NANOFILTRATION: FOULING AND CHEMICAL CLEANING

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Abstract

The challenge of providing developing rural areas in South Africa with sufficient potable water is substantial. North West Province, among others, is water-stressed, semi-arid, and largely rural with a high dependence on groundwater as a strategic resource. Some parts of the province are having poor water quality which ends up affecting households, farming and livestock. The aim of this study is to evaluate the performance of nanofiltration (NF) membranes in detrimental ion (fluoride, nitrate and sulphate) rejection and to monitor fouling on membranes with their subsequent chemical cleaning.

Five commercial membranes (D12, D11, CTC1, NF90 and NF70) were characterized using scanning electron microscopy (SEM), single salt retentions and clean water permeation studies. The three-layered structure of the membranes was observed using SEM, viz.: smooth dense layer, loosely networked sublayer and the support. D12, D11 and CTC1 showed higher water flux than NF90 and NF70. Membranes showed more retention of divalent ions than of monovalent ions. All tested membranes showed a negative surface charge density.

During treatment of sampled rural water, all the membranes tested (D12, D11, CTC1, NF90 and NF70) gave different ion retention results and were mostly influenced by water composition. All tested membranes satisfactorily rejected sulphate. NF70 effectively rejected all the ions of interest (fluoride, nitrate and sulphate) from rural water, indicating that NF70 behaves more like a reverse osmosis (RO) than an NF-membrane.

During fouling experiments, it was found that salts crystallize on the membrane surface, thus decreasing the membrane performance. Cake formation was observed on the membranes fouled with rural water. During chemical cleaning, acid was not an effective cleaning agent. Alkali and surfactant solutions separately proved to be moderate cleaning agents (flux

recovery ranged from 50% to 75%) while their combination (alkali and surfactant) gave the best results (100% flux recovery).

Opsomming

Die uitdaging om ontwikkelende landelike gebiede in Suid-Afrika van genoegsame drinkwater te voorsien, is aansienlik. Die Noordwes Provinsie, soos ook ander provinsies, is watergestrem, semi-aried en grotendeels landelik met 'n hoë afhanklikheid van grondwater as 'n strategiese bron. In sekeredele van die provinsie is die waterkwaliteit wat uiteindelik huishoudings, boerdery en vee beïnvloed. Die doel van die studie is om die prestasie van nanofiltrasiemembrane tydens die verwerping van skadelike ione (fluoried, nitraat en sulfaat) te evalueer en om bevuiling van die membrane, asook die daaropvolgende chemiese reiniging, te monitor.

Vyf kommersiële membrane (D12, D11, CTC1, NF90 en NF70) is met behulp van skandeerelektronmikroskopie (SEM), enkelsoutterughouding en skoon water permeasie studies gekarakteriseer. Die drielaagstruktuur van die membrane is m.b.v. SEM waargeneem. Die lae bestaan uit 'n gladde, digte laag, 'n sublaag met 'n los netwerk en 'n steunlaag. 'n Hoër waterfluks is waargeneem by D12, D11 en CTC1 as by NF90 en NF70. Die membrane vertoon groter verwerping van divalente as van monovalente ione. Al die getoetste membrane was negatief gelaai.

Gedurende behandeling met water monsters uit die landelike gebiede het al die getoetste membrane (D12, D11, CTC1, NF90 en NF70) verskillende ioonretensieresultate getoon wat grootliks deur die watersamestelling beïnvloed is. Al die getoetste membrane het sulfaat bevredigend verwerp. NF70 het effektiewe verwerping van al die ione van belang (fluoride, nitraat en sulfaat) uit landelike water getoon, wat daarop dui dat NF70 meer soos 'n tru-osmose membraan as 'n nanofiltrasiemembraan optree.

Gedurende bevuilingseksperimente is gevind dat soute op die membraanoppervlak kristalliseer en dus die membraanprestasie verlaag. Aanpakking is waargeneem op die membrane wat met landelike water bevuil is. Gedurende chemiese reiniging was suur nie 'n effektiewe reinigingsmiddel

nie. Alkaliese- en surfaktantoplossings op hul eie was gemiddelde reinigingsmiddels (fluksherstel het gewissel tussen 50% en 75%), terwyl hul kombinasie (alkalie en surfaktant) die beste resultate gelewer het (100% fluksherstel).

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List of Abbreviations and Symbols

Abbreviations

AA	deionized water
AFM	atomic force microscopy
ED	electrodialysis
FESEM	field emission scanning electron microscopy
FR_s	flux reduction
FR	flux recovery
MF	microfiltration
MDI	modified fouling index
NF	nanofiltration
NOM	natural organic matter index
PWF	pure water flux
RF	relative flux
RO	reverse osmosis
RR	resistance removal
SDI	silt density index
SEM	scanning electron microscopy
TDS	total dissolved solids
UF	ultrafiltration

Symbols

A	Water permeability coefficient	$(m^3.m^{-2}.s^{-1}.bar^{-1})$
c	Concentration	$(mg.\ell^{-1}$, ppm)
c_f	Feed concentration	$(mg.\ell^{-1}$, ppm)
c_m	Concentration of charged groups on surface	$(mg.\ell^{-1}$, ppm)
c_x^m	Concentration of membrane charge	$(mg.\ell^{-1}$, ppm)
c_p	Permeate concentration	$(mg.\ell^{-1}$, ppm)
MWCO	Molecular weight cut-off	(Da)
J	Flux	$(m^3.m^{-2}.s^{-1}, m.s^{-1})$
ΔP	Pressure difference	(bar)

R	Retention coefficient	(-)
t	Time	(s)
x	membrane thickness	(m)
ε	Permitivity	($C.m^{-1}.V^{-1}$)
η	Viscosity	(Pa.s)
α	Separation factor	(-)

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CHAPTER 1

AN OVERVIEW

"'A sorting demon', a demon able to discriminates between molecules".
Marcel Mulder

CHAPTER 1

1.1 Background

The challenge of providing developing rural areas in South Africa with sufficient and potable water is substantial. It is estimated that some 80% of South Africa's rural citizens do not have access to formal water supply systems. It is believed that 75% of the remaining 20% have access to supply systems that are not functional [1]. It is therefore essential that all water supply schemes should be properly planned. Factors such as community organisation, operation and maintenance, logistic backup, system administration and finance rather than the purely technical considerations, are frequently the major constraints. However, the selection of a suitable technology and appropriate scientific resource evaluation techniques remain very important [1].

In the natural environment there is no "pure" water available for general use [2]. All water contains impurities. Surface water sources are contaminated with microorganisms, suspended solids and, in most cases, acceptable levels of dissolved solids, while groundwater (mainly from boreholes) can contain high levels of dissolved solids [2].

Many studies have been conducted on the effect of water quality on human and animal health [2] and on the life threatening conditions of water conveying structures such as pipes, dams, tanks, water heaters and plumbing fixtures. Following such studies, guidelines have been proposed [2] for quality standards to which domestic water supplies should comply.

Various approaches can be used for the purification of water, of which chemical treatment is still most widely used. In the past, membrane filtration techniques were not considered to be technically feasible separation processes, the most important reason being the membrane performance over time resulted in a flux decline. This behaviour is due to concentration

polarization and fouling (see Chapter 2). However, due to new developments in this field, the usage of, and the developments in, membrane technology is rapidly growing and promising [3].

1.2 Chemical pollutants

There are a number of chemical parameters and components, which should be assessed when determining the quality of a water source. These include fluoride, nitrate, sulphate, iron, total salts (groundwater), hardness and stability. The degree of toxicity and recommended level of some of these components are briefly discussed below [2].

An excessive consumption of fluoride results in the mottling of teeth and bone fluorosis. In some parts of Southern Africa, groundwater contains fluoride levels as high as 15 to 20 mg.ℓ^{-1} as a result of the natural geological formations in the area [2]. Some industrial effluents contain high levels of fluoride, which by law should not be disposed into rivers without sufficient ion treatment [2].

Nitrate is relatively non-toxic to adults but potentially harmful to infants. Fatal *methaemoglobinaemia* ("blue baby syndrome") can occur at nitrate concentrations in excess of 10 mg.ℓ^{-1}. Nitrate occurring in groundwater originates from natural formations, from excessive use of fertilizers by farmers and from leachates from pit latrines and other waste disposal sites [2].

Sulphate is a common constituent of water. Consumption of an excessive amount in drinking water causes diarrhoea [4]. The target water quality range is 0 to 200 mg.ℓ^{-1}. Sulphate contaminated water has a salty taste.

Level of iron in water is due to corrosion in the piping distribution system. At concentrations above 0.3 mg.ℓ^{-1}, iron is toxic while giving rise to discoloration, staining and taste problems. Irrespective of the harmful

condition mentioned above, iron is still used as a flocculant in water purification [2].

Some groundwater in South Africa are highly saline. Such high salt levels [total dissolved solids (TDS)] are not good for human consumption due to their osmotic effects. Saline water may be corrosive while causing scaling in nature. Salinity is usually measured in terms of the electrical conductivity of the water [2].

The presence of multivalent cations (especially calcium and magnesium as hardness) is not harmful, although the correct level of hardness in the water is desirable as a protective factor against heart diseases [2]. Excessive hardness, however, results in an excessive consumption of soap for laundry and washing. The degree to which water will either corrode a metal pipe or form a scale deposit within the pipe is a measure of stability of the water. The stability of the water is determined by the measurement of the pH, calcium content, alkalinity, total salts, and temperature.

1.3 Membranes

Membranes can be classified by morphology, structure or material composition. There are two classes of membrane structures: symmetric and asymmetric. These two classes can be subdivided further as shown in Figure 1.1. Symmetric membranes (porous or nonporous) vary in thickness roughly ranging from 10 to 200 μm. Since the thickness of the membrane is proportional to the resistance of mass transfer, a decrease in membrane thickness results in an increased permeation rate. Therefore, asymmetric membranes with dense toplayer or skin thickness of 0.1 to 0.5 μm, were developed. These high permeation rate membranes are supported by a porous sublayer with a thickness of about 50 to 150 μm [3]. In general, most membranes have an asymmetric structure, except membranes used for microfiltration, which are symmetric [3].

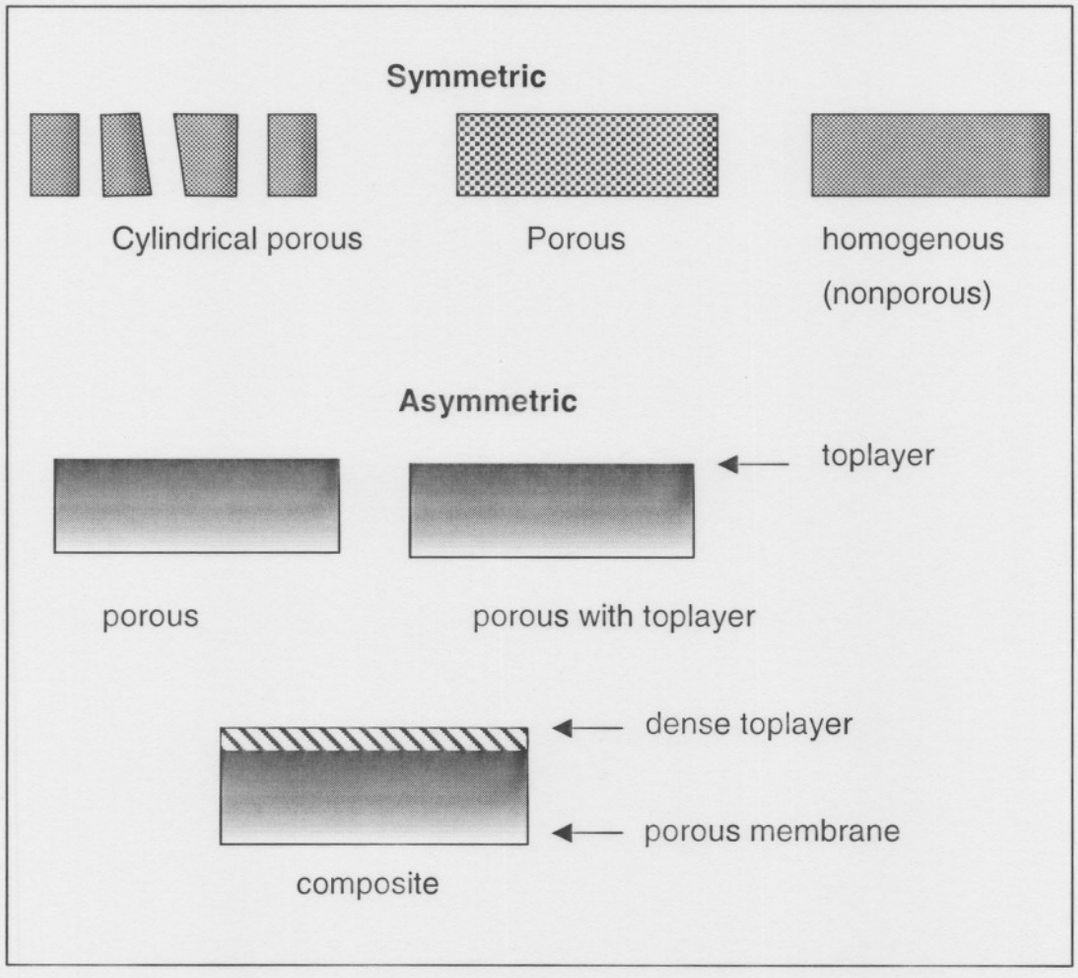

Figure 1.1: Schematic representation of membrane cross-section (symmetric and asymmetric) as adapted from Mulder [3].

Membranes can also be classified on the basis of their material composition, either being organic or inorganic. Materials used for organic membranes are polymers while for inorganic membranes, ceramics, porous carbon, glass and sintered metal are used. Of these, the ceramic and polymer membranes are the most widely used groups [5].

1.3.1 Membrane modules

Large membrane areas are normally required when using membranes on a commercial scale. The smallest unit into which the membrane is packed is called the module, which is then also the central part of a membrane

installation. Modules that have been developed are based on two types of membrane configurations, namely:

- Flat, or
- Tubular

Plate-and-frame and spiral-wound modules are examples of flat membranes whereas tubular, capillary and hollow fiber modules are based on tubular membrane configurations. A plate-and-frame module can be seen in Figure 1.2 and a spiral-wound module in Figure 1.3.

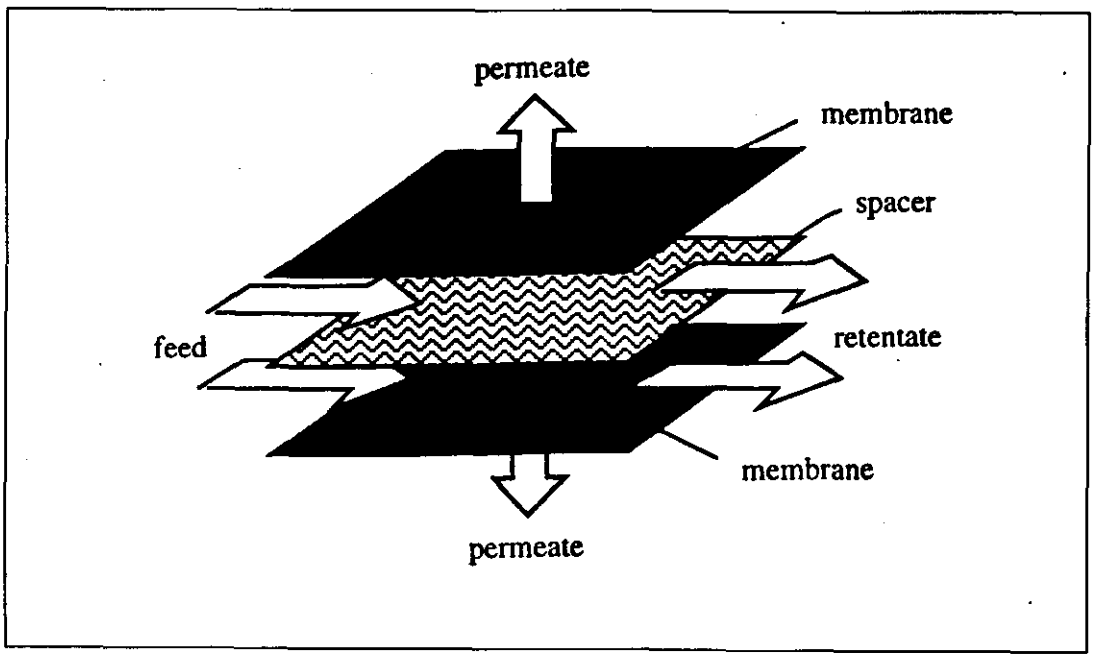

Figure 1.2: Schematic representation of a plate-and-frame module [3]

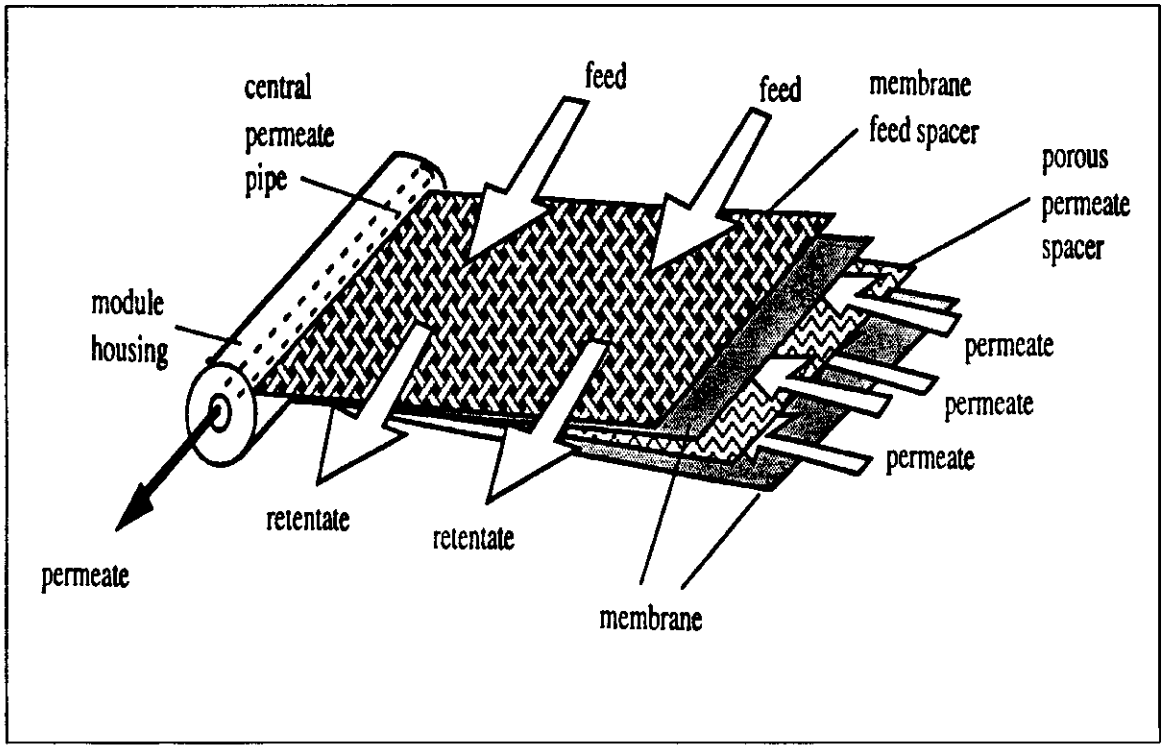

Figure 1.3: Schematic representation of a spiral-wound module [3]

1.3.2 Membrane processes

A membrane can be defined as a permselective barrier existing between two homogenous phases [3]. The two words, permselective and barrier, are the most important criteria from the above definition. The membrane physically separates the feed side from the permeate side, and is therefore a barrier. It is selectively permeable, meaning that certain entities are allowed to pass through and others to a lesser extent. Transport through the membrane takes place when a driving force is applied to the components in the feed.

The driving force can result from a:

- pressure difference (ΔP)
- concentration (or activity) difference (ΔC)
- temperature difference (ΔT), or
- electrical potential difference (ΔE)

Usually pressure-driven membrane processes are used to concentrate or purify a dilute solution. The characteristics of these processes are that the solvent is a continuous phase and that the concentration of the solute is relatively low. According to the particle size of the solute rejected, the membrane processes: microfiltration, ultrafiltration, nanofiltration and reverse osmosis can be distinguished (
Figure 1. 4). In Figure 1. 5, a schematic representation of these processes is given [3].

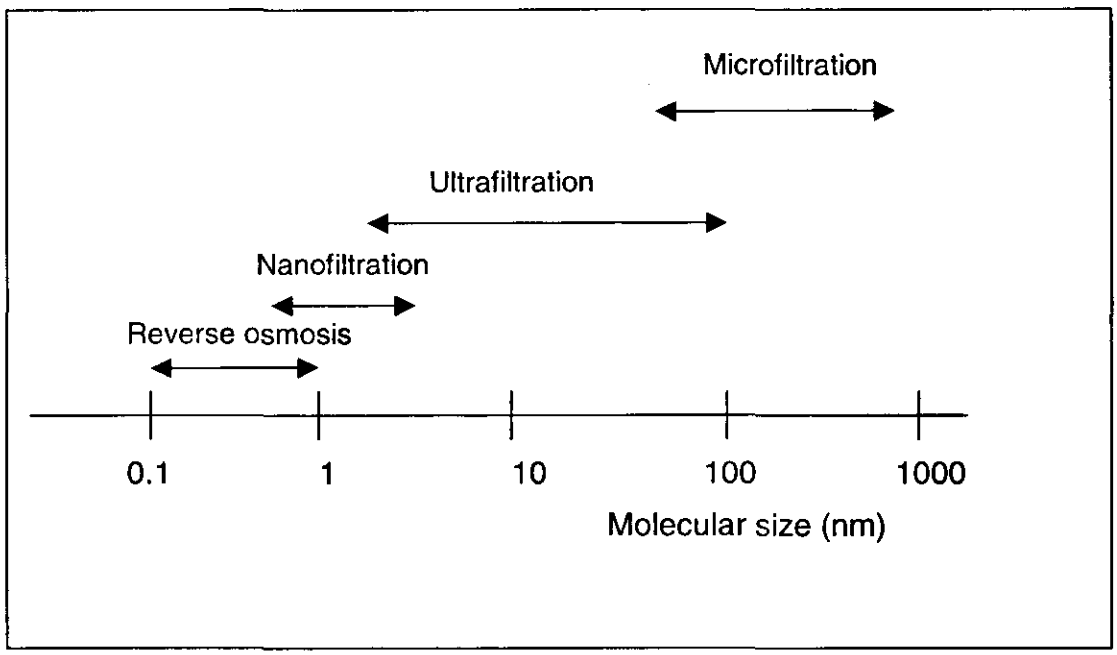

Figure 1. 4: Classification of pressure driven membrane processes. Structure adapted from Schaep [6].

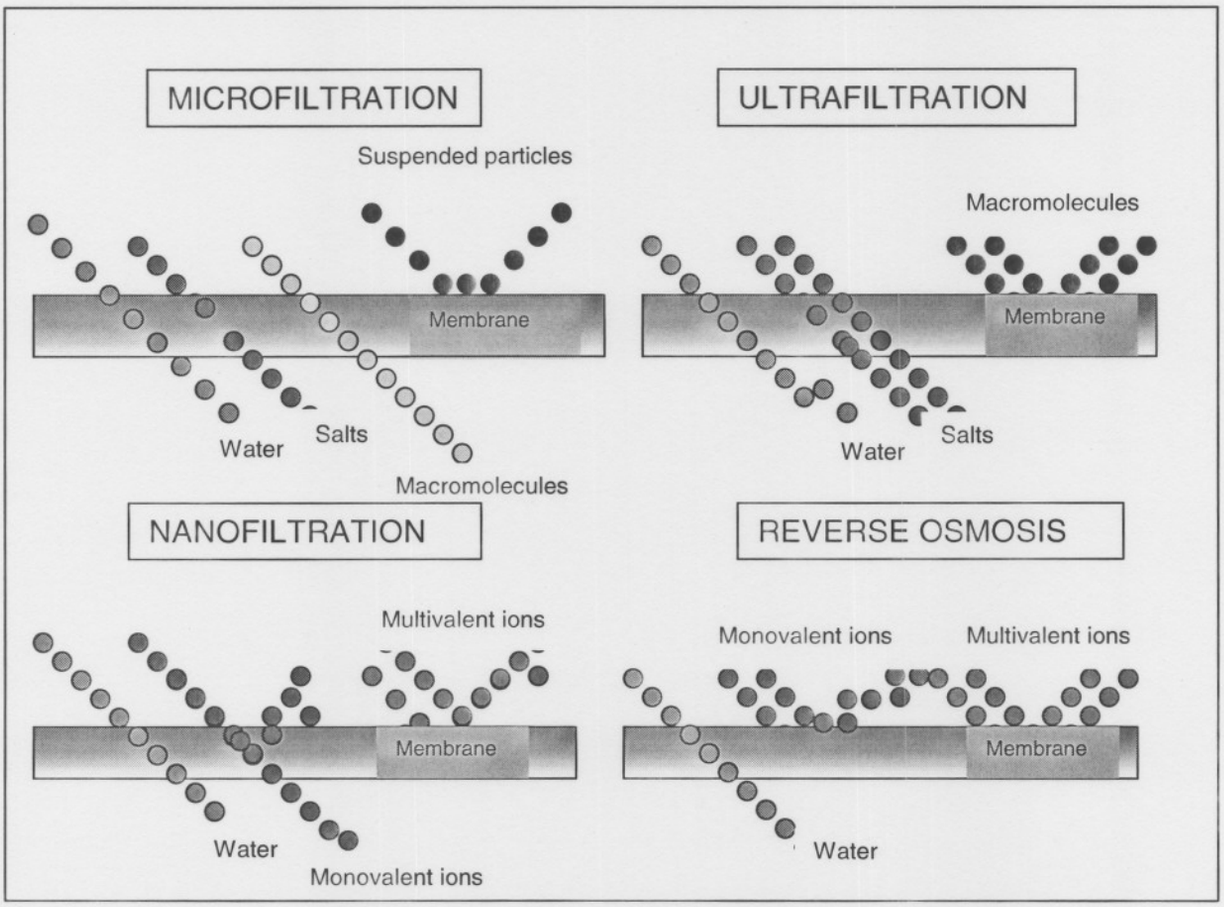

Figure 1. 5: Schematic representation of various membrane processes [6]

The design of membrane filtration systems can differ significantly because of the large number of applications and module configurations. Membrane processes, however, operate mainly in two modes: dead-end flow or cross-flow as illustrated in Figure 1.6. In dead end flow, the feed is forced through the membrane, increasing concentration of the rejected components in the feed, usually resulting in a quality decrease of the permeate with time. In cross flow, the occurrence of concentration polarization and fouling of the membrane is reduced [3].

The applied pressure and the membrane resistance or permeability determines the product flux. An indication of the range for pressure and flux is given in Table 1.1 [3].

Table 1.1: Pressure and flux for various pressure driven membrane processes

Membrane process	Pressure range (bar)	Flux range ($\ell m^{-2}.h^{-1}.bar^{-1}$)
Microfiltration	0.1 – 2.0	> 50
Ultrafiltration	1.0 – 5.0	10 – 50
Nanofiltration	5.0 – 20	1.4 – 12
Reverse osmosis	10 – 100	0.05 – 1.4

There are three properties to keep in mind when evaluating membranes: flux, selectivity and stability. Flux can be described by (Equation 1.1):

$$J = -L_p \frac{dP}{dx} \qquad (1.1)$$

where J is the flux ($m.s^{-1}$), L_p is the water permeability coefficient ($\ell.hr^{-1}.m^{-2}.bar^{-1}$), P is the pressure (bar) as the driving force and x is the membrane thickness (m).

The selectivity of a membrane towards a component in a mixture is generally expressed either as the retention of liquids (R) or the separation factor (α)

The retention is given by:

$$R = \frac{c_f - c_p}{c_f} \qquad (1.2)$$

where c_f is the solute concentration (ppm) in the feed and c_p is the solute concentration in the permeate (ppm).

The separation factor is given by:

$$\alpha_{\frac{A}{B}} = \frac{y_A / y_B}{x_A / x_B} \qquad (1.3)$$

where y is the concentration of A or B in the permeate and x is the concentration of A and B in the feed, where A is the higher concentration.

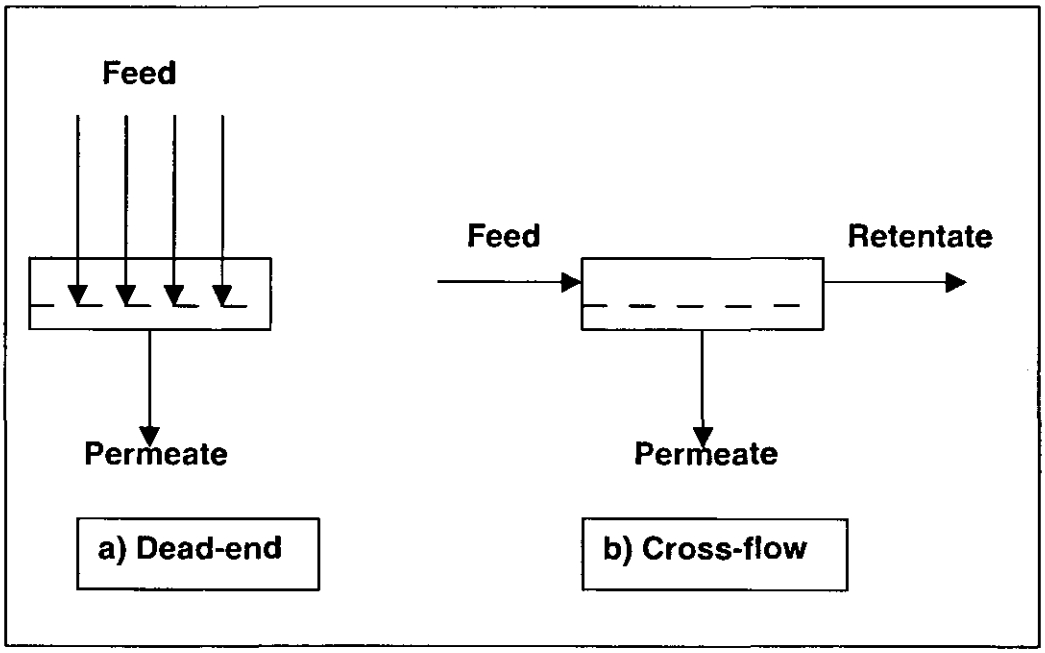

Figure 1.6: Modes of flow

1.3.2.1 Membrane fouling and chemical cleaning

The performance of the membrane deteriorates due to polarization phenomena (concentration or temperature polarization) [3]. Polarization phenomena are reversible processes. It is this polarization which causes the flux to decrease over time. Such a continuous flux decline is the result of membrane fouling, which may be defined as the irreversible deposition of retained particles, colloids, emulsions, suspensions, macromolecules and salts on or in the membrane. Mulder [3] identified three types of foulants, namely:

- Organic precipitates (macromolecules, biological substances, etc.)
- Inorganic precipitates (metal hydroxides, calcium salts, etc.)
- Particulates

The type of membrane, the composition of the feed as well as the process conditions will determine the extent of the deterioration (fouling) of the membrane. Apart from other cleaning techniques, chemical cleaning is an important method for reducing fouling. Chemical cleaning is usually attained by using acid, alkaline, surfactant and detergent solutions. Cleaning efficiency depends on the type of cleaning agent and its concentration.

