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FORWARD OSMOSIS: A DESALINATION TECHNOLOGY FOR THE TEXTILE INDUSTRY

by

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DECLARATION

I, **Estella Zandile Jingxi**, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

ABSTRACT

Similar to the energy crisis, the critical state of the water supply in South Africa (SA) is a combination of (i) resource exhaustion and pollution; (ii) increasing demand; and (iii) poor infrastructure. Despite its importance, water is the most poorly managed resource in the world. The disposal of industrial effluents contributes greatly to the poor quality of water. The textile industry consumes great quantities of water and produces enormous volumes of wastewater which requires appropriate treatment before being released into the environment. In an attempt to address the water issues, research globally has focused on advanced technologies such as desalination to increase limited pure water resources. The need for alternative desalination methods for the production of clean water from alternative water resources, such as seawater and brackish water, has gained worldwide attention. Reverse osmosis (RO) and Nanofiltration (NF) have been used as unswerving approaches to yield freshwater. Forward osmosis (FO) is a developing membrane technology that has increased substantial attention as a possible lower-energy desalination technology. However, challenges such as suitable FO membranes, membrane fouling, concentration polarisation, and the availability of effective draw solutions (DS), limit FO technology. FO is seeking more importance in novel areas where separation and recovery of the DS is not required.

The aims of this study was to: i) identify alternative water resources and evaluate their potential as suitable feed solution (FS); ii) Identify dyes and evaluate their potential as suitable draw solutions (DS) at different concentrations; iii) assess the use of aquaporin biomimetic membrane and iv) assess a FO system for the production of dye solutions.

Osmotic pressure (OP) is the pressure exerted by the flow of water through semi-permeable membrane, separating two solutions with different concentrations of solute. The DS should always have OP higher than the FS in order to achieve high water flux. Three basic dyes (i.e. Maxilon Turquoise, Red and Blue) and three reactive dyes (i.e. Carmine, Olive Green and Black) were selected, based on their common use in the SA textile industry. The respective dye samples were prepared at different concentrations and dye-to-salt mass ratios ranging from 1:10 to 1:60 and assessed for OP using a freezing point osmometer. A lab-scale FO unit was used for all the studies. Feed and draw channels were circulated in a counter-current flow at a volumetric flow rate of 600 mL/min. Feed solutions(FS) included deionised water (DI) as a control, brackish water (BW), synthetic seawater (SSW) and textile wastewater (TWW) collected from two textile factories. OP of the FS (DI, BW5, SSW and SW, Factory 1 and Factory 2) was 0, 414, 2761, 2579, 1505 and 3308 kPa, respectively. Basic Blue and Reactive Black generated a higher OP compared to other selected dyes in the study and were therefore selected to be used as DS at a 1:10 dye-to-salt ratio and 0.02 M concentration. An aquaporin biomimetic FO membrane (Aquaporin, Denmark) was used for all the experiments conducted in the FO mode.

In assessing FO for the production of a dye solution, at a target dye concentration, which is the concentration at which the dye solution was produced, two controls were performed. Control 1 was an experiment with DI as a FS and Reactive Black as a DS and control 2 was an experiment with DI is a FS and Basic Blue a DS. The total amount of water permeated through the membrane from FS to DS per unit time which is referred to as feed recovery rate for control 1 and control 2 was at 60 and 45%, respectively at reaching target concentration, while at osmotic equilibrium a feed recovery rate of 95 and 80% was achieved, respectively. The initial fluxes for the two control experiments for the target dye concentration were 16.18 and 19.73 L/m^{2}h respectively. The reverse solute flux (J_s) in FO refers to the diffusion of solutes from a high-concentration draw solution (DS) to a low-concentration feed solution (FS). At equilibrium the J_s was 6.74 and 1.08 g/m^{2}h for Control 1 and Control 2, respectively. The study of SSW and Reactive Black generated a driving force (osmotic gradient) of 13658 kPa and a 20.24 L/m^{2}h initial water flux was achieved, with flux decline to 5.22 L/m^{2}h at target concentration, achieving a 75% feed recovery rate. For the studies between TWW as a FS and Reactive Black as a DS, an initial water flux of 19.51 and 13.43 L/m^{2}h was achieved for TWW from Factory 1 and Factory 2 respectively, and a 30% feed recovery rate was achieved at target concentration. For the studies between SSW and Basic Blue, an osmotic driving force of 6962 kPa with an initial water flux of 18.72 L/m^{2}h and a 50 % feed recovery rate was generated. In the studies involving TWW as a FS and Basic Blue as a DS, initial water flux of 15.13 and 13.42 L/m^{2}h was achieved for TWW from Factory 1 and Factory 2, respectively; and a 20 % feed recovery was achieved at reaching target concentration. It was noted that the colour concentration on the DS dropped due to the water transportation from FS to the DS, but the colour concentration on the FS increased with progression of time and this was referred to as reverse flux. The averaged reverse solute permeation for the studies between Reactive Black and the FS was found to be ranging from an initial of 47.30 to 104.94 g/m^{2}h at target concentration and was evidenced by the Hazen Colour test, while for the studies conducted between Basic Blue and the FS ranged from 0.25 to 21.02 g/m^{2}h.

This study contributes to the FO technology by addressing one of the challenges faced in FO technology, which is identifying suitable draw solution. To this end, the potential of dyes as such a draw solution was tested.

Research outputs

The following outputs are the contributions made by the candidate towards scientific knowledge during her Masters candidacy:

Publication

Sheldon,M.S., **Jingxi, E.Z.**, De Jager, D., Augustine, R., Korenak, J Helix-Nielsen, C & Petrinic' I. 2017. Forward osmosis in a South African context: Part A: Dye solutions as draw solutions in the textile industry. *Water SA 3477.* Under review

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Poster

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DEDICATION

I would like to dedicate this thesis to my late mother, Lizeka Nozolile Jingxi, who has always been my source of strength, my biggest fan and my lifelong cheerleader. Gone too soon but never forgotten. To her, education has always been a priority and it has always been her dream to see her children succeed academically. Without a doubt she would be the proudest woman in the entire world for this work, *sithi Lala ngo xolo Xesi*.

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SYMBOL	EXPLANATION
Cf,f	Feed salt concentration final
Cf,i	Feed Initial salt concentration
c_2	Solute concentration (mol/L)
i	Van 't Hoff's solute factor (dimensionless)
J_s	Reverse solute flux ($kg.m^{-2}.s^{-1}$)
J_w	Experimental water flux ($L.m^{-2}.s^{-1}$)
L	Litre (m)
k	Conductivity (mS/cm)
M_w	Molecular weight ($g.mol^{-1}$)
mS	Mili Siemen
m_2	Solute molal concentration (mol /L)
m'_2	Volume molal concentration (mol / L)
N	Moles (mol)
R	Universal gas constant ($m^3.Pa.mol^{-1}.K^{-1}$)
T	Temperature (K)
V	Volume (m^3)
Vf,i	Feed volume initial
Vf,f	Feed volume final

Greek symbols

Π	Osmotic pressure (kPa)

GLOSSARY

Word	Definition
Draw solution (DS)	Highly-concentrated solution (Zhao *et al*., 2012).
Feed solution (FS)	The solution of low-concentration (Zhao *et al*., 2012).
Forward Osmosis (FO)	A developing technology for desalination which consumes low energy and uses the change in the osmotic pressure to push the solvent from a state of lower solute concentration to that of higher solute concentration, through a semi-permeable membrane (Nicoll, 2012; Zhao, *et al.*, 2012).
Internal Concentration Polarisation	the emergence of concentration gradients at a membrane/solution interface resulted from selective transfer of some species through the membrane under the effect of transmembrane driving forces (Zhao, *et al.*, 2012)
Membrane Technology	Separation process of two solutions by making use of the semi-permeable membrane (Plannekamp & Frieldrich, 2003).
Osmotic Pressure (OP)	Pressure applied by water flow across a semi-permeable membrane that divides the two solutions (Kutchai, 2003).
Recycle	Process of changing waste material in order to produce a new product (Carl, 2005).
Flux	The quantity of permeate collected over time (i.e. flow rate) for a given membrane area, hence a flow density by dimension (Boddeker, 2007)

ABBREVIATIONS

Abbreviation	Explanation
As	Arsenic
ABMS	Aquaporin Biomimetic Membranes
ABPMS	Aquaporin-based Biomimetic Polymeric Membrane
AOSB	Atlantic Ocean Seaboard
AQP	Aquaporin
AQPZ	Aquaporin Z
BW	Brackish Water
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
Cu	Copper
CP	Concentration Polarisation
C&T	Clothing & Textile
CTA	Cellulose Triacetate
Cr	Chromium
D	Dialysis
DI	Deionised water
DS	Draw Solution
EC	Electric Conductivity
FS	Feed Solution
FO	Forward Osmosis
GS	Gas Separation
HPLC	High Performance Liquid Chromatography
ICP	Internal Concentration Polarisation
IOSB	Indian Ocean Sea Board
MF	Micro Filtration
MW	Molecular Weight
MO	Methyl Orange
NF	Nano Filtration
Ns	No salt
OP	Osmotic Pressure
PI	Potassium Indigo trisulfonate

PFD	Process Flow Diagram
RR	Remazol Red
RO	Reverse Osmosis
SA	South Africa
SANAS	South African National Accreditation Systems
SW	Seawater
SSW	Synthetic Seawater
SS	Suspended solids
SWRO	Seawater Reverse Osmosis
TFC	Thin Film Composite membrane
TWW	Textile Waste Water
TDS	Total Dissolved Solids
UF	Ultra filtration
VRF	Volume reduction factor
Ws	With salt
Zn	Zinc

CHAPTER 1

CHAPTER 1

INTRODUCTION

1.1 Background

The scarcity of resources in South Africa (SA) means that there are significant trades-offs between food, energy and water. Water is the most significant resource constraint, since SA is a water-scarce country that experiences enormous dissimilarities in sequential and spatial distribution of rainfall (Von Bormann & Gulati, 2014). Water is a requirement for the production of food and quantity of water that is required is gigantic (Von Bormann & Gulati, 2014). It is a significant contribution in manufacturing of manures and farming chemicals, growing crops, raising livestock and accessing marine food resources (Besade & Werner, 2015). Water is also a precondition for production of energy and supplying water systems consume energy for all the stages of the water production and supply chain process, which includes water abstraction, treatment and distribution to end-users, wastewater reticulation and treatment (Von Bormann & Gulati, 2014; Besade & Werner, 2015).

The extent of water scarcity within SA has affected the economy of the country considerably, since the economy of any state is mostly centred on resources such as food, water and energy. Innovative techniques need to be established to resolve the stresses on these key resources (Von Bormann and Gulati, 2014). South Africa, and particularly the Western Cape, is highly industrialised and is experiencing a water scarcity crisis.

Various methods of treatment have been used for the treatment of wastewater from industries. One such industry is textile dyeing, which consumes substantial quantities of potable water, while producing enormous volumes of wastewater, which is ecologically detrimental. The wastewater that is produced from the printing and dyeing sectors is normally strong in colour, with deposits of responsive dyes and chemicals, and therefore have need of an appropriate treatment method before being discharged into the environment (Chougule & Sonaje, 2012). The current methods for the treatment of textile wastewater are biological, physiochemical and filtration-based. Biological treatments are effective in reducing chemical oxygen demand (COD) but fail to decolourise the wastewater, while the physiochemical treatment and filtration treatment methods behave like oxidation processes decolourisation of textile wastewater (Han *et al*., 2016).

The necessity for the improvement and development of technologies to utilise other water resources, such as seawater and brackish water desalination, as well as wastewater recovery, has gained worldwide attention. Desalination is one of the technologies used for treating alternative water resources (Liu, 2013; McGovern & Lienhard, 2014) and such a process should consume significantly less energy and yet produce large volumes of water. Membrane processes, like reverse osmosis (RO) and nanofiltration (NF) have been used as reliable methods to produce freshwater from alternative water resources (McGovern & Lienhard, 2014). The ultrafiltation (UF), NF and RO are potential technologies for the treatment of textile wastewater (TWW) but the rejection of UF membranes in low molecular weight (Mw) dyes is inefficient (Han *et al*., 2016). Forward osmosis (FO) is a developing membrane process that is under examination for providing improved water production (Phuntsho, 2012). FO has great potential in the treatment and reuse of impaired water streams (Han *et al*., 2016). FO technology has the capability to play a most important role in resolving the water scarcity and energy issues, not only in SA but globally, since this technology has the potential of reducing energy consumption during wastewater treatment and has attracted more interest in novel areas where separation and recovery of the draw solution (DS) is not required (Phuntsho, 2012; Liu, 2013; McGovern & Lienhard, 2014; Han *et al*., 2016).

1.2 **Problem statement**

FO technology is challenged with scarcity of effective DS for desalination and DS recovery and re-concentration.

1.3 Research questions

- Can concentrated dye solution be used as a DS?
- Can FO be used to produce a dye solution?
- Can the textile wastewater be re-used in the process of producing a dye solution?
- How does the dye solution produced from the FO process compare to the solution produced using potable water?
- Will the application of FO be successful in the textile industry?

1.4 Aims and objectives

The aim of this research project was to evaluate and critically assess the FO technology in the application of producing dye solutions using alternative water resources.

The objectives of this research study were to:

- Identify alternative water resources and evaluate their potential as suitable feed solutions (FS).
- Identify dyes and evaluate their potential as suitable draw solutions (DS) at different concentrations.
- Construct, commission and assess a FO system for the production of dye solutions using alternative water resources, as well as reclaimed textile wastewater.

1.5 Delineation

This research project did not focus on:

- Fouling;
- The modelling of the water transport across the membrane.

1.6 Significance of the study

The significance of this research project is developing a new application of the FO membrane technology. It will contribute towards developing potential feed solutions and draw solutions to the FO technology. This project will be embracing FO technology to improve and add value to the textile industry by assessing the FO technology for production of dye solution and channelling the textile wastewater to be the feed solution.

CHAPTER 2

CHAPTER 2
LITERATURE REVIEW

2.1 The water and energy crisis in South Africa

In the past years, energy prices have more than doubled and a shortage of power has the net outcome of compromising the whole water services value chain, in which water plays a major part in the electricity value chain (Sparks *et al.,* 2014). The relationship amongst water and energy is intimate, with the utmost level of co-dependency (Sparks *et al.,* 2014; Von Bormann & Gulati, 2014). Load-shedding has been a critical challenge in SA over the past years, and water-shedding is an even more challenging issue. Similar to the energy crisis, the critical state of the water supply in SA results from a combination of at least three factors: (i) increasing demand (ii) resource exhaustion and pollution, and (iii) ineffectual infrastructure (Besade & Werner, 2015). Rainfall levels are reducing swiftly due to climate change. Many dams and rivers across the country have low water levels due to prolonged drought. During the December 2015 summer holidays, the eThekwini municipality took the unexpected step of requesting citizens and tourists to considerably lessen their water use to avoid universal cutbacks (Fioramonti, 2015). Additionally, level five water restrictions were instituted by the City of Cape Town on the 3rd of September 2017, and this involved a prohibition on all use of potable water for outside and non-essential purposes. This resulted from the repeated failure of the city's populace to reach the intended 2017 water savings target of 600 million litres of collective water use per day (Etheridge, 2017).

It has been anticipated that SA will face severe water deficiencies by 2020 (Fioramonti, 2015). In 2014, the Department of Water and Sanitation reported that 37% of SA's potable water was lost through pipe leaks, dripping taps and other infrastructure inadequacies. SA is already using 98% of its available water supply and 40% of its wastewater treatment is in a critical state (Fioramonti, 2015).

The common causes that bring about the shortage of water and energy supply include (Von Bormann & Gulati, 2014):

- Population growth: Statistics have shown that SA's population has developed by 25% from 2000 to 2013, and the population is estimated to be 55, 9 million by the end of June 2016 (Statistics SA, 2016).

- Increasing affluence and urbanisation is placing extra pressure on the sources of energy and water, as more societies depend on purified tap water, with minimum people depending on and/or using rainfall and solar energy.
- Availability of cultivable lands: About 13% of land in SA is appropriate for crop production, with most of that only having low production potential. Only 3% is regarded to be high potential land.
- Soil degradation: Water contamination, deforestation which causes soil erosion, waste disposal and over-exploitation of the land contributes immensely to soil degradation.

The consequences of both water and energy supply shortages include (Kafeero, 2007; Eichelberger, 2010; Von Bormann & Gulati, 2014):

- Droughts; famine; extinction of animal species; adverse impact on aquatic life; load-shedding and change in lifestyle.

In SA the water shortage, the level of water scarcity and deteriorating water quality is a major challenge. Advanced technological processes have been implemented for the treatment of wastewater produced during industrial activities. The purpose of re-use, recycling and reclamation water strategies is to relieve the strain on energy supplies (Kafeero, 2007; Segal, 2009).

2.2 South African textile industry and water usage

The clothing and textile (C&T) industry is a very broad industry in terms of raw materials, processes, products and equipment, with a complex industrial chain. It is one of the leading and oldest industries and considered vital to many developing countries. Even though there is a great diversity of developments and skills within the textile industry, this sector can be divided into dry and wet processing (Chougule & Sonaje, 2012). Dry processing consists of yarn manufacturing, fabric weaving and knitting, whereas wet processing includes preparation, dyeing and finishing (Chougule & Sonaje, 2012).

The textile industry can be categorised into three classes, namely cotton, wool and synthetic fibres, each category based on the raw materials used. The dyes are mainly fragrant, and sweet-smelling and consist of six carbon ring compounds, with colour-display and polar groups (Wang *et al.* 2010). These dye structures are complex and stable, resulting in greater difficulty in the process of degrading dye in wastewater. The textile industry is categorised as one of the major threats to the environment (Wang *et al.,* 2011; Ananthashankar, 2013).

Attention paid to environmentally-friendly textile dyeing techniques has increased recently, due to environmental campaigns that have increased worldwide (Ananthashankar, 2013). The textile industries use extensive amounts of water and toxic compounds in the wet dyeing processes. It is estimated that about 80 to 150 m^3 of water is used to make 1 kg of fabric and about 1,000-3,000 m^3 of wastewater is generated after processing about 12 to 20 tons of textiles per day. These toxic compounds include chemicals, polymers and organic products, which are used in different processes, including scouring, bleaching, dyeing, printing and finishing. The products associated with the dyeing process number more than 8 000 and includes the use of acidic, reactive, basic, dispersed and metal-complex dyes (Babu *et al*., 2007; Truett & Truett, 2010; Ananthashankar, 2013).

The SA textile industry (incorporating both textiles and clothing) is the 6th leading manufacturing sector employer and the 11th largest manufactured goods exporter. The SA government considers textiles and apparel to be a very important part of the economy (Truett & Truett, 2010). The SA textile industry is the 2nd largest user of electricity and the 2nd major payer of rates and taxes (Gravelet-Blondin *et al*., 1997). Over the past years the SA textile industry has been deteriorating, with the lowering of textile tariff rates and the industry becoming increasingly exposed to international competition. With the introduction of the environmental management standard ISO 14 000, it has been increasingly difficult to export goods to the European Union and North America unless the textiles are manufactured in accordance with the environmental legislation.

In addition to this international trade pressure, the industry is also faced with increasing pressure from local authorities to reduce their environmental impact due to limited water resources within SA. Among industrial wastewaters produced in SA, textile wastewaters are reflected to be one of the most problematic in certain parts of the country, especially in terms of colour, COD, salinity and TDS (Gravelet-Blondin *et al*., 1997). The textile industry not only consumes enormous capacities of water, but it produces massive volumes of toxic, highly coloured water with low levels of biodegradability, which requires appropriate treatment (De Jager *et al*., 2012; De Jager *et al*., 2014).

The environmental difficulties in the SA textile industry are mostly connected to liquid wastewater. Water consumption and wastewater production differ from one factory to the other, provisional to the point of integration, type of fibre processed, number of operations, type of dyestuff used, method of dyeing and, lastly, type of equipment at hand. The dye house wastewaters are multifaceted, comprising an extensive and diverse range of dyes and other products such as acids, levelling agents, dispersants, salts and sometimes heavy metals (Gravelet-Blondin *et al.,* 1997; De Jager *et al*., 2012; De Jager *et al*., 2014). It is of utmost importance to encourage industries to reduce water consumption, recycle and re-use water and wastewater where possible (Gravelet-Blondin *et al.,* 1997).

2.3 Characteristics and composition of textile wastewater

In the textile industry, the wastewater that is released contains dyes and toxic chemicals which harm the environment. The textile wastewaters are extremely coloured wastewaters contaminated with high concentrations of dyes, textile auxiliaries, pigments, heavy metals and other toxic chemicals that are resistant to biological treatment methods. It also contains a variety of impurities such as salts, enzymes and surfactants (De Jager *et al*., 2012; Ananthashankar, 2013). The level of toxicity is dependent on the industry and the product produced. In any procedure of dyeing, there is a highly concentrated amount of unfixed dye that is carried away with water and these characteristics differ between textile industries (Chougule & Sonaje, 2012). The normal daily textile dyeing and finishing operations vary considerably, to the extent that the dyestuff used in a mill can vary from day to day and sometimes several times a day as the dyeing processes are batch processes (Ananthashankar, 2013). The constant changing of the dyestuff used in the dyeing processes leads to variations in the wastewater characteristics, particularly pH, colour and COD, biological oxygen demand (BOD) and salinity. The strong colour and high turbidity of the wastewater is caused by the combination of the strong colour of the textile wastewater and high dissolved solid content. Table 2.1 illustrates the characteristics and effects of the textile wastewater (Wang *et al*., 2010; Buthelezi *et al.*, 2012; De Jager *et al*., 2012; Ananthashankar, 2013).

Table 2.1: Characteristics and effects of textile wastewater (Wang *et al*., 2010; Buthelezi *et al.*, 2012; De Jager *et al*., 2012; Ananthashankar, 2013).

Characteristics	**Effects**
High amounts of agents.	Damage to the environment and human health including suspended and dissolved solids
Unpleasant Odour.	Health risks.
Unpleasant Colour.	The ratio of BOD/COD are frequently found to be around 1:4, which indicates the presence of non-biodegradable substances.
Trace elements i.e. copper (CU), zinc (Zn), Chromium (Cr) and arsenic (As), etc.	Capable of harming the environment and blocking the penetration of sunlight to water surfaces.
Toxic, low biodegradable and highly coloured.	Destroy the natural water environments.
Non-Biodegradable organic substances and inorganic chemicals e.g. dyes, pigments, salts, heavy metals and enzymes.	These results in suspended solids, high temperature, fluctuating pH and a strong colour of wastewater.
Solid waste.	This may result in anaerobic sludge layers in receiving streams.
High concentration of organic salts, acids or alkali.	Will cause the receipt water inappropriate for most industrial and municipal purposes.
Organic compounds with high BOD.	Will result to anaerobic state in natural water sources results to death of the aquatic life.

