Treatment and reuse of reactive dye effluent from textile industry using membrane technology

A thesis submitted in fulfilment of the academic requirements for the degree of

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Declaration

I Martha Noro Chollom, student number (21144183), hereby declare that unless indicated, this thesis titled *Treatment and reuse of reactive dye effluent from the textile industry using membrane technology* is the result of my own investigation and has not been submitted in part or in full for any other degree at another University or Institution.

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Signature

Abstract

The textile industry consumes large volumes of water and in turn produces substantial quantities of polluted effluents. Approximately 30% of reactive dyes used during the textile processing remain unfixed on fibres and are responsible for the colouration in effluents. Various conventional methods are being used to treat textile effluent. However, the disadvantage of these methods is that total colour removal is not achieved and chemical by-products are introduced from the use of chemicals. The water quality produced therefore does not meet the requirement for textile reuse. Membrane based processes provide interesting possibilities of separating hydrolysed dye stuff and dyeing auxiliaries, thereby reducing colouration and COD content. They can be employed to treat reactive dye bath effluent to recover the salts and water for the purpose of reuse.

This study aimed at integrating membrane processes into the reactive dye bath of a textile industry. The objectives were to determine the quality of permeate produced in terms of removal of organics, ascertain its reusability for dyeing, investigate the production rate in terms of permeate fluxes and finally to investigate the cleanability and flux recovery of the membranes. Three effluent samples were chosen for this study based on the dyeing recipe; Light shade, Medium shade and Dark shade.

Ultrafiltration (UF) and Nanofiltration (NF) membrane processes were employed to treat the reactive dye bath effluents to recover the salts and water. Investigations were conducted firstly with UF as a pre-treatment to NF. Secondly, evaluations were carried out on the performance of two types of NF membranes (SR90 and NF90) in terms of permeate quality and fluxes for the investigated samples. The effect of cleaning on membrane performance was done. A reusability test was carried out on the permeate samples for dyeing.

It was found that the use of UF as a pre-treatment yielded an increase in permeate of 5–25% of the NF fluxes and 90% in organics reduction for all treated samples, hence increasing the water recovery. High rejection of >90% by NF90 for COD, TOC and colour were obtained for all the treated samples. SR90 rejection was 80–90% for colour and >90% for COD and TOC. Salt recovery for NF90 was 60–90% and for SR90 was 40–50%.

The reusability tests carried out showed that permeate recycled from NF90 can be used for any section in the textile industry including the most critical such as dyeing on light shades, while that from SR90 can be used for dyeing dark shades only. It was then concluded that membrane based processes can be integrated into the dye bath of the textile process for the purpose of reuse, thereby saving on the cost of chemicals (salts), reducing fresh water usage and reducing the extent of final effluent treatment.

Dedication

This research work is dedicated to GOD almighty, without your Grace, Mercy and Divine direction this project will not have been a reality. I am Grateful.

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Abbreviations

DS	Dark shade
Lc50	Lethal concentration
LS	Light shade
MWCO	Molecular weight cut-off
MS	Medium shade
NF	Nanofiltration
NTU	Nephelometric turbidity units
Pt-Co	Platinum- Cobalt units
POTW	Public owned treatment works
PWF	Pure water flux
RO	Reverse Osmosis
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
WFR	Water flux recovery

List of Symbols

J_v	Volumetric flux (Jv, m s^{-1})
J_s	Solute flux (Js, mol m^{-2} s^{-1})
σ	Reflection coefficient (–)
P_s	Solute permeability (mol N^{-1} s^{-1})
L_p	Hydraulic coefficient ($m^3N^{-1}s^{-1}$)
$\Delta\pi$	Change in osmotic pressure (Pa)
ΔC	Concentration difference between permeate and retentate (mol m^{-3})
ΔP	Applied transmembrane pressure (Pa)
J	Flux (L m^{-2}h)
T	The period over which permeate is collected (h)
A	Effective membrane area (m^2)
R	Retention
C_p	Solute concentration in permeate (mg^{-1})
C_f	Solute concentration in feed (mg^{-1})
ΔP	Applied pressure (Pa)
$\Delta\pi$	Osmotic pressure (Pa)
μ	Feed viscosity (Pa.s)
Jc	Flux after cleaning and (LMH)
$J0$	Flux of the virgin membrane (LMH)
Rm	Intrinsic membrane resistance deter. using pure water as feed (m^{-1})
Rf	Fouling layer resistance due to pore clogging, gel layer, and adsorption (m^{-1})

Chapter 1 - Introduction

1.1 Textile wastewater

Fresh water supply is increasingly becoming scarce and expensive; this is due to an increase in human population, industrial and agricultural activities that consume large amounts of this resource. Globally, about half of the freshwater available for consumption is used by households, and the rest is for industrial and agricultural activities. In addition to the shortage in freshwater supply, increase in industrial activities has led to most environmental pollution problems through the discharge of untreated wastewaters into the receiving water bodies (Naim and Abd, 2002).

Although treatment of these wastewaters before discharge has been made compulsory to all industries by the relevant environmental protection legislations, not all the industries have the treatment facilities to adequately treat these effluents. As a result, the water quality in the receiving environment is rapidly deteriorating. Hence shortage of water supplies has forced the industrialists to pay more for their fresh water consumption and wastewater generation. Thus, finding sufficient water supply and using water appropriately have become a vital matter of concern (Goodman and Porter, 1980; Nouha *et al.*, 2012).

The textile industry utilizes huge quantities of freshwater and in return produces substantial quantities of effluent (Schoeberl *et al.*, 2005). The wastewater generated has got high chemical oxygen demand (COD), high salinity and are made up of non-biodegradable components such as dyes, pigments, sizing polymers or chemicals, and oftentimes heavy metals. Their amounts in effluent is dependent on the textile processes used (ElDefrawy and Shaalan, 2007).

There are a number of processes that are in use in the textile industry for the conversion of fibres of natural origin such as cotton, silk and wool and those of synthetic origin such as nylon, into fabrics. These include: pre-treatment, dyeing, printing and finishing. These processes are used to treat the fibres using chemicals such as:

dispersing agents, salts, emulsifiers, levelling agents, and in some cases heavy metals. These fibres often require additional washing, rinsing, and drying, and hence large consumption of fresh water, energy, and chemicals. In terms of waste generation and environmental impact, the wet processes (dyeing, preparation and finishing) are the most significant textile operations.

The textile wastewater is made up of different components due to variations in the dyeing procedures, techniques, machinery, raw materials and fabrics. As a result, it becomes difficult to assess the effluent characteristics and the load pollution in the effluent. The main source of waste is from the washing and bleaching of natural fibres, and the dyeing and finishing processes. Therefore wastewater of different composition and huge chemical complexities are produced due to the different fibres types and their methods of treatment, the different ranges of dyes used, process aids and finishing products employed. Some of the pollutants found in the textile wastewater include: colour, persistent organics, toxicants, surfactants, absorbable organic halides and sometimes heavy metals (Slokar and Marechal, 1998; Vandevivere, Bianchi and Verstraete, 1998).

1.2 Problem statement

Three processes are used for the treatment of textile wastewater: biological, physical and chemical methods. However this manner of treating textile wastewater is not sufficient. Physical treatment methods and physico-chemical methods such as flocculation are limited due to the high electrolytic strength of the dye liquor. Chemical methods such as ozonation methods are also used, however, degradation products which results from ozonation and chlorination increases in the recycled liquor and act as colourless dyes which then obstruct the dyeing process. Activated carbon seems a very viable method, colour removal is limited, due to the fact that only a single dye can be treated in a run and only 70% efficiency is achieved (Erswell, Brouckaert and Buckley, 1988; Chakraborty *et al.*, 2003).

The carry-over of the impurities from these methods is undesirable to the environment due to the fact that it affects the quality of water in the receiving bodies, which could lead to the build-up of dyes in certain forms to aquatic life, and might lead to toxic and carcinogenic degradation products. Dyes limit aquatic plant growth by reducing the rate at which light is transmitted into these water bodies, thereby prohibiting or reducing photosynthetic activities in the receiving water bodies (Akbari, Remigy and Aptel, 2002).

Moreover the cost of treating these effluents is on the increase. As a consequence, most textile industries have their own effluent treatment plants where most of the waste coming from various processes are combined and treated prior to its discharge to the environment. There are those that do not treat their effluents but, collect it in a sump, and then send it to the municipal water treatment facilities.

The biological and chemical methods are usually applied for end-of-pipe treatment. The effluents from different processes are collected and treated together. The mixture of these streams makes the characteristics of the effluent complex. Therefore, the water quality obtained from these treatments is not satisfactorily high because the majority of the compounds cannot be easily degraded. The reclaimed water still contains remaining colour and COD. In addition, these processes are unable to decrease salinity and most of them are expensive and require expertise in the operation of the equipment employed (Gozálvez-Zafrilla *et al.*, 2008; Bes-Piá *et al.*, 2009). The conventional methods are therefore limited due to their inability to recover the valuable components in the waste water and the quality of water produced do not meet the reuse guidelines.

It is therefore imperative to use treatment methods that can treat the effluent to recover salt and water for reuse in order to save on the costs incurred by treating the effluents and disposing into rivers and also reduce fresh water consumption. This can be done by the use of membranes as treatment option in the dyeing process such that the most polluted streams are treated at the point of collection. The advantage of this process is the recovery of the salts and the water for reuse in the dye baths. Also, treating of the most polluted stream separately can minimise the size of the treatment plant because the less polluted streams such as rinsing can be handled by biological processes alone (Erswell, Brouckaert and Buckley, 1988; Wenzel *et al.*, 1996).

Membrane based processes provide interesting possibilities of separating the hydrolysed dye stuff and dyeing auxiliaries thereby reducing the effluent colours and COD content. The choice of membrane processes to separate contaminants is guided by the quality of permeate required for reuse by the textile company. Therefore they can easily be integrated to treat effluents at the point of collection so that reclaimed water and chemicals are reused.

1.3 Membrane Technology

A membrane is a barrier that allows some substances to pass through it (permeate) while hindering others (retentate), in a rather specific manner (Strathmann, 1990). Membranes are widely used in various industries for separation processes due to their ability to control the substances that pass through the membrane, hence a high degree of separation is always achieved, which then makes these processes widely acceptable (Baker, 2004).

There are basically four categories of membrane processes, which include; Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). The principle of operation in each of these membranes is different; this may be based on size, solubility, charge and also the driving force for transport across the membranes.

MF and UF membranes removes suspended solids or colloidal particles through a sieving mechanism based on the pore size of the membranes. The separation mechanism in both MF and UF is based mainly on molecular size and pore size distribution. They can be applied to the textile industry mainly for the treatment of the rinsing sections and to serve as pre-treatment to NF and RO, but cannot be used to achieve high levels of separation because the polluting substances such as dyes are still visible in the permeate even after separation (Baker, 2004).

NF and RO membranes are specifically designed to remove dissolved solids. RO membranes are referred to as tight membranes, they are asymmetric with homogeneous skin and microporous support. The molecular weight is around 100 Da.

RO has the ability to retain more than 90% ionic compounds, mineral salts, hydrolysed reactive dyes and the auxiliaries used in the textile industry in a single step, thereby allowing a clear permeate through the membrane for reuse. The separation in most RO systems is achieved by the solution diffusion mechanism and is energy intensive (Cheremisinoff, 2002).

The characteristics of NF membranes lie between those of UF (loose membrane) and RO (tight membrane). For NF membranes, the sodium chloride rejection is between 20-80% with molecular weight cut-offs for dissolved organic solutes of 200-800 Da. The rejection mechanism of NF is based on the following: molecular size, whereby separation is achieved by size exclusion or due to the effect of charge, i.e. Donnan exclusion (the electrostatic repulsion of the co-ions by the fixed membrane charge). NF is preferred over RO due to its performance in terms of water flux recovery and the quality of permeate as well as relatively low energy consumption (Cheremisinoff, 2002; Baker, 2004).

Various studies have been carried out using NF processes for the treatment of textile effluents (Wenzel *et al.*, 1996; Chakraborty *et al.*, 2003; Koyuncu, Topacik and Yuksel, 2004; Tang and Chen, 2005; Irena *et al.*, 2007; Nouha *et al.*, 2012; Vergili *et al.*, 2012).

To the best of the author’s knowledge previous studies of this kind had focused on the use of diluted streams or by making synthetic feed simulating dye bath effluent. Others have used effluents obtained from biological processes or other conventional methods and this served as feed to NF (Van der Bruggen *et al.*, 2005; Irena *et al.*, 2007). In some instances, the effluents from the dye bath were diluted to meet NF requirements (Chakraborty *et al.*, 2003; Fersi, Gzara and Dhahbi, 2005). The required reuse criteria were met, however, the dilution or making of synthetic feed does not give a true representation of the effluent from the dye bath and the effects it has on the membrane performance in terms of permeate quality and recovery of chemicals for reuse.

For this study NF was used to treat effluent directly from the dye bath for reuse and a reusability test was carried out on the permeate samples. The feed was a mixture of various dyes and dyeing auxiliaries with other additives such as bleaching agents from other production stages during the fibre preparation. NF was chosen for the treatment of the textile effluent because of the following reasons (Lau and Ismail, 2009; Kurt *et al.*, 2012):

(i) It is operates at reasonable pressures but fairly higher fluxes, which results in low energy consumption, and higher water recovery.

(ii) It allows the passage of monovalent ions such as NaCl, which makes the recovery of salt possible for reuse.

(iii) It achieves excellent removals of dyes as well as chemical oxygen demand (COD), so that the quality of permeate produced can be reused in the delicate process such as dyeing (Kurt *et al.*, 2012).

1.4 Selection of feed

The feed selection was based on the following criteria:

I. Reactive dyes were selected because they represent about 20-30% of the sum total of market demand for dyes, and they are used to dye cotton which is about 50% of the fibre used in textile (Cuhorka and Mikulášek, 2010).

II. The fixation rate is poor, a huge portion of the dyes is lost during dyeing, about 30% of it remains unfixed on the fibre and are washed off into water bodies which accounts for the high colours in the textile effluents. Most of them are not biodegradable; therefore they resist degradation by conventional methods of treatment and processes such as oxidation is always too expensive.

1.5 Aim and objectives

The main aim of this research study was to evaluate the feasibility of using NF processes for the treatment of reactive dyebath effluents from the textile industry in order to recover the water and chemicals (salts) for reuse purposes. The specific objectives are:

- (I) To study the efficiency of two NF membranes (SR90 and NF90) for the treatment of reactive dye effluent in terms of removal of organics for reuse purposes.
- (II) To study the rate of flux decline for the three different samples to be treated and also the effect of using UF as a pre-treatment to NF.
- (III) To evaluate the efficiency of membrane cleaning by physical methods and also with the use of chemicals.

1.6 Approach

The feed water (effluent) was obtained from Mediterranean textile industry KwaZulu-Natal, South Africa. The company carries out most of its dyeing with reactive dyes thereby generating substantial amounts of effluents; these are then combined with wastewater from other streams of production and are discharged to the municipality sewer for treatment. The disadvantage of this is that the effluent is usually in various degrees of composition and this makes the municipality process more cumbersome while recovery of water for reuse is not feasible. Also, most reactive dye compounds are properly structured polymers, hence they are not easily broken biologically, and other processes of treatment are not sufficient.

This study was conducted in two stages. The first stage of the experiment was carried out using UF as a pre-treatment to feed NF. These membranes were supplied by Inge GmbH. The effect of feed pre-treatment was investigated on the performance of both NF membranes in terms of flux.

The second stage was carried out using two NF units (SR 90 and NF 90). Both NF membranes were supplied by Dow film Tech. The distinction between the two membranes is based on their molecular weights cut-off (MWCO). NF90 had a MWCO of 100-200 Da while SR90 had a MWCO of 200 Da. The performance of both NF membranes in terms of the rate of fouling for the treatment of three different dye samples (light, medium and dark shades) was evaluated. Permeate and feed samples were analysed for the following parameters TOC, colour, TSS, turbidity, pH, COD, and conductivity. The following equipment was used: Hach DR 3900 spectrophotometer, Hach pH meter, Hach turbidity meter and Hach conductivity meter.

Cleaning of all membranes was carried out using 0.1 wt. % NaOH and 0.2 wt % HCl, based on membrane manufacturer recommendations. The effect of once-off cleaning and several cleans on membrane performance was investigated. Evaluation of the efficiency of membrane cleaning was also performed.

Finally permeate obtained was used for dyeing in order to evaluate its reusability for the dyeing process.

1.7 Thesis organisation

The thesis consists of five chapters. The first chapter is the introduction; it presents a brief background to the study and the problem statement.

Chapter two presents a review of the literature relevant to the study; the processes used in the production of fibres in textiles are reviewed. It also covers the treatment strategies that have been adopted for the treatment of textile effluents; their short- comings and the need for new and more effective methods are elaborated.

Chapter three presents the methodology used in this research. It gives a brief description of the equipment and procedures used for the treatment of the effluents.

In chapter four, the results and discussion is presented. The results are presented and discussed as follows: the effects of pre-treatment of the feed on permeate flux; rate of fouling on the membranes; and the separation efficiency of the membranes regarding the parameters of interest for reuse in the textile industries. Also, membrane cleaning and efficiency of the cleaning methods are discussed and finally the reusability of permeate for the dyeing of fibres.

Finally, Chapter five is the conclusions and recommendations. It summarises the important findings from the study and gives some recommendations for further research.

Chapter 2 - Literature Review

2.1 Introduction

The processes used for the production of fibres and the characteristics of the effluent and its impact on the environment are to be reviewed. Membrane processes mainly UF and NF are the focus of this work. UF is used for pre-treatment of the feed to NF; and NF is used as the main method to treat textile effluent. This chapter presents the separation mechanism and transport phenomena of UF and NF membranes, and the limitations of using these processes. Finally the regeneration of the membranes for reuse wraps up the literature survey. At the end of this chapter, a summary of the literature reviewed is provided and the gaps in knowledge which are the basis of this study are clearly identified.

2.2 Global water scarcity

Water is becoming a scare and rare commodity. Despite the fact that it appears to be plenteous in supply on the earth's surface, only about 0.03% of the earth's water is available for human activities (Allègre *et al.*, 2006). According to UNEP (2002) about one third of the world's population is at present living in countries distressed with moderate to high water stress, where water utilisation is more than 10% from renewable fresh water resources (Mara, 2003). Amongst these countries, Africa and Asia are the parts suffering the most, with low water availability. The increase in growth of the world's population, urbanization, agriculture, industrial development and natural occurrences like drought, have increased the demand for water resources in many parts of the world. Thus, there is the need for water resource planners to look for supplementary sources of water to increase the inadequacy of water accessible to their region. Also, as industries continue to increase, there is a corresponding increase in wastewater generation and is raising concerns about environmental pollution resulting from the quality of wastewater disposed. The water shortage worldwide makes industrial wastewater reuse a good option to conserve and extend available water supplies and at the same time presents an opportunity for pollution reduction when water reuse replaces effluent discharges (Avlonitis *et al.*, 2008).

2.2.1 **Challenges of water usage in textile industries**

For most textile industries in the past, water supply and effluent disposal costs were not a vital aspect of the total operating costs and hence most industries focused on other aspects of the industries. This however has to change, due to the fact that water is becoming a limited resource relative to demand, and the rate of water supply and effluent disposal charge have risen and will continue to increase (Van der Bruggen, Curcio and Drioli, 2004)

In South Africa, most textile industries are faced with significant challenges which are mainly due to stricter governmental legislation on environmental and water related issues, some of which include:

I. Increase in costs of effluent treatment or disposal as textile companies adhere to municipalities directives to reduce the pollution levels of sewage. Most of the textile finishing plants in Southern Africa treat and discharge their effluent to municipality sewers for further management in public owned treatment works (POTW) (Ntuli *et al.*, 2009).

II. More stringent legislation concerning effluent quality, e.g. for toxicity and colour.

III. Rising water supply costs as most water companies are now investing to improve water quality to meet increased demand.

2.2.2 **The need for wastewater treatment for reuse**

South Africa is a country that is faced with the scarcity of fresh water supply. Its water stress is between 40–60% due to the low volumes of rainfall (averagely 500 mm per annum). The evaporation rate is to a great extent high (an average of 1700 mm per annum). The irregular and shortage of rainfall throughout the country has increased the shortage of clean water. South Africa depends mainly on surface water for its urban, industrial, and agricultural usage (Adewumi, Ilemobade and Zyl, 2010).

The rate at which freshwater sources are consumed is higher than they are restored due to increases in population and industrial activities. This increase reduces freshwater sources because of the huge quantities of water needed by manufacturing facilities and also contaminants from manufacturing processes could contaminate the remainder of the freshwater sources.

Textile industry uses a large amount of water for manufacturing purposes. It roughly takes about 70 to 150 ℓ of water to produce 1 kg of textile (Allgre *et al.*, 2004). The quantity of water required for production in each textile industry is different. Basically there are two ways in which water is used: (I) for the application of chemicals on the fibres and (II) for the rinsing of the manufactured fibres (Hessel *et al.*, 2007)

The environmental effect of the textile industry is related with its high water utilisation, colour, conductivity and the mixture of pollutants that is contained in the wastewater. Due to this, most municipalities are confronted to think about alternatives to water and efficiently manage water use and supply. At present, wastewater reclamation and reuse is becoming very important in the textile industry because of the shortage of clean water and increasingly stringent regulation concerning its discharge (Bes-Piá *et al.*, 2009; Singh and Arora, 2011).

2.2.3 **Reuse standards**

The definition of a generally acceptable standard for water reuse has not been fully adopted in the textile industry. This is so because the water quality requirements for each textile are different. Usually, softened water is needed for scouring, dyeing and for preparation of printing pastes, but it is not necessary for all the washing cycles. The critical conditions that are considered are water turbidity, which should be lower than the turbidity of the ground water, or 0‒15 NTU for reclaimed water. Water hardness, can be between 50–60 mg/ℓ. This is moderately soft ground water

(Van der Bruggen, Curcio and Drioli, 2004; Giwa and Ogunribido, 2012). This is shown in Table 2-1. Furthermore, high amounts of other constituents such as heavy metals are not permitted in the reclaimed water (Capar *et al.*, 2006). The use of reclaimed water using various treatment methods in the textile dyeing processes has been studied by various researchers and in their studies they found that it is possible to use reclaimed water for textile dyeing processes (Wenzel *et al.*, 1996; Van der Bruggen, Curcio and Drioli, 2004).

Table 2-1 Reuse criteria for textile wastewater (Capar *et al.*, 2006; Alcaina-Miranda *et al.*, 2009)

Parameter	**Reuse criteria**
Colour (Pt-Co)	0-20
COD (mg/l)	8-40
Total solids (mg/l)	500
Total hardness (mg/l)	60
Turbidity (mg/l)	15
Conductivity (µS/cm)	1000
pH	6-8

2.3 Textile industry

The word textile means to weave; this was adopted from the Latin word “texere’’. The fabrication of textiles is one of the world’s oldest art and bases of civilization (Smith and Block, 1982). It has over the years developed from small scale into large scale production. In the early culture, wool was easily spun into yarn using simple instruments by housewives, but by the late 16th century textile manufacture had developed the characteristics of an industry. This was due to demand for new items which encouraged industrialists to invest in this sector, hence its growth and prosperity (Smith and Block, 1982).

The raw materials for textile are fibres which can be of natural or synthetic origin. Throughout most of human history people have used the natural fibres (cotton, linen, wool and silk). Due to the advancement of technology, synthetic fibres are now available in a wide range of different synthetic fibres (Smith and Block, 1982; Babu *et al.*, 2007).

The textile industries are classified based on the types of textile fibre they produce, namely, those involved in the production of cellulose fibres, protein fibres and synthetic fibres or a combination of two or all three classes. The methods used for the processing of the raw fibres into finished apparel and non-apparel textile products is difficult, as a result most of the textile mills specialize in just one process. The quality of a textile depends on the kind of raw material used and the nature of the yarn spun (Verma, Dash and Bhunia, 2012).

2.3.1 **Textile effluent**

Textile wastewaters can be described by their severe variations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, colour and salinity .The wastewater pollutants depends on the different compounds, chemicals and dyes used. The most significant contaminants from the dry and wet-processing steps are shown in Table 2-2 (Santos, Cervantes and Lier, 2007; Aouni *et al.*, 2012).

The wastes generated from the textile industry can be in the solid, liquid or gaseous forms, and are usually from manufacturing processes. The solid wastes are mostly from the dry process while the wet processes yield only a small amount of solid waste. The majority of solid wastes are made of pieces of fabric and packaging materials. The dried up sludge from the textile production is also a major source of solid waste. These wastes are generally not found to be hazardous. However the emptied chemical containers may contain traces of harmful substances.

Some of the processes that are carried out in the textile industries produce gaseous emissions in one form or another. The main sources of gaseous emissions are the boilers, ovens and storage tanks. The boilers generate sulphur oxides and nitrogen, while the high temperature processes such as drying emit hydrocarbons. Other processes where gases can be emitted are the fibre and dye processes (Babu *et al.*, 2007).

Table 2-2 Ranking of environmental issues of textile wet processing (Ren, 2000)

Sub process	**Major environmental problems**	**Ranking**	**Remarks**
Desizing	It has the highest BOD (> 50%), from the use of chemicals	High	Sizing operations significantly affects the BOD.
Scouring	Low BOD (20–30%), high COD, low toxicity from surfactants.	High	Low toxic chemicals are preferred to low BOD
Bleaching	AOXs (adsorbable organic halogens) in effluent	Low	No much problem from H_2O_2 bleaching
Mercerising	High alkalinity in effluent	Lowest	Seldom practised by all textiles
Dyeing	Colour, BOD (10–20%), metals, mostly heavy, salts, COD (30%), high water/energy consumed	Highest	Mainly water pollution, and energy-related impacts
Printing	Urea, solvents, binders	Low	Mainly air emission
Finishing	Urea-aldehyde, energy	Middle	Mainly air/energy-related impacts

In terms of waste generation and environmental impact, the wet processes (dyeing, preparation and finishing) are the most significant textile operations. The water discharged after the production of textiles contains a large amount of dyes and other chemicals which are harmful to the environment. The level of toxicity or harmfulness of the textile effluents differs among industries due to the different processes (Singh and Arora, 2011; Vergili *et al.*, 2012).

2.3.2 **Environmental impact of textile effluent**

The characteristics of textile effluents vary and are dependent on the type of fabric manufactured and the chemicals used. The textile effluents may contain high amounts of substances that cause damage to the environment and human health. They are characterised by high amounts of suspended and dissolved solids, BOD, COD, chemicals, odour and colour. Most of the BOD/COD ratios are around 1:4 (Bisschops and Spanjers, 2003). This is an indication of the presence of non-biodegradable substances. Typical characteristics of textile effluent vary considerably, some of which will be discussed briefly in this study. The textile effluents are not only associated with dyes and chemicals but also with some trace metals like Chromium, Arsenic, Copper and Zinc, which are capable of harming the environment .

Dyes in water can block the penetration of sunlight from the water surface preventing photosynthesis (Verma, Dash and Bhunia, 2012). Inorganic substances in the textile effluents make the water unsuitable for use due to the presence of an excess concentration of soluble salts. These substances even in a lower quantity are found to be toxic to aquatic lives. The organic components are found to undergo chemical and biological changes that result in the removal of oxygen from the water, while some of the inorganic chemicals like hydrochloric acid, sodium hypochlorite, sodium hydroxide, sodium sulphide and reactive dyes may be poisonous to aquatic life.

2.3.3 **Characteristics of textile effluents**

I. **Colour**

One of the obvious indicators of pollution is colour which is usually from synthetic dye. Reactive dyes are often used because of their bright, wide range shades and ease of application on cotton and also their great wet fastness. The main disadvantage of using these dyes for dyeing is that a huge portion of the dye is wasted during the dyeing process, about 10-50%, and up to 0.6-0.8 g dye/dm^3 can be detected in the effluent (Al-Degs *et al.*, 2008).

The colour from wastewaters can be harmful to the water bodies (Nigam *et al.*, 1996). For instance, colour absorbs the sunlight which is accountable for the photosynthesis of aquatic plants, however this sunlight is prevented from penetrating into the water (Nigam *et al.*, 1996).

The two most important sources of dye being released into the water bodies and surroundings are from textile and dye manufacturing companies. The effluent composition is dependent on the dyeing process. Dyes that belong to different chemical classes may be used for a single dyeing procedure (Correia, Stephenson and Judd, 1994).

