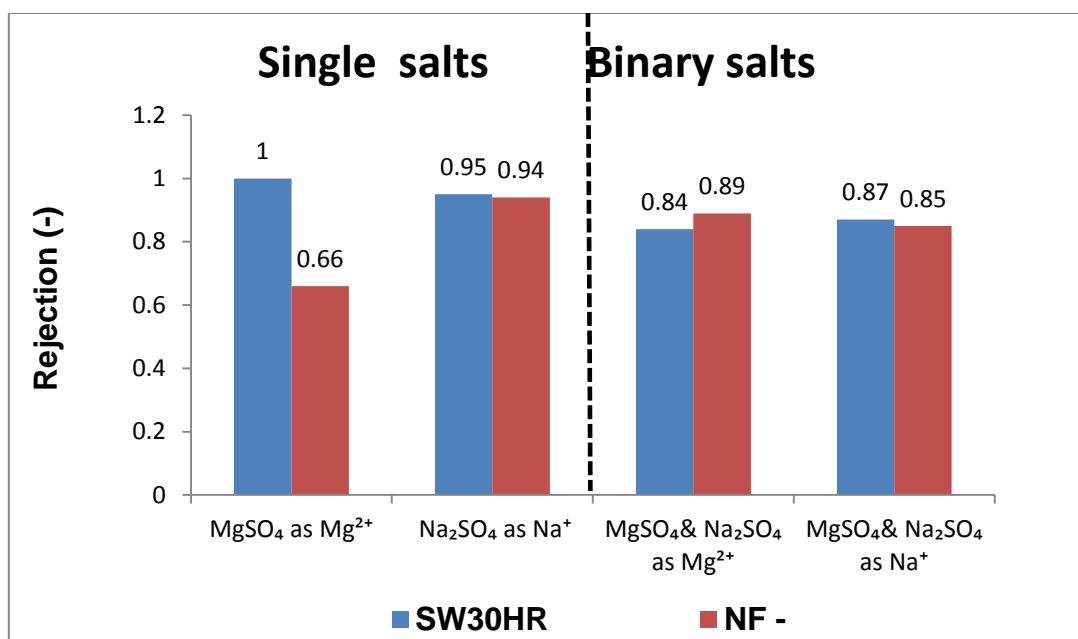


Figure 4.21 Rejection of single and binary salts ions (Na⁺ / Mg²⁺)

SECTION B: INDUSTRIAL APPLICATION

4.9 DMS Powders process water

Routine analysis for DMS process water monitored for two years are illustrated in Table 4.5, which indicates average pollutants levels at three different plants. Pollutants are calcium hydrogen (CaH), magnesium hydrogen (MgH), total hardness (TH), conductivity (cond) and pH. The M8A showed lower levels of pollutants on conductivity and total hardness as compared to M8B and M9. The average pH was stable at all plants, which was around 9. Figure 4.22 for M8A, Figure 4.23 for M8B and Figure 4.24 for M9 also showed DMS Powders pollutants for each plant.

Table 4.5 DMS Powders pollutants levels

Pollutants	M8A	M8B	M9
Conductivity	900ppm	2800ppm	2600ppm
Total hardness	400ppm	500ppm	500ppm
pH	9	9	9