1.3.3 Development of membranes in South Africa

Membrane research started in South Africa in 1953 on electrodialysis (ED) systems at the Council of Scientific and Industrial Research (CSIR). This research laid the foundation for a better understanding of the thermodynamic and physical processes involved in ED [7, 8].

The initial research development on polymeric membranes started in 1973 at the Institute for Polymer Studies (IPS) at Stellenbosch University. This research initiated the establishment of the first local membrane manufacturing company (Bakke industries) in 1979. In conjunction with the IPS, the company developed low cost tubular reverse osmosis (RO) and ultrafiltration (UF) systems in the 1980's. These beginnings lead to the current situation where the research on, and development of, membranes is actively pursued, not only in tertiary institutions, but also at private companies as well as water and power utilities [7, 9]. More recent research and products by the IPS include an outer-skinless ultrafiltration polysulphone membrane and the coating of ceramic membranes and other inorganic membranes with catalytic, conducting material for the oxidation or combustion of components in water [7, 10, 11, 12]. Tubular woven fibre microfiltration (MF) technology was developed at the Pollution Research Group (University of Natal) [7, 13], while research in cost-efficient manufacture of ozone using membranes and anodic oxidation was conducted at the University of Stellenbosch [7, 13].

At the University of the Western Cape, novel proton-conducting composite ceramic membranes are being designed for electrochemical decomposition of organic pollutants such as phenols [7, 14].

UF membrane bioreactors were developed in joint studies by the IPS and Rhodes University [7, 15]. Some membrane fouling studies were performed at the University of Stellenbosch (Department of Biochemistry) [7, 16] and the University of South Africa (UNISA) [7, 17].

Some of the membrane developments at the Potchefstroom University include: the use of supported liquid membranes for the extraction of metals such as nickel from liquid streams [7, 18], the removal of copper (II) from polluted water with alumina/chitosan composite membranes, the manufacture of ceramic membrane tubes using centrifugal casting techniques and the coating with chitosan [19, 20], the enantioselective catalytic hydrolysis of racemic 1,2-epoxyoctane in a batch and in a continuous process [21, 22], the enrichment of chlorthalidone enantiomers by an aqueous bulk liquid membrane containing β-cyclodextrin [23], the removal of acid sulphate pollution by nanofiltration [5] and the analysis and treatment of inorganics with nanofiltration and adsorption [24].

Since 1985, Weir-Envig Membrane Company in South Africa designed, manufactured and commissioned water treatment plants for both private and public sectors within and outside South Africa. The clients in South Africa such as Sun International, ESKOM, Dept of Public works, Clover, SCI etc, use membrane units for desalination of brackish water and cooling tower blowdown. SFW, CFG, CFI, Gilbeys, Granor Passi etc, use the units for clarification of wine and juice, while African Products, Sastech, Saldanha Steel etc., use membranes for industrial effluent treatment. Due to secrecy, some of the membrane developments have not been disclosed [25].

From the above discussion, it is evident that research in membrane processes is growing in South Africa. The focus is not only on a specific membrane process, but on broad membrane research.

1.4 Objectives

It is the aim of this study to show that membrane processes can make a most valuable contribution to restore or improve the quality of water resources and aqueous effluent streams.

The objectives of this study are:

- To characterize various nanofiltration (NF) membranes.
- To study rejection of NO_3^-, F^- and SO_4^{2-} from ground- and surface water using NF-membranes.
- To monitor fouling of NF-membranes used for treatment of ground and surface water.
- To recover the flux of fouled NF-membranes by a chemical cleaning process.

1.5 Scope of the study

In this Chapter, an overview is presented on the health related impact of chemical pollutants in water. It includes some introductory comments on membrane, fouling and chemical cleaning. In Chapter 2, an extensive literature review concerning the objectives of this study is given. The experimental work that has been done is described in Chapters 3, 4, and 5. Characterization (by scanning electron microscopy, clean water flux and ion retention) of the selected NF-membranes in both dead-end and cross-flow is presented in Chapter 3. Some results obtained on treatment of rural water, fouling (by salts and sampled water) and chemical cleaning (by bases, acids, chelates and surfactants) in dead-end and cross-flow are discussed in

Chapters 4 and 5. Evaluation and recommendations of the results are presented in Chapter 6. Possible further studies are also suggested in this Chapter.

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CHAPTER 2

LITERATURE SURVEY

CHAPTER 2

2.1 Introduction

Membrane filtration was not considered a technically important separation process until 25 years ago [1]. Today membrane processes are used in a wide range of applications and the number of applications is still growing [1]. In this Chapter, literature on various aspects of NF is reviewed, including the processes, applications and characterization of NF membranes. Finally, the advantages, disadvantages (membrane fouling) and chemical cleaning of membranes will be discussed.

2.2 Nanofiltration (NF)

2.2.1 NF-membrane processes

Pressure driven membrane processes are often used for water purification. NF is the latest addition to this class of membrane processes [2]. NF finds its origin in the development of modified reverse osmosis membranes, reported in 1970 [3]. It was, however, only at the end of the 1980's that the name NF was given to these specific membranes, when it was observed that non-charged solutes larger than 1 nanometer were retained. Since then, NF has become a promising technique for future water treatment, extending the applications of membrane processes [3].

In terms of its separation characteristics, NF falls between reverse osmosis (RO) and ultrafitration (UF), as illustrated in Figure 2. 1, and can be used for the removal of low molecular weight organics and multivalent ions from a solution.

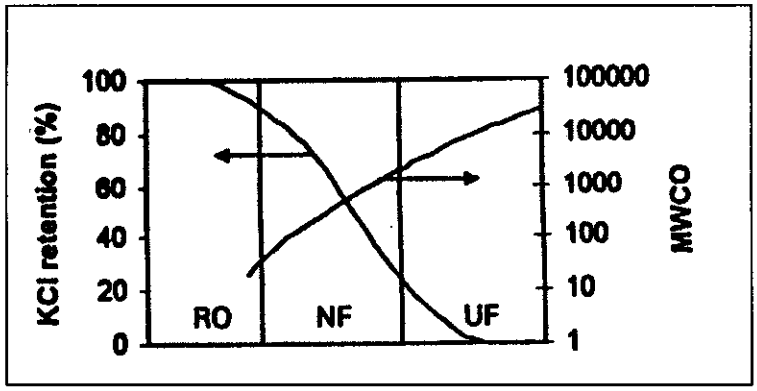

Figure 2. 1: Diagram of the region of NF membrane performance relative to RO and UF membranes [3].

NF gives low rejection of salts with monovalent anions and nonionized organics with molecular weight below 150 Da. For organic components above 150 Da (membrane cut-off between 200 and 1000 Da), a high rejection is obtained, as well as for salts with di- and multivalent ions. This behaviour is illustrated in Figure 1.5 (Chapter 1). As a pressure driven membrane process, NF is closely related to ultrafiltration, microfiltration and reverse osmosis. The differences between these processes are mainly the pore sizes, the transport mechanism, the applied pressure and the range of applications as shown in Table 1.1 (Chapter 1). The pore sizes, which correspond to the size of the molecules retained by membranes, are illustrated in Figure 1.4 (Chapter 1) [3].

Due to the lower energy requirement, using NF instead of reverse osmosis can save energy. Retentions may be somewhat lower, but the removal of multivalent ions and relatively small organic molecules is nearly complete [3]. When a high retention is required, for example NaCl with high feed concentrations, reverse osmosis is the preferred process [1].

NF operates at the interface of porous and nonporous membranes as the transport system has characteristics of both sieving as well as solution diffusion. Since NF-membranes have a surface charge, the electric interactions with the salts also contribute to the transport and retention behaviour [3].

The two most important applications for NF are [3]:

- Partial water desalination, and
- The removal of monovalent and divalent ions and low molecular weight organic molecules.
- The separation of monovalent ions from divalent ions.

A stream with high TDS (total dissolved solids) can be treated with NF to reduce TDS and the concentration of specific species, while not significantly influencing specific other specific components. This characteristic of specific selectivity gives NF an advantage above reverse osmosis where all components are rejected. As some monovalents are allowed to pass through the NF-membrane, the electrolyte concentration will be higher in the permeate stream than in the case of reverse osmosis [4].

It is well known that transport through membranes occurs as a result of a driving force acting on the components in the feed and that permeation through the membrane is directly proportional to this driving force. The equation showing proportionality between the flux and the driving force was given in Chapter 1 (Equation 1.1) [1]:

2.2.2 Applications of NF-membranes

2.2.2.1 Drinking water treatment in the US

Membrane technology is playing an increasingly important role in the treatment of water and wastewater in the United States. Jacangelo *et al.* [5] listed some of the roles of membrane technology in drinking water treatment. Both NF and RO have been used for the removal of natural organic matter (NOM). NF was primarily used for the treatment of groundwaters containing relatively low total dissolved solids, high total hardness, colour, pathogens, inorganic and synthetic organic chemicals. A plant having a capacity of more than 270 000 $m^3.day^{-1}$ was installed and over 90% of trihalomethane (THM)

haloacetic acid precursors and 95% or more of the simulated distribution system THM were removed.

2.2.2.2 European potable water production

Ledondo and Lanari [6] studied membrane selection and design considerations for European potable water production, based on different feedwater conditions. Their study was based on the latest developments and specifications of FILMTEC membranes and elements for reverse osmosis and nanofitration. Two new membranes (FILMTEC NF70-345 and NF70-400) were also investigated. The removal of nitrate, hardness, sulphate, and bicarbonate was studied. A plant, fitted with FILMTEC NF70-345, with permeation capacity of 21 000 $m^3.day^{-1}$ and a blend capacity of up to 30 000 $m^3.day^{-1}$ was installed in Spain. This was used for the reduction of sulphate to less than 250 $mg.\ell^{-1}$ as ion, of magnesium to less than 50 $mg.\ell^{-1}$ as ion and of total water salinity (TDS) as recommended by Spanish Guidelines. The plant contained six FILMTEC NF 70-345 modules and operated at a recovery rate of 70%. After a year of operation the ionic analysis had values of about 40% lower for the permeate TDS, irrespective of the increase in the feed TDS. This value corresponds to an element salt rejection of 97.8%, which is very high for an NF 70 plant [6].

An NF drinking water plant was built by the Syndicat des Eaux d'Ile de France (SEDIF) in Mery-sur-Oise, a suburb located in the north of Paris (France) [7]. The water plant is capable of producing a maximum of 340 000 m^3 of water per day for the North Paris Region. The membrane facility has been coupled with a conventional biological facility. The membrane facility on its own operates with a maximum production of 140 000 $m^3.day^{-1}$. Risks of biofouling were reduced by running the plant continuously with limited stops of 24 to 48 hours to rinse the concentrate side of the membranes.

The FILMTEC NF70-345 membranes showed salt rejections of 97.8%, a behaviour that is characteristic of RO membranes where almost all the ions

are rejected. Membranes used in Europe (France and Spain) obtain about 370 000 m^3 of water per day.

2.2.2.3 Electrolyte rejection

Choi *et al.* [8] investigated the effect of co-existing ions (nitrate, fluoride, sulphate, chloride, calcium and magnesium) on the removal of nitrate and fluoride using NF-membranes (NTR 7250 and NTR 7450). Experiments treating groundwater indicated that sulphate was rejected most effectively. Chloride ions were rejected more than nitrate and fluoride. The permeated divalent cations caused a strong demand for divalent anions to ensure eletroneutrality; therefore least repulsive anions in the solution passed a membrane with a higher surface potential more readily than one with a lower surface potential.

They also found that the hydration effect of nitrate would be stronger in a membrane with a low surface potential. The reduction in rejection rates of monovalent ions were more significant for a membrane with a low surface potential. At high salt concentrations, cations tend to shield negatively charged groups on the membrane. Although divalent anions were highly rejected, calcium ions shielded membrane charges more effectively than magnesium ions. Rejection rates of some ions studied are presented in Table 2.1 [8].

Table 2.1: Rejection of ions by NTR-7250 and NTR-7450 [8]

	Rejection rate (%)	
Feed	NTR-7250	NTR-7450
Nitrate	72.2	85.7
Fluoride	70.4	72.0
Sulphate	98.5	99.6

Xiao-Lin Wang *et al.* [9] did some permeation experiments using KCl, NaCl, LiCl, $MgCl_2$, $MgSO_4$ and K_2SO_4 solutions on NF45 and SU200 commercial membranes. The effect of the type and concentration of electrolytes, as well as the pH, on separation performance was investigated. Separation potential on the 1-1 (LiCl, NaCl and KCl) inorganic electrolyte types was similar for different concentrations, but differed significantly from the separation of electrolytes containing divalent ions ($MgCl_2$, K_2SO_4 and Mg_2SO_4), which were more readily rejected than monovalent ions. An increase in electrolyte concentration led to a decrease in electrolyte rejection. The sizes of the electrolyte-ions were compared to the pore radii of the NF-membranes. Both tested membranes behaved similarly in terms of the rejection of electrolytes such as LiCl under various pH values of the feed solution.

Visser *et al.* [10] studied the removal of acid sulphate pollution in mine water (gold and coal mines in South Africa) on D11, D12 (Envig), NF70, NF90 (Filmtec) and CTC1 (Hydranautics) commercial NF-membranes. A dead-end module with a capacity of about a litre operating at pressures of up to 25 bar was used. Different pH values were compared. At neutral pH, all membranes showed a sulphate rejection of 95 – 99% with the water flux ranging from 2 – 7 $\ell.m^{-2}.h^{-1}.bar^{-1}$. At lower pH, the membrane performance decreased. This was due to the presence of a higher fraction of monovalent HSO^-_4 ions and a possible change in the membrane charge from negative to positive. NF70 and NF90 (Filmtec) membranes with fluxes below 4 $\ell.m^{-2}.h^{-1}.bar^{-1}$ were shown to be suitable for mine water with pH 4 and salt concentrations of up to 2500 ppm.

Modise [11] studied the analysis and treatment of inorganics with NF and adsorption. Selected South African rural groundwaters within the North West Province (Lerome, Kaallaagte, Rhenosterfontein and Rietvlei) and the stream water of the Vaal River were chosen for treatment by NF and adsorption techniques. The membranes TFC-S, TFC-ULP, D11, D12, NF70, NF90, TFC-SR and CTC1 were used. The experiments were performed in a ~1 ℓ dead-

end module at pressures of 20 bar and a temperature of 20°C. Analysis was done for copper, fluoride, nitrate, sulphate, calcium and magnesium.
All the tested membranes showed rejections above 60% for the divalent sulphate anion. The divalent cations (magnesium and copper) were not so well retained. The retention of the monovalent anions (fluoride and nitrate) depended on the different compositions of the rural water samples. The nitrate content in all sampled water was already within acceptable levels. Nevertheless, only NF90 could reject nitrate satisfactorily. Fluoride in Lerome water was in excess of the acceptable value (~4.00 ppm) and was reduced by ~76% and 91% using NF70 and TFC-ULP, respectively.

Peters [12] studied over 150 covered landfills in Germany and Spain and found that the dissolved components in the leachate ranged from 2000 – 15000 mg.ℓ^{-1}, comprising organic components (100 and 3000 mg.ℓ^{-1}), inorganic components (1600 – 14300 mg.ℓ^{-1}) and ammonia (300 to 2000 mg.ℓ^{-1}). The DTF-module designed to optimise the interaction of flow parameters such as feed flow velocity, pressure drop, efficient membrane cleaning and insensitivity to micro-particles was fitted in an NF system. The high rejection rate for sulphate ions and dissolved organic matter, together with very low rejection for chloride and sodium, reduced the volume of the concentrate. Some examples of rejection rates for different components dissolved in leachate landfills are shown in Table 2. 2. The permeate recovery rate of 95 to 97.5% was achieved when a reverse osmosis process was combined with nanofitration.

Table 2. 2: NF rejection rates of components dissolved in leachate [12]

Parameter	Feed	Permeate	Rejection*
BOD mg O_2/ℓ	480	280	41.62
COD mg O_2/ℓ	17000	700	95.88
Ammonia mg. ℓ^{-1}	3350	1420	57.61
Sulphate mg. ℓ^{-1}	31200	2345	92.48
Chloride mg. ℓ^{-1}	12760	17730	38.95
Magnesium mg. ℓ^{-1}	1030	72.7	92.94
Calcium mg. ℓ^{-1}	2670	187	93.00
Sodium mg. ℓ^{-1}	10900	5010	54.04

* rejection given as percentage (%)

The results obtained in electrolyte rejection studies were comparable and confirmed the tested membranes as NF. Divalent ions were highly rejected by all the tested membranes while monovalents were partially rejected. According to electrolyte research, NF membranes can be used to serve the purpose of separation, mainly discriminating between monovalent and divalent ions.

2.2.2.4 NF rejection of organic pollutants

Kiso *et al.* [13] studied the effects of hydrophobicity and molecular size on rejection of hazardous organic micro-pollutants, such as aromatic pesticides. Four types of flat sheet membranes (NTR-729HF, NTR-7250, NTR-7450 and NTR-7410) were used. In their study, NF-membranes rejected 11 aromatic pesticides (nominal NaCl rejection was 92, 60, 51 and 15% respectively). The most effective desalting membrane (NTR-729HF) rejected pesticides at >92%, except for tricyclazole. Even though the other membranes showed least effectiveness in rejection of salts, of the pesticides isoxathion, chloroneb and asprocarb were rejected more than 95% by all the membranes. The experiment indicated that all the pesticides were adsorbed on the membranes and adsorption properties were controlled by both the hydrophobicity and molecular shape of the solute.

Kiso *et al.* [14] also examined the rejection properties of NF-membranes for alkyl phthalates. The same membranes as above were used. In this case, more than 99% of the hydrophobic alkyl phthalates were rejected by the least effective desalting membranes (NTR-7410 and NTR-7450). The most effective desalting membrane (NTR-7250 and NTR-729HF) rejected more than 96% of almost all alkyl phthalates.

The removal of organic pollutants of petroleum and agrochemical origin was investigated using commercial reverse osmosis (RO) and NF-membranes of characterized porosities [15]. The experiments revealed that the rejection of organics was dependant on membrane properties such as pore size, membrane material, membrane charge and solute characteristics such as molecule size, charge and polarity. Solute and pore size, as well as the physiochemical interactions, influenced the rejection of the small nonionized organic molecules. Physiochemical interactions became dominant when the same pollutants were exposed to membranes with wider pores. The rejection of pesticides was fully governed by the separation mechanism based on the size of the solute molecule and the membrane pore size. Physicochemical effects contributed to the rejection of some pesticides using certain membranes.

The studies by Kiso *et al.* [13, 14] showed that NF membranes could reject most of the hazardous organics from polluted water streams. According to NF-membrane theory, all organic pollutants are rejected, but since the organic retention obtained during this study was only as high as 92%, the theoretical rejection of 100% was not achieved.

2.2.2.5 Industrial water treatment

Lee Comb [16] did a study on treatment of water for beverage production using NF membrane processes. Soft drink producers have always had an interest in the water that goes into their products, as it is not only 80 – 90% of the product, but also influences the taste of the product. Comb [16] found that NF

proved to meet the greatest needs of the soft drink industry, i.e. fine filtration of particles and only a slight reduction of dissolved contaminants. NF also provides the advantage of lower cost of operation ($0.75 - $0.95/1000 gallons). The soft drink facility studied obtained its water from the Colorado River in Riverside, California, where dissolved solids levels are in the range of 500–700 ppm. The NF unit was pre-treated by chlorine injection for disinfection and backwashable dual media filtration (anthracite or manganese greensand). A permeate was post-treated by additional chlorination and activated carbon before being sent to the can line and blending areas. The feed, permeate and concentrate water qualities are shown in Table 2. 3:

Table 2. 3: The feed, permeate and concentrate water qualities for the beverage industry [16].

	Riverside City water (mg. ℓ^{-1} as $CaCO_3$)	NF Permeate (mg. ℓ^{-1} as $CaCO_3$)	NF Concentrate (mg. ℓ^{-1} as $CaCO_3$)
Calcium	56	12	280
Magnesium	68	15	400
Sodium	199	78	768
Alkalinity	76	8	152
Sulphate	58	15	731
Chloride	189	82	565
Silica	14	8	32
Conductivity (μmho)	575	175	2178

The NF unit reduced the dissolved solids level by about 70%, while the inorganic levels were within the criteria for soft drink water production.

Charles [17] did some work on treating various industrial water streams with membranes while showing current applications of NF-membranes for the industry in general. Rejections of 95% for divalent ions, 40% for monovalent ions and organics with sizes ranging from 150 – 300 MW were obtained.

A NF/RO combination membrane process was developed by Rautenbach and Linn [18] to treat a leach solution in order to achieve a recovery rate of more than 95%. It was found that the implementation of an NF stage into the process can extend the limits of the RO set by scaling and/or osmotic pressure considerably. Rautenbach, Vossenkaul, Linn, Katz and Al-Gobaisi further refined the NF/RO combination process [19 20]. Figure 2. 2 shows the flow diagram of such a combined membrane process.

Rautenbach and Mellis [21] did a study on hybrid processes involving the use of membranes for highly organic or inorganic contaminated wastewater. A combined bioreactor (ultrafiltration and NF) was designed in Germany. Experiments were carried out with dumpside leachate on a pilot-plant scale. By recycling the concentrate of the NF process several times, the elimination rate of COD's increased by 9 – 17% while the nitrate concentrations remained below 2 ppm.

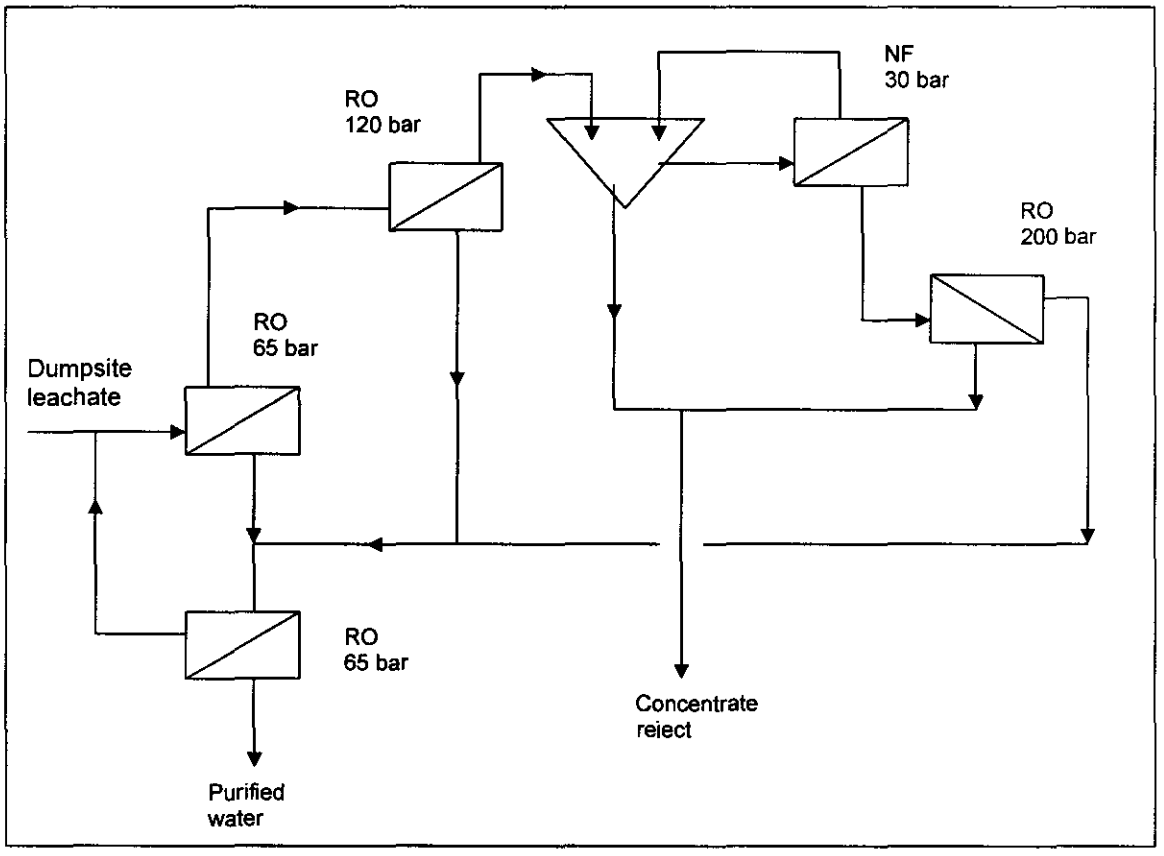

Figure 2. 2: A flow diagram of a combined RO and NF system as adapted from Rautenbach and Linn [18]

Rosberg [22] identified a major advantage in the combination of UF module upstream of RO/NF for the treatment of surface water. This is called the double barrier concept as it provides a double barrier for the removal of viruses and cysts of *Giardia* and *Cryptosporidium.*

2.3 Characterization of NF membranes

The aim of membrane characterization is to relate the morphological properties of the membranes to their separation characteristics. A difference should be made between organic and inorganic NF-membranes when selecting a characterization method for these membranes. The morphology of ceramic membranes remains unchanged whether wet or dry. In the case of polymeric membranes, there is a change in morphology due to swelling when a dry membrane is wetted. Hence, polymeric membranes are altered much more by solutions in contact with them, as well as by process parameters, than ceramic membranes [2].

Characterization can be performed in several ways. Firstly by retention measurements, which are used to understand the morphology and charge of the membrane. Another characterization method is permporometry where the actual pore size and pore size distribution are determined. The third method is gas adsorption-desorption to determine the pore area within a sample and from that a mean pore size and pore size distribution can be determined. Microscopic techniques can also be used to visualize the structure and give information on morphological aspects. The last characterization methods discussed are the membrane charge related measurements. A summary of characterization techniques of polymeric and ceramic membranes is given in Table 2. 4 [2]:

Table 2. 4 Characterization methods for NF membranes

Characterization method	Characteristic	
	Porous charged membranes	Swollen networks
Solvent flux measurements	Ratio of porosity and membrane thickness	Solvent permeability
Retention measurements		
➢ Uncharged molecules	Pore size	Solute permeability and size hindrance factor
➢ Electrolyte solution	Pore size and membrane charge	Solute permeability, size hindrance factor, charge hindrance factor, and membrane charge
SEM and AFM	Pore size and porosity	Overall structure and defects
Permporometry	Pore size and porosity	-
Gas adsorption-desorption	Pore size and surface pore area	Surface pore area
Charge determining method		
➢ Titration	Bulk membrane charge	Bulk membrane charge
➢ Electrokinetic measurements:		
1. Along membrane surface	Membrane surface charge	Membrane surface charge
2. Through membrane	Surface pore wall charge	Bulk membrane charge
➢ Membrane potential	Bulk membrane charge	Bulk membrane charge
➢ Membrane resistance	Bulk membrane resistance	Bulk membrane resistance

2.3.1 Retention measurements

This is the most frequently used characterization method for NF-membranes. Retention is a measure of the ability of the membrane to retain certain solutes. It is expressed as the retention or rejection coefficient (R):

$$R = 1 - \frac{c_p}{c_f} \qquad (2.1)$$

where c_p is the permeate concentration and c_f the feed concentration. A retention coefficient of 1 refers to total exclusion of the solutes on the

membrane, while a retention coefficient of 0 means no retained solutes. Retention of a solute depends on the solute and membrane used, while it is also affected by the feed concentration and the pressure applied over the membrane [2].

2.3.1.1 Uncharged solutes

Uncharged molecules are excluded differently from a solution by the two types of NF-membranes mentioned previously i.e. porous membranes and swollen network membranes. For porous membranes, the separation is mainly due to a sieving mechanism, as is the case for micro- and ultrafiltration. In the case of a swollen network, structure exclusion is based on a solution-diffusion mechanism. Smaller molecules may have a higher diffusion coefficient through the network than large molecules. A molecular weight cut-off with values ranging from 200 to 1000 dalton (Da) can be used as a characteristic for NF-membranes. This molecular weight cut-off value corresponds to 90% of retained particles by the membrane [2].

2.3.1.2 Electrolyte solutions

For charged molecules, both sieving properties and the electrostatic repulsion between the charged membrane and the solute is important. Charge effects will for example, determine differences in retentions of ions of comparable sizes. Multivalent (di- or trivalent) ions with the same sign of charge as that of the membrane surface (co-ion), are more effectively repelled than monovalent ions with the same sign of charge. In case of ions with a charge opposite to the membrane charge (counter-ions), the counter ion with the lowest charge will show the highest retention.