2.4 Membrane technologies

Membrane processes are one of the growing and fascinating technologies used for desalination and wastewater treatment and they play a substantial role in water and energy sustainability. Membrane technology involves separation of substances with the membrane operating as a filter (Pinnekamp & Frieldrich, 2003; De Jager *et al.,* 2014; Le & Nunes, 2016). In the treatment of wastewater, membrane technology can be combined or used concurrently with other techniques. Membrane technologies have been widely applied in the water sector, with a focus on the treatment of wastewater and the desalination of brackish water and seawater. Membrane technologies are recognised as economical and efficient techniques for the treatment of wastewater (Strathmann *et al*., 2006). On the other hand, Le and Nune (2016) argue that these technologies require improvements in terms of cost and affordability, energy consumption and expertise and to achieve these improvements, advances in membrane materials are needed. Membrane technologies are well recognised for their advanced purification effectiveness through the broad retention of particles and bacteria. Membrane technologies demonstrate significant potential in the treatment of textile wastewater, as they have the potential to eliminate the dyestuff, allowing reuse of the auxiliary chemicals used for dyeing. Membrane processes also distillate the dyestuffs and auxiliaries producing purified water (De Jager, *et al*., 2014). Membrane technologies include micro-filtration (MF), ultra-filtration (UF), nanofiltration (NF), reverse osmosis (RO), membrane bioreactors (MBR) and a developing membrane technology, forward osmosis (FO) (Pinnekamp & Frieldrich, 2003; Strathmann *et al*., 2006; De Jager *et al*., 2012; De Jager *et al*., 2014; Le & Nunes, 2016). Some of the membrane technologies are applied in industries and these include RO, wastewater treatment by MBR and membrane-based fuel cells. The membrane technologies not only address water and energy shortage but meet sustainable criteria in ways of environmental effects, land practice, ease of use, flexibility and adaptability (Le & Nunes, 2016).

2.4.1 Micro- and Ultra-filtration (MF and UF)

MF and UF are both under pressure-driven membrane processes. The separation mechanism used by these two processes is comparable and the fields in which they are applied may resemble one another (McGovern & Lienhard, 2014). The operation mode of these two processes can be either in cross-flow or dead-end. The difference between MF and UF is the operating pressure and pore sizes. MF, with pore sizes of 0.003 to 10 microns, operates between 0.1 to 3 bars, while UF, with pore sizes of 0.002 to 0.1 microns, operates between 0.5 to 10 bars. MF and UF are used in wastewater treatment for separation purposes and for the retention of constituents in the emulsified wastewater (McGovern & Lienhard, 2014; De Jager *et al*, 2014). In municipal wastewater treatment, MF and UF are used for separating the sludge and water fractions (Pinnekamp & Frieldrich, 2003; Strathmann *et al*., 2006; Fersi & Dhahbi, 2008; McGovern & Lienhard, 2014; De Jager *et al.*, 2014).

MF has extensive applications in modest dead-end filtration for water filtration, sterile bottling of fruit juices, wine and sterilized uses in the pharmaceutical industry (Pinnekamp & Frieldrich, 2003). MF has an enormous market in cross-flow filtration, which includes wine production, milk de-fatting and brewing (Fersi & Dhahbi, 2008). UF is used for the elimination of emulsified oils, metal hydroxides, emulsions, dispersed material, suspended solids (ss), viruses, bacteria and other large molecular-weight materials from water (McGovern & Lienhard, 2014). In addition, UF is used in oil and water separation, potable water production, fruit juice clearing; paint filtration and wastewater reuse (Pinnekamp & Frieldrich, 2003; Strathmann *et al*., 2006; Fersi & Dhahbi, 2008; McGovern & Lienhard, 2014).

Fersi and Dhahbi (2008) treated textile plant wastewater with UF and NF for water reuse, where UF was used as a pre-treatment stage for the NF process. An evaluation between direct NF and UF/NF combined performances was conducted by Fersi and Dhahbi (2008). The outcomes from the experimental work illustrated that the UF/NF combination enhanced the textile permeate quality by amassed retention values. The colour retention was 95%, conductivity and total dissolved salts (TDS) retentions approximated to 80% and the bivalent ions retention values exceeded 95%, while with direct NF, the permeate flux was constant while waiting for the volume reduction factor (VRF) to reach 1.35. After combining UF with the NF process, a stable permeate flux was observed until the VRF of 2.77 was reached. These results indicate that using UF as pre-treatment for NF enhances the competence of textile wastewater treatment by increasing the membrane run-time (Fersi & Dhahbi, 2008).

De Jager *et al.* (2014) conducted a study for colour removal from textile wastewater using a pilot-scale dual stage membrane bioreactor (dsMBR) system that incorporated two UF side stream membrane modules. The residual colour and remaining suspended solids in the UF permeate were treated with NF and RO. The objectives of the study were met by taking hydraulic retention time (HRT) of both UF-dsMBR and RO pilot plants while operating the RO system using the RO membrane. The HRT samples showed the removal of above 80% for the parameters measured and met the South African National Standards (SANS) drinking water specification of 241-1:2011. Overall colour removal competences of 99.1% and 90.4% were recorded for the dark and light HRT samples (De Jager *et al.,* 2014).

2.4.2 Nano-filtration (NF)

NF is a membrane process that is mainly utilised in the reprocessing of watery solutions. This technique is normally operated between UF and RO systems (Plannekamp & Frieldrich, 2003). A cross flow operation is employed in this process, with the operating pressure between 2 to 40 bars. The pore sizes for NF range from 1 to 5 nm (Shon *et al.*, 2013). This technique has only been applied in industrial wastewater treatment for the (i) textile and (ii) paper and pulp industries, where it was used to remove colour in the wastewater (Dashtpour & Al-zubaidy 2012). It has also been applied in separation of high molecular weight components from low molecular weight components in aqueous solutions (Pinnekamp & Frieldrich, 2003; Strathmann *et al*., 2006; Dashtpour & Al-zubaidy, 2012).

De Jager *et al.* (2012) conducted a study that involved a membrane bioreactor (MBR), followed by NF/RO application within the treatment of high-strength textile wastewater. The NF/RO process was used as a subsequent treatment. It was found that after the operation and setup of the UF dual stage MBR, the UF permeate still contained residual dye and salts, and it was of utmost importance to remove those for successful reclamation. The permeate was then treated using an NF/RO system. The system was operated with a NF membrane for four days under the following operating conditions: 13 bar feed pressure, 0.609 bar differential pressure, 950 L/h cross velocity and 11.5 L/m^{2}h average flux. It was observed that the salts were being removed from the permeate and with the NF membrane maximum conductivity and TDS removal achieved were 53% and 54%, respectively. Higher colour removal was obtained with NF, 97.6% than RO, 96.0%, but the RO treatment achieved higher conductivity and TDS removal 91% and 92%, while NF treatment achieved 21.2% and 29%, respectively (De Jager *et al*., 2012).

Effective management and textile wastewater treatment would permit water recycling, decrease contamination of surface waters and minimum bioaccumulation of dyes and other dyeing chemicals within the environment. In textile wastewater treatment, the UF efficiently eliminates particles and macro molecules from the wastewater; however, the removal of polluting substances percentage, such as colour, typically ranges between 31% to 76%. NF separates organic compounds of low molecular weight (<1000 g/mol), divalent salts or large monovalent ions such as hydrolysed reactive dyes and dyeing auxiliaries from textile wastewater. RO eliminates all mineral salts, hydrolysed reactive dyes, chemical auxiliaries, ions and larger species from the wastewater. However, the higher the concentration of salt in the wastewater, the more significant osmotic pressure becomes when using RO membranes and the better the energy requirements (De Jager *et al*., 2014).

2.4.3 Reverse Osmosis (RO)

RO is a pressure-driven membrane process, in which the driving force arises from the alteration of the electrochemical potential on the two sides of the membrane (Strathmann, *et al*., 2006; Mehta, 2015). RO uses a cross flow operation with the operating pressure between 5 to 70 bars. However, in some cases, it can go as high as 120 bar (Pinnekamp & Frieldrich, 2003). RO has a pore size range of 0.0001 to 0.001 micron. RO does not play a significant part in municipal wastewater treatment; however its utmost importance is in the treatment of industrial wastewater. This membrane process is also used in the practice of treatment of landfill leachate and the management of wastewater from textile dying industries (Pinnekamp & Frieldrich, 2003; Strathmann *et al*., 2006; Dashtpour & Al-Zubaidy, 2012; Mehta, 2015).

A study conducted by Greenlee *et al.* (2009) on RO desalination concluded that seawater RO (SWRO) recovery is predominantly limited by an increase in osmotic pressure (OP) and fouling of organic material. The system design consisted of chemical and filtration pre-treatment and one RO stage. A system of brackish water treated with a RO membrane consisted of two RO stages that were in series. The key RO issues include salt precipitation and salt concentrate management. While the RO systems i.e. seawater and brackish have been adequately industrialized to be used in large scale commercial plants, several significant challenges remain (Greenlee *et al*., 2009).

Garud *et al.* (2011) studied the applicability and efficiency of RO systems for treating beverage industry wastewater, distillery spent wash and groundwater treatment, including phenol compound recovery wastewater and SWRO. It is stated that feed water containing suspended particles, organic matter and inorganic salt may deposit on the membrane and cause fouling or damage of the membrane because of applied pressure and particle size. Pre-treatment is then required and will determine the RO efficiency. Hence, RO membrane performance should be evaluated to avoid irreversible damages to the RO membrane. The success of a RO system hinges on the efficiency of a pre-treatment method used (Garud *et al*., 2011).

De Jager *et al.* (2012) reported that the percentage of conductivity and TDS rejection were observed to be extremely low, and then a NF membrane was replaced with the RO membrane. The operating conditions for the RO membrane were adjusted and the feed pressure was 10 bar, differential pressure at 0.0609 bar and average flux at 5 L/m^{2}h. The successive treatment by NF and RO membranes appropriated most of the salts that were remaining in the UF dual-stage membrane bioreactor. The removal efficiencies of conductivity and TDS by the RO membrane were 91% and 91.8%, respectively (De Jager *et al*., 2012).

2.4.4 Forward Osmosis (FO)

FO is a membrane process that uses a porous membrane for effective separation of dissolved solute from water. It is a developing membrane technology for wastewater reclamation and seawater desalination, with established research importance across the world. FO technology has emerged as a strong candidate among potential technologies to mitigate water and energy shortages. FO has the ability to create clean water, and also clean energy, by making use of an osmotic pressure gradient across a semi-permeable membrane as the driving force for water production and power generation. FO needs requires much lower energy to make a net flow of water across the semi-permeable membrane, compared to traditional pressure-driven membrane processes such as RO. The semi-permeable membrane acts as a wall that permits water to pass through and discards substances such as salts or unwanted elements. FO processes take place only if there is a semi-permeable membrane separating the feed from the DS and there is an osmotic pressure difference across the membrane (Chung *et al.*, 2012). The feed solution (FS) is the solution with the low concentration while the draw solution (DS) is the solution with the higher concentration. The FS and DS are separated by a semi-permeable membrane. The pure water is transported from the low concentrated FS to the highly concentrated DS, because of the OP difference generated across the membrane. The OP of the DS must be higher than that of the FS. Techniques that are energy efficient are used to draw pure water from DS. The most expensive stage in FO desalination process is the regeneration of the DS (Lin & Cheng, 1995; Zhao *et al*. 2012; Zhao *et al*., 2015; Mehta *et al*., 2014).

2.5 Forward Osmosis Technology

Current research in this technique focuses on the development of new membranes, fouling mechanisms, optimising the DS and characterisation of fouling behaviour. FO is appropriate for application in many areas, as it is described as a technology that uses low energy which can be supplied by resources that are renewable (Cath *et al*., 2006; Salter, 2006; Wang *et al*., 2012; Phuntsho *et al.,* 2012; Zaviska & Zou, 2014).

2.5.1 The FO process operation

Figure 2.1 illustrates the FO process with OP difference between the DS and FS. On stage one the water levels are equivalent, and there OP is at a maximum since there is zero hydrostatic pressure working against the OP. As a result, there is a movement of water (indicated by the arrow) through the porous membrane (indicated by the dotted line), moving from the low OP compartment into the higher OP compartment. During the stage 2 of the process, the low OP compartment, consisting of the aqueous solution, has been concentrated and the aqueous solution that is in the higher OP compartment has been diluted due to the movement of water. In addition, the water flow into the higher OP compartment has resulted in high water levels that result in an opposing hydrostatic pressure (Achilli *et al*., 2010; Zhao *et al*., 2012a; Motsa *et al.,* 2014; McGovern & Lienhard, 2014). Consequently, the overall driving force decreases, thus decreasing the movement of water through the semi-permeable membrane. During the third stage of the process, the OP difference decreases and is equal to the opposing hydrostatic pressure. Hence, the overall driving force disappears, thus stopping the flow of water (Achilli *et al.,* 2010; Motsa *et al.,* 2014).

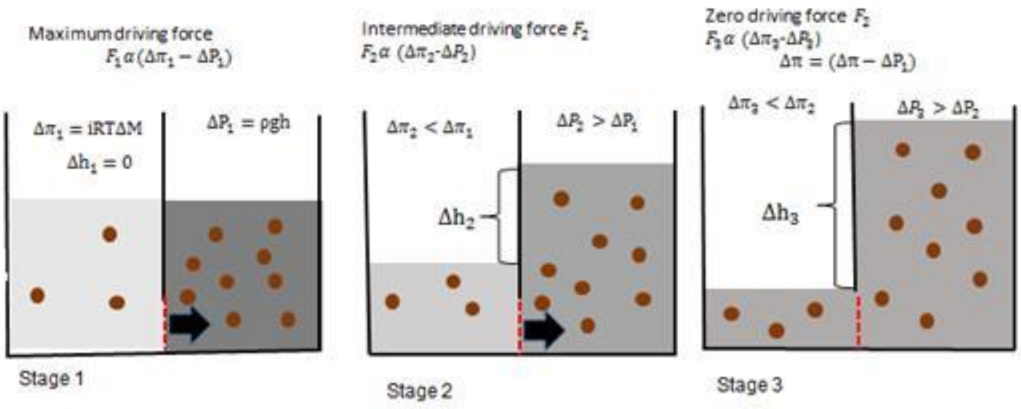


Figure 2.1: Diffusion of water molecules from the feed solution (FS) to the draw solution (DS) via osmotic pressure (OP) (Woode*,* 2013)

2.5.2 The Feed Solution (FS)

The FS is referred to as the solution that has the lower OP. The FS must have a lower OP than the DS so that water can be withdrawn from the FS. The FS permeates through the semi-permeable membrane (Achilli *et al*., 2010) and deionised water (DI) is mostly used as a FS on control experiments for comparative studies (Archili *et al.,* 2010; Phunthso *et al.,* 2011; Phuntsho, 2012; Zhao *et al.,* 2015b).

2.5.3 The Draw Solution (DS)

The DS is referred to as a solution that has a higher OP. To identify a suitable DS, certain characteristics are considered (Wang *et al*., 2012; Chung *et al.*, 2012; Shaffer *et al*., 2015; Akther, *et al.,* 2015; Han, *et al*., 2016):

(i) OP must be higher than the FS in order to achieve a higher water flux.
(ii) Easy water separation from the DS.
(iii) The DS should not be toxic and must be chemically compatible with membrane materials.
(iv) Resistance to different pH ranges along with mechanical and performance stability.
(v) Inexpensive.
(vi) Stable.
(vii) Efficient at minimal energy consumption.
(viii) Using simple and efficient techniques, DS must be completely regenerated.
(ix) To limit reverse solute flux through the FO membrane active layer, DS must possess a molecular size that is large enough, yet small enough to be highly mobile and mitigate internal concentration polarisation (ICP).
(x) Minimal reverse draw solute flux, so that there is insignificant diffusion of solutes from a high-concentrated DS to a low-concentrated FS.

Achilli *et al.* (2011) conducted a study on the selection of organic optimal based DS for specific FO applications. A procedure for the collection of optimal DS was used with flat-sheet cellulose triacetate (CTA) FO membrane. The protocol encompassed a process of desktop screening and laboratory analyses and modelling. The screening process performed identified 14 DS as being suitable for FO applications. The 14 DS were then verified in the laboratory to assess water flux and reverse salt diffusion through the flat-sheet cellulose triacetate (CTA) FO membrane. From the DS selection procedure established in this study, it appeared that an expansive variety of DS must be well-thought-out for future FO applications and that magnesium chloride ($MgCl_2$) specifically, should be further investigated for environmental engineering applications. The most widely employed DS for FO investigations are calcium chloride ($CaCl_2$), calcium nitrate ($Ca(NO_3)_2$), sodium chloride (NaCl), and a thermolytic DS based on ammonia and carbon dioxide, similar to ammonium hydrogen carbonate (NH_4HCO_3).

2.5.4 Advantages of FO

The advantages of the FO process in water treatment are as follows (Nicoll, 2012; Zhao *et al.*, 2012; Akther *et al.,* 2015; Han *et al*., 2016):

(i) Low temperature and pressure utilisation.
(ii) Minimal fouling.
(iii) Brine discharge minimisation.
(iv) Low energy consumption resulting in low costs.
(v) High water recovery rate.
(vi) Has the ability to assist in attaining a high-water flux and recover a large volume of water because the OP gradient across the membrane is high.
(vii) Cake layer formation reduced.
(viii) High fouling reversibility.
(ix) Greater rejection of a wide range of contaminants.

2.5.5 Challenges encountered in the FO process

Regardless of the modern developments in FO, there are still numerous challenges that need to be overcome for successful implementation of this technology (Shaffer *et al*., 2015). Challenges that have been reported in the FO process from previous studies include (Chung *et al*., 2012; Phuntsho *et al*., 2011;Zhao *et al*., 2012a; Kim *et al*., 2014; Akther *et al.,* 2015; Nguyen *et al*., 2015; Shaffer *et al*., 2015):

(i) Shortage of an effective semi-permeable FO membrane.
(ii) Scarcity of effective DS for desalination.
(iii) Internal concentration polarisation (ICP).
(iv) DS recovery and re-concentration.
(v) Membrane fouling is a major obstruction in many membrane applications, which compromises process efficiency.
(vi) Reverse draw solute flux (J_s): The reverse solute flux from the draw solution not only reduces the water flux but also increases the cost of draw solute replenishment.

Table 2.2 illustrates the advantages and challenges of FO per application:

Table 2.2: Advantages and challenges in FO applications (Chung *et al.*, 2012; Zhaoa *et al.*, 2012; Akther *et al.,* 2015; Shaffer *et al*., 2015)

Application of FO	**Advantages**	**Challenges**
Desalination	Transportation of water across the semi-permeable. requires low energy consumption.	Ineffective membranes, lack of cost effective DS.
Direct fertigation	Fertilisers are natural DS, diluted DS is useful for irrigation.	Limited application sites.
Osmotic power generation	Seawater is natural DS.	Pre-treatment of seawater and river water.
Osmotic membrane bioreactor	Low fouling and energy consumption.	Need to discover low cost and easy to recycle DS.

2.5.6 Applications of the FO membrane process

The FO process has a considerable extensive variety of applications which include desalination, direct fertigation, and osmotic power generation. However, only a few of these applications have currently been commercialised, such as water treatment (Akther *et al.,* 2015), desalination (Chung *et al.,* 2012) and water substitution (Chung *et al.,* 2012). FO technology can be applied in the above mentioned processes and many more, including emergency drinks; power generation; enhanced oil recovery; produced water treatment; fluid concentration and thermal desalination feed water softening (Cath *et al.* 2006; Salter, 2006; Chung *et al.,* 2012; Zhaoa *et al.,* 2012; Akther *et al.,* 2015; Shaffer *et al.,* 2015).

A study conducted by Han *et al.* (2016) investigated a combination of the FO process integrated with a coagulation/flocculation (CF) stage for potential textile wastewater treatment. In this process, the FO was used to remove water from a wastewater stream and reduce its volume with high water flux, high recovery and low energy consumption fouling. The CF process was used to remove dye from the FO concentrate, with much improved efficiency and reduced dosage. The FO-CF was tested by using a synthetic dye solution of acid, basic and reactive dyes (Indigo Carmine, Alcian Blue and Reactive Black) and using synthetic textile wastewater containing multiple salts. From the FO-CF system it was reported that a great advantage was achieving high water flux, recovery rate and well controlled membrane fouling and minimal environmental impact. An initial flux of 36.0 L/m^{2}h was obtained using (TFC) FO membrane in FO mode operation with dye rejection of 99.9%, where the draw solute (DS) was 2M NaCl and a synthetic textile wastewater with salts and additives was used as a feed solution (FS). The flux was maintained at 12 L/m^{2}h when the recovery rate of wastewater reached 90% (Han *et al*., 2016). Phuntsho *et al*., (2011) investigated the application of the FO technology for desalination of saline water for irrigation, using fertiliser as a DS. The diluted fertiliser DS can be directly applied for fertigation rather than separating the DS from the desalinated water. Common fertilisers were used as the FO DS and the pure water flux and reverse draw solute flux were used to assess their performances. The results indicated that most soluble fertilisers can produce osmotic pressure much higher than seawater (Phuntsho *et al*., 2011; Phuntsho, 2012).

A study by Zaviska and Zou (2014) used a method of modelling to endorse the desalination process by FO as a pre-treatment. The operating conditions were selected by means of modelling and were validated experimentally by using ground BW as FS. Zaviska and Zou (2014) reported a method of optimisation that combined FO and RO membrane processes by modelling results from experimental and theoretical studies. This method has been confirmed that it can be used on large scale, in continuous mode and with different FO hydrodynamic conditions. Zaviska and Zou (2014) confirmed that the modelling approach used for the improvement of the experimental conditions was successful. The modelling results were validated by the application of the FO process on brackish water (Zaviska and Zou, 2014).

Zhao *et al*., (2015) conducted a study on the polyelectrolyte-promoted FO process for dye wastewater treatment, investigating the possibility of using polyacrylamide (PAM) as DS. Reactive Brilliant Red K-2BP was utilised for the synthetic wastewater preparation. A thin film composite (TFC) membrane was used and it was concluded that the FO process treatment of Reactive Brilliant Red K-2BP dye solution was possible, where membrane fouling produced by Reactive Brilliant Red dye solution was insignificant and high dye rejection was achieved.

2.6 Membrane selection

Synthetic membranes are made up of two main geometries:

(i) **Flat sheet**: utilised in the construction of flat sheet, disc, spirally wound, plate and frame modules (McCutcheon *et al*., 2006).

(ii) **Cylindrical**: utilised in tubular, capillary or hollow fibre modules.

The range of membranes used in wastewater treatment is broad. However, most are synthetic membranes and these fall into two categories, namely organic (i.e. polymer) and inorganic. Inorganic materials are advantageous compared to organic, due to their high chemical and thermal stability. The most important class of synthetic membranes are the organic membranes, as they are easier to process and less expensive (Chen *et al*., 2011). Based on structure, the two basic types of membranes are symmetric and asymmetric membranes (Khulbe *et al.*, 2008).