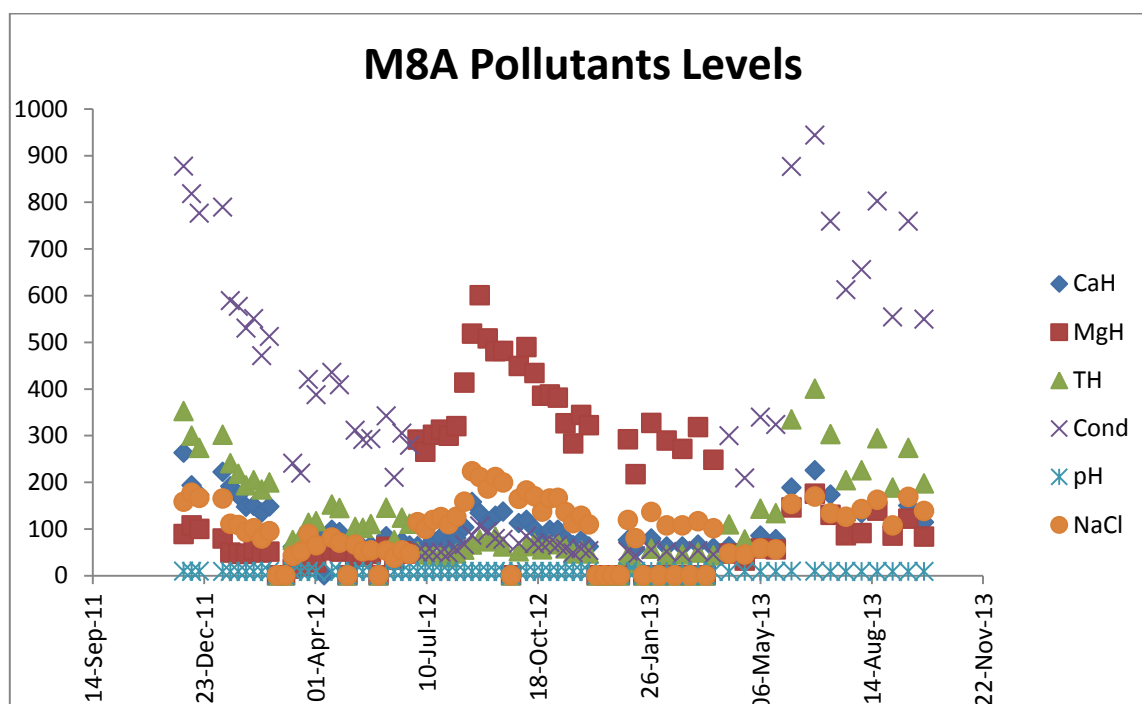


Figure 4.22 M8A pollutants levels

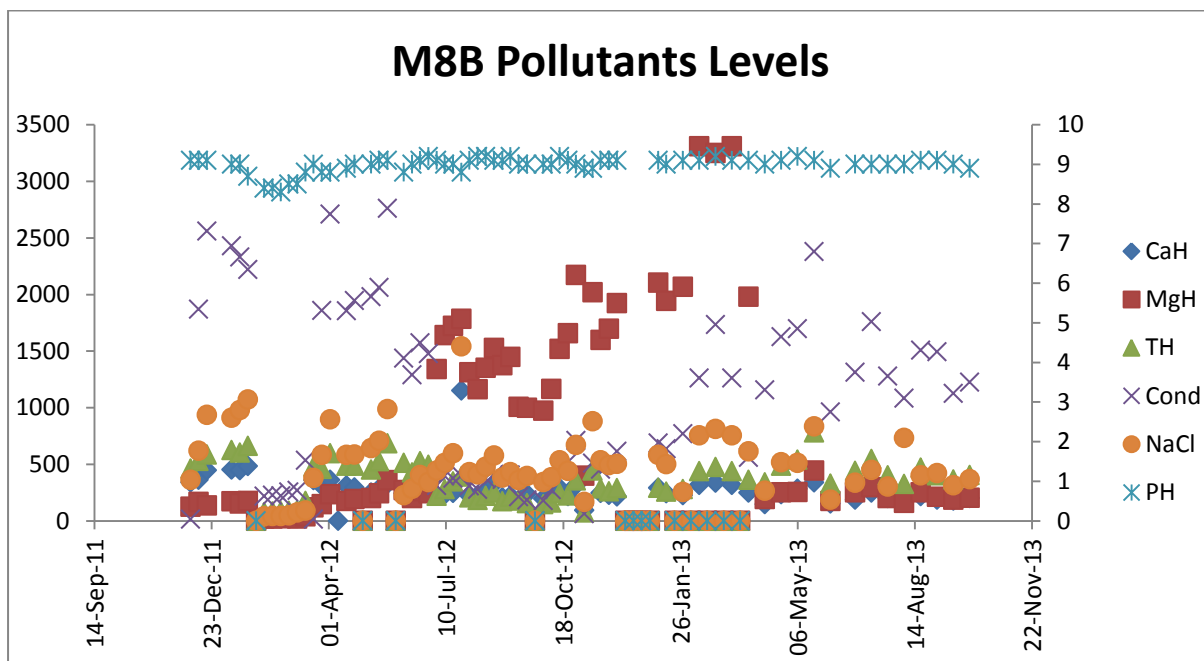


Figure 4.23 M8B pollutants levels

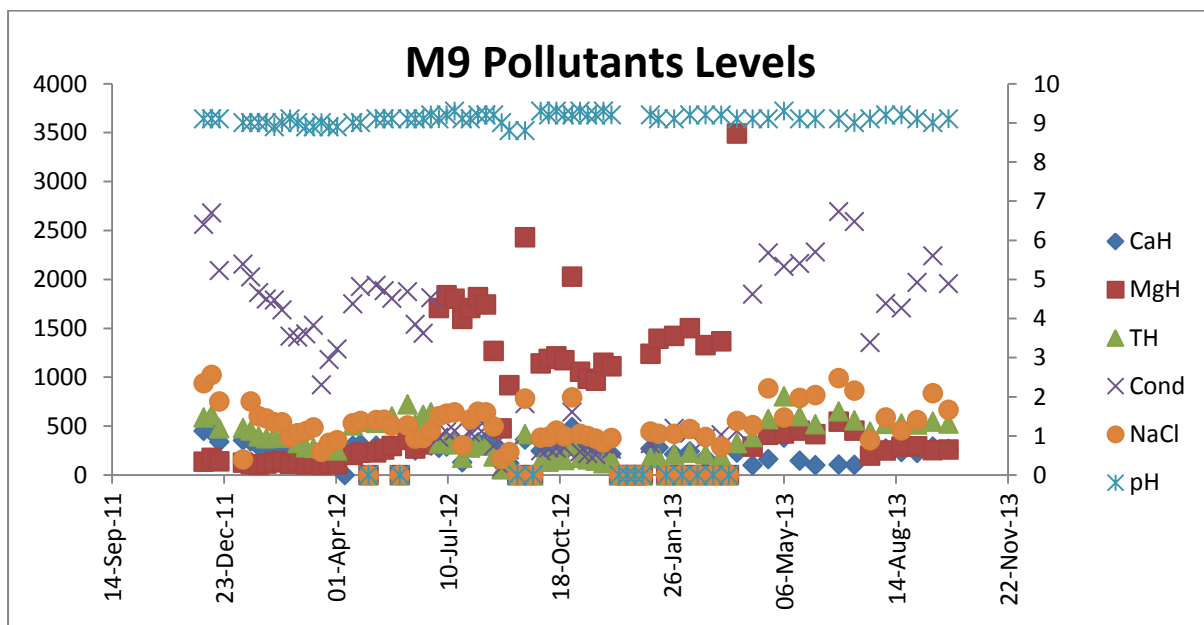


Figure 4.24 M9 pollutants levels

4.9.1 Flux on DMS Powders process water

In August and September 2013, process water samples were collected at DMS Powders, twice in a month at three different sampling points (M8A, M8B, and M9).

On the 5th of August 2013, M8A showed the highest flux of 63.0 L.m⁻².hr⁻¹ at a pressure of 20 bar as compared to M8B (40.2 L.m⁻².hr⁻¹) and M9 (13.3 L.m⁻².hr⁻¹) on NF- membranes. On the 19th August 2013, M8B showed the highest flux of 59.1 L.m⁻².hr⁻¹ as compared to M8A (52.1 L.m⁻².hr⁻¹) and M9 (33.9 L.m⁻².hr⁻¹). M8A again showed the highest flux of 77.5 L.m⁻².hr⁻¹ on the 16th September 2013 as compared to M8B (69.4 L.m⁻².hr⁻¹) and M9 (38 L.m⁻².hr⁻¹). Lastly on the 30th September 2013 both M8A and M8B have the same highest flux of 72.6 L.m⁻².hr⁻¹ and M9 still with the lowest flux of 35.4 L.m⁻².hr⁻¹. M9 showed the lowest flux all through these months compared to M8A and M8B. On average fluxibility through NF- were 3.3 L.m⁻².hr⁻¹.bar⁻¹ for M8A, 3.0 L.m⁻².hr⁻¹.bar⁻¹ for M8B and 1.5 L.m⁻².hr⁻¹.bar⁻¹ for M9.

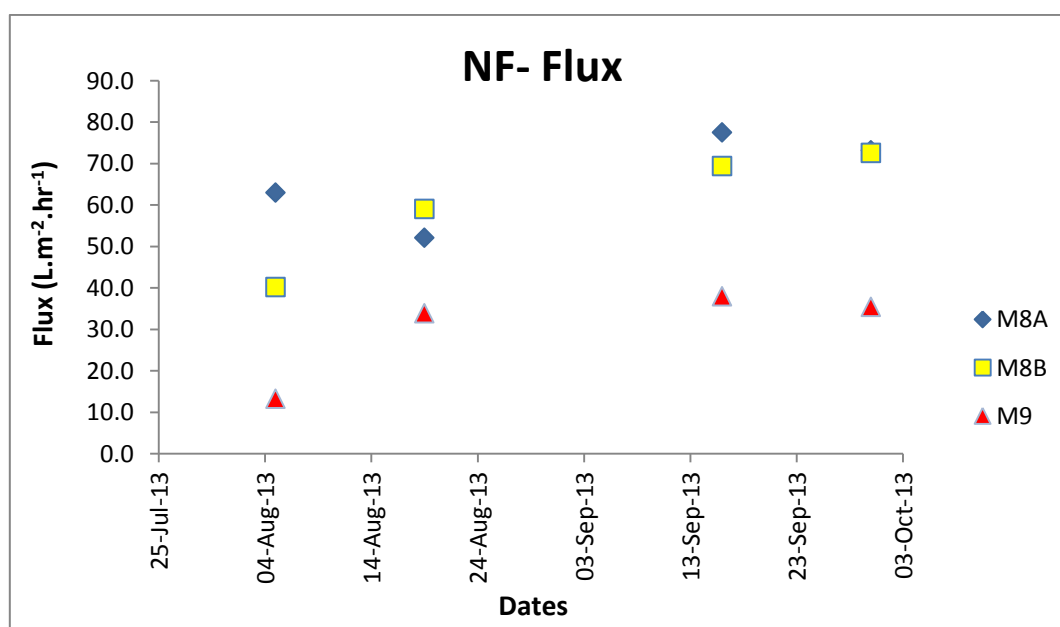


Figure 4.25 Flux on DMS process water for NF- membrane

On the 5th of August 2013, M8A showed the highest flux of 7.8 L.m⁻².hr⁻¹ at a pressure of 20 bar as compared to M8B (7.3 L.m⁻².hr⁻¹) and M9 (5.6 L.m⁻².hr⁻¹) on SW30HR membrane. On the 19th August 2013 both M8A and M8B showed the same highest flux of 8.9 L.m⁻².hr⁻¹ as compared M9 (6.1 L.m⁻².hr⁻¹). M8A again showed the highest flux of 6.5 L.m⁻².hr⁻¹ on the 16th September 2013 as compared to M8B and M9 both showed lowest flux of 5.5 L.m⁻².hr⁻¹. Lastly on the 30th September 2013 M8A showed the highest flux of 7.9 L.m⁻².hr⁻¹ as compared to both M8B and M9 with the same lowest flux of 6.8 L.m⁻².hr⁻¹. The flux for all three (M8A, M8B, and M9) sampled process water was very poor on SW30HR compared to NF- membrane flux. On average fluxibility through SW30HR were 0.39 L.m⁻².hr⁻¹.bar⁻¹ for M8A, 0.35 L.m⁻².hr⁻¹.bar⁻¹ for M8B and 0.30 L.m⁻².hr⁻¹.bar⁻¹ for M9.