Feed concentration has a strong effect on the retention of salts by NF-membranes. The higher the concentration of ions, the lower the retention. The decrease in retention is caused by the Donnan equilibrium [2] (potential build-up which is determined by the ionic distribution at the membrane-solution

interface [1]), which will be discussed in more detail later. The Donnan equilibrium is not affected by the pressure difference applied [2].

A number of authors showed experimentally that for mixtures of various ions, the retention of the co-ion with the lowest charge is lower compared to the same co-ion in a single salt solution, whereas retention of the co-ions with the highest charge in a mixed salt solution stayed almost the same. This indicates that separation does not only depend on the charge, but that the difference in mobility of the ions through the membrane also play an important role. The ion with the lowest mobility is retained best. Both the charge and mobility influence separation similarly. Variation in retention measurements with single salts and salt mixtures can also be explained in terms of porosity-membrane thickness ratio's, membrane charge density and the effective pore size. For salt mixtures, retention measurements can give qualitative information on the separation mechanism [2].

Bowen *et al.* [23] characterized the Hoechst PES5 asymmetric NF-membrane. Permeation experiments with single salts solutions (KCl, NaCl and LiCl) were carried out. These three single salts have the same co-ion, but different counter ions. The order of rejection was KCl>NaCl>LiCl which follows the order of decreasing diffusivities of the counter-ion $K^+>Na^+>Li^+$. This allows interpretation of experimental data with model calculations in order to characterize the membrane for effective pore radius, the ratio of the effective thickness over porosity and the effective volumetric membrane charge density. The rejection of uncharged solutes, i.e. Vitamin B_{12}, raffinose, sucrose, glucose and glycerin was also investigated and the effective pore radius and effective thickness over porosity was calculated.

Hafiane *et al.* [24] investigated the removal of chromate by means of an NF-membrane as a possible alternative to the conventional methods of hexavalent chromium removal from an aqueous solution. Solutions of NaCl, Na_2SO_4 and $CaCl_2$ were used as reference to study the influence of anion charge density and cation interaction on the membrane, an aromatic polyamide thin-film membrane in this case. Potassium chromate was used to

study the retention of chromium and the pH was adjusted by addition of hydrochloric acid. For solutions with pH 2 – 4, 60% retention of chromate was obtained. The retention increased progressively to reach values of 77% at pH 7. Retention measurements with single reference salts revealed that Donnan exclusion (see section 2.4 for detailed explanation) played an important role.

Visser [4] characterized NF-membranes (D12, D11, CTC1, NF90 and NF70) using NaCl, $CaCl_2$ and Na_2SO_4. He found that there was poor rejection of salt solutions containing monovalent anions, except by NF90 and NF70. All the membranes, except D11, effectively rejected sulphate. The author concluded that D12 and CTC1 were negatively charged membranes while the charge of D11 was not clear compared to the other membranes. NF90 and NF70 showed characteristics more of an RO than an NF-membrane since almost all the ions were rejected.

Modise [11] did similar experiments confirming the results obtained by Visser [4]. Instead of using D11 and D12, TFC-S and TFC-SR were used. The two substituted membranes were negatively charged.

2.3.2 Microscopy

Microscopic techniques visualize the membrane structure and give information about the surface pore shape and size (if visible), porosity and cross-sectional structure.

In scanning electron microscopy (SEM), resolutions of about 5 nm can be reached [1, 2]. Low voltages should be applied for polymeric membranes to avoid damage of the sample surface, resulting in lower resolution. A conductive coating is applied to avoid the electron beam to charge the membrane material or even burn the sample. Pores of NF membranes cannot be visualized by SEM technique, because resolution of the method is too low to detect the small pores. Only a general structure of the membrane showing different layers can be observed [2].

Both Visser [4] and Modise [11] characterized NF membranes using SEM. They both observed that most NF-membranes are composed of three layers i.e. the top smooth and dense layer, the loosely networked sublayer and the support layer.

Another visualizing technique is Atomic Force Microscopy (AFM). The method can be applied to investigate the surface roughness of a membrane by scanning the sample surface with a sharp tip at the end of a flexible cantilever [1, 2]. By moving this tip at a constant force over the membrane surface, an image of the surface can be obtained. Unlike SEM, AFM does not require a vacuum and samples can be measured in air or even in a liquid. AFM has been mainly used to investigate surface morphologies of ultrafiltration membranes. Most probably the size of the tip with a radius of 10 – 40 nm restricted the resolution of this technique and, therefore, AFM has not often been used for the characterization of nanofiltration membranes. A pore size distribution of porous NF membranes can be obtained from AFM pictures by determining the diameters of the pores at the membrane surface. However, to obtain suitable information from AFM pictures, a good method should be used to distinguish between pores and surface roughness [2].

Bowen *et al.* [23] used atomic force microscopy (AFM) to determine surface pore radius and porosity. According to their study, the AFM images provided direct confirmation of the presence of discreet surface pores in such membranes. Bowen *et al* added that it is better to describe the transport through such NF-membranes as occurring through discreet pores rather than using a homogenous description of a membrane structure. The complexity of a "space-charge" description of the electric field distribution of pores in the nm range is not warranted; hence both sieving effects and electrical (Donnan) effects may have an influence on the separation achieved.

Johan *et al.* [25] studied the characteristics and retention of a mesoporous γ-Al_2O_3 membrane for NF. The γ-Al_2O_3 membrane was characterized using both FESEM (Field emission scanning electron microscopy) and SEM (Scanning

electron microscopy). From the data the specific surface area, mean pore size and porosity were obtained. The experiments for both techniques were carried out with both single salts and mixtures of salts at different concentrations. The retention of ions was interpreted in terms of Donnan exclusion (the formation of an electrical double layer within the pores). They found that one of the advantages of using γ-Al_2O_3 as an NF-membrane is that it is negatively charged at pH > 7 and positively charged at pH < 7 (amphoteric behaviour).

2.4 Donnan distribution

The distribution of charged species between the membrane and the solution is affected by the interactions between the charge at the membrane surface and the ions in the solution [2]. This distribution is influenced by interactions between different ions. In the case of a charged membrane, the concentration of the co-ions in the membrane becomes lower than that in the solution, whereas the counter-ions have a higher concentration in the membrane than in the solution. A potential difference caused by the concentration difference of the ions is generated at the interface between the membrane and solution. This potential difference is called the Donnan potential. The influence of this potential causes the co-ions to be repelled by the membrane, whereas the counter-ions are attracted.

An equilibrium, caused by a charged membrane in contact with a single solution, will be established between the membrane and the solution. The Donnan equilibria for NaCl (1-1), $CaCl_2$ (2-1) and Na_2SO_4 (1-2), after some equation solving steps, can be specifically written as follows:

(1-1) $$\frac{c_B^m}{c_B} = \frac{c_B}{c_B^m + c_X^m} \qquad (2.2)$$

(2-1) $$\frac{c_B^m}{c_B} = \left(\frac{2c_B}{2c_B^m + c_X^m} \right)^2 \qquad (2.3)$$

(1-2) $$\frac{c_B^m}{c_B} = \sqrt{\frac{c_B}{c_B^m + c_X^m}} \qquad (2.4)$$

This difference in co-ion distribution, as a function of the feed salt concentration, is shown in Figure 2.3.

The Donnan equilibrium depends on the salt concentration, the fixed charge concentration in the membrane and the valence of both the co-ion and counter-ion. An increase in salt concentration and decrease in fixed membrane charge leads to an increase of co-ion concentration in the membrane and hence to a lower rejection of salts. The co-ion in the membrane will increase with increasing counter-ion valence and decreasing co-ion valence. Calculating the Donnan equilibrium becomes much more complex when studying salt mixtures.

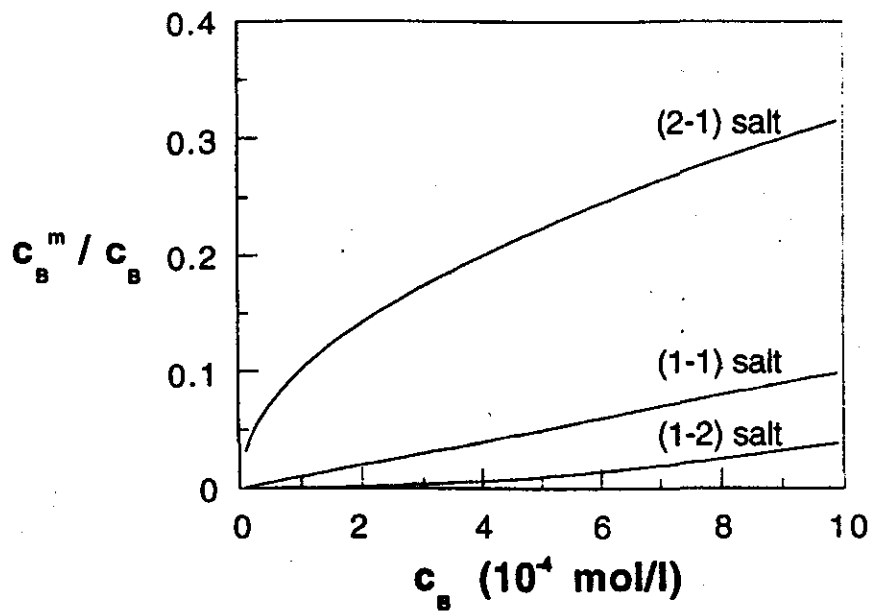

Figure 2.3: Distribution coefficient of co-ions between membrane and solution in case of a negatively charged membrane [2]

2.5 *Membrane fouling*

Membrane fouling can be defined in terms of the reduction in permeate flux that cannot be reversed. Nonetheless, both reversible and irreversible decreases in permeate flux are often referred to as membrane fouling, while the materials causing the permeate flux decline are collectively referred to as foulants. Usually flux decline is partly reversible and partly irreversible [26]. The difference between reversible and irreversible fouling could be explained as follows: take an initial pure water flux of 100; the water flux decreases to 70; when using the membrane again the final water flux is 90. One could thus say that the flux decline is 30%, of which 20% is reversible and 10% is irreversible.

The deterioration in flux performance of the membrane is due to polarization phenomena, which will be discussed later in this section [27]. The transport of foulants and their accumulation on and within the membranes are affected by the fluid dynamics of the membrane, membrane chemistry [28], the nature of the foulants [29] as well as the flow rate and concentration of a feed solution. To reduce fouling, systems can be designed to operate with the feed flow tangential to the membrane.

2.5.1 *Principles of fouling*

Fouling can be due to concentration polarization, pore blocking and adsorption of hydrophobic species on the membrane [28, 30]. NF-membranes retain substances with molar masses higher than ~300g.mol^{-1} as well as monovalent and multivalent ions, which contribute to membrane fouling [31]. The main foulants include soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants and microorganisms [32, 33]. Flux decline and membrane fouling cause an increase in the cost and thus indirectly a reduction in the applicability of membrane processes.

2.5.1.1 *Concentration polarization*

In pressure driven membrane processes, concentration polarization arises when the membrane rejects a solute. This phenomenon leads to a supersaturated concentration of soluble salts at the NF-membrane surface even though the bulk concentration is not saturated [28]. The solute and other species in the feed stream are transported towards the membrane surface by convective flow at a velocity equivalent to that of the permeating solvent. Solutes larger than the pores of the membrane will be retained on the membrane surface. The cross-flow velocity which prevails in the boundary region is essentially laminar and backtransport of retained solute into the bulk stream occurs due to diffusion. In Figure 2.4, this build-up on the membrane surface is illustrated [27, 30]. In order to balance the backdiffusion of the solute [D(dC/dx)] and the convective flow of the solute towards the membrane surface (JC), the concentration of the retained solutes at the membrane interface (C_s) must be much higher than the concentration in the bulk solution (C_b).

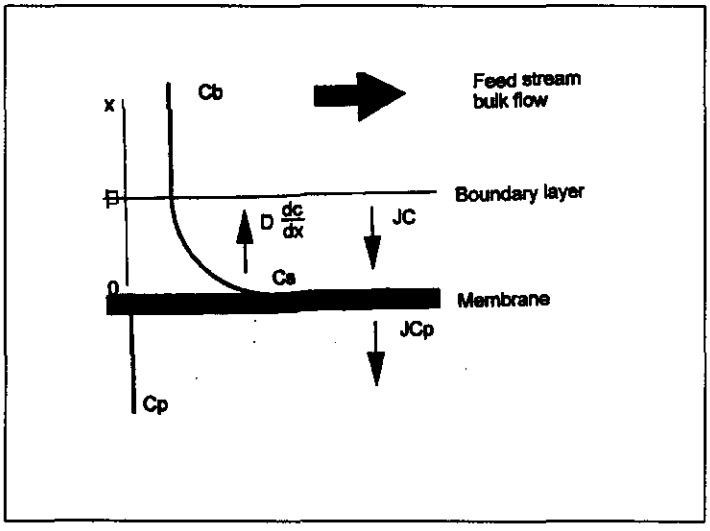

Figure 2.4: The concentration polarization phenomenon [30]

2.5.1.2 *Pore blocking*

Pore blocking refers to the accumulation of materials on, in and near a membrane. These accumulated materials create an additional layer of resistance to the permeate flux. Materials smaller than the pore size are absorbed onto the inner walls of the pores. Except by back flushing, the inner wall adsorbed materials (Figure 2.5, C) are difficult to remove [27, 30]. The schematic presentation of modes of pore blocking is shown in Figure 2.5.

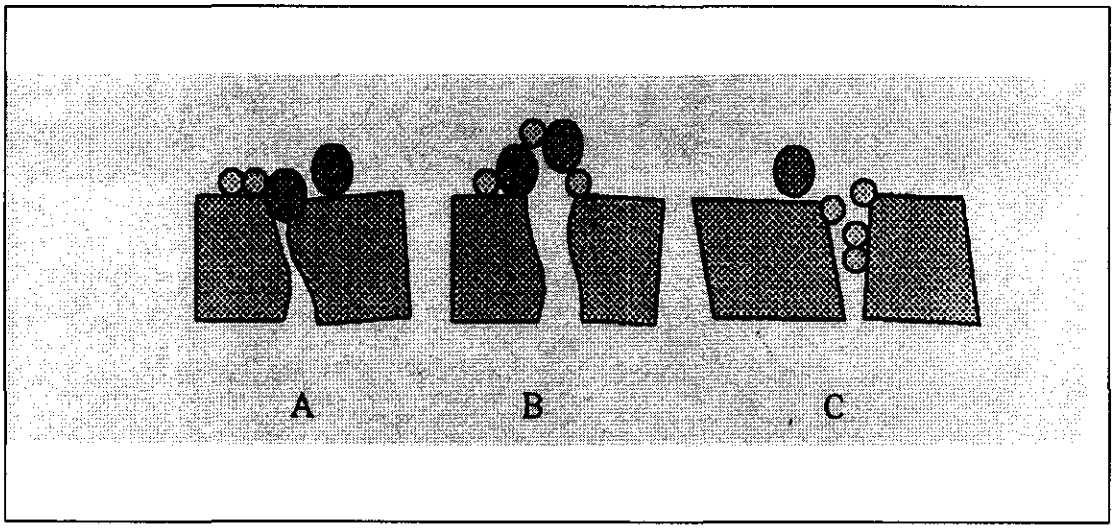

Figure 2.5: Modes of pore blocking [30]

In Figure 2.5, A illustrates complete pore blocking, B pore bridging which is a partial obstruction of an entrance, and C internal pore blinding, entrapment or adsorption of non-retained species.

2.5.2 Fouling indices

2.5.2.1 Silt Density Index (SDI)

The likelihood of polluted water to foul a membrane can be assessed by means of an empirical test of filterability (silt density index, SDI) using a

0.45μm membrane in a dead-end filtration cell. The SDI can be calculated from the initial time t_i required to filter a fixed volume, typically 500 cm^3, of polluted water through a clean membrane and the final time t_f required to filter the same volume after the membrane has been used for a defined period of time. The standard measurement of SDI includes a 47mm diameter filter with a driving force of 2 bar pressure applied and a total test time t_t of 900 seconds. The SDI can be calculated as:

$$SDI = \frac{100(1-\frac{t_i}{t_f})}{t_t} \qquad (2.16)$$

where t is expressed in seconds. Upper SDI limits of approximately 3-5 have been found to apply for the successful operation of outside hollow fibers and spiral-wound reverse osmosis membranes [27]. For the other membranes, MF, NF and UF, the same method of quantifying fouling can be used and the SDI range can be approximated.

2.5.2.2 Modified fouling index (MDI)

The modified fouling index (MDI) is determined by the same principles and equipment used for the SDI index determination. In this index, however, the volume is recorded every 30 seconds over a 15 minute filtration period [34] and the thickness of the cake layer formed on the membrane surface is assumed to be proportional to the filtrate volume. The total resistance is the sum of the filter and the cake resistances.

2.5.3 Scale formation

Scaling occurs when there is a precipitation of salt in the polluted water due to an increased concentration on the membrane surface. Concentration of scale-forming species can occur due to: (1) bulk concentration of the salts as water permeating through the membrane is removed from the salt solution and (2) concentration polarization. The common scaling enhancing compounds

present in polluted water are calcium/magnesium carbonate, barium/magnesium sulphate and calcium phosphate [27].

Manttari *et al.* [35] studied the fouling effects of polysaccharides and humic acid on NF membranes. Various concentrations of vanillin, humic acid, locust bean gum and karaya gum were studied and the NF-membranes used were NTR-70 and Desal-5. Before the filtration of any solution was carried out, RO-treated water was permeated through the membrane until a stable flux was obtained. After pure water filtration, the model substance solution was introduced without decreasing the pressure. Permeation was again continued until a stable flux was obtained. Finally the pure water flux was measured again.

Figure 2.6 shows the effect of locust bean concentration on the flux of the NTR-7450 membrane. From Figure 2.6, it is clear that the concentration of the model substance solutions is directly proportional to fouling.

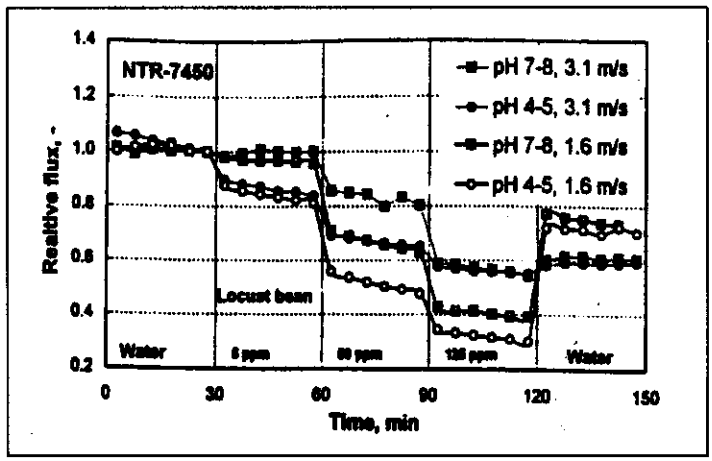

Figure 2.6: Effects of locust bean concentration on the flux of the NTR-7450 membrane [35]

Nyström *et al.* [31] used four different membranes (NF40, NTR-7450, NTR-7410 and NTR-7250) to study fouling. Initially, the membranes were stabilized for ~4h at a pressure of 10 bar at 25°C, and the pure water flux was measured. Fluxes for pure water, salts, vanillin and humic acid solutions were tested at different pressures between 4 and 12 bar, a flow rate of 2.0 ms^{-1} and a

temperature of 25°C. Thereafter, the module was washed with pure water and the flux of the pure water was measured. The original solutions, retentate and permeate were analysed. It was observed that multivalent salts foul more when in combination with organic compounds, which was to be expected.

Benkahla *et al.* [36] described the fouling mechanism in cross-flow filtration of a mineral $CaCO_3$ (average diameter of 6μm) suspension. The tests were carried out on membranes of 2.8 mm inner diameter and an average pore diameter of 0.2 μm. A pump circulated the test sample through the membrane module and stirred reservoir. The suspension flow rate, membrane inlet and exit pressures, filtrate compartment pressure and the permeate flux were continuously measured. The permeate flux variation presented a hysteresis which was interpreted as an irreversible compression of the cake deposited on the membrane.

In the second experimental set-up, the pressure between the deposited cake (foulant) and the corresponding pure water flow rate were continuously measured. The study was focused on determining the variation of the void fraction (porosity) of the cake resulting from the relative particle displacements under the compressive action of the pressure. The porosity was found to be a function of the pressure gradient in the cake. The cake thickness was 0.54 mm representing 38% of the inner radius.

Vrijenhoek *et al.* [37] studied the influence of RO as well as NF-membrane surface properties on the initial fouling rate of colloidal silica particles. Using a cross-flow membrane filtration test unit, they found that, regardless of operating conditions, the rate and extent of colloidal fouling was most significantly influenced by the physical roughness of membrane surfaces.

It was observed by atomic force microscopy (AFM) images that more particles accumulated in the valleys of rough membranes (valley clogging) and that this clogging caused a more severe decrease of flux than is observed for smooth membranes.

Van der Bruggen *et al.* [38] performed experiments on flux decline during NF due to adsorption of organic compounds. UTC-20 (Toray Ind. Inc., Japan) and NF 70 (FilmTec/Dow, MI, USA) membranes were used to measure flux decline caused by 11 organic compounds. The flux decline was compared to pure water flux. Organic solutions, which contained less than 1000 mg. ℓ^{-1} of organic compounds, showed a flux decline of more than 50% compared to pure water flux. For the NF70 membrane, over 50% flux decline was obtained mainly for the aromatic compounds e.g. benzaldehyde, benzonitrile and p-tolualdehyde, while the flux decline values were less for saccharides, alcohols and gycols. UCT-20 membranes, with flux declines less than 50%, appeared to be less susceptible to organic fouling than the NF70's. However, fouling caused by saccharides, alcohols and gycols was comparable for both membranes.

The presence of calcium, humic acid or natural organic matter (NOM) in surface water can cause severe fouling of NF membranes [39]. Schafer *et al* [39] studied the conditions of fouling using a stainless steel stirred cell of volume 185 ml and a membrane area of 21.2×10^{-4} m^2 at a transmembrane pressure of 5 bar. Three commercial thin film composite membranes (TFC-S, TFC-SR and TFC-ULP from Fluid Systems, USA) and one cellulose acetate (CA-UF) membrane were used. The deposition of organic matter was determined by mass balance in feed and concentrate samples. Electron microscopy and X-ray photoelectron spectroscopy (XPS) were used to study the morphology and composition of the fouling layer. It was found that both the calcium and the organic matter played a major role in fouling of the membranes. The calcium forms complexes with some of the organics, which is deposited on the membrane surface. Irreversible fouling occurred with all membranes at high calcium concentrations.

Seidel and Elimelech [40] investigated the role of hydrodynamics (initial permeate flux and crossflow rate) and divalent cations (calcium) in NOM fouling of thin film composite NF70 (Dow-FilmTec) membranes. The fouling run was continued for 50 hours and permeate flux was continuously

monitored. The NOM, total dissolved salts (TDS) and Ca^{2+} rejection from the feed and permeate solution were periodically determined. At higher initial flux and/or low crossflow rate, the concentration of the rejected Ca^{2+} at the membrane surface increased due to concentration polarization, thus enhancing fouling by Ca-NOM complexes. This showed that membrane fouling and performance are governed by the coupled influence of chemical and hydrodynamic interactions.

Research done on fouling confirmed that membranes could experience flux decline with time during the filtration process. The fouling problem has been identified, but how could the performance of the membrane be regenerated?

2.6 Chemical cleaning

Due to fouling, cleaning is an essential requirement for membrane processes. Membranes can be cleaned every few minutes, hours or even after a month, depending on the rate of fouling. Some of the chemical cleaning techniques are given in Table 2.5.

Table 2.5: Membrane chemical cleaning techniques [41, 42]

Category	Major function	Foulant	Typical chemicals	Comment
Pure water flush	Remove unbound species	Loosely-bound species	Water	First useful step in cleaning
Caustic	Hydrolysis, solubilization	Proteins, biomolecules	NaOH	Usually for UF
Acids	Solubilization	Inorganic scale	Citric acid, nitric acid	Usually for RO
Enzymes	Chelation	Proteins, biomolecules	Enzymes	Cleaning temperature may be important
Chelating Agents	Oxidation, disinfection	Metals	Citric acid, EDTA	Form complex compounds
Oxidants/Disinfectants	Oxidation, disinfection	Biofilms and oxidasable deposits	NaOCl, H_2O_2, peroxyacetic	Caution! Chlorine can damage some membranes
Surfactants/detergent	Emulsifying, dispersion, surface conditioning	Hydrophobic species e.g. oils	Surfactants, detergents	Detergent may be a mixture of base, enzymes and dispersants

Since little research has been done on the chemical cleaning of NF-membranes, some of the literature cited on chemical cleaning will be based on other membrane classes.

Chemical cleaning can help to restore the membrane flux. Once the overall resistance caused by retained species accumulating on the membrane surface reaches the critical point, some chemical cleaning procedure must be applied [30].

In order to understand membrane fouling, one has to understand interactions between the fouling materials and the membrane, between cleaning

chemicals and fouling, and within the fouling materials [42]. Once the cause of membrane fouling is identified, various cleaning chemicals (Table 2.5) may be used to remove foulants and restore the membrane flux.

Madaeni *et al.* [43] studied chemical cleaning of fouled membranes. Membranes fouled by seawater showed that 90% of the foulant on the membrane surface was calcium sulphate and the rest mainly calcium phosphate. They found that the type of the fouling material determines the choice of the cleaning agent. The concentration of the cleaning agent was 0.05 %. Acids had the lowest cleaning ability, alkali moderate while the combination of chelating agents (EDTA) with alkali provided the best cleaning efficiency. The chemicals used in this study included:

- Acids (hydrochloric, nitric, sulphuric, phosphoric, citric, and sulphamic acid)
- Bases (sodium, potassium and ammonium hydroxide)
- Surfactants (sodium hypochlorite, ammonium chloride, EDTA, and sodium dodecyl sulphate)
- Commercial dish washing liquids (Yekta and Goli)

The efficiency of various chemicals for cleaning fouled NF-membranes was studied by Liikanen *et al.* [44]. The pilot plant was fed with conventionally treated surface water from a water treatment plant in Southern Finland. Fouled membranes were cleaned on a weekly basis with various chemicals and procedures. The cleaning efficiency was compared both in terms of flux recovery and foulant removal. The study revealed that alkaline cleaners with chelates resulted in the most efficient cleaning both in terms of flux recovery and foulant removal. Alkaline cleaners modified the membrane and improved the flux substantially in comparison to the virgin state (membrane before use).

Mohammadi [45] investigated chemical cleaning efficiency on a polyamide RO-membrane fouled by precipitation of materials (petroleum industry) on the membrane surface. He found that a combination of sodium dodecyl sulphate,

Na-EDTA and sodium hydroxide should be used as a chemical cleaner for optimum recovery of the polyamide membrane.

Hong and Elimelech [46] used an EDTA-chelating agent to reduce natural organic matter (NOM) fouling which has complexed with calcium present in the feed water. The formation of a Ca-NOM complex has been discussed above (fouling section) [40]. Both free and NOM-complexed calcium ions were removed. EDTA improved the cleaning efficiency by disrupting the fouling layer structure through a ligand exchange reaction between EDTA and the NOM-calcium complexes.

Sadhwani and Vesa [47] did cleaning experiments on reverse osmosis membranes. The selected membranes had a spiral-wound configuration and where thin-film composite membranes obtained from Filmtec. Experiments were carried out in a seawater desalination plant known as Las Palmas, which was commissioned in 1989. The tests consisted of the initial measurement of the performance, cleaning of the membrane by recycling the cleaning solution for an hour and a final measurement of performance. Cleaning solutions were acids, bases and detergents prepared at three different doses of 0.5%, 0.8% and 1.0%. Feed pressure was 67 bar and the temperature 20-22°C. The cleaning agents that proved most effective for increasing product water flow rate were alkaline (NaOH) chemicals with detergent, acid (HCl) with detergent and acid (HCl) with caustic soda. The introduction of a detergent resulted in a higher effectiveness of cleaning.

A bench-scale crossflow unit was used to evaluate cleaning strategies with a sulfonated polyethersulfone (PES) ultrafiltration (NTR7410) membrane [48]. The crossflow velocity was adjusted and maintained at approximately ~8.6 cms^{-1} by setting a constant feed flow rate of 0.20 $\ell.min^{-1}$. The temperature was maintained at 23-25°C and the transmembrane pressure at 345 kPa. Ultrafiltration (UF) membranes were fouled by relatively hydrophilic and hydrophobic NOM-sources (Horsetooth Resevoir surface water, HT-SW and Orange County groundwater, OC-GW) and humic acid. The three different cleaning agents used included 0.1 M citric acid, 0.1 M NaOH and 0.001 M

sodium dodecyl sulphate (SDS, an anionic surfactant). Caustic cleaning (NaOH) was more effective than citric acid cleaning for the membrane fouled with OC-GW NOM due to the high percentage (54.7%) of hydrophobic acids present in the desorbed NOM (foulants). Cleaning with SDS was not as effective as caustic or acid cleaning. For membranes fouled with HT-SW NOM, none of the three cleaning agents were very effective in recovering flux after fouling. NOM-rejection showed almost the same trends before and after application of cleaning agents.

Munoz-Aguado *et al.* [49] studied the enzymatic and detergent cleaning of a polysulfone ultrafiltration membrane fouled with bovine serum albumin (BSA) and whey protein concentrate. A Millipore PTTK polysulfone membrane, which completely retains the foulant, was used in all experiments. Cetyl-trimethyl-ammonium bromide (CTAB), a cationic surfactant, Terg-A-Zyme (TAZ), a complex mixture of detergent and enzymes and *α-chymotrypsin* (α-CT) were used as cleaning agents. The experiments were performed in a batch cell of 110 mℓ capacity and with a membrane area of 15.2 cm^2. The amount of foulant deposited on the membrane was kept constant by maintaining a fixed permeate volume.

Enzymatic cleaners were most effective when operated at concentrations that optimise the cutting of the proteins. The use of higher concentrations did not increase the enzymatic cleaning efficiency. The efficiency of the detergent increased with concentration until a point where the cleaner damaged the membrane itself.