2.6.1 Symmetric membranes

Symmetric membranes are membranes that do not possess a top dense layer, although most of the practically useful membranes are asymmetric. Some membranes have symmetric structures and include (Khulbe *et al.*, 2008):

- Non-porous (dense) symmetric membranes; and
- Porous symmetric membranes.

2.6.2 Asymmetric membranes

Asymmetric membranes are the most common membranes used in industry. The asymmetric membranes are most commonly formed by a phase inversion (polymer precipitation) process. They contain one polymer and consists of two layers: the top layer, which is a very thin dense layer (active layer) and the bottom layer, which is a porous sub-layer (support layer). The top dense active layer manages the performance of the membrane and the porous support layer provides mechanical strength to the membrane. The active layer is thin (from 0.1 to 1 μm) and the membrane resistance to water transport (which is proportional to the dense skin thickness) is much lower and, as a result, water fluxes appear much higher than those through comparable symmetric membranes. Mechanical support is provided by a mesh entrenched in the porous polymer matrix. This allows for a thinner support layer, which results in a decreased occurrence of ICP. The ICP which is reduced leads to a better use of the osmotic driving force, which in turn results in either higher water fluxes or increased recovery (Khulbe *et al.*, 2008). Asymmetric membranes include (Khulbe *et al.*, 2008; Wu, 2015):

- Integrally skinned asymmetric membrane.
- Coated asymmetric membranes.
- Composite membranes.

The top layer and porous sub layer have the same material in the integrally skinned asymmetric membrane. However membranes whereby the top layer material is different from the porous sublayer are reffered to as composite membranes. In composite membrane the material for the top layer and porous sublayer can be selected separately in order to optimise the efficiency of the membrane and that is the advantage that composite membranes have over integrally skinned membranes (Khulbe *et al.*, 2008; Chen *et al.*, 2011; Wu, 2015). Chen *et al.* (2011) compiled a list of commercial membranes in terms of their composition and application and it was noted that most of the membranes are used for filtration processes.

2.6.3 FO Membranes

FO membranes are aimed to be more or less exclusively selective towards water, and that allows them to distinct water from all other contaminants. These membranes are of the asymmetric composite nature and consist of a nanometre-thin rejection layer (typically 100 to 200 nm in thickness) which is attached with a micrometre-sized underlying support layer (typically 100 to 200 μm in thickness), that gives mechanical support and total strength to the membrane material. One of the most important factors that contribute to the success or failure of the application of the FO technology is the selection of the membrane (Woode, 2013). Tables 2.3 to 2.6 show the membranes that have been used in FO.

2.6.4 Ideal FO Membrane

The ideal membrane for the FO process must have the following properties (Chung *et al*., 2012; Wang *et al*., 2012; Shaffer *et al*., 2015):

- Salt retention must be high.
- Water flux must be high.
- Be resistant to chlorine.
- Be resistant to different pH and have a stable performance for long periods.
- High water permeability stability in synthetic DS.
- Completely reject feed and draw solutes.
- Mechanically robust.

2.6.5 Membranes used in forward osmosis applications

FO membranes are divided into three groups which are (Woode, 2013):

- Flat-sheet FO membranes, which are assembled into plate-and-frame (i.e. stacked) or spiral wound modules. One commonly used is cellulose triacetate (Woode, 2013).
- Hollow fibre FO membranes, which are assembled into hollow fibre modules (Woode, 2013).
- Tubular FO membranes, which are assembled into tubular modules (Woode, 2013).

Table 2.3: **Categories of FO membranes** (Woode, 2013)

FO Membrane	Advantages	Disadvantages	Application
Flat-sheet	Simple operation when there is high amount of fouling agents in the waste streams.	Not appropriate for application of high volume of waste.	Water treatment.
Hollow Fibre	Proper for application of large volume because of the high packing density.	Membrane blockages at concentrations of fouling that are low.	Desalination, downstream water processing steps and large water treatment.
Tubular	Simple operation when waste streams contain high amounts of fouling agents.	Thickness of a tube may limit water flux.	Water treatment industry.

2.6.5.1 Thin film composite membrane

Thin film composite (TFC) membranes comprised of more than one polymer layers. In comparison to the integrally skinned asymmetric membranes, TFC membranes have the potential to obtain a high permeation rate and maintain high selectivity (Wu, 2015). TFC membranes consist of three layers namely ultra-thin top layer (01 to 0.3 µm), microporous sub-layer (20 to 50 µm) and a non-woven backing (100 to 200 µm) (Kim *et al*., 2003). The ultra-thin top layer is the selective barrier which is accountable for the separation. The top layer is supported by a micro porous sub-layer; which typically is an MF membrane that provides a suitably even surface to support a defect-free ultrathin top layer. Micro-porous sub-layer is further supported by a non-woven strengthening fabric that provides additional mechanical strength to the composite structure while offering little resistance to mass transport through the membrane. Several techniques used to form the top layer of TFC include: solution casting, *in situ* graft polymerisation and interfacial polymerisation (Wu, 2015). The interfacial polymerisation process is used to prepare the most important TFC membranes where by a highly porous membrane (usually polysulfone) is covered with a polymer or monomer and then reacted with a cross-linking agent. Tables 2.4 and 2.5 illustrate the application of TFC membrane.

A study by Ren and McCutcheon (2014) reports a new commercial TFC membrane for FO that is considered to be an early generation TFC (FO) membrane from Hydration Technology Innovation (HTI). This newly-designed TFC membrane from HTI has been introduced as a commercially-available FO membrane which is made in a continuous process on a 40-inch production line. This TFC membrane inherits the mesh-embedded structure from the cellulose acetate (CA) membrane, but it goes further by possessing a porous support layer that promotes high water flux, low salt crossover and hydrolytic resistance. A comparison between CA and TFC membranes was carried out and it was found that water permeance of the TFC membrane is twice that of CA membrane. For the pre-wetted TFC, the water permeance was reportedly to be almost 50% higher than the virgin TFC and three times that of the CA membrane. In the standard method tests, the two TFC membranes achieved nearly double the level of water fluxes as the CA membrane (Ren & McCutcheon, 2014).

Table 2.4: Comparison of the Membranes used in FO process (McCutcheon *et al*., 2006; Alturki, *et al*., 2012; Phuntsho, 2012)

Parameters	**CTA**	**NF90**	**CTA**	**TFC**	**CTA**	**TFC**	**SWRO***	**NF Membrane**
References	(Alturki *et al.,* 2012)		(McCutcheon *et al.,* 2006)		(Phuntsho, 2012)			
Application	FO		FO		FO			
Material of rejection	CTA	PA	CTA	PA	CTA	PA	-	PA
Material support later	Polyester mesh embedded	TFC polysulfone	Polyester mesh embedded	TFC polysulfone	Polyester mesh embedded	TFC polysulfone	TFC polysulfone	TFC polysulfone
Water permeability A(x10^{-12} ms/Pa)	1.08	4.36	-	-	1.02	5.215	1.87	10
Salt rejection (%)	-	-	>95	<80	93	85.2	99.5	85
Operating conditions	Temperature (FS & DS): 22.5 °C Standard: Milli-Q water pH: adjusted by KOH and HCl;		DS: NH_3-CO_2 and FS: NaCl Heat required: 35 – 40°C Ambient Temp: 15-20°C		membrane Area = 2.00x10^{-3} m^3 Temperature = 25 +-1; Flow rate = 400ml/min pH (FS)= 6.80 – 7			

*SWRO – Seawater Reverse Osmosis

Table 2.5: Comparison of membranes used in FO application, dye wastewater as a FS (Zhao *et al*., 2015a)

Parameters	**Cellulose triacetate**	**Thin Film Composite**
Material of rejection	Cellulose triacetate	Polyamide
Operating pH	3-8	2-12
Zeta potential as a function of pH	-2.1 at pH =6	86 at pH = 6
Membrane thickness (µm)	93	116
Operating conditions	T = 25,35,45 °C; DS: PAM- 20, 30, 40g/l; FS : dye wastewater (0.05g/l)	
Application	Polyelectrolyte-promoted forward osmosis process for dye wastewater treatment – Exploring the feasibility of using polyacrylamide as draw solute	

Table 2.6: **Aquaporin biomimetic membranes for desalination** (Aquaporin (FO Flat Sheet Test Membrane) data sheet 1.8)

Parameters	**Aquaporin biomimetic membrane**
Membrane thickness	110 µm (±15 µm)
NaCl reverse flux	<2 g/m2/hr (H_2O vs 1M NaCl: FO)
Boron Rejection	>70 %
Arsenic rejection	>95 %
Shelf Life	6 months
Operating conditions	Temperature range: 5-50°C Short term exposure: 65°C pH: 2-11

2.6.5.2 Biomimetic membrane

Biomimetic membranes are referred to as efficient membranes, and they are dependent on their complex structures. They follow a certain pattern and consist of (i) surface layer proteins (S-layer), (ii) lipid bilayers, (iii) ionophores, (iv) membrane protein facilitated lipid bilayers and (v) a biological antifouling surface (Shen *et al*., 2014).

(i) S-Layer

Shen *et al*. (2014) refers to a surface layer (S-layer) protein as arrays of proteins that are ordered and gathered on the cell walls of prokaryotic cells externally. The S-layer proteins found in different shapes of arrangements such as oblique, square or hexagonal arrays and form porous membranes with sizes ranging from 2 to 8 nm and porosities from 30% to 70%. The purposes of the S-layer include cell protection, cell adhesion, molecular sieving, and molecule and ion traps (Shen *et al*., 2014).

(ii) Lipid bilayers

The lipid bilayers are responsible for providing a dynamic but stable barrier between extracellular and intracellular compartments of a biological cell. The permeation of small uncharged molecules through a bilayer is described by the solution diffusion model, where molecules must enter the membrane and diffuse through the hydrocarbon section of the membrane in a two-step transport mechanism. This transport is due to a chemical potential gradient (Shen *et al*., 2014).

(iii) Ionophores

Ionophores are macro cyclic peptides that have oxygen atoms or other compatible ligands to provide a binding pocket for a specific ion. When the ion is bound to the ionophore, the ion's charge is delocalised to create a membrane soluble complex, which can diffuse across a bilayer with a maximum turnover rate on the order of thousands per second. The diffusion of molecules across biological membranes can be facilitated by carriers called ionophores residing in the hydrophobic core of the lipid membrane (Shen *et al*., 2014).

2.6.6 Aquaporin biomimetic membrane (ABM)

The water channel proteins with excellent water permeability and solute rejection are referred to as Aquaporins. The high-performance of biomimetic membranes is prepared by aquaporins. Aquaporin biomimetic membranes (ABMs) are made from combining three components: aquaporins (AQPs), which are membrane protein water channels; amphiphilic molecules, in which the AQPs are embedded; and a polymer support structure. The amphiphilic molecules can generally be either lipids or polymers. Due to superior performance in terms of stability and flexibility, block copolymers have been predominantly investigated, resulting in aquaporin-based biomimetic polymeric membranes (ABPMs). Table 2.6 illustrates the parameters for an aquaporin biomimetic membrane (Zhao *et al*., 2012b; Habel *et al.,* 2015).

Zhao *et al*. (2012b) prepared a thin film composite (TFC) ABM using an interfacial polymerisation method, where aquaporins that contains proteoliposomes were added to the m-phenylene-diamine aqueous solution. Control membranes, either without aquaporins, or with inactive (i.e. mutant) aquaporins, were also prepared. The cross flow reverse tests were used to evaluate the separation performance of these membranes. The active ABM achieved significantly high-water permeability (4 L/m^{2}h bar) with comparable NaCl rejection of 97% at an applied pressure of 5 bars. The permeability was found to be 40%, higher compared to a commercial brackish water RO membrane and an order of magnitude was higher when compared to a seawater RO membrane, which clearly demonstrated great potential (Zhao *et al*., 2012b).

Zhonga *et al.* (2012) conducted a study on the aquaporin-embedded biomimetic membranes for NF. This study carried a demonstration of aquaporin-z (AQPZ) fixed planar biomimetic membranes with a high flux and a reasonable salt rejection for water reuse. Zhonga *et al.* (2012) stated the performance of the membrane was improved by the combination of nanoparticles and biological elements in such. The incorporation of the transmembrane called Aquaporins are one of the key attractions of this aspect of water purification

The aims of the study were to: (1) Fabricate a substrate from a commercially-available CA polymer with pore sizes within an appropriate range; (2) modify the CA substrate inorder to be compatible with AQP and suitable for vesicle rupture and (3) molecularly design AQP-embedded biomimetic membranes with negligible weaknesses for NF. The known boundaries of current NF membranes, included low flux and requirement to use of high hydraulic pressure, it was expected that the AQP incorporated biomimetic membranes in order to generate a higher flux and lower energy consumption for the NF process, as well as open up a new frontier in water purification technology. This preliminary study on the NF process served as a continuing effort towards the well-developed RO process. NF experiments were performed in a home-based stirred dead-end filtration cell. The active membrane surface area had a diameter of 3 mm. All filtration experiments were carried out at 5 bars and at room temperature (22 °C). It was found that the NF membranes comprising AQPZ: ABA ratio of 1:50 gave an impressive water permeability of 34 L/m^{2}h bar and NaCl rejection of more than 30% (Zhonga *et al.,* 2012).

2.6.7 Determining of basic membrane properties

2.6.7.1 Determining the experimental water flux (Jw)

The experimental water flux (J_W) across the FO membrane was calculated based on the change in weight increments of the FS. Volume changes in the FS were recorded hourly by recording the mass on the balance. Water flux, J_W (L/m^2h) was calculated by Equation. (2.1). Phuntsho, 2012):

$$\boldsymbol{J_w = \frac{\Delta V}{\Delta t \times A\ (m^2)}} \tag{2.1}$$

Where, ΔV is the volume of the permeate water (L), Δt is the time interval (h) and A is the effective membrane surface area (m^2) (Han *et al*., 2016).

2.6.7.2 Determining the reverse solute diffusion of the draw solutes

The reverse solute diffusion of draw solutes towards the FS was measured in terms of reverse solute flux (J_S). J_S was calculated based on the changes in volume increments in the FS. Volume changes in the FS were recorded at one-hour intervals by reading mass of the FS on the balance. J_s (g/m^2h) was calculated by using Equation (2.2) (Han *et al*., 2016).

$$\mathbf{J_s = \frac{\Delta(C_t V_t)}{\Delta t\ (h) \times A\ (m^2)}} \tag{2.2}$$

Where, C_t is the reverse solute concentration at the end of the FO bench scale analyses (M); V_t is the feed volume measured at the end of the FO bench scale analyses (L); Δt is the time interval (h); and A is the effective membrane surface area (m^2).

2.6.7.3 Feed recovery rate

Feed recovery rate is the amount of water permeated per unit time.

$$\boldsymbol{R_e = \frac{\Delta V}{V_{f,i}} \times 100}\ \% \tag{2.3}$$

Where, $V_{f,i}$ (L) is the initial volume of the feed solution, and ΔV is the change in volume of the FS (L) (Han *et al*., 2016).

2.7 Dye

A dye is an element that, when put to fabrics, imparts a permanent colour and the colour is not detached by washing with water or soap or an exposure to light (Madan, 2005). The dyes are preserved in the substrate by adsorption, solution, mechanical retention and by any ionic or covalent bond. The dye's colour is subject to the alteration amongst different molecular orbitals of the molecule, the probability of these changes determining the intensity of the colour. The difference in energy between the orbitals determines whether the colour falls in the electromagnetic spectrum's visible range and if it does, determines the exact shade and type (Standen, 2004; Madan, 2005).

2.7.1 Classification of the dye

Dyes can be classified by many different methods; every type of a dye has its own unique chemistry, structure and method of bonding. Certain dyes can react chemically with the substrates and form strong bonds, yet other dyes can be held by physical forces. The prominent methods of dye classification include (Kolorjet Chemical Pvt. Ltd, 2017):

- Natural/synthetic;
- Organic/inorganic;
- By area and method of application; and
- Chemical classification – based on the nature of their chromophores.

2.7.2 Industrial classes and application of dyes

Dyes are classified into different classes and comprise of acidic, azoic, basic, direct, disperse, reactive, mordant, solvent, sulphur and vat dyes (Standen, 2004). Table 2.7 illustrates the different classes of dyes and their application.

Table 2.7: Classes of dye and their application (Standen, 2004)

Dyes classes	Application
Acid	Wool, silk, paper, synthetic fibres and leathers
Azoic	Printing inks and pigments
Basic	Silk, wool and cotton
Direct	Cotton, cellulosic and blended fibres
Disperse	Synthetic fibres
Reactive	Cellulosic fibres and fabric
Organic pigments	Cotton, cellulosic, blended fabric and paper
Sulphur	Cotton and cellulosic fibre
Vat	Cotton, cellulosic and blended fibres

2.7.3 Factors in selecting a dye

There are many factors that are considered when selecting a dye for textile application and such include (Baumann & Fletcher, 1951; Madan, 2005):

- Economy: The dye must be affordable and inexpensive.
- Shade (i.e. brightness / dullness).
- Fastness: characterises the resistance of the material's colour to fading.
- Level dyeing properties including chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, color and salinity.
- Ease of dispersion and / or dissolving (i.e. dyes must be water-soluble).
- Fixation: fixation of the dye molecules by adhesion.
- Environmental concern: Avoid harming the ecosystem in the long run.

2.7.4 Commonly used dyes in the textile industries

2.7.4.1 Reactive Dyes

Reactive dyes are referred to as strongly-coloured organic substances. A chromophore which contains substituent that has the ability to react directly with a fibre substrate is used by reactive dyes. The reactive dye forms a covalent bond with the substrate and is responsible for the attachment of the reactive dye to the natural fibre. The reactive dyes are classified to be the permanent dyes because of the covalent bond. Reactive dyes are used for dyeing cotton, other cellulose fibres, nylon and wool (Horst *et al*., 2000).

2.7.4.2 Advantages of reactive dyes

The advantages of reactive dyes include (Horst *et al*., 2000):

- Permanencies of the colour - Reactive dyes are alleged as the most everlasting of all dye types.
- Easy to wash - The fibres that are dyed with reactive dyes can be washed without the fear of colouring the white fibres.
- Chemical binding **-** The chemical bonds improves the product's colour stability and washability.

2.7.4.3 Types of reactive dyes

(i) Bi-functional dyes

Bi-functional dyes are dyes that show more than one type of reactive group in the molecule. These reactive dyes are designed to react with the fibre in more than a one way. Bi-functional dyes can be more tolerant to temperature deviations (Horst*, et al*., 2000).

(ii) Vinylsulphone dyes

Vinylsulphone dyes are temperately reactive. When using the mixture of soda ash and caustic soda the dyeing temperature is at 600°C and the pH 11.5. The excellent fixation properties under alkaline conditions are demonstrated by these types of dyes (Horst *et al*., 2000).

(iii) Monochlorotriazine dyes

Monochlorotriazine dyes are not as reactive as the vinylsulphone dyes. In energetic reaction conditions the chemical reactions for monochlorotriazines can occur. For proper fixation on cellulosic fibres a temperature of 800°C and a pH value of 10.5 are required.

2.7.4.4 Basic dyes

A positively charged stain that reacts with material that is negatively charged is referred to as a basic dye. They are mostly synthetic. The colour base of the basic dyes is not water soluble, however converting the base into a salt can make basic dyes soluble. The basic dye characteristics consist of the dyeing strength, brightness and display cationic functional groups like $-NR_3^+$ or $=NR_2^+$ (Baumann & Fletcher, 1951).

2.8 Osmotic Pressure (OP)

The OP is described as the pressure that is applied by the movement of water across a semi-permeable membrane which separates two solutions with different solute concentrations. It is also referred to as the pressure gradient that is a driving force of solvent through the semi-permeable membrane stop. The OP of a solution increases with an increase in the molar concentration of the solute particles in solution. OP is given by Equation 2.4 (Kutchai, 2003).

$$\boldsymbol{\pi = \frac{n}{V_m}\, i\, RT} \qquad (2.4)$$

Where, Π represents the osmotic pressure (kPa); i is the number of ions into which the dissolved species dissociates (dimensionless); R is the universal gas constant (J / mol. K); T represents absolute temperature (K); $\mathrm{V_m}$ the volume of solute (mol/L); and n the number of moles (mol).

Factors affecting OP include the concentration of the solutes, volume and temperature. OP is directly proportional to both the concentration of the solutes and the temperature; and is inversely proportional to the volume.

2.8.1 Methods to measure Osmotic Pressure

2.8.1.1 Van’t Hoff Equation

The Van’t Hoff equation is a common connection between the osmotic pressure (π) and concentration (c). This association is named after a Dutch physical chemist who came up with this theory. The Van’t Hoff Law applies only for dilute solutions and is given by the following Equation 2.5 (Kutchai, 2003).

$$\boldsymbol{\pi = iRTC_2} \qquad (2.5)$$

Where, Π represents the osmotic pressure (kPa); i is the number of ions into which the dissolved species dissociates (dimensionless); R is the universal gas constant (J / mol. K); T represents absolute temperature (K); and $\mathrm{C_2}$ is the solute concentration (mol/L).

The purpose of the Van’t Hoff factor (i) is to account/compensate for abnormalities that arise from an ideal solution which includes a finite volume. In the use of diluted solutions the Van’t

Hoff equation has been known to be unsuccessful/limited. However, the solutions behave ideally when the concentrations of these molecules are sufficiently low (Grattoni & Merlo, 2007).

2.8.1.2 Morse Equation

The Morse equation has similar limitations as the Van't Hoff equation. The Morse equation is given by Equation 2.6 (Grattoni & Merlo, 2007).

$$\boldsymbol{\pi = RTm_2'} \tag{2.6}$$

Where, Π represents the osmotic pressure (kPa); R is the universal gas constant (J / mol. K); T represents absolute temperature (K); and m_2' the volume molal concentration (mol/L).

m_2' is defined by the Equation 2.7.

$$\boldsymbol{m_2' = m_2 \overset{\circ}{\rho_1}} \tag{2.7}$$

Where, m_2 is the solute molal concentration (mol /L); and $\overset{\circ}{\rho_1}$ the density of pure solvent (kg/m^3)

2.8.1.3 OLI Stream Analyser software

OLI Stream Analyser is a software application which estimates the properties of a solution over a comprehensive temperature and concentration by using thermodynamic modelling that is based on experimental data that has been published. This software measures full phase steadiness and speciation, together with the thermophysical properties. The stream analyser is a small component of the analyser studio and offers methods that are understandable and allow for assessment of the quality of research laboratory data by finding missing or incorrect dimensions (Phuntsho *et al*., 2011).

The OLI Stream Analyser software was used in the evaluation process and determination of the OP of the fertiliser DS and FS in a study by Phuntsho *et al*. (2011). The results obtained from the study indicated that all the selected fertilisers generate OP higher than seawater (~28 atm) or brackish water when used as an osmotic draw agent (Phuntsho *et al*., 2011).