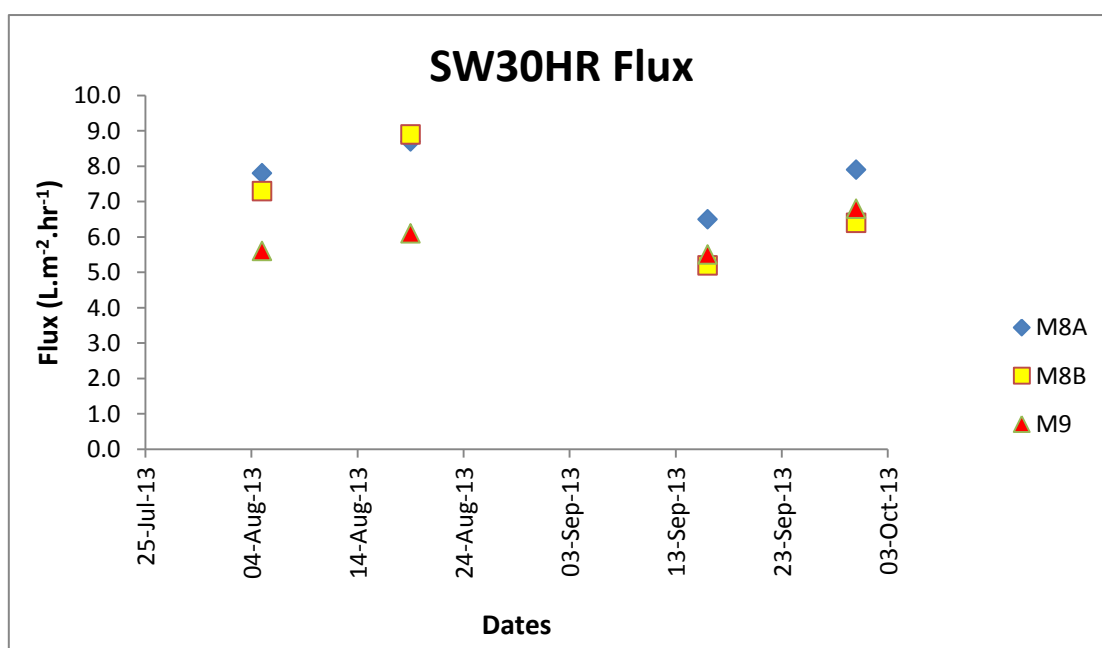


Figure 4.26 Flux on DMS process water for SW30HR membrane

For M8A process water fluxibility on both membranes was illustrated in Table 4.6. NF- showed the higher fluxibility than SW30HR, as it was expected. Fluxibility of M8A Plant was similar to that of single salt. SW30HR fluxibility was very poor, because of the dense pores on the membrane surface.

Table 4.6 Fluxibility on both membranes (NF- and SW30HR) for M8A Plant

DATES	NF-	SW30HR
05 August 2013	3.15	0.39
19 August 2013	2.60	0.44
16 September 2013	3.88	0.33
30 September 2013	3.66	0.40
Average	3.32	0.39

NF- membrane fluxibility was higher than SW30HR membrane on M8B process water in **Error! Reference source not found.** The behaviour of both membranes (NF- and SW30HR) for M8B process water was the same as M8A.

Table 4.7 Fluxibility on both membranes (NF- and SW30HR) for M8B Plant

DATES	NF-	SW30HR
05 August 2013	2.00	0.37
19 August 2013	3.00	0.45
16 September 2013	3.50	0.26
30 September 2013	3.63	0.32
Average	3.03	0.35

Table 4.8 showed fluxibility of both membranes (NF- and SW30HR) on M9 process water. NF- membranes showed the higher fluxibility than SW30HR membrane. The fluxibility was expressed in decreasing order as M8A > M8B > M9 for both membranes (NF- and SW30HR). The behaviour of the membranes was the same as compared to synthetic water.

Table 4.8 Fluxibility on both membranes (NF- and SW30HR) for M9 Plant

DATES	NF-	SW30HR
05 August 2013	0.67	0.28
19 August 2013	1.70	0.31
16 September 2013	1.90	0.28
30 September 2013	1.77	0.34
Average	1.51	0.30

4.9.2 Rejection of DMS Powders process water

The two figures (Figure 4.27 and Figure 4.28) illustrate the rejection of DMS Powders process water on selected membranes (NF- and SW30HR).

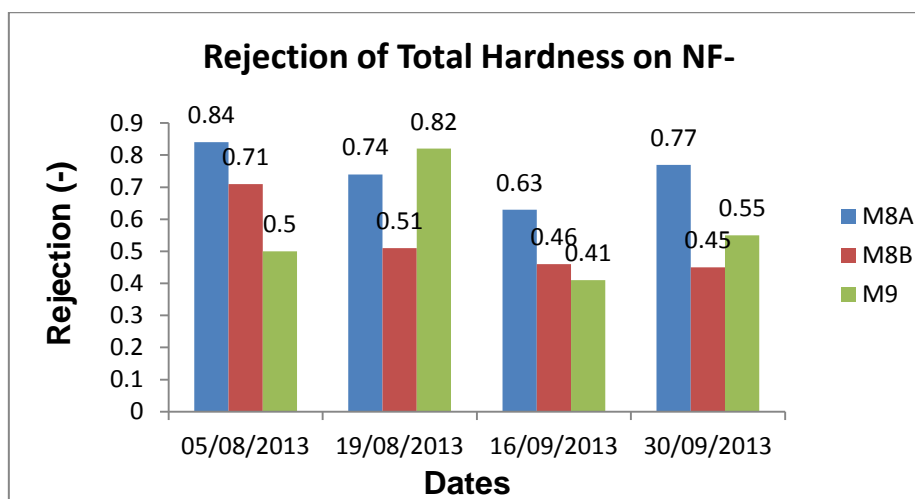


Figure 4.27 Rejections of Total Hardness on NF- membranes

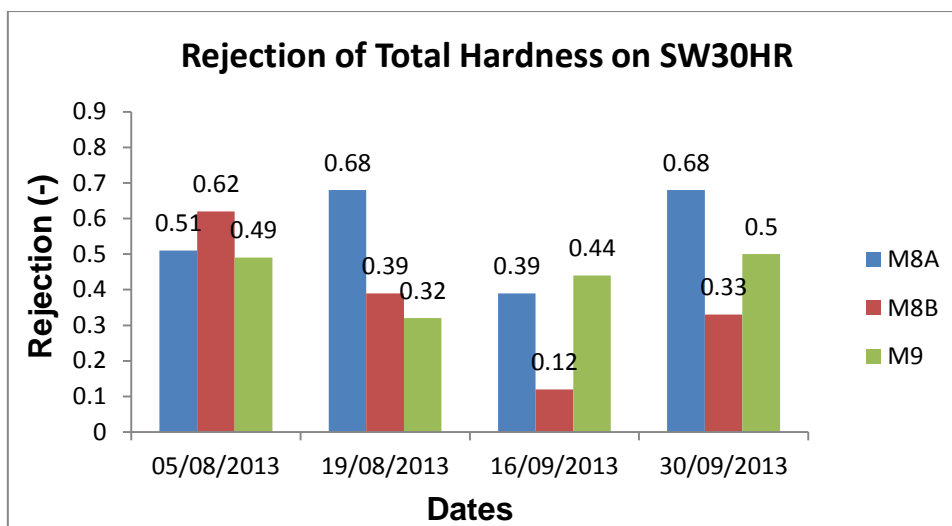


Figure 4.28 Rejections of Total Hardness on SW30HR membranes

NF- and SW30HR membranes behaviour were not the same as compared to rejection on the synthetic water. NF- membrane showed higher rejection than SW30HR membrane, which the cause could be pollutants rejected on process water and how they reacted on the surface membrane.

4.10 Fouling of DMS Powders process water

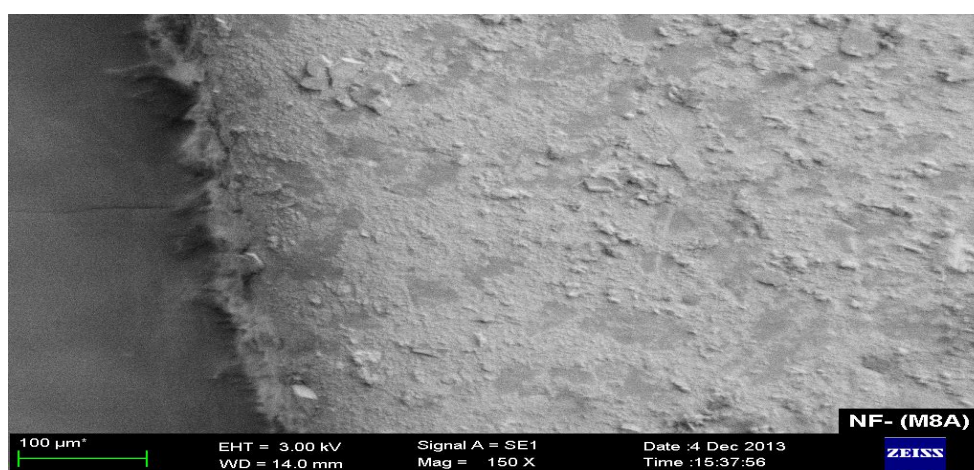


Figure 4.29 Fouling on NF- membrane for M8A effluent

The assumption was that the charge density on the membranes surface also played a part in rejection of DMS Powders process water.