II. Persistent organics

The wet processes (preparation, dyeing and finishing), contribute largely to the organics that are found in textile effluents. The persistent organic molecules found in these effluents are used in small amounts and belong to diverse chemical classes. These include: polyacrylates from the dyeing and auxiliaries from the finishing stage that are used to improve properties of the fibre. The highest amounts of organics are from the preparation stages, where, scouring, sizing, desizing, and bleaching are carried out (Vandevivere, Bianchi and Verstraete, 1998).

III. Toxicants

Textile effluent comprises of various organic substances, among which are the biocides. Biocides are toxicants which can contribute generally to the toxicity of the textile effluent. Several studies have been evaluated on the effect of dyes to aquatic life (Chung and Cerniglia, 1992; Chung and Stevens, 1993; Beydilli, Pavlostathis and Tincher, 1998). It was found that the LC_{50} (lethal concentration) of the majority of dyes is lower in rivers; hence it is considered they will not cause acute toxicity to the aquatic life. It is worthy to note that the data for the chronic exposure of most commercial dyes and their derivatives is inadequate, however, some dyes are said to be mutagenic (Vandevivere, Bianchi and Verstraete, 1998; Chung, 2000).

IV. Surfactants

Surfactants are consumed by wet processing streams which include: sizing, desizing, spinning, weaving, scouring and washing. Surfactants are grouped into two namely anionic and non-ionic. Textile processes use the Alkyl phenol ethoxylates; they are the principal non-ionic substances. They can be biodegraded to alkyl phenols which can be absorbed and with time are build-up in the sewage sludge (Slokar and Marechal, 1998; Vandevivere, Bianchi and Verstraete, 1998; Bisschops and Spanjers, 2003).

V. Absorbable organic halides (AOX)

The absorbable organic halides are usually from the bleaching process. Sodium hypochlorite and other bleaching agents are used for the bleaching of fibres. Hypochlorite bleaching effluents are made up of 100 mg dm^{-3} AOX which include substantial quantities of carcinogenic chloroform. Certain reactive dyes also contain the AOX (Vandevivere, Bianchi and Verstraete, 1998).

VI. Heavy metals

Most of the metals in the textile effluent are usually from the dyeing process. Most dyes contain metals such as: chromium, copper, mercury, zinc, and cadmium. Other sources of metals are from reducing and oxidising agents, electrolytes, acids and alkalis (Bisschops and Spanjers, 2003). These heavy metals may affect all forms of aquatic life when discharged into the receiving water bodies. However, some organisms require some traced amounts (µg/ℓ) of metals like copper, zinc iron nickel and cobalt as cofactors for their enzymatic activities. However, heavy metal ions at higher levels (mg/ℓ) are poisonous to most of the organisms due to the irreversible retardation in the enzymatic activities by heavy metal ions (Pamukoglu and Kargi, 2007).

2.3.4 Textile manufacturing processes

The textile industry comprises mainly of three to four stages of converting textile fibres into apparels. These processes are yarn formation, fabric formation, wet processing, and textile fabrication (finishing) (Babu *et al.*, 2007). Figure 2-1 shows the stages used in processing fibres into apparels at the Mediterranean Textile Mills. Each of the above mentioned process contributes significantly to the pollution of textile wastewater but in varying degrees (Babu *et al.*, 2007).

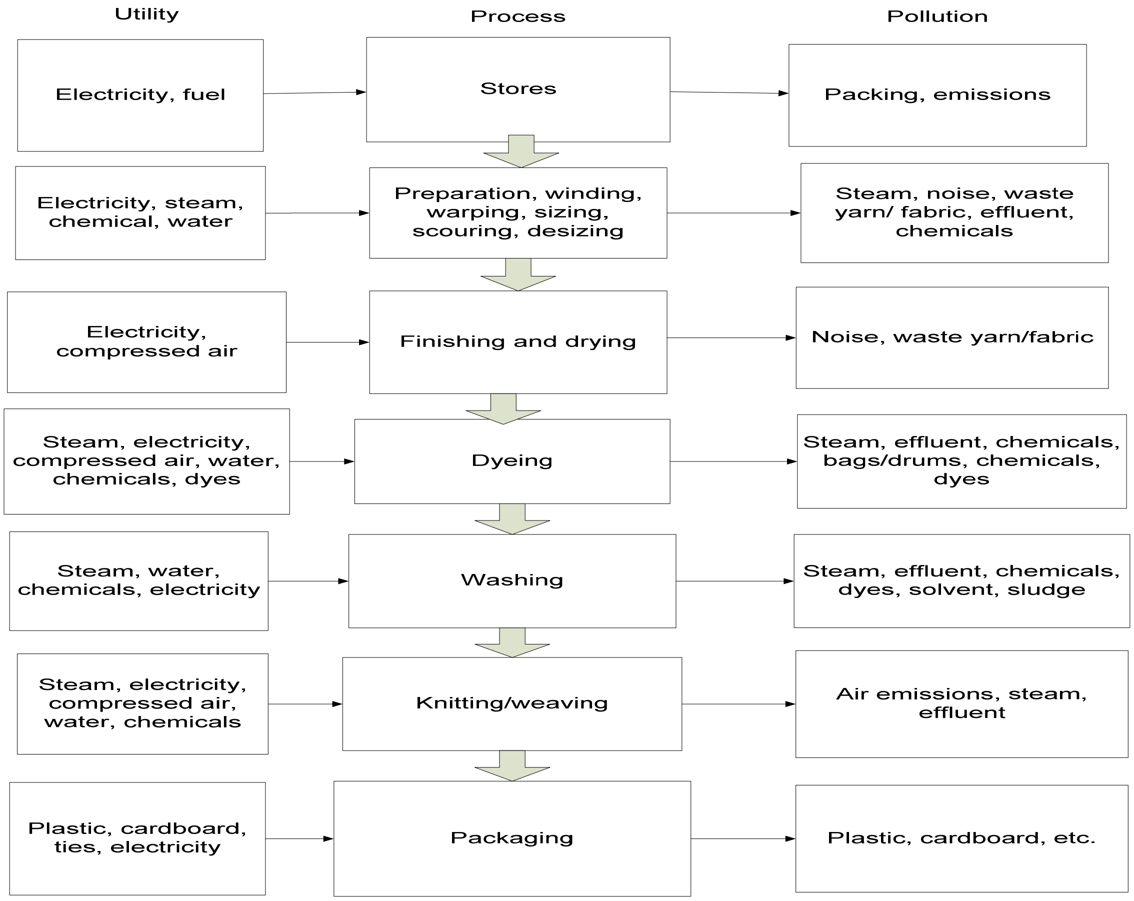

Figure 2-1 Shows a simplified process diagram for Mediterranean Textile Mills and the stages used in processing fibres into apparels (Barclay, 2012).

The consumption of water is highest in the yarn preparation and the dyeing sections. These sections are discussed as follows:

2.3.5 **Yarn preparation**

Preparation or pre-treatment is carried out on both natural and synthetic fibres to make them suitable for dyeing and finishing. It can be carried out on loose fibres or yarns of fabrics. The effluent with the highest COD/BOD is from the preparation stages. The stages that require the most water and consume considerable amounts of chemicals include: sizing, desizing, scouring, bleaching and mercerising in some cases when yarns of fabrics are used. Several types of chemicals are used in preparation, which include: enzymes, alkalis, bleach bath stabilisers, sequestrants, oxidative and reducing agents. To the main components, auxiliaries such as surfactants are usually added to assist in wetting, scouring and detergency (Correia, Stephenson and Judd, 1994; Babu *et al.*, 2007).

I. **Sizing**

Sizing is the process of coating warp yarns with film-forming polymers so as to reduce the frictional properties of the fibre. It also improves weaving productivity by increasing weft (these are fibres that lie across a piece of cloth when it is woven) insertion speeds and decreasing yarn breakages. Typical sizing materials are of two types: (1) Water-soluble, such as gelatine used on synthetic fibres and (2) Water-insoluble ones such as starch, which are used on cotton and rayon yarns (Smith and Block, 1982; Correia, Stephenson and Judd, 1994; Hickman, 1995).

II. **Desizing**

This is the process of removing the sized materials that were used during sizing. The sized materials covers the yarns, hence acts as an obstacle to dyes and chemicals. Depending on the type of size that is used, water soluble sizes that are used on synthetic fibres are easily removed by washing with detergents and hot water, whereas the water insoluble starch is removed with the use of enzymes and sodium bromite. This break the starch into smaller molecules after which it can then be easily washed off with water (Smith and Block, 1982; Bisschops and Spanjers, 2003).

III. **Scouring**

Scouring is the process of treating the fibres to remove impurities on the natural fibres and synthetically made fibres. The intensity depends on the kind of cloth that is used. Cotton is scoured to get rid of the natural waxes, pectin, spinning oils and other non-cellulosic substances that are naturally found in it. This is usually carried out with one to three percent sodium hydroxide which is based on the weight of the cloth (Smith and Block, 1982). However, the addition of other alkalis such as trisodium phosphate, sodium silicates and tetrasodium pyrophosphate can also be used (Smith and Block, 1982; Correia, Stephenson and Judd, 1994; Hickman, 1995) Wool and synthetic fibres such as nylon and polyester are scoured with synthetic detergents containing alkali.

IV. **Bleaching**

Bleaching is the process of treating the fibres with chemicals to remove unwanted colouring materials especially from natural fibres. The main purpose is to prepare the fabric for further processing for instance dyeing or printing. Bleaching is carried out on the yarn as well as on the cloth stage of manufacturing. The bleaches used are dependent on the type of fibre (Smith, 2009).

Cellulosic fibres such as cotton are bleached with sodium hypochlorite or sodium chlorite as well as hydrogen peroxide. Wool is bleached with sodium dioxide gas or with hydrogen peroxide. Synthetic fibres are generally white; hence usually require little or no bleaching. If necessary, nylon, acrylic and polyester fibres may be bleached with sodium chlorite under acidic conditions (Smith and Block, 1982; Correia, Stephenson and Judd, 1994; Hickman, 1995).

There are three steps involved in the bleaching process: (I) saturation of the cloth with bleach, (II) raising the temperature to that required by each fibre, and keeping it constant till the bleaching action is complete, and (III) washing of the cloth thoroughly to free it of all bleaching chemicals (Smith and Block, 1982).

V. **Mercerising**

Mercerisation is the treatment given to the yarn or fabric to impart properties like lustre and increase in strength of the fabric and as well as maximum uptake of dye. It is carried out with 15‒30% sodium hydroxide. The period of treatment is dependent on the particular desired properties and also on the type of fibre used, which can either be yarn or fabric. Cotton undergoes a longitudinal shrinkage and swells laterally when saturated with the solution. When the fabric have been mercerised, the excess NaOH can be gotten rid of by a number of washes under tension, while the reminder of the alkali maybe neutralised with a cold acid, then more rinsing (Babu *et al.*, 2007).

VI. **Wet processing**

The wet processes consume a lot of water and the resulting wastewater is usually accompanied with residual of the dyes. The process entails dyeing, printing and washing.

The art of imparting colours on the treated fabric is termed dyeing. There are basically three methods of dyeing:

I. Mass dyeing: this is the dyeing of a synthetic polymer before the formation of the fibre.

II. Pigment dyeing: is the process of fixing a colorant that is insoluble on the surface of the fibre using a binder.

III. Exhaustion dyeing: The fibres here have great affinity for the dyes; they are dyed from the aqueous baths.

The exhaustion method of dyeing involves the transporting of the dye which is not completely soluble in the dye-bath to the fibre surface by the movement of the dye liquor or fabric; the dye is then adsorbed onto the fibre surface and hence diffuses into the fibre. The dye could be fixed physically or chemically, this depends on the interaction between the fibre and the dye. The diluted solution of the dye can be applied to the fibre discontinuously this is exhaustion dyeing from long liquor, or continuously by immersion of the fibre in the concentrated dye solution and then the excess liquor squeezed-off (Hunger, 2003).

2.3.6 **Dyes used in the manufacturing process**

Many types of dyes are used for the dyeing of fibres and are mostly grouped based on their chemical structures and method of application (Kurbus, Slokar and Marechal, 2002). Dyes are aromatic organic compounds, and are based on the structure of benzene, toluene or naphthalene as they originate from coal tar and petroleum-based substances. They are used for the dyeing of natural and synthetic fibres. There are two key components that can be found in the dye molecule; chromophore which is accountable for its colour and the functional group which binds the dye to the fibre.

Table 2-3 Types of fibre and the common dyes used for dyeing (Wang *et al.*, 2011)

Fibre type	**Dyes used on fibre**
Cellulose	Direct dyes, Reactive dyes, Vat dyes, sulphide dyes, Azo dyes
Wool	Acid dyes
Silk	Direct dyes, Acid dyes
Polyester	Azo dyes, Disperse dyes
Polyester-cotton	Disperse/Vat dyes, Disperse/Insoluble dyes
Polyacrylonitrile	Cationic dyes, Disperse dyes
Polyacrylonitrile-wool	Cationic dyes, Acid dyes
Vinylon	Direct dyes, Vat dyes, Sulphur dyes, Acid dyes

The exact amount of dye produced has not been fully documented, but it is approximated that over 10 000 tons are produced each year (Forgacs, Cserhati and Oros, 2004). Each dye class is suitable to a specific type of fibre; therefore the fixation rate of each class is different. Disperse dyes have a higher percentage of fixation to the fibre compared to acid and reactive dyes. Most of the fibres dyed in the textile industries are cotton with about 50% of these dyed using reactive dyes. Table 2-3 shows the different fibres and the common dyes that are used for dyeing each type of fibre.

2.3.7 Classification of dyes

Dyes are grouped based on their chemical composition or the methods of application onto the fibre (dyeing properties). The classification of dyes in textile based mostly on their methods of application which include: basic, acid, direct, disperse, reactive, sulphur and vat dyes. Usage of these dyes differs from industry to industry, based on the type of fibre that is manufactured.

I. Basic dyes

Basic dyes are also referred to as cationic dyes because the dye molecule is positively charged. They are applied to synthetic fibres such as acrylics, and may also be used on modified nylons and polyesters. They have excellent colour fastness and give bright colours. Because of the poor light and wash fastness, they are not used on natural fibres (Trotman, 1975; Smith and Block, 1982).

II. Acid Dyes

These dyes are modified from the basic dyes, the molecules are negatively charged. They are applied mostly to protein and polyamide fibres, but not on any cellulosic and other fibres that are sensitive to acid solutions. They have poor colour fastness (Trotman, 1975; Smith and Block, 1982).

III. Direct dyes

Direct dyes are defined as anionic dyes and are used mostly to dye cellulosic fibres. They are often referred to as substantive dyes. What makes these dyes attractive for dyeing cellulosic fibre is the simplicity of the dyeing process; they can be applied directly to cellulosic fibres to give bright and deep colours. The dyestuff is soluble and is adsorbed onto the fibre. Their solubility reduces their wet fastness, and may therefore bleed, hence the need for an after treatment. (Trotman, 1975; Smith and Block, 1982).

IV. **Disperse dyes**

Disperse dyes are not soluble in water, they are mostly in suspensions of finely divided organic compounds with slight aqueous solubility (Trotman, 1975). They are adsorbed onto the fibre at the point at which they touch and are not sensitive to fibre chemistry; they are only slightly affected by surface chemistry. They were originally developed to dye acetate, but can now be used for all fibre types (Smith and Block, 1982).

V. **Sulphur dyes**

These dyes contain sulphur or its compounds in an alkali soluble form. They are used to dye only dark shades of cellulosic fibres; this is because the colour lacks brightness, and also lighter colours exhibit poor resistance to light and laundry.

VI. **Vat dyes**

Vat dyes are insoluble in water but are with good solubility in alkaline solutions. Vat dyes are derived from indigo or anthraquinone. Most of those derived from indigo contain highly condensed aromatic systems and are mostly used for dyeing cellulosic fibres.

2.3.8 **Reactive dyes**

Considerable research has been carried out on how to increase the wet fastness on cellulosic dyeing, without converting the soluble dye to an insoluble compound in the fibre. However, this is usually accompanied by a measure of difficulty in application. By the end of the 19th century, methods of joining the dye molecule to the cellulose with a covalent bond had become feasible.

Reactive dyes are different from other dyes because of their ability to form covalent bonds with the fibre during the process of application. The dye molecule are made up of some functional groups that undergoes addition or substitution reactions with the OH and NH_2 groups present in the fibres (Hunger, 2003).

Reactive dyes are soluble in water and they are attached to the fibre covalently. They react with the OH group in the water molecule thereby resulting in hydrolysis of the dye. When this happens, the dye can no longer bond to the fibre, and are therefore washed off as the excess dye (Kurbus, Slokar and Marechal, 2002).

2.3.9 **Dyeing chemistry**

The dye is dissolved in the application medium, which is usually water, at some point during colouration. There are four types of forces that are involved during dyeing and the dyeing of the fibre can involve one or more of these forces.

a. Ionic bonding: this is due to the opposite ionic charges on the fibre and the dye molecule (Smith, 2009).

b. Hydrogen bonding: the interactions here are weak and usually formed by the sharing of a lone pair of electrons on nitrogen, oxygen or fluorine in a molecule with the covalently bonded hydrogen atom. Wool, silk and some synthetic fibres are involved with hydrogen bonding. Dyeing of cellulose cannot be explained through this type of bond because water has more affinity for cellulose than dye molecules (Smith, 2009).

c. Van der Waals interaction: weak interactions occur here, and are mainly due to molecules being close to one another. During dyeing, the orbital of the dye and the fibre molecule orientate in a linear fashion and these forces become stronger between similar groups, e.g. in arylin polyester dyes (Smith, 2009).

d. Covalent bonds: these bonds are formed between the dye and the fibre molecule as a result of the reaction between the reactive dye and the OH group in the fibre. When a reactive dye having a dichloroazine reactive system undergoes a reaction with the cellulose structure having an alcoholic hydroxyl, one of the chlorine atoms undergoes a reaction with the hydroxyl group of the fibre yielding a dye-fibre attachment. Therefore, one chlorine atom gets replaced by the oxygen of the hydroxyl groups originally present in the cellulose while the other chlorine atom gets replaced by hydroxyl group by the reaction with water.

2.3.10 Challenges of treating of textile reactive dye effluent

Even though reactive dyes are preferred for dyeing cotton, they are rated as one of the least environmentally friendly dyes, because they have low fixation rates and huge amounts of salts are needed to fix the dyes to the fibres (Hessel *et al.*, 2007).

The treatment of reactive dye effluent is therefore difficult due to the following:

I. Reactive dyes represent about 20-30% of the market for dyes as a whole, and are used to dye cotton which accounts for a large quantity of the world's fibre production.

II. Large fraction of the dyes is wasted during dyeing, about 30% of it remains unfixed on the fibre and are washed off into water bodies which accounts for the high colours in the textile effluents.

III. Most of the dyes are not biodegradable, therefore they resist degradation by conventional methods of treatment and other processes such as oxidation is always too expensive (Hessel *et al.*, 2007).

IV. Dyeing using reactive dyes requires the usage of huge amounts of salts for the dye fixation; as a result, the effluent is usually associated with high salinity. Salts are not easily separated by standard wastewater treatment processes which mean that they are released in the final effluent (Allègre *et al.*, 2006; Hessel *et al.*, 2007).

2.3.11 Typical treatment of textile effluent

Choosing a particular treatment method is guided by the expected quality of reclaimed water. The effluents can be treated for the purpose of meeting the strict environmental regulations set and then discharged off into the receiving bodies, or are treated for the purpose of reuse. There are basically four steps in treating these effluents: primary, secondary, tertiary and quaternary treatments. Each treatment level is aimed at removing a more specific class of contaminants (Naim and Abd, 2002).

The removal of suspended solids and oils from the waste stream is best handled by the primary treatment methods, while soluble materials such as dissolved solids can be removed by the secondary methods. Tertiary and quaternary treatments are used to polish the effluent to remove specific contaminants that are not removed in the first and second treatment steps (Naim and Abd, 2002).

In addition to the levels of treating the effluents, treatment methods are classed into four: physical, chemical biological and thermal. These processes can be used singularly or combined with other methods to remove contaminants from the wastewater (Naim and Abd, 2002).

2.3.12 **Physical treatment**

The main purpose of physical treatment is to eliminate those chemicals that did not dissolve and particulate matter present in wastewater. Though these processes are not dye-specific, they are used to treat textile effluents to some extent. Some of the physical methods include: adsorption, coagulation and flocculation, irradiation, membrane technology and ion exchange.

I. Adsorption

Adsorption as a method of treating textile effluent has been used over the years and has gained acceptability in most treatment plants; this is due to its efficiency in the removal of contaminants that are not easily treated by other treatment methods (Robinson *et al.*, 2001). A lot of work has been done on the adsorption characteristics and their capability to remove dyes. The adsorbents used can be organic or inorganic. Inorganic provides good mechanical and chemical stability, high specific area, and resistance to microbial degradation. The organic has its benefits due to the fact that that it can be renewed (Singh and Arora, 2011).

Activated charcoal is an adsorbent and is most commonly used for the treatment of textile effluents due to its effectiveness in the adsorption of dyes. The ability of activated carbon to decolourise completely textile waste water is affected by the molecular size and the solubility of the dyes, for water-soluble hydrophilic dyes, the polar nature of the dyes verses the non-polar nature of carbon can also be a factor (Singh and Arora, 2011). The lowest adsorption is achieved with acid and reactive dyes, this is due to their small molecular masses, while medium to high adsorption is achieved using disperse dyes which are hydrophobic in character. High adsorption can also occur with basic and direct dyes that has higher relative molecular mass (Singh and Arora, 2011).

The removal rate can be enhanced by using huge doses of the adsorbent thereby regenerating the used ones for reuse, but there is usually a huge reduction in its performance such that the effectiveness of the dye removal becomes uneven and a high reliance on the doses of carbon.

This adsorbent can therefore be suitable for some dye and not suitable for others. It is a costly process, the carbon has to be regenerated which usually results in a 10-15% loss in the adsorbent or otherwise its disposal is considered (Robinson *et al.*, 2001).

II. Ion-exchange

Ion-exchange is not a common method for the treatment of textile effluents due to the inability of the ion-exchangers to put up with a wide range of dyes. Anionic (e.g., acid, mordant, reactive, direct, metal complexes) as well as cationic (basic) dyes, if treated with ion-exchange resins, will form complexes in the form of large flocs, capable of separation by filtration. The waste water is passed through the ion exchange resin until the resins become saturated, by so doing both the cationic and ionic dyes in the effluent can be removed from the effluent (Singh and Arora, 2011).

The successful elimination of the dye depends on dye type and number of interactions. Ion-exchange is not an appropriate method for the treatment of disperse dyes, this is due to their hydrophobic nature (Anjaneyulu, Sreedhara and Samuel, 2005). The ion-exchange method is limited by its poor hydrodynamic properties which make it difficult to withstand the high pressures necessary to make huge volumes of effluent go through the bed of the resin thereby sustaining high flow rate. Other drawbacks are its high cost of recharging the resins and the production of huge volumes of sludge (Robinson *et al.*, 2001; Singh and Arora, 2011).

2.3.13 **Chemical treatment**

Chemical methods of treatment involve chemical reactions due to the use of oxidizing agents such as ozone and hydrogen peroxide. The efficiency of these methods relies on the interaction between the contaminants that are found in the wastewater which are to be removed and the type of chemical used. These chemicals can either aid in the separation, or assists to ruin and neutralise some of the harmful effects associated with the contaminants (Robinson *et al.*, 2001).

I. **Oxidation**

For dyes that are resistant to biodegradation, the oxidation methods are usually applied. The main oxidizing agent used is hydrogen peroxide. The agent used is usually activated in most cases by ultra violet light. The manner in which the dye is removed from the coloured effluent is by the oxidation process which results in the formation of an aromatic ring cleavage of the dye molecule (Robinson *et al.*, 2001).

II. **Ozonation**

This an effective method used for decolourising textile dyes, it is carried out by the breaking of the double bond in the dye. It can slow down or eliminate the foaming properties of the left over surfactants and it can oxidize a great portion of COD. Most of the fibre dyed in the textile industry is carried out mainly by dyes that resist degradation like the reactive dyes. This method can be used to increase the biodegradability of the effluents that are made up of dyes having high portions of non-biodegradables and poisonous components that are difficult pollutants into more easily biodegradable intermediates (Wang *et al.*, 2011).

The dosage applied depends on the colour of the effluent and the residual COD to be removed. One benefit of ozonation is that it can be applied in its gaseous state and as a result does not add to the volume of the wastewater or that of the sludge. Its limitation is that it has a short life, which is just about 20 minutes (Robinson *et al.*, 2001).

III. Coagulation and flocculation

Coagulation has been used for many years for the treatment of dye waste waters. The coagulants used are alum, ferric sulphate, ferric chloride and polyelectrolyte. Its efficiency is determined by the quantity of coagulant dosed and usually varies with the quality of wastewater to be treated; the more contaminated the wastewater, the higher the required quantity of coagulants to be used. The disadvantage of this method is the use of large quantities of chemicals which leads to increased sludge production, and mostly the dye removal is very poor (Rajkumar and Kim, 2006; Zahrim, Tizaoui and Hilal, 2011).

2.3.14 Biological treatment

The use of microorganisms for the biodegradation of coloured effluents such as textile dyes is a satisfactory and easy method by operation. However, the biological mechanisms can be difficult. Most of the dyes used during dyeing are not biodegradable and therefore resist degradation, due to the fact that the microorganisms do not consume the colour components as their food source (Anjaneyulu, Sreedhara and Samuel, 2005).

The biological methods of treatment include: the removal of colour by white rot fungi which is also degradation; use of other microbial cultures, pseudomonas strains, Sphingomonas under aerobic, anaerobic, or mixed conditions; and adsorption by living or dead microbial biomass (Slokar and Marechal, 1998; Mukesh and Anil, 2005).

Because the azo dyes resist degradation to a large extent, they are not easily metabolised at aerobic conditions, while with anaerobic states the electrophilic bonds in them are reduced by bacteria into colourless amines. The produced amines resist additional anaerobic breakdown. They are however good substances for aerobic degradation (Mukesh and Anil, 2005).

Decolourisation of the textile effluent by the aerobic bacteria is as a result of adsorption onto the cell surface as opposed to biodegradation, which results in low colour removal efficiencies. With respect to COD and TOC it is more enhanced by the aerobic bacteria as to compare to anaerobic bacteria. Hence a combination of anaerobic and aerobic methods of treatment is effective (Mukesh and Anil, 2005).

Table 2-4 Advantages and disadvantages of current textile effluent treatment methods (Robinson *et al.*, 2001)

Processes	**Advantages**	**Disadvantages**
Biodegradation	Rates of elimination by oxidizable substances is about 90%	Low biodegradability of dyes
Coagulation – flocculation	Elimination of insoluble dyes and economically feasible	High sludge production
Activated carbon	Fine removal of variety of dyes	Very expensive
Ozonation	Applied in gaseous sate: no alteration of volume	Short half-life (20 mins)
Electrochemical processes	Breakdown compounds and are non-hazardous	High cost of electricity
Photochemical	No sludge production	Formation of by-products
Ion-exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Membrane treatment	Reuse of water salts and heat	Handling and disposal of concentrate stream, flux decline

2.4 Use of membrane technology

2.4.1 **Overview of membrane filtration**

A membrane is defined as a barrier that allows some substances to pass through it (permeate) while hindering others (retentate), in a specific manner (Strathmann, 1990). Membranes became feasible means of treating water back in the 1960. The use of membranes for water treatment has since then improved, by using highly developed membranes made from new materials and are engaged in various configurations (Pellingro and Sikdar, 2004).

Membranes are widely used in various industries for separation processes due to their ability to control the substances that passes through the membrane, hence a high degree of separation is always achieved, which then makes these processes widely acceptable (Baker, 2004).

Membrane processes can be integrated into the dyeing processes of a textile industry such that the most polluted streams are treated at the point of collection using the appropriate membrane process. The advantage of this process is the recovery of the salts and the water for reuse in the dye baths. Also, treating of the most polluted stream separately can minimise the size of the treatment plant because the less polluted streams such as rinsing can be handled by biological processes alone (Erswell, Brouckaert and Buckley, 1988; Wenzel *et al.*, 1996). A variety of membrane treatment process trains can be implemented for the treatment of textile effluent. In this study UF was used as a pre-treatment to NF, hence permeate from UF was further filtered using NF.