At Stellenbotch University, paper effluent arriving from the Mondi Kraft paper mill at Piet Retief, South Africa, was filtered through a tubular poly(ether sulphone) (PES) ultrafiltration membrane under constant pressure cross-flow conditions [50]. The tubular UF membrane test rig was operated in a complete recycle system at zero recovery. This system allowed changes in the feed end permeate to be monitored throughout the filtration process. The effluent deposited into the membranes and the permeate were characterized by UV-

VIS (Beckman DU640) light spectroscopy. Untreated and Pluronic F108-treated membranes were fouled for a period of 24 hours. Cleaning with sodium dodecyl sulphate (SDS) and NaOH solutions slightly restored the permeate water flux of uncoated PES-membranes. The use of Titron X-100 in place of SDS for Pluronic coated membranes proved to be more effective. Enzymatic cleaning did not increase the permeate water flux of the membranes. In some cases it appeared as if the enzyme itself adsorbed onto the membrane, causing additional fouling.

The literature of cleaning showed that generally, the cleaning efficiency depends on the type of membrane foulants. The alkaline solutions and surfactants have good cleaning efficiency, while acids generally gave poor results unless used in combination with for example surfactants. For seawater, EDTA was an effective chemical cleaner as there was higher metal concentration in the sample. Alkaline solutions were also effective when used for membranes fouled with surface water. This is evident since surface water has a high NOM-content, which can easily be removed by alkali.

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CHAPTER 3

CHARACTERIZATION OF NF-MEMBRANES

CHAPTER 3

3.1 Introduction

Various characterization methods can be used to compare NF-membranes [1]. These methods provide information on structure, morphological and on performance related properties.

In this study, NF-membranes were characterized using scanning electron microscopy (SEM), clean water flux and the retention of electrolyte solutions (NO_3^-, F^- and SO_4^{2-}) both in the dead-end and cross-flow mode.

3.2 Experimental

3.2.1 Materials and methods

3.2.1.1 SEM

SEM was used to investigate surface properties as well as to obtain an understanding of the nature of the membrane support layer and the elemental composition. The SEM instrument used was a Philips XL 30 coupled with an EDAX CDU Leap Detector.

For scanning electron microscopy, samples were first mounted onto the sample plates using carbon glue. The samples were dried at about 50°C before being coated in a vacuum with either gold/palladium or carbon. The top and bottom surfaces and a cross-section of the membranes were subsequently investigated.

3.2.1.2 Clean water flux

Water flux through a membrane can be described by the model of Darcy [2] (Equation 3.1):

$$J_w = A_w \cdot (\Delta P - \Delta \pi) \qquad (3.1)$$

where A_w is the water permeability ($\ell .m^{-2}.h^{-1}.bar^{-1}$), which can be determined experimentally from a figure of J_w versus ΔP (equation (3.2)), ΔP is the applied trans-membrane pressure (bar) and $\Delta \pi$ is the osmotic pressure difference. If the feed and the retentate sides contain clean water, i.e. the osmotic pressure difference across the membrane becomes zero, then equation (3.2) reduces to:

$$J_w = A_w \cdot \Delta P \qquad (3.2)$$

This equation (3.2) can be related to the Hagen-Poiseuille model [2,3] (Equation 3.3):

$$J_w = \frac{\varepsilon . r^2}{8 \cdot \eta \cdot \tau} \cdot \frac{\Delta P}{\Delta x} \qquad (3.3)$$

where Δx is the membrane thickness (m) and η is the viscosity of water (Pa.s). By combining the Darcy and Hagen-Poiseuille models, i.e. models (3.2) and (3.3), Equation 3.4 is obtained:

$$A_w = \frac{\varepsilon}{\tau} \frac{r^2}{8 \cdot \eta \cdot \Delta x} \qquad (3.4)$$

where ε is the porosity, which gives an approximation of how many pores there are in a medium and τ is the tortuosity. For cylindrical pores perpendicular to the membrane surface, $\tau = 1$ [3]. When it is approximated that:

$$\tau \approx \frac{1}{\varepsilon} \tag{3.5}$$

When combining (3.4) and (3.5), the following equation is obtained:

$$(\varepsilon \cdot r)^2 = A_w \cdot 8 \cdot \eta \cdot \Delta x \tag{3.6}$$

3.2.1.2.1 Dead-end module

A bench scale dead-end module with a capacity of ~1 ℓ was used. The unit could be operated at pressures of up to 20 bar, using the pressure difference as a driving force and the pressure is obtained from a nitrogen cylinder. A magnetic stirrer is used to homogenize the feed sample. The membrane area is 0.0064 m^2. All the experiments were performed at room temperature. A diagrammatical presentation of the experimental apparatus can be seen in Figure 3.1.

Samples of the various membranes were cut to fit into the dead end unit and were immersed in deionised water for ±30 minutes to remove membrane preservatives before being placed on a porous metal support disc in the high-pressure module. Clean water (feed) was poured into a module and rates of permeation ($\ell.min^{-1}$) were determined with the aid of a Sartorius electronic balance. These experiments were done at pressures of 5, 10, 15 and 20 bar for all the tested membranes at ambient temperature. The clean water flux for five membranes was determined (see Table 3.2).

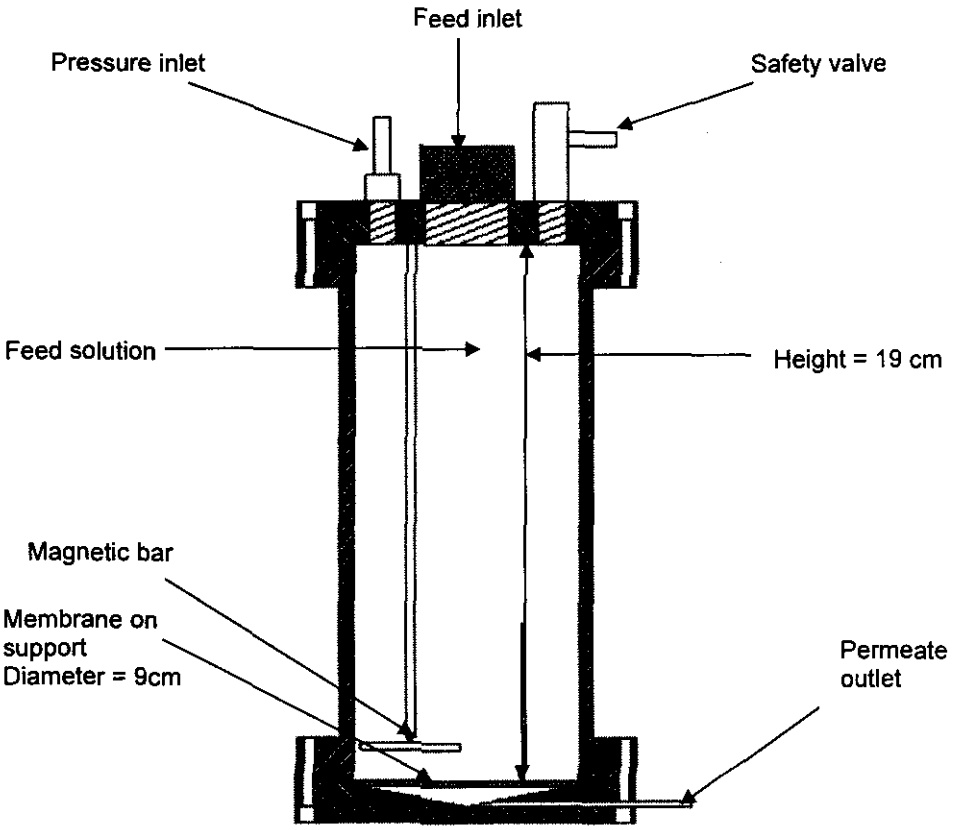

Figure 3.1: Dead-end unit for NF-experiments

3.2.1.2.2 Cross-flow module

A pilot-scale cross-flow NF-unit was manufactured combining a sand filter, a MF-module and a NF-module. The unit was designed in such a way that any combination of the three filtration techniques can be used for the treatment of water. The feed tank before the MF-unit has a capacity of 1000 litres. After the MF process is another reservoir with a capacity of ±300 litres, which feeds the NF-membrane process. Experiments were performed at room temperature. Unlike a bench-scale unit, the pilot-scale unit can be operated at pressures above 20 bars. The spiral-wound NF-membranes of 2.5 inch (0.0635 m) diameter and 40 inch (1.016 m) length were fitted into a stainless steel 2.5" GRP pressure vessel. A diagrammatical presentation of the cross-flow NF-plant is presented in Figure 3.2.

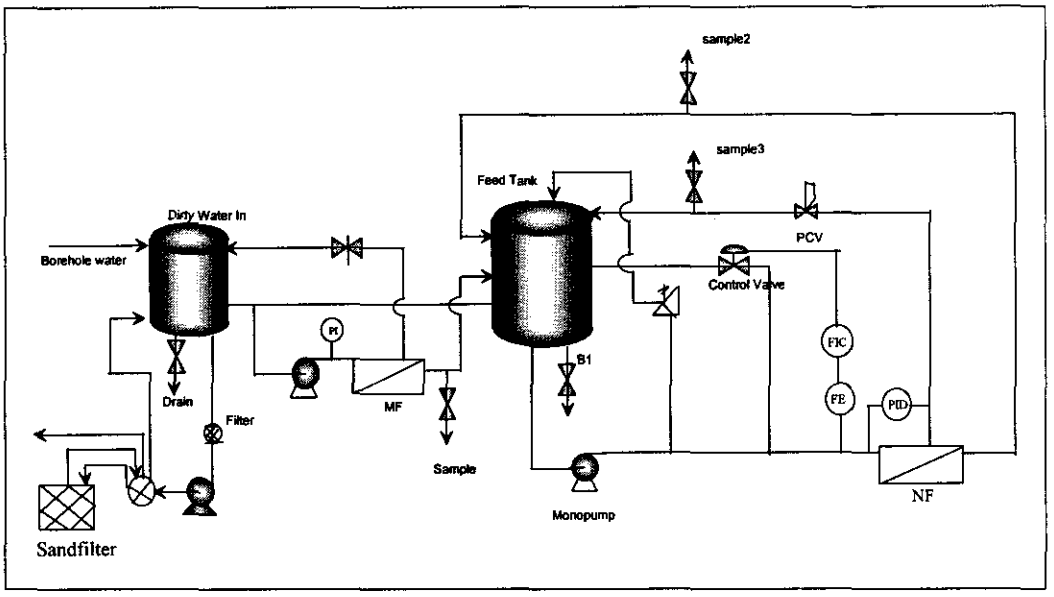

Figure 3.2: Process flow diagram of NF-membrane pilot plant

For the pilot-scale cross-flow module, clean water flux was determined using the same membranes as in the bench-scale dead end module, except for NF70. To ensure the removal of membrane preservatives, clean water was permeated through the membranes for 2-3 hours.

The experiments were performed at ambient temperature. The feed flow was kept constant at 1.50 $\ell.min^{-1}$ and the flow rate of the permeate was measured. The surface area of the membranes was 2.60 m^2 and operational pressures of 5, 10, 15 and 20 bar were applied.

3.2.1.3 Electrolyte solutions

20 ppm of three salts prepared as NO_3^-, F^- and SO_4^{2-} were investigated for retention on NF-membranes in both the dead-end and cross-flow modules. For dead-end module, three experimental repetitions were done while collecting a 100 mℓ permeate sample, which is only 10% of the initial solution while for cross-flow module 100 mℓ permeate samples were collected at intervals of 30 minutes for about three hours. The experimental errors were

then calculated for both modules. The chemical details given by the suppliers are shown in Table 3.1. An operational pressure of 5 bar was applied at ambient temperature.

Table 3.1: Detailed information of chemical used

	Supplier	Assay	Purity	MW* (g/mol)
$NaNO_3$	SAARCHEM	99%	AR*	84.99
NaF	MERCK	99%	AR	41.99
$MgSO_4$	SAARCHEM	62-70%	CP*	120.39

* MW = molecular weight AR = analytical reagent CP = chemically pure

The analysis of the permeate, retentate and feed was carried out colorimetrically using a HACH DR/890 colorimeter. The procedure used was adapted directly from the instrument's manual.

The retention coefficient (R) was obtained using Equation (3.7):

$$R = 1 - \frac{C_p}{C_f} \tag{3.7}$$

where C_p (permeate concentration, ppm) was obtained from the colorimeter analysis value and C_f was obtained from the average of the initial feed concentration and the retentate (the feed solution remaining in the module at the end of the experiment) concentration.

3.2.1.4 Membranes used

The tested membranes were obtained from different suppliers as presented in Table 3.2. All the membranes except for NF70, which was not available as a cross-flow module, were used for both dead-end and cross-flow modules.

Table 3.2: Different membranes used and their suppliers

Membrane	Supplier	Membrane Type	Operating conditions (°C & bar)*	MW cut-off (Da)	Operational pH range
D12	Weir-Envig	FS*/SWM*	50 & 41	180	4 – 11
D11	Weir-Envig	FS/SWM	50 & 41	180	4 – 11
CTC1	Hydranautics	FS/SWM	45 & 41.6	(-)*	3 – 10
NF90	Filmtec	FS/SWM	35 & (-)	200	3 – 9
NF70	Filmtec	FS/SWM	35 & (-)	200	3 – 9

* SWM = Spiral-wound module, FS = Flat sheet, Pressure = bar, Temperature = °C, (-) = no value

According to the manufacturer, CTC1 (chlorine tolerant composite) membranes have a minimal NaCl rejection of 90% and a flux of 0.3 $m^3.d^{-1}$ at maximum pressure of 41.6 bar. The two FilmTec® membranes (NF70 and NF90) have a minimum magnesium sulphate rejection of 95% for solutions of 2000 ppm at a pressure of 5 bar and temperature of 25°C. The clean water flux for NF70-2540 and NF90-2540 are 3.2 $m^3.d^{-1}$ and 2.6 $m^3.d^{-1}$, respectively. The flow rates for individual elements may vary by ±20%.

Similarly, Envig membranes (D11 and D12) have minimum magnesium sulphate and fructose rejections of 96% and 98%, respectively. In terms of NaCl rejection, D11 has 50% minimum rejection while D12 has 15%. A pressure range of 5-28 bar can be used. For chemical cleaning purposes, the pH must be between 2 and 11.5. The flux for the 4040 module (with an area of 7.90 m^2) of D11 and D12 is 7.57 $m^3.d^{-1}$ and 10.61 $m^3.d^{-1}$, respectively and the estimated flux for the 2540 module (with an area of 2.6 m^2) for D11 and D12 is 4.73 $m^3.d^{-1}$ and 6.63 $m^3.d^{-1}$, respectively.

3.3 Results and Discussion

3.3.1 SEM

The scanning electron microscopy was mainly used to study the morphology of the membranes. The instrument's images gave information about the membrane surface, support layer and cross-section. Images of a D12

membrane studied under SEM are shown in Figure 3.3 and Figure 3.4. All the other NF-membranes had a similar morphology as a D12 membrane.

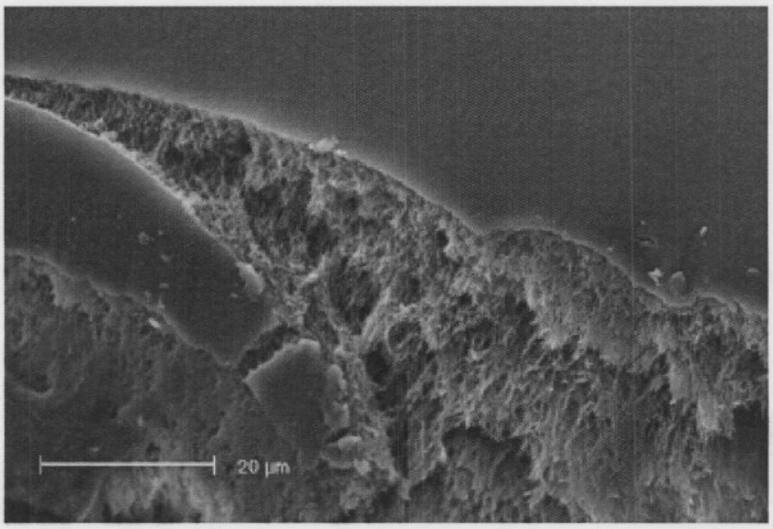

Figure 3.3: The top layer and the cross-section of a D12 membrane

According to Figure 3.3, the top-layer is smooth, thin and dense. This dense layer, which lies over the porous sublayer, is responsible for the separation characteristics. This observation confirms that usually NF-membranes are composite membranes in accordance with findings of Mulder [3].

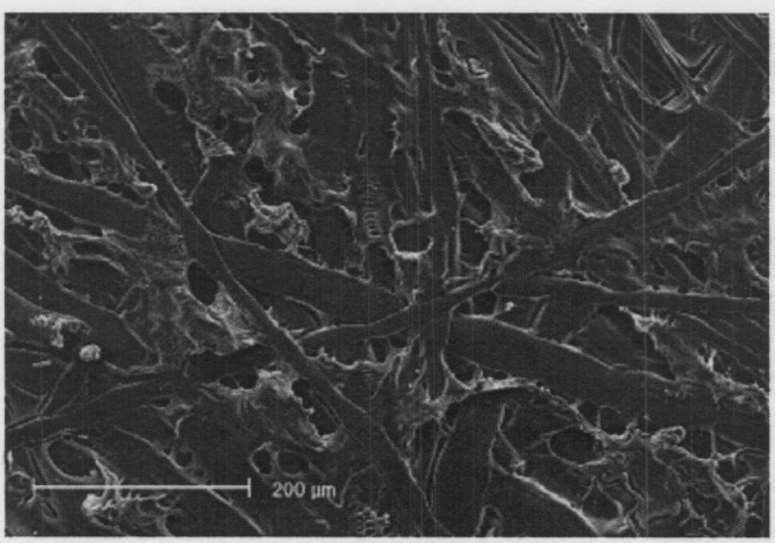

Figure 3.4: The structure of a support layer (D12)

Figure 3.4 shows the loosely packed layer of the support on which the NF thin film is coated (Figure 3.3). According to EDAX, the D12 membrane is composed of carbon, oxygen and sulphur, which suggests that the membrane contains polysulphone.

3.3.2 Clean water flux

3.3.2.1 Dead-end module

The values of A_w (water permeability, $\ell.m^{-2}.h^{-1}.bar^{-1}$) for each membrane can be obtained experimentally from a plot of water flux ($\ell.m^{-2}.h^{-1}$) versus pressure (bar) as shown in Figure 3.5. The viscosity of clean water is usually 0.001 Pa.s and Δx is taken as 1μm [4]. If τ is approximated as per Equation 3.5, $\tau \approx \varepsilon^{-1}$, the value of $\varepsilon.r$ (Equation 3.6) can be calculated from the flux data. The values of ε and r are dependent on each other as shown by the hyperbolic relationship presented in Figure 3.6. The relationship implies that if the polymer porosity is known, the pore radius can be estimated. Since water molecules have a kinetic radius of 0.15 nm [5], they should not be restricted by these membranes. The calculated values of A_w and εr are shown in Table 3. 3.

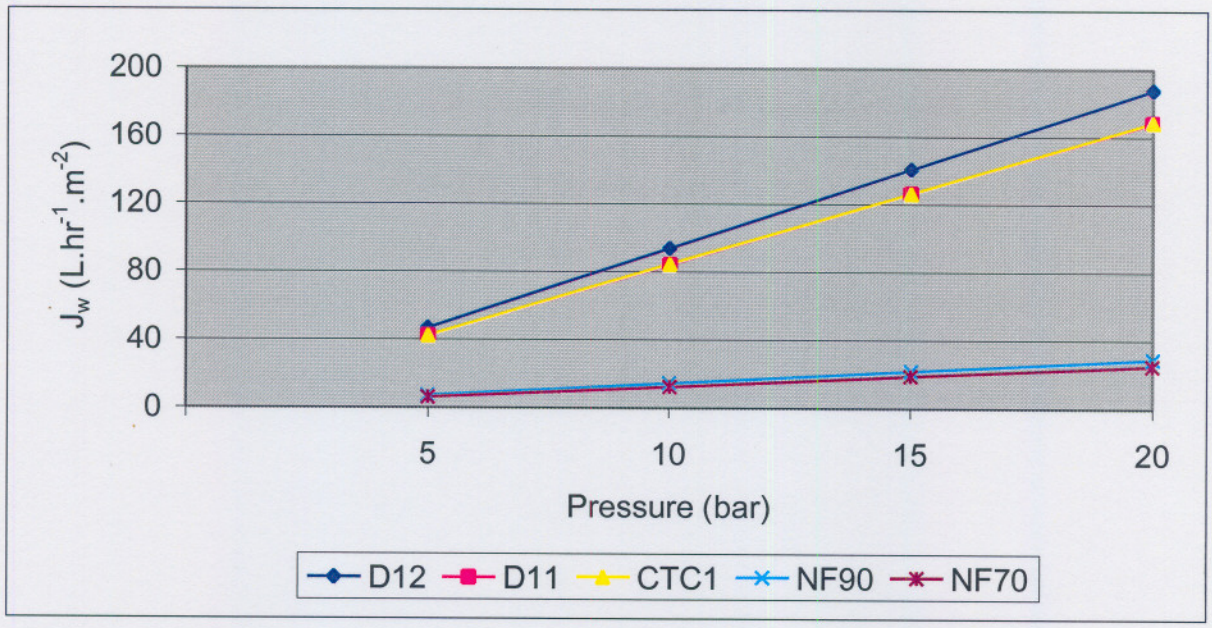

Figure 3.5: Clean water flux for different membranes in dead end-module

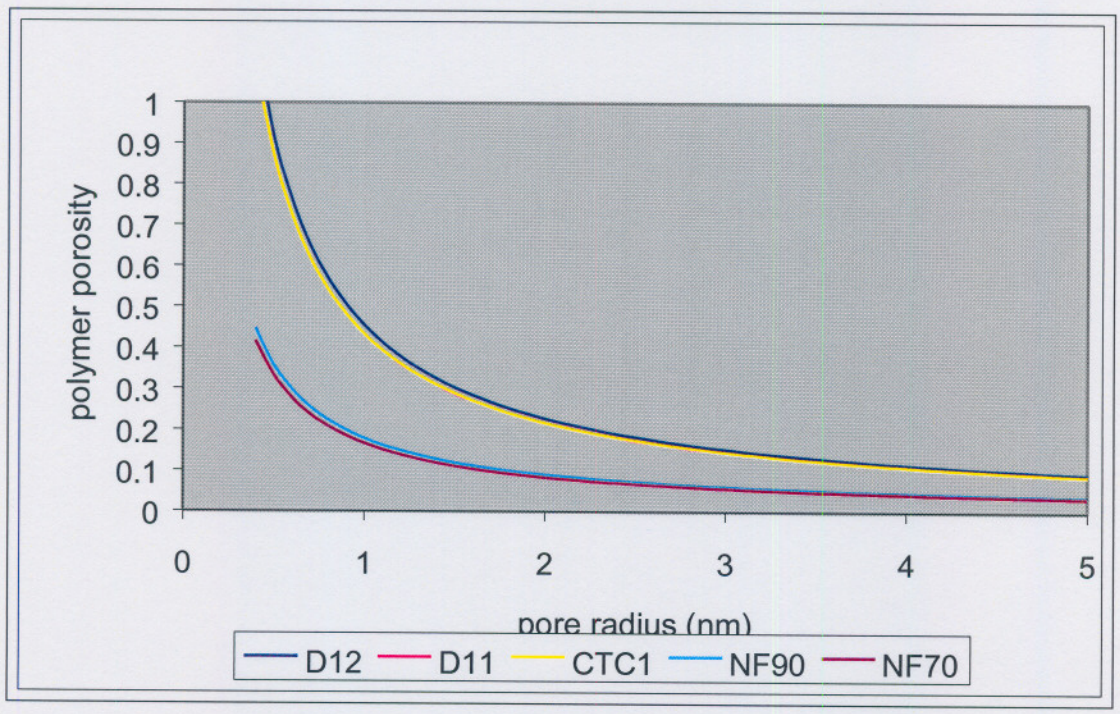

Figure 3.6: Hyperbolic relationship between porosity and pore radius (dead-end module)

Table 3. 3: Clean water permeability and porosity data (dead-end module)

Membrane	A_w (ℓ.m^{-2}.h^{-1}.bar^{-1})	ε.r (10^{-10} m)
D12	9.36	4.55
D11	8.41	4.32
CTC1	8.42	4.33
NF90	1.43	1.78
NF70	1.25	1.66

The A_w results in Table 3. 3 can be compared to the flux ranges given in Table 1.1 [3] for different types of membrane processes. Accordingly, D12, D11, CTC1 and NF90 are NF-membranes because of their water flux range (1.4 - 12 ℓ.m^{-2}.h^{-1}.bar^{-1}) as defined by Mulder [3]. The NF70 flux range was not within the NF-range and can hence rather be classified as an RO-membrane (flux range 0.05 - 1.4 ℓ.m^{-2}.h^{-1}.bar^{-1}). D12, D11 and CTC1 gave fluxes above 8 ℓ.m^{-2}.h^{-1}.bar^{-1} while NF 70 and NF90 had comparable fluxes between 1 and 2 values just close to 1.4 ℓ.m^{-2}.h^{-1}.bar^{-1}.

3.3.2.2 Cross-flow module

As with the bench-scale water permeation, the values of A_w (water permeability, ℓ.m^{-2}.h^{-1}.bar^{-1}) for each membrane in the cross-flow module were experimentally obtained from a plot of water flux (ℓ.m^{-2}.h^{-1}) versus pressure (bar) as shown in Figure 3.7 (points at the origin of this figure should be ignored since they are not experimental points).

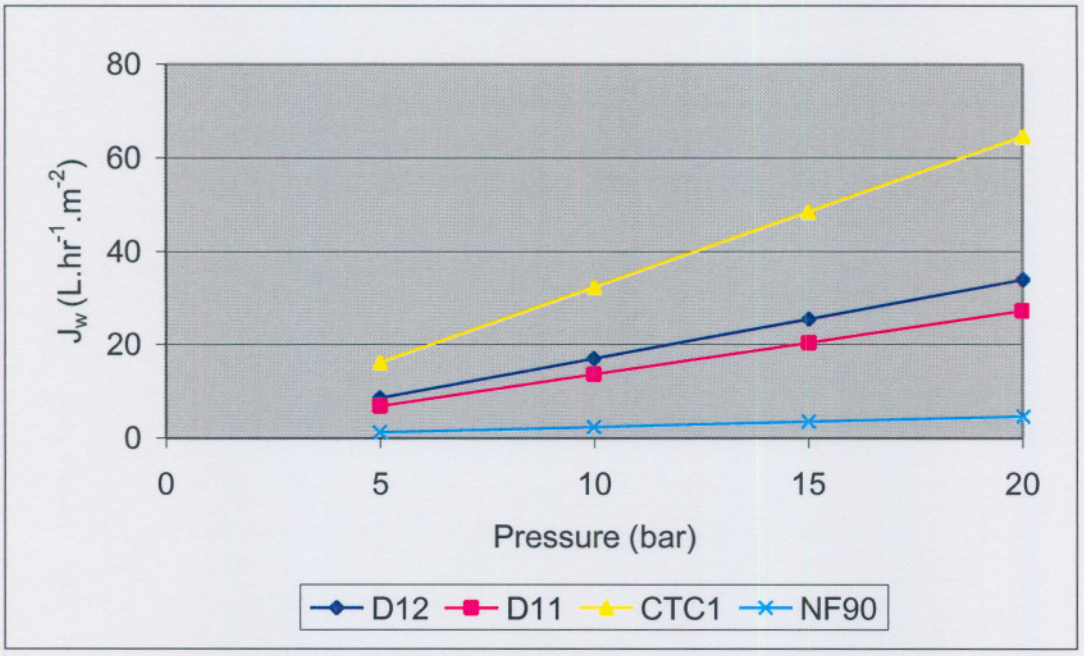

Figure 3.7: Clean water flux for different membranes in cross-flow module

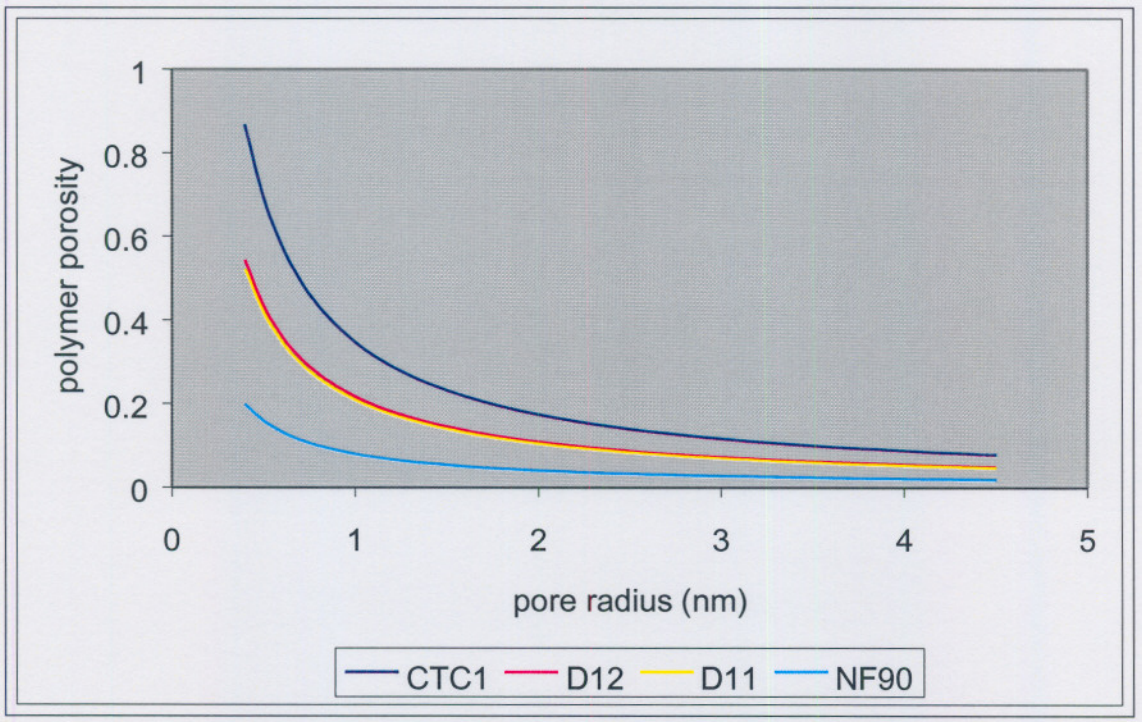

Figure 3.8: Hyperbolic relationship between porosity and pore radius (cross-flow)

The values of ε and r are dependent on each other as shown by the hyperbolic relationship in Figure 3.8. The calculated values of A_w and εr are presented in Table 3.4.