Concentration polarization was formed on NF- membrane for M8A process water as shown in Figure4.29. The pores were starting to block on the surface of the membrane that lead to fouling. M8A pollutants on NF- membrane were highly rejected by 63.0 – 84.0%.

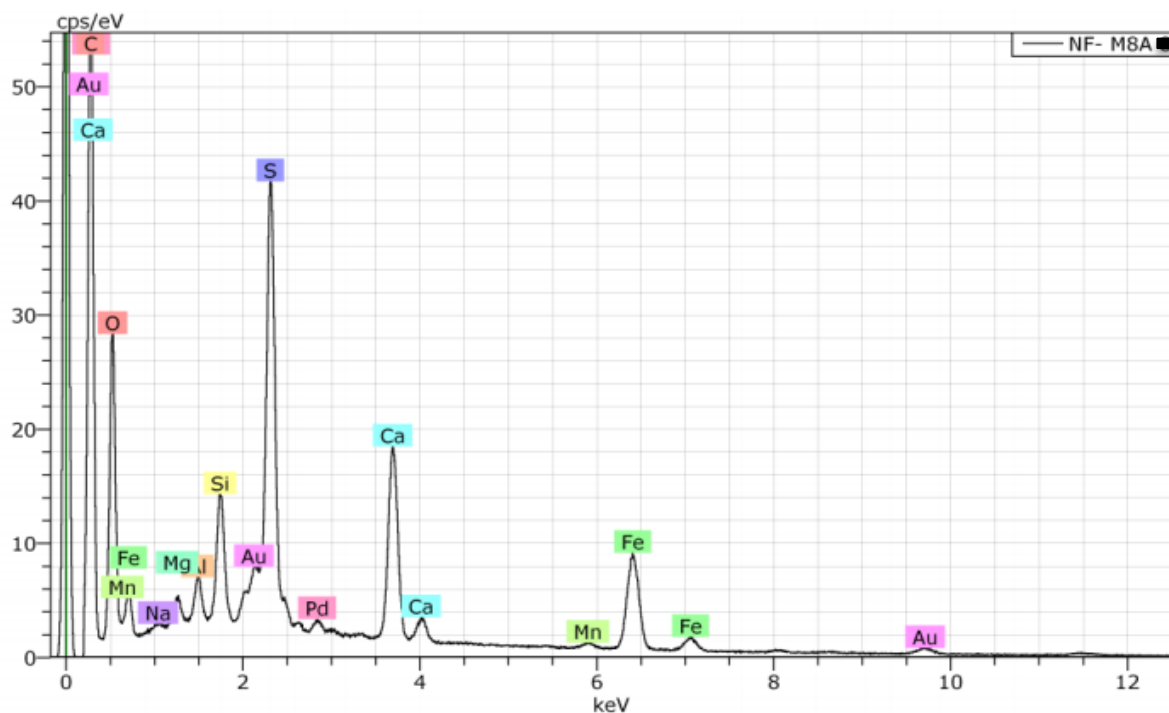


Figure 4.30 EDX analyses on NF- membrane for M8A effluent

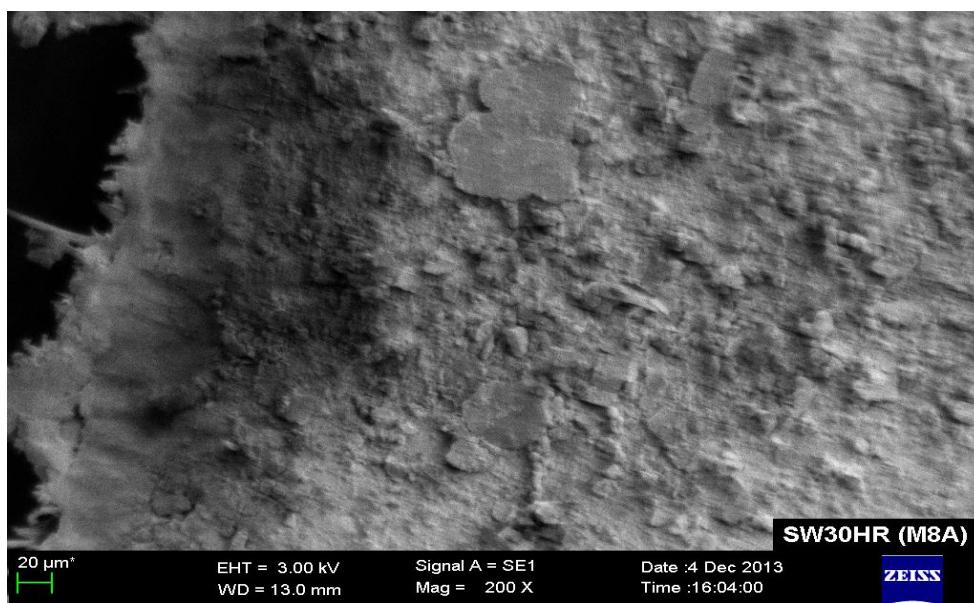


Figure 4.31 Fouling on SW30HR membrane for M8A effluent

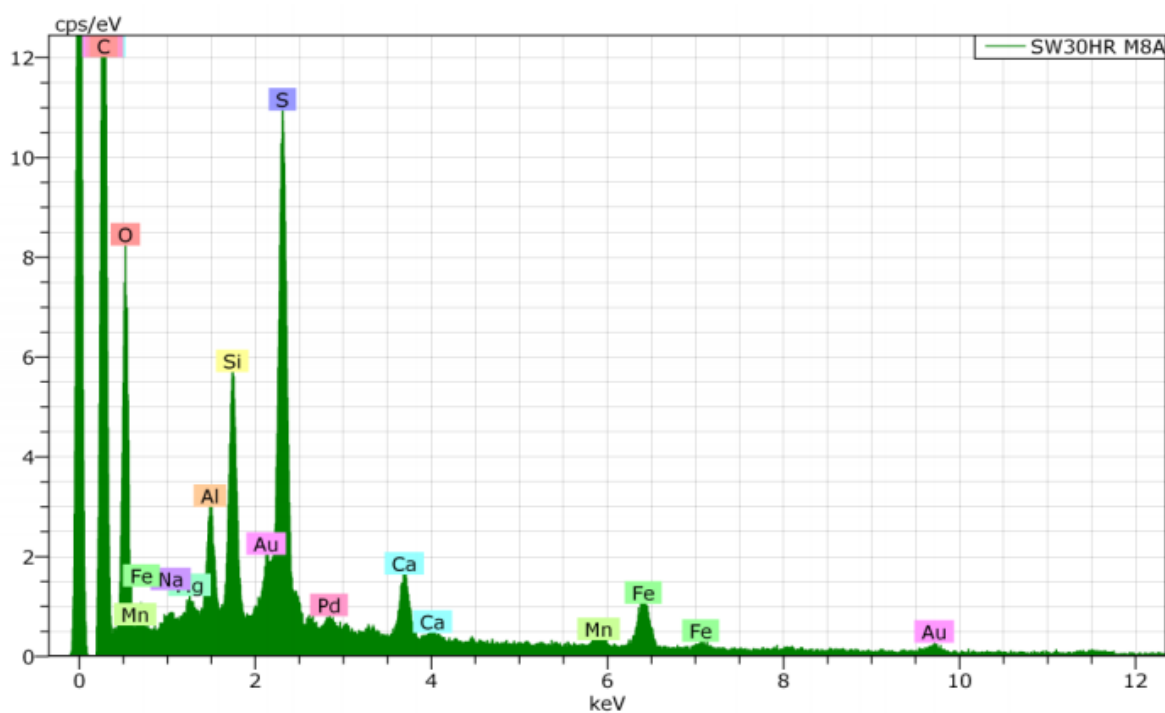


Figure4.32 EDX analyses on SW30HR membrane for M8A effluent

The surface area of SW30HR membrane was fouled by M8A pollutants found in process water. Crystals were formed on the top layer of the SW30HR as indicated in

Figure 4.. SW30HR rejection was poor (39.0 – 68.0%) when compared to NF-membrane. This could be the suspended solids were not highly concentrated at M8A plant.