There are four types of pressure membrane processes: microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF). The difference between these processes is related to the membrane pore sizes Figure 2-2. For instance, MF membranes have the largest pore size and usually reject large particles and a range of microorganisms. UF membranes have pores which are less than MF membranes and, therefore, with addition to what MF can reject, the UF rejects bacteria and soluble macromolecules such as proteins. RO membranes are non-porous, they reject particles and as well many low molar mass substances such as salt ions, organics, etc. (Baker, 2004; Pellingro and Sikdar, 2004). NF membranes are fairly new and are referred to as "loose" RO membranes (Ong, Lau and Ismail, 2012). These membranes are porous. They have pore sizes in the order of ten angstroms or less, and demonstrate its performance between that of RO and UF membranes (Baker, 2004; Pellingro and Sikdar, 2004).

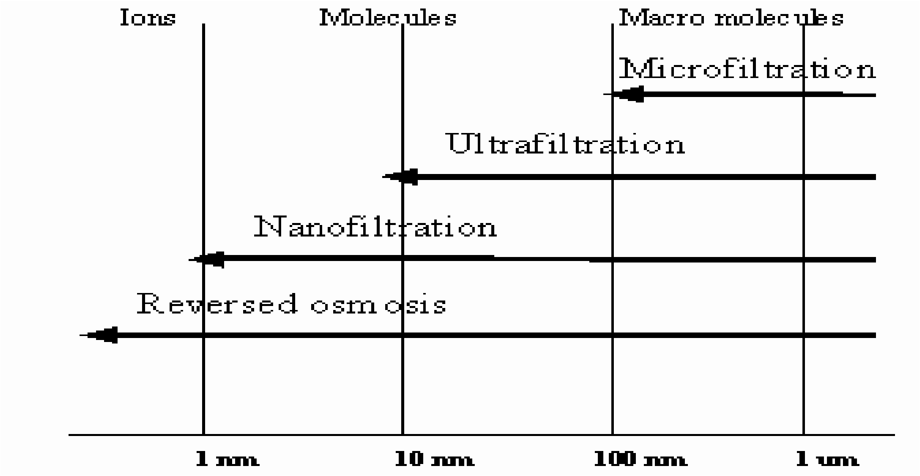

Figure 2-2 Range of nominal membrane pore sizes (Baker, 2004).

2.4.2 **Microfiltration**

Microfiltration (MF) is used for the treatment of liquid such that the particles that have more than 0.1 µm are retained. As the sizes of the particles retained by MF are greater than the sizes of solutes retained by UF, NF and RO, the osmotic pressure for the MF process is negligible, and the required transmembrane pressure (TMP) is relatively small, generally less than 2 bar. The permeate flux is typically greater in MF than other membrane processes because of the large pore sizes.

MF is usually applied in the processes such as separation of oil-water emulsions, dehydration of lattices, clarification (beverages), and sterilisation in the pharmaceutical and food industries. The separation principle for MF is based on the sieving mechanism and a very low driving force is used usually below 2 bars (Mulder, 1996).

2.4.3 **Ultrafiltration**

Ultrafiltration (UF) is used for retention of macromolecules and colloids from solution and the pore sizes ranges between 0.005 µm to 1 nm (Mulder, 1996). UF membranes have the ability to retain larger organic macromolecules and are characterized by some manufacturers by the use of molecular weight cut-off (MWCO) rather than by a particular pore size. Cut-off is defined as that molecular weight which is 90% rejected by the membrane (Mulder, 1996; Pellingro and Sikdar, 2004).

Therefore UF membranes with definite MWCO are supposed to act as a barrier to compounds or molecules with a molecular weight exceeding the MWCO. UF can be used for a variety of applications especially where high molecular substances have to be separated from low molecular ones. In the food and dairy industries it is used for the concentration of milk and cheese making and clarification of juices and alcohols. In the chemical processing industries such as textile it is used for the treatment of some of the waste streams, especially the sizing wastewater and also for the treatment of indigo dyes. UF membranes can also be used to pre-treat the feed for nanofiltration and reverse osmosis (Cheryan, 1986; Mulder, 1996).

2.4.4 **Nanofiltration**

NF is sometimes referred to as “loose” RO due to their more open network structure. The separation capability of NF is between that of UF and RO. The typical pore size of NF membranes is 0.5-5 nm, and the applied pressures are typically 5-20 bars, which are lower than those for RO process, but yield higher fluxes (Mulder, 1996). NF membranes retain low molecular weight solutes which include inorganic salts small organic molecules such as glucose and contaminants such as pesticides and dyes. It has low salt retention, and can only reject molecules which are 200 Da to a few thousand Da. NF processes retains higher percentage of divalent ions such as ($Ca^{2+,}$ Mg^{2+}) and less of monovalent ions (Na^+, K^+, Cl^-) (Aouni *et al.*, 2009). The rejection of

NaCl by NF is 60%, 80% for calcium bicarbonate and 98% for magnesium sulphate, glucose and sucrose (Scott, 1995). This is due to the fact that NF polymers have charges which are ordered, and can therefore retain higher valence ions more than monovalent (Bowen, Mohammad and Hilal, 1997; Aouni *et al.*, 2009).

The application of NF and RO is almost similar, but the difference is the network structure. NF is the preferred process when a high retention is not required for NaCl (Mulder, 1996). NF is widely applied for water softening, removal of trihalomethanes and natural organic matter (NOM), for the retention of dyes and metals, and wastewater treatment and recovery. Lately it is used as a feasible alternative to the conventional treatment methods in the environmental engineering field due to its outstanding separation ability with the possibility of recovery valuable material (He *et al.*, 2010).

2.4.5 **Reverse osmosis**

Reverse osmosis (RO) is a means of separating dissolved solids from water molecules in aqueous solutions, this is due to the fact that the membranes are made up of special polymers which allow water molecules to pass through while retaining other types of molecules (Cheremisinoff, 2002). RO membranes are referred to as tight membranes, they are asymmetric with homogeneous skin and microporous support, the molecular weight is around 100 Da, less than 2 nm. RO has the ability to retain more than 90% ionic compounds, mineral salts, hydrolysed reactive dyes and the auxiliaries used in the textile industry in a single step, thereby allowing a clear permeate through the membrane for reuse. The separation in most RO systems is achieved by the solution diffusion mechanism and is energy intensive, the operating pressure for most RO systems is 20-40 bars, hence the reason for high energy requirement (Cheryan, 1986; Cheremisinoff, 2002). Table 2-5 give a summary of the membrane mechanisms.

Table 2-5 Summary of membrane processes showing their mechanism of operations (Mulder, 1996)

	MF	**UF**	**NF**	**RO**
Membrane type	Symmetric microporous	Asymmetric microporous	Composite	Asymmetric or composite
Pore size	0.05-10 (μm)	1-10 nm	<2 nm (200-250 Da)	< 2 nm (100 Da)
Driving force (bar)	< 2	1-10	10-25	10-70
Separation principle	Sieving mechanism	Sieving mechanism	Solution-diffusion	Solution diffusion
Membrane material	Polymeric, ceramic	Polymer (polysulfone, polyacrylonitrile)	Polyamide (interfacial polymerisation)	Cellulose triacetate, aromatic polyamide, interfacial polymerisation

2.4.6 Use of UF and NF in textile effluent treatment and the benefits

For textile water reuse, membrane processes can either be integrated in the process or used as an end-of-pipe treatment method. Integrated solutions seem most advantageous with respect to the potential economic gain by recycling recovered chemicals and water. Although membrane technology requires an initial high setup cost, it is outweighed by the significant cost savings achieved through the reuse of chemicals, dyes and water (Mo *et al.*, 2007). The costs can be reduced by the implementation of pre-treatment processes and regular cleaning to eliminate fouling problems and by choosing the most appropriate membrane system.

UF and NF processes have been applied for the treatment of textile waste water because of the advantages it offers over other membrane processes. Due to the ability of UF membranes to retain large molecular substances as stated earlier, it is usually used as a pre-treatment for the feed to NF in most applications especially textile waste water. Few factors are considered for the use of UF as a pre-treatment method, a few were considered for this study including low energy requirement due to low operating pressure, high permeate flux production, its retention ability of colloidal and other substances.

NF is employed for the treatment of textile effluent due to some of the factors that were considered for this study. Nanofiltration retains organic compounds of relative low molecular weight, divalent ions or large molecular ions such as hydrolysed reactive dyes of 700–1000 molecular weight, as well as dyeing auxiliaries. It has the advantage of recovering valuable materials and it is to be preferred to reverse osmosis which has higher maintenance and operational costs. The reasons for choosing NF instead of RO include:

(i) NF membranes require low pressure for operation and can simultaneously produce high fluxes, resulting in low energy consumption, hence an increase in water recovery.

(ii) Its permeability to monovalent ions such as NaCl is high, which makes the recovery of salt possible for reuse.

(iii) The removal of dyes and COD is high, so that the quality of permeate produced can be reused (Kurt *et al.*, 2012).

2.4.7 **Mechanism of separation (transport)**

The mechanism of separation in UF and NF will be discussed for the purpose of this work. Literature on separation using MF and RO can be found elsewhere (Mulder, 1996; Baker, 2004).

I. **Separation mechanism**

Separation in NF is largely due to the sieving (steric hindrance) effect and the Donnan (electrostatic) exclusion (Schaep *et al.*, 1998; Teixeira, Rosa and Nystrom, 2005). Separation mechanism in NF can be understood in terms of charge and/or size effects. The transport of uncharged solutes takes place by convection due to a pressure difference and by diffusion due to a concentration gradient across the membrane. For the retention of uncharged solutes, sieving mechanism is responsible for it, while for charged components an electrostatic interaction takes place between the component and the membrane since most NF membranes are charged negatively (Schaep *et al.*, 1998).

II. Transport in UF and NF

The transport of the solute through UF and NF membranes can be demonstrated using different approaches and this is dependent on the membrane type (Hilal *et al.*, 2005c). The first instance, regards the membrane as a dense layer, transport is based on the solution-diffusion model. The second approach regards the membrane as a porous medium, based on the extended Nernst-Planck equation (Wang *et al.*, 1997; Szymczyk and Fievet, 2005; Cuhorka and Mikulášek, 2010). The approach assumes that the flux of every ion passing through the membrane is caused by pressure, concentration and electrical potentials. These models describe the transport of ions in terms of an effective pore radius, effective membrane thickness/porosity ratio and effective membrane charge density (Cuhorka and Mikulášek, 2010).

The final approach is based on irreversible thermodynamics. In this model, the membrane is assumed to be a black box, and is applied for the prediction of transport mechanism through NF membranes for binary systems (Wang *et al.*, 1997).

This is seen in the equation of Kedem and Katchalsky (1963) were they introduced the relation of the volumetric flux (Jv, m s^{-1}) and the solute flux (Js, mol m^{-2} s^{-1}) through a membrane

$$Jv = Lp(\Delta P - \sigma \Delta \pi) \qquad \text{Equation 2-1}$$

$$Js = Ps\Delta C + (1 - \sigma)CJv \qquad \text{Equation 2-2}$$

Where,

σ, reflection coefficient (−)

P_s, solute permeability (mol N^{-1} s^{-1})

L_p, Hydraulic coefficient ($m^3N^{-1}s^{-1}$)

$\Delta\pi$, change in osmotic pressure (Pa)

ΔC, concentration difference between permeate and retentate (mol m^{-3})

ΔP, applied transmembrane pressure (Pa)

The solute flux is shown by the sum of the diffusive and convective. The transport through the membrane is possible because of the applied pressure gradient across the membrane, while the diffusive transport is as a result of concentration difference on both sides of the membrane (Hilal *et al.*, 2005a; Hilal *et al.*, 2005b).

Selectivity and flux are two factors that define how the membrane performs (Mulder, 1996). Flux describes the amount of fluid passing through the membrane, which is the volumetric flowrate of permeate and this defines the productivity of the membrane. It is determined by the rate at which solutes or the particles are transported towards the membrane, this is measured in terms of its flux. The permeate flow through the membranes is described by Darcy's law, whereby the flux (J) through the membrane is directly proportional to the applied pressure (Mulder, 1996).

$$J = \frac{V}{A}.t \qquad \text{Equation 2-3}$$

Where,

J: flux (LMH)

t: The period over which permeate is collected (h)

A: effective membrane area (m^2)

V: Volume (m^3)

Selectivity of the membrane defines whether it will be useful or not as it is an indication of how pure the product stream is and how much of it is recovered at the desired purity. Selectivity can be expressed by one of the two parameters: retention or rejection (Mulder, 1996). The solute is partially retained while the solvent (water) molecules pass liberally through the membrane. The retention is given by:

$$R(\%) = 100 * (1 - \frac{Cp}{Cf}) \qquad \text{Equation 2-4}$$

Where,

R: is the retention

C_p: solute concentration in permeate (mg^{-1})

C_f: Solute concentration in feed (mg^{-1})

The value of R is between 1 when there is total retention of the solute and it is 0 when both the solute and the solvent pass through the membrane.

2.4.8 **Membrane module configurations**

There are four major classes of modules: plate-and-frame, tubular, spiral wound, and hollow fibre (Pellingro and Sikdar, 2004). Figure 2-3 to Figure 2-6 shows the types of membrane modules that are commonly used. The simplest module is the plate-and-frame, it consists of two end pates, the flat sheet membranes and spacers, while the tubular module is often on the inside of a tube, and the feed solution is pumped through the tube. The spiral wound module is generally used in the industry for nanofiltration and reverse osmosis processes. It consist of a flat sheet membrane which is wrapped round the perforated permeate collection tube. The flow of the feed is one side of the membrane, while permeate is collected on the other side of the membrane and then spirals in towards the centre of the collection tube (Baker, 2004; Pellingro and Sikdar, 2004).

Their main benefit is that they are easily packed into modules, hence providing a higher surface area. The disadvantage with these membranes is that they have low fluxes as compared to the flat-sheet membranes which are prepared from the same material. The fibres are packed into bundles and potted into tubes to form a membrane module (Baker, 2004). To maintain high fibre production and reproducibility, the process of producing this membrane bundle must be carried with care such that there are no broken or defective fibres.

If the diameter of fibre is 50-200 um, then the feed fluid can be applied to the outside of the fibres and the permeate collected down the fibre bore otherwise the feed fluid should be applied to the inside bore of the fibre and the permeate removed from the outer shell with fibre diameter greater than 200-500 (Baker, 2004).

The hollow fibre modules that are used for seawater desalination are made up of bundles of hollow fibres in a pressure vessel. They consist of a shell-side feed form where the feed passes along the outside of the fibres and exits on the other end. Hollow fibres employed for waste water treatment and in membrane bioreactors are not always used in pressure vessels. Bundles of fibres can be suspended in the feed solution, and permeate is collected from one end of the fibres (Baker, 2004; Pellingro and Sikdar, 2004).

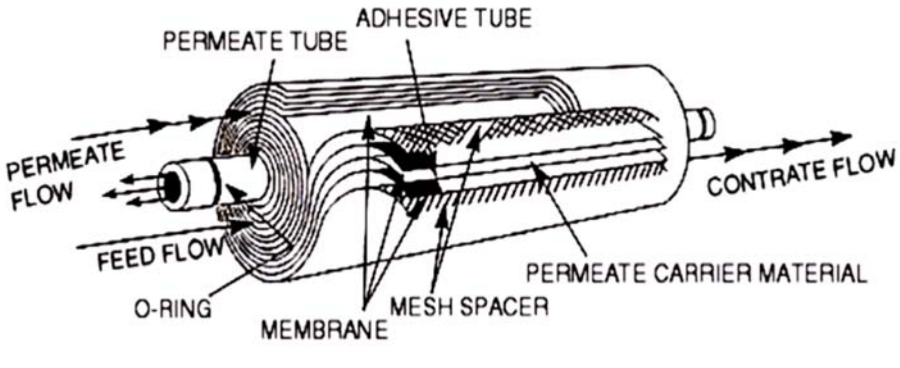

Figure 2-3 Spiral wound membrane module showing the filtration operation (Baker, 2004)

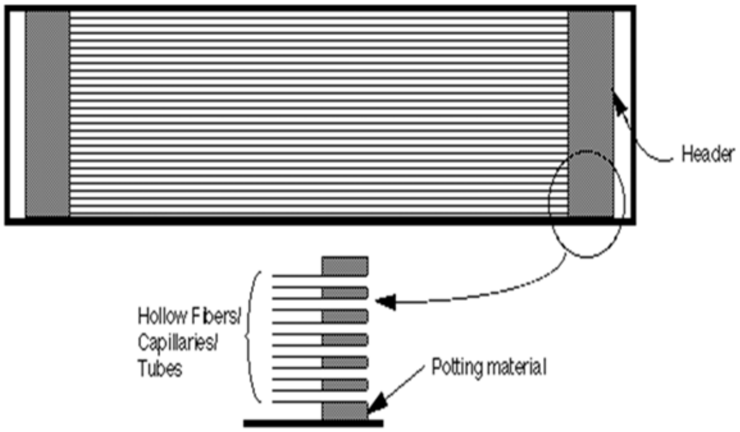

Figure 2-4 Schematic representation of a hollow fibre membrane module (Baker, 2004)

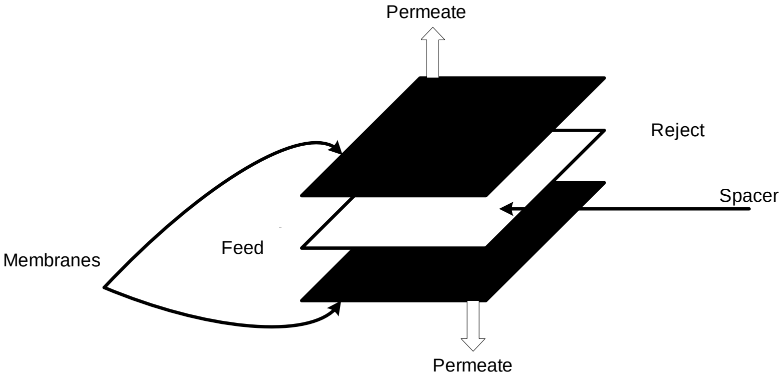

Figure 2-5 Plate-and-frame membrane showing its operation (Baker, 2004)

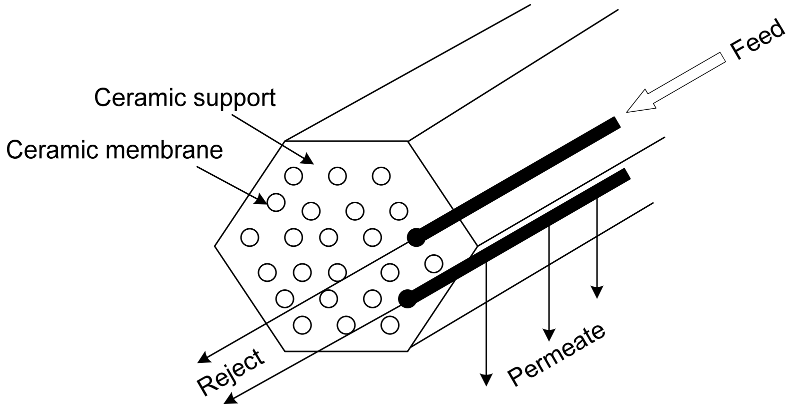

Figure 2-6 Tubular membrane showing its operation (Pellingro and Sikdar, 2004)

2.4.9 **Membrane filtration modes**

There are two modes used for most membrane processes: dead-end and cross-flow. In dead end filtration mode the particles are simply collected on a filter media under an applied pressure, and the liquid flows perpendicular to the filter media and causes the accumulation of the retained particles, leading to the formation of a cake layer at the surface (Baker, 2004). The thickness of the cake increases with filtration time and causes an increase in the pressure drop or a decrease in the filtration rate. When the pressure drop becomes too high, or the filtration rate becomes too low, the cake is removed and the filter media is cleaned. However, in most practical cases, the filter media is simply replaced. This concept is still used for MF (Murkes and Carlsson, 1988; Mulder, 1996).

Most industrial applications are carried out using the cross flow mode of operation. In cross-flow filtration the feed water is recycled under an applied pressure, and the feed flow is parallel to the filter media Figure 2-7 (b). The reason for the flow is to manage the thickness of the cake, such that the suspended solids are transported away, thereby reducing the rate at which the particles are retained on the membrane, improving the life span and providing longer service for the filter media before cleaning or replacing.

Cross-flow filtration and membrane filtration has become synonymous, although they are not, in principle, as the term "membrane filtration" implies nothing about the flow pattern and the term "cross-flow" does not mean anything for the filter media. However, in practice, cross-flow filtration overlaps membrane filtration almost completely. In other words, membrane filtration is almost always carried out by cross-flow, as dead-end filtration through a membrane would end very rapidly due to total clogging (Murkes and Carlsson, 1988; Mulder, 1996).

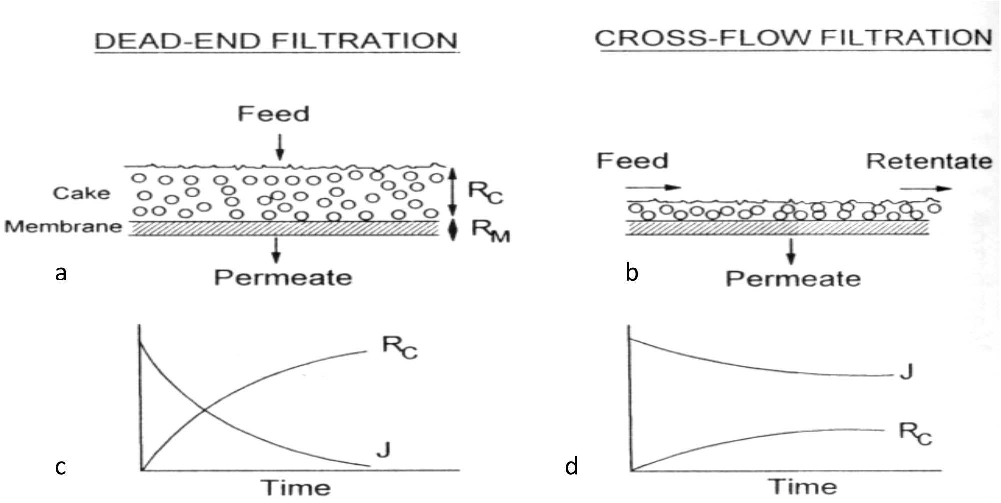

Figure 2-7 (a-d) Membrane filtration modes; dead end (a and c), cross flow (b and d) (Cheryan, 1986).

Figure 2-7 (c) and Figure 2-7 (d) shows the rate of deposition of substances on the membrane at different modes of filtration. In dead end filtration, there is a constant build-up of particles on the surface of the membrane thereby leading to a cake layer formation. This usually results into a resistance to filtration and hence a decrease in membrane fluxes. During cross flow filtration, the cake layer is not built indefinitely, but rather, due to the high force applied on the feed flowing tangentially to the membrane surface, the particles which are deposited on the membrane are swept off towards the exit of filter and results into making the cake layer remaining thin. This makes it possible for high fluxes to be maintained over prolonged periods of time as shown in Figure 2-7 (d) a steady state flux is achieved once the cake layer has attained its steady state.

2.5 Membrane fouling

Fouling is defined as the reduction in flux with time of a membrane below the pure water flux (Cheryan, 1986). This is a limitation to all pressure driven membranes, especially with MF and UF, where the flux decline is very severe because of their porosity which makes them susceptible to fouling (Mulder, 1996). For NF and RO which are tighter forms of membranes, the fouling is limited (Schäfer *et al.*, 2004).

Figure 2-8 illustrates the fouling mechanism mostly in UF. The extent of fouling in membranes depends on the type of separation and the type of membrane used to carry out the separation. It affects the performance of membranes by a gradual decrease in flux, increase in transmembrane pressure (TMP) and a decrease in rejection. This leads to deterioration in the membrane properties and results in high costs of operation and cleaning of the membranes to restore its initial flux.

The pressure–flux behaviour observed for pressure driven membranes processes can be expressed using the following equation (Mulder, 1996)

$$J = (\Delta P - \Delta\pi) / \mu(Rm + Rf) \qquad \text{Equation 2-5}$$

Where,

J is the flux (l m^{-2} h)

ΔP is the applied pressure (Pa)

$\Delta\pi$ is the osmotic pressure (Pa)

μ is the feed viscosity (Pa.s)

R_m is the intrinsic membrane resistance determined using pure water as feed (m^{-1})

R_f is the fouling layer resistance due to pore clogging, gel layer, and adsorption (m^{-1})

The term $\Delta\pi$ is negligible because the osmotic pressure of the molecules is negligible compared to the applied pressure.

The factors that affect membrane fouling can be classified into three categories: membrane properties, operating parameters and the nature of the waste water to be treated (Aouni *et al.*, 2009; Zahrim, Tizaoui and Hilal, 2011). Foulants are colloidal materials with different properties which interact with the membrane thereby causing fouling. They are grouped into four: organic precipitates, inorganic precipitates, biological and particulates (Cheryan, 1986; Schäfer *et al.*, 2004; Al-Amoudi and Lovitt, 2007; Field, 2010).

Figure 2-8 illustrates the forms of fouling commonly found in porous membranes.

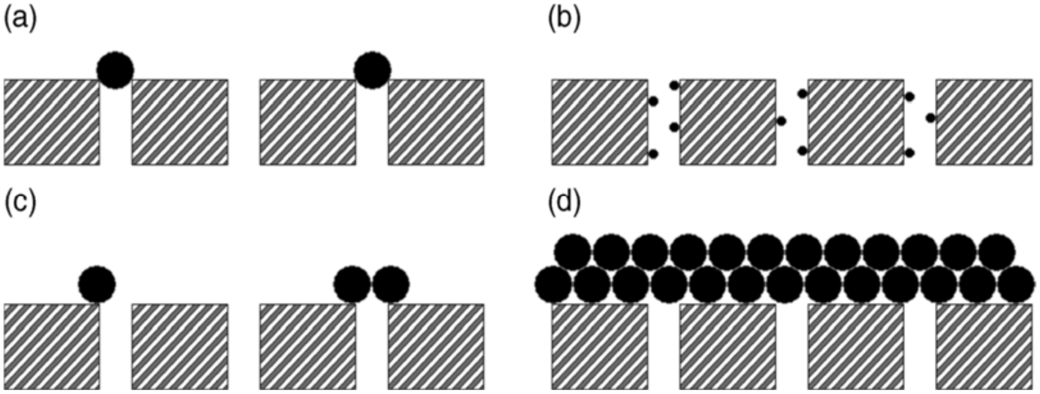

Figure 2-8 Fouling mechanisms of porous membranes (a) Complete pore blocking (b) Internal pore blocking (c) Partial pore blocking (d) Cake filtration (Field, 2010)

I. **Adsorption**: It occurs when there is a relationship between the membrane and the solute. In the absent of permeate flux, a layer of particle and solutes can be formed which can lead to supplemental hydraulic resistance. However concentration polarization can be worsened by the amount of adsorption, if the degree of adsorption is concentration-dependent (Field, 2010).

II. **Pore blockage**: During filtration, the blocking of the pores of the membrane can occur, which can lead to a decline. This can occur as partial or full blockage.

III. **Deposition:** This is the deposition of particle with time as the filtration proceeds, the deposition can grow in on the membrane surface, thereby leading to a crucial hydraulic resistance by the membrane. This is often referred to as a cake resistance (Field, 2010)

IV. **Gel formation**: During the filtration of certain macromolecules, the level of concentration polarization may lead to gel formation in the immediate vicinity of the membrane surface, for example, a solution of concentrated proteins (Cheryan, 1986; Field, 2010).

Fouling in NF membranes depends mostly on the type of membrane and its characteristics. The retention of ionic species results in a concentrated layer of ions at the membrane surface (known as salt concentration polarisation), which creates an osmotic pressure drop across the membrane. It can occur due to the interaction of sub-micrometer colloids; these colloids are highly Brownian and are influenced by diffusive and convective transport mechanisms, and also by deposition and aggregation due to colloidal forces (Schäfer *et al.*, 2004).