Table 3.4: Clean water permeability and porosity data (cross-flow module)

Membrane	A_w (ℓ.m^{-2}.h^{-1}.bar^{-1})	ε.r (10^{-10} m)
D12	2.12	2.17
D11	1.95	2.08
CTC1	5.41	3.47
NF90	0.28	0.79

Again, the A_w results in Table 3.4 can be compared to the flux ranges given in Table 1.1 [3] for different types of membrane processes. Similar to the dead-end process, D12, D11 and CTC1 have fluxes typical of NF-membranes according to Mulder [3], while NF90's flux was below the NF-range (1.4 – 12 ℓ.m^{-2}.h^{-1}.bar^{-1}) falling in the RO-range. This confirms that the FilmTec® (NF70 and NF90) membranes should actually be classified as RO membranes. Overall, CTC1 gave the highest flux. All the flux values obtained with the cross-flow were less than those obtained with the bench-scale.

By comparing the two modes of flow, higher water permeabilities were obtained in dead-module than cross-flow. For spiral-wound membranes (cross-flow), a permeating component that enters the permeate envelope far from the perforated permeate tube, must spiral inward several feet [6, 7]. Depending on the path length, permeate spacer design and permeate flux, significant permeate side pressure drop can be encountered, thereby reducing the mass transfer driving force, hence the low water permeabilities in cross-flow modules. Similar results were obtained by Nuortila-Jokinen *et al.* [8] using laboratory scale flat sheet cross-flow (53 cm^2) and pilot scale spiral wound (6.1 m^2) modules.

The porosity values (ε.r) for both dead-end and cross-flow modules should be the same (same membrane material was used), The difference observed in Table 3. 3 and Table 3.4 is due to the fact that the ε.r values were not obtained experimentally, but calculated from the A_w, and since the A_w values differ, so will the ε.r values.

3.3.3 Electrolyte solutions

3.3.3.1 Dead-end module

Single salt permeations on the small-scale dead-end unit have been extensively studied previously in our membrane laboratory [2, 4]. The results obtained in this study and their standard deviations are summarized in Table 3. 5.

Table 3. 5: Rejection of single salts in a dead-end module

	Single salts* (%)		
Membrane	NO_3^-	F^-	SO_4^{2-}
D12	60.3 ± 0.21	50.1 ± 3.72	>99.9 ± 0.01
D11	57.7 ± 2.70	19.9 ± 0.14	64.7 ± 4.32
CTC1	49.5 ± 2.19	62.9 ± 1.93	>99.9 ± 0.01
NF90	74.6 ± 2.33	66.0 ± 3.18	>99.9 ± 0.01
NF70	85.5 ± 1.75	89.5 ± 1.13	96.5 ± 0.80

*Concentration = 20 ppm; Temperature = Ambient; Pressure = 5 bar

Accordingly it was shown that all the tested NF-membranes (D12, D11, CTC1, NF90 and NF70) are negatively charged membranes as they have a higher rejection for the divalent anion than for the monovalent anion. This preferential rejection of divalents is typical of NF-membranes as discussed in Chapter 2. NF70 showed typical characteristics of RO rather than NF since the membrane showed little difference in the rejection of multivalent and monovalent ions. Both Modise [4] and Visser [2] came to a similar conclusion for this membrane. It is possible that NF70 might be an amphoteric NF-

membrane that acquires a charge depending on the nature of the electrolyte. NF90 showed high rejection of all the tested ions, mostly sulphate, suggesting that the membrane is negatively charged. Peeters [1] cited that multivalent ions with the same sign of charge as that of the membrane surface (co-ion) are more effectively rejected than monovalent ions.

Although D11 gave good rejection for sulphate and low rejection for monovalent anions, the membrane generally showed lower separation when compared to the other tested membranes, confirming a result previously reported by Visser [2].

3.3.3.2 Cross-flow module

Figure 3. 9 shows rejection of the four tested membranes in the cross-flow module. These results show that, for all four the membranes, the rejection remained constant during a 3-hour experiment period.

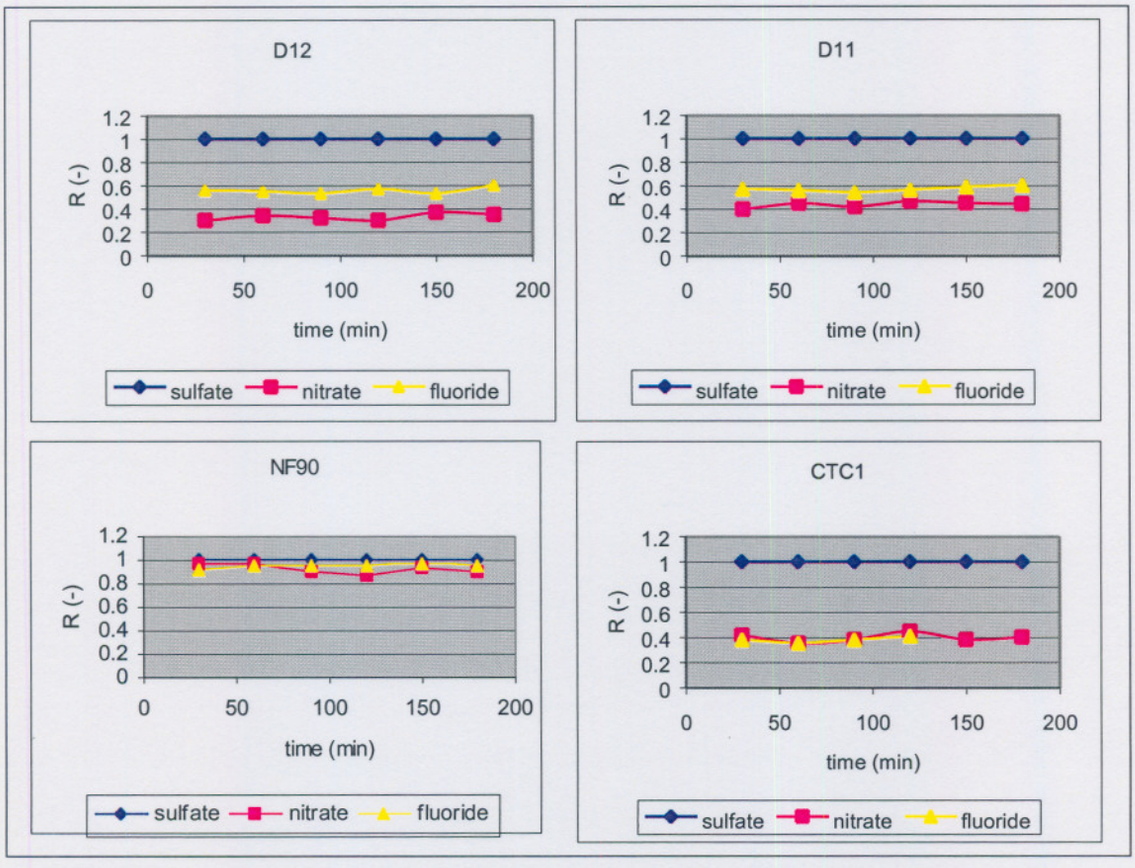

Figure 3. 9: Membranes performance using single salts in pilot plant

The rejection results for the three salts NO_3^-, F^- and SO_4^{2-}, deduced from the graphs in Figure 3. 9 are summarized in Table 3. 6.

Table 3. 6 Rejection of single salts in a cross-flow module

	Single salt rejection* (%)		
Membrane	NO_3^-	F^-	SO_4^{2-}
D12	32.8 ± 0.03	55.6 ± 0.03	>99.9 ± 0.01
D11	43.7 ± 0.02	57.0 ± 0.02	>99.9 ± 0.01
CTC1	39.7 ± 0.03	38.3 ± 0.02	>99.9 ± 0.01
NF90	95.5 ± 0.01	94.4 ± 0.02	>99.9 ± 0.01

*Concentration = 20ppm; Temperature = ambient; Pressure = 5 bar

The results show that the divalent anion has been effectively rejected for all the membranes used. This repulsion is mainly determined by the co-ion (the ion with a similar charge as the membrane), which again confirms the negatively charged NF-membrane behaviour found previously (monovalent ions partially rejected and multivalent completely rejected). NF90 showed characteristics that are more of RO rather than NF.

When comparing data from Table 3. 5 and Table 3. 6 for dead-end and cross-flow modules, it can be observed that less rejection of monovalent ions was found during cross-flow than during dead-end.

For nitrate, rejection in dead-end for D12, D11 and CTC1 (~50 – 60%) was higher than in cross-flow (~30 – 40%). It is expected that cross-flow should have a higher ion retention due to the flux and selectivity relationship (usually selectivity increases as flux decreases) [9]. However, Nuortila *et al.* [8] also obtained better organic compound and ionic retention with a laboratory scale flat sheet cross-flow module than with a pilot scale spiral-wound cross-flow module. Since no satisfactory explanation currently exists, further studies are recommended to explain this behaviour.

While all membranes performed better in dead-end than cross-flow for nitrates, no clear trend is visible when comparing cross-flow and dead-end rejection of fluoride. Only D12 shows similar rejections, i.e. ~50% for dead-end and ~55% for cross-flow.

For both cross-flow and dead-end, sulphate rejection was >99.9, except for D11 dead-end (~65%). Overall however, D11 had the worst rejection.

For the NF90 membranes, rejection of nitrate and fluoride of above 90% was achieved by cross-flow. Nitrate and fluoride rejection of ~75% and ~70% was achieved by dead-end, respectively, which does not correlate with the general better rejection of nitrate in the dead-end module.

3.4 Conclusion

D12, D11 and CTC1 gave pure water fluxes within the NF-membrane range (1.4 – 12 $\ell.m^{-2}.hr^{-1}.bar^{-1}$). According to this characterization data, the two FilmTec® membranes i.e. NF90 and NF70 can be considered to be RO-membranes.

Three layers of NF-membranes (top, sub and support) were clearly identified by scanning electron microscopy (SEM).

Rejection of single salts was typical for NF-membranes except for the FilmTec® membranes. Single salts rejection further confirmed that the NF70 and NF90 membranes carry characteristics of RO-membranes by showing high rejection for all the monovalent and divalent ions.

3.5 References

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CHAPTER 4

NF-MEMBRANE PROCESSES (DEAD-END)

CHAPTER 4

PART I: Rural water treatment

4.1 Introduction

NF is a relatively new method for removing ions from water and consumes less energy than RO. In this section (Part I), the results on water treatment of various water samples using on NF-membrane process for the dead-end module are presented.

4.2 Experimental

4.2.1 Materials and methods

The instrumentation described in Chapter 3 (Section 3.2.1.2.1 and 3.2.1.3) was used. The membranes (D12, D11, CTC1, NF90 and NF70) described in Chapter 3, Section 3.2.1.4, were used.

4.2.2 Water sampling

Groundwater samples were collected from the Rustenburg rural area of the North West Province including Kaallaagte, Lerome, Rhenosterfontein and Rietvlei. The choice of sampling is based on previous research conducted at Potchefstroom University revealing high levels of potentially harmful ions such as fluoride and nitrate. The water in rural areas was previously found to have fluoride and nitrate concentrations as high as 8 ppm and 14 ppm (as mg.ℓ^{-1} N), respectively [1], which are above the recommended levels of 1 ppm (fluoride), 10 ppm (nitrate as mg.L^{-1} N) and 200 ppm (sulphate) [2]. Another groundwater sample from Haaskraal farm about 10 km from Potchefstroom University was added in this study.

Surface water samples were collected from the Vaal River at Bothaville and the Mooi River (mainly used for fouling studies) at Potchefstroom. All the samples were kept in plastic (PTFE) bottles and were refrigerated to retain the water composition.

4.2.3 Water treatment

Groundwater and river samples were permeated through five membranes (D12, D11, CTC1, NF90 and NF70). The experiments were operated with a pressure of 20 bar at ambient temperature using the set-up described in (3.2.1.2.1). Haaskraal groundwater experiments were operated at 5 bar to be able to compare to the cross-flow module, which is also operated at 5 bar (see Chapter 5). The collected samples i.e. feed, permeate and retentate were analysed for NO_3^-, F^- and SO_4^{2-} using a colorimeter (HACH DR/890).

4.3 Results and Discussion

4.3.1 Water sampling

The sampled water composition (in ppm) is given in Table 4. 1.

Table 4. 1: Characteristics of sampled water from rural areas before treatment

Sampling point	Fluoride*	Nitrate*(as N)	Sulphate*
Kaallagte	0.96	1.30	41.90
Lerome	4.65	3.08	25.20
Rhenosterfontein	1.15	0.82	39.70
Rietvlei	0.41	2.52	51.40
Vaal River	1.13	4.57	30.40
Haaskraal	2.75	4.20	186.00
Mooi River	3.41	5.60	204.00

* Concentration in ppm

In Table 4. 1, Kaallaagte and Rietvlei showed fluoride concentrations within the recommended level, while Lerome was the highest with concentrations about five times as high as the minimum-safe level. Nitrate and sulphate concentrations were all within the recommended level. Haaskraal and Mooi River showed high sulphate levels, which could be due to fertilizers used on farms.

4.3.2 Water treatment

The results for Kaallaagte groundwater are shown in Figure 4. 1 (R is given as percentage fractions in Figure 4.1 - 4.6). Fluoride was negatively rejected by CTC1 and NF90 while D12 and NF70 showed poor rejection of fluoride (~20% and 30% respectively). Modise [1] cited that the monovalent co-ions are "pushed" through the membrane in the presence of high valence co-ions. Therefore, the negative rejections observed are due to increased transport induced by the high valence co-ions, causing the permeate concentration to be higher than the feed concentration. The highest fluoride rejection was shown by D11 (~70%).

Nitrate was poorly rejected by D12, D11 and CTC1 (up to 33%). The two FilmTec® membranes (NF70 and NF90) rejected nitrate well for this sampled water (above 70%). Visser [3] obtained a negative nitrate rejection for D12 and CTC1 membranes while NF90 showed a poor rejection using mine water as a feed. Only D12 and NF70-membranes showed nitrate rejections above 75%.

Sulphate rejection was above 90% for all tested membranes. Choi *et al.* [4], Visser *et al.* [5] and Peters [6] obtained similar results of high sulphate rejection (above 90% rejection) using NF-membranes.

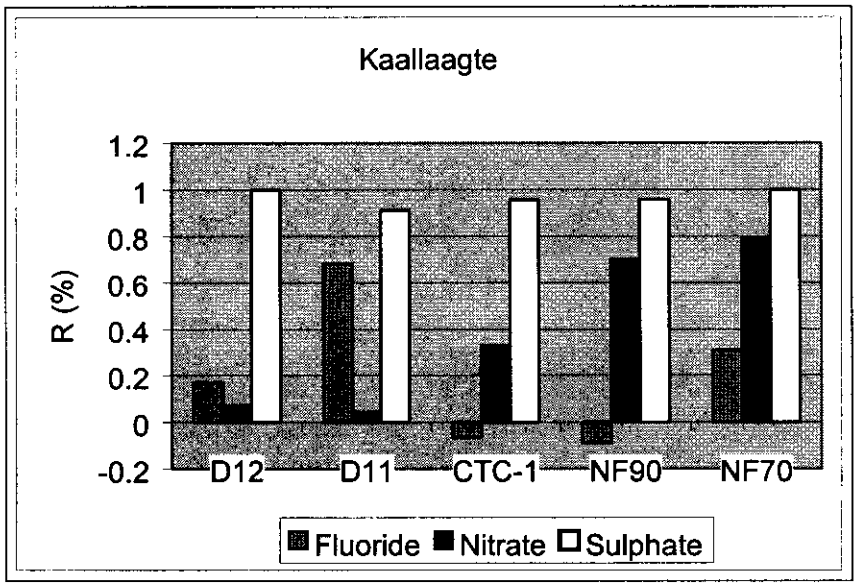


Figure 4. 1: Rejection of salts in Kaallaagte water by NF-membranes

Figure 4. 2 shows the performance of NF-membranes on Lerome groundwater. In this figure, the rejection (R) of fluoride was poor for membranes D11, NF90 and CTC1 (up to 20%), with NF70 again displaying the highest fluoride rejection (~80%). Due to its high fluoride rejection, NF70 could be a suitable membrane for Lerome water treatment. Nitrate was negatively rejected by D11 and CTC1. A moderate performance was achieved using NF90 (about 45% rejection), while D12 and NF70 rejected nitrate relatively well (~60%). Sulphate was again well rejected by all tested membranes (above 90%).

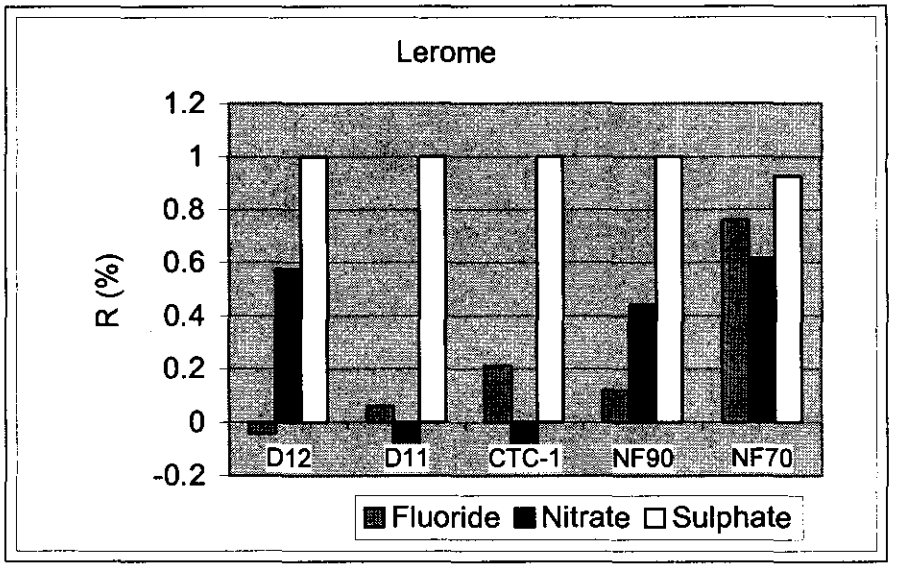


Figure 4. 2: Rejection of salts in Lerome water by NF-membranes

The results for Rhenosterfontein groundwater are shown in Figure 4. 3. Nitrate was negatively rejected by NF90 and poorly rejected by D12, D11 and CTC1 (up to ~15%). Good rejection was again attained when using NF70 (~70%). Poor rejection of fluoride was found for D12, NF70, NF90 and D11 (up to 35%). About 50% fluoride was rejected by CTC1 (moderate performance). Sulphate was rejected well by all membranes (70 – >99.9%).

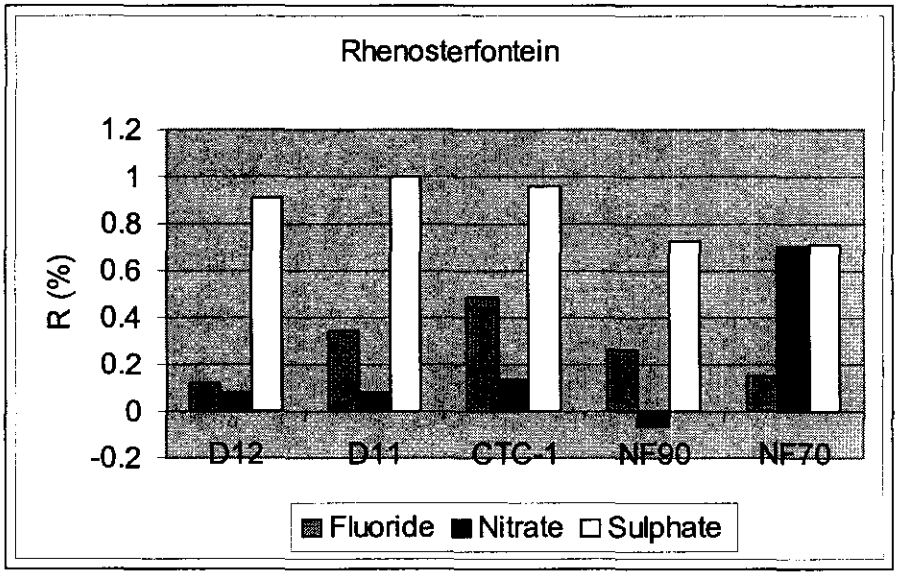


Figure 4. 3: Rejection of salts in Rhenosterfontein water by NF-membranes

Figure 4. 4 shows the results of Rietvlei groundwater.

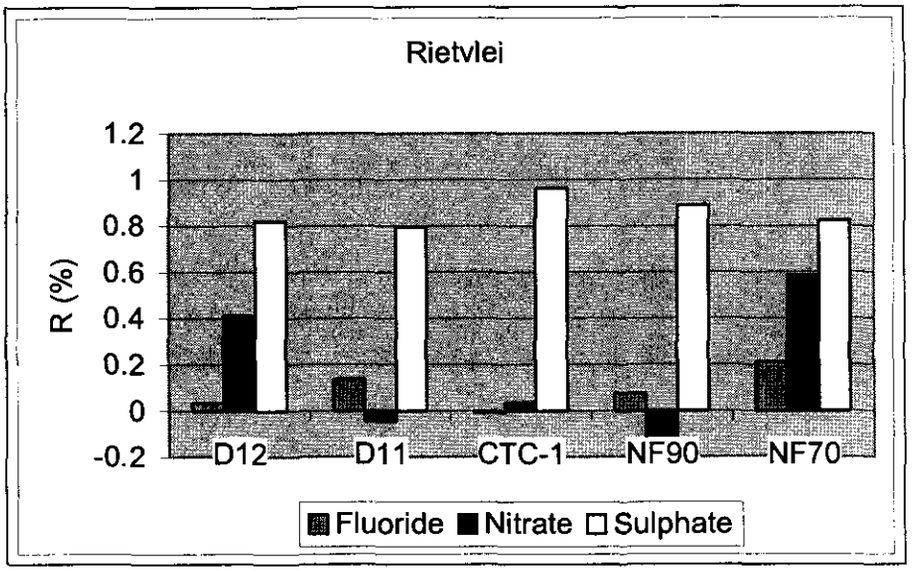


Figure 4. 4: Rejection of salts in Rietvlei water by NF-membranes

All membranes showed poor or negative (CTC1) fluoride rejection (up to 20%). Nitrate was negatively rejected by D11 and NF90 with very poor performance by CTC1. Only D12 (~40%) and NF70 (~60%) showed a moderate performance. Rejection of above 80% was achieved for sulphate.

The results for Haaskraal groundwater are shown in Figure 4. 5. Fluoride and sulphate were effectively rejected by all the tested membranes (by above 60% and 90% respectively). Good nitrate rejection was attained with CTC1, NF90 and NF70. The Envig membranes (D12 and D11) showed a poor nitrate rejection.

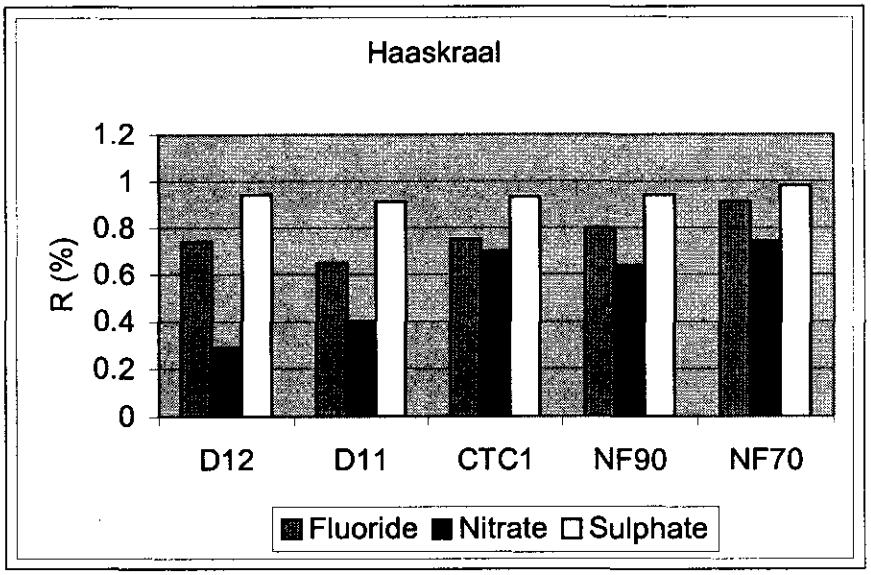


Figure 4. 5: Rejection of salts in Haaskraal water by NF-membranes

Figure 4. 6 shows the results obtained from Vaal River samples. Here fluoride was negatively rejected by CTC1 and poorly rejected by D12 and D11 (up to about 20%). Good fluoride rejection was achieved by NF70 (>99.9%). Nitrate was poorly rejected by D11 and NF90 (~40%) and moderately rejected by D12, CTC1 and NF70 (~50%). Rejection values of above 60% were achieved for sulphate.

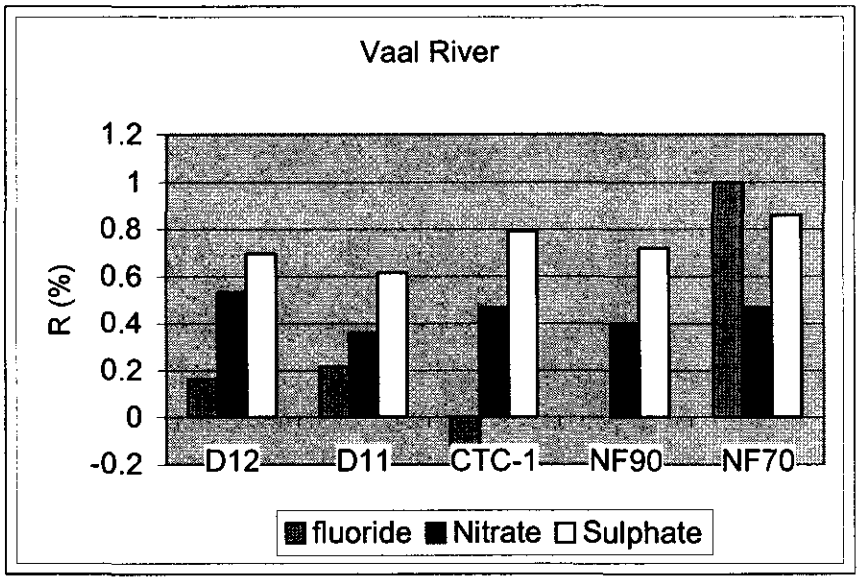


Figure 4. 6: Rejection of salts in Vaal River water by NF-membranes

As membranes are charged, the concentration of the co-ion (ion with the same charge as the membrane) in the membrane will be lower than that in the solution [7]. The results shows that sulphate ions (bivalent) were effectively repelled from the membrane surface (due to the negative charge of the membrane). In the case of different counter-ions (ion sign opposite to that of a membrane), the counter-ion with the lowest charge will show the highest retention. Multivalents will be more attracted to the membrane surface generating a potential difference at the interface between the membrane and the solution, which is called the Donnan potential [7].

NF70 and D11-membranes showed a good fluoride rejection for varying water samples i.e. for Lerome, Kaallaagte and Vaal River. Only NF70 was able to effectively reject nitrate for Kaallaagte, Lerome, Rhenosterfontein and Haaskraal water samples. D12 and D11 showed good nitrate rejection for Lerome and Kaallaagte, respectively. In general, membranes tested showed little or negative rejections for monovalent ions. The results obtained for both monovalent and divalent ions were in accordance with findings of Modise [1]. The membrane performance differs for different water compositions. There could not be found any relation between initial fluoride, nitrate and sulphate and rejection behaviour for various water samples.

PART II: Fouling

4.4 Introduction

The performance of a membrane flux decreases due to concentration polarization and fouling [8]. With the polarization phenomenon, the flux at a finite time is always less than the original value. However, when steady state conditions (constant flux as a function of time) have been reached, no further decrease in flux is observed. A continuous flux reduction results in membrane fouling.

During permeation, there is a membrane flux decrease with time caused by the retained materials. The reduction in the pure water flux [see Figure 4.7, step (A) and (C)], which is a measure of membrane irreversible fouling, can be calculated by comparing the pure water flux before and after filtration as: [9]

$$FR_{PWF} = \frac{PWF_b - PWF_a}{PWF_b} \times 100 \qquad (4.1)$$

where FR_{PWF} (%) is the flux reduction of pure water flux, PWF_a ($\ell.m.^{-2}.h^{-1}$) is the pure water flux after filtration and PWF_b ($\ell.m.^{-2}.h^{-1}$) is the pure water flux before filtration.

In the filtration of the prepared and sampled feed solutions, the reduction of a permeate flux can be calculated by comparing the steady permeate flux (no further flux decrease is observed) with the initial water flux (using Equation 4.2):

$$FR_s = \frac{PWF_b - PF}{PWF_b} \times 100 \qquad (4.2)$$

where FR_s (%) is the flux reduction during the filtration of the sample and PF ($\ell.m.^{-2}.h^{-1}$) is the steady flux during the filtration of the sample.

The relative flux (RF) is defined as the steady flux of the sample solution divided by the initial water flux (Equation 4.3):

$$RF = \frac{PF}{PWF_b} \tag{4.3}$$

In this section (Part II), results on fouling of NF-membrane D12, using single salts, chemical cleaning agents and various water samples are presented.