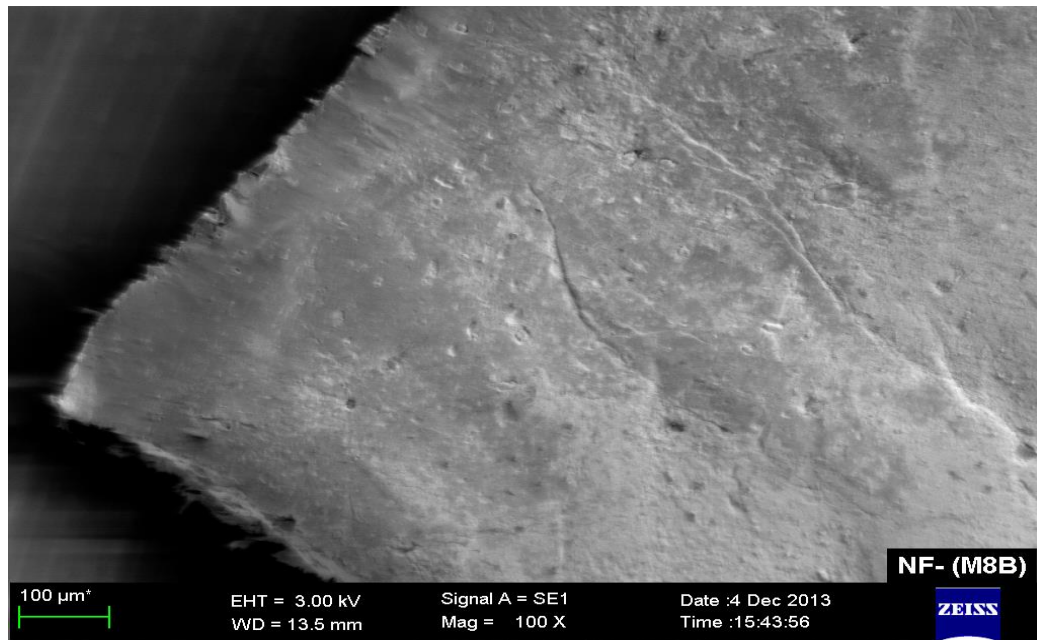


Figure 4.33 Fouling on NF- membrane for M8B effluent

A cake layer was formed on the surface area of NF- membrane for rejection on M8B process water as illustrated in Figure 4.. The pores on the NF- membrane surface were blocked by suspended solids in process water. Charge density played a bigger role on the NF- membrane surface.

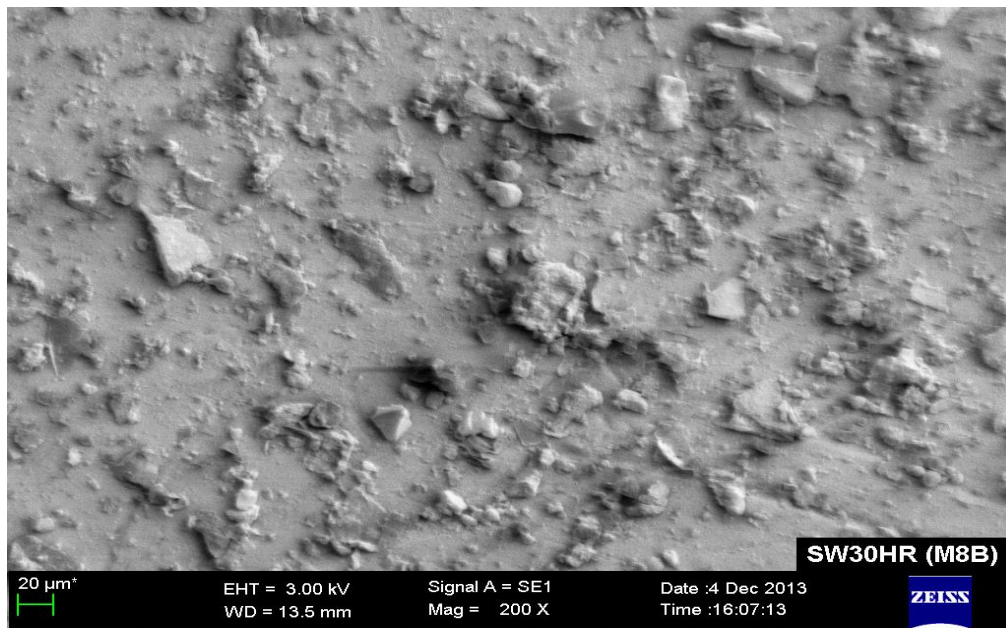


Figure 4. 34 Fouling on SW30HR membrane for M8B effluent

Figure4.34 showed crystals formed during M8B process water on SW30HR membrane. SW30HR membrane poorly rejected M8B pollutants as compared to NF-membrane rejection. This could be the suspended solids may have smaller size that managed to pass through the dense pores of SW30HR membrane.

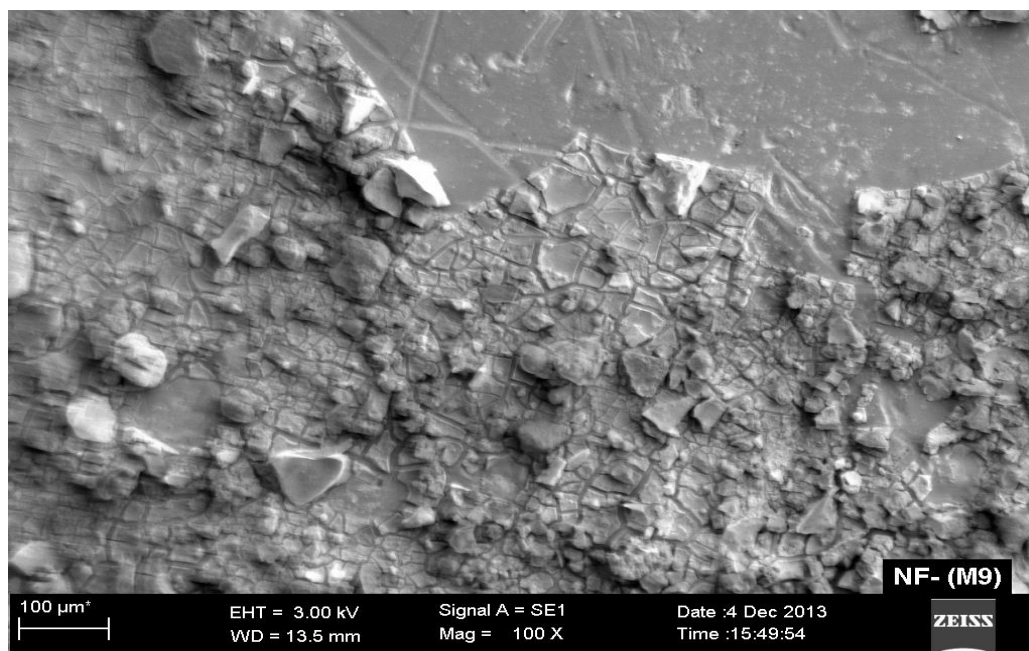


Figure 4.35 Fouling on NF- membrane for M9 effluent

Two layers (cake and crystallisation) were formed on NF- in Figure 4. for M9 process water. The crystallization was also due to concentration polarization at the membrane surface, which means M9 pollutants were highly rejected (41.0 – 82.0%) by NF- membrane. This indicated that at M9 plant suspended solids were highly concentrated.

Crystals were formed on the surface area of SW30HR for M9 process water in

Figure 4.. SW30HR still showed the poor rejection (30.0 to 50.0%) compared to NF- membrane. The assumption could be the membrane surface of SW30HR was neutral and the sizes of suspended solids were smaller than the pore size of the membrane.