Colloidal fouling in NF is worsened by the polarised layer of rejected ionic solutes by greatly reducing electrostatic interactions, also the dissolved (organic, inorganic or biological) and colloidal matter aggregates at the membrane surface thereby presenting an opportunity for additional fouling mechanism. These mechanisms arise from the interactions between rejected ions and colloids passing through the concentration polarisation layer and at the membrane surface. Fouling in NF membranes can be due to external surface fouling (build-up of a cake/gel-like layer on the upstream face of a membrane) and pore blocking fouling (Schäfer *et al.*, 2004; Al-Amoudi and Lovitt, 2007).

Minimisation of membrane fouling depends on the nature of the fouling process. The following techniques are used:

- Pre-treatment of feed to reduce the amount of particles reaching the membranes thereby reduce fouling. It is one of the most effective methods to use.

- By adjusting the operating conditions, e.g. pressure, cross flow and backwashing velocities.

- Membrane regeneration by cleaning the membrane with or without using chemicals can also reduce fouling.

2.5.1 **Membrane cleaning**

Fouling in membranes can be reduced by pre-treating the feed and optimising the operating conditions. This will greatly assist in the performance of the membrane filtration; however, cleaning methods are always applied. The frequency in which a membrane can be cleaned depends on the operating conditions of the process. Cleaning methods can be divided into three categories: hydraulic cleaning, mechanical cleaning and chemical cleaning (Cheryan, 1986; Mulder, 1996; Sohrabi *et al.*, 2011; Shi *et al.*, 2014).

The choice of cleaning method will depend on the module configuration, its resistance to the cleaning chemicals, the type of membrane and also the type of foulants (Sohrabi *et al.*, 2011).

I. **Hydraulic cleaning**

Hydraulic cleaning includes back flushing, by varying pressure or depressurising and changing the flow direction at a given frequency. This is carried out so that the particles are loosen and are dislodged from the membrane. This can be done by back flushing as shown in Figure 2-9. This method of cleaning is applicable to MF and UF. The limitations however is reduction in the overall operation time and the loss of permeate. Also only particles that are partially attached on the surface of the membranes can be flushed out (Mulder, 1996).

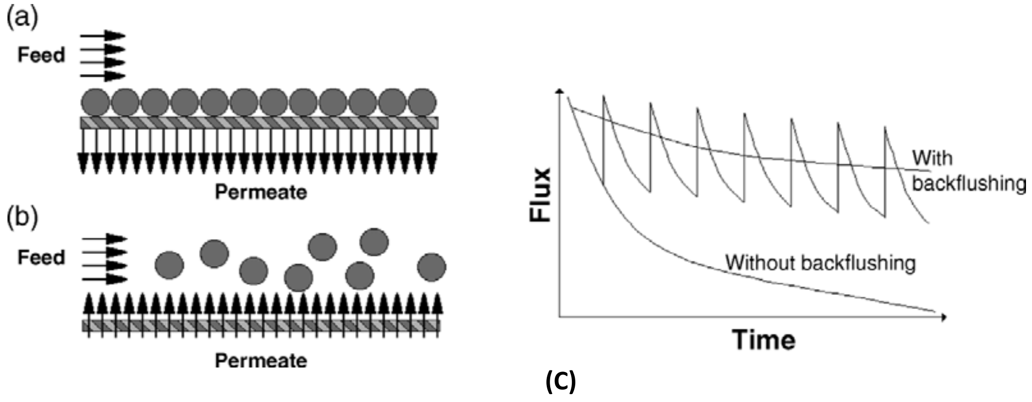

Figure 2-9 Back flushing (a) Standard operational mode (b) Back flushing concept and anticipated outcome (c) Flux-time on a regenerated membrane (Mulder, 1996; Field, 2010)

II. **Mechanical cleaning**

Mechanical cleaning involves the physical removal of the fouling matter. It can be done using oversized sponge balls, ultrasonic waves and air scouring. This is applied in tubular systems.

III. **Chemical cleaning**

Chemical cleaning is the most frequently used method. It is usually applied when hydraulic cleaning has not been achieved (irreversible fouling). Chemical cleaning depends on chemical reactions to break bonds that have been formed, and also the cohesion forces between membranes and foulants (Schäfer *et al.*, 2004; Shi *et al.*, 2014). The cleaning chemical to be used should be efficient against several foulants. It should be mild to the membranes so that its characteristics are not distorted but rather preserved. The choice of the cleaning chemical is a function of the membrane characteristics and the foulants, even though, the cleaning procedures and cleaning products are usually specified by membrane manufacturers (Al-Amoudi and Lovitt, 2007).

2.5.2 **Cleaning chemicals**

There are different types of chemical cleaning agents which are available. They are categorised into six: alkalis, acids, metal chelating agents, surfactants, oxidising agents and enzymes (Al-Amoudi and Lovitt, 2007; Shi *et al.*, 2014). Selection of the cleaning product and procedure is made based on the feed characteristics. The cleaning products available commercially are in most cases mixtures of these chemicals. However, their real composition will not be discussed in this work. The reason being is that two cleaning chemical were recommended by the manufacturers of membranes used in this study. More details on other chemical cleaning methods are found in (Schäfer *et al.*, 2004; Al-Amoudi and Lovitt, 2007; Shi *et al.*, 2014).

I. **Alkaline**

This is at times the most important because several foulants from the natural and wastewaters are of organic origin, or the inorganic colloids maybe coated by organics. The purpose of alkaline cleaning is to eliminate organic foulants from the surface and pores of the membrane. Sodium hydroxide and sodium carbonate are usually used which is the reason for the high pH. Anionic and non-ionic surfactants are added sometimes alongside alkaline agents, this is carried out so that the particles containing fats are emulsified to prevent the foulants from sticking firmly on the surface of the membrane. Ethylene diamine tetra acetic acid (EDTA) which is a sequestering agent is added to remove multivalent ions like calcium and magnesium (Schäfer *et al.*, 2004).

II. **Acids**

Acid cleaning is mainly used to eliminate precipitated salts from the surface and pores of the membrane. Nitric acid is often used due to its mild oxidising ability, alongside other acids and cleaning formulations. The latter includes detergents, cationic or non-ionic, as well as some sequestering agents can be present. The recommended pH for the cleaning solution should be between 1 and 2.

2.5.3 **Efficiency of cleaning methods**

Various methods are used to determine how efficient and successful a cleaning method is. These include: water productivity and membrane resistance; foulant content of cleaning solution; membrane surface investigation; and membrane retention. The most common method is the water productivity (flux measurement) (Schäfer *et al.*, 2004; Al-Amoudi and Lovitt, 2007)

Flux measurement is a direct measurement of fouling and the cleaning process. Pure water flux (PWF) of the membrane is carried out on the virgin membrane with deionised water by varying the pressure and measuring the flux, after which a plot of flux against pressure is done. PWF can be measured on the virgin membrane and compared to the PWF obtained immediately after filtration with effluent to determine if flux was recovered due to cleaning. The water flux recovery (WFR) can be calculated as: (Schäfer *et al.*, 2004; Al-Amoudi and Lovitt, 2007)

$$WFR = Jc/Jo$$ Equation 2-6

Where,

J_c is the flux after cleaning and (LMH)

J_0 is the flux of the virgin membrane (LMH)

2.6 Summary

Water is becoming a scare resource due to industrial activities, increased human population, and strict government rules and so on, therefore the need to treat effluent to meet the standards for reuse. Furthermore large volumes of water and chemicals are consumed by different processes for the conversion of fibres into fabric resulting into the production of effluents which are characterised by high amounts of suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour. Cotton is one of the fibres that enjoys the greatest usage by the textile industries and is dyed with reactive dyes.

Reactive dyes are commonly used in textile because of their bright, wide range of colours, ease of application and their high wet fastness on these fibres. However, their disadvantages include: low fixation rate (20-30%), require high salts of NaCl and Na_2SO_4 before dyeing, therefore high salinity in effluent and finally they resist biodegration.

Conventional methods of treating effluents favour the end-of-line pipe treatment. This is the point at which waste stream from different processes are collected and treated collectively, which then means that the properties of the effluent is a representation of an overall average of the different effluent streams.

A more realistic option of treating dye effluent is by integrating treatment options in the dyeing process such that the most polluted streams can be treated at the point of collection. The advantage of this is the recovery of the salts and the water for reuse in the dye baths.

The implementation of pre-treatment processes is of the most important criteria for implementing membrane technology. In this study, UF membranes were evaluated as a pre-treatment step to NF membranes.

In this study, NF membranes were integrated into reactive dye baths of a textile industry for its effluent treatment to enhance its reusability. Previous studies of this kind focused on the use of diluted streams or by making synthetic feed simulating dye bath effluent (Aouni *et al.*, 2012). Others have used effluents obtained from biological processes or other conventional methods and this served as feed to NF (Van der Bruggen *et al.*, 2005; Irena *et al.*, 2007). In some instances, the effluents from the dye bath were diluted to meet NF requirements (Chakraborty *et al.*, 2003; Fersi, Gzara and Dhahbi, 2005). The required reuse criteria were met, however, the dilution or making of synthetic feed do not give a true representation of the effluent from the dye bath and the effects it has on the membrane performance in terms of permeate quality and recovery of chemicals for reuse.

This study will carry out a feasibility study by integrating NF processes for the treatment of three different reactive dyebath effluents from the textile industry (without dilution). The feed samples will be collected from the dye bath. In contrast to laboratory-made feeds, the feed samples used in this study include the dyes and other processing chemicals from the fibre processing steps. The performances of the membranes in terms of permeate quality and fluxes will be evaluated. The aim therefore will be to recover the water and chemicals (salts) for reuse purposes. The dye bath effluents were classified as: light shade, medium shade and dark shade.

Chapter 3 - Methodology

3.1 Introduction

The dyes from a local textile industry were collected and then treated using two-stage membrane system. In the first stage, UF was used as a pre-treatment step. In the second stage, the permeate from UF step was used as the feed solution for the NF membranes. Standard methods of analysing the parameters for water reuse were used. Both UF and NF membrane rigs were operated in the cross flow mode under constant pressure. Both membranes were cleaned by physical and chemical methods to recover the flux.

3.2 Materials and analytical equipment

3.2.1 Samples

Effluent samples were obtained from Mediterranean Textile Industry in KwaZulu-Natal, South Africa. The company carries out about 80% dyeing on cotton and 20% on polyester. Most of the dyes used are reactive dyes, while the salts are sodium chloride. However, rarely sodium sulphate (which is for dye fixation) and sodium carbonate salts are used to raise the dye liquor pH. The quantity of salts used for dyeing is dependent on the shade of colour required; for light shades, 10 g/ℓ of NaCl is required, medium shades require 40 g/ℓ, while darker shades require 80 g/ℓ. Dye recipe typically range from 0-5% of the fibre mass, or sometimes it can be more than this depending on the colour shade that is required (Erswell, Brouckaert and Buckley, 1988). The fixation rate is between 70-80%. The dye bath effluents therefore consist of 20-30% hydrolysed dyes, salts and other additives that are used in the manufacturing process. The wide variability of the physico-chemical composition of the effluent makes it a challenge to treat and dispose safely.

The characteristics of the effluent depended on the dye process being carried out at the time of collection. Three different dye shades were evaluated in this study. Light shade (**LS**), medium shade (**MS**) and Dark shade (**DS**) as described in Table 3-1.

Table 3-1 Sample composition based on the dye type and salt concentration as provided by the Mediterranean Textile Industry

Sample	Abbrv. for samples	Dye type	Salt concentration
Light shade 1 (Green)	LS 1	Reactive green,	10 g/ℓ NaCl, 5 g/ℓ Na_2CO_3
Light shade 2 (Grey)	LS2	Semi fixed yellow 3RS, semi fixed red 4BNS,	20 g/ℓ NaCl, 8 g/ℓ Na_2CO_3
Medium shade (cobalt blue)	MS	Remazol brilliant yellow, Remazol red 3RSA 150 %, Synozol blue.	50 g/ℓ NaCl, 20 g/ℓ Na_2CO_3
Dark shade	DS	Remazol black, Remazol BTE Red 3BS	80 g/ℓ NaCl, 20 g/ℓ Na_2CO_3

3.2.2 **Chemicals**

The chemicals that were used for cleaning of the membranes were selected according to the manufacturers' guides as shown in Table 3-2.

Table 3-2 List of chemicals used for membrane cleaning and their concentrations

Nature	Caustic	Acid	Chelating agent	Surfactant
Chemical	NaOH	HCl	EDTA	Sodium lauryl sulphate
Concentration (wt. %)	0.1	0.2	1	0.025
pH	12	2	12	12

3.2.3 Analytical Equipment

The most important parameters that determine the reuse of water in a textile industry include chemical oxygen demand (COD), total organic carbon (TOC), turbidity, conductivity and colour. These parameters were analysed using the equipment listed in Table 3-3. The Spectrophotometer was used for COD, TOC and colour at the following ranges respectively (435 nm, 425 nm and 465 nm). The step by step description of each procedure is shown in Appendix I.

Table 3-3 Equipment and methods used for analysis

Parameter	**Instrument used**	**Method**
Conductivity	HACH conductivity meter	Standard method
Turbidity	HACH turbidity meter	Standard method
Colour	HACH DR 3900 Spectrophotometer	Platinum- cobalt standard. Method 8025
pH	HACH pH meter	Standard method
TOC	HACH DR 3900 spectrophotometer	Direct method. Method 10128
COD	HACH DR 3900 spectrophotometer	USEPA reactor digestion. Method 8000
TDS	HACH conductivity meter	Standard method
TSS	HACH DR 3900 spectrophotometer	Photometric method

Table 3-4 Characteristics of UF and NF membranes used in this study

Membrane	**UF**	**SR 90**	**NF 90**
Supplier	Inge GmbH	Dow film tech	Dow film tech
Membrane type	Polyethersulphone	Polyamide	Polyamide
MWCO	0.02µm (Pore size)	200-300 Da	150-200 Da
Contact angle	-	54°	27°
Effective filtration area	0.0397 m^2	0.003 m^2	0.003m^2
Hydrophilicity	Hydrophilic	Hydrophilic	Hydrophilic
pH range	1-13	1-13	1-13

3.2.4 **Membranes**

UF and NF rigs were used for the experiments. Characteristics of the membranes used are shown in Table 3-4

3.3 Experimental Apparatus

3.3.1 **NF rig Components**

a. **Feed tank**

The dimensions of the feed tank were 80 mm in diameter and 600 mm in height. The capacity was 20L. Cooling coils were immersed into it. A mercury thermometer was fitted into the feed tank to measure the temperature of the feed water.

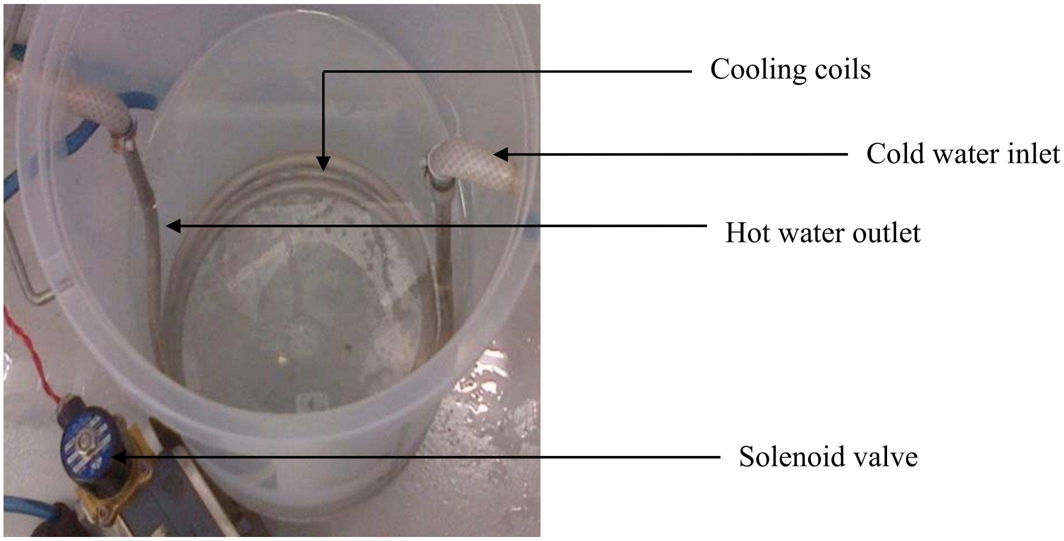

Figure 3-1 NF feed tank fitted with cooling coils

b. Membrane cell

The cross flow cell was rectangular and was made of two stainless steel plates which were similar, one was porous and the other was non-porous. A piece of membrane was cut to size and fitted on the porous stainless steel. The neoprene rubber gaskets were placed over the membrane, while the non-porous cell was then placed above the porous plate so as to provide mechanical support to the membrane. The cells were then tightened by nuts and bolts.

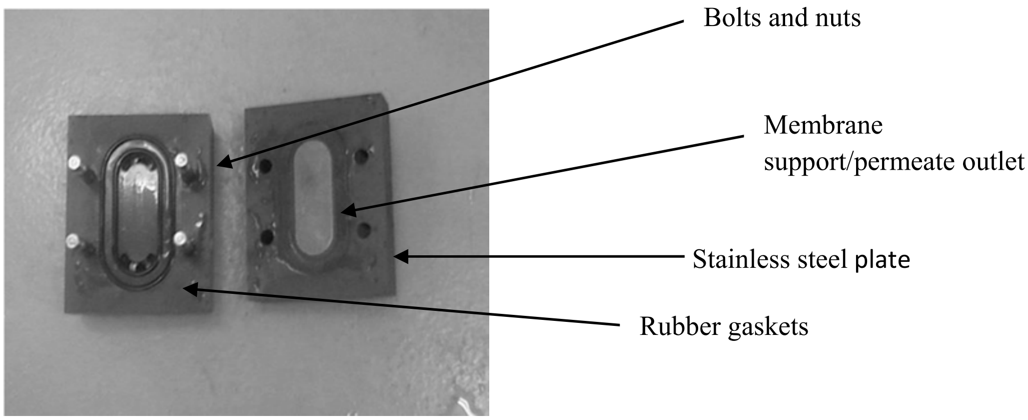

Figure 3-2 Parts of the NF membrane cell

c. **High pressure pump**

A high pressure pump was used on the NF test rig. It was a stainless steel Fluid-o-Tech magnet drive rotary vane pumps TH series. The highest output pressure of the pump was 15 bars, and the temperature was between 20–70°C, its maximum speed was 1725 rpm.

3.3.2 **Cooling system for NF**

Water was pumped through the inlet of the immersed coil and was re-directed back to the feed tank. The process diagram is shown in Figure 3-3 Process flow of the cooling water to each NF rig. A chiller unit, water tank and a circulation pump (centrifugal) were used to circulate water from the feed tank to the cooling coils of each test rig. Water was chilled to 20^{o}C. The temperature was kept constant because of the effect it has on flux, it is reported that every rise in 1 ˚C in temperature affects the flux of the membrane. Flux is inversely proportional to the viscosity of the permeate passing through the membrane pore.

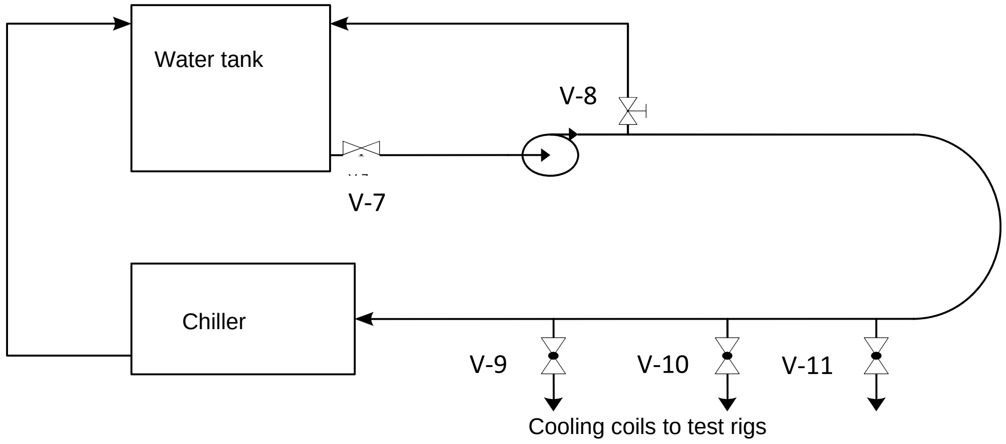

Figure 3-3 Process flow of the cooling water to each NF rig

V$_9$-V-$_{11}$ are ball valves controlling cooling water inlet. V-$_7$ is ball valve controlling feed flow into the pump; V-$_8$ is a ball valve on the bye-pass line for flow control.

A cooling coil was immersed in the feed tank. Fresh tap water was used to cool the feed tank contents.

Figure 3-4 Chiller for supplying cooling water

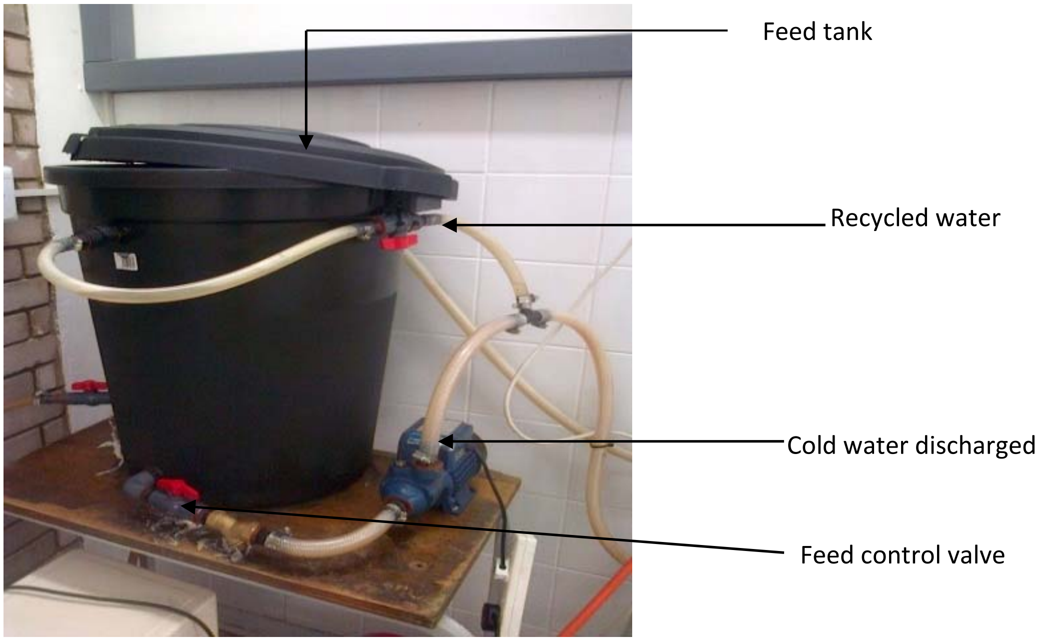

Figure 3-5 50 ℓ cooling water tank

The chiller was a 2900W Puron carrier NANOCHIL. The water tank Figure 3-5 had a capacity of 50L; attached to it was an HPE60 Centrifugal pump with maximum capacity of 35L/min and rotational speed of 2850 rpm which was used to pump cooling water attached to each feed tank of NF rigs.

3.3.3 **Components of the UF test rig**

a. **Feed tank**

The feed tank was a 10 ℓ container connected to the peristaltic pump.

UF membranes

Figure 3-6 Loose UF capillaries membrane

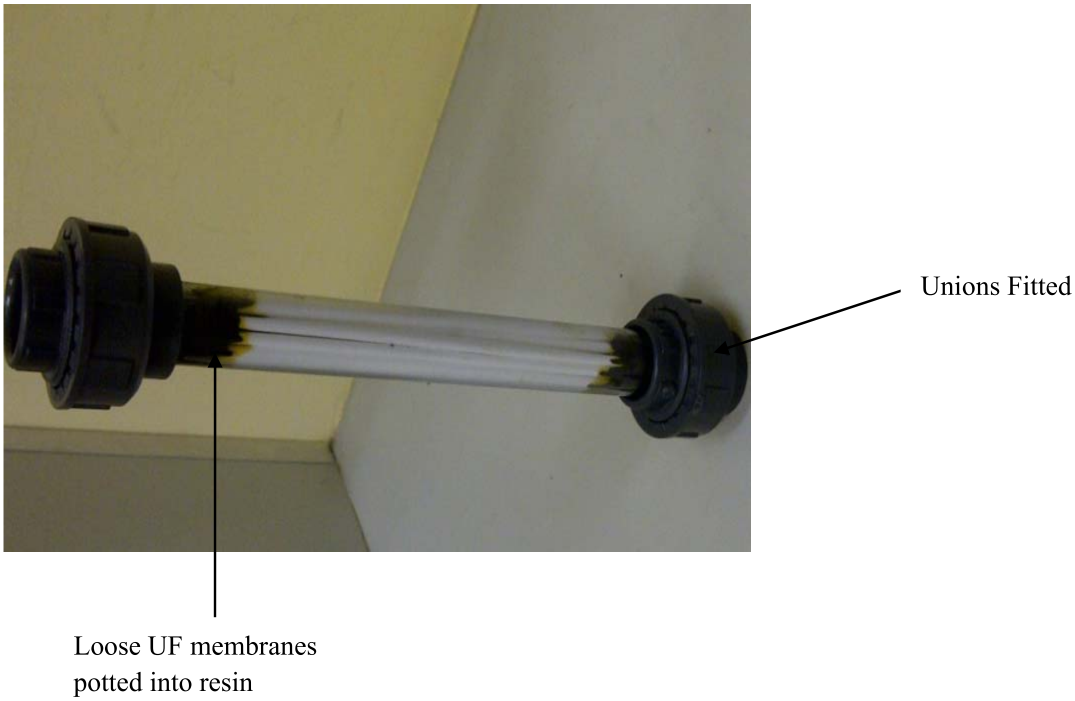

Figure 3-7 UF capillary membranes potted into resin

The loose capillary tube membranes were supplied by Inge GmbH chemical company.

The modules consisted of 8 loose hollow fibre membranes, fitted into a 25 mm clear PVC pipe. Two 25 mm unions were attached to the module as shown in the Figure 3-9.

b. **Pump**

The pump that was used in the UF test rig was a Watson Marlow 313S peristaltic pump.

3.4 Equipment and Experimental procedures

3.4.1 Procedures for module preparation

The procedures for UF and NF membrane operations are described below.

3.4.2 **Construction of UF module**

The following steps were used in the construction of the UF module.

- A hole which was 5 mm in diameter is drilled on 25 mm clear PVC pipe for permeate outlet; the PVC used is shown in Figure 3-9.
- Both ends of the loosed membranes were blocked with clear silicone gel; this was to prevent permanent damage of the pores during the potting.
- The loosed membranes from step two were then bundled into the 25 mm clear polyvinyl (PVC) pipe.
- Two parts (A and B) of the Membralock were mixed in a ratio of 1:1 and then poured into the moulds to more than half way of the moulds.
- They membranes were then potted into the resin on both ends to keep them together.
- A small part of both ends were cut off in order to allow flow since they were blocked by the resin.
- 25 mm union was then attached to both ends of the modules.

3.4.3 **Procedure for UF Wetting**

UF membrane modules were wetted using 80% ethanol solution so as to open up the pores of the membranes. The rig was then operated in a cross flow mode and the pressure was set at 0.2 bars for thirty minutes in order to open the membrane pores. The membrane module was rinsed properly with deionised water to remove the alcohol before operation. The membranes were kept wet in deionised water to prevent them from getting dry. This was carried out on all the UF modules used throughout the experiment.

3.4.4 **NF membranes preservation**

The membranes were cut into the sizes that would fit properly into the membrane cell and were soaked in deionised water until the time it is required for use. The soaking of the membranes was to prevent them from drying so that the structure is not deformed.

3.4.5 **Filtration rig and assembly**

The filtration rigs for UF and NF were operated in cross flow modes of filtration, the retentate stream was recycled to the feed tank, while permeates were collected in a beaker and analysed. The operating parameters were: cross flow velocity, pressure, temperature and concentration of the feed as shown in Table 3-5 and 3-6.