4.5 Experimental

4.5.1 Materials and methods

The instrumentation described in Chapter 3 (Section 3.2.1.1; 3.2.1.2.1 and 3.2.1.3) was used. Only D12 was selected for fouling experiments because of its high water flux and good rejection performance. NF90 and NF70 had better rejection behaviour but their flux was very low.

A number of selected salts were used to monitor the extent of fouling in the D12 membrane. The chemical details are given in Table 4. 2.

Table 4. 2: Detailed information on chemicals used

	Supplier	Assay	Purity	MW* (g/mol)
$NaNO_3$****	SAARCHEM	99%	AR**	84.99
NaF****	MERCK	99%	AR	41.99
Na_2SO_4	MERCK	99%	CP***	142.04
$MgSO_4$****	SAARCHEM	62-70%	CP	120.39
NaCl	SAARCHEM	99.5%	AR	58.44

* MW = molecular weight, **AR = analytical reagent, ***CP = chemically pure and **** Chemicals used in cross-flow module

Figure 4.7 shows a schematic diagram of the procedure followed during fouling and chemical cleaning (see Part III).

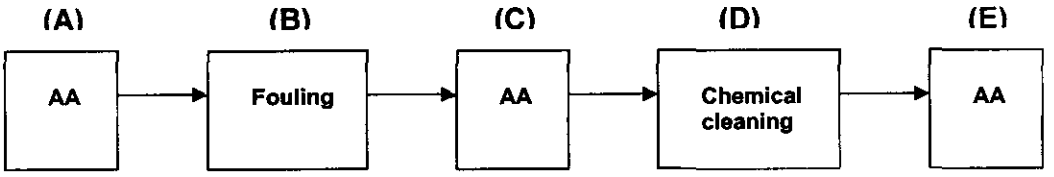


Figure 4. 7: A schematic diagram for the fouling experiment procedure

According to Figure 4.7, step (A) is the initial introduction of deionised (AA) water, (B) is the sample introduction, (C) is the washing step with clean water, (D) is the cleaning step with various chemicals and (E) is the washing step with AA-water after cleaning. The membranes were rinsed using AA-water between step (B) and (C), and step (D) and (E) to remove any unbound species of the sample and cleaning chemicals respectively.

4.5.1.1 Single salts

Different salt ($NaNO_3$, NaF, Na_2SO_4, $MgSO_4$, and NaCl) solutions were prepared at different concentrations (50ppm, 100ppm, 150ppm and 200ppm as anions). AA-water was initially introduced to the reactor module and the permeate flow was measured. Salt solutions were then permeated through the D12-membrane following an ascending order of concentrations. AA-water permeation (flushing) was done every time before and after each salt solution concentration on the membrane. After the last salt concentration (200ppm), the membrane was flushed using AA-water. The lines showed in Figure 4. 8 shows represent the stabilized flux i.e. the region where flux decrease is no longer observed for a period of an experiment.

The initial and final AA-water fluxes were compared. The flux reduction was then calculated using Equation 4.1. The permeate flow was determined using a Sartorius electronic balance.

4.5.1.2 Chemical cleaning reagents as foulants

In Table 4. 3, the chemicals investigated in Part III for their cleaning behaviour were investigated in Part II for their contribution to membrane fouling. 0.05%

(w/v) solutions of HCl, H_2SO_4, HNO_3, H_3PO_4, $C_6H_8O_7$, $HO\text{-}SO_2NH_2$, NaOH, KOH, NH_4Cl, EDTA and SDS were prepared.

Table 4. 3: Chemicals used for chemical cleaning

Chemical	Supplier	Assay	Purity	MW* (g/mol)
HCl	MERCK	32.0%	AR**	36.46
HNO_3	F.C Scientific	55%	AR	63.01
H_3PO_4	MERCK	85%	AR	98.00
$C_6H_8O_7$	Koch Lient	100%	AR	191.93
$HO\text{-}SO_2NH_2$	ALDRICH	99.3%	AR	97.09
NaOH***	BDH chemicals	97.5%	AR	40.00
KOH	LABCHEM	85%	AR	56.11
NH_4Cl	SAARCHEM	99.5%	AR	53.48
EDTA*****	BDH chemicals	98%	AR	372.24
SDS*****	MERCK	99%	AR	288.38

* MW = molecular weight, ** AR = Analytical reagent, *** Chemical used in cross-flow, **** EDTA = ethylene diamine tetrachloride-acetic acid and *****SDS = sodium dodecyl sulphate.

4.5.1.3 Groundwater and river water treatment

Fouling studies were performed using groundwater (Lerome, Rietvlei and Kaallaagte) and river water samples (Mooi and Vaal rivers). All experiments were carried out at a pressure difference of 20 bar. This was done by measuring the permeate flow of the initial (A) and final (C) water flux as well as that of the sampled water (B) [Figure 4.7]. After step C of this scheme the membrane was thoroughly rinsed to remove unbound species on the surface.

4.5.1.4 SEM

The same procedure as the one described in Chapter 3 (Section 3.2.1.1), was used.

4.6 Results and Discussion

4.6.1 Single salts as foulants

All data presenting fluxes during different treatments (for example AA before, fouling, cleaning and AA after) show the flux after steady state had been reached. Steady state was assumed when a flux remained constant for at least 3 hours.

The purpose of this study was to investigate the extent of fouling by various single salts at different concentrations. The results of relative flux (RF) at steady state are shown in Figure 4. 8. According to Figure 4. 8, the relative flux in the presence of monovalent ions was generally lower than in the presence of divalent ions. This is due to the negative charge of the membrane, which repels divalent anions more from the membrane surface than monovalent anions, while allowing water molecules to permeate easily.

The relative flux for all the tested salt solutions decreased in direct proportion with the increase in salt concentration. In general, monovalents caused a greater decrease in relative flux than the divalents with increasing order of the concentrations. Peeters [7] cited that, in the case of ions with an opposite charge as that of a membrane (counter-ions), the counter ion (Na^+) with the lowest charge would show the highest retention, which can cause concentration polarization with time, as confirmed in this study.

Sodium chloride caused a greater flux reduction than the other salts. Visser [3] observed spike-like crystals of NaCl on the membrane surface from mine brine solution using SEM-EDAX analysis. This confirms that this salt crystallizes on the membrane surface, retarding its performance.

An improvement in flux (~20%) was observed for sodium chloride after the final clean water flush. This shows that the concentration polarization or crystallization formed by salts on the membrane surface can be easily removed by water flushing, again confirming the formation of crystals on the

membrane surface. Less flux improvement (<10%) was observed for other tested salts.

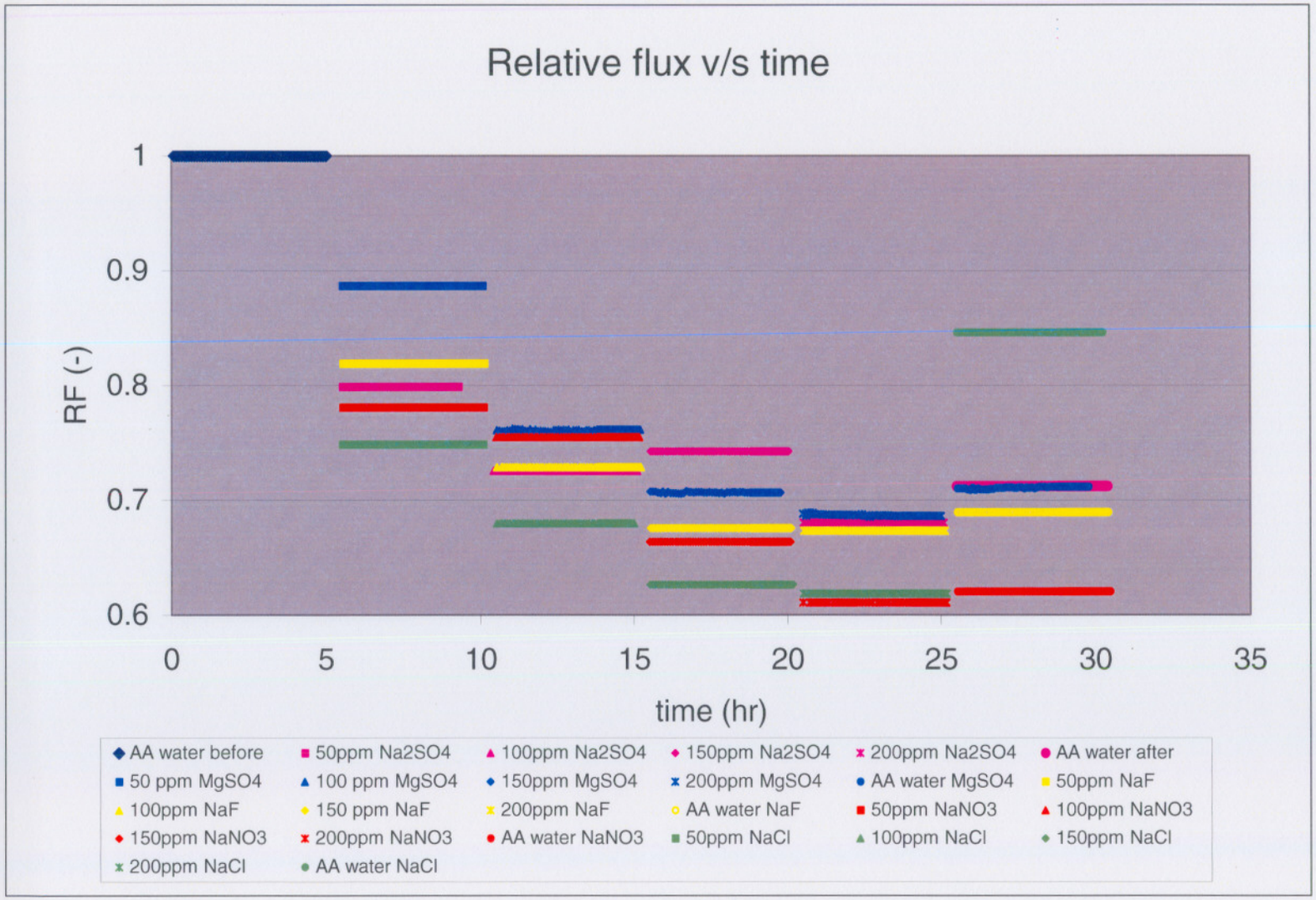


Figure 4.8: A plot of steady state RF at ambient temperature and 20 bar pressure

4.6.2 *Cleaning agents as foulants*

The results obtained for cleaning chemical agents (acids and bases) as foulants are shown in Figure 4. 9 and Figure 4. 10 respectively.

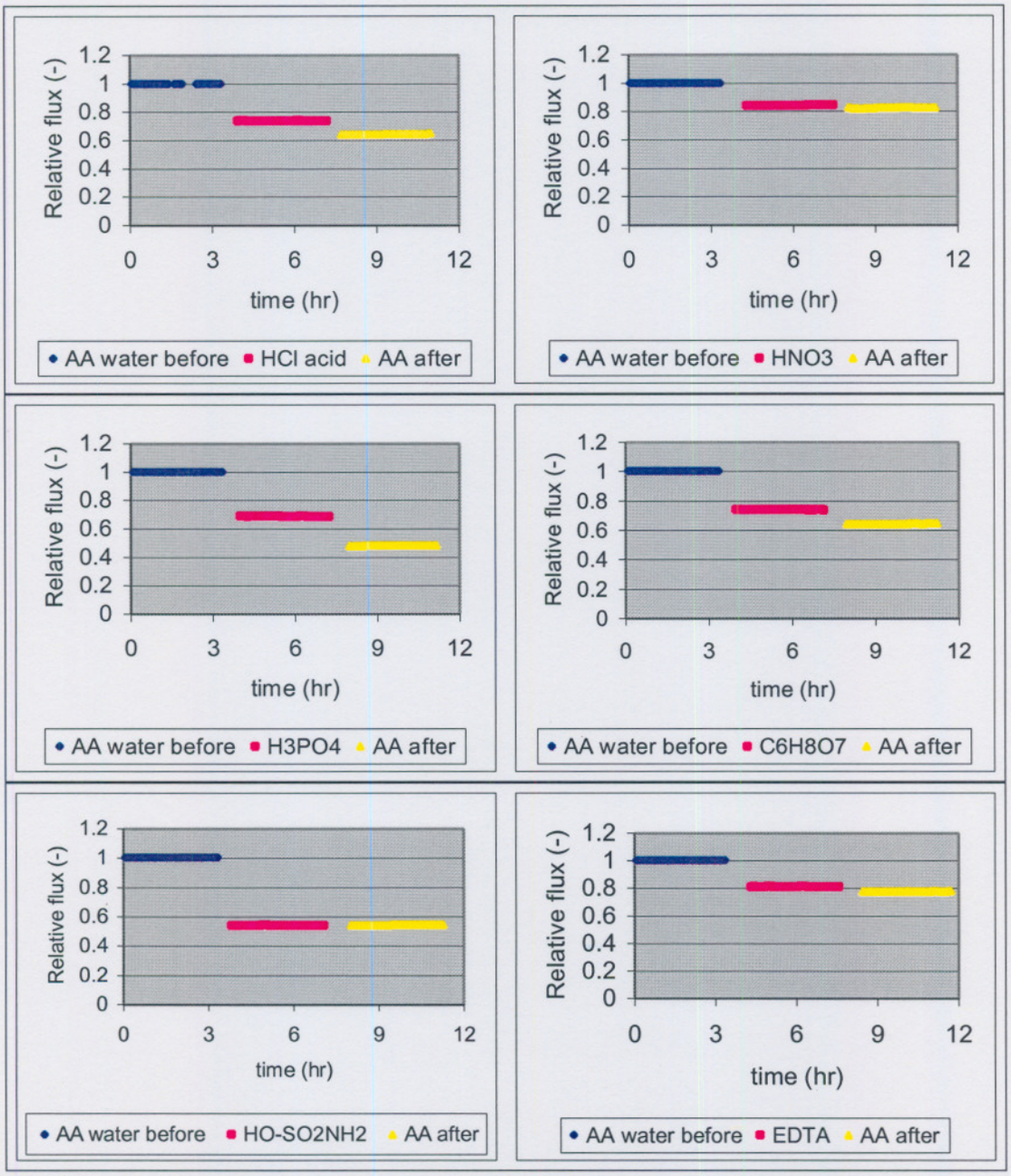


Figure 4. 9: The effect of acid cleaning agents on the steady state flux of a D12-NF-membrane at ambient temperature and 20 bar pressure

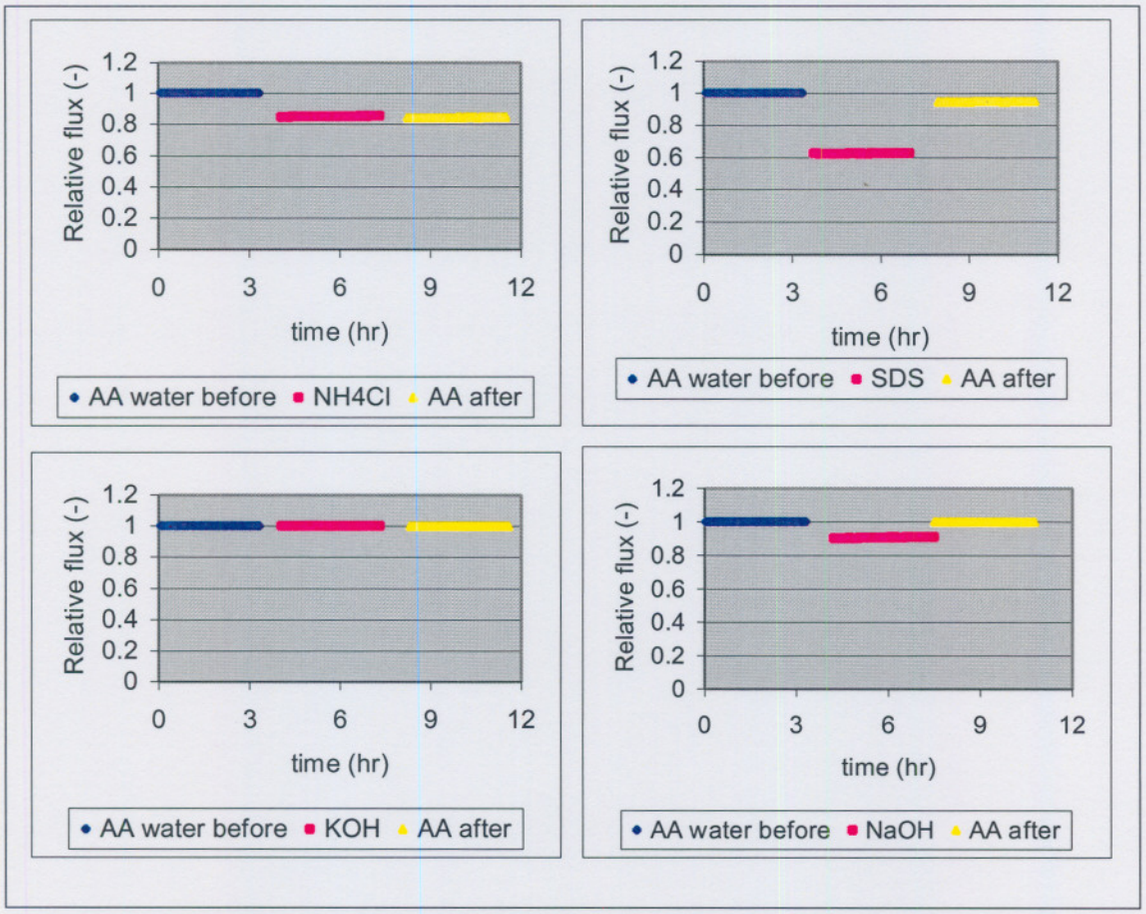


Figure 4. 10: The effect of bases cleaning agents on the steady state flux of a D12-NF-membrane at ambient temperature and 20 bar pressure

From Figure 4. 9, acids (HCl, HNO_3, H_4PO_3, $C_6H_8O_7$ $HO\text{-}SO_2NH_2$ and EDTA) curves show a greater relative flux reduction than bases (Figure 4. 10). All acids caused a 20% or more decrease in flux, which remained even after washing with AA-water (Figure 4. 7, step C). Sulphamic acid had the worst affect on flux (~45%).

For bases (NH_4Cl, SDS, KOH and NaOH), only ammonium chloride did not show a flux improvement after the final AA-water flush. Final AA-water fluxes after treatment with SDS, KOH and NaOH showed improvement after washing, suggesting that fouling caused by these bases is reversible. For sodium hydroxide and potassium hydroxide, the initial AA-water fluxes were completely recovered. Potassium hydroxide did not foul the membrane at all. This shows that, while both acids and bases cause fouling, the fouling is worse in the presence of acids while furthermore being irreversible.

The AA-water flux reduction [Figure 4.7, steps (A) and (C)] was calculated by Equation (4.1) and is presented in Figure 4.11. Phosphoric and sulphamic acids showed the highest flux reduction (above 55%), citric and hydrochloric acids showed ~40%, EDTA showed ~28% and nitric acid showed ~20%. The results confirm that acids, even at low concentrations, can foul the D12-NF-membrane. Mantarri *et al* [9] previously reported that membranes are fouled more in acidic solutions where the electrostatic repulsion of the membrane is lower. In an acidic environment, fouling is mainly caused by adsorption.

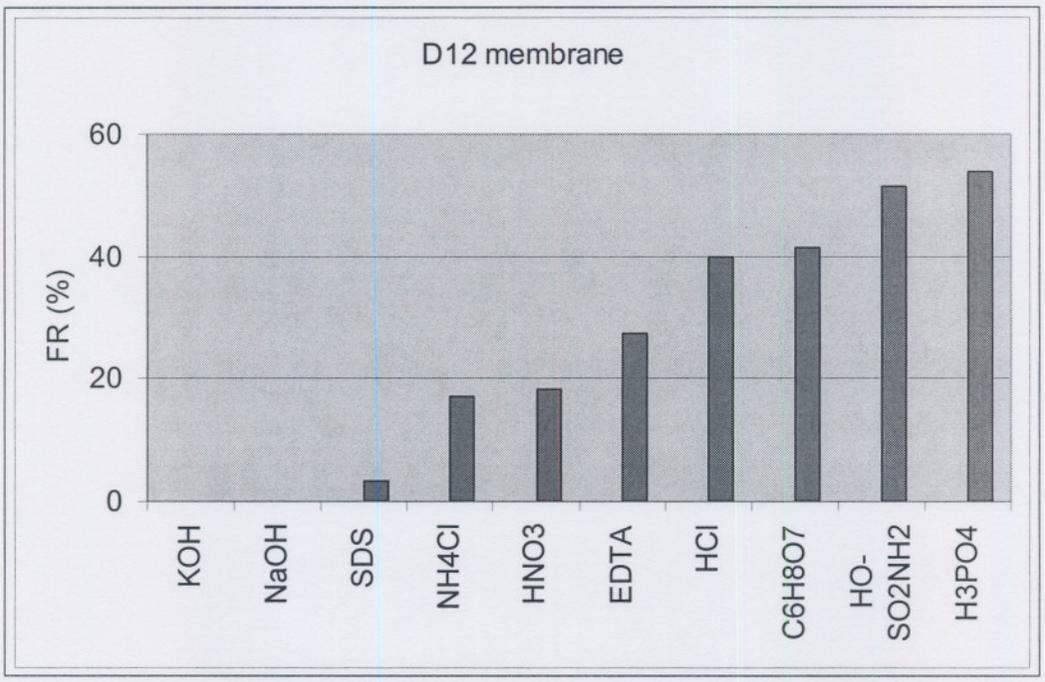


Figure 4.11: Pure water flux reduction due to cleaning agents

While bases also showed flux reductions, they were lower than those observed for acids. Ammonium chloride and SDS showed flux reductions of about ~20% and ~5% respectively. Potassium hydroxide and sodium hydroxide did not show any irreversible fouling.

4.6.3 Fouling by groundwater and river water

The relative flux for various groundwater and river water samples is shown in Figure 4.12.

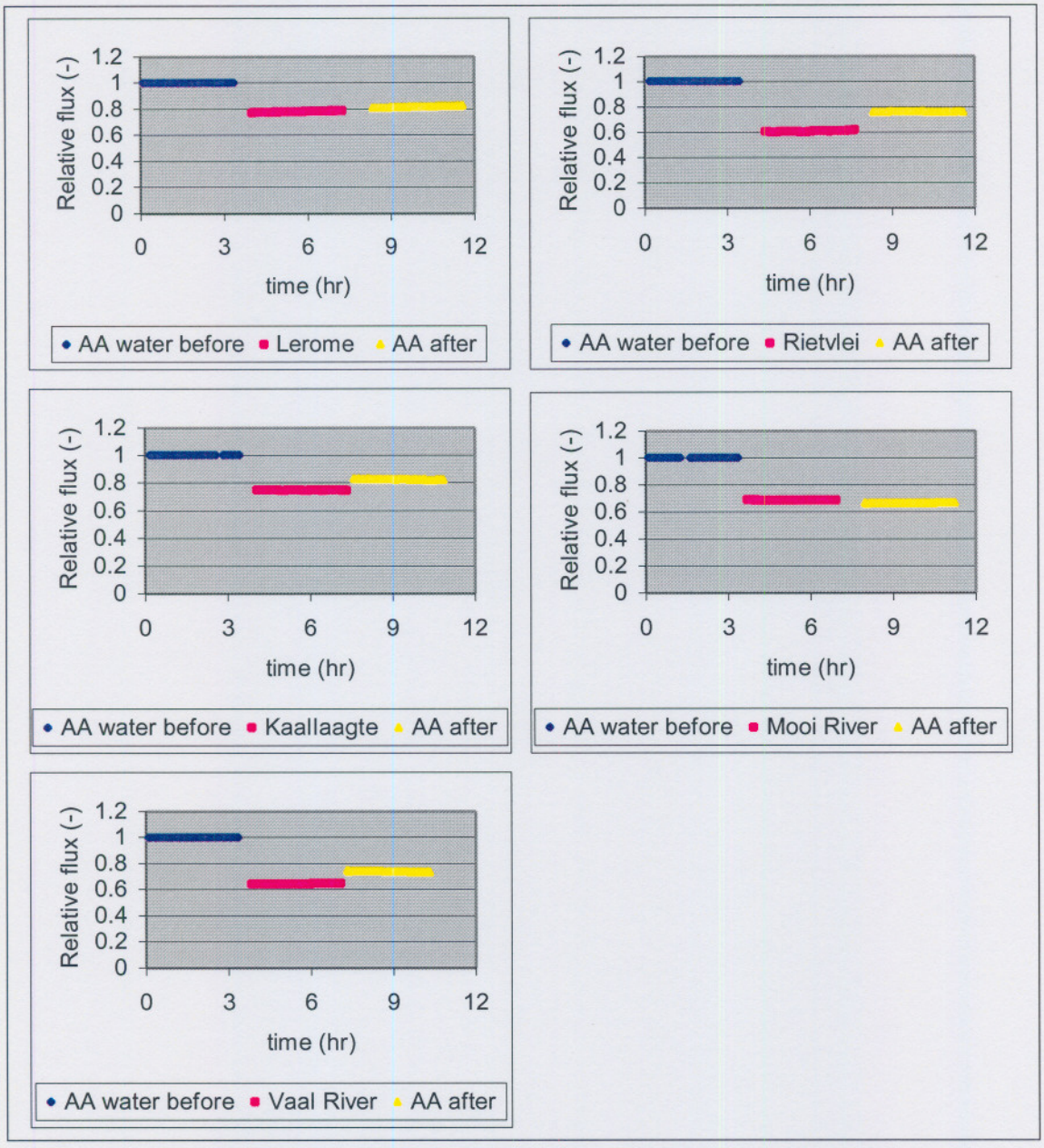


Figure 4.12: The effect of various groundwater samples on the steady state flux of a D12-NF-membrane, ambient temperature and pressure = 20 bar

For all groundwater and river water samples, the original AA-water flux could not be recovered. Only slight flux improvements of less than 10% were observed for all samples during washing (Figure 4.7, step C). For the Mooi River, the flux actually decreased further during washing. The little flux improvement for the Vaal River sample treatment could be because some silica and/or suspended materials were covering the membrane surface, which could have been removed by thorough rinsing.

The calculated water flux reduction (Equation 4.1) results are presented diagrammatically in Figure 4.13. The results show that the irreversible fouling of Lerome, Rietvlei and Kaallaagte was about 30% (FR_s). Groundwater, particularly boreholes, are reported to be mainly polluted by inorganic salts [1], hence less fouling than observed for the Mooi River and Vaal River samples.

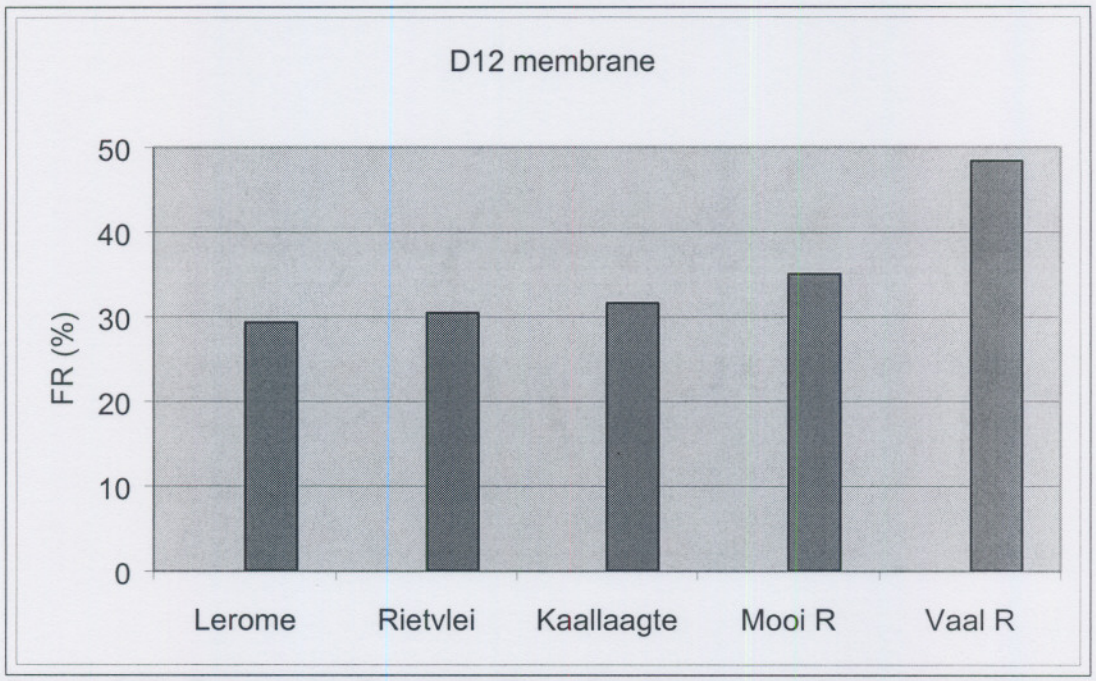


Figure 4.13: Pure water flux reduction of various groundwater and river water samples

According to Lee *et al.* [10], the natural organic matter (NOM), which is mainly found in surface water, largely contributes to the reduction of the membrane performance. While the FR_s of the Mooi River sample was ~35%, an FR_s of about ~50% was observed during the treatment of Vaal River water, which is ~20% higher than the groundwater samples. The excess water flux reduction seen in surface water can be due to NOM (main problematic foulant) and suspended solids, and this flux cannot be easily recovered by flushing with water.

4.6.4 SEM

Scanning electron microscopy was used to visualize scale or cake formation (Figure 4.14 and 4.15). Crystallization during fouling due to the various foulants on the membrane surface is presented in Figure 4.16.