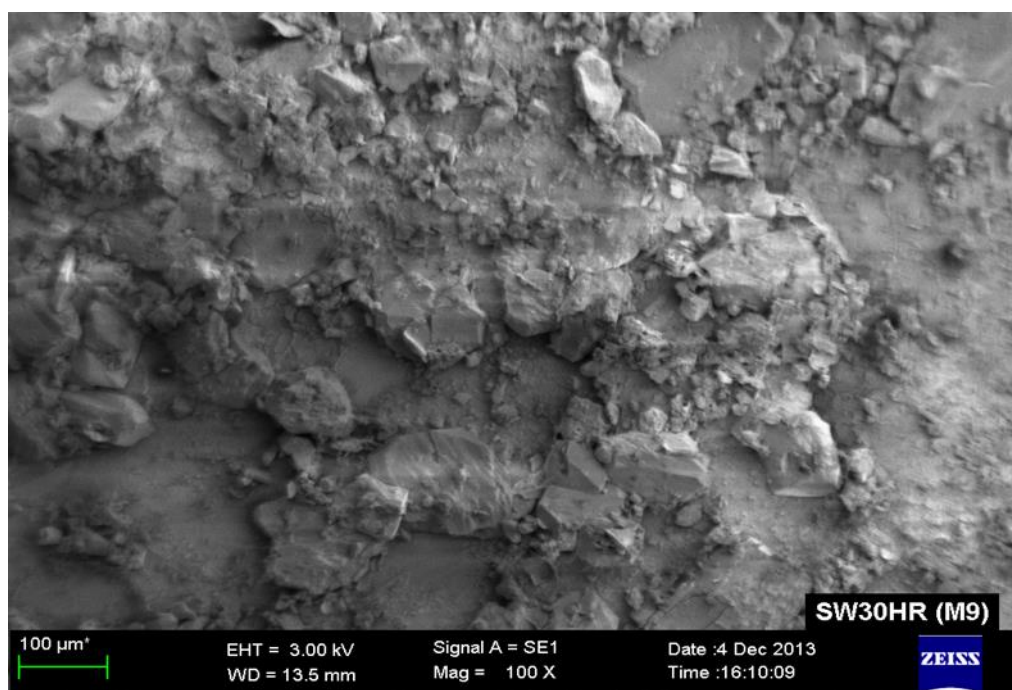


Figure 4.36 Fouling on SW30HR membrane for M9 effluent

Bibliography

Bandini, S., Drei, J. & Vezzani, D., 2005. The role of pH and concentration on the iron rejection in polyamide nanofiltration membranes. *J. Membr. Sci*, Volume 264, pp. 65 - 74.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

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5.1 Conclusion

Water is used for various applications during processes taking place in the industry and its quality changes due to introduction of contaminants. Industries are facing challenges of maintaining the current standards related to the quantity and quality of discharging wastewater into the environment. Pollution from industrial discharge produce high levels of suspended solids that can subsequently contaminate sediments within the surface water system. DMS Powders process water needs to be treated to maintain the water used in the plants and to comply with the legislature before effluent are being discharged. Membrane technology was considered as the best available technologies in many industrial processes and waste management applications.

In this study the aim was to treat DMS Powders process water using selected membrane processes. NF and RO were the most investigated membrane processes with a potential use in the chemical industries. During membrane characterization, flux measurements using pure water revealed the characteristics of the membranes before a sample was introduced to the membrane. The fluxibility of pure water and single salts (NaCl, MgCl₂, Na₂SO₄, and MgSO₄) at a concentration of 20ppm with varying pressure of 5 to 20 bar were expressed in decreasing order as NF⁻ > NF90 > SW30HR. Amongst the membranes investigated, NF- gave a higher flux than NF90 and SW30HR. This was because of the bigger pore size on the membrane surface.

Rejection studies on charged solutes (Na⁺ and Mg²⁺) were performed on single salts and binary salt system. For single salts at a concentration of 20ppm with varying pressure of 5 to 20 bar, charged solutes (Na⁺ and Mg²⁺) were highly rejected in all membranes (NF⁻, NF90, and SW30HR). For binary salt system (Na⁺ / Mg²⁺), the suggestion was that each cation rejection was compromised. The rejection of binary salt system was still high but not higher than single salts. NF⁻ membrane highly rejects binary salt system (NaCl / Na₂SO₄) than when they were single salts. This could cause by high electronegativity of the sulfate. Same results were observed in binary salts system of MgCl₂ / MgSO₄. The assumption was that NF⁻ membrane could be switching charge density to positive.

Investigations on selected membranes conclude that NF- membrane will be the suitable membrane for treatment of DMS Powders process water because of its high fluxibility and rejection. Discharged effluent of DMS Powders could comply with the legislature and environmental pollution could be minimised.

Selected membranes were successfully characterized by using clean water, SEM, TGA and DTA, and FTIR instruments. SEM revealed a smooth surface morphology of the selected membranes. TGA and DTA revealed the physical properties of the membranes and lastly FTIR revealed the polypiperazine and polyamide chemical structure and functional group of the NF- and SW30HR membranes.

DMS Powders permeate water was successfully quantified for suitability of recycling. The high flux on the suitable membrane selected will make the operation easier and save the energy costs in the plants.

Rejections of DMS Powders process water was successfully achieved by using the suitable membrane. The recovery of species such as suspended solids and metal ions were considered for recycling and reclamation.

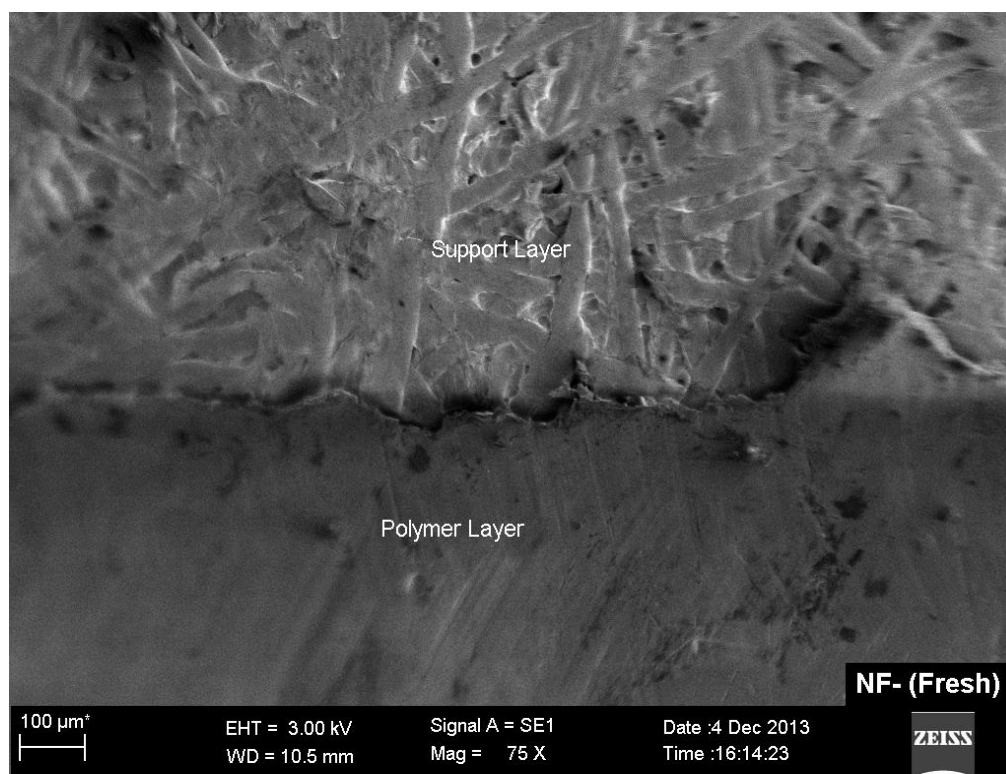
Fouling studies were also performed using samples from three different Plants (M8A, M8B, and M9) at DMS Powders. The study revealed that fouling does occur during treatment of process water. SW30HR showed that M9 Plant had more fouling for M9 samples than other Plants (M8A and M8B). It was because of higher concentrations in suspended solids.

5.2 Recommendations

- ❖ Membrane processes can be implemented at DMS Powders for process water treatment and for recycling closed loop water treatment plant.
- ❖ Industries that have similar effluent as DMS Powders can also use membrane processes.