Table 3-5 Operating parameters for membrane rigs

Operating parameters	**UF**	**NF**
Pressure (bar)	1	10-15
Crossflow velocity (m/s)	1	0.0003
Temperature (˚C)	20	20
Velocity (m/s)	1	0.3
Area of membrane (m^2)	0.040	0.003
pH	10-12	10-12
Feed concentration (g/l)	Varies	Varies

Table 3-6 Analysis of feed samples without any form of pre-treatment

Parameter	**LS 1**	**LS 2**	**MS**	**DS**
Colour (pt-co)	711	1068	1141	23115
COD (mg/l)	208	449	1353	6454
TOC (mg/l)	127	143	143	1984
TSS (mg/l)	93	172	193	209
pH	10	10	11	11
Turbidity (NTU)	22	28	89	98
Conductivity (mS/cm)	10	21	32	123

3.4.6 **Operating conditions**

The operating conditions for the membranes are shown in Table 3-5. Because of the effects temperature has on permeate flux, it was kept constant by the use of a chiller unit which was connected to the membrane rigs. The pressure and crossflow velocity were chosen to give reasonable fluxes and permeate quality. A constant pressure mode of operation was used and filtration time was kept constant (He *et al.*, 2008). The membranes used were positive pressure driven membranes and not vacuum driven. Positive pressure driven membranes run at constant pressure mode, where flux (or permeate flow rate) is monitored to track membrane fouling status. This mode of operation therefore ascertained that the performance of each membrane with respect to flux and the fouling rate was monitored.

Flux which is one of the important parameter during this study was calculated using equation 2-3

$$J = \frac{V}{A}.t$$ Equation 3-1

3.4.7 **Operation of membrane rigs**

The procedures described below were used for obtaining pure water of the membrane and also the fluxes when the effluent samples were treated.

3.4.8 **Pure water flux**

Before a membrane was used to filter an effluent sample, clean water flux was determined. The reason for this was to evaluate permeate flux decline during effluent filtration and compare it to clean water flux of the virgin membrane in order to determine the effect of fouling and cleaning.

3.4.9 **Procedures for UF**

Figure 3-8 shows the schematic diagram of the UF rig

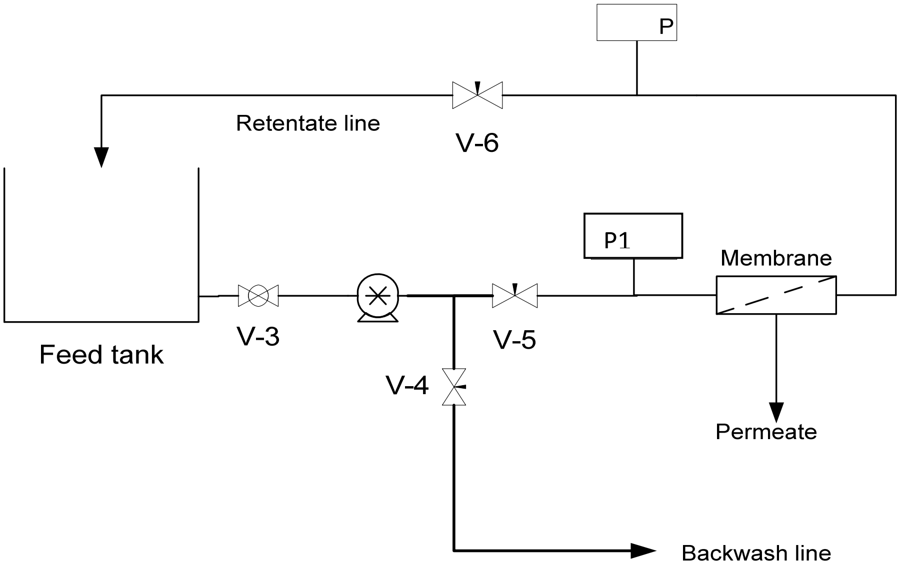

Figure 3-8 Schematic representation of UF rig

V-$_3$ is a ball valve attached to the feed tank, V-$_4$ is ball valve controlling flow during backwash, V-$_5$ controls feed flow into the membrane as well as the crossflow velocity; V-$_6$ is a needle valve for pressure control. P1 and P2 are gauges indicating the pressure difference of the membrane module.

The preliminary start-up of the rig was carried out to make sure that everything was alright. This was done by opening the appropriate valves as described in the procedures below.

The pure water flux was determined in two modes; constant pressure and varying pressure. The membrane module shown in Figure 3-9 was fitted into the UF rig.

- Needle valves V-$_4$ (Backwash line) was closed
- 10L of deionised water was poured into the feed tank
- The feed tank outlet valve V-$_3$ was opened.
- Then the valves V-$_5$ and V-$_6$ which were connected to the membrane to control flow inlet and pressure were opened.
- The pump start-up button was switched on and the valve V-$_6$ was adjusted to the required operating pressure.
- For varying pressure the valve V$_6$ was adjusted to the following pressures; 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 kPa. While for PWF at a constant pressure, the valve was adjusted to set the pressure 100 kPa.
- For each of the varied pressure, permeates were collected in a beaker after every 30 minutes and measured in a volumetric flask.
- Permeates sample were also collected every 30 minutes during the constant pressure experiment for 3 hours

- After the PWF, the deionised water in the feed tank was discarded and filled with the effluent sample to be treated and the same procedures above were followed. The filtration of the effluent samples was carried out at operating conditions shown in Table 3-5. Permeates were analysed using the equipment as mentioned in Table 3-3 and its rejection was calculated using Equation 2-4.

$$R(\%) = 100 * (1 - \frac{Cp}{Cf}) \qquad \text{Equation 3-2}$$

3.4.10 **Procedure for NF membranes**

Preliminary start-up procedures for the rig

Figure 3-9 shows the schematic diagram for the NF rig. It was used for all the NF filtration experiment.

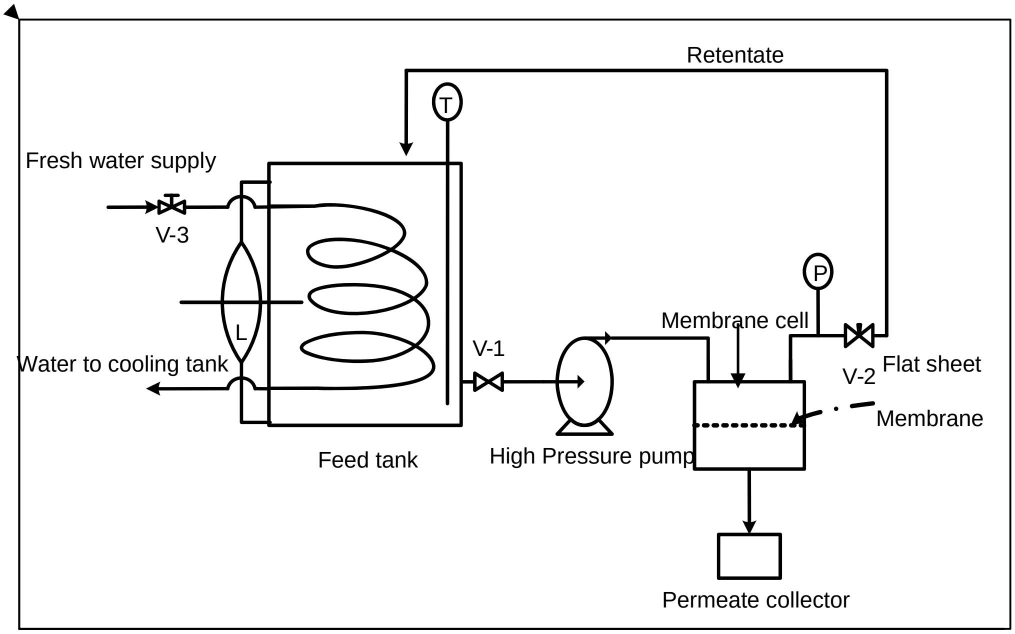

Figure 3-9 Schematic representation of NF rig

V-1 is a solenoid valve controlling feed into the pump, V-2 is a diaphragm valve for pressure control and V-3 is a ball valve to control cooling water.

The preliminary start-up described below was used for both pure water flux (PWF) and effluent samples. The feed tank outlet valve V-1 was opened. The manual needle valve V-8 on the bye pass stream was fully opened. The cooling circulation pump was then started to circulate chilled water into the chiller and the chilled water was allowed to flow into the cooling coils through V-9 to V-11.

- After the start-up procedures, the actual membrane operation was continued. 20 l of deionised water was poured into the feed tank
- The high pressure pump was started by pressing the start-up bottom on the rig and thereafter the pressure control valve V-2 was adjusted so as to set the required operating pressure; the operating pressures were 2.5, 5, 7.5, 10, 12.4 and 14. 5 bars.
- For each of the varied pressures, permeates were collected in a beaker after every 30 minutes and measured in a volumetric flask.
- To carry out filtration on actual feed samples, the deionised water in the feed tank was discarded and refilled with the sample to be treated. Filtration of the feed sample was carried out at a constant pressure of 10 bars. The control valve V-2 was therefore adjusted to 10 bars and filtration was carried out for 3 hours. Permeate samples were collected every 30 minutes. Permeates were analysed using the equipment mentioned in Table 3-3 and its rejection was calculated using Equation 2-4.

$$R(\%) = 100 * (1 - \frac{Cp}{Cf})$$

Equation 3-3

- The flux of the membrane was then calculated and also the rate of fouling of the membrane was monitored from these calculations. This was repeated for all the feed samples.

- The decline in flux was calculated by finding the difference between the initial pure water flux and the studied sample flux divided by the initial pure water

$$Decline\ in\ Flux\ = (PWF - Sample\ flux)/PWF \qquad \text{Equation 3-4}$$

- Cleaning of the membrane was the last thing to be done on the membrane to restore its flux.

3.4.11 **Regeneration of fouled membranes**

Membranes were regenerated by physical and chemical methods for both membranes. Forward flushing for NF and backward flushing for UF was used. Pure water flux was then carried out to determine flux recovery. If low volumes were recorded for the PWF after flushing, a chemical cleaning was carried out following the manufacturer's guidelines. Hence fluxes were determined in two stages:

- Initial pure water flux: this was the first flux determined on the virgin membrane and is same as the membrane permeability.

- Clean water flux after chemical cleaning: this was the flux on the cleaned membrane after a chemical cleaning had been carried out on the fouled membrane. This was compared to the flux of the virgin membrane to determine if the membrane was regenerated. The effectiveness of the cleaning protocol was calculated using the water flux recovery ratio. Equation 2-6 was used to determine the efficiency of cleaning on membrane flux.

$$WFR = Jc/Jo \qquad \text{Equation 3-5}$$

3.4.12 **Regeneration of UF membranes**

During the backwash of the UF membranes, the flow of the feed was changed and was redirected to the permeate side of the membrane module. Chemical cleaning was carried out using the chemicals in Table 3-2.

- The feed tank was filled with the deionised water.
- The feed tank outlet valve V-$_3$ was opened
- The bye pass/backwash valve V-$_4$ was opened and then Valve V-$_5$ was closed. By this, the direction of flow into the membrane was changed to the permeate outlet, but the reject route was still the same.
- The pump start-up button was switched on and the valve V-$_4$ was fully opened so that the flow into the membrane was high to push out the suspended particles on the membranes. The backwash duration was for 45 minutes.
- A pure water flux was then carried out following the procedure described earlier in section 3.4.8
- Each module was backwashed twice and then chemical cleaning was carried out on the membrane in the case when regeneration could not be achieved by physical cleaning.
- The procedures described in section 3.4.8 were used for chemical cleaning; however, the valves V-$_5$ and V-$_6$ were fully opened so that the cross flow velocity was very low to allow more contact time between the solution and the membrane for effective removal of suspended particles. The chemical cleaning was for the duration of 30 minutes, and the rinsing step was 40 minutes.
- Pure water flux was then carried using the procedure described in section 3.4.8 and was then compared to the pure water flux of the virgin membrane.

3.4.13 **NF Chemical Cleaning**

Recovery of the membrane was first carried out by flushing and relaxation at low pressure (2.5 bars) on the fouled membrane with deionised water and the cleaning chemicals. The valves on the cooling units were closed because cooling was not required during cleaning since cleaning was carried out at a low pressure.

- The feed tank outlet valve V-1 was opened.
- The manual needle valve V-2 on the reject stream was fully opened
- 20 ℓ of cleaning solution was poured into the feed tank
- The high pressure pump was started by pressing the start-up bottom on the rig and thereafter the pressure control valve V-2 was adjusted so as to set the required cross flow velocity. Circulation through the membrane was allowed for 1 hour for the physical cleaning which was forward rinsing with deionised water. The pump was stopped and the feed tank emptied and refilled with deionised water.
- Each NF membrane sheet was physically cleaned twice and then chemical cleaning was carried out on the membrane in the case when regeneration could not be achieved by physical cleaning.
- The procedures described in section 3.4.8 were used for chemical cleaning; however, the pressure control valves V-2 was fully opened so that the cross flow velocity was very low to allow more contact time between the solution and the membrane for effective removal of suspended particles. The chemical cleaning was for the duration of 30 minutes, and the rinsing step was 40 minutes.
- Pure water flux was then carried out on the membrane to determine the flux recovered as described in section 3.4.9

3.4.14 **Sample collection and testing**

The samples were collected immediately directly from the dye bath in 25 l containers and were stored at room temperature. Experiments were carried out immediately with the collected samples.

The most important parameters that determine the reuse of water in a textile industry include COD, TOC, turbidity, conductivity and colour. The reagents that were used for measuring TOC, COD and colour were bought from the supplier of the spectrophotometer. These reagents had already been prepared and were therefore ready for use. The COD test used potassium dichromate in a 50% sulphuric acid solution that oxidizes both organic and inorganic substances in a wastewater sample. TOC contains Persulfate pillows which are added to the solutions. The observed rejection for each quality was calculated using equation 2-4. The procedures for the analysing of parameters are discussed in appendix A

Chapter 4 - Results and discussion

4.1 Introduction

This chapter discusses the experimental results obtained from the pre-treatment of the effluent followed by those obtained by the use of NF membranes. The results discussed will include: the effects of pre-treatment of the feed on permeate flux; rate of fouling on the membranes; and the separation efficiency of the membranes regarding the parameters of interest for reuse in the textile industries. Also, membrane cleaning and efficiency of the cleaning methods will be discussed and finally the reusability of permeate for the dyeing of fibres will be presented.

Three types of dye bath effluent were treated, and were denoted by LS, MS and DS. They represent the colour shades that were used for the dyeing of the fibres. LS represent the light shade, MS the medium shade and DS was for the dark shade. What differentiated these effluents were the dye composition and the quantity of salt used. The composition of the feed samples has early been discussed in **section 3.2.1 and 3.4.5**

For NF90, only three of the samples were treated, LS1, LS2 and MS shade. The dark shade had a higher osmotic pressure which was not overcome by the NF90. The NF rig that was used for the experiment had a maximum operating pressure of 15 bars, which was not large enough to overcome the osmotic pressure in the dark shade due to high salt contents.

4.2 Membrane productivity

One of the most important parameters in membranes is the permeate flux; it is routinely used to evaluate the performance of a membrane. In most cases when the retention of solute by the membrane has been met, permeate flux then become important. This can be improved by studying the process conditions, by optimization and carrying out a suitable pre-treatment on the feed.

The membrane area is the major determinant of the capital cost for a membrane system, therefore to minimise capital costs, it is desirable to have a high permeate flux. Due to the small surface area of the membrane used for this study, it was difficult to study the influence of feed water recovery; therefore the membrane productivity in terms of flux production with respect to feed type was evaluated.

4.2.1 **Pure water flux**

The pure water flux for the two NF membranes is shown Figure 4-1.

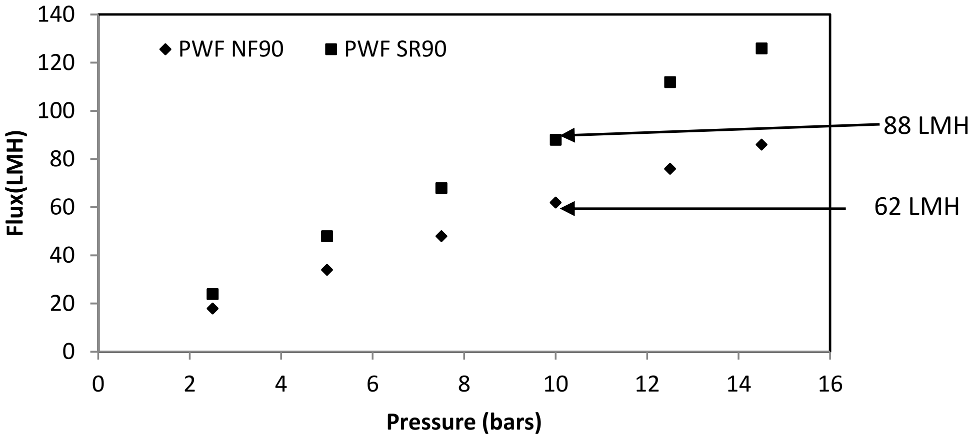

Figure 4-1 Pure water flux on SR90 and NF90 membranes

The filtration experiment was carried out at pressures of 2.5-14.5 bars at a temperature of 20˚C. The permeate flux increased linearly with increase in operating pressure, resulting in higher flux at higher pressure. It was observed that SR90 had higher fluxes due to the larger molecular weight cut-off (MWCO) as given Table 3-4. The higher the MWCO of the membrane, the faster the water molecule is transported through the membrane due to its relatively low transport resistance. The pure water flux at 10 bars, which was the set pressure for all the effluent filtration experiments were 62 LMH for NF90 and 88 LMH for SR90 and NF90 membranes respectively.

4.2.2 Permeate flux as a function of time for UF membranes

To reduce the significance of membrane fouling and the decline in flux of which is caused by the building up of particles, bacteria and other suspended solids on the NF membrane, UF was used as pre-treatment to NF (Nouha *et al.*, 2012). The variation in the permeate flux as a function of time for the feed samples is presented in Figure 4-2.

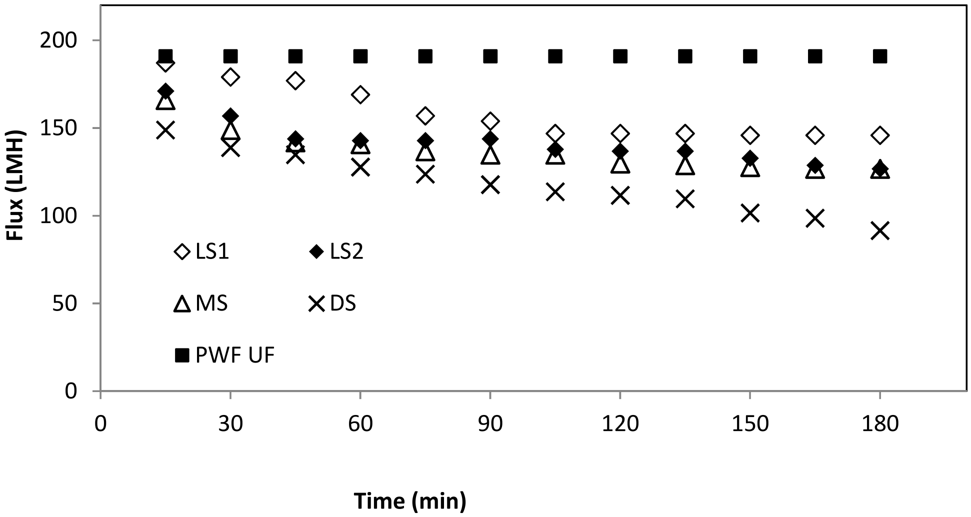

Figure 4-2 Flux as a function of time using UF membranes

The graph is a representation of filtration flux with time using UF as a pre-treatment for all the dye bath samples used. The average flux values for LS1, LS2, MS and DS were 159, 142, 137 and 118 LMH respectively.

A gradual decrease in flux for all the samples was observed. This loss in flux was assumed to be due to the fouling of the membrane as a result of the deposition of substances on the membrane that caused some pore blockage and hence a restriction in the flow of permeate through the membrane.

With respect to individual permeate fluxes for the feed samples; LS1 had the highest flux, with DS having the least flux. The fluxes in LS2 were lower as compared to those obtained from LS1 even though they were both light shades. The low fluxes are an indication of high fouling by this feed sample which was presumed to be as a result of the different feed composition due to the dye mixtures. LS1 represented a single dye consisting of reactive green, while LS2 had a combination of two dyes. The electrolyte concentration and turbidity were higher in LS2 than LS1, Table 3-6 and could have been responsible for lower fluxes recorded in the filtration of this sample.

The volume produced though from the 3 h experiment suggests that the more permeate volume can be achieved using the medium and light shades. The DS is associated with a less volume at the start of experiment indicating a more immediate fouling effect once the system is operational. For the other shades, there is a gradual decline in flux towards a stabilised operation (although this was not achieved due to the experiments being limited to 3 h).

Sample MS and DS had higher flux loss as compared to the light shades. The high loss was also attributed to the different feed compositions as shown in Table 3-6. DS had a high dye concentration of 14,900 mg/l with a higher turbidity of 98 NTU as compared to MS and the LS.

4.2.3 **Permeate flux for SR90**

Figures 4-3 and 4-4 show the flux with time relationship for SR90. Figure 4-3 is the flux–time graphs for all the feed samples on SR90 without pre-treatment while 4-4 is a flux time graph on the feed after pre-treatment.

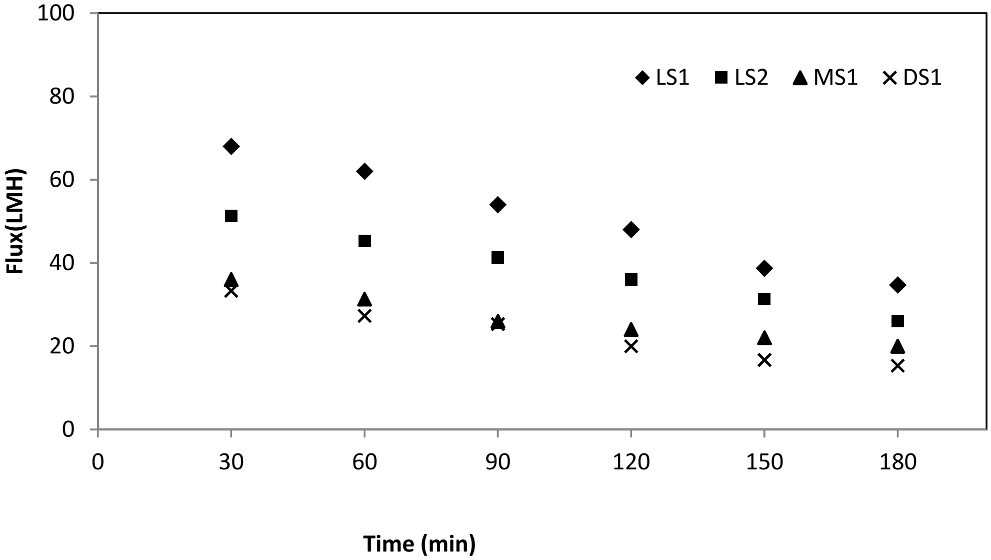

Figure 4-3 Flux as a function of time for SR90 without pre-treatment

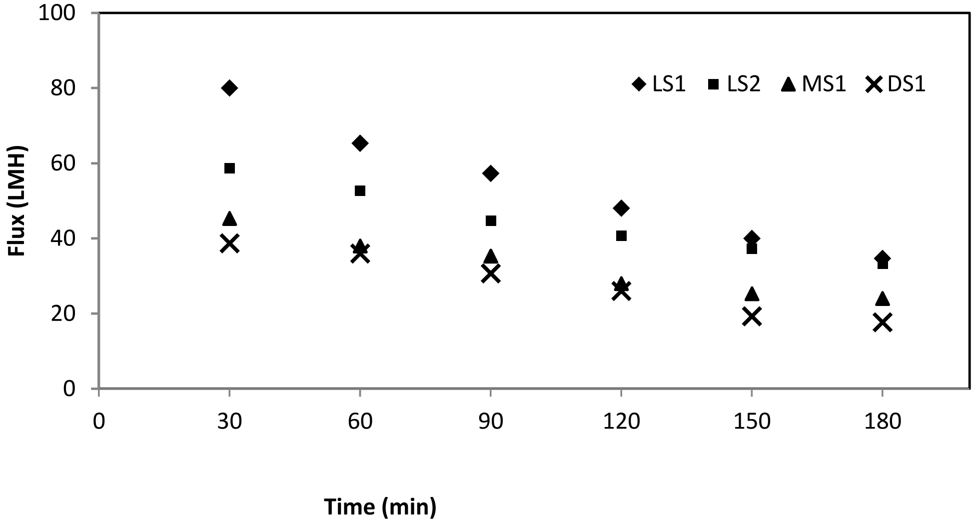

Figure 4-4 Flux as a function of time after pre-treatment for SR90

The average flux values for LS1, LS2, MS and DS before pre-treatment were 87, 66 46 and 39 LMH. The feed samples were subjected to UF filtration in order to evaluate the performance of NF membranes after pre-treatment. The fluxes for LS1, LS2, MS and DS after pre-treatment were 93, 76, 56 and 48 LMH respectively.

There was a decline in flux for all the feed samples as seen in the case of the UF membranes. The decline in flux was progressive, and this was noticed in the case of both pre-treated feed and the un-treated feed samples. The Figures indicate that there is not much difference at the end of the run. LS2 and MS1 have higher fluxes at the end and have not reached a stable stead. But they could possibly do so if the experiment was run longer. With respect to the flux in individual feed samples, LS1 had the highest flux with the dark shade having the least flux.

4.2.4 **Permeate flux for NF90**

Figures 4-5 and 4-6 show the flux with time for NF90. Figure 4-5 is the flux–time graphs for all the feed samples on NF90 without pre-treatment while 4-6 is a flux time graph on the feed after pre-treatment.

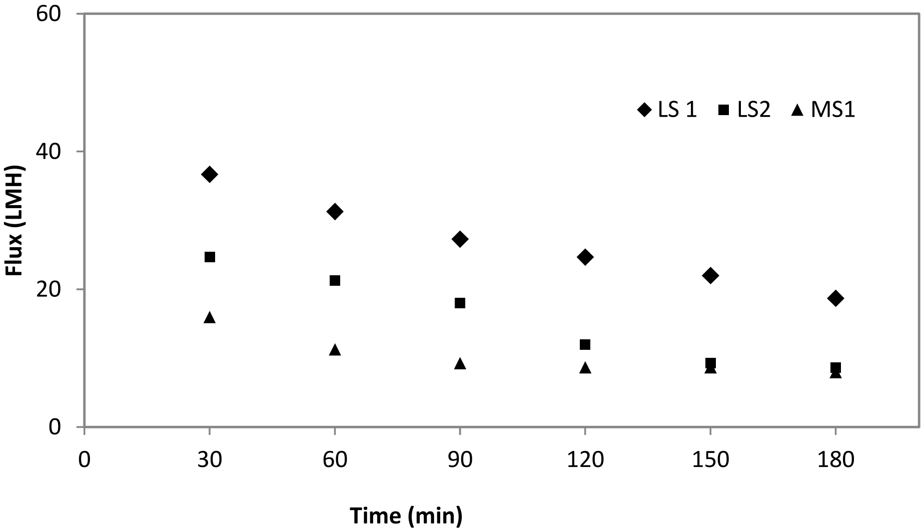

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Figure 4-5 Flux as a function of time without pre-treatment for NF90

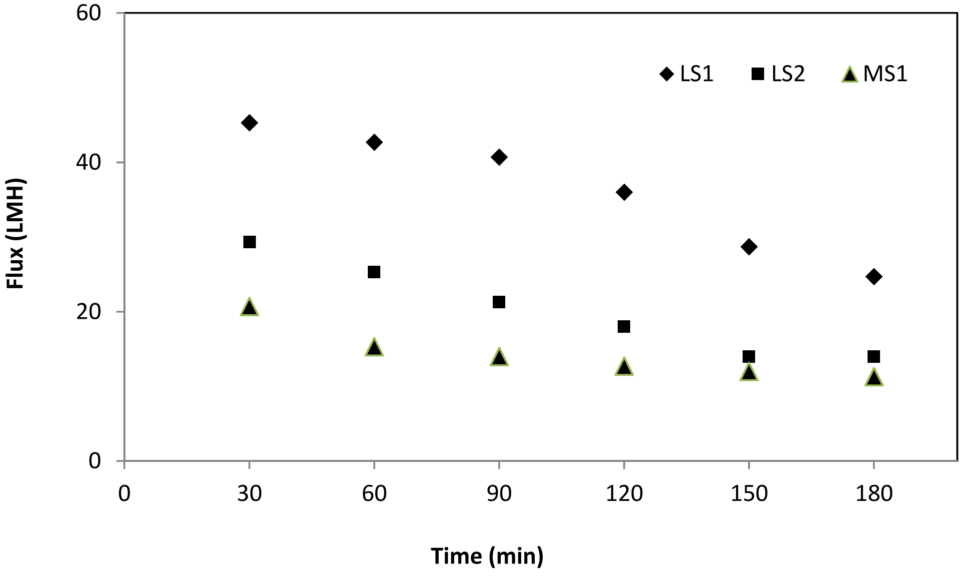

Figure 4-6 Flux as a function of time with pre-treatment for NF90

A similar trend was observed when NF membranes were used.