2.8.1.4 Osmometer

An osmometer is an instrument that is used to measure the osmotic strength of a solution or compound. Osmometers are available in three different classes and each one influences a certain property to produce the necessary results. The three classes of osmometer are freezing point osmometers, vapour pressure osmometers and membrane osmometers. The freezing point osmometer makes use of the freezing point depression to find the solution's osmotic strength. The vapour pressure osmometer analyses the concentration of a particle that is osmotically active and decreases the vapour pressure of the solution. The membrane osmometer calculates the OP of a solution that is divided by the porous membrane (Mary & Tetraut, 1995).

Zhao *et al.* (2015) conducted a study on exploring the feasibility of using polyacrylamide (PAM) and KCl as a DS with dye wastewater as the FS. The PAM and KCl were prepared in different concentrations (20 g/L, 30g/L and 40 g/L). It was stated that the OP of both KCl and PAM was measured by the freezing point osmometer, sourced from Germany. It was then reported that the OP varied approximately linearly with concentration. The OP for PAM at 20, 30 and 40 g/L was reported to be 366, 544 and 824 mOsm/kgH_2O, respectively. The OP for KCl at 20, 30 and 40 g/L was found to be 508.5, 814 and 1055.5 mOsm/kgH_2O, respectively.

2.9 Salinity

Salinity refers to the existence of salts that are soluble in the water. The soluble salts have the ability to cause stress or toxicity to crops and vegetation, increase sodicity and soil erosion; pollute drinking water and damage roads, fences, railways, buildings and natural ecosystems (Phuntsho, 2012).

2.9.1 Salinity of seawater

Seawater is composed of many chemicals that make it salty. Many of these chemicals are carried from rivers carrying dissolved salts out of rock and soil. The main chemical is sodium chloride. Throughout the world, seawater is not consistently saline. Seawater can be less saline in regions where fresh water occurs such as runoff from the river mouths or melting glaciers. The most saline sea is the Red Sea because of the high rate of evaporation and low precipitation (Chester & Jickells, 2012).

The masses of evaporation in other parts of the ocean are caused by the absence of rainfall, and occurrence of warm dry winds. The salinity of the sea increases when the evaporation eliminates water, and water vapour rises to the atmosphere, leaving salt on the ground. This causes seawater to be denser. In some parts of the ocean the seawater is less dense because there is a lot of rain and fresh water dilutes the seawater reducing salinity, however near the land where rivers deposit fresh water, seawater can also be less saline (Chester & Jickells, 2012).

Among factors that contribute to change in salinity is a very large river emptying into the ocean. large rivers can cause the ocean to have little or no salt content for over a mile (i.e. 1.6 km) or more out to sea. Little effects on salinity is when the runoff from small streams and rivers is quickly mixed with ocean water by the currents (Chester & Jickells, 2012).

Phuntsho *et al*. (2011), conducted a study evaluating the performance of fertiliser DS and using different types of feed solutions (FS). The FS also consisted of model brackish water (BW) of 5,000 mg/L NaCl and synthetic seawater (SW) of 35,000 mg/L NaCl. Phuntsho*, et al*. (2011), report that seawater has an osmotic potential of about 28 atm, while the OP of brackish groundwater can differ liable on its total dissolved solids, Grey *et al*. (2006) report OP of BW to be 395 atm. Water transfer from saline FS to DS by natural osmotic process will occur when OP of the DS remains higher than the FS. If the volume of the saline FS remains unrestricted, the water transfer will continuously dilute the DS during the FO process, to a point where net water movement will cease. This occurs at a point when osmotic equilibrium is reached (zero osmotic gradients). It was found that, based on the volumetric mass balance and the osmotic equilibrium, all fertiliser draw solutions are shown to extract water from saline feed water as long as the fertiliser draw solution can generate OP much higher than the FS.

CHAPTER 3

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter focuses on the experimental procedure for all the bench-scale experiments carried out in this study. This chapter is divided into five phases; (1) evaluating the potential of water resources as suitable feed solutions (FS), (2) identifying dyes and evaluating their potential as suitable draw solutions (DS) at different concentrations (3) evaluating basic and reactive dyes as suitable draw solutions, (4) FO bench scale experiments and (5) membrane integrity tests. The FO process was investigated as a process that could be used to produce a dye solution using alternative water resources. The FO process was carried out using different types of dye solutions as the DS.

3.2 PHASE 1: Evaluating potential of alternative water resources as suitable feed solutions (FS)

Preliminary experiments were carried out based on the readily available water resources, which included brackish water (BW), synthetic seawater (SSW), actual seawater (SW) and textile wastewater (TWW). The seawater (SW) was collected from three areas along the Indian Ocean sea board (IOSB) and three areas along the Atlantic Ocean sea board (AOSB). Duplicate samples were prepared and sent to a SANAS-accredited independent laboratory (Bemlab, South Africa) for full chemical and OP analysis. Table 3.1 indicates the NaCl concentration on the FS.

Table 3.1: **Feed solutions evaluated for osmotic pressure**

Types of FS	Composition
Deionised water (DI) – Control	Pure water – Control
Brackish water (BW)	5000 mg/L NaCl
Synthetic seawater (SSW)	35000 mg/L NaCl
Collected seawater (SW)	30392 mg/L NaCl
Textile wastewater Carmine	46156 mg/L NaCl
Textile wastewater Olive Green	63749 mg/L NaCl
Textile wastewater Factory 1	573 mg/L NaCl
Textile wastewater Factory 2	32065 mg/L NaCl

3.2.1 Preparation of brackish water (BW) and synthetic seawater (SSW)

Brackish water (BW) and synthetic water (SSW) were prepared at a concentration of 5000 and 35000 mg/L NaCl, respectively. The samples were sent for full chemical and OP analysis to a SANAS-accredited laboratory (Bemlab).

3.2.2 Seawater (SW) collection

Seawater was collected in areas, along AOSB and IOSB, as listed in Table 3.2. The seawater was collected in duplicate, filtered and sent for full chemical and OP analysis to a SANAS-accredited laboratory, Bemlab. See Table A1: Appendix A for full seawater analysis results.

Table 3.2: Collected seawater from areas in Western Cape, S.A

AOSB	IOSB
Camp's bay	Gordon's bay
Clifton 4th	Strand: Location 1
Sea Point	Strand: Location 2

3.2.3 Textile wastewater (TWW)

Textile wastewater samples were collected from a textile company in Cape Town. The textile wastewater (TWW) samples were collected from the outlet stream after the dye bath operation. TWW samples were of reactive dye. TWW Carmine and TWW Olive Green were TWW samples collected from Factory 1 after the dye processing of those two reactive dyes, while Factory 1 and Factory 2 yielded TWW samples of the same dye (Reactive Beige) from the two different factories. The TWW samples were collected in duplicate and sent to a SANAS-accredited laboratory for full chemical and OP analysis. See Appendix A: Table A1 for full chemical analysis results.

3.3 PHASE 2: Identification and evaluation of available dyes as potential draw solutions

For the identification of a suitable DS, the readily available dyes in the laboratory, Methyl orange (MO), Remazol Red (RR) and Potassium Indigo trisulfonate (PI) were used to determine the OP generation at different concentrations. These samples were prepared and sent to Bemlab for OP analysis. Table 3.3 illustrates the dyes tested, their molecular weight (Mw) and tested concentration range.

Table 3.3: **Preliminary dyes analysed as draw solutions**

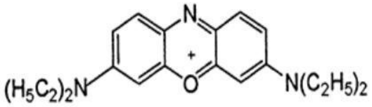
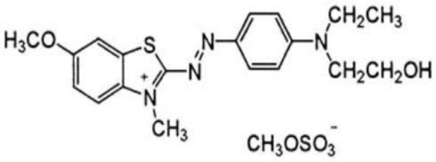
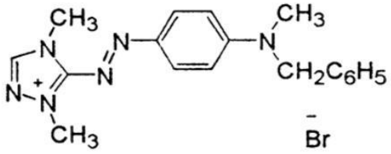
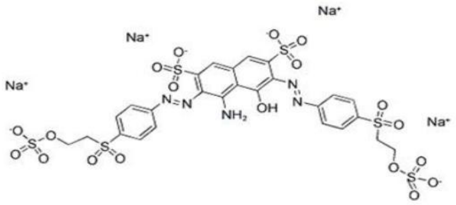
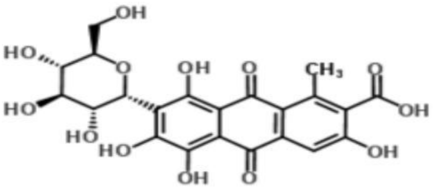
Preliminary Dyes	Chemical formula	Molecular weight (g/mol)	Concentration range (g/L)
Methyl Orange (MO)	$C_{14}H_{14}N_3NaO_3S$	327	0.5 to 2.5
Remazol Red (RR)	$C_{27}H_{18}ClN_7Na_4O_{16}S_5$	985	0.5 to 2.5
Potassium Indigo trisulfonate (PI)	$C_{16}H_7K_3N_2O_{11}S_3$	616	0.5 to 2.5

3.4 PHASE 3: Evaluation of selected dyes as suitable draw solutions

After the initial preliminary analysis on the readily available dyes in the laboratory as suitable DS for FO, it was deduced that dyes do generate a substantial OP, and a further investigation was conducted on textile dyes used in industry. From the conducted investigation it was concluded that two types of dyes, (i) basic and (ii) reactive dyes are the most commonly used dyes.

From the range of basic and reactive dyes, three dyes were selected for OP analysis using the osmometer. Basic dyes were Maxilon Blue 5G; Maxilon Red GRL; and Blue 41 GRL and reactive dyes were Reactive Black; Carmine and Levifix Olive Ca. The dyes that were evaluated as the suitable DS were selected based on the solubility, fixation, application and demand in the textile industry. The OP analysis was performed on dyes at 0.02 to 0.2 M concentration. Since there are auxiliary chemicals used in the textile and dyeing industry such as salt, soda ash and urea, the OP analysis was also performed on dyes with the addition of salt. Different salt ratios were applied in the preparation of the dye solutions, from 1:10 to 1:60 dye-to-salt ratios, depending on the textile recipes from textile industries. Table 3.4 illustrates the basic and reactive dyes with their molecular weight (Mw) and structures of dyes.

Table 3.4: **Basic and reactive dyes evaluated for osmotic pressure (OP)**

Dyes		**Referred to**	**(M_W) (g/mol)**	**Chemical Formula**	**Chemical Structure**	**Reference**
Basic	Maxilon Blue 5G	Turquoise	359	$C_{20}H_{26}ClN_3O$		Mahir *et al*., (2008)
	Maxilon Blue GRL	Blue	482	$C_{20}H_{22}N_4O_6S_2$		Aljeboree *et al*., (2014)
	Maxilon Red GRL	Red	402	$C_{18}H_{22}BrN_6$		El-sayed *et al*., (2014)
Reactive	Reactive Black	Black	991	$C_{26}H_{21}N_5Na_4O_{19}S_6$		Han *et al*., (2016)
	Remazol Red**:**	Carmine	492	$C_{22}H_{20}O_{13}$		Chemical book (2016)
	Levifix Olive Ca	Olive Green	585	$C_{20}H_{17}N_3Na_2O_9S_3$	Not available	Dystar product selection guidance (2014)

3.5 PHASE 4: Control experiments and FO bench scale experiments

3.5.1 Introduction

The control experiments were done with DI as a FS and Reactive Black dye and Basic Blue as the DS. This experiment was carried out to determine the duration of osmotic equilibrium (OE) between the FS and DS. FO bench scale experiments were done in order to assess the FO system for the production of dye solutions with a target dye concentration, using alternative water resources as well as reclaimed textile wastewater under different dye concentrations.

3.5.2 Experimental setup

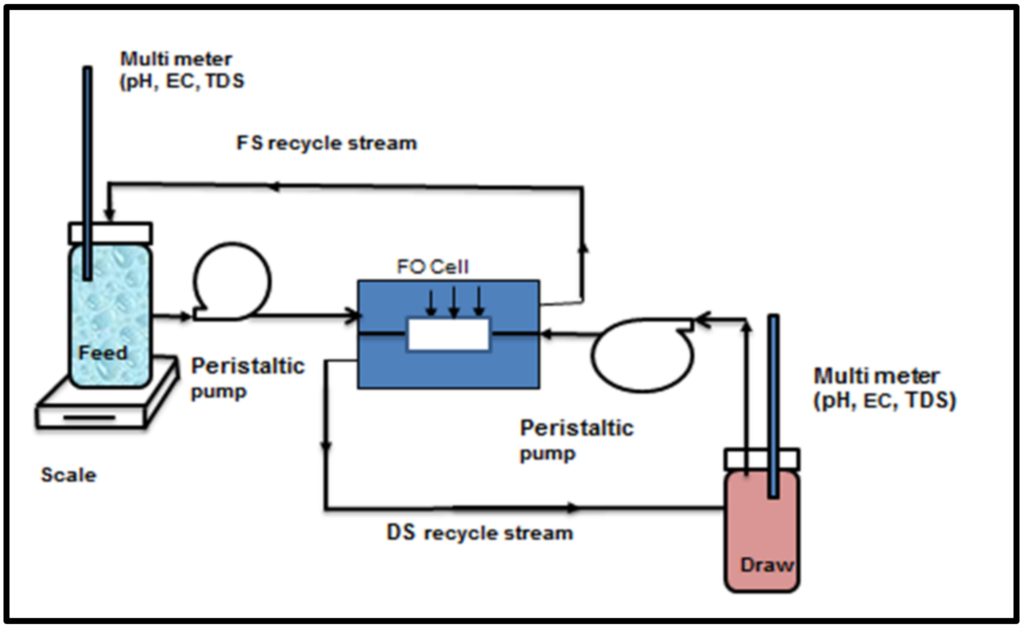


Figure 3.1: Process flow diagram (PFD) of a laboratory bench-scale FO process with FS and DS recycled

3.5.3 Experimental procedures

Figure 3.1 illustrates the bench-scale FO process. The main unit in this process was the FO cell (CFO42D) which was connected to the FS and DS. The FS was synthetic seawater (35000 mg/L NaCl) and textile wastewater from two different factories, and DI water was used as a FS for control experiments. The DS was a dye solution, (i) Basic Blue 41 GRL and (ii) Reactive Black. The FS and DS were pumped using identical peristaltic pumps (Watson Marlow, 323S), from storage tanks of 2L and 1L respectively, to the FO cell at a flow rate of 600 mL/min. The Marprene tubing (1/4" I.D. 3/8" O.D. and1/16" wall) was used on the pumps.

The weighing balance (Labex, WA606), with a range of 0 to 6 kg, was used to record the mass of the FS. 2L FS was fitted with a multi meter (Lovibond sensor direct) used to measure the pH, TDS, EC and salinity. There was no external form of hydraulic pressure for this process; the only energy required for this process was for the running of the two pumps. The purpose of the weighing balance was to measure the mass of water moving across the membrane used in order to calculate the flux.

3.5.4 Operating conditions

The experiments were accomplished at room temperature (±25 °C). The pumps (Watson Marlow 323S) were set at 200 rpm, equivalent to a flow rate of 600 mL/min. The DS concentration was 0.02 M. The starting volume of the FS and DS was 2L and 1L respectively. pH, EC, TDS, salinity and mass were measured every hour during operation parameters. Each experiment was operated in duplicate and for every new experiment a new membrane was used. Table 3.5 lists the set of FO experiments with the respective FS and DS. The control experiments were carried to osmotic equilibrium (OE), hence, they have a longer duration of operation compared to other experiments. The duration of the experiments with SSW and TWW was based upon reaching the target dye concentration, where by the system was allowed to run up to 30 hours in order to observe enough water transportation from feed side to the draw side.

Table 3.5: Experiments operated in the FO unit

Feed solutions (FS)	Draw solutions (DS)	Duration of experiments
DI (control)	Reactive Black	55 hours
SSW (35 000 mg/Nacl)	Reactive Black	30 hours
TWW (Factory 1)	Reactive Black	30 hours
TWW (Factory 2)	Reactive Black	30 hours
DI (Control)	Basic Blue	140 hours
SSW (35 000 mg/Nacl)	Basic Blue	30 hours
TWW (Factory 1)	Basic Blue	30 hours
TWW (Factory 2)	Basic Blue	30 hours

3.5.5 FO CELL: CF042D Reactor

The CF042D Cell (Sterlitech, USA) is a unit for cross flow filtration and is intended to measure flat sheet membranes in different applications. It imitates the flow dynamics of greater, commercially-available membrane elements such as industrial spiral wound membrane elements. Users can alter the operating conditions and fluid dynamics over comprehensive ranges. Table 3.6 outlines the features and technical specifications of the CF042D Cell.

Table 3.6: CF042D features and technical specification (Sterlitech Corporation CFO42D- FO Cell Manual V.1)

Parameter	Description
Membrane Active Area	42 cm^2
Maximum Pressure	69 bar
Maximum temperature	82 °C
O-rings	Buna
pH	Membrane dependent
CF042D cell	Delrin
Cross Flow Velocity	Variable
Dimensions	
• Slop depth	2.3 mm
• Slop width	39.2 mm

3.6 FO mode

FO mode is when the active side of the membrane is facing the FS and the porous side is facing the DS. A lab-scale FO unit with membrane area 42 cm^2 consists of channels (slope depth 2.3 mm and slope width 39.2 mm) on both sides of the membrane that allow FS to flow on the active side of membrane and DS on the support side of the membrane.

3.7 Samples and Analysis of the Feed solution (FS) and Draw solution (DS)

3.7.1 Phase 1 and Phase 2 analysis

The FS and DS were analysed for conductivity (EC), total dissolved solids (TDS), pH and osmotic pressure (OP). In addition, trace element analysis was undertaken, and elements found included calcium (Ca), carbon trioxide (CO_3), chlorine (Cl), iron (Fe), bicarbonate (HCO_3), potassium (K), magnesium (Mg), Manganese (Mn), sodium (Na) and sulphate (SO_4). These were tested on the FS and SS at the SANAS-accredited laboratory, refer to Appendix A: Table A1 for FS and Table A2 for DS for full chemical analysis. The OP for FS and DS was obtained via three methods, (i) calculated, (ii) analysed at a SANAS accredited laboratory and (iii) measured using a freezing point Genotec 3000 osmometer. With the calculated method, the OP of the dye DS and various FS was calculated using the Van't Hoff's equation (i.e. Equation 2.2), since it is applicable to dilute aqueous solutions (Grattoni & Merlo, 2007; Phuntsho *et al.,* 2012). Samples of both the FS and DS were sent for OP analysis at a SANAS-accredited laboratory (Bemlab).

3.7.2 Phase 3 analysis

A freezing point Genotec 3000 osmometer (Scientific Group, Germany) was used to measure OP in the laboratory of both the FS and dye DS, whereby the dye DS was divided into dyes with salt and dyes without salt. Refer to Appendix B for the analytical procedure of OP analysis and calculations and conversions involved.

3.7.3 Phase 4 samples and analysis

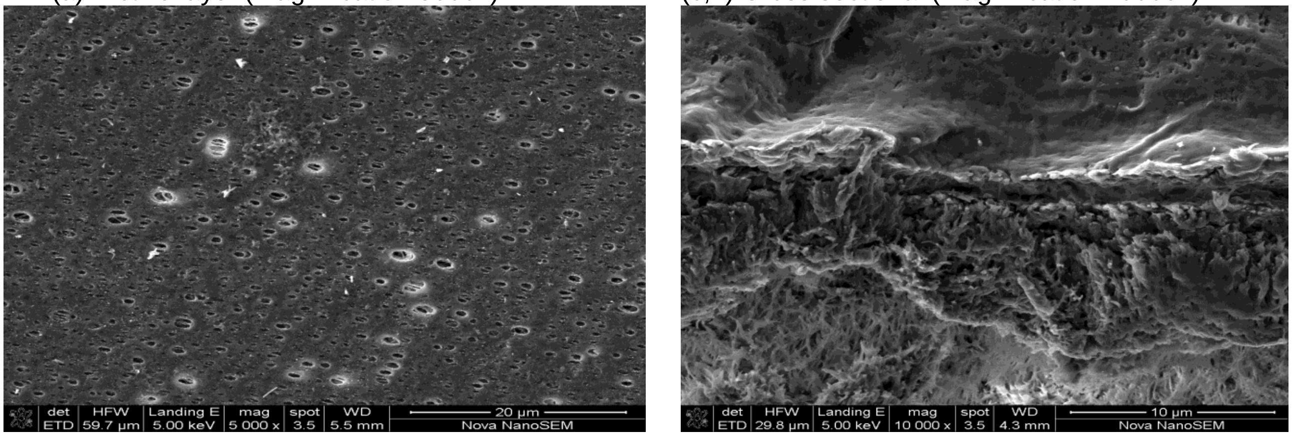
During Phase 4 experiments, pH, EC and TDS were measured using sensor direct multipurpose meter every hour and the mass on the balance of the feed was also measured every hour. A 1 mL sample was collected every second hour on both the FS and DS to measure the OP using freezing point osmometer. A sample was taken initially and at the end of the experiment for Hazen Colour analysis.

3.8 PHASE 5: Membrane integrity

The membrane used in this research project is the FO flat sheet Aquaporin biomimetic membrane, sourced from Aquaporin (Denmark). The aquaporin membrane properties and strength compared to other FO membranes reported in Chapter 2 (section 2.7.7), led to the utilisation of the aquaporin biomimetic membrane. The membrane integrity experiments were carried out in order to evaluate the strength, the capacity of the membrane and the flux at which the membrane will function maximally. Table 3.7 illustrates the specifications of the Aquaporin biomimetic membrane. Figure 3.2 illustrates the structure of the membrane; (a) active side, (b) support layer and (c1 & c2) cross section.