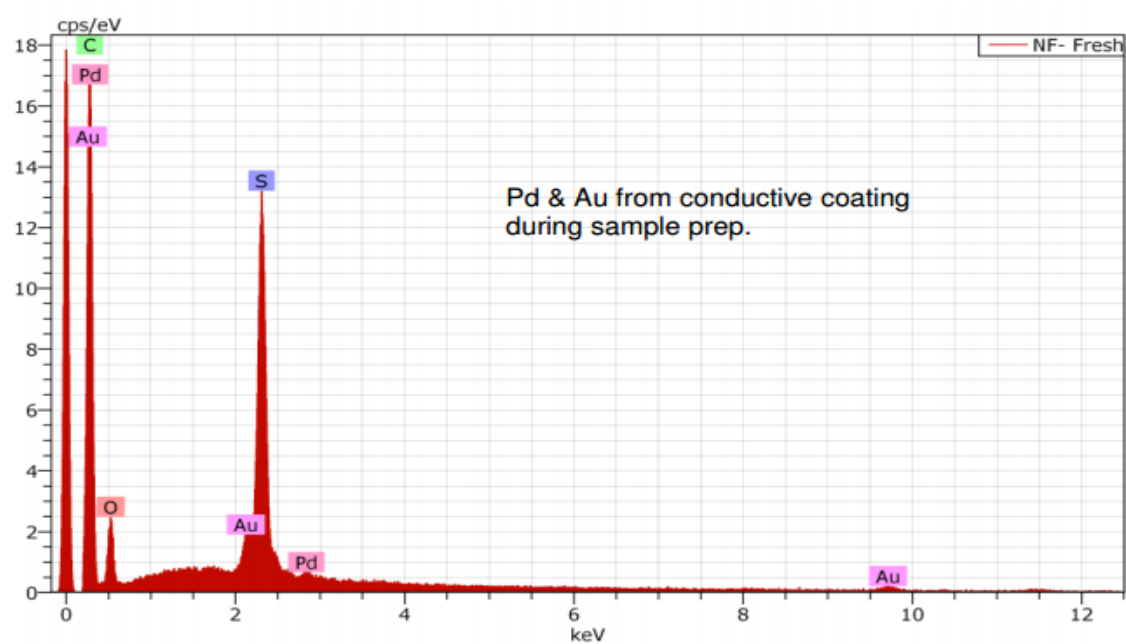
- ❖ Further studies can be done on other membrane processes for DMS Powders process water.
- ❖ Further studies can also be done on cleaning of membrane fouling and this can be avoided by pre - treatment.

APPENDIX A



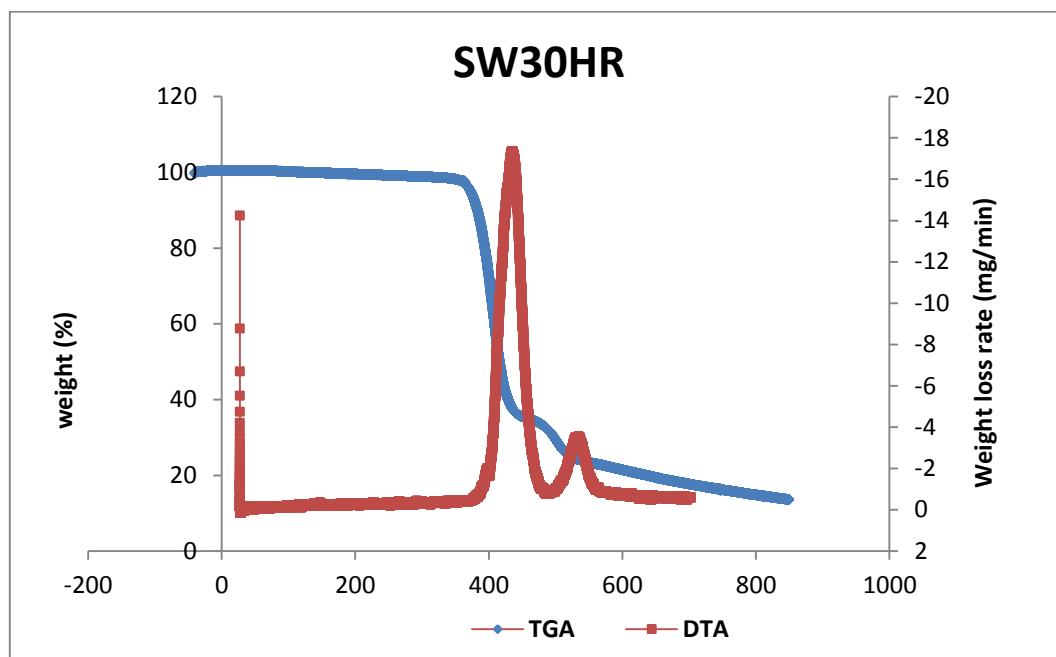
Cross Sectional view of NF- (Virgin) – membrane