The average fluxes for the un-treated samples were 46, 27 and 18 LMH while for the treated sample; they were 62, 35 and 25 respectively. This shows again a decline in flux.

Comparing the nature of the graphs obtained from all the membranes used for this experiment with that of the pure water flux, the fluxes obtained for the effluent were significantly lower than that of the pure water flux due to deposition of substances on the membranes; therefore this indicated that fouling effects were significant.

The flux time graphs for UF and SR90 membranes shows that fluxes obtained were above 20 LMH after 3 hours of filtration. NF90 experienced a significant flux drop to below 20 LMH after 3 hours of filtration. Comparing these results to what is obtainable in literature; the UF and SR90 membranes used for this study were therefore more sustainable as compared to NF90. According to a work carried out by Lopes, Petrus and Riella (2005), they considered a permeate flux within the range of 30-60 LMH acceptable in terms of cost effectiveness for nanofiltration processes at pressures of 15–30 bars.

In terms of individual fluxes for the feed samples; the light shades had higher fluxes as compared to the MS and DS samples. A number of reasons could have led to this variation such as: the interaction between the membrane and the feed solution, the sample concentration and composition in terms of its dye and salt contents.

The DS sample had high initial dye and salt contents from the results of the characterization of feed; the colour tested in the feed was 149,000 Pt-Co units, while its conductivity was 122 Ms/cm. The huge loss in permeate flux for the MS and DS was ascribed to a cake layer formation and adsorption of dyes on the membrane surfaces as a result of the high salinity of these samples and also the dye content. This was confirmed by the visible colour layer observed on the membrane at the end of the filtration process. This happened because the dye molecules had attached strongly to the surface of the membrane thereby reducing permeates flux.

This finding is in agreement with the literature (Lopes, Petrus and Riella, 2005; Van der Bruggen *et al.*, 2005). Studies by (Van der Bruggen *et al.* (2005); Al-Rashdi, Johnson and N.Hilal, 2013) found that reduction in flux can be attributed to osmotic pressure. One of the factors that influence osmotic pressure is the ionic concentration of the solution. Solutions with higher ionic strength will contribute more to osmotic pressure. This is because a larger fraction of the ions will be retained by the membrane, and as a result, the concentration difference on both sides of the membrane will thus give rise to an increased osmotic pressure.

Other substances that could contribute to flux decline include dye auxiliaries which are commonly applied to enhance the uptake of dyes. Flux decline by the membranes could also have resulted from the interaction of the membrane and the divalent salt of Na_2CO_3 which was also in the feed solution. Na_2CO_3 is used during dyeing to raise the liquor pH which will increase dye hydrophobicity and hence its attachment to the fibre. Osmotic pressure is strongly dependent on the composition of the dye bath. For the feed samples used in this study, it was a combination of monovalent salts and divalent salts, therefore the presence of the divalent salts also lowered the membrane fluxes.

Finally, comparing the fluxes of both NF membranes, SR90 had higher fluxes than NF90. The major influencing parameter here was assumed to be the membrane properties. SR90 was a looser membrane as compared to NF90. Consequently, the flux is expected be higher in this membrane. Similar findings have been reported by Lau and Ismail (2009) they found that a significant improvement in flux could be obtained using looser NF membranes (Aouni *et al.*, 2012; Ong, Lau and Ismail, 2012).

4.2.5 **Effect of pre-treatment of feed on NF membrane performance**

Figure 4-7 shows the flux improvement by both NF membranes after pre-treatment.

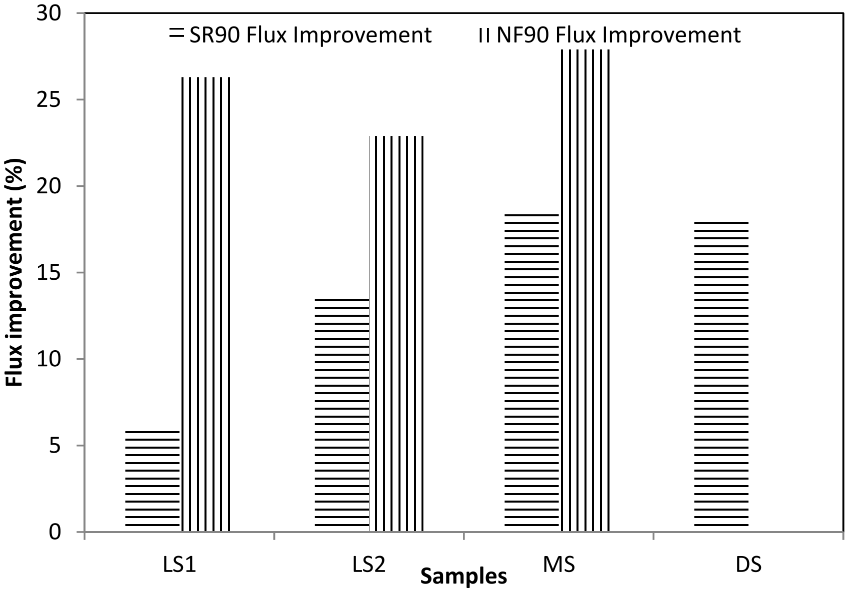

Figure 4-7 Flux improvement by NF membranes after a pre-treatment with UF

A higher improvement was observed with NF90 with the highest observed for the MS while for SR90 it varied significantly depending on the type of effluent used. Comparing permeates obtained with the NF membranes without pre-treatment and with the pre-treatment stage; the differences were 5–15% for SR90 and 20–25% for NF90 respectively. This indicated that the particles that caused the membrane fouling were reduced in the pre-treatment stage hence an improvement in NF performance in terms of its fluxes. The results observed were for a 3 h filtration run. The importance of pre-treating each feed therefore shows that a great improvement in flux can be achieved.

4.2.6 Summary of permeate flux with time for all the membranes

According to the literature, a system with 30-60 LMH fluxes can be made comparable with industrial processes (Petrova and Stoychev, 2003; Lopes, Petrus and Riella, 2005). High fluxes above the stipulated flux above were obtained by all the membranes used for this study, which means that these membranes can be scaled up for the treatment of textile effluents. SR90 achieved higher fluxes than NF90, this was due to the membrane pore size; SR90 was a looser membrane as compared to NF90.

The effect of feed pre-treatment was also noticeable in the flux of each membrane. A significant flux improvement of 5–25% was recorded for NF membranes.

4.3 Membrane Fouling

Fouling is a major operational challenge in membrane processes. It is indicated by flux decline and therefore productivity over time. In this section the flux decline over time (limited to 3 h) is presented. In this study, no differentiation was made between pore blocking and adsorption as both were considered to contribute to membrane fouling. To limit fouling in the NF membranes, the feed solution was pre-treated using an UF membrane. This section will therefore consider fouling rate in UF and NF membranes and the effect of feed pre-treatment on the rate of fouling.

4.3.1 Fouling in UF membranes

Figure 4-8 shows the variation of fouling on the UF membrane for the different feed samples.

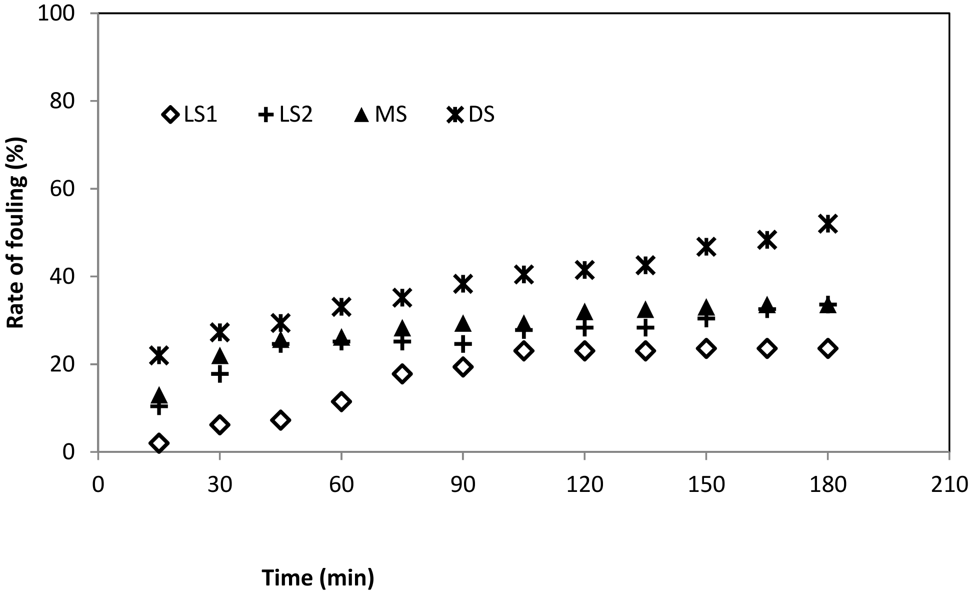

Figure 4-8 Variation of fouling rate with time using UF membrane

Flux decline in UF is usually very severe because of their porosity. The rate of fouling in LS1 and MS fluxes stabilised after 2 hours of filtration, while LS2 and DS continued to experience a gradual change. This behaviour was assumed to be due to the interaction of the feed and the membrane as a result of the different dyes in the feed composition, since each feed contained different dyes.

The highest rate of fouling was observed with DS samples (27–52%) while the lowest rate was for LS1 (6–24%). The rate of fouling at the beginning of the experiment was low. After 3 hours of filtration, the rate had increased and a large decline in permeate flux was now noticeable probably due to a cake layer formation on the membrane, and possibly concentration polarisation. The fouling rate in the UF membranes were however lower as compared to both NF membranes.

4.3.2 **Fouling in SR90 membranes**

Figure 4-9 shows the rate of fouling on SR90 without feed pre-treatment while 4-10 shows the rate of fouling on SR90 membrane after pre-treatment.

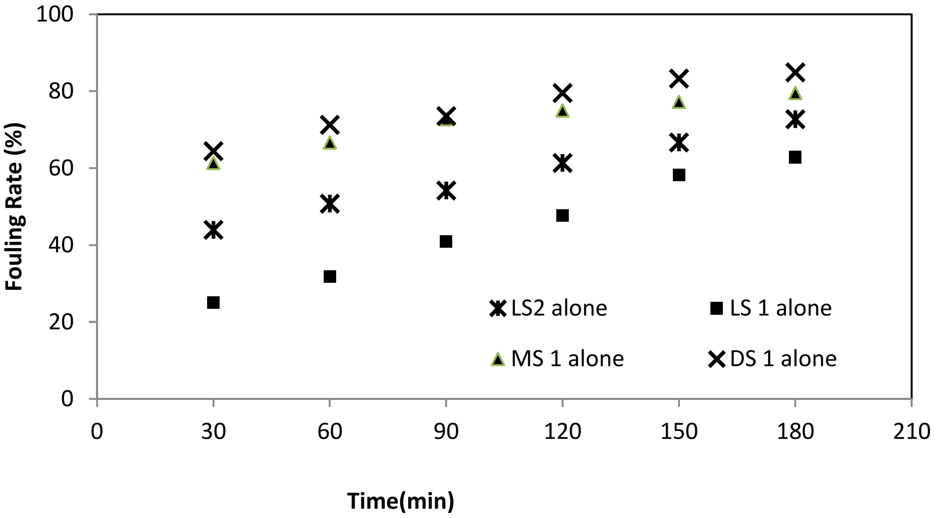

Figure 4-9 Variation of fouling rate with time without pre-treatment SR90

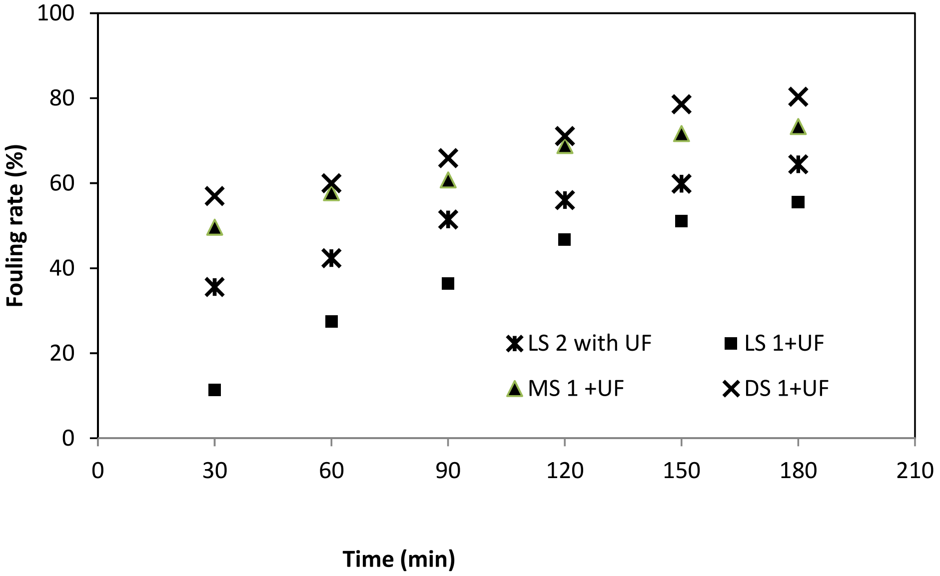

Figure 4-10 Variation of fouling rate with time with pre-treatment SR90

An increase in the rate of fouling in the membrane was observed for all the treated samples which indicated a decrease in permeate flux, this was observed for both the treated and untreated feed samples. The rate of fouling was however more severe for the untreated samples.

A higher loss was recorded for the dark shade followed by the medium shade. The rate of fouling for dark shade was from 57% for the first 30 minutes and it went further up to 80% after 3 hours of filtration, similar trend was observed for the other feed samples, though with lower values. The rate of fouling for the first 30 minutes for LS1, LS2 and MS were 11, 36 and 50% and after 3 hours a further decrease in flux of 56, 64 and 73% was recorded. This behaviour was attributed to the composition of the feed samples and its interaction with membrane. Flux loss in membranes was thought to be the result of adsorption or pore blocking.

4.3.3 **Fouling in NF90 membranes**

Figure 4-11 and 4-12 shows the variation in the rate of fouling for NF90 on both treated and un-treated feed samples.

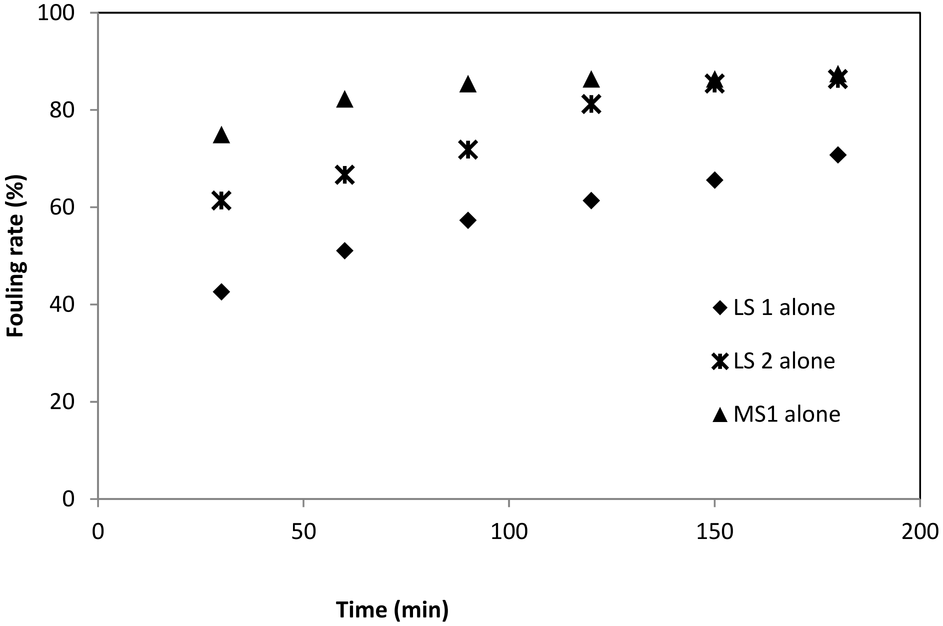

Figure 4-11 Variation of fouling rate with time without pre-treatment NF90

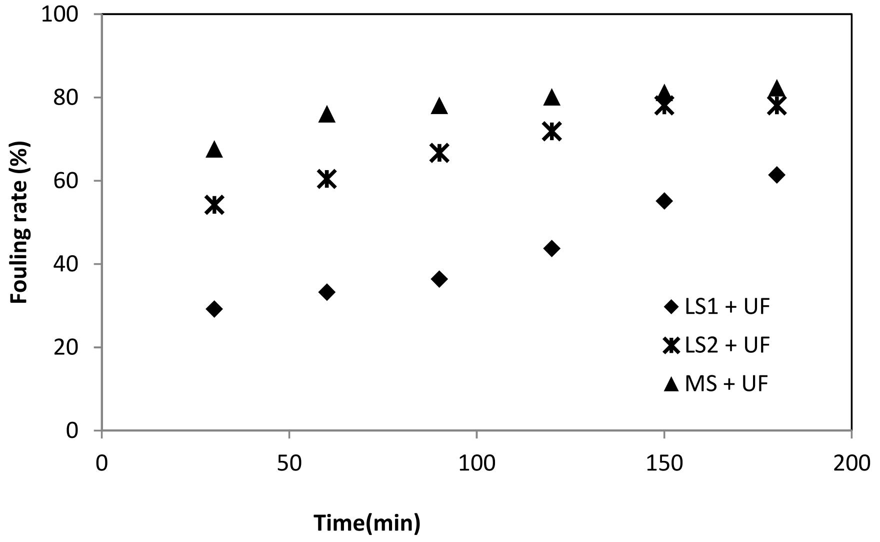

Figure 4-12 Variation of fouling rate with time with pre-treatment NF90

Rate of fouling was more pronounced in NF90 even though the same feed samples were used with SR90. The dark shade was not treated with NF90 as earlier stated. For the NF90 membranes, the MS shade had the highest rate of fouling. Can be seen in Figure 4-11; the plots asymptotes at a faster rate than those in Figure 4-12. The difference in the fouling rates was attributed to the UF pre-treatment of the samples.

Similarly like the SR90, rate of fouling was attributed to the different feed composition and its interaction with membrane. For the MS sample, about 67–82% of the membrane flux was lost indicating a severe fouling and hence a reduction in permeate for the treated samples; while the un-treated sample yielded about 75–87% flux reduction.

The rate of fouling for the first 30 minutes indicated an important osmotic pressure effect due to high salt concentration especially for the MS and DS samples with higher salt contents and after 3 hours of filtration the flux had further dropped, this decline was probably due to concentration polarization.

The severe fouling rate in the NF membranes was assumed to be as a result of the reaction between the dyes and the membranes since the feed sample had a combination of one or two dyes. From literature it have been reported that each dye class could cause membrane fouling and the manner of interaction between the membrane and these dyes differ. A study by Ismail and Dincer (2003) showed that dye molecule adsorbed on the membrane surface affects permeate flux thereby increasing fouling due to physicochemical interactions, e.g. hydrophobic interactions, polar interactions and charge transfer.

There are various factors that can influence the adsorption of dyes on the membranes. These include nature of the membrane material, the type of solutes, solute concentration, and pH (Aouni *et al.*, 2012). During all experiment, the membrane surface was observed to be coloured with the intensity varying according to the feed solution that was filtered. The photographs of the coloured membranes is shown in appendix D

Another factor for the high rate of fouling was attributed to the salinity of the feed sample. The feed samples with the highest salinity had the highest rate of fouling. Jiraratananon, Sungpet and Luangsowan (2000) explained that, the penetration of reactive dye onto the membranes could be enhanced by the use of NaCl during the dyeing process thereby resulting in the NF membranes being heavily coloured after the experiments. This subsequently led to a flux decline in the membrane process.

Furthermore, high rate of fouling was due to the high pH of the feeds which were high signifying that most of the feed samples were alkaline in nature. Ismail and Dincer (2003) stated that under alkaline conditions, the formation of a strong and stable dye-salt complex will result in an increase in hydrophobicity and as such, the adsorption of dye molecules on the membrane surface increased therefore increasing the membrane fouling. This was probably due to differences in the material and the membrane manufacturing process including contact angle, surface roughness, and membrane hydrophilicity/hydrophobicity.

Comparing the rate of fouling between the NF membranes, NF90 had a higher fouling rate. This was due to the membrane properties such as contact angle, surface roughness, membrane hydrophilicity/hydrophobicity.

The contact angle of a membrane is a semi-quantitative index which is connected to the hydrophilicity/hydrophobicity of a membrane surface. With a low contact angle, the hydrophilicity will increase while the propensity of fouling in the membrane is decreased (Aouni *et al.*, 2012). Lau and Ismail (2009) found out that a small contact angle which corresponds to the hydrophilic surface of a membrane could reduce the tendency of the membrane fouling through preferential wetting of the membrane material by water. The greater contact angle in NF90 (54˚) compared to SR90 (27˚) could possibly be a reason for high fouling shown in NF90.

4.3.4 **Summary of fouling in membranes**

The study found that the degree of fouling in the NF membrane was influenced majorly by the feed composition. The darker shade which had a high content of salts and dyes lead to a heavy fouling of the membranes. Fouling was more severe in NF90 than SR90; this was due to the difference in membrane characteristics.

4.4 Quality of permeate

The quality of water is defined as acceptable as long as the impurities in the water do not affect its functions. Before process water is recycled for reuse, the impurities in the waste water must be reduced to a level that is acceptable (Goodman and Porter, 1980). NF permeate quality were analysed after the pre-treatment stage, therefore the parameters discussed here represent the samples taken for the feed to the NF membrane only. Permeate quality was evaluated by measuring COD, TOC, conductivity, colour, turbidity and suspended solids.

The composition of each effluent sample is given in

Table 4-1 Characteristics of the feed samples used for the study after pre-treatment with UF. The feed composition before pre-treatment was earlier discussed in section in section **3.4.5** and its collection storage in **3.4.14**.

Table 4-1 Characteristics of the feed samples used for the study after pre-treatment

Parameter	**LS 1**	**LS 2**	**MS**	**DS**
Colour (pt-co)	574	978	1050	14900
COD (mg/l)	890	206	1100	4800
TOC (mg/l)	98	98	102	570
TSS (mg/l)	54	46	68	127
pH	10	10	11	11
Turbidity (NTU)	18	75	11	48
Conductivity (mS/cm)	10	21	32	122

It can be seen from the table that the quality of the feed samples were quite different. The dark shades had the highest organic load, colour and salinity. This is due to the higher quantity of the dyes and salts required to achieve dark shades for dyeing process. Variations in feed samples are also as a result of the different recipes that are used to obtain the right colour shades.

4.5 Performance of membranes in terms of organic removal

4.5.1 **Percentage removal after UF treatment**

Table 4-2 shows the characteristics of the various permeates obtained with the use of UF membrane.

Table 4-2 Characteristics of the various permeates from UF of the various samples

Parameter	**LS1 (%)**	**LS2 (%)**	**MS (%)**	**DS (%)**
Colour	19	8	8	36
COD	57	54	19	26
TOC	56	54	37	71
TSS	72	73	65	39
pH	1	0	0	4
Turbidity	82	51	89	38
Conductivity	0	0	0	1

The rejection of polluting substances was high. Turbidity rejection was more than 80% for LS1 and MS. LS2 and DS were 51 and 38%. Low removal was achieved for the LS2 and DS. The reason for this was not clear but was not investigated further as this was for pre-treatment only. The rejection of total suspended solids was highest in LS1 and MS, while LS2 and DS had lower rejection values of 65 and 39%. Low colour rejection was achieved by the UF. The rejections were between 8–36% for all the feed samples. DS had the highest colour removal; this was achieved possibly due the adsorption of dyes onto the layer of the membranes which further acted as a barrier to the passage of the dyes.

The rejection of conductivity was however not significant; no values were recorded for all the feed samples this was due to the nature of the membrane. This was expected because UF membranes are used for removal of macromolecules and other suspended solids but are unable to retain monovalent and divalent salts (Baker, 2004; Alcaina-Miranda *et al.*, 2009). Therefore, the use of UF as a pre-treatment leads to an improvement in NF permeate quality in terms of colour and organic content retention.

4.5.2 Performances of NF with respect to solutes rejection

I. COD rejection

Figure 4-13 shows the performances of both NF membranes in terms of COD rejection.

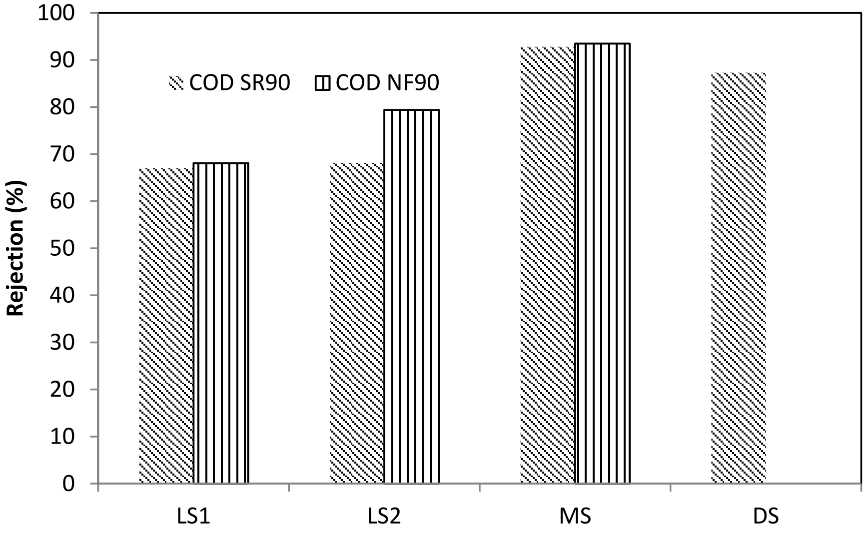

Figure 4-13 Performances of NF with respect to COD rejection

Higher percentages of COD removal were recorded when filtration was carried out using NF as shown in Figure 4-13. NF90 gave a better performance in terms of COD removal for both samples LS1 and LS2, while for MS; its performance was almost the same as SR90. The COD in the permeates sample for NF90 was less than 100 mg/l representing a rejection of over 80–90%. While in SR90, the COD was between 30–140 mg/l with a rejection of 60–90%.

From these results, the LS1 sample had the lowest COD value in the permeate; its initial feed sample was 206 mg/l which was lower than other samples measured (900–4800 mg/l COD) as shown in Table 4-1. The least rejection was observed when the DS sample was filtered using SR90. The high COD in permeate was therefore attributed to the high initial feed concentration of 4800 mg/l. This suggested that feed concentration plays a significant role in membrane rejection performance. In a study by Alcaina-Miranda *et al.* (2009) they considered that a 76–83% COD reduction in textile industry wastewater as satisfactory values. According to Sojka-Ledakowicz *et al.* (2010) they found that high reduction of COD (up to 99 %) could only be achieved by RO membranes. The reminder of the COD in permeate was perhaps from the solutes and other oxidizable low molecular weight materials that went through the membrane. Both NF membranes had achieved high COD rejection, but higher rejections were achieved by NF90.

On comparing the COD values with those obtained in literature and the reuse criteria, it was concluded that the permeates from NF90 met the reuse criteria while only the light shades and the medium shades from SR90 were considered satisfactory for reuse purposes.

II. Membrane rejection of pure salts

Figure 4-14 and 4-15 shows pure salt rejection of NF membranes with feed at different concentrations using NaCl and $NaSO_4$. The study of pure salt removal is important because they are commonly used in the textile industry during the dyeing process to enhance the dye fixation onto the fabric.