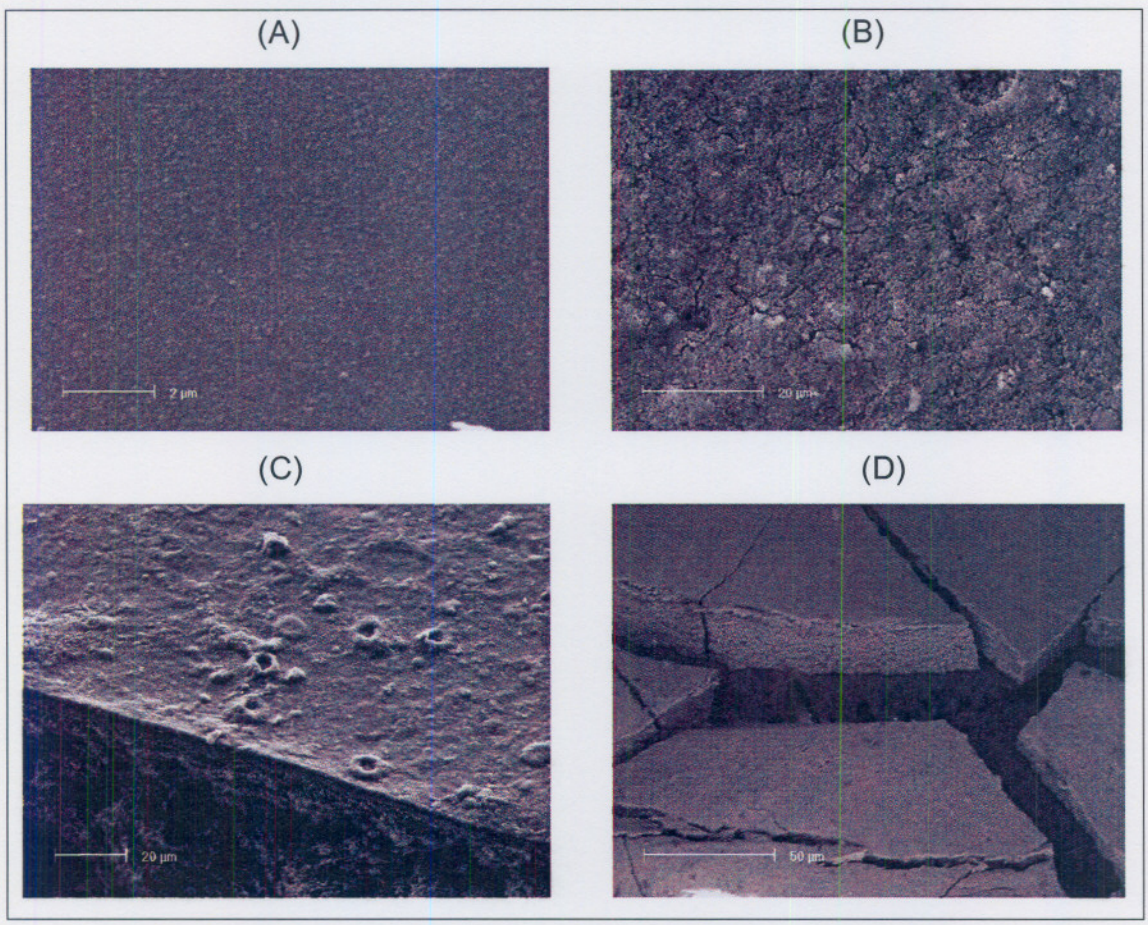


Figure 4.14: D12-NF-membranes fouling

Figure 4.14, (A) shows a virgin D12-membrane, (B) shows a D12-membrane after it has been fouled by Lerome groundwater, (C) shows a D12-membrane fouled by Mooi River water and (D) shows a cake formed of the surface on the D12-membrane by a Vaal River water sample. The best image magnification view were elected to show fouling clearly.

A scaly deposit on the membrane is observed in (B), (C) and (D), as compared to the smooth surface observed in (A). This build-up due to the deposit of materials on the membrane surface during permeation, results in

the observed poorer performance of the membrane. The D12-membrane was characterized to have three layers i.e. dense, sub and support layers (Figure 3.3 and Figure 3.4). An additional cake layer, formed by foulants on the membrane surface, can be clearly observed in both (C) and (D).

Similar results (Figure 4.15) were observed for the Mooi River water sample.

(A) (B)

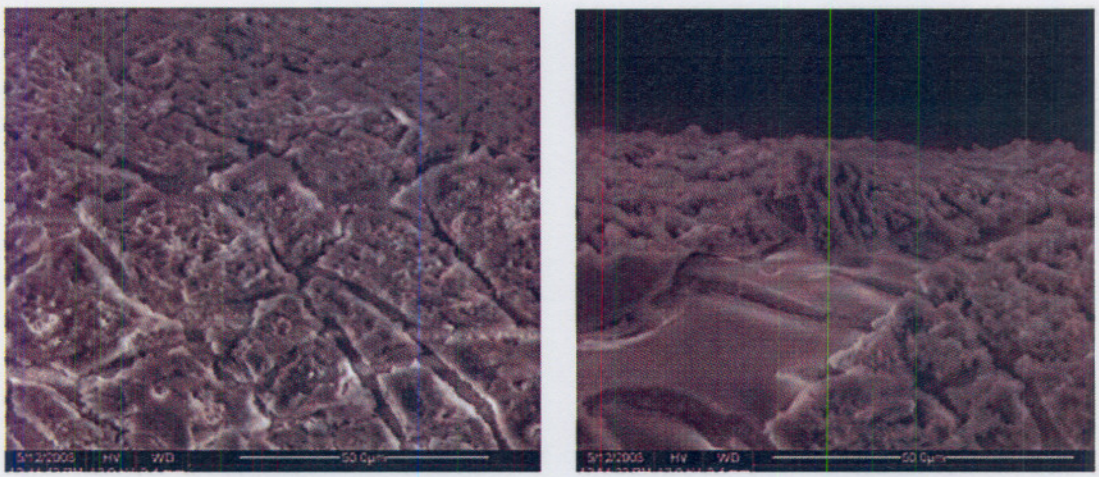
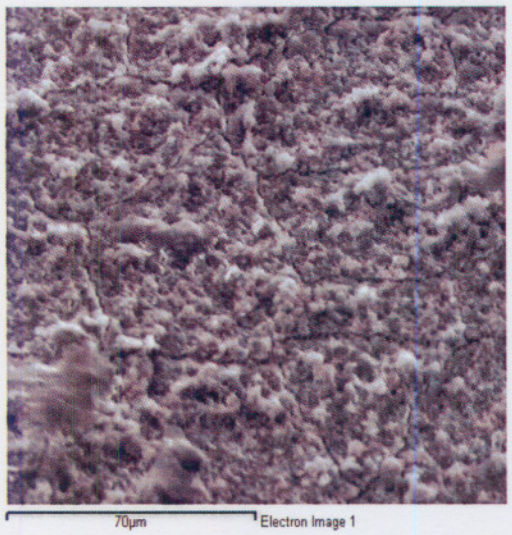
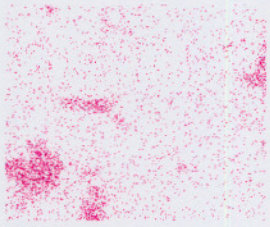


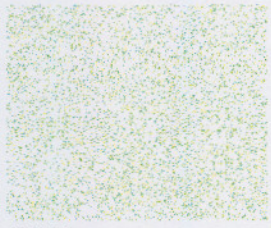
Figure 4.15: D12 NF membrane fouling

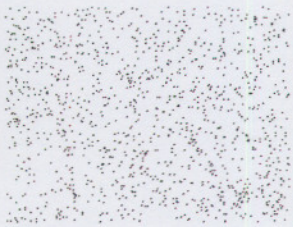
Figure 4.15, (A) shows the cake formation on the membrane surface while (B) is showing a portion of a smooth virgin membrane surface as well as the cake layer formed on the top of the surface.

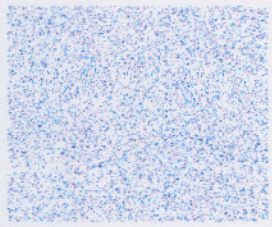
The colour mapping and elemental composition (given by weight percentage) of the membrane fouled by Mooi River are shown in Figure 4.16.

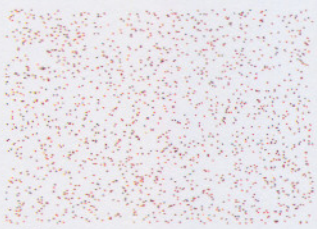


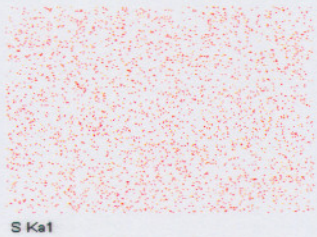












Element	C	O	F	Mg	P	Ca	Si	S
Composition	24.03	43.81	12.53	3.14	6.00	8.95	0.16	1.38

Figure 4.16: Colour mapping and elemental composition by weight %.

The colour mapping gave an idea of how foulants (elements) are distributed on the membrane surface. It was observed that all the elements analysed (Mg, P, Ca, Si and S) were evenly distributed on the membrane surface, except fluoride, which seemed to be concentrated in certain areas, indicating crystallization. A cluster of dots concentrated on the same position can be related to the visible foulants on the SEM-micrograph taken of the fouled membrane.

Part III: Chemical cleaning

4.7 Introduction

Chemical cleaning is currently one of the most important methods in reducing fouling. Cleaning chemicals can be used separately or in combination. The increase in resistance during filtration can be used to quantify fouling and the efficiency of cleaning can be defined by the removal of this resistance [11]. The resistance is due to the formation of a cake or gel layer on the membrane surface. According to Darcy's law, the flux (J) through the cake and the membrane can be described as [11]:

$$J = \frac{\Delta P}{\eta \cdot \sum R} \tag{4.4}$$

where ΔP (bar) is the transmembrane pressure (driving force), η (Pa.s) is the viscosity of the fluid and $\sum R$ is the sum of the resistances. Initial membrane resistance (R_m) can be obtained from the initial water flux (Figure 4. 7, step A) (Equation 4.5):

$$R_m = \frac{\Delta P}{\eta \cdot J_{wi}} \tag{4.5}$$

where J_{wi} is initial water flux. The resistance, which appeared after fouling (R_f) i.e. step B (Figure 4. 7), can be calculated from the water flux after washing with water (Equation 4.6):

$$R_f = \frac{\Delta P}{\eta \cdot J_{ww}} - R_m \tag{4.6}$$

where J_{ww} is water flux after washing (step C, Figure 4. 7). The resistance that remained after cleaning (R_c) in step D can be calculated from the water flux after chemical cleaning (Equation 4.7):

$$R_c = \frac{\Delta P}{\eta \cdot J_{wc}} - R_m \qquad (4.7)$$

where J_{wc} is water flux after cleaning, (step E in Figure 4. 7). The resistance removal (RR), which can be used to quantify cleaning, is obtained from (Equation 4.8):

$$RR(\%) = \frac{R_f - R_c}{R_f} \times 100 \qquad (4.8)$$

Another term that can be used to quantify cleaning efficiency is flux recovery (FR) (Equation 4.9) [11]:

$$FR(\%) = \frac{J_{wc} - J_{ww}}{J_{wi} - J_{ww}} \times 100 \qquad (4.9)$$

Both resistance removal and flux recovery have been used previously to demonstrate cleaning efficiency [11].

4.8 Experimental

4.8.1 Materials and methods

The instrumentation described in Chapter 3 (Section 3.2.1.1; 3.2.1.2.1; and 3.2.1.2.2) was used. For this study only D12 was used due to the reasons described earlier in this chapter. The cleaning efficiency was tested on the D12-membrane fouled with a water sample from the Mooi River.

0.05% (w/v) solutions of HCl, H_2SO_4, HNO_3, H_3PO_4, $C_6H_8O_7$, $HO\text{-}SO_2NH_2$, NaOH, KOH, NH_4Cl, EDTA and SDS were prepared for chemical cleaning. This concentration (0.05%) could comply with the cleaning pH-range specification (2 – 11.5) of a D12-membrane for both acids and bases. A

Hanna instrument HI 9321 pH-meter was used to determine pH-values of these reagents. Cleaning chemicals were initially applied separately. Depending on the individual effectiveness of the cleaning reagents, combinations of reagents were used to determine any further improvement of cleaning effectiveness.

Cleaning was done after deliberately fouling the membranes with the river sample using the same scheme as before (Figure 4. 7). The initial AA-water flux was measured [step (A)]. After fouling [step (B)], the membrane was thoroughly rinsed to remove unbound materials [between (B) and (C)] and AA-water flux was again measured [step (C)]. The cleaning reagent was introduced to the reactor [step (D)], and left for 2 hours with no pressure applied while stirring. The cleaning solution was discarded and the reactor was thoroughly rinsed [step (2)] with AA-water. The AA-water flux was measured again [step (E)]. The graphs obtained are shown in Figure 4. 17, Figure 4. 18 and Figure 4. 19 (Section 4.9).

4.8.2 SEM

The same procedure as described in Chapter 3 (Section 3.2.1.1) was used

4.9 Results and Discussion

The behaviour of relative flux versus time graphs for acids, combinations and alkali are shown in Figure 4. 17, Figure 4. 18 and Figure 4. 19.

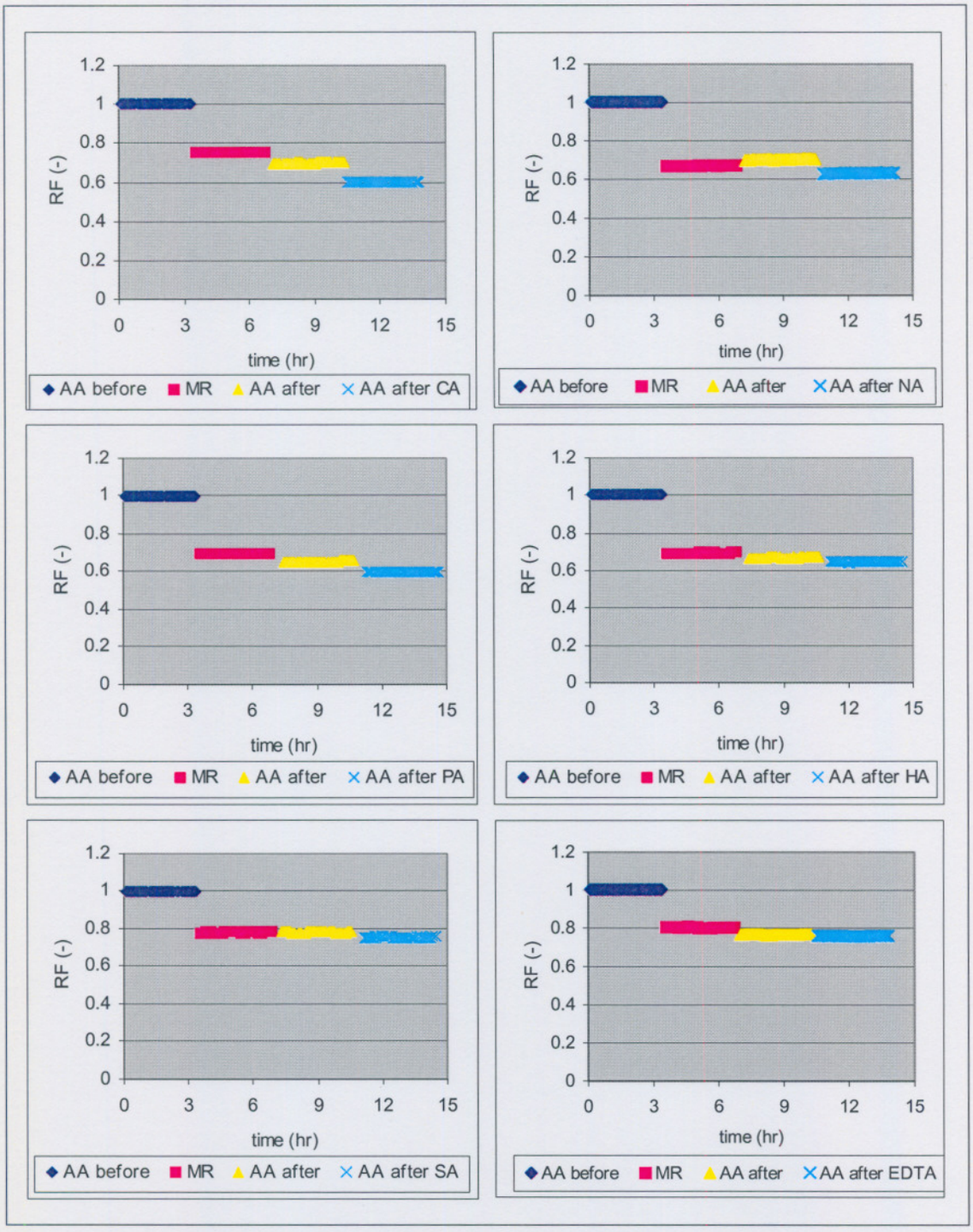


Figure 4. 17: The effect of chemical cleaning (acids) on the steady state flux of a D12-NF-membrane at ambient temperature and 20 bar pressure. AA = deionized water, MR = Mooi River, CA = citric acid, NA = nitric acid, PA = phosphoric acid, HA = hydrochloric acid, SA = sulphamic acid and EDTA = ethylene diamine tetrachloride-acetic acid.

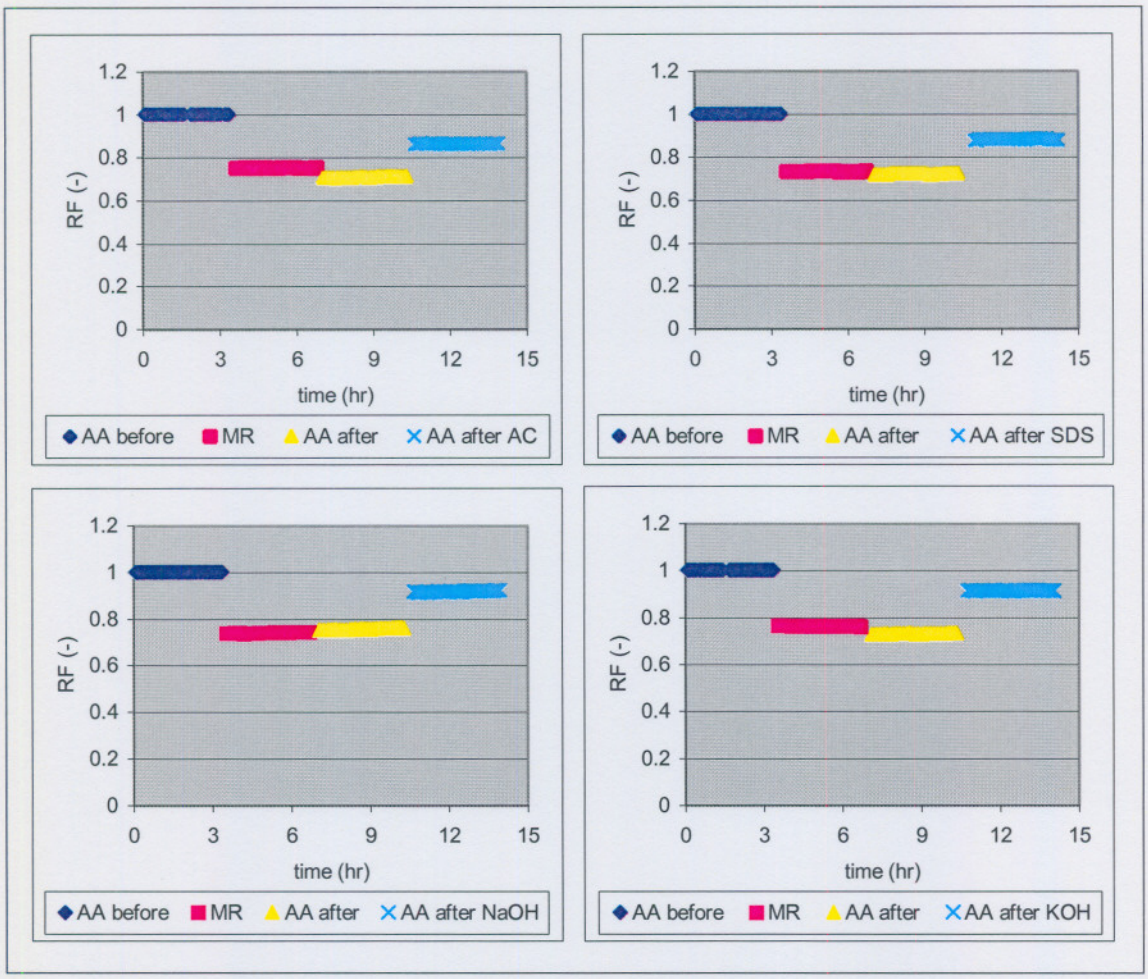


Figure 4. 18: The effect of chemical cleaning (alkali) on the steady state flux of a D12-NF-membrane at ambient temperature and 20 bar pressure. AC = ammonium chloride.

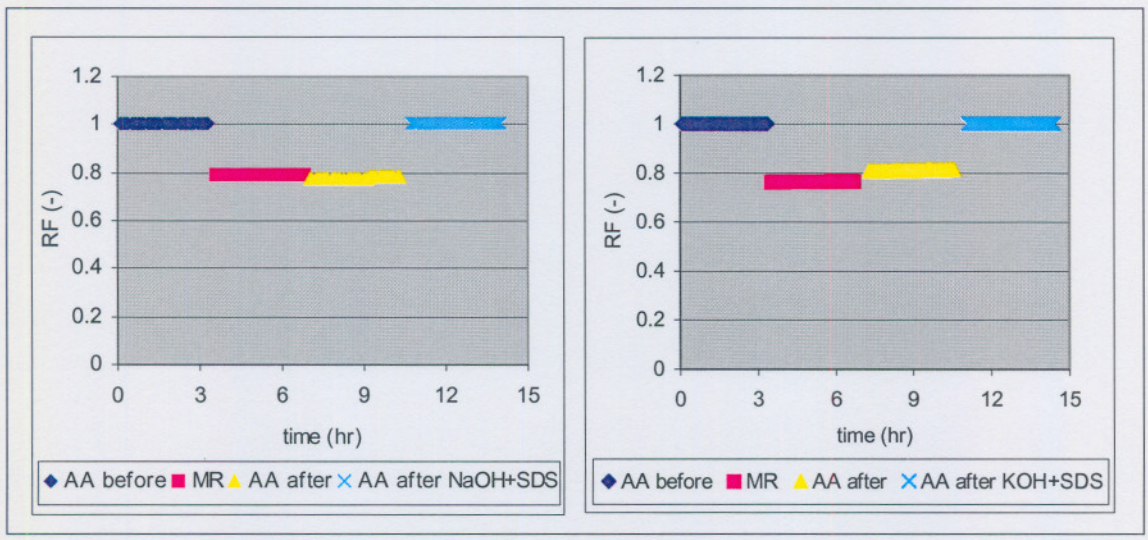


Figure 4. 19: The effect of chemical cleaning (combination) on the steady state flux of a D12-NF-membrane at ambient temperature and 20 bar pressure.

Table 4. 4 shows the cleaning efficiency as flux recovery ($FR,\%$) and resistance removal ($RR,\%$) for various chemicals used, which were calculated using Equation (4.8) and (4.9) from the graphs obtained in Figure 4. 17, Figure 4. 18 and Figure 4. 19.

Table 4. 4: The cleaning efficiency for different cleaning chemicals

Chemical	Solution pH	*FR*, %	*RR*, %
$C_6H_8O_7$	3.05	-36	-66
HNO_3	2.66	-33	-57
H_3PO_4	2.42	-23	-41
HCl	2.87	-20	-34
$HO\text{-}SO_2NH_2$	2.24	-11	-16
EDTA	4.89	-08	-11
NH_4Cl	6.17	42	51
SDS	6.40	50	59
NaOH	11.56	61	68
KOH	11.43	66	74
NaOH + SDS	11.36	100	100
KOH + SDS	11.28	100	100

The cleaning agents were compared using a Mooi River sample on a D12-membrane. From the results, acids and chelates were not effective cleaning agents (1) for this particular water sample and (2) under these experimental conditions. The flux reduction and resistance removal obtained by calculation were negative.

The effect of the acids can be clearly seen from Figure 4. 17, i.e. instead of the flux increasing as required as cleaning objective, for all acids the flux worsened, shown by the negative flux recovery (Table 4. 4). This confirms that acids are not suitable cleaning agents for this particular sampled water (Mooi River water sample) and the type of membrane used. All tested acids

had negative flux recoveries in the range of –36% to –11% as shown in Table 4. 4.

Alkali and surfactants (Figure 4. 18), on the other hand, had a moderate cleaning effect. A combination of the alkali and surfactant (Figure 4. 19), however, provided the best cleaning efficiency. An improvement of water flux after cleaning with alkali cleaning reagents was from 42% to 66%, while being 100% for alkali and surfactant combinations.

According to literature, flux improvements are due to membrane charge modifications in alkaline environments and their ability to remove some of the constituents from the membrane structure, both of which make the membrane more open [12].

EDTA is a chelating agent known for its ability to chelate metals [11]. Its negative performance shows that there were no or few amount of metal pollutants in the sampled water as confirmed by the SEM analysis. As recommended by the supplier [13], low pH solutions (acids) are used for cleaning metalic scales, while alkaline solutions are used for biological and/or organic fouling. The statement implies that the performance of alkaline solutions shows that biological and/or organic substances mainly polluted the Mooi River water sample. Madaeni *et al.* [11] previously found that NaOH/KOH and SDS had good cleaning ability when combined with EDTA. However, their water was seawater, which contained high concentrations of metals.

4.9.1 SEM

The effect of cleaning membranes was observed under SEM and the results are shown in Figure 4. 20.

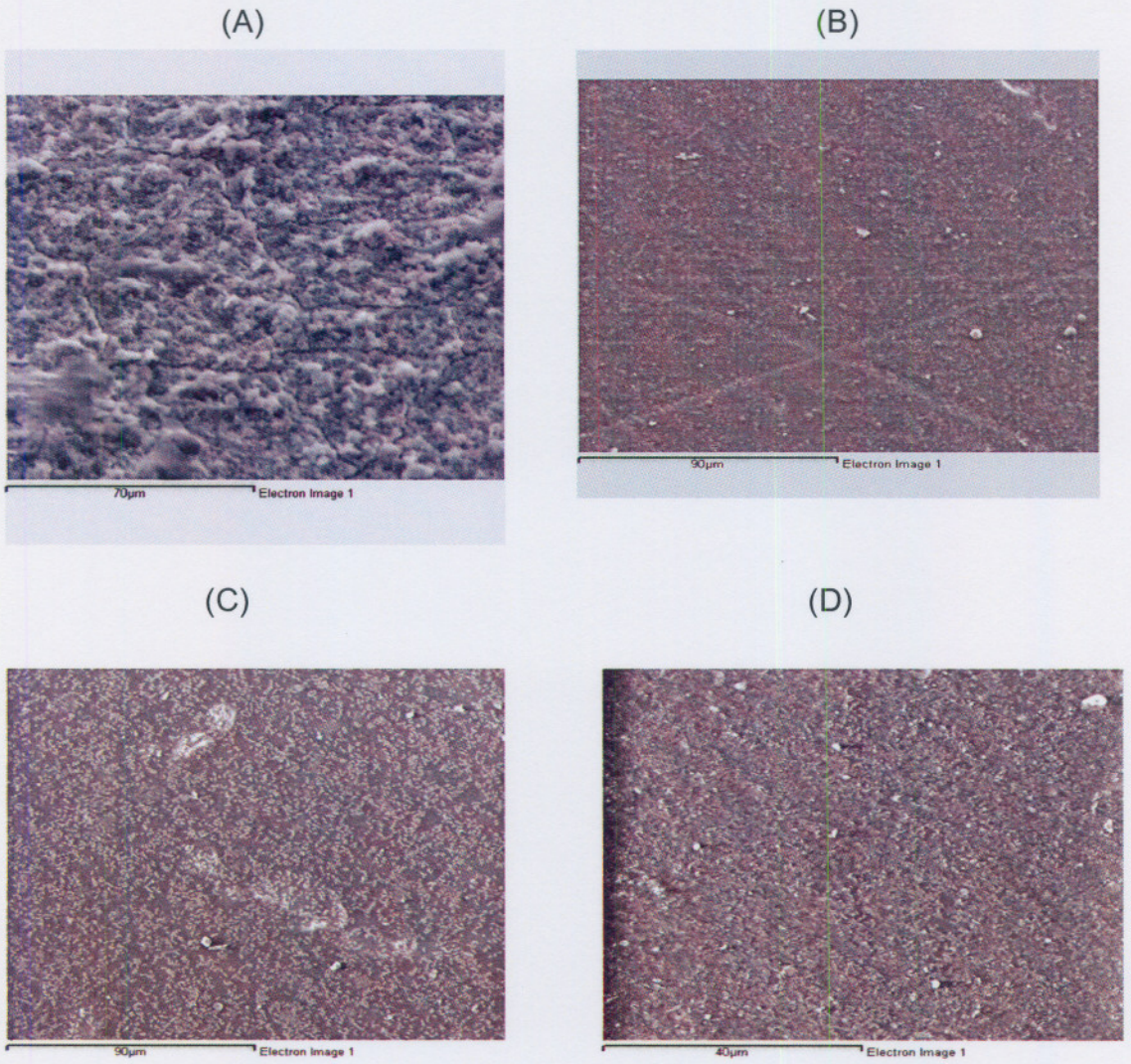


Figure 4. 20: The effect of cleaning D12-membranes as seen under SEM.

According Figure 4. 20, (A) shows the fouled D12-membrane (Mooi River water), (B) shows D12 after cleaning with a combination of potassium hydroxide and sodium dodecyl sulphate, (C) shows D12 after cleaning with potassium hydroxide and (D) shows D12 after cleaning with nitric acid.

An elemental composition analysis was done for these membranes. Membranes cleaned with KOH on its own and a combination of KOH and SDS showed elements similar to those of a virgin membrane, i.e. carbon, oxygen and sulphur, while for HNO_3, 0.5% of sodium was observed.