APPENDIX B



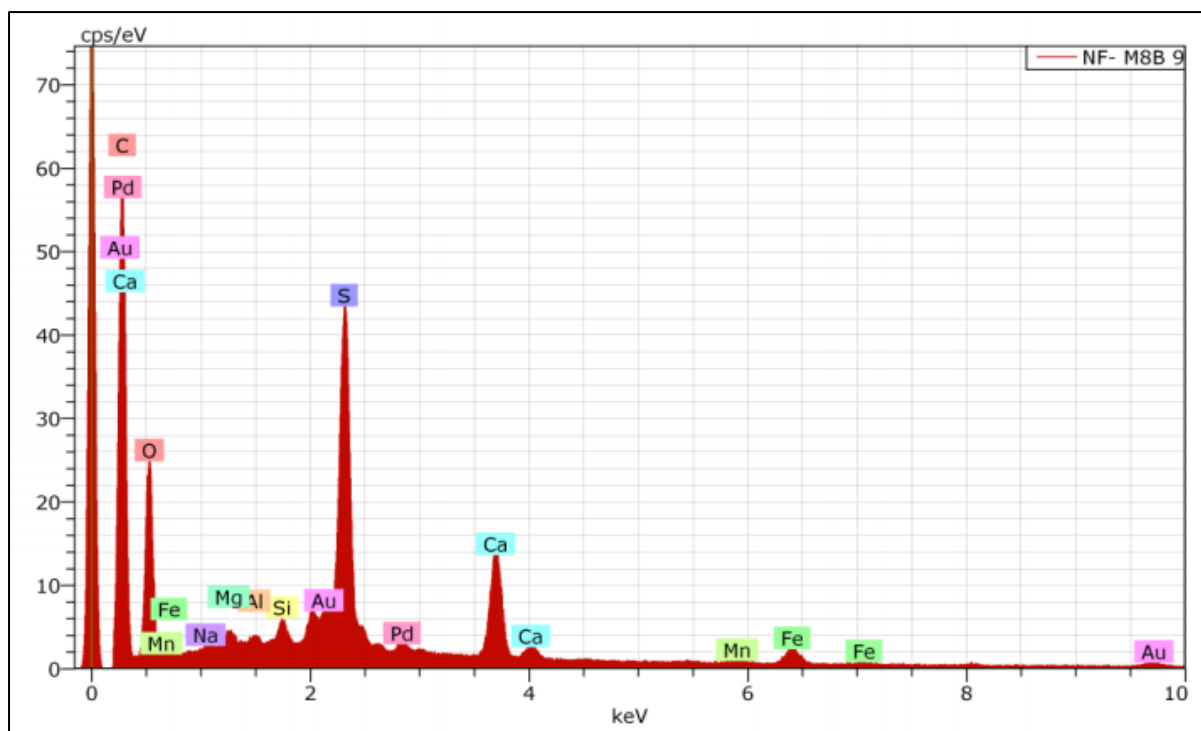
EDX analysis on NF- membrane

APPENDIX C



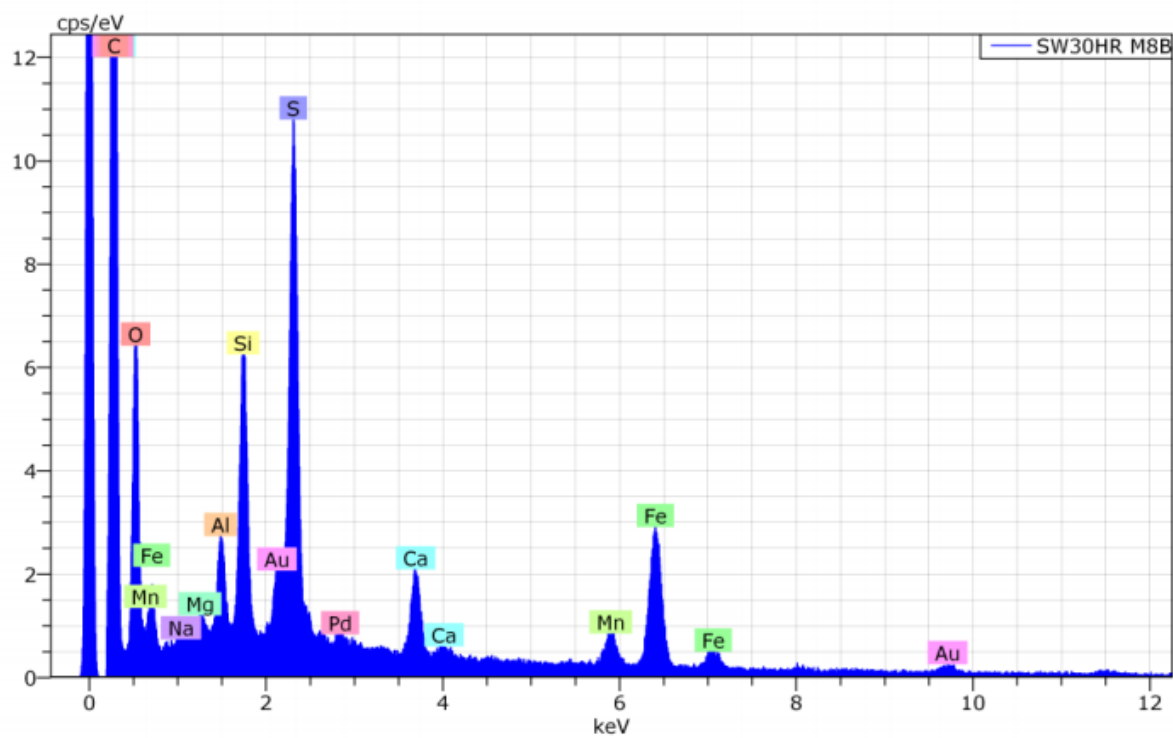
DTA and TGA graphs for SW30HR membrane

APPENDIX D



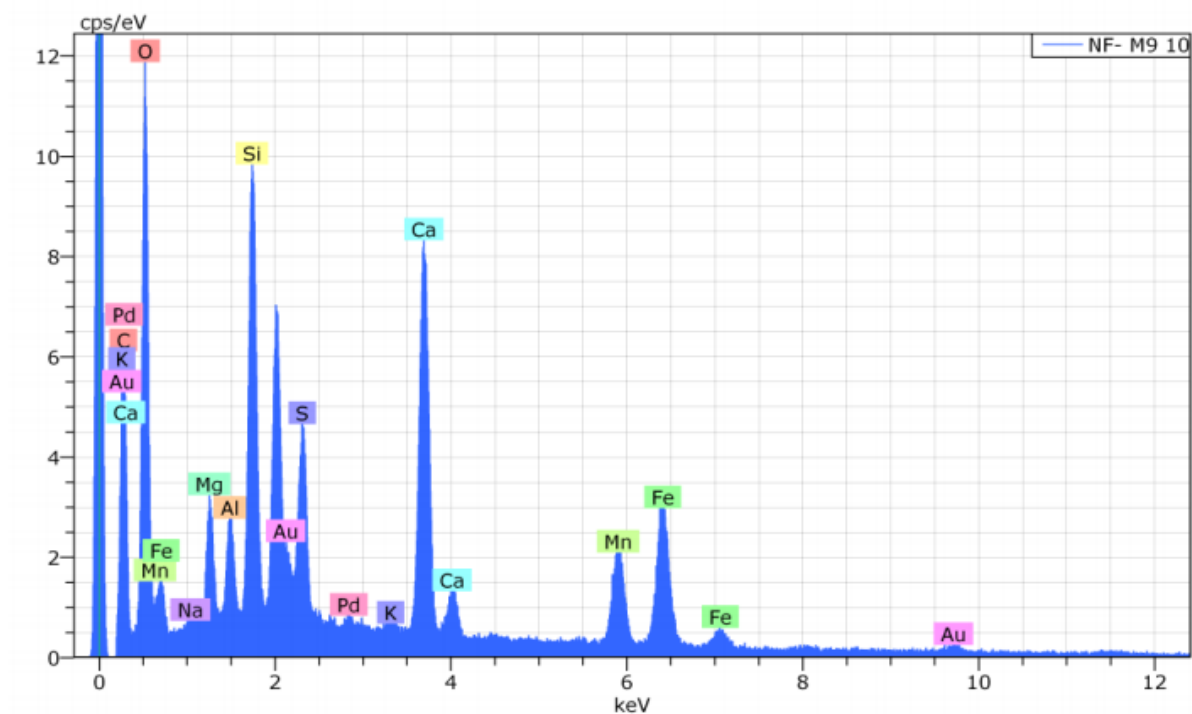
EDX analyses of NF- membrane for M8B fouling

APPENDIX E



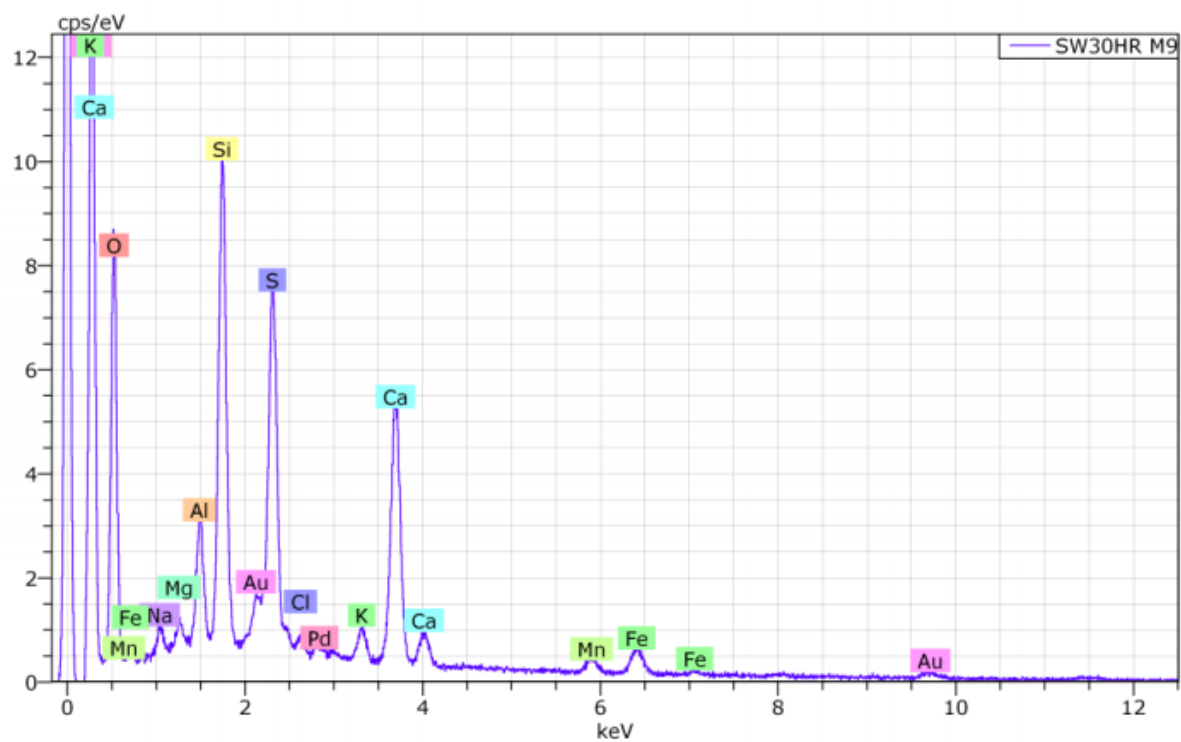
EDX analyses on SW30HR membrane for M8B fouling

APPENDIX F



EDX analyses on NF- membrane for M9 fouling

APPENDIX G



EDX analyses of SW30HR membrane for M9 fouling