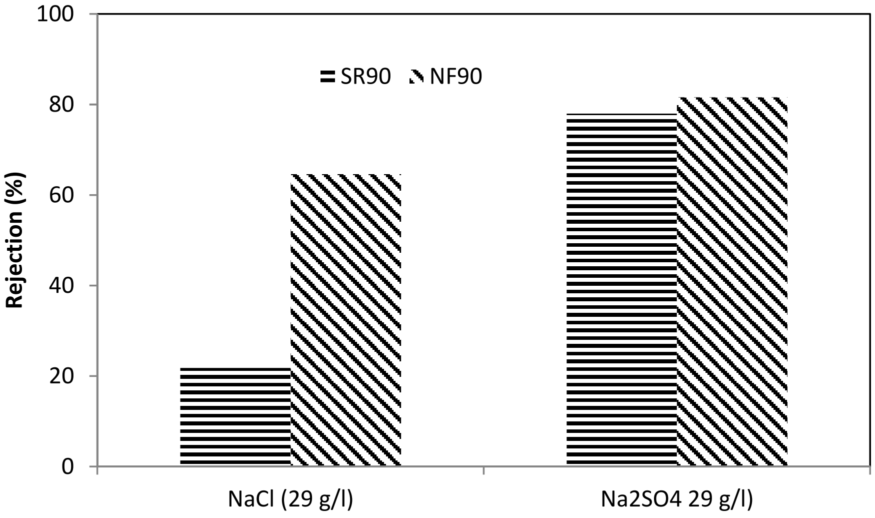

Figure 4-14 Pure salt rejection of NF membranes with feed concentration of 29 g/l

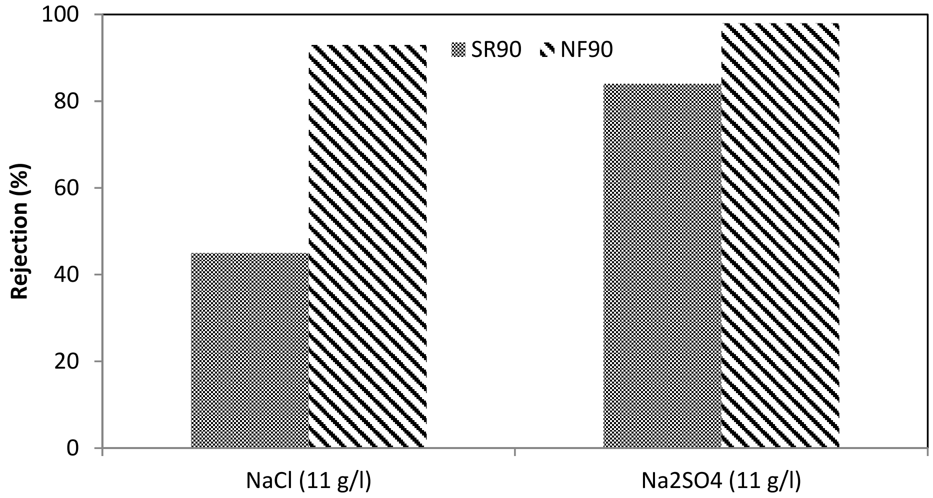

Figure 4-15 Pure salt rejection of NF membranes with feed concentration of 11 g/l

Pure salt solutions were prepared and filtration was carried out using both NF membranes on the single salts to determine the performance of the NF membranes in terms of the rejection of the salts. This provided information that was used to compare the rejection of salts by the NF membranes with effluent samples. The rejection was studied by setting the same operating parameters that were used for the filtration of the effluent samples.

From Figure 4-15 and 4-16; it is found that NF90 showed higher salt rejection for both NaCl and Na_2SO_4 as compared to SR90, despite its low water permeate fluxes. The higher separation efficiency of NF90 was attributed mainly to its relatively smaller pore structure which restricted the passage of the dissolved salt. The salt rejection of Na_2SO_4 for both tested membranes was apparently much higher than NaCl rejection; this was in agreement with the Donnan exclusion mechanism where divalent anions are highly rejected by NF membranes with negative surface charge (SO_4^{2-}) than that of monovalent anions (Ong, Lau and Ismail, 2012).

Furthermore, Ong, Lau and Ismail (2012) attributed the high rejection rate of Na_2SO_4 to the effect of size exclusion where the observed order of ion rejection was SO_4^{2-} $>Na^+>Cl^-$.

The rejection of NaCl by SR90 membrane is similar to those reported in literature. However lower rejection of Na_2SO_4 by SR90 was observed in this study compared to others (Ong, Lau and Ismail, 2012). This might be partly due to different testing conditions (e.g. salt concentration, feed pH, applied pressure, etc.). The selectivity of NF is altered during filtration due to the fact that the behaviour of salt in solution differs as a result of the size of the hydrated ions formed (Wang *et al.*, 2011; Ong, Lau and Ismail, 2012).

III. Membrane rejection of effluent salt

Figure 4-16 shows the salt rejection by SR90 and NF90 for effluent samples.

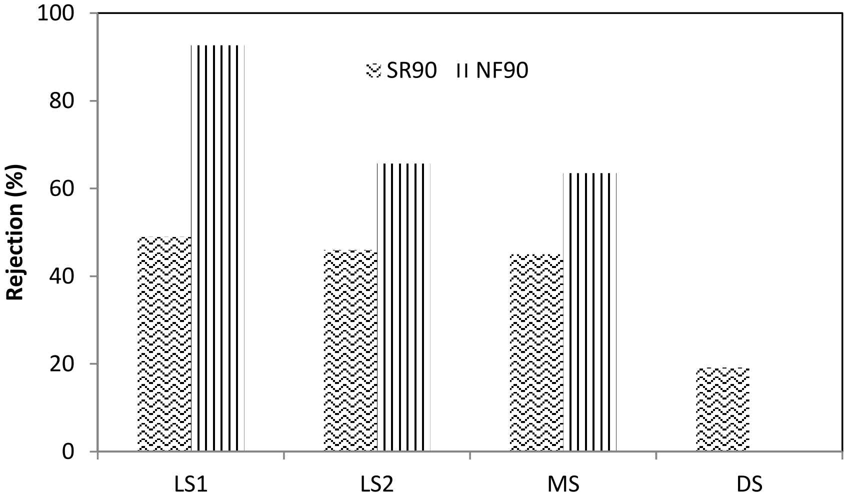

Figure 4-16 Salt rejection by SR90 and NF90 for the feed samples

The rejections were from 65–90% for NF90. SR90 had lower rejection of 20–50%. Like other parameters as shown in Table 4-1; there was a variation in sample conductivities with the DS and MS shades having the highest conductivities of 122 mS/cm and 32 mS/cm, respectively. For the lighter shades, the conductivities were 21 and 10 mS/cm respectively.

Comparing the performance of NF membranes for the effluent samples and the pure salt filtration, it was observed that for both cases, at higher salt concentration the rejection of salts by NF decreased. This is in agreement with observation in literature (Denyer, Shu and Jegatheesan, 2007). For example, (Lau and Ismail, 2009) have shown that the transport of salt through the membrane is proportional to the salt concentration difference, but independent of the applied pressure.

More so, salt rejection in a membrane depends mainly on membrane type; it is either charged with positive or negative ions or it is neutral. Lau and Ismail (2009) stated that monovalent salts such as NaCl are usually completely ionized into Na^+ and Cl^- in alkali or pure water. When there is an increase in the salt concentration, it is accompanied by an increase in the ions in solution. Therefore based on the Donnan principle, the repulsive force from the negatively charged membrane will decrease on increasing concentration of the salt. Lower repulsive force therefore means that more Cl^- anions will be allowed to pass through the membrane and thus salt rejection is reduced. In general, the increase in salt concentration usually reduces electrostatic repulsion for NF, causing salt rejection rate to decrease.

However for NF90, the rejections were between 60–90% for the samples irrespective of the feed concentration which then means that salt rejection was by both the sieving and Donnan exclusion principle. Unlike NF90, the tendency of salt rejection decrease was very obvious in SR90 and this is largely due to the remarkable decreasing Donnan exclusion effect as a result of membrane type. Even though NF90 had a higher conductivity rejection than SR90, the performance of SR90 met the objective of the study in terms salt recovery.

IV. **Dye rejection**

Figure 4-17 shows the performance of the NF membranes with respect to dye rejection

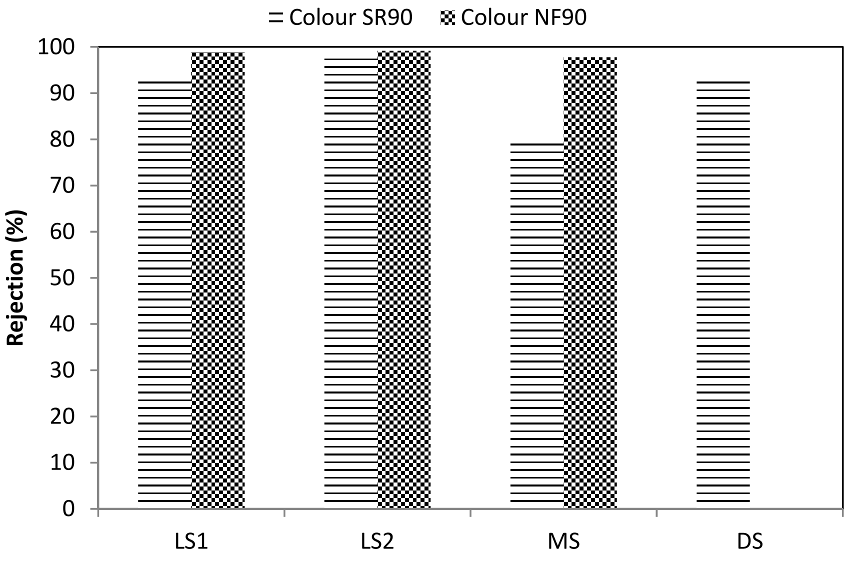

Figure 4-17 Colour rejection by SR90 and NF90 for the feed samples

Colour rejection by NF90 was higher than SR90 for all treated samples, even though both membranes achieved a high rate of rejection above 90% for all the samples. Higher colour removal was achieved for light shades as compared to the darker shades. It is expected that dye rejection at lower feed concentrations will be higher. And since the darker shades had more salt contents, the rejection were lower. These results were in agreement with the findings of Tang and Chen (2002) who reported that lower colour rejection removal was observed with increasing NaCl concentration.

However, contrasting views were reported by Lopes, Petrus and Riella (2005) who stated that initial dye concentration in the feed does not significantly affect dye rejection, but rather rejection is affected by the membrane type used in terms of its molecular weight cut-off.

Nevertheless, for this study, the rejection of dyes by the NF membranes was concluded to be as a result of variation in the salt content of the feed sample composition and membrane type. With respect to the reuse criteria, permeate samples from NF90 were considered satisfactory, while only the light shades were considered acceptable for the SR90. However studies by Lopes, Petrus and Riella (2005) on the purification of water contaminated with reactive dye, using different NF membranes, considered dye retention of 85‒90% satisfactory for reuse especially for some of the washing streams and using dyeing of dark colours.

V. **TOC rejection**

Figure 4-18 shows the TOC rejection by SR90 and NF90 for the feed samples.

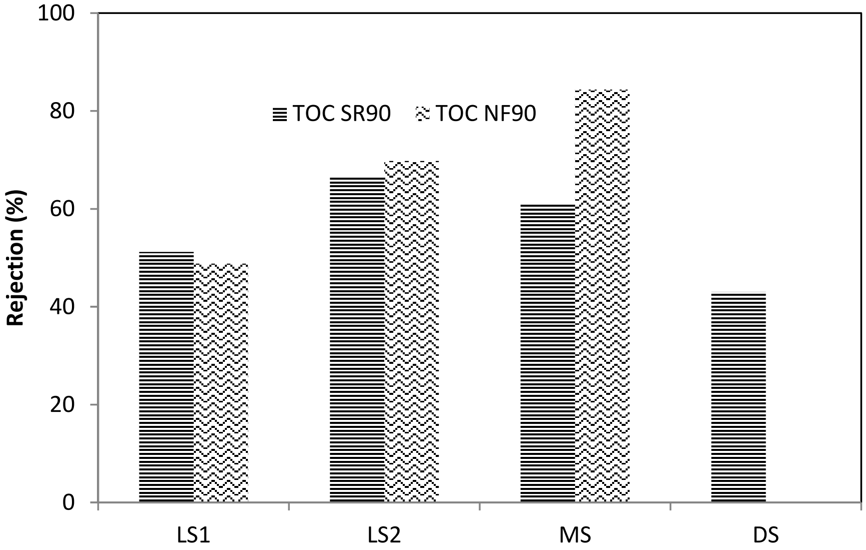

Figure 4-18 TOC rejection by SR (90) and NF90 for the feed samples

Both NF membranes achieved high TOC rejections. The final TOC concentration from SR90 ranged from 21-64 mg/l representing a rejection of between 40‒70%. The highest rejections were achieved using LS shades while the least rejection occurred treating the DS shades. TOC in NF90 permeates were between 10‒22 mg/l indicating removal rates of 50‒85% for NF90. TOC obtained by both NF membranes met the reuse criteria, and similarly like in the previous parameters discussed, the dark shades did not meet the criteria.

VI. **TSS**

Figure 4-19 shows the TSS rejection by SR90 and NF90 for the feed samples.

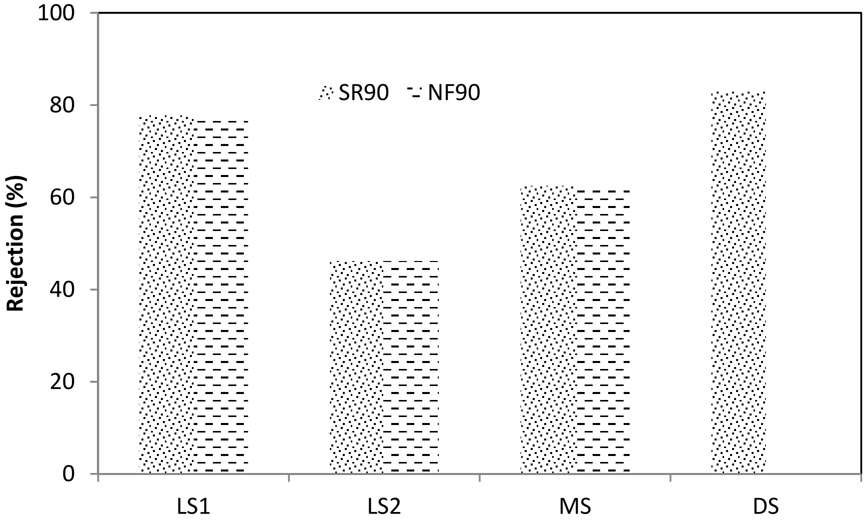

Figure 4-19 TSS rejection by SR90 and NF90 for the feed samples

The SR90 achieved the highest removal of TSS whilst treating the DS shade. This equated to an average removal of 83% which represent final effluent TSS concentration of 12 mg/l in permeate. The removal rates for the other samples were between 45–80%. The high removal rate for DS was probably due to higher initial TSS concentration in the DS solution to the NF membrane. The TSS removal performances of both NF membranes were nearly identical for all feed solutions tested.

VII. Turbidity

Because of the pre-treatment of the feed, most of the suspended particles were removed by the UF membranes; as a result the turbidity removal observed by the NF membranes was negligible because all turbidity measured was below 1 NTU.

4.5.3 Summary on permeate quality

The results obtained therefore shows that permeates from NF90 were of higher quality as compared to SR90 in terms of the reuse criteria. Even though NF90 permeate were of a higher quality to permeates from SR90, more salts were recovered from SR90 thereby meeting the objective of the study.

4.6 Efficiency of cleaning methods

Fouling causes a decrease in permeate flux due to the deposition of substances on the membrane. Regenerating the membrane by cleaning is therefore critical so as to make the process a viable one for application in industries. All the membranes used in this study were subject to cleaning by using physical (backwashing) for UF while forward flushing was used for the NF membranes followed by chemical cleaning for all the membranes. Cleaning was carried out at the end of each run. See section for **3.4.12 and 3.4.13** for contact times and detailed procedures of cleaning. The membranes were cleaned at the end of each experimental run.

This section will describe briefly the flux recovered for each membrane after cleaning and the efficiency of the cleaning methods. The manufactures specification for cleaning was followed for the membranes chemical cleaning.

4.6.1 **UF regeneration**

Permeate flux in UF membrane after physical and chemical cleaning is shown in figure 4-20.

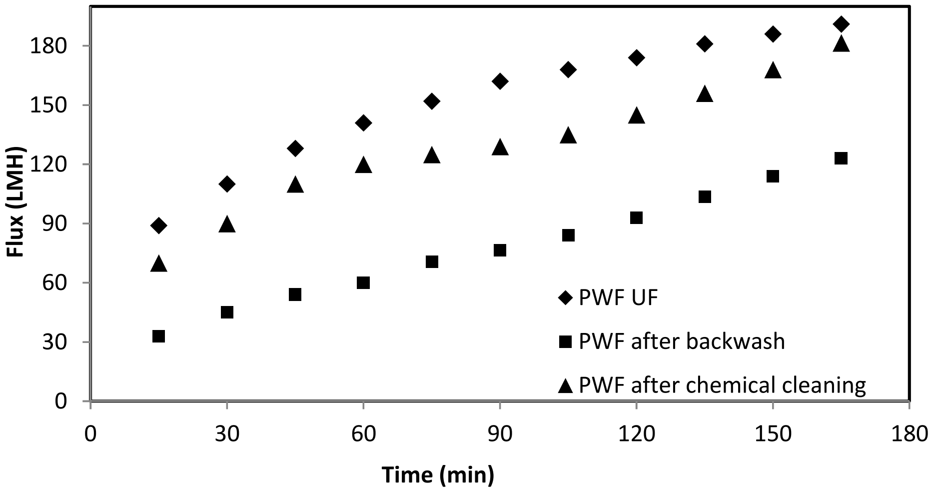

Figure 4-20 UF membrane regeneration

During the backwash, the permeate flow was reversed so that the surface foulants on the membrane were dislodged. Flux recovery after backwash was 64%. This was considered low since 34% of the membrane was still fouled. Because of the low flux recovery after the backwash, it was assumed that different types of fouling might have occurred on the membrane (cake formation and adsorption). Therefore in order to get rid of the adsorbed foulants, chemical cleaning was performed on the membrane. This was elaborated in section 2.5.1 of the literature. The flux recovery after chemical cleaning was 95%, such that only 5% of the flux was lost.

4.6.2 **SR90 regeneration**

Figure 4-21 shows the flux recovery curves after chemical cleaning on SR90. Flux recovery in NF membranes was determined by forward flushing for the physical cleaning and by the use of chemicals for the chemical cleaning.

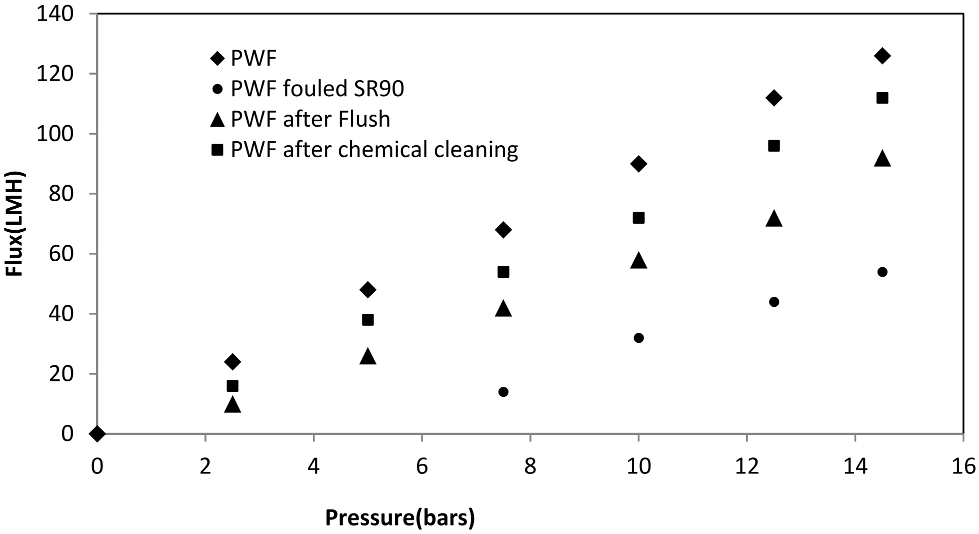

Figure 4-21 Flux recovery after chemical cleaning SR90

From the results in Figure 4-21, the water flux recovery (WFR) after flushing was 66% and 82% after a chemical cleaning. The loss in flux after physical cleaning was 44% and 12% after chemical cleaning. This shows that physical cleaning was not able to recover the flux but chemical cleaning was able to achieve a satisfactory recovery.

4.6.3 NF90 regeneration

Flux recovery after physical and chemical cleaning on NF90 is shown in Figure 4-22.

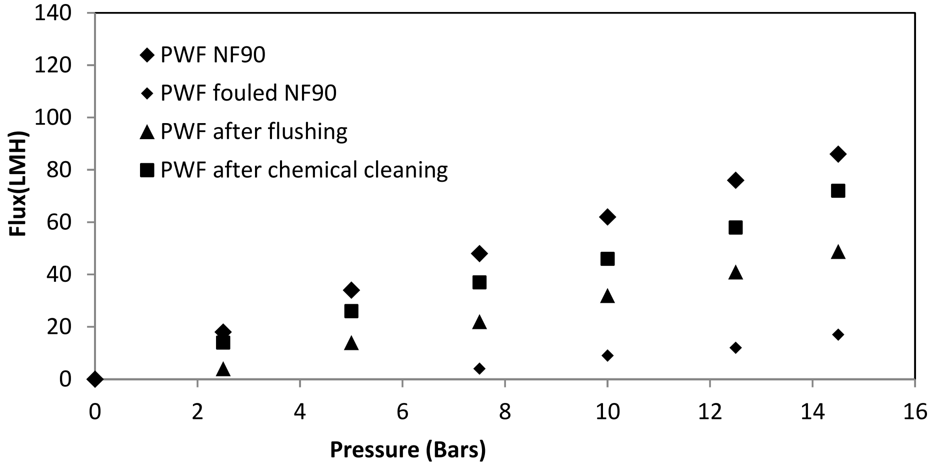

Figure 4-22 Flux recovery after chemical cleaning on NF90

The flux recovery after flushing and chemical cleaning was 51% and 76%, respectively. From the cleaning results; there was a loss in flux for both membranes, a higher flux loss was recorded for the NF90 membranes. The loss in flux was assumed to be due to irreversible fouling and therefore could not be recovered. Jiraratananon, Sungpet and Luangsowan (2000) reported that flux recovered in NF could be as high as 80–100% if the chemical cleaning is carried out periodically. Photographs of the fouled and cleaned membrane are shown in the appendix D

With respect to the membrane regeneration, the results were said to be satisfactory since almost 80% of the flux was recovered in all the membranes. This went further to suggest that the membranes used can be implemented for similar processes in large scales. However the cleaning cycles will have to be carried out intermittently to avoid huge losses in membrane flux.

4.6.4 Evaluation of membrane performance after chemical cleaning

The NF membranes performances in terms of permeate flux and its rejection was determined after chemical cleaning for the second cycle; this was to evaluate the effect of prolonged chemical cleaning on their performances. Only MS feed sample was used for this analysis. Same procedure for PWF and effluent filtration were used. Also the performance of the membranes in terms of rejection of substances was evaluated in a similar way as when the first experiment was carried out on the virgin membrane.

4.6.5 **PWF on the membranes after a second chemical cleaning**

The PWF after chemical cleaning for the first and second time is shown in Figure 4-23 and 4-24 for SR90 and NF90.

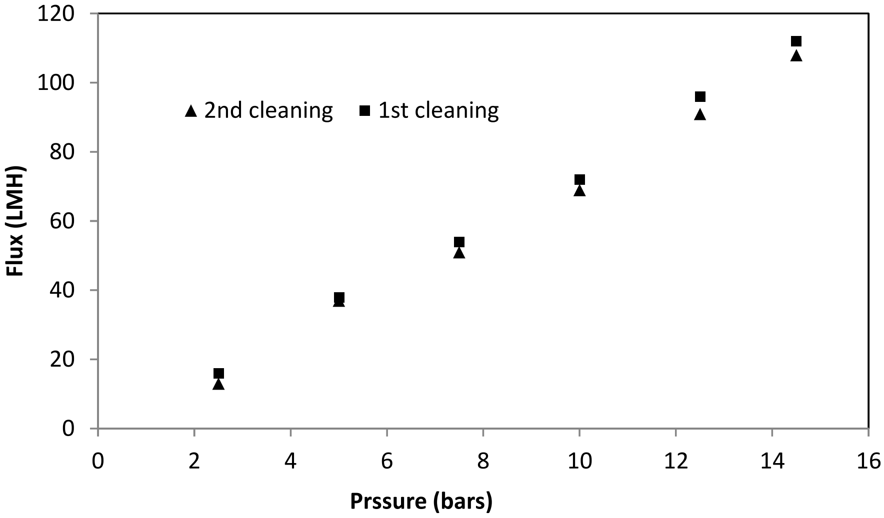

Figure 4-23 PWF on SR90 after the 1st and 2nd chemical cleaning

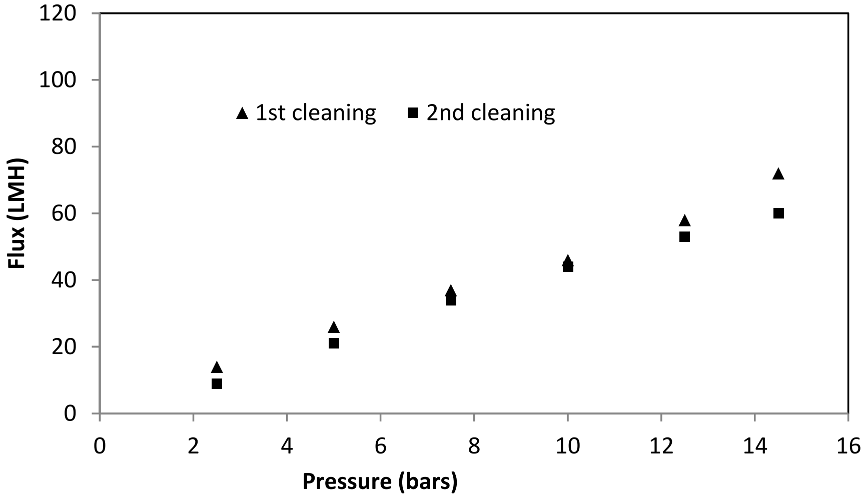

Figure 4-24 PWF on NF90 after 1st and 2nd chemical cleaning on NF90

The Figure compares the PWF in both membranes after cleaning for the second time. From the graph it was observed that 70–80% of the initial flux was recovered, which means that the cleaning chemicals did not have much effect on the membrane properties. Therefore the membrane morphology was not affected considerably after the chemical cleaning. Effluent filtration was carried out after chemical cleaning so as to ascertain the performance of the membrane with respect to filtration with the effluent samples.

4.6.6 **Performance of NF membranes after a second chemical cleaning**

Figure 4-25 and 4-26 shows the effect of membrane cleaning on permeate fluxes for NF90 and SR90 with effluent samples.