4.9.2 Disadvantage of chemical cleaning

While storing the membranes (1 month), it was discovered that chemical cleaning creates a suitable medium for bacterial growth as is clearly visible in Figure 4. 21. (A) shows the footprints of the bacterial growth on the membrane after cleaning with KOH, (B) shows a minimum growth after cleaning with a combination of KOH and SDS while (C) shows no growth after applying HNO_3. This seems to indicate that chemically cleaned membranes should be used continuously to avoid this growth, or discarded or sterilized if it has been stored for a period of time.

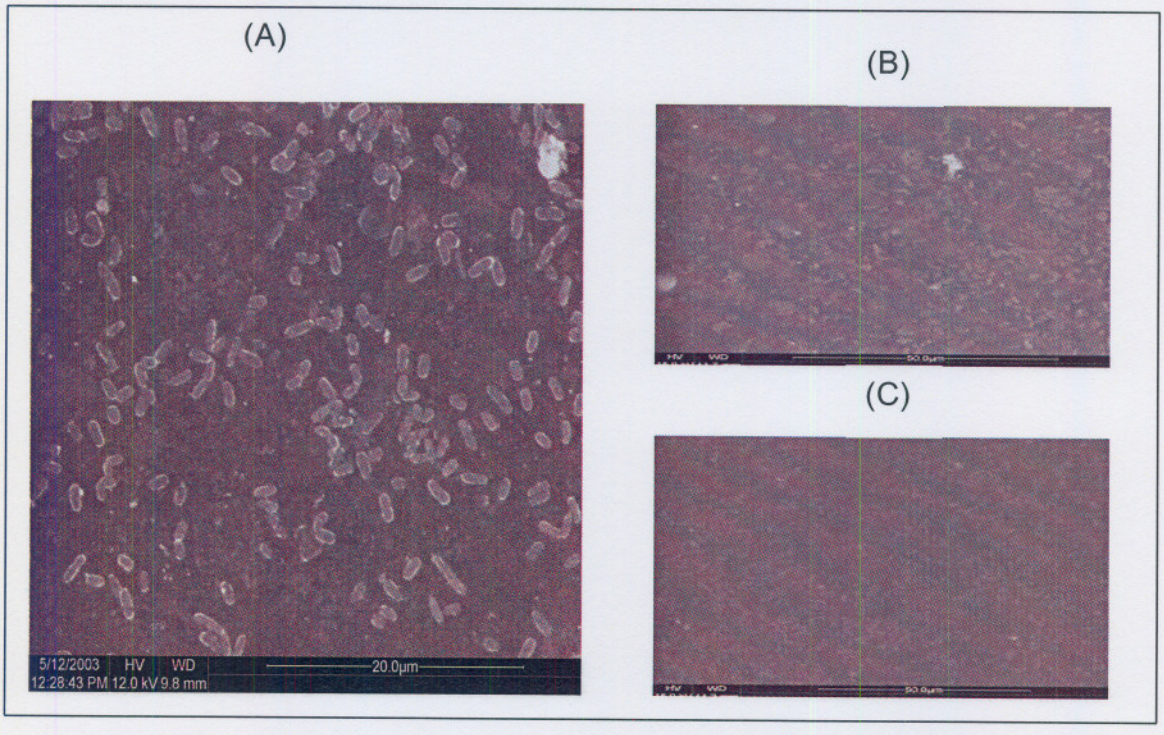


Figure 4. 21: Bacterial growth on a D12-membrane as seen under SEM

4.10 Conclusion

All membranes (D12, D11, CTC1, NF90 and NF70) were effective in rejecting sulphate (divalent) as compared to nitrate and fluoride (monovalents). For sampled water dead-end experiments, D11 and NF70 showed good rejection

of fluoride. NF70 was able to reduce the excess fluoride content from Lerome (4.65 ppm in feed) to less than 1 ppm (~80% rejection). According to the cross-flow results, all NF-membranes rejected fluoride effectively which means that NF can be considered for fluoride reduction in water. The nitrate content in all the water samples was within the acceptable values. Nevertheless, the FilmTec® membranes (NF70 and NF90) most effectively rejected nitrate. Generally, D12 and D11 showed poor performance in nitrate reduction and therefore are not recommended membranes for treatment of rural water with high nitrate concentrations. CTC1, NF90 and NF70 could be good choices since all moderately rejected nitrate and fluoride. All NF-membranes tested can be used for sulphate rejection.

Crystallization occurred on the membrane surface, which could be removed by washing with plenty of water. Irreversible fouling is observed when cleaning membranes with acids, while when using bases, fouling is reversible. It was also found that river water samples caused more fouling of NF-membranes than groundwater samples.

Finally, it was shown that acids are not effective cleaning agents for the sampled river water (Mooi River). However, alkaline (ammonium chloride, potassium hydroxide and sodium hydroxide) and surfactant (sodium dodecyl sulphate) solutions can be used for NF-membrane flux recovery. A combination (alkaline and surfactant) seems to be most effective as a cleaning agent.

4.11 References

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CHAPTER 5

NF-MEMBRANE PROCESSES (CROSS-FLOW)

CHAPTER 5

Part I: Rural water treatment

5.1 Experimental

5.1.1 Materials and methods

The instrumentation described in Chapter 3 (Section 3.2.1.2.2) was used at an operational pressure of 5 bar at ambient temperatures. All the membranes (Section 3.2.1.4) except NF70, which was not commercially available for a cross-flow module, were used.

5.1.2 Water sampling

Groundwater sample were collected at the Haaskraal farm as mentioned in Chapter 4 (Section 4.2.2)

5.1.3 Water treatment

Groundwater samples from Haaskraal were permeated through four membranes (D12, D11, CTC1 and NF90). The experiments were operated with a pressure of 5 bar at ambient temperature using the set-up described in (3.2.1.2.2). The collected samples i.e. feed, permeate and retentate, at random time intervals for the minimum of ~10 hours to the maximum of ~24 hours were analysed for NO_3^-, F^- and SO_4^{2-} using a colorimeter (HACH DR/890).

5.2 *Results and Discussion*

The rejection of sulphate, nitrate and fluoride from groundwater samples from Haaskraal farm treated by nanofiltration membranes is shown in Figure 5. 1. Accordingly, sulphate was effectively rejected by all the tested membranes. A sulphate rejection of greater than 97% was observed for NF90, followed by CTC1 with a rejection above 90%. D12 and D11 showed sulphate rejections of above 80%.

A moderate nitrate rejection (~50%) was obtained by CTC1 and rejections of above 70% were achieved by NF90. D12 and D11 poorly rejected nitrate. Fluoride was rejected well by all the NF-membranes except for CTC1. Fluoride rejection of above 70% was achieved in D12, D11 and NF90. Again NF90 behaved more like an RO-membrane than an NF-membrane by rejecting almost all the ions.

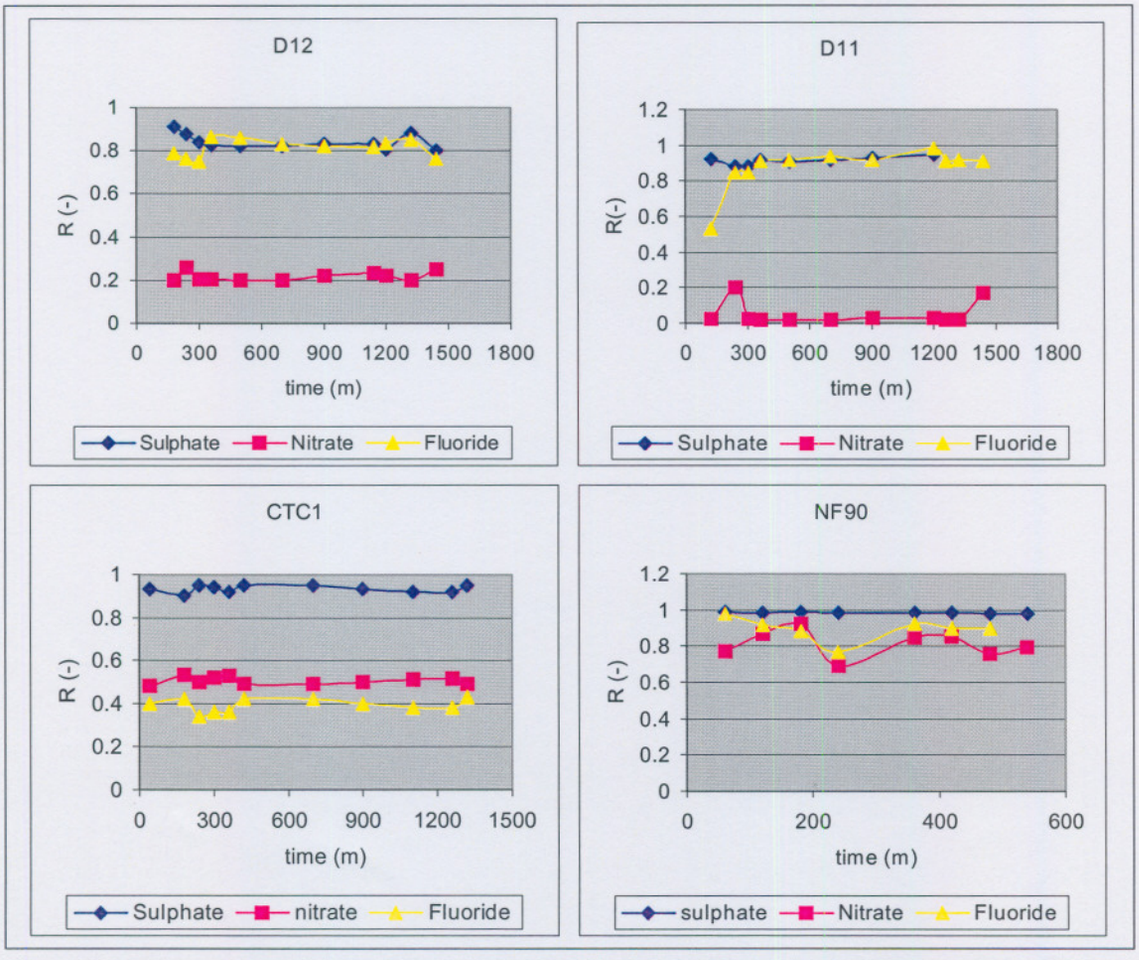

Figure 5. 1: Rejection of salts from Haaskraal water by NF-membranes

5.3 Dead-end versus cross-flow module

Table 5. 1 shows a comparison in salt rejection between dead-end and cross-flow modules.

Table 5. 1: Average rejection of SO_4^{2-}, NO_3^- and F^- from Haaskraal water sample by dead-end and cross-flow

	D12		D11		CTC1		NF90	
Ions	DE*	CF**	DE	CF	DE	CF	DE	CR
SO_4^{2-}	0.93±0.02	0.85±0.04	0.90±0.03	0.91±0.03	0.92±0.03	0.93±0.02	0.94±0.02	0.98±0.01
NO_3^-	0.29±0.38	0.22±0.02	0.40±0.33	0.06±0.07	0.70±0.28	0.51±0.02	0.64±0.30	0.81±0.07
F^-	0.74±0.31	0.80±0.04	0.65±0.27	0.86±0.13	0.76±0.25	0.38±0.03	0.81±0.26	0.90±0.06

* dead-end, **cross-flow

Sulphate rejection in all the tested membranes was relatively high (Table 5. 1). With the D12-membrane, ~95% sulphate rejection was attained for dead-end while 85% was achieved in cross-flow. A sulphate rejection of above 90% was observed for both modules using D11 and CTC1-membranes. NF90 rejected sulphate effectively (~95%) in dead-end while a >99.9% rejection was observed in the cross-flow module.

For nitrate, poor rejections (~30% in dead-end and 20% for cross-flow) were observed for the D12-membrane in both the modules. The two modules also showed poor nitrate rejection by the D11-membrane, that is 40% in dead-end and less than 10% in cross-flow, while the CTC1-membrane showed good nitrate rejection of ~70% for dead-end and ~50% in cross-flow. For the NF90-membrane ~65% and ~80% nitrate rejection was observed for dead-end and cross-flow, respectively.

The D12-membrane showed a good rejection of fluoride with both modules (~75% in dead-end and cross-flow ~80% retention obtained), which is relatively comparable (Table 5. 1). The D11-membrane showed good rejection, but a difference of ~20% in performance was obtained. About ~65% and ~85% fluoride rejection was observed for dead-end and cross-flow respectively. The difference could be due to the increased transport of

monovalent co-ions induced by the presence of high valence co-ions. Fluoride rejection for the CTC1-membrane was ~75% and ~40% for dead-end and cross-flow, respectively. Rejections by the NF90 membrane were comparable for both modules (up to 80% fluoride rejection in dead-end and ~90% cross-flow).

Part II: Fouling

5.4 Experimental

5.4.1 Materials and methods

The instrumentation set-up described in Chapter 3 (Section 3.2.1.2.2) was used. For this part, a D12-spiral-wound membrane was selected for fouling experiments using Mooi River water samples. The permeate flow of the initial AA-water flux, the Mooi River water flux and the final AA-water flux were determined following the sketch shown in Figure 4.7, Step (A) - (C). An operational pressure of 5 bar was used at ambient temperature.

5.5 Results and Discussion

The flux reduction with time is shown in Figure 5. 2 and is mainly due to concentration polarization and fouling.

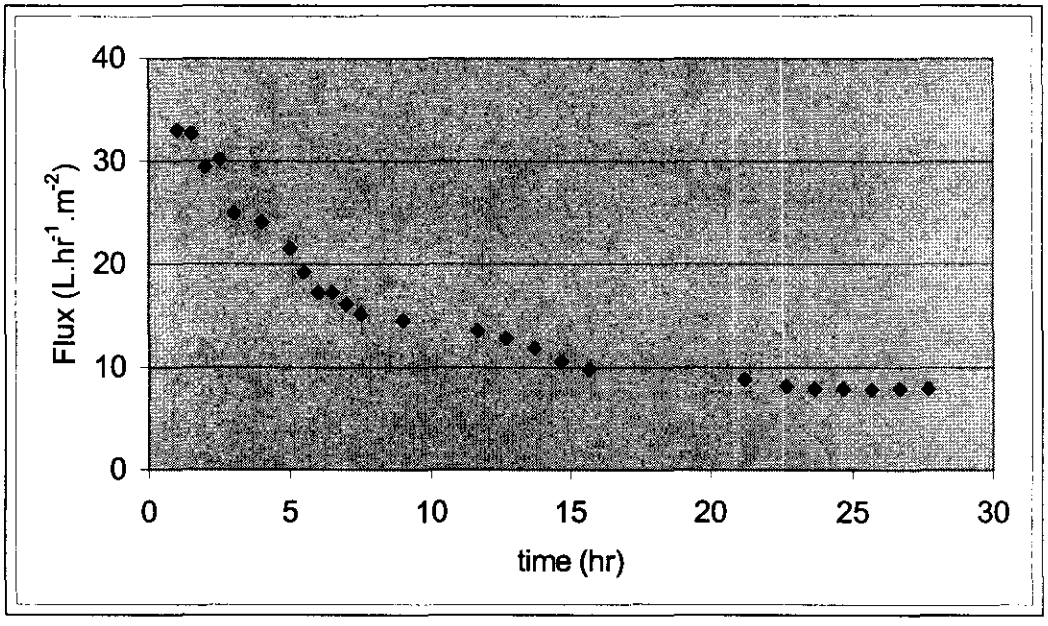

Figure 5. 2: Flux reduction as a function of time; ambient temperature and pressure = 5 bar

As in Section 4 the effect of fouling and cleaning on the flux is illustrated by presenting the flux at steady state for the various treatments (Figure 5.3). All data presenting fluxes during different treatments (for example AA before, fouling, cleaning and AA after) show the flux after steady state had been reached. Steady state was assumed when a flux remained constant for at least 3 hours.

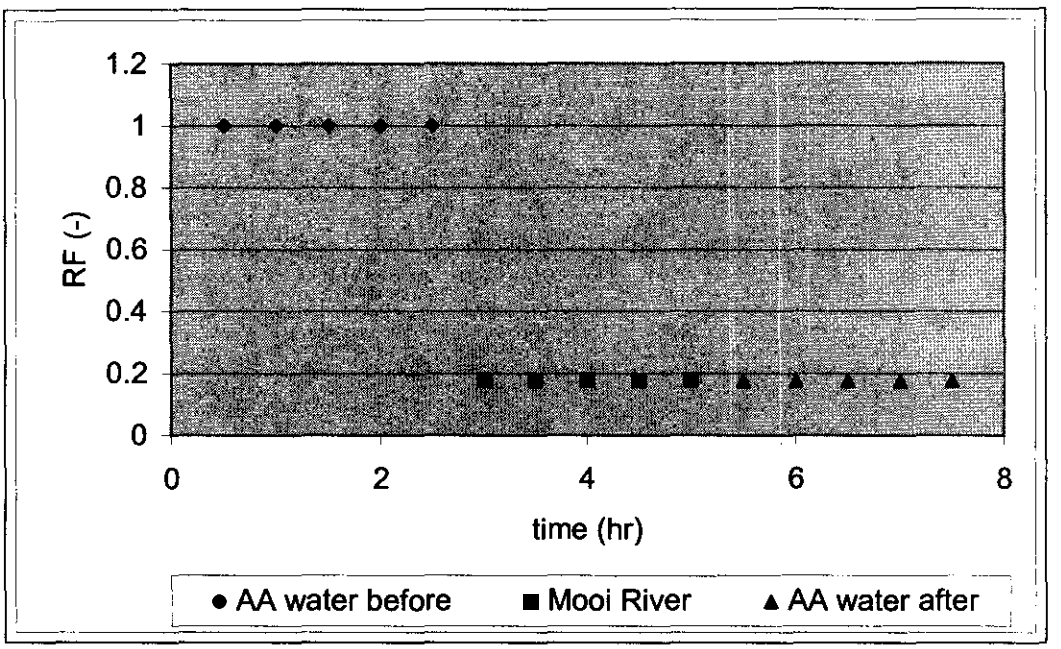

Figure 5.3: A graph of relative flux at steady state at ambient temperature and pressure = 5 bar

The curve in Figure 5.2 shows that there has been an accumulation of materials (foulants) on the surface of the membrane, which causes a reduction in flux with time. Such continuous flux decline is a result of membrane fouling. A steady-state condition was established after 20 hours and no further flux decrease was observed thereafter.

Using Equations (4.1) and (4.2), the water flux reduction (FR) and sample flux reduction (RF) were calculated as 83% and 80%, respectively.

5.6 Dead-end versus cross-flow

Theoretically, more fouling can be expected in the dead-end than cross-flow module [1]. While dead-end usually reached the steady within 3 hours, the cross-flow module took about 25 hours before a steady state condition was observed.

Part III: Chemical cleaning

5.7 Experimental

5.7.1 Materials and Methods

0.05% KOH solutions were prepared for chemical cleaning. The Hanna instruments HI 9321 pH-meter was used to determine pH-values of these reagents. Cleaning chemicals were initially applied separately. Depending on the individual effectiveness of the cleaning reagents, combinations of reagents were used to determine any further cleaning effectiveness.

The permeate flow of the initial AA-water flux, the Mooi River water flux, AA-water flux after membrane fouling and AA-water after chemical cleaning as shown by sketch in Figure 4.7, Step (A) - (E) were determined. For the cross-flow experiments, a fouled membrane was immersed in the cleaning solution (Step (D) in Figure 4.7) for about 12 hours. Thereafter, water flux was measured again (Step (E) in Figure 4.7) and compared with initial water flux [step (A)].

The curves shown in Figure 5.4 represent the steady state of the experiment, even though the duration of the filtration was longer. For these experiments, an operational pressure of 5 bar was used at ambient temperature.

5.8 Results and Discussion

For cross-flow experiments, only potassium hydroxide was used as a cleaning agent on a D12-spiral-wound membrane. Potassium hydroxide was chosen due to its effective cleaning performance in bench-scale (dead-end) experiments where it did not foul the membrane during filtration. Flux recovery

(FR) and resistance removal (RR) were 25% and 65%, respectively. A graph of relative flux at steady state can be seen in Figure 5.4.

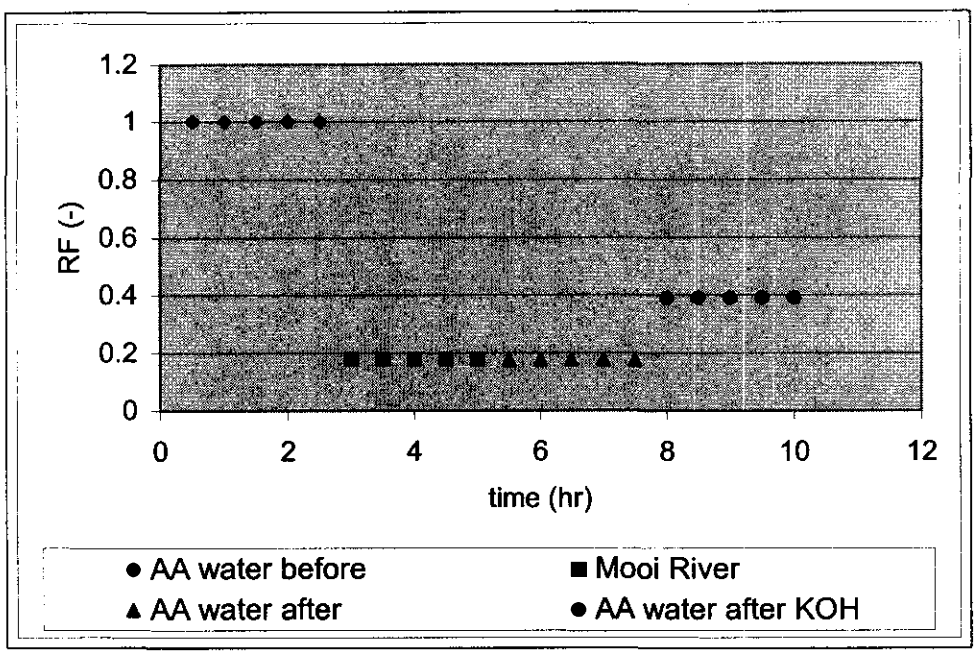

Figure 5. 4: A graph of relative flux at steady state; ambient temperature and pressure = 5 bar

5.9 Dead-end versus cross-flow

A flux recovery for KOH as a cleaning agent in dead-end was 66% while in cross-flow only 25% was achieved. Only the resistance removal, 74% for dead-end and 65% in cross-flow, was relatively comparable. Results in both modules confirm that chemical cleaning can be used as a method for membrane regeneration even though the flux recovery is minimum for cross-flow.

5.10 Conclusion

NF membranes rejected sulphate (divalent) and fluoride (monovalent) effectively, while nitrate (monovalent) was poorly rejected except by NF90-membranes. A moderate nitrate rejection was achieved using CTC1.

The Mooi River water sample caused ~80% fouling of an NF-membrane (D12). About 20% final AA-water improvement was observed after cleaning with KOH as a cleaning agent. KOH cannot effectively remove resistance on the membrane surface for membrane regeneration.

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CHAPTER 6

EVALUATION AND RECOMMENDATIONS

Chapter 6

6 Evaluation and Recommendations

This Chapter gives an overview of the entire study. The main findings in the characterization of the membranes, their performance, fouling and chemical cleaning are briefly discussed. Some recommendations for further study are made.

6.1 Evaluation

The scarcity of quality drinkable water and the degradation of water resources are important problems. South Africa is a water scarce country where about 12 – 16 million people have insufficient potable water [1]. Most rural areas depend on groundwater as a strategic resource. Some of this water is exposed to hazardous organic and inorganic pollutants, which threaten human health.

Sampling in some selected areas of the North West province indicated that nitrate and sulphate levels were within the acceptable limit, while fluoride was above the limit.

All the tested membranes were negatively charged. D12, D11 and CTC1 showed high water fluxes compared to NF90 and NF70. The two FilmTec® membranes, NF90 and NF70, showed characteristics which are closer to those of RO-membranes than NF-membranes by rejecting almost all ions.

The general performances of the membranes for the prepared single salts solution and sampled water are shown in Table 6. 1. The range of proposed performance (given in signs, Table 6. 1) for both single salt and sampled water are interpreted as follows:

Table 6. 1: General performance of different membranes for single salt solutions

Membrane performance								
	Dead-end				Cross-flow			
	SO_4^{2-}	NO_3^-	F^-	Overall*	SO_4^{2-}	NO_3^-	F^-	Overall
D12	++	+	+	++	++	-	+	+
D11	+	+	-	+	++	+-	+	+
CTC1	++	+-	+	++	++	-	-	+-
NF90	++	++	+	++	++	++	++	++
NF70	++	++	++	++	NR	NR	NR	NR

A negative rejection = (--), 0 – 40 = (-), 41 – 50 = (+-), 51 – 70 = (+) and 71 – >99.9 = (++). NR = no results. * overall performance of the membrane.

Membranes in both the modules performed well in terms of single salt retention. An overall good rejection was observed for the dead-end module compared to the average performance observed for cross-flow. Nitrate was not well rejected by D11 and CTC1 for both modules. NF90 was generally a very effective membrane.

The ability of nanofiltration membranes (D12, D11, CTC1, NF90 and NF70) to remove fluoride, nitrate and sulphate from rural water samples of Lerome, Kaallaagte, Rhenosterfontein, Rietvlei, Vaal River and Haaskraal was evaluated (Table 6. 2). Haaskraal water was used for cross-flow module experiments. Sulphate was sufficiently rejected by all the tested membranes in both dead-end and cross-flow modules. This achievement qualifies nanofiltration membranes as a good choice for the application of sulphate removal, especially in mining industries were sulphate-containing acid effluents are problematic. This efficiency in the removal of sulphate ions from acid mine water was previously shown in our laboratory [2]. Nitrate and fluoride were well retained by NF70 only, while the other membranes showed poor or even negative rejections in some cases. For the cross-flow module, the two Envig membranes, D12 and D11, poorly rejected nitrate. Accordingly,

NF90 and/or NF70 are recommended, after screening all the tested membranes, for a pilot plant built to treat polluted rural water for the community.

Table 6. 2: General performance of different membranes on rural water

Membrane performance										
		Dead-end					Cross-flow			
Sample	Ions	D12	D11	CTC1	NF90	NF70	D12	D11	CTC1	NF90
Lerome	F^- NO_3^- SO_4^{2-}	-- + ++	- -- ++	- -- ++	- +- ++	++ + ++	NR	NR	NR	NR
Kaallaagte	F^- NO_3^- SO_4^{2-}	- - ++	+ - ++	- - ++	-- + ++	- ++ ++	NR	NR	NR	NR
Rhenoster	F^- NO_3^- SO_4^{2-}	- - ++	- - ++	+- - ++	- -- ++	- + ++	NR	NR	NR	NR
Rietvlei	F^- NO_3^- SO_4^{2-}	- +- ++	- -- ++	- - ++	- -- ++	- + ++	NR	NR	NR	NR
Vaal River	F^- NO_3^- SO_4^{2-}	- + ++	- - ++	-- +- ++	- - ++	+- +- ++	NR	NR	NR	NR
Haaskraal	F^- NO_3^- SO_4^{2-}	++ - ++	+ - ++	++ ++ ++	++ + ++	++ ++ ++	++ - ++	++ - ++	- +- ++	++ ++ ++

NR = no results

For the Haaskraal groundwater sample, all the tested membranes showed an effective fluoride rejection, except for CTC1 in the cross-flow module. D12 and D11 showed a poor nitrate rejection in both the dead-end and cross-flow modules, while a medium rejection was attained in cross-flow. Sulphate was effectively rejected in all the tested membranes. NF90 was generally effective in removing both monovalent and divalent ions from rural water both for dead-end and cross-flow modules.

It is evident that membranes foul during the filtration process. Foulants tend to form a cake on the membrane surface, which retard the membrane performance by reducing flux and retention. Chemical cleaning can be a

remedy to this problem. The cleaning efficiency will depend on the type of water composition and membrane used. Alkaline and surfactant solutions were effective in cleaning NF-membranes fouled by the Mooi River water sample. By using acids, a further flux decline was observed showing that acids are not effective cleaning agents for the Mooi River water sample. D12 was the tested NF-membrane for both fouling and chemical cleaning.

6.2 Recommendations and further research

Monitoring of harmful pollutants in groundwater should be broadened to other parts of the North West province.

Consumers should be made aware of the side effects caused by polluted water, e.g. mottling of teeth and dental fluorosis caused by high levels of fluoride.

Universities doing water research should have a close collaboration with the Department of Health where the results above the limit for human health will be presented. A follow-up to purify water in such polluted areas should be done in order for consumers to have potable water.

Further research needs to be done in the investigation of membrane performance for treatment of polluted water using RO and/or low-pressure RO-membranes. The results must be compared with those of previous research projects on NF-processes.

Research on the analysis of inorganic pollutants has been extensively done in our laboratory [2, 3, 4]; and should be extended to the analysis of organic components.

Furthermore, membrane autopsies can be done. Dead membranes can be collected from different companies for investigation to discover the cause of

the death. This study can comprise a complete Masters or even a Ph D study.

Another study could be done on the variation in data obtained in this study i.e. a difference in ion retention for NO_3^-, F^- and SO_4^{2-} by the same membrane, but different sampling sites, which could not be explained. Also the difference in ion retention behaviour between dead-end and cross-flow could also be investigated.

6.3 Closing remarks

This research has provided insightful information on the general application of nanofiltration membranes. A number of NF-membrane plants were visited during the two years of study. These excursions (Sasol Secunda and Lethabo power station) gave background on where and how nanofiltration can be applied in South African industries i.e. treatment of process water using NF and RO-membranes for reuse.

This study was mainly focused on trying to compare the dead-end module with the cross-flow module. Life was not easy during these experiments, especially working on the cross-flow module where some modification e.g. automation, still needs to be done. This dissertation does not represent a complete picture of the experience gained during this study.

During my two years of study, certain skills were developed i.e. leadership role, teamwork, organization, and communication skills.

6.4 References

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