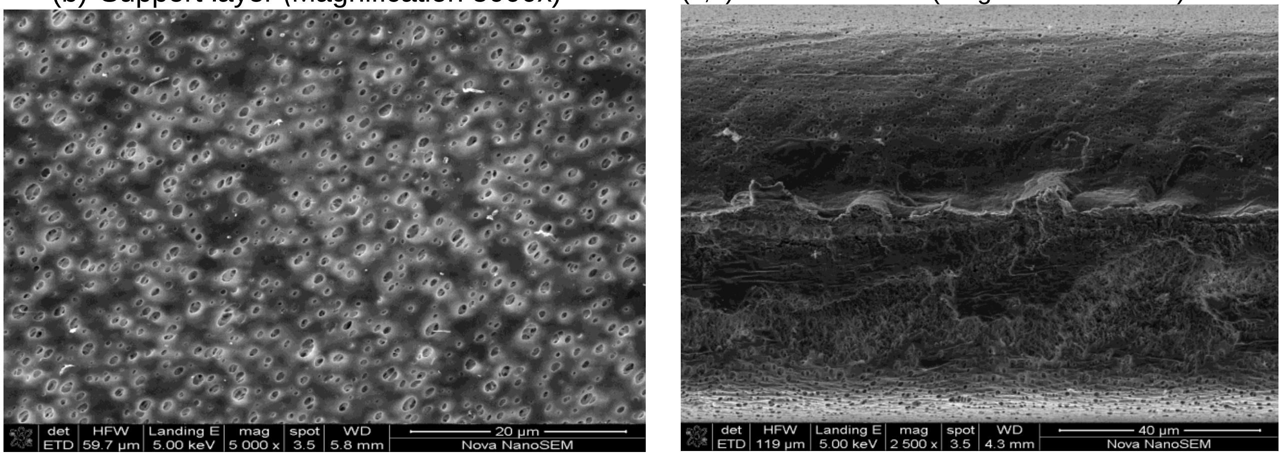
Table 3.7: **Specifications of the Aquaporin biomimetic membrane** (Aquaporin Inside™ data sheet 1.8)

Specifications	FO flat sheet membrane
Membrane thickness	110µm (+/ - 15 µm)
Shelf life	6 months
Water flux	>7 L / m^{2}hr
NaCl reverse flux	<2 g /m^{2}hr
Boron rejection	>70%
Arsenic rejection	>95 %



(a) Active layer (Magnification 5000x)

(c,1) Cross sectional (Magnification 10000x)



(b) Support layer (Magnification 5000x)

(c,2) Cross sectional (Magnification 2500x)

Figure 3.2: **Scanning electron microscopy images of the aquaporin biomimetic membrane (a) active layer at 5000x magnification, (b) support layer at 5000x magnification, c(1) cross section at 10000x magnification and c(2) cross section at 2500x magnification**

3.8.1 Membrane integrity test experiments

The membrane was cut using scissors and soaked in DI water for approximately 30 minutes prior to the experiment. DI was used as the FS and BW (5000 mg/L NaCl) was used as a DS. The membrane was then placed in the CFO42D- FO (Sterlitech, USA) unit (see Figure 3.1). The membrane integrity was then tested by varying the flow rate of each experiment for a duration of five hours. The tested flow rates are listed in Table 3.8 and the purpose was to observe at which flow rate the membrane would tear. Parameters that were measured included pH, EC, salinity, mass on the feed and flux determination was carried out using equation 3.1.

Table 3.8: **Flow rates used for membrane integrity test**

Flow rate (mL/min)	Pump speed (rpm)
290	100
450	150
600	200
800	250

3.9 FO parameters

3.9.1 Water flux

The experimental water flux (J_w) across the FO membrane was calculated based on the changes in weight deduction of the FS. Volume changes in the DS were recorded at every 2 hour time intervals by water flux J_w (L/m^{2}h) was calculated by Equation (2.1).

$$\boldsymbol{J_w} = \frac{\Delta \boldsymbol{V}}{\Delta \boldsymbol{t} \times \boldsymbol{A}\ (\boldsymbol{m^2})} \tag{2. 1}$$

Where, ΔV is the volume of the permeate water (L), Δt is the time interval (h) and A is the effective membrane surface area (m^2) (Han *et al*., 2016).

3.9.2 Reverse solute flux

The reverse solute diffusion of draw solutes towards the FS was measured in terms of reverse solute flux (J_S). J_S was calculated for control experiments where DI was a FS and was based on the changes in volume increments in the FS. Volume changes in the FS were recorded at 2 hour time intervals by recording the mass on the balance of the feed. J_s (g/m^{2}h) for controls was calculated by using Equation (2.2) where a standard curve of conductivity versus feed concentration was prepared to determine the reverse solute concentration. For other experiments i.e the production of dye solution using different FS, the reverse solute flux was monitored by recording of the conductivity of the FS while operating the FO system.

$$\mathbf{J_s} = \frac{\Delta(\mathbf{C_t V_t})}{\Delta\mathbf{t}\ (\mathbf{h})\times\mathbf{A}\ (\mathbf{m^2})} \tag{2.2}$$

Where, C_t is the reverse solute concentration at the end of the FO bench scale analyses (M); V_t is the feed volume measured at the end of the FO bench scale analyses (L); Δt is the time interval (h); and A is the effective membrane surface area (m^2) (Han *et al*., 2016).

3.9.3 Water recovery rate

The feed water recovery rate was calculated using equation 2.3.

$$\boldsymbol{R_e} = \frac{\boldsymbol{\Delta V}}{\boldsymbol{V_{f,i}}} \times \mathbf{100}\ \% \tag{2.3}$$

Where, $V_{f,i}$ (L) is the initial volume of the feed solution, and ΔV is the change in volume of the FS (L) (Han *et al*., 2016).

CHAPTER 4

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Phase 1 results: Evaluating potential of water resources as suitable feed solutions (FS)

The objectives of this study were to identify alternative water resources and evaluate their potential as suitable feed solutions (FS). Water sources such as synthetic brackish water (BW), seawater (SW), synthetic seawater (SSW) and textile wastewater (TWW) were identified as potential feed solutions. Their potential was then assessed by measuring their osmotic pressure (OP) using the freezing point Genotec 3000 osmometer, sending water samples for analysis to a SANAS-accredited laboratory for OP analysis, and calculating their OP using Van’t Hoff’s equation.

4.1.1 Feed solutions (FS)

Table 4.1 illustrates the FS that were identified and their OP. One of the greatest contributors to OP is salinity. The actual seawater was collected in two regions within the Western Cape, Atlantic Ocean seaboard and the Indian Ocean seaboard (see Table 3.2). As illustrated in equation 2.4 (Chapter 2), the OP is directly proportional to the solute concentration and this is evident in the OP of DI (used as the control) which was 0 kPa since there are no solutes dissolved in DI. The OP of BW was found to be 414, 377 and 384 kPa using the freezing point Genotec 3000 osmometer, Van ’t Hoff equation and from the SANAS laboratory analysis, respectively. Previous research reported the OP of BW to be 395 kPa (Grey *et al*., 2006; Phunthso *et al*., 2011), implying that the DS for BW as a FS must have an OP higher than 414 kPa. The OP of SSW ranged from 2057 kPa from the SANAS laboratory OP analysis to 2761 kPa using the freezing point osmometer. Phunthso (2012) reported the OP of SSW to be 2800 kPa. The actual seawater (AOSB and IOSB) ranged from 1710 kPa to 2589 kPa and was found to have a lower OP compared to the SSW, and this was due to the lower NaCl concentration found in the actual seawater, which was found to be 30392 mg/L NaCl (see Appendix A: Table A1). The OP of the SSW is based on the 35000 mg/L of NaCl, while the actual seawater concentration is greatly influenced by many factors, such as evaporation and precipitation (Huber *et al*., 2000). Precipitation decreases salinity, hence the OP of the actual seawater is found to be lower than the OP of SSW, because the OP is influenced by salinity (Huber *et al*., 2000). From these results, it was then concluded that for both SW and SSW a DS with OP higher than 2800 kPa is required.

TWW was collected, after the dyeing process of the two reactive dyes that were selected for the study, i.e. (TWW Carmine and TWW Olive Green). The OP was 7821 and 6020 kPa for TWW Carmine and TWW Olive Green, respectively. More TWW was then collected from two different factories, Factory 1 and Factory 2, using the same dye (Reactive Beige) under different recipes and was assessed for OP potential, which was found to be 1505 and 3308 kPa for Factory 1 and Factory 2, respectively. The TWW from Factory 1 and Factory 2 generated a lower OP compared to TWW Carmine and TWW Olive Green, and this was due to the lower salt content on the recipe for the dyeing process of Reactive Beige from Factory 1 and Factory 2. It was then concluded that TWW from Factory 1 and 2 will be used as FS on the FO operation, as they had a lower OP, creating a higher OP gradient between the TWW as FS and potential DS.

Table 4.1: Osmotic pressure of the feed solutions

Feed solution	Measured (kPa) Bemlab	Measured (kPa) Osmometer	Calculated (kPa) Van ’t Hoffs	Literature (kPa)	Literature References
DI	0.135	0	0	0	Gray *et al*., 2006
BW5	384	414	377	395	Gray *et al*., 2006
SSW	2057	2761	2636	28 atm = 2800 kPa	Phunthso *et al*., 2012
AOSB					
Camps bay	1861	2571	2368		
Clifton 4th	1818	2585	2246		
Sea point	1856	2566	2383		
IOSB					
Gordon’s Bay	1847	2589	3667		
Strand location 1	1858	2583	3852		
Strand location 2	1710	2358	3453		
Averaged SW	1825	2542	2994		
Textile wastewater					
TWW Carmine	7245	7821	8125		
TWW Olive Green	6249	6020	6495		
TWW Factory 1	1319	1505	1616		
TWW Factory 2	2259	3308	4558		

4.2 Phase 2 results: Evaluate readily-available dyes and their potential as suitable draw solutions (DS) at different concentrations

The readily-available dyes in the laboratory were used in order to determine if dye solutions could generate sufficient OP. Three dyes, Methyl orange (MO), Remazol Red (RR) and Potassium Indigo trisulfonate (PI), were available and were therefore accessed for their potential as suitable DS by measuring their OP. The OP for this part of the study was measured in a SANAS-accredited laboratory. The OP of the dyes was first assessed without salt and then with salt.

4.2.1 Dyes as draw solution

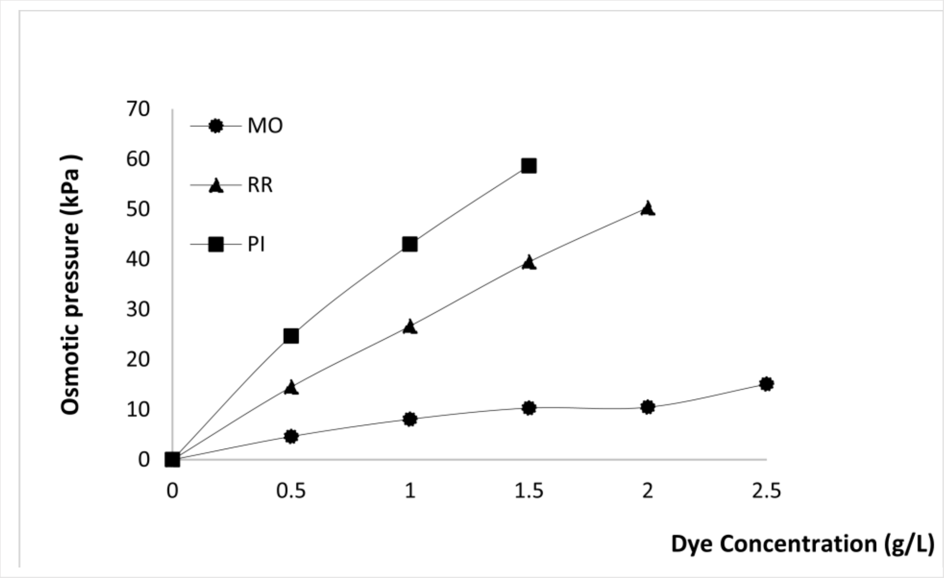


Figure 4.1: OP of different types of dyes with no salt

Figure 4.1 illustrates the OP of the three dyes, Methyl orange (MO), Remazol Red (RR) and Potassium Indigo trisulfonate (PI) at different dye concentrations with no salt addition. It was evident that OP increased with an increase in dye concentration (Figure 4.1). The (PI) dye had a higher OP compared to the other two dyes and that is due to its chemical composition when in aqueous phase and its dissociation properties, which form a number of species. However, it was still not a suitable DS as its OP was lower compared to that of the FS presented in Table 4.1. The OP of all three dyes were lower than that of the FS presented in Table 4.1 and operationally DS should have a considerably greater OP than the FS in order to achieve a high-water flux (Wang *et al*., 2012; Chung *et al.*, 2012 Shaffer *et al*., 2015; Akther *et al.,* 2015; Han *et al*., 2016) and were therefore concluded not to be suitable DS without addition of salt.

Remazol Red was selected from the three dyes because of its abundant availability in the laboratory, common use in the textile industry and of its known class of belonging which is reactive dye and a dye-to-salt mass ratio of 1:158 was applied following the recipe received from a textile factory when this dye is being used for fabric dyeing. Figure 4.2 illustrates the OP of a reactive dye RR with and without salt addition. . The RR without salt had a lower OP while, that with salt showed higher OP, meaning the dye samples without salt do not have the potential to draw the FS in Table 4.1, while dyes with salt have the potential to draw FS such as BW, SW and SSW from a concentration as small as 0.5 g/L.

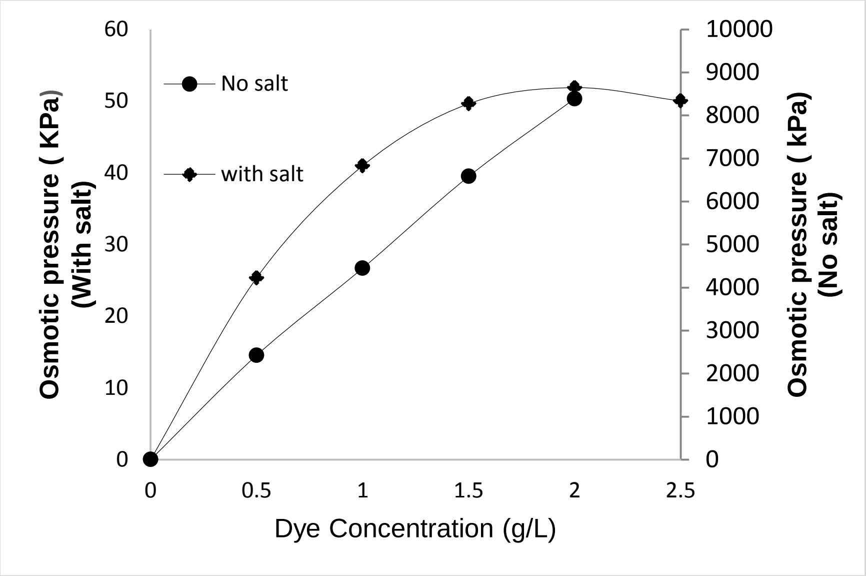


Figure 4.2: Reactive Remazol Red (RR) dye with salt and without salt

4.3 Phase 3 results: Evaluating identified basic and reactive dyes as a suitable draw solution

It was evident from Phase 2 that dye solutions without salt are able to generate an OP, however this OP is insufficient for an alternative DS. Basic dyes and reactive dyes were selected based on their high demand and popularity of use as dyestuff in the textile dyeing industries. Three dyes were selected from the two groups and the selection criteria were based on the solubility, fixation and application in the textile industry (Mackin, 2008).

Basic dyes (Turquoise, Red and Blue) and reactive dyes (Carmine, Olive Green and Black) were the dyes selected for an OP analysis at different concentrations, in order to be assessed as suitable DS. All calculations involved are illustrated in a sample calculation in Appendix C.

4.3.1 Basic and reactive dyes without salt addition

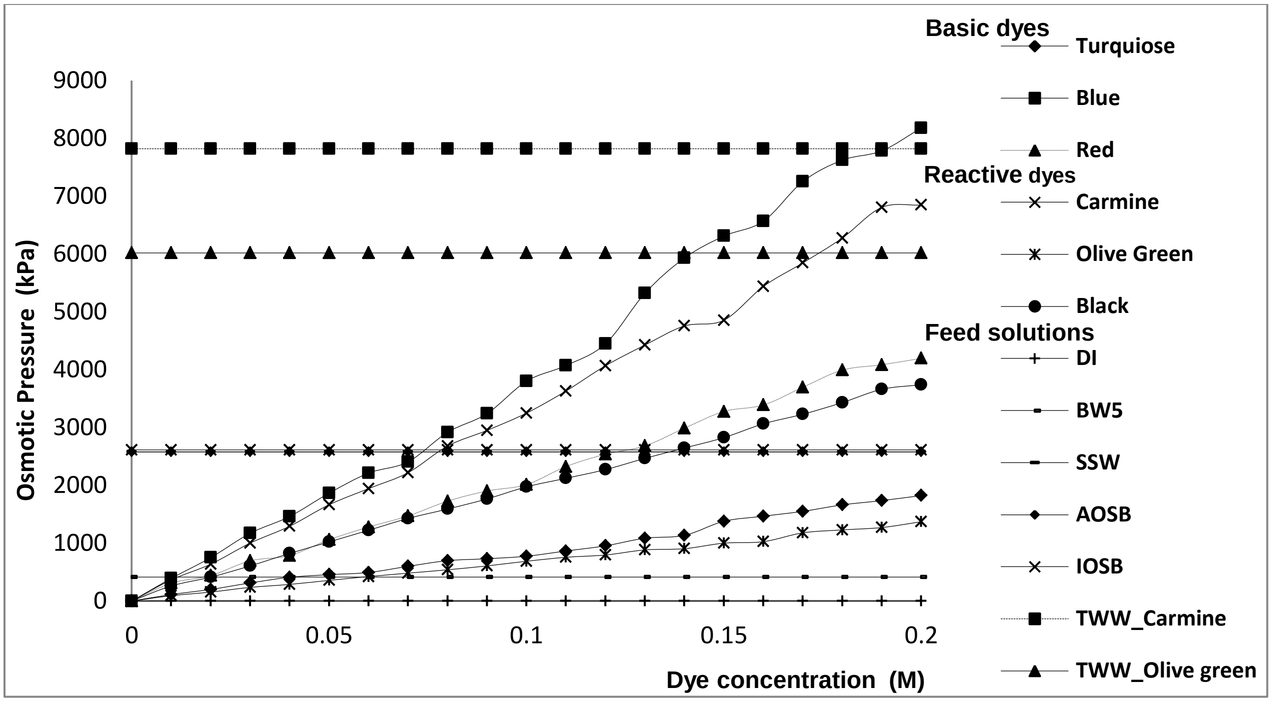


Figure 4.3: **Osmotic pressure of basic and reactive dyes (without salt addition) and alternative feed solutions**

Figure 4.3 illustrates an evaluation of OP of potential DS (basic and reactive dyes) with no addition of salt and the OP of the identified water resources. The dye concentration in which the OP was assessed is from 0 to 0.2 M. From Figure 4.3, it can be observed that the OP increases with an increase in concentration for all the selected dyes. It was also noted that the basic dyes without salt have a higher OP compared to the reactive dyes, yet the reactive dyes have a higher molecular weight (Mw) than the basic dyes. The reactive dyes with no added salt generate a lower OP when in aqueous solution, because they form a chemical reaction with water and hydrolyses (Christie, 2014). Hydrolysis involves a reaction of the reactive dye with hydroxide ($^{-}$OH) anions present in an aqueous dye bath in competition with the dye-fibre reaction (Christie, 2014). Hydrolysis of reactive dye increases the loss of dyes, and therefore the concentration drops (Christie, 2014; Burkinshaw, 1995). A salt concentration is required when working with reactive dyes, as a higher salt concentration decreases hydrolysis.

Basic dyes are water-soluble cationic dyes, and their positive charge allows them to adhere to anionic material. By analysing the acquired OP of the dyes, it was concluded that the OP generated by these dyes at these concentrations is not sufficient enough to draw the identified feed solutions in order to carry the FO process and therefore salt as an auxiliary chemical used in the textile industry was added in order to generate the higher OP.

At small concentrations of 0 to 0.03 M, all the dyes cannot be considered for the FO, due to lower OP compared to the available FS. BW had an OP of 414 kPa, but it can only be successfully considered as a suitable FS for all the presented dyes from a concentration higher than 0.1 M. The SSW and actual seawater generated a higher OP of 2761 kPa and 2596 kPa respectively, hence these FS can only be used with Basic Blue and Carmine dye at a concentration above 0.08 M and at a concentration higher than 0.15 M with red and black dye. Dyes such as Olive Green and Turquoise generated an OP lower than that of the SSW and the actual seawater and therefore cannot be considered a suitable dye DS.

4.3.2 Addition of salt to both reactive and basic dyes

After the assessment of the OP of dyes without salt was completed and it was concluded that dye DS without addition of salt cannot be considered as suitable DS, the addition of salt was then necessary in order to increase the OP of the dye DS.

Figure 4.4 (a) to (f) illustrate the mass of salt addition applied to each dye in different dye-to-salt mass ratios, ranging from 1:10 to 1:60. The salt was added following the dye-to-salt ratio applied in the textile dyeing industry. Among other auxiliary chemicals that are used in the textile dyeing industry, such as soda ash and urea and salt, salt acts as a catalyst and has affinity for water. The salt is required in the textile dyeing industry in three ways, (i) dye is driven into fabric during the dyeing process (ii) salt leads to full exhaustion of dye molecules during the dyeing process in textiles and (iii) salt is used as an electrolyte for movement, adsorption and fixation of the dyestuff to the cellulose material (Talukder *et al*., 2017; Samanta *et al*., 2015). From Figure 4.4, it can be seen that salt addition demonstrated a linear relationship with dye concentration and a linear relationship with the Mw of the dyes. The dyes with higher Mw required a higher amount of salt in order to achieve the stipulated dye-to-salt ratios. The addition of salt indeed increased OP of the dyes to be used in the FO operation.