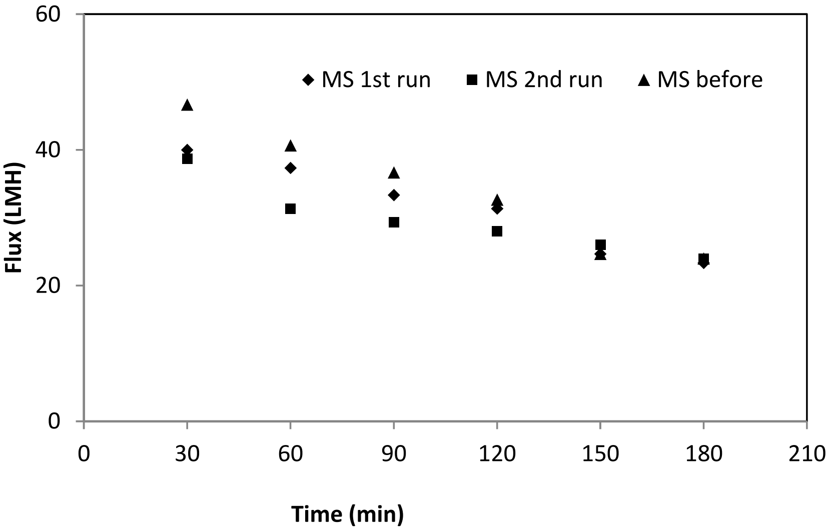

Figure 4-25 Variation in fluxes with time for SR90 on the virgin membrane, and after 1st and 2nd chemical cleaning

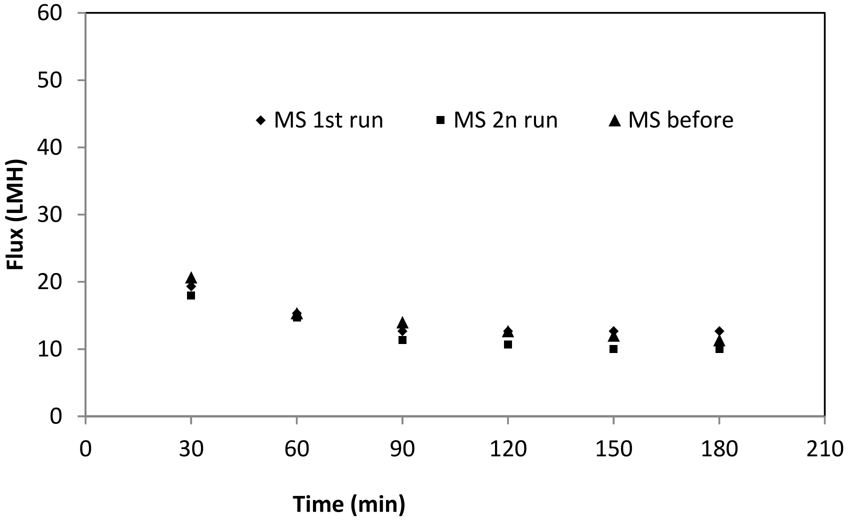

Figure 4-26 Variation in fluxes with time for NF90 on the virgin membrane, and after 1st and 2nd chemical cleaning

The results show that there was a little drop in flux after chemical cleaning from the initial flux of the membrane before cleaning. MS flux for SR90 before cleaning was 47 LMH and after cleaning for the first time, the flux was 40 LMH. For the second run, it was 39 LMH. For NF90, the flux before cleaning was 21 LMH while for the first and second runs they were 19 and 18 LMH. The results showed that even though there is still a flux decline for both membranes types after chemical cleaning, this difference was not significant. The performance of the membrane in terms of their rejection was also evaluated. Table 4-3 shows the rejection of both membranes after chemical cleaning.

Table 4-3 Analysis of NF membranes before and after cleaning

Parameter	**SR90** **Before cleaning**	**SR90** **After cleaning**	**NF90** **Before cleaning**	**NF90** **After cleaning**
Colour (Pt-Co)	193	201	21	25
COD (mg/l)	64	62	58	59
TOC (mg/l)	25	30	10	15
TSS (mg/l)	3	5	3	4
Turbidity (NTU)	0.81	0.80	0.91	0.87
Conductivity (mS/cm)	17	18	12	14

From these results it was observed that both the flux and rejection of the membranes was not affected significantly. The findings show that membranes used for the treatment of the effluent were recovered by means of chemical cleaning. The recovered fluxes were about 80% of the original PWF even after cleaning for the second time. It was concluded that the NF membranes are suitable for the treatment of textile effluents since the major problem which is fouling, can be overcome by carrying out intermittent chemical cleaning.

4.7 Comparative analysis of NF treated water with reuse criteria and MTM process water

There are advantages related with reuse of reactive dye house wastewaters after treatment with NF membranes. These include the reduction of fresh water consumption and the recycling of chemicals. The NF permeates quality were compared to the initial fresh water (process water) quality and the reuse criteria as shown in Table 4-4 and 4-5.

Table 4-4 Comparison of SR90 permeates with reuse standards

Parameter	**Reuse criteria**	**Freshwater**	**SR90 LS1**	**SR90 LS2**	**SR90 MS**	**SR90 DS**
Colour (Pt-Co)	0-20	0	23	30	193	640
COD(mg/l)	8-40	15	30	103	64	135
TOC (mg/l)	0	7	21	21	25	61
TSS mg/l	500	0	2	7		12
Turbidity (NTU)	15	0.67	0.97	0.73	0.81	0.89
Conductivity mS/cm	< 0.5	0.086	5.30	12	17	98

Table 4-5 Comparison of NF90 permeates with reuse standards

Parameter	**Reuse criteria**	**Fresh water**	**NF90 LS1**	**NF90 LS2**	**NF90 MS**
Colour (Pt-Co)	0-20	0	5	7	21
COD (mg/l)	8-40	15	29	84	58
TOC (mg/l)	0	7	22	19	10
TSS (mg/l)	500	0	2	7	3
Turbidity (NTU)	15	< 1	< 1	< 1	< 1
Conductivity mS/cm	< 0.5	0.086	0.076	3	12

For SR90 membranes, the COD concentration was higher than the reuse criteria for all permeate samples except in LS1. Even though the LS1 and LS2 membrane permeate appeared colourless to the naked eye, their values were slightly above the reuse standards. MS and DS were still clearly coloured and their values were above the reuse standards. However, even though a slight concentration of dyestuff in solution is usually visually noticeable.

NF90 permeates were much closer to the reuse guidelines and process water. The COD for LS1 was below the reuse standard and the process water, while LS2 and MS were above. Permeates samples all appeared to be colourless and were below the reuse standard except for the MS which was 1 point above the reuse standard. TSS and turbidity were at acceptable values. Conductivity for LS1 met the reuse values, while for LS2 and MS it was above.

Even though the quality of permeates from NF varied from the process water and reuse guidelines, the reuse test was still carried out on permeates.

Dyeing was carried out using permeate samples from NF in a laboratory scale at Mediterranean Textile where the effluent originated from. The dyeing was carried out on a fibre composed of 80% cotton and 20% polyester. A light shade recipe was chosen, which means that the salt content should be less than 10 g/l with 0-2% of the dye stuff added. Photographs of the dye cloth is shown in the appendix D

From the results of the dyeing, LS1 and LS2 samples from NF90 gave satisfactory results on dyeing with no colour difference even when compared to using the process water. However a variation was noticed when the MS sample was used. For permeates from SR90 only the LS1 sample was dyed successfully without any visible variation in colour while difference in colour was noticed for the remaining samples. However; the permeate samples were dyed using a light shade recipe. This could have been the reason for the variation in colours for the other sample permeates. These samples were observed to have higher conductivities.

Carrying out dyeing procedures with reuse water is limited in literature. However a few authors performed similar studies. Vreese and Bruggen (2007) studied cotton and polyester dyeing using effluents treated by nanofiltration. They came to a conclusion that the limited colour in permeate cannot be a hindrance to dyeing but instead the conductivity of the permeate has a higher impact on possibility of its reuse.

From the dyeing test it was therefore concluded that both NF membranes permeates from the light shade samples could be used for dyeing of light shades while the darker shades be dyed with dark shade permeates or alternatively. If NaCl concentration required for the dye bath recipe is lower than in the permeate, the salt can be supplemented by an addition so as to get the desired concentration. However, if it is higher, the permeate stream should be diluted.

Chapter 5 - Conclusions and Recommendations

This chapter summarises the conclusion and recommendations drawn from this study.

Conclusions

The feasibility of applying membrane processes in the textile industries to treat reactive dye effluents and to carry out reusability test on permeate was the focus of this study.

The following observations were made from the experimental results;

- SR90 achieved higher average fluxes above 20 LMH after three hours of filtration as compared to NF90 which were below 20 LMH for the treated sample with the lighter shades generating more permeate.
- Rate of fouling was more pronounced in NF90 as compared to SR90. The rate of fouling for the darker shades was more enhanced in both membranes as compared to the lighter shades.
- Permeate flux in NF membranes was improved with the use of UF as a pre-treatment, an average of 15–25 LMH improvement was observed for both NF membranes.
- High rejection of >90% by NF90 for COD, TOC and colour were obtained for all the treated samples. SR90 rejection was 80–90% for colour and >90% for COD and TOC. Salt recovery for NF90 was 60–90% and SR90 was 40–50% for all the treated samples.
- Chemical cleaning resulted in more than 80% flux recovery for both membranes. This indicated that the manufacturer's chemical cleaning specifications for the membranes was satisfactory for the treatment of textile wastewater.

Based on the observation the following conclusions were deemed suitable.

- ✓ The use of UF as a pre-treatment was able to reduce the effect of fouling on the NF membranes. The fluxes produced by the membranes were high enough and therefore the membranes can be made comparable with industrial processes.
- ✓ The study found that the degree of fouling in the NF membrane was influenced majorly by the feed composition. The darker shade which had a high content of salts and dyes lead to heavy fouling of the membranes. Fouling was more severe in NF90 than SR90, due to the difference in membrane characteristics.
- ✓ High rejection in terms of COD, TOC and colour were obtained for both NF membranes. NF90 showed averagely slightly better removal of colour and COD as compared to SR90.
- ✓ The reusability tests carried out showed that permeate recycled from NF90 could be used for any section in the textile industry including the most critical such as dyeing on light shades.
- ✓ The good recovery of membrane after cleaning suggests that the membranes used can be implemented for similar processes in large scales with the cleaning cycles carried out intermittently to avoid a high loss in membrane flux.
- ✓ Finally it was concluded that the performance of a membrane in terms of permeate quality and flux is dependent on the properties of the membrane and the characteristics of the feed.

Comparing both NF membranes, NF90 accomplished better results than SR90 in terms of permeate quality while SR90 accomplished better results in terms of permeate flux and salt recovery.

In summary we conclude that membrane based processes can be integrated into the water circuits of the textile industry to treat even the difficult effluent streams such as the dye bath despite its variations in composition.

Recommendations

The following recommendations were made based on the study

1. Future work on fouling mechanism should be carried out extensively. Therefore for a better understanding of fouling and its occurrence, the membrane used for the treatment of reactive dye effluent should be characterised in detailed as well as the feed samples. This will help in the identification of individual components which are responsible for fouling and the rejection mechanism of the membrane.

2. Future work should be carried out on a pilot plant scale. This should be studied in detail for a period of time for the purpose of scaling up, especially in terms of water recovery.

3. The duration of the experiments was limited to 3 h only. During the investigation of the permeate flux and the rate of fouling, it was observed that the LS shades graphs reached a steady. However, the DS graphs in some instances did not. It is recommended that the experiment be extended for a longer time. This will further give an understanding on the behaviour of the DS on a longer period of filtration

4. Further study on the economic feasibility should be investigated to determine if the process is practicable for implementation at the industrial scale.

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Appendix A Analytical Procedures

I. COD MEASUREMENT

COD

The COD’s were measured in three ranges depending on the strength of the effluent samples, although the procedure for measuring each range was the same. Measurements were done by means of HACH Method No. 8000 certified by USEPA using HACH DR-3900 model spectrophotometer at a wavelength of 430 nm for high range measurements (up to 1500 mg/L) and at a wavelength of 435 nm for low range measurements (up to 150 mg/L).

The following procedure was followed:

1. The COD reactor/heating (150°C) block and a colorimeter were turned on so that both instruments are allowed to stabilize.
2. The vials were selected for the COD test based range on expected results.
3. The caps were removed from the vials
4. The first vial was marked as a blank and the other effluent sample.
5. The vial marked blank was held at a 45- degree angle and 2 ml in the case of low range and 0.2 ml for high range of deionised water was pipette into the vial and swirl
6. The second vial marked effluent was also held at a 45-degree angle and 2 ml of the effluent sample was pipette into the vial for low range and 0.2 ml for high range.
7. The vials were then capped back properly and rinsed with water and wiped with a clean cloth to remove stains from the body of the vials.
8. Then they were inverted two to three times to enhance proper mixing.

9. The vials were then inserted into the reactor and the lid closed properly and allowed to heat for two hours. After heating for two hours, the reactor was turned off and the vials allowed cooling to a temperature of 120˚C.

10. The vials were then taken out and inverted while still hot and were place on the test tube rack and allowed to cool to room temperature.

11. The programme was selected on the spectrophotometer depending on the range and the vials were wiped again with a damp cloth followed by a dry one to remove stains on the vials. The blank vial was first inserted into cell and the instrument was zero, after which the effluent sample was vial was inserted and the reading was taken.

II. **TOC**

1. DR 3900 reactor was turned on and the TOC programme selected and the temperature set at 105°C

2. 10 ml of the sample was turned into a flask and 0.4 ml of a buffer solution was at pH 2 was added to the sample and the flask was placed on the stirrer and stirred for 10 minutes.

3. The vials were selected for the TOC test based range on expected results.

4. The caps were removed from the vials; the first vial was marked as a blank and the other effluent sample.

5. Persulfate powder pillow was added to each acid digestion vial and then 1 ml of deionised water was added to the vial tagged reagent blank and also 1 ml of the other tagged sample

6. Depending on the range of the TOC, either high range or medium range, the right ampule was selected and was rinsed with deionised water and cleaned off with a lint free clothe.

7. The ampule was lower into the acid digestion vial still uncapped, and the score mark on the ampule was levelled with the top of the acid digestion vial and was snapped off and dropped into the acid digestion vial the n capped properly. No mixing was needed.
8. The capped vials were then placed into the reactor and allowed to digest for two hours at 105˚C.
9. The vials were then taken out carefully and allowed to cool off for one hour
10. The programme was selected on the spectrophotometer depending on the range and the vials were wiped again with a damp cloth followed by a dry one to remove stains on the vials. The blank vial was first inserted into cell and the instrument was zero, after which the effluent sample was vial was inserted and the reading was taken.

III. Colour

Colour was measured with the same equipment used for COD and TOC at a wavelength of 455 nm and 465 nm. True colour was tested and not apparent. The difference between true and apparent colour is the extra step of filtering out suspended matter from the sample, but the other procedures remain the same.

1. The first step to determine the true colour was by taking 200 ml of the sample and the pH was adjusted to 7.6 using 1.0 N HCl
2. The filter apparatus was assembled this comprised of 0.45 micron membrane filter, filter holder, filter flask and aspirator
3. About 50 ml of deionised water was filtered using the filter apparatus and rinsed properly with the filtered deionised. Another 50 ml of deionised water was again filtered. The prepared sample was also filtered
4. Two samples of 10 ml each were properly washed to get rid of grease and other things that will interfere with the results and were marked sample and blank.

5. 10 ml of the filtered deionised water was turned into the cell marked blank and it was properly wiped with a clean cloth and was inserted into cell holder on the spectrophotometer and the right programme selected and was zero
6. Finally 10 ml of the filtered sample was turned into the cell marked sample and was wiped with a clean cloth and inserted into the cell holder and the reading was taken.

IV. **Conductivity, pH and turbidity**

Conductivity was measured by the use of a Hach conductivity meter. This was done placing the electrode probe into the solution to be tested and the reading taken and recorded. Similarly for pH, a Hach pH meter was used, the probe was also inserted into the solution and the reading taken and recorded.

Turbidity was measure by the use of a Hach turbidimeter also. This equipment had a sample test cell, its volume was 10 cm. the cell was properly rinsed with deionised water to get rid of any contaminants and the filled to the mark with the sample to be measured. This cell was then placed into the turbid meter and the reading taken and recorded. These procedures were carried for the samples to be tested.

Appendix B Characterization of Feed and Permeates Samples

The rejection of the polluting parameters were calculated using the rejection equation 2-4

$$R(\%) = 100 * (1 - \frac{Cp}{Cf}) \qquad \text{Equation 0-1}$$

B-1 Characteristics of LS1 with UF

Parameter	Feed	Permeate	Rejection (%)
Colour	574	470	18
COD	206	91	56
TOC	98	43	56
TSS	46	9	83
pH	10.47	10.35	1
Turbidity	18	1	93
Conductivity	10.4 mS/cm	10.4 mS/cm	0

B-2 Characteristics of LS1 with SR90

Parameter	Feed	Permeate	Rejection (%)
Colour	470	29	94
COD	91	30	67
TOC	43	21	51
TSS	9	2	78
pH	10.35	10.23	1
Turbidity	1.28	0.97	24
Conductivity	10.4 mS/cm	5.30 mS/cm	49

B-3 Characteristics of LS1 with NF90

Parameter	Feed	Permeate	Rejection (%)
Colour	470	5	99
COD	91	29	68
TOC	43	22	49
TSS	9	2	78
pH	10.35	10.21	0.3
Turbidity	1.28	0.84	34
Conductivity	10.4 mS/cm	76.1 µS/cm	93

B-4 Characteristics of LS2 with UF

Parameter	Feed	Permeate	Rejection (%)
Colour	978	903	8
COD	890	407	54
TOC	204	93	54
TSS	54	23	57
pH	10.50	10.50	0
Turbidity	115	0.87	99
Conductivity	32.4 mS/cm	32.4 mS/cm	0

B-5 Characteristics of LS2 with SR90

Parameter	Feed	Permeate	Rejection (%)
Colour	903	23	98
COD	407	103	68
TOC	93	21	67
TSS	23	7	46
pH	10.50	9.87	6
Turbidity	0.87	0.73	16
Conductivity	21.2 mS/cm	11.5 mS/cm	46

B-6 Characteristics of LS2 with NF90

Parameter	**Feed**	**Permeate**	**Rejection (%)**
Colour	903	7	99
COD	407	84	79
TOC	93	19	70
TSS	23	7	46
pH	10.50	9.73	7
Turbidity	0.87	0.87	0
Conductivity	21.2 mS/cm	3.23 mS/cm	85

B-7 Characteristics of MS with UF

Parameter	Feed	Permeate	Rejection (%)
Colour	1050	970	17
COD	1100	890	19
TOC	102	64	37
TSS	68	8	88
pH	10.80	10.78	0.1
Turbidity	11.4	2.51	78
Conductivity	32.4 mS/cm	32.4 mS/cm	0

B-8 Characteristics of MS with NF90

Parameter	Feed	Permeate	Rejection (%)
Colour	970	21	98
COD	890	58	94
TOC	64	10	84
TSS	8	3	63
pH	10.78	10.34	4
Turbidity	2.51	0.92	63
Conductivity	32.4 mS/cm	11.8	64

B-9 Characteristics of MS with SR90

Parameter	Feed	Permeate	Rejection (%)
Colour	970	193	78
COD	890	64	93
TOC	64	25	61
TSS	8	3	63
pH	10.78	10.23	5
Turbidity	2.51	0.81	68
Conductivity	32.4 mS/cm	16.7 mS/cm	45

B-10 Characteristics of DS using UF

Parameter	Feed	Permeate	Rejection (%)
Colour	14,900	9580	36
COD	4800	1056	78
TOC	570	107	81
TSS	127	70	45
pH	10.27	9.89	4
Turbidity	47.7	3.8	92
Conductivity	122.4mS/cm	120.8 mS/cm	1

B-11 Characteristics of DS with SR90

Parameter	Feed from UF	Permeate	Rejection (%)
Colour	9580	640	93
COD	1056	135	87
TOC	107	61	43
TSS	70	12	83
pH	9.89	9.80	1
Turbidity	3.8	0.89	77
Conductivity	120.8 mS/cm	97.6 mS/cm	19

Appendix C Permeate fluxes for the membrane

Permeate fluxes were calculated using equation 2-3

$$J = \frac{V}{A}.t$$

Equation 0-2

Permeates fluxes from UF membrane

C-1 UF LS 1

Cum.time (min)	Volume(litres)	Area(M^2)	Time(Hr.)	Flux (LMH)
15	1.86	0.040	0.250	187
30	1.78	0.040	0.250	179
45	1.76	0.040	0.250	177
60	1.68	0.040	0.250	169
75	1.56	0.040	0.250	157
90	1.53	0.040	0.250	154
105	1.46	0.040	0.250	147
120	1.46	0.040	0.250	147
135	1.46	0.040	0.250	147
150	1.45	0.040	0.250	146
165	1.45	0.040	0.250	146
180	1.45	0.040	0.250	146

C-2 UF LS 2

Cum Time (min)	Vol. (L)	Area (m^2)	Time (Hr.)	Flux (LMH)
15	1.7	0.040	0.250	171
30	1.56	0.040	0.250	157
45	1.43	0.040	0.250	144
60	1.42	0.040	0.250	143
75	1.42	0.040	0.250	143
90	1.43	0.040	0.250	143
105	1.37	0.040	0.250	138
120	1.36	0.040	0.250	137
135	1.36	0.040	0.250	137
150	1.32	0.040	0.250	137
165	1.28	0.040	0.250	129
180	1.26	0.040	0.250	127

C-3 UF MS

Cum. Time (min)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
15	1.65	0.040	0.250	166
30	1.48	0.040	0.250	149
45	1.41	0.040	0.250	142
60	1.4	0.040	0.250	141
75	1.36	0.040	0.250	137
90	1.34	0.040	0.250	135
105	1.34	0.040	0.250	135
120	1.29	0.040	0.250	130
135	1.28	0.040	0.250	129
150	1.27	0.040	0.250	128
165	1.26	0.040	0.250	127
180	1.26	0.040	0.250	127

C-4 UF DS

Cum. time (min)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
15	1.48	0.040	0.250	149
30	1.38	0.040	0.250	139
45	1.34	0.040	0.250	135
60	1.27	0.040	0.250	128
75	1.23	0.040	0.250	124
90	1.17	0.040	0.250	118
105	1.13	0.040	0.250	114
120	1.11	0.040	0.250	112
135	1.09	0.040	0.250	110
150	1.01	0.040	0.250	102
165	0.98	0.040	0.250	99
180	0.91	0.040	0.250	92

Permeates from SR90 without pre-treatment

C-5 SR90 LS 1

Cum Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	110	0.11	0.003	0.5	73
60	93	0.093	0.003	0.5	62
90	84	0.084	0.003	0.5	56
120	72	0.072	0.003	0.5	48
150	58	0.058	0.003	0.5	39
180	54	0.054	0.003	0.5	36

C-6 SR90 LS2

Cum. time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	81	0.081	0.003	0.5	54
60	72	0.072	0.003	0.5	48
90	66	0.066	0.003	0.5	44
120	59	0.059	0.003	0.5	39
150	51	0.051	0.003	0.5	34
180	43	0.043	0.003	0.5	29

C-7 SR90 MS

Time (min)	Volume collected	Vol.(L)	Area (m^2)	Time(Hr.)	Flux (LMH)
30	58	0.058	0.003	0.5	39
60	50	0.05	0.003	0.5	33
90	45	0.045	0.003	0.5	30
120	42	0.042	0.003	0.5	28
150	40	0.04	0.003	0.5	27
180	38	0.038	0.003	0.5	25

C-8 SR90 DS

Cum Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	54	0.054	0.003	0.5	36
60	46	0.046	0.003	0.5	31
90	42	0.042	0.003	0.5	28
120	34	0.034	0.003	0.5	23
150	29	0.029	0.003	0.5	19
180	27	0.027	0.003	0.5	18

Permeates from SR90 after pre-treatment

C-9 SR90 LS 1

Cum Time (min)	Vol.(ml)	Vol.(L)	Area(m^2)	Time (Hr.)	Flux (LMH)
30	120	0.120	0.003	0.5	80
60	98	0.098	0.003	0.5	65
90	86	0.086	0.003	0.5	57
120	72	0.072	0.003	0.5	48
150	66	0.066	0.003	0.5	44
180	60	0.060	0.003	0.5	40

C-10 SR90 LS 2

Cum Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	88	0.088	0.003	0.5	59
60	79	0.079	0.003	0.5	53
90	67	0.067	0.003	0.5	45
120	61	0.061	0.003	0.5	41
150	56	0.056	0.003	0.5	37
180	50	0.05	0.003	0.5	33

C-11 SR90 MS

Cum Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	68	0.068	0.003	0.5	45
60	57	0.057	0.003	0.5	38
90	53	0.053	0.003	0.5	35
120	42	0.042	0.003	0.5	28
150	38	0.038	0.003	0.5	25
180	36	0.036	0.003	0.5	24

C-12 SR90 DS

Cum. Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	58	0.058	0.003	0.5	39
60	54	0.054	0.003	0.5	36
90	46	0.046	0.003	0.5	31
120	39	0.039	0.003	0.5	26
150	29	0.029	0.003	0.5	19
180	26.5	0.0265	0.003	0.5	18

Permeates from NF90 without pre-treatment

C-13 NF90 LS 1

Cum. Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	55	0.055	0.003	0.5	37
60	47	0.047	0.003	0.5	31
90	41	0.041	0.003	0.5	27
120	37	0.037	0.003	0.5	25
150	33	0.033	0.003	0.5	22
180	28	0.028	0.003	0.5	19

C-14 NF90 LS 2

Cum. time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	37	0.037	0.003	0.5	25
60	32	0.032	0.003	0.5	21
90	27	0.027	0.003	0.5	18
120	18	0.018	0.003	0.5	12
150	14	0.014	0.003	0.5	9
180	13	0.013	0.003	0.5	9

C-15 NF90 MS

Cum. Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	24	0.024	0.003	0.5	16
60	17	0.017	0.003	0.5	11
90	14	0.014	0.003	0.5	9
120	13	0.013	0.003	0.5	9
150	13	0.013	0.003	0.5	9
180	12	0.012	0.003	0.5	8

Permeates from NF90 after pre-treatment

C-16 NF90 LS 1

Cum. Time (min)	Vol. (ml)	Vol.(L)	Area(m^2)	Time (Hr.)	Flux (LMH)
30	68	0.068	0.003	0.5	45
60	64	0.064	0.003	0.5	43
90	61	0.061	0.003	0.5	41
120	54	0.054	0.003	0.5	36
150	43	0.043	0.003	0.5	29
180	37	0.037	0.003	0.5	25

C-17 NF90 LS 2

Cum. Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	44	0.044	0.003	0.5	29
60	38	0.038	0.003	0.5	25
90	32	0.032	0.003	0.5	21
120	27	0.027	0.003	0.5	18
150	21	0.021	0.003	0.5	14
180	21	0.021	0.003	0.5	14

C-18 NF90 MS

Cum Time (min)	Vol.(ml)	Vol.(L)	Area (m^2)	Time (Hr.)	Flux (LMH)
30	31	0.031	0.003	0.5	21
60	23	0.023	0.003	0.5	15
90	21	0.021	0.003	0.5	14
120	19	0.019	0.003	0.5	13
150	18	0.018	0.003	0.5	12
180	17	0.017	0.003	0.5	11

Appendix D Photographs of fouled membrane and permeate samples

The photographs below sow the sample of feed before filtration and after filtration. The photographs the NF membrane sheets are shown before the filtration with dyes as well as after filtration. Permeates from UF membranes are not shown here because most of them were visually still coloured. The pieces of dyed fibre are also shown.

Figure D-1 DS feed and NF membrane permeates

Figure D-2 MS feed and NF permeates

Figure D-3 LS1 feed and NF permeates

Figure D-4 LS2 feed and NF permeates

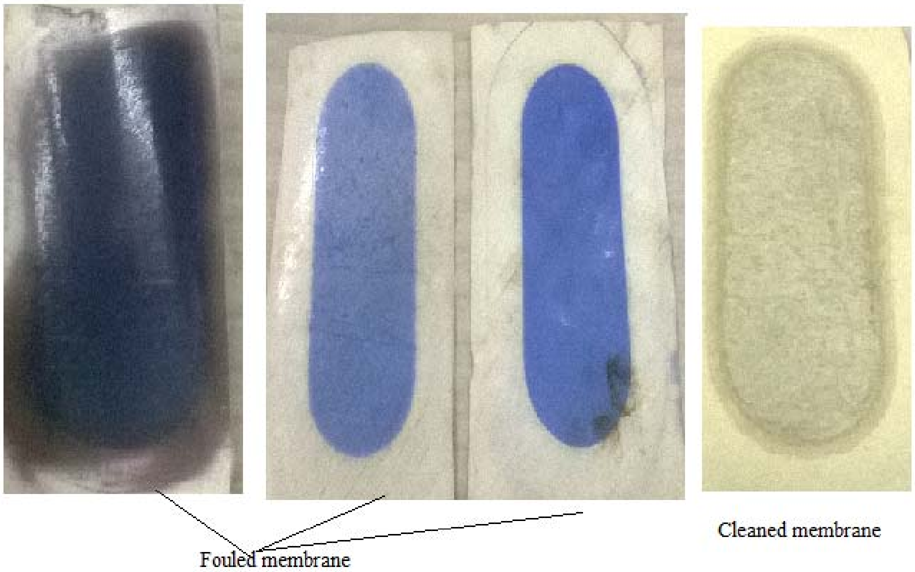

Figure D-5 Fouled and chemically cleaned membrane

Figure D-6 Dyed pieces of fibres