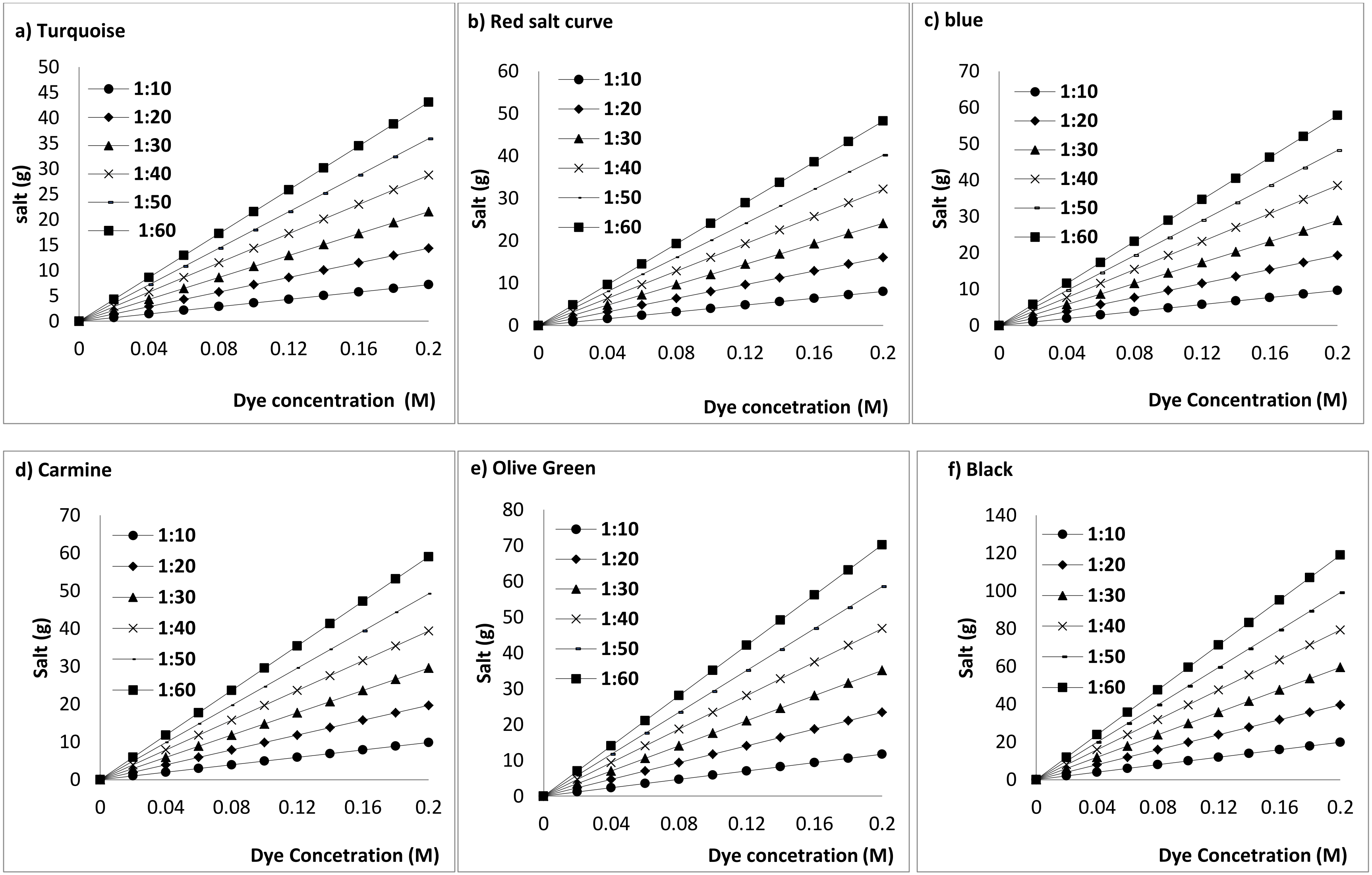


Figure 4.4: Addition of salt in different dye-to-salt ratios (1:10 to 1:60) for both basic (a-c) and reactive (d-f) dyes

4.3.3 Osmotic pressure of dyes with the addition of salt in different salt ratios

Reactive dyes used in the dyeing of cotton fabric using conventional dyeing processes, generally require large amounts of salt to help drive the dye onto the fabric. Therefore, further studies were conducted where these dyes were combined with salt in different dye-to-salt mass ratios. Figures 4.5 (a) to (f) illustrates the OP of potential DS, basic dyes (Turquoise, Red and Blue) and reactive dyes (Olive Green, Reactive Black and Carmine) at different dye concentrations and varied application of dye-to-salt ratios of 1:10 to 1:60. Figure 4.5 (a) to (f) indicates a linear relationship between the concentration of the dye solution and OP, as well as increasing dye-to-salt ratio. The reactive dyes have a higher Mw than the basic dyes and the OP of the reactive dyes is also higher than the OP of the basic dyes with addition of salt. The OP for the basic dyes follows the trend of Blue>>Red>Turquoise which is the same order of the Mw trend with Blue (482 g/mol)>>Red (402 g/mol)>Turquoise (359 g/mol). The OP for the reactive dyes follows the trend Black>>Olive>Carmine which is also the same order of the Mw trend with Black (991 g/mol)>>Olive (585 g/mol)>Carmine (492 g/mol). A linear relationship between the OP and Mw of the dyes is observed when there has been addition of the salt and the OP of the dyes combined in the salt ratio’s generated higher OP than the dyes with no salt in Figure 4.3.

Furthermore, the OP of the DS with addition of salt in different dye-to-salt mass ratios is higher than that of the FS tested in Table 4.1 and Figure 4.3. Therefore, dye DS with addition of salt has the potential to draw all the FS at all the stipulated concentration. Among factors that contribute to the OP is the concentration of solute. Reactive Black dye demonstrates the highest OP compared to all other dyes at all different dye-to-salt ratios, and it has the highest Mw of all the dyes, because of its chemical composition. However, OP is a colligative property and does not depend on the nature of species formed when the dye is in the aqueous state, but on the number of species formed when the dye molecule dissociates.

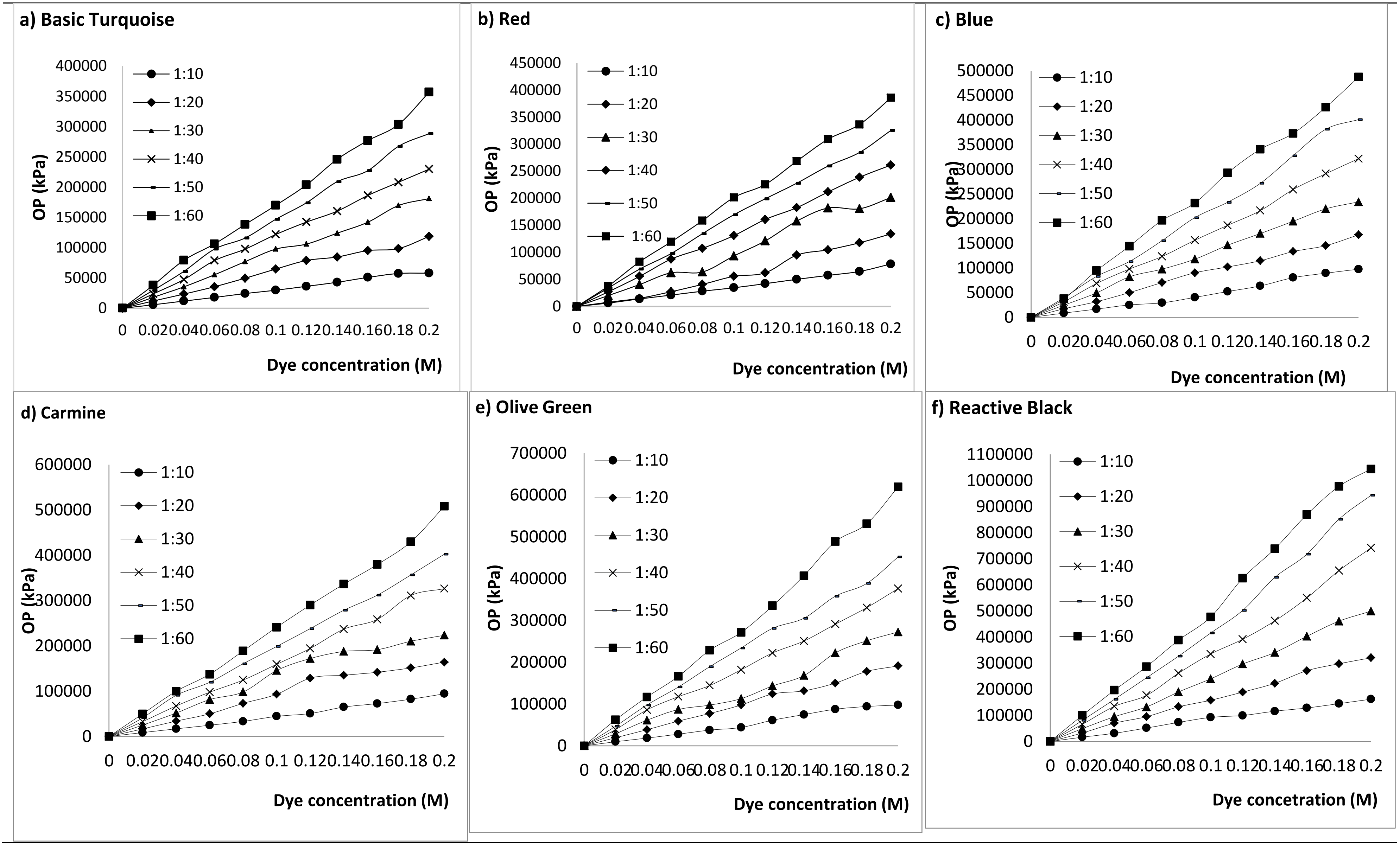


Figure 4.5: Osmotic pressure (OP) of dye solutions at different concentrations in different dye-to-salt mass ratios: (a) to (c) basic dyes and (d) to (f) reactive dye

4.3.4 Comparison of OP of different dye solutions at different concentrations at the same dye-to-salt mass ratio

Figures 4.6 (a) to (f) illustrate the comparison of the OP of the different dye solutions at the same dye-to-salt ratios. Figure 4.6 shows that for all the different dye-to-salt ratios, the OP increases as the Mw increases. The trend for each of the different dye-to-salt ratio graphs are: Black>Olive>Carmine>Blue>Red>Turquoise, ranked from the reactive dyes to the basic dyes, from the dye with the highest Mw to the dye with lowest Mw. Comparing the dye with highest Mw with the dye with lowest Mw, the black dye possesses a higher Mw (991 g/mol) and has the highest OP, compared to the Turquoise dye with lower Mw (359 g/mol). According to Han *et al.,* (2016), Reactive Black dye possesses four sulfonic acid groups, signifying that they continue to be in the anionic state in the solutions because of the low pKa value (pKa is the 10 logarithm base of the acid that is negative dissociation constant of a solution) (Perrin, 2013). The lower the pKa value, the weaker the acid. The Turquoise dye belongs to the basic dye group and basic group dyes are salt organic bases. They are called cationic dyes because they ionise in solution, causing the coloured component to become an act of positively charged acids (Baumann & Fletcher, 1951; Venkataraman, 2012). The trend for the OP for the different dye-to-salt ratio was found to be 1:60>1:50>1:40>1:30>1:20>1:10.

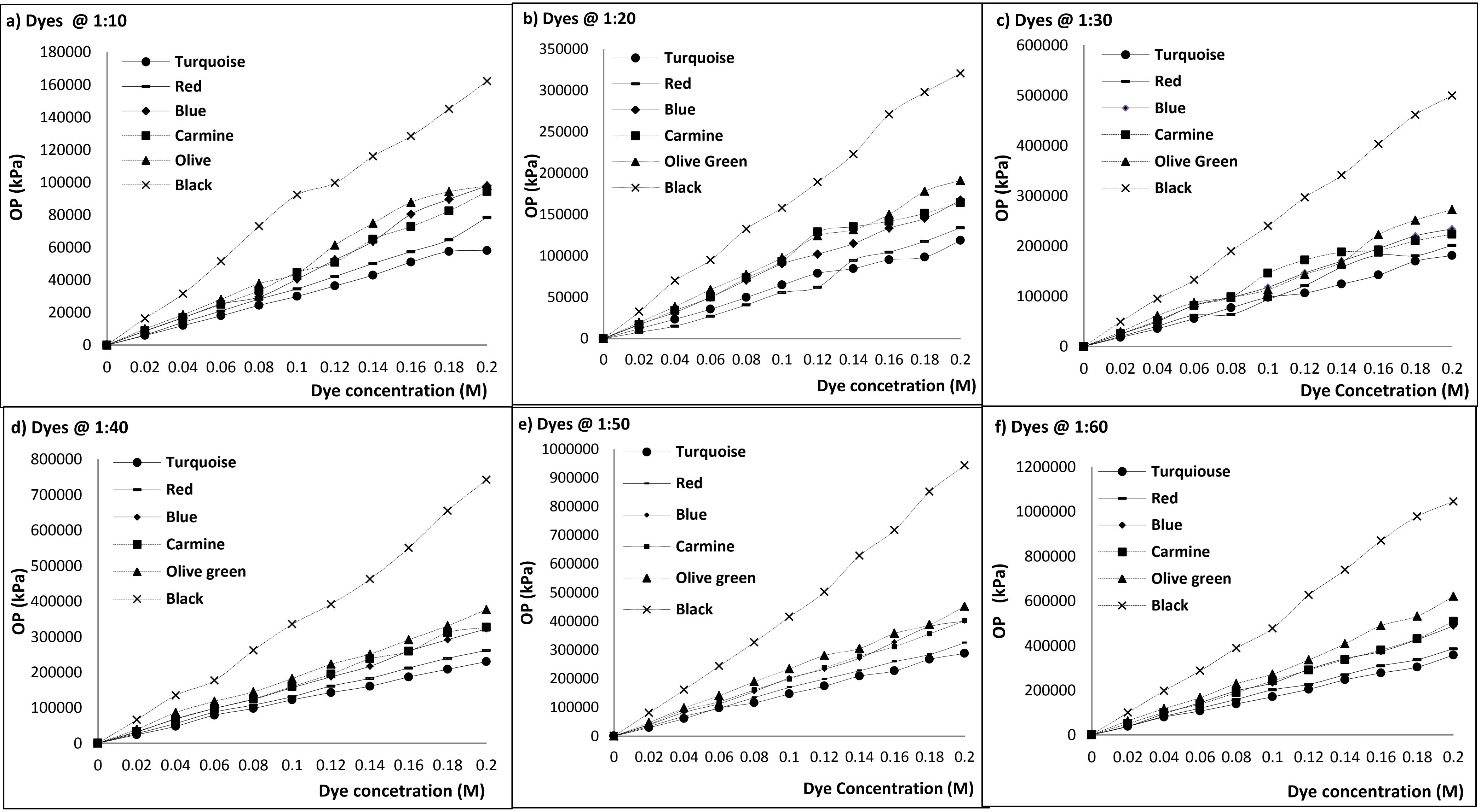


Figure 4.6: Comparison of osmotic pressure (OP) of different dye solutions at different concentrations at the same dye-to-salt mass ratio

4.4 Phase 4: The FO bench scale experiment

As explained in Chapter 2 (section 2.6.1) FO operation is about transportation of water across a semi-permeable membrane which hinders the solutes from passing through the membrane. For FO to be considered successful, the generation of a natural OP gradient in the absence of external hydraulic pressure must be evident. The natural OP gradient therefore is a result of a highly-concentrated DS and a FS with a low concentration. A semi-permeable membrane separates the two aqueous solutions. OP difference between FS and DS acts as the driving force for the movement of water through the semi-permeable membrane**.** From the dye solution OP analysis, the two dyes were selected (reactive dye: Reactive Black and basic dye: Basic Blue) as these dyes generated the highest OP for the two types of dyes classes evaluated.

4.4.1 FO bench scale experiments

The FO experiments in the FO mode were carried out using dye DS (Reactive Black and Basic Blue) both at a solute concentration of 0.02 M and a dye-to-salt ratio of 1:10. Basic Blue and Reactive Black, at 1:10 dye-to-salt ratio and 0.02 M, generated an OP of 9773 and 16231 kPa, respectively. The solute concentration and dye-to-salt mass ratio were selected on the basis of the recipe received from a textile industry, where producing an ideal dye solution for Basic Blue and Reactive Black had to have the OP of 8853 and 8580 kPa, respectively. The measured solute and water flux from these experiments are presented in Appendix C Table C1 to Table C8. The experiments were carried out with the different FS (SSW and TWW) listed in Table 4.1. The DI was used as a FS for the control experiment and the purpose for this experiment was to evaluate the duration to achieve osmotic equilibrium, while also producing an ideal dye solution that can be used directly in the textile industry.

4.5 Osmotic Equilibrium test results

Osmotic equilibrium is when the OP of both FS and DS reach an equilibrium state or become equal. An osmotic equilibrium experiment was carried out for the control experiments, i.e. Control 1 was an experiment between Reactive Black (DS) and DI (FS) and Control 2 an experiment between Basic Blue (DS) and DI (FS). Table 4.2 illustrates the findings from the two experiments

Table 4.2: Comparison of the two control experiments

Parameters	Units	Control 1	Control 2
OP (FS)	kPa	0	0
OP (DS)	kPa	16568	9773
ΔOP	kPa	16568	9773
Initial Flux (J_W)	L/m^2h	16.18	19.73
Flux @ 2hr (J_W)	L/m^2h	8.14	5.73
Final Flux (J_f) @ target concentration	L/m^2h	4.01 @ 25h	5.72 @ 6h
Final Flux (J_f) @ equilibrium	L/m^2h	2.32 @ 52h	1.61 @ 140h
Reverse flux (J_S)@ equilibrium	g/m^2h	6.74	1.08
Recovery Rate (Re) @ target concentration	%	60	45
Recovery rate @ equilibrium	%	95	80

4.5.1 Water flux for controls

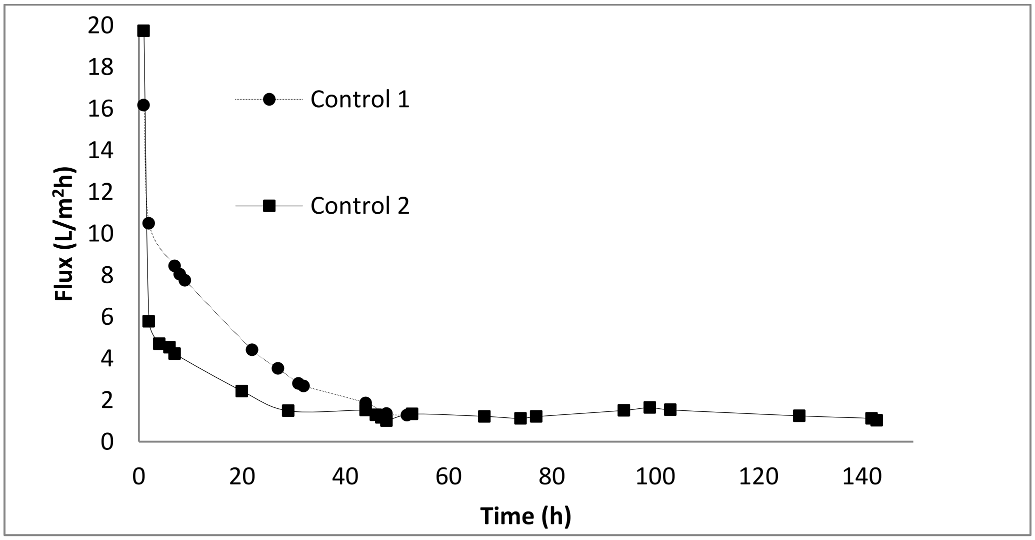


Figure 4.7: Water flux (Jw) of control experiments

The water flux is the flow rate of water applied per unit area of the membrane (Chun, *et al*., 2017; Zhao *et al*., 2015). The initial OP gradient for control 1 was 16568 kPa, while the inital OP gradient for Control 2 was 9773 kPa. Control 1 reached osmotic equilibrium at approximately 55 hours, with FS having an OP of 5391 kPa and DS having an OP of 6667 kPa. Control 2 reached OP equilibrium in approximately 140 hours, with FS having an OP of 3978 kPa and DS having an OP of 4045 kPa. The OP equilibrium is highly influenced by the OP gradient i.e. the higher the initial OP gradient the quicker the OP equilibrium is reached. As illustrated in Figure 4.7 Control 1 initial flux was at 16.18 L/m^2 and after two hours, there was a decrease in water flux to 8.14 L/m^{2}h, while Control 2 had an initial flux of 19.73 L/m^{2}h and after two hours decreased to 5.73 L/m^{2}h. The significant decrease of the water flux occurring in the first two hours was primarily due to the decline in the net osmotic pressure difference across the membrane.

For Control 1, the system reached the target concentration of 0.002 M at approximately 25 hours, with a water flux of 4.01 L/m^{2}h, since the OP difference between the DS and target concentration was 7651 kPa, the system took longer to reach the target concentration. For Control 2 the target concentration of 0.0041 M was reached at approximately 6 hours, with a water flux of 5.72 L/m^{2}h. The OP difference between DS of Control 2 and the target concentration was 920 kPa, hence the system attained the target concentration in a relatively short time. The final flux (J_f) for Control 1 after 55 h was 2.32 L/m^{2}h and, for Control 2 after 140 h was 1.61 L/m^{2}h. There was no driving force between the two solutions and the system was declared to be at equilibrium.

4.5.2 Reverse solute flux for controls

Table 2.6 illustrate the aquaporin membrane specification with NaCl reverse flux of less than 2 g/m^{2}h, with DI as a FS and 1 M NaCl as a DS. In this study at the osmotic equilibrium the average reverse solute flux (J_S) was 6.74 and 1.08 g/m^{2}h for Control 1 and Control 2, respectively. The high J_s for control 1 is possibly due to several factors which may include (i) different DS used in this study (dyes) (ii) high molecule weight of the dyes as DS, as a significant amount of dye had a tendency to adhere to the surface or pores of the membrane more easily, (iii) use of membrane after the lapsed 6 months shelf life after production as stated in Table 2.6 and (iv) the membrane used in this study was still at a development stage.

Furthermore, a Hazen Colour analysis was performed initially and after the completion of the experiments for the purpose of assessing solute fluxing. The Hazen Colour analysis is represented in Appendix D: Table D1 and D2 for all experiments relating to Reactive Black and Basic Blue, respectively. However, solutes diffused through the membrane from DS to the FS, colouring the

DI. The initial DI colour was 0 mg/L Pt for control experiments and the final DI colour at completion of the experiment was found to be approximately 7 and 2.5 mg/L Pt for Control 1 and Control 2, respectively, indicating the number of solutes that have fluxed through the membrane during the experiment. At the osmotic equilibrium for the average reverse solute flux (J_S) was 6.74 and 1.08 g/m^2h for Control 1 and Control 2 respectively.

4.5.3 Water recovery rate for controls

It was noted that with progression of time, water moved across the permeable membrane diluting the DS, reaching a recovery rate of 60% at target concentration in Control 1 and 95% recovery rate at the completion of the experiment. This was evidenced by a decline in the colour concentration of the DS from an initial colour concentration of 805 mg/L Pt to 500 mg/L Pt at the end of the experiment. For Control 2, a 45% recovery rate was achieved at target concentration and at the completion of experiment 80% recovery rate was achieved. The colour concentration on the DS dropped from an initial colour concentration of 553 mg/L Pt to 402 mg/L Pt at the completion of the experiment, indicating water transportation from the FS to the DS.

4.6 Production of reactive dye solution using alternative feed solutions

Table 4.3 illustrates the averaged fluxes of duplicate FO mode experiments with Reactive Black as a DS at an initial concentration of 0.02 M with SSW and TWW as FS. For Reactive Black, the target concentration of dye solution that needed to be produced was 0.002 M corresponding to OP of 8580 kPa, as was received from a standard recipe for Reactive Black in the textile industry.

Table 4.3: **Comparison of parameters obtained in FO operation using alternative feed solutions**

Parameters	**Units**	**SSW**	**TWW: Factory 1**	**TWW: Factory 2**
OP (FS)	kPa	2851.50	1503.50	3308.94
OP (DS)	kPa	16510.4	16492	16349.9
ΔOP	kPa	13658	14988	13040
Initial Flux (J_W)	L/m^2h	20.24	19.51	13.43
Flux @ 2hr (J_W)	L/m^2h	8.61	5.93	5.74
Final Flux (J_f) @ target Concentration (0.002 M)	L/m^2h	5.22 @ 44 h	4.05 @ 22 h	4.15 @ 22 h
Final flux (J_f)	L/m^2h	5.65 @ 44 h	0.76 @ 30 h	0.98 @ 30 h
Recovery Rate @ Target Concentration (0.002)	(%)	75	30	30
Recovery rate @ 30 hrs.	(%)	65	65	65

4.6.1 Water Flux (J_W) for Reactive black

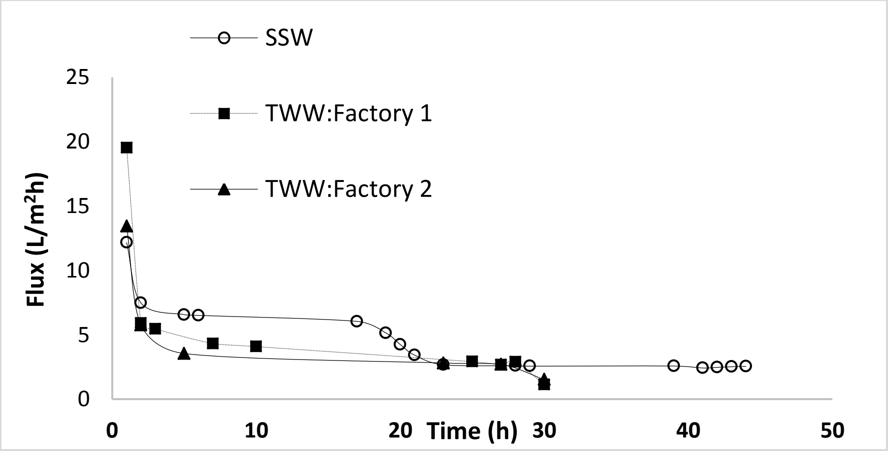


Figure 4.8: Flux profiles of FO experiments with Reactive Black as DS and different FS

The FS (SSW, TWW Factory 1 and TWW Factory 2), unlike DI, contained a certain amount of salt, though the salt concentration differs as evidenced by the OP (FS) in Table 4.3.

For the experiment using SSW as the FS the initial OP gradient which is the driving force for FO, was 13658.9 kPa and for TWW Factory 1 and TWW Factory 2 was 14988 and 13040 kPa, respectively. Figure 4.8 illustrates the flux profiles obtained when producing a target concentration reactive dye solution. From Figure 4.8 it was observed that the initial water flux (J_W) for SSW experiment was 20.24 L/m^{2}h and after 2 hours declined to 8.61 L/m^{2}h. For TWW Factory 1 and Factory 2, the initial water flux (J_W) was 19.51 and 13.43 L/m^{2}h, and after two hours, it declined to 5.93 and 5.74, respectively. For all FS the flux had a gradual decrease after 2h. In pressure-driven membrane processes, the cake enhanced osmotic pressure leads to water flux decline (Zhao *et al*., 2015a). The main mechanism leading to the gradual decline in water flux is the cake enhanced osmotic pressure, whereby the cake layer of dyes deposited on the feed side prevents the back diffusion of salt into the bulk solution, hence resulting in higher OP near the membrane surface of the feed side. This contrivance leads to a drop in the net driving force and therefore a decline in the water flux. For the experiments with TWW, another contributing factor for this decline in the water flux is the dye in the feed solution that accumulates within the porous structure and on the membrane surface of the substrate, and therefore enhances the transport resistance and increases the structural parameters.

For the experiment using SSW as the FS, the target concentration was reached at approximately 44 hours, with water flux of 5.22 L/m^{2}h. The SSW is a composition of an ionic solid, NaCl, which is dissolved in water, a polar solvent. Therefore, the drop-in water flux is caused by the positive charges in the SSW solution that induces strong interaction between the negative charges of the dye molecules. Thus the system took longer to reach the target concentration and the recovery rate was at 75%, indicating a significant amount of water was transported across the membrane.

For experiments where FS was TWW from Factory 1 and Factory 2, the target concentration was reached at 22 hours, with water flux of 4.05 and 4.15, respectively. The TWW shows the lowest reduction in water flux when the system reached target concentration, with a recovery rate of 30%. Since both TWW are of reactive dye origin and they possess a negative charge and the DS (which is Reactive Black) also possesses a negative charge, the greater decline in water flux was due to larger molecular weight of the TWW. It was noted, however, that at 30 hours, the water flux had declined. For all the FS the feed water recovery rate was the same at 65%.

4.6.2 Reverse solute flux for Reactive Black

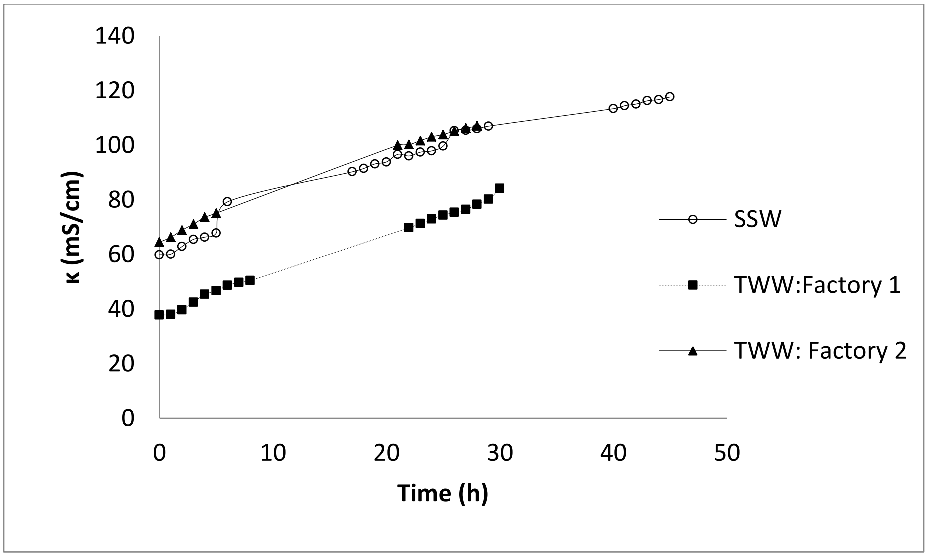


Figure 4.9: Conductivity of different FS in the FO operation with Reactive Black as a DS

The reverse permeation of draw solutes in osmotically-driven membrane processes is the outcome of the difference in solute concentration across the membrane. The reverse flux of solute decreases the OP difference across the membrane, and therefore compromises the competence of the FO system (Yong *et al.,* 2012).

The reverse solute flux was monitored by measuring of the feed solution conductivity during the FO operation. For the SSW experiment the conductivity of the SSW (FS) ranged from 59.9 to 110 mS/cm and the experiment was conducted up to approximately 44 h, where the system reached the target concentration while experiment with TWW Factory 1 and TWW Factory 2 the conductivity ranged from 37.8 to 84.2 mS/cm and 64.4 to 115 mS/cm, respectively. This is due to the back diffusion of solutes from the DS, which increase the internal concentration polarisation. The SSW experiment and TWW Factory 2 demonstrated higher conductivity with implied a higher reverse solute flux compared to the TWW Factory 1 experiments, this is due to the salts that were present in the FS (SSW and TWW Factory 2) before the FO operation and because of the interaction between the FS and DS, as explained above. For the TWW experiments, reverse solute flux is also closely associated with the recipe of the dye used in the textile industry, as more solutes were used to make the recipe in which the TWW was collected. It was therefore noted that conductivity increases with progression of time.

Furthermore, a Hazen Colour analysis was executed at the initiation and completion of the experiment for the purpose of attesting the reverse solute flux. For the experiment between the SSW as FS and Reactive Black as DS, the FS did not initially show colour concentration, but over time it was observed that the FS colour began to change to that of the DS. The Initial FS colour was 0 mg/L Pt and the final FS colour was at 496 mg/L Pt. The change of colour and colour concentration of the FS occurred rapidly compared to the control experiment. From the Hazen Colour analysis that was performed, it was observed that initially the TWW from Factory 1 had a Hazen Colour of 200 mg/L Pt. Over time, the colour concentration increased to 500 mg/L Pt, indicating reverse solute flux that was occurring from the DS to the FS. TWW from Factory 2 initially had Hazen Colour of 288 mg/L Pt and increased over time to 500 mg/L Pt.

4.6.3 Recovery rate for Reactive black

The TWW experiments both achieved a recovery rate of 30% and took 22 hours to reach the target concentration, while the experiment of SSW achieved 75% at target concentration after 44 hours. At 30 hours all the experiments achieved a feed solution recovery rate of 65 %. Feed recovery rate increased with time, as was evidenced by the Hazen Colour analysis done on the DS at the beginning and end of the experiment, for purpose of assessing the water transportation from the feed side to the DS. For the SSW experiment, the DS colour concentration decreased from 794 mg/L Pt to 500 mg/L Pt, indicating water transportation from the FS to the DS. Using Factory 1 TWW, the DS was initially at 799 mg/L Pt and decreased to 694 mg/L Pt at the end of the experiment, and for Factory 2 TWW the DS colour concentration was initially at 809 mg/L Pt, then decreased to 712 mg/L Pt.

4.7 Production of basic dye solution using alternative feed solution

Table 4.4 illustrates averaged flux results of duplicate FO experiments carried in FO mode. Using a basic dye (Basic Blue) as a DS at a 0.02 M concentration and dye-to-salt mass ratio of 1:10. SSW and TWW were used as alternate FS. The TWW was collected from two different factories, both using a reactive dye in the dyeing process. The dye solution that had to be produced had a target concentration of 0.0041 M solution corresponding to 8853 kPa, as was calculated from a standard recipe for Basic Blue in the textile industry.

Table 4.4: comparison of parameters with basic dye as DS using alternative feed solutions

Parameters	**Units**	**SSW**	**TWW: Factory 1**	**TWW: Factory 2**
OP(FS)	kPa	2811	1513	3281
OP (DS)	kPa	9773	9774	9776
ΔOP	kPa	6962	8260	6495
Initial Flux (J_w)	L/m^{2}h	18.72	15.13	13.42
Flux @ 2 hrs. (J_w)	L/m^{2}h	3.15	3.195	4.65
Final Flux (J_f) @ target concentration (0.0041)	L/m^{2}h	2.81 @ 20 h	3.54 @ 4 h	3.22 @ 4 h
Final Flux (J_f) @ 30 hours	L/m^{2}h	2.21	1.52	2.56
Recovery Rate @ target concentration	(%)	50	20	20
Recovery rate @ 30 hrs.	(%)	75	50	65

4.7.1 Water Flux for Basic Blue

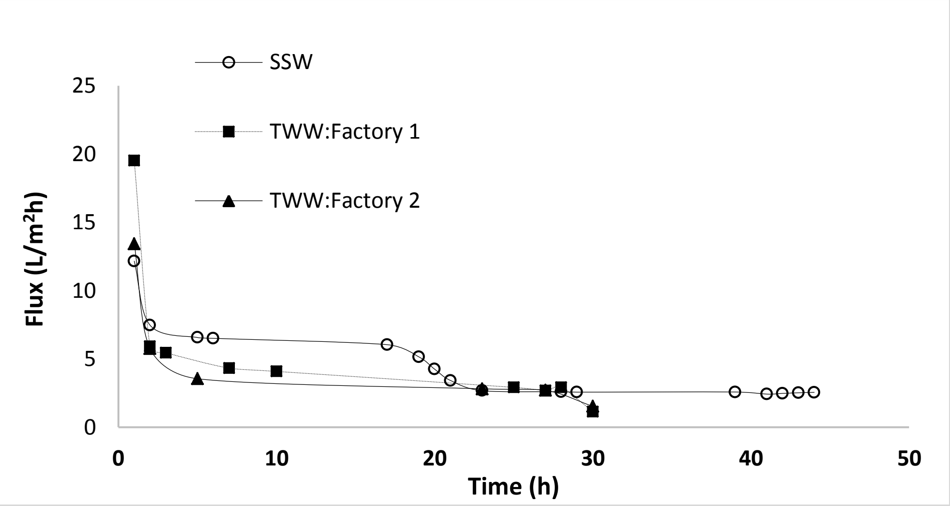


Figure 4.10: Flux profile of FO experiments with Basic Blue as the DS and different FS

Figure 4.9 illustrate flux profiles when producing basic dye solution using Basic Blue as a DS and different FS (SSW, TWW 1 from Factory 1 and TWW 2 from Factory 2). For the SSW experiment, the initial OP gradient was 6962 kPa, resulting in an initial water flux (J_W) of 18.72 L/m^{2}h, similar to other reported studies, such as Zhao *et al.* (2015) and Han *et al.* (2016). A significant drop in the water flux occurred after two hours to 3.15 L/m^{2}h. For the experiments using TWW as a FS initial flux from Factory 1 and 2, these values were found to be 15.13 and 13.42 L/m^{2}h respectively. The initial OP gradient was 8260 and 6495 kPa for TWW from Factory 1 and 2, respectively. After two hours, the flux declined to 3.20 and 4.65 L/m^{2}h respectively. This flux decline is characterised by two factors (i) the deposition of dye molecules on the surface of the membrane and (ii) a decline in the net osmotic pressure across the membrane.

The FO system was operated for 30 hours for all the experiments. Using the SSW as the FS, the system reached the target concentration approximately at 20 hours of the operation, with water flux 2.81 L/m^{2}h, while for TWW experiments the target concentration was reached within 4 hours, with water fluxes at 3.54 and 3.22 for TWW Factory 1 and Factory 2, respectively. It was noted that when the fouling had developed and the system was stable, the flux decline became slower and minor. The difference in time (20 hours for SSW experiment and 4 hours for TWW experiments) to reach the target concentration is due the chemistry of the DS dye solution, whereby Basic Blue is a cationic dye possessing a positive charge and the TWW solution are of reactive dye origin and possess a negative charge, TWW was attracted to the DS, while for the SSW a strong interaction between SSW and dye molecules occurred hence declining the water flux. At 30 hours where the final water flux (J_f) for the SSW experiment was found to be 2.21 L/m^{2}h and for the TWW experiments, Factory 1 and Factory 2 was at 1.52 and 2.56 L/m^{2}h, respectively.

4.7.2 Reverse solute flux for Basic Blue

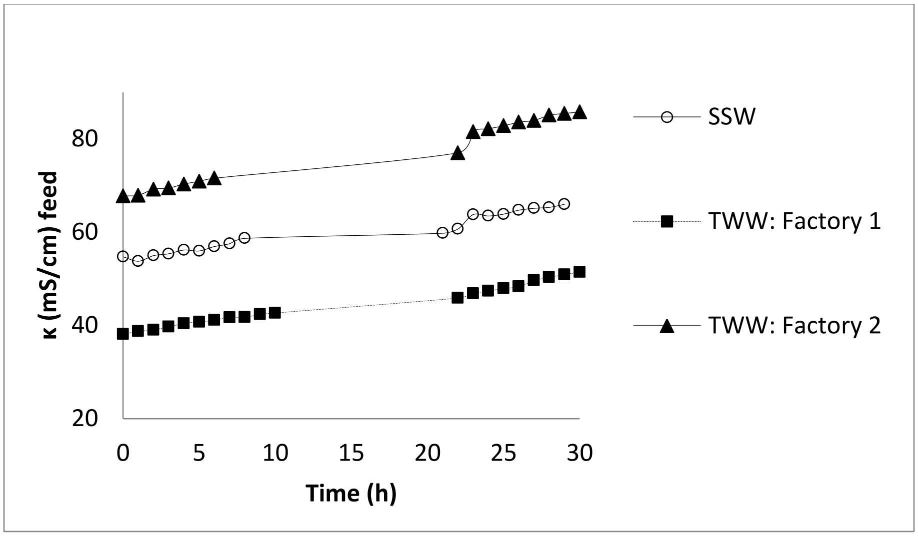


Figure 4.11: Conductivity of different FS in the FO operation with Basic Blue as a DS

Figure 4.11 illustrates the conductivity of three FS (SSW, TWW Factory 1 and TWW Factory 2) with Basic Blue as a DS, used as a measure of the reverse solute flux. In the experiment where SSW was used as a FS, the conductivity ranged from an initial conductivity of 54.3 to 65.9 mS/cm and at target concentration it was about 59.75 mS/cm. For the TWW experiments, the conductivity ranged from 38.1 to 51.4 mS/cm and 67.7 to 86.4 mS/cm, respectively, for TWW Factory 1 and TWW Factory 2. The conductivity increased with time on the FS as a result of solutes moving from DS to the FS. It was obvious that the reverse solute flux is a function of time, as was also evidenced by the colour change of the FS to that of DS. Colour Hazen analysis was carried out to measure the change in colour concentration on both the FS and DS. The initial colour on the FS was 0 mg/L Pt and at the end of the experiment, it was found to be 24 mg/L Pt for the SSW experiment. It was noted that the colour concentration. For Factory 1 the colour increased from 200 mg/L Pt to 256 mg/L Pt, illustrating the fluxing of solutes from DS to FS. Factory 2 experiments showed that the colour concentration increased from 288 to 383 mg/L Pt. The initial conductivity and colour of the TWW FS is associated with the recipe of the dye.

4.7.3 Recovery rate for Basic Blue

Feed water permeated across the membrane from the FS to the DS was found to be 50 % for SSW and 20% for both TWW experiments at the target concentration. The recovery rate increased with the progression of time, demonstrating significant water transportation. At 30 hours for the experiment with SSW, 75% feed water was achieved, while for TWW experiments, 50 % and 65% recovery rates were achieved for Factory 1 and Factory 2, respectively. Moreover, Hazen Colour analysis was done on the DS at the initial and final stages of the experiments. The initial colour on the DS was at 553 mg/L Pt and at completion of the experiment it was 402 mg/L Pt. for the SSW experiment. For the TWW experiments, in the Factory 1 experiment the initial colour of the DS was at 541 mg/L Pt, and this decreased to 402 mg/L Pt, indicating water transport from FS to DS. For the Factory 2 experiment, DS decreased from 540 to 286 mg/L Pt, which clarifies the 65 % feed recovery rate.

CHAPTER 5

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This study focused firstly on (i) identifying and evaluating possible alternative feed solutions (FS); (ii) the evaluation and assessment of basic and reactive dyes as potential and suitable draw solutions (DS) and (iii) assessing a FO system for the production of dye solutions using alternative water resources as well as reclaimed textile wastewater. The FS included deionized water (DI) for control experiment, brackish water (BW), synthetic seawater (SSW), seawater (SW) and textile wastewater (TWW).

Assessing the OP of the identified FS, it was found that measured OP of FS was (DI, BW5, SSW and SW) 0 kPa, 414 kPa, 2761 kPa and 2579 kPa, respectively. The identified FS were suitable for FO processes where the DS has a higher OP. Assessing the OP of the dyes, from the selected basic and reactive dyes, it was found that both basic and reactive dyes combined with salt in different dye to salt ratios generated higher OP than the dyes with no salt. The higher concentrations of dye solutions generated a higher OP. The higher dye to salt mass ratios produced higher OP and the trend followed by the dyes with the application of dye to salt ratio were Black>Olive>Carmine>Blue>Red>Turquoise. The OP generated by the basic and reactive dye solutions ranged between 160 000 kPa to more than 1 000 000 kPa. It was concluded that the OP of the dyes at different concentration and dye to salt ratios is influenced more by the dye chemistry and Mw of the dye rather than the type of dye.

Assessing the FO system for the production of a dye solution, it was concluded that the target concentration was reached at different times depending on the FS. Both the Reactive Black and Basic Blue are suitable DSs. Using the Aquaporin biomemetic membrane as the semi-permeable membrane a highest flux of 19.73 (L/m^{2}h) was achieved. It was also found that production of dye solutions using FO is possible with feed water recovery rate of ranging from 20 to 75 % using SSW and TWW. The use of dyes as DS was successful; however, challenges such as reverse solute flux still remain, as the reverse solute flux of Control 1 was at 6.74 g/m^{2}h. SSW, TWW1 and TWW2 illustrated the potential to be a suitable FS, however based on the reverse solute flux results it was concluded that the TWW is a better FS than SSW

5.2 Recommendation

Among the challenges that were faced in this study is high rate of back diffusion of solutes, especially when using SSW as a FS. It is therefore recommended that a study which will incorporate the use magnetic nanoparticles which function by polyacrylic acid and yield high OP and high water flux (Chung *et al.,* 2012) be undertaken at a dye concentration lower than 0.02 M, as this will reduce reverse solute flux. Moreover on this study the energy used was delineated; it is recommended that a study which will focus on the use of energy for this technology in the textile industry be undertaken.

REFERENCES

Achilli, A., Cath, T.Y. & Childress, A.E. 2010. Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science*, 364(1-2):233-241.

Alturki, A. A., Mc Donald, J., Khan, S., Price, W. & Nghiem, L. 2012. Removal of trace organic contaminants by the forward osmosis process. *Seperation and Purification Technology*, 103:258-266.

Aljeboree, A., Alkaim , A. & Alshirifi , A. 2014. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian Journal of Chemistry, 150* (10) 1016:1-14.

Akther, N., Sodiq, A., Giwa, A., Daer, S., Arafat, H.A. & Hasan, S.W. 2015. Recent advancements in forward osmosis desalination: A review. *Chemical Engineering Journal,* 281:502-522.

Ananthashankar, A.G. 2013. Production, characterization and treatment of textile effluents: a critical review. *Journal of Chemical Engineering and Process Technology*, 5(1):1-18.

Babu, B.R., Parande, A.K., Raghu, S. & Kumer, T.P. 2007. Cotton textile processing:Waste Generation and effluent treatment. *The journal of cotton Science* 11:141-153.

Baumann, H. & Fletcher , J. 1951. *Textile dyeing.*: International Textbook company. United States of America.

Besade, H. & Werner , K. 2015. An assessment of the effects of Africa's water crisis on food security and management. *International Journal of Water resources development,* 31(1):120-133.

Buthelezi, S.P., Olaniran, A.O. & Pillay, B. 2012. Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates. *Molecules*, 17(12):14260 - 14274.

Burkinshaw. S.M. 1995. *Chemical Principles of synthetic fibre dyeing*. Black academic & professionals. London.

Cath, T., Childress, A. & Elimelech, M. 2006. Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science*, 281 (1-2):70-87.

Chen, J. P., Wang , L. & Hung , Y.T. 2011. *Membrane and desalination technologies.* New York Springer Science & Business Media LLC.

Chester, R. & Jickells, T. 2012. *Marine Geochemistry*.Wiley-Blackwell publishers. Scotland.

Chemical book 2016. Carmine. 02 October 2016. (https://www.chemicalbook.com/Price/CARMINE-2.htm).

Chongule, M.B. & Sonaje, N.P. 2012. Novel techniques of water recycling in textile wet processing through best management practices (BMP's). *International Journal of Applied and Advance Technology*, 1(1):29-30.

Chung, T.S., Zhang, S., Wan, K.Y., Ling, M.M. & Su, J. 2012. Forward osmosis processes: Yesterday, today and tomorrow. *Desalinatio*n, 287(15):78-81.

Chun, Y., Mulcahy, D., Zou, L. & Kim, I.S.2017. A short Review of Membrane Fouling in Forward Osmosis Processes*. Membranes journal Membranes*, 7(2):30 doi:10.3390/membranes7020030.

Christie, R. 2014. *Colour Chemistry 4th edition*. The Royal Society of Chemistry. United Kingdom.

Dashtpour, R. & Al-Zubaidy, S.N. 2012. Energy efficient reverse osmosis desalination process. *International Journal of Environmental Science and Development*, 3(4):339-345.

De Jager, D., Sheldon, M.S. & Edwards, W. 2012. Membrane bioreactor application within the treatment of high textile effluent. IWA Publishing*. Water Science & Technology*. 65 (5):907-914.

De Jager, D., Sheldon, M.S. & Edwards, W. 2014. Colour removal from textile wastewater using a pilot-scale dual stage MBR and subsequent RO sysem. *Separation and Purification Technology,* 135 (2014) 135-144*.*

DyStar Product Selection Guidance. 2014 H&M Chemical Restrictions Version May 2014 Part 3

El-sayed, G.O., Awad, M.S. & Ayad, Z.A. 2014. Electrochemical Decolorization of Maxilon Red GRL Textile Dye. *International Research Journal of Pure and Applied Chemistry*, 4(4):402–416.

Etheridge, J. 2017 News24 https://www.news24.com/SouthAfrica/News/city-of-cape-town-approves-level-4-water-restrictions-20170531.

Fersi. C & Dhahbi, M. 2008. Treatment of textile plant effluent by ultrafiltration.*: Desalination,* 1(222):263-271.

Fioramonti, L. 2015. Water shortages about to put load-shedding in the dark. Business Day http://www.waterrhapsody.co.za/2015/06/30/water-shortages-about-to-put-load-shedding/downloaded 8 Dec 2016).

Garud, R., Kore, S. & Kulkarni, G.2011. A short review on process and application of reverse osmosis. *Universal Journal of Environmental Research and Technology,* 1(3): 233-238.

Gray, G.T., McCutcheon, J.R. & Elimelech, M. 2006. Internal concentration polarization in forward osmosis: Role of membrane orientation. *Desalination*, 197:1-8.

Greenlee, L. F., Lawler.D. F., Benoit, M. & Philippe, M. 2009. Reverse osmosis desalination: Water sources, technology. *Water Research,* 43(9): 2317-2348.

Grattoni, A. & Merlo, M. 2007. Osmotic pressure beyond concentration restriction. *Journal of Physical Chemistry,* 111:11770-11775.

Gravelet-Blondin, L.R., Barclay, S., Carliel, C. & Buckley, C.1997. Management of water resources in South Africa with respect to the textile industry. *Water Science & Technology* (2-3):303-310.

Han, G., Liang, C.,Zeng, C., Tai Shung, W.,Staudt,M.C. & Maletzko, C. 2016. Combination of forward osmosis (FO) process with coagulation/flocculation (CF) for potential treatment of textile wastewater. *Water Research*, 91:361–370.

Habel, J., Hansen, M., Kynde, S., Larsen, N., Midtgaard, S.R., Jensen G. V., Bomholt, J., Ogbonna, A ., Almdal, K., Schulz, A. & Claus, H. 2015. Aquaporin-based biomimetic polymeric membranes: *Membranes,* 1(5):307-351.

Horst, T., Helming, W., Mischke, P., Rebsamen, K., Reiher, U., Russ, W. & Vermehren, P. 2000. *Reactive dyes in Ullmann's Enyclopedia of Industrial Chemistry.* Weinheim: Wiley-VCH.

Huber, C., Klimant , I., Krause , C., Werner , T., Mayr, T., & Wolfbeis , O. 2000. Optical sensorfor seawater salinity. *Fresenius J Anal Chem*, 196-202.

Kafeero, F. 2007. The impact of water shortage on forest resources: The case of Uganda. *Unasylva*, 58(229):38-52.

Kim, Y., Elimech, M., Shon, H.K. & Hong, S. 2014. Combined organic and colloidal fouling in forward osmosis: Fouling reversibility and the role of applied pressure. *Journal of Membrane Science,* 460:206-212.

Kolarjet chemicals PVT .Ltd (n.d) viewed 08 October 2015, from http://www.dyes pigments.com/profile.html (http://www.dyes-pigments.com/reactive-dyes.html) viewed on the 16/11/15.

Kutchai, H. 2003. *Self-instructional packages on diffusion, osmosis, ionic equiilibria and resting membrane potential: General physiology course*. Sackler School of Medicine, Tel Aviv University.

Khulbe, K., Feng , C.& Matsuura, T. 2008. *Synthetic polymeric membranes.* Springer publishers. Canada.

Liu, Y. 2013. Fouling in forward osmosis membrane processes: characterization, mechanisms, and mitigation. Unpublished PhD thesis, University of Maryland, United State of America.

Lin, S. & Cheng, M. 1995. treatment of textile wastewater by chemical. *Elsevier Science*, 31(4): 868-876.

Mahir, A., Turhan , Y., Demirbas , O. & Turan , P. 2008. Adsorption kinetics and mechanism of maxilon blue 5Gdye on sepiolite from aqueous solution . *The Chemical Engineering Journal* , 139 (2):213-223.

Mary, H. & Tetraut, G. 1995. *Laboratory Instrumentation.* 4th edition. John Wiley and Son. Canada.

Mackin J.F. 2008. Dye selection & combination. *Society of Dyers and colours*. 91 (3):61-80.

Madan, R.L. 2005. S. Chad Success guide in organic chemistry.s. Chad & Company Ltd Ram Nagar, New Delhi.

Mehta, D., Gupta, L. and Dhingra, R. 2014. Forward Osmosis in India: Status and comparison with other desalination technologies. *International Scholarly Research Notices,* Volume 2014 (Article ID 175464):9 .

Motsa, M.M., Mamba, B., D'Haese, A., Hoek, E. & Verliefde, R.D. 2014. Organic fouling in forward osmosis membranes: The role of feed solution chemistry and membrane structural properties. *Journal of Membrane Science*, 460:99-109.

McGovern, R.K. & Lienhard, V.J.H. 2014. On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *Journal of Membrane Science*, 469:245-25.

McCutcheon, J.L., McGinnis, R.L. & Elimelech, M. 2006. Ammonia-Carbon dioxide forward osmosis desalination. *Water Conditioning and Purification*.

Mehta, D., Gupta, L. & Dhingra, R., 2014. Forward osmosis in India: status and comparison with other desalination technologies. *International Scholarly Research Notices*, *2014:* (1-9) Article ID 175464.

McGovern, R.K. & Lienhard J.H. 2014. On the potential of forward osmosis to energetically outperform reverse osmosis desalination, *Journal of Membrane Science,* 469: 245-250.

Nicoll, P. 2012. Forward osmosis applied to desalination and evaporative cooling make-up Water. *Modern water* 11:1-13.

Nguyen, H.T., Nguyen, C.N., Chen, S.S., Ngo, H.H., Guo, W. & Wang Li, C. 2015. A new class of draw solutions for minimizing reverse salt flux to improve forward osmosis desalination. *Science of the Total Environment* 538:129–136

Le,N.L. & Nunes, S.P. 2016. Materials and membrane technologies for water and energy sustainability. *Sustainable Materials and Technologies,* 7: 1–28.

Phuntsho, S., Shon, H.K., Hong. S., Lee, S. & Vigneswaran, S. 2011. A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions. *Journal of Membrane Science,* 375(1-2):172-181.

Phuntsho, S. 2012. A novel fertiliser drawn forward osmosis desalination for fertigation PhD thesis. sydney: School of civil and Environmental Engineering. Faculty of Engineering and Information Technology University of Technology, Sydney (UTS), New South Wales, Australia.

Phuntsho, S., Shon, H.K., Hong, S., Lee S., Vigeswara S. & Kandasaby, J. 2012. Fertiliser drawn forward osmosis desalination: The concept, performance and limitations for fertigation. *Reviews in Environmental/Science Biotechnology*, 11:147-168.

Pinnekamp, I.J. & Frieldrich, H. 2003 Municipal Water and Waste Management. *Membrane Technology for wastewater treatment.* FiW Verlag (2):1-239.

Perrin.D. 2013. pKa Prediction for Organic Acids and Bases, springer-science and business media, Australian national university.

Ren, J. & McCheon, J. R.2014. A new commercial thin film composite membrane for forward osmosis. *Desalination.*343:187-193.

Salter, B.R.J. 2006. Forward osmosis. *Water Conditioning and Purification*, 48(4):36–38.

Segal. N. 2009. Does South Africaface a water crisis? A report to business leadership in South Africa.

Shaffer, D.L., Werber, J.R., Jaramillo, H., Lin, S. & Elimelech, M. 2015. Forward osmosis: Where are we now? *Desalination,* 356:271-284.

Shen, Y., Saboe, P., Sines, I., Erbakan, M. & Kumar, M. 2014. Biomimetic membranes :A review. *Journal of Membrane Science,* 454: 359-381.

Shon, H. K., Phuntsho, S., Chaudhary, D. S., Vigneswaran, S. & Cho, J. 2013. Nanofiltration for water and wastewater treatment – a mini review. *Drinking Water Engineering and Science.*6:47-53.

Standen, A. 2004. dye. In: *Encyclopedia of Chemical Technology.*: John Wiley and Sons, Inc , 464-507. New York.

Statistics South Africa. 2016. Mid-year population estimates 2016 Mid-year population estimates 2016.

Sparks, D., Madhlopa, A., Keen, S., Moorlach, M., Dane, A., Krog, P. & Dlamini, T**.** 2014. Renewable energy choices and their water requirements in South Africa. *Journal of Energy in Southern Africa,* 25(4):80-92.

Strathmann H, Giorno L, Drioli E.2006. An introduction to membrane science and technology, chapter 2. CNR Publisher, Roma. ISBN 88-8080-063-9.

Shen, Y., Saboe, P., Sines, I., Erbakan, M. and Kumar, M. (2014). Biomimetic membranes: A review. *Journal of Membrane Science*, 454, pp.359-381.

Talukder, E., Kamruzzaman,M.D., Majumder, M, Shakhawat, M.D., Hossain, R., Hossain, M & Das, S. 2017. Effects of salt concentration on the dyeing of various cotton fabrics with reactive dyes, *International Journal of Textile Science* 6(1): 7-14.

Truett, L. J., & Truett, D. (2010). New challenges for the south african textile and apparel industries in the global economy. *Journal of economic development,* 35 (4) 73-91.

Venkatarama,K. 2012, *The Chemistry of Synthetic Dyes*, academic press. New York.

Von Bormann, T. & Gulati, M. 2014. The food energy water nexus: Understanding South Africa's most urgent sustainability challenge WWF-SA, South Africa:1-35.

Wang, R., Setiawan, L. & Fane, A.G. 2006. Forward osmosis: Current status and perspectives. *A Journal of Membrane Science Virtual Special Issue*, 281:70-87.

Wang, Z., Xue, M., Huang, K. & Liu, Z. 2011.Textile dyeing wastewater treatment. *Advances in textile effluent*. Prof. Peter Hauser (Ed.), ISBN: 978-953-307-704-8, InTech, Available from: http://www.intechopen.com/books/advances-in-treating-textile-effluent/textile-dyeing-wastewater-treatment.

Wu, D. 2015. Thin film composite membrane derived from interfacial polymerisation for nanofiltration and pervaporation. PhD thesis.University of Waterloo Faculty of engineering in Chemical Engineering Waterloo, Ontario, Canada.

Yong,J.S., Phillip, W.A & Elimelech. M. 2012. Reverse Permeation of Weak Electrolyte Draw Solutes in Forward Osmosis. *Industrial & Engineering Chemistry Research.51:* (41) 13463–13472.

Zaviska, F. & Zou, L. 2014. Using modelling approach to validate a bench scale forward osmosis pre-treatment process for desalination. *Desalination,* 350(1):1-13.

Zhao, S., Zou, L., Tang, C. & Mulcahy, D. 2012a. Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science,* 396(1):1–21.

Zhao, Y., Qiu, C., Li, X., Vararattanavech, A., Shen, W., Torres, J., He´lix-Nielsen, C., Wang, R., Hu, X., Fane, A.G & Tang, C.Y. 2012b. Synthesis of robust and high perfomance aquaporin based biomimetic membrane by interfacial polymerisation membrane preparation and RO perfomance characterisation. *Journal of Membrane Science ,* (423):422-428.

Zhao, P., Gao, B., Xu, S., Kong, J., Ma, D. & Shon, H. K. 2015a. Polyelectrolyte-promoted forward osmosis process for dye wastewater. *Chemical Engineering Journal*, 264:32-38.

Zhao, S., Huang, K and Lin, H. 2015b. Impregnated Membranes for Water Purification Using Forward Osmosis. *Industrial and engineering chemistry research.* 54(49): 12354–1236.

Zhonga, P.S, Chung, T.S., Jeyaseelan, K & Armugam, A. 2012. Aquaporin-embedded biomimetic membranes for nanofiltration. *Journal of Membrane Science*, (407-408): 27-33.

APPENDIX A: Water samples chemical analysis

Table A1: Water chemical analysis

Sample	pH @ 25^0C	EC @ 25^0C (mS/m)	OP (kPa)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Cl (mg/l)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	SO_4(mg/l)	B(mg/l)
DI	5.3	0.4	0.14	22.5	0.4	0.6	0.6	0.8	0.04	3	0	3	6	0.34
DI	5.4	0.5	0.18	11.7	0.2	0.1	0.2	0.4	0.01	3	0	3	5	0.2
BW5	5.6	1066	384	2040	0.2	0	0.1	0.3	0.01	3140	0	0	5	0.13
BW5	4.7	1067	384	2098	0.2	0.1	0	0.2	0.01	3040	0	0	5	0.09
BW35	5.8	5716	2058	9390	2.1	7.8	1	0.08	0	23660	0	0	5	0.05
BW35	5.8	5713	2057	9445	0.7	0.3	0	0.09	0	24120	0	0	5	0.02
Clifton	7.8	5615	1807	11036	393	344	488	0.1	0	16740	0	138	2492	4.03
Clifton	7.9	5587	1829	11102	394	344	483	0.1	0.01	19720	0	153	2493	4
Camps Bay	7.6	5682	1850	12232	380	330	464	0.2	0	18440	0	140	2396	3.77
Camps Bay	7.7	5651	1872	12197	390	342	485	0.2	0	18720	0	148	2472	3.93
Sea Point	7.9	5518	1861	10859	391	343	481	0.1	0	19560	0	145	2474	3.99
Sea Point	7.9	5537	1850	11791	394	346	482	0.1	0	19960	0	141	2507	4.07
Gordon’s Bay	8.0	4301	1548	33000	0.3	0	0.3	0	0	16664	0	157	37	0.01
Gordon’s Bay	8.0	4481	1857	31000	0.4	0	0.3	0	0	15431	0	188	36	0
Strand Location 1	8.1	5026	1857	29000	0.4	0	0.4	0	0	17370	0	163	39	0.01
Strand Location 1	8.1	5034	1812	37000	0.4	0	0.4	0	0	17583	0	157	41	0.01
Strand Location 2	8.1	4885	1713	40000	0.5	0	0.4	0	0	18973	0	168	44	0.01
Strand Location 2	8.0	5351	1706	39000	0.5	0	0.4	0.01	0	18731	0	132	44	0.01
TWW Carmine	10.4	11830	7245	18113	23	1.2	2.3	0	0	45061	39315	31878	840	0.19
TWW Carmine	10.5	11760	7245	18518	19.8	1.4	2.5	0	0	47221	39315	31875	1148	0.19
TWW Olive Green	10.7	17360	6249	25297	31.7	0.9	1.6	0	0	91707	39315	4.02	1148	0.25

TWW Olive Green	10.7	17360	6249	25290	30.8	0.8	1.5	0	0	92208	39318	4.02	1148	0.27
TWW Factory 1	11.1	3680	1324	9853	13.2	13.6	11.2	0.1	0	351	4702	4.02	5225	0.79
TWW Factory 1	11.1	3650	1314	9897	13.1	13.6	11.5	0.1	0	340	7611	4.02	5097	0.81
TWW Factory 2	10.9	6200	2286	12424	28.9	3.8	1.0	0.1	0	24282	5575.2	4.02	586	0.16
TWW Factory 2	10.9	6350	2232	13024	32.9	3.5	1.0	0.1	0	30943	11635	4.02	598	0.16

Table A2: Dye chemical Analysis

Sample @ 25°C	pH	EC (mS/m)	OP (kPa)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Cl (mg/l)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	SO_4 (mg/l)	B (mg/l)	Nacl (mg/l)
MO (0.5g.L^{-1})	6.2	13.2	4.75	34.8	0	0	0	0	0	8	0	28	136	0.01	42.8
MO (0.5g.L^{-1})	6.1	12.6	4.54	37	0	0	0	0	0	499.6	0	22	149	0.01	536.6
MO (1g.L^{-1})	6	23.6	8.5	78.4	0	0.1	0	0	0	539.6	0	85	310	0.01	618
MO (1g.L^{-1})	5.9	21.3	7.67	70.5	0	0.1	0	0	0	499.6	0	56	277	0.01	570.1
MO (1.5g.L^{-1})	6.2	31.2	11.2	108	21.5	0	0	0.1	0	0	0	169	407	0.01	108
MO (1.5g.L^{-1})	6.2	26.1	9.4	109	2.6	0	0	0.9	0	3	0	94	355	0.01	111.9
MO (2g.L^{-1})	6.3	33.1	11.9	137	12.4	0	0	0.1	0	0	0	179	493	0.01	137.1
MO (2g.L^{-1})	6.1	25.1	9.04	124	2	0	0	0.1	0	0	0	55	415	0.01	123.6
MO (2.5g.L^{-1})	6.3	39.8	14.3	166	0.2	0	0	0.1	0	3	0	213	558	0.01	168.8
MO (2.5g.L^{-1})	6.2	44	15.8	177	0.2	0	0	0.1	0	3	0	192	587	0.01	179.5
PI (0.5g.L^{-1})	3.1	64.9	23.4	7.1	107	1	0	0.1	0	0	0	0	271	0.01	7.1
PI (0.5g.L^{-1})	3.1	72.4	26.1	1.4	128	0.2	0	0.1	0	0	0	0	307	0.01	1.4
PI (1g.L^{-1})	3.5	108	39.1	70.5	206	0.3	0	0.13	0	0	0	0	558	0.01	70.5
PI (1g.L^{-1})	2.9	131	47.0	1.2	213	0.1	0	0.1	0	3	0	0	520	0.01	4.2
PI (1.5g.L^{-1})	2.6	163	58.7	7.6	313	0.4	0	0.12	0	0	0	0	875	0.01	7.6
RR (0.5g.L^{-1})	4.8	41.3	14.9	110	0.1	0	0	0.12	0	40	0	0	239	0.01	149.9
RR (0.5g.L^{-1})	4.7	39.5	14.2	102	0.1	0	0	0.12	0	35	0	0	226	0.01	137.4
RR (1g.L^{-1})	4.6	69.4	25.0	188	2.4	0	0	0.13	0	65	0	0	427	0.01	253
R.R (1g.L^{-1})	4.6	78.9	28.4	210	0.8	0	0	0.13	0	76	0	0	472	0.01	286
RR (1.5g.L^{-1})	4.3	110	39.5	289	1.9	0	0	0.14	0	105	0	0	633	0.01	394
RR (1.5g.L^{-1})	4.4	110	39.5	297	0.8	0	0	0.16	0	120	0	0	663	0.02	416.8
RR (2g.L^{-1})	4.2	133	47.9	376	1.3	0	0	0.16	0	134	0	0	836	0.02	509.8
RR (2g.L^{-1})	4.2	147	52.8	412	0.6	0.1	0	0.17	0	156	0	0	928	0.02	568.4

APPENDIX B: Dye DS calculations

Sample Calculation

Table B1: Dye known properties

Dye: Turquoise	M_r (dye): 359 g/mol
Salt: Nacl	M_r (salt):58.44 g/mol
Volume:	10 mL = 0.01 L

1.Identify molarity

Molarity = 0.01 M (mol/L)

$C = 0.01\, mol/L$

2. *Find the mass of dye to make up a 0.01 mol/L of dye solution*

$n = \frac{m}{M_r} \quad \therefore m = n \times M_r$

$m = \boldsymbol{n} \times M_r$

Calculating moles of the dye

$C = \frac{n}{V} \quad \therefore n = C\,.V$

$n = \left(0.01 \frac{mol}{L}\right)(0.01\, L)$

$n = 1 \times 10^{-4}\ mols$

$\therefore m = n \times M_r$

$m = (1 \times 10^{-4}\ mol)(359 \frac{g}{mol})$

$m = 0.0359\, g$

3. Calculating mass of salt

- *Apply dye-to-salt mass ratio of 1:50*

$m = 0.0359\, g \times 50$

= 1.795 g

4. ***Verify if dye-to-salt ratio is correct***

1.795/0.0359 = 50

2.) Determining the target concentration from the factory recipe

Table B2: Dye receipt from textile industry

FABRIC	1	Kg
water	20	L
DYE	40	G
Salt	2000	G
soda Ash	40	G
Temp	60	Deg C
Time	30	mins
Dye-to-salt ratio	50	(Mass ratio)

From the recipe:

$m = 40\ g$

$V = 20\ L$

Known

$Reactive\ black\ M_r = 991\ g/mol$

$c = ?\ mol/L$

1. *Determine the number of moles*

$n = \frac{m}{M_r}$

$n = \frac{40g}{991g/mols}$

$n = 0.04\ mols$

2. *Determine concentration*

$C = \frac{n}{V}$

$C = \frac{0.04\ mols}{20L}$

$C = 0.0020\ mols/L$

3. Converting From $mOsmol$ to kPa

Conversion of mOsmol/kg to kPa Unit

$1\ osmol = 2.48\ MPa$ .... (Lange, et al., 1983)
$1 osmol = 2480\ kPa$

$1\ mOsmol = 0.001\ Osmol$
$1000mOsmol = 1\ Osmol$

$\therefore 1000\ mOsmol = 2480\ kPa$
$mOsmol = \frac{2480\ kPa}{1000}$
$mOsmol = 2.48\ kPa$

3. Converting From $mOsmol$ to kPa

Conversion of mOsmol/kg to kPa Unit

$1\ osmol = 2.48\ MPa$ ………………………………… (Lange, et al., 1983)
$1osmol = 2480\ kPa$
$1\ mOsmol = 0.001\ Osmol$
$1000mOsmol = 1\ Osmol$

$\therefore 1000\ mOsmol = 2480\ kPa$
$mOsmol = \frac{2480\ kPa}{1000}$
$mOsmol = 2.48\ kPa$

Osmolality to kPa

1. At 25°C the relationship between concentration and pressure is:

$$1\frac{Osmole}{kg}H_2O = 2.48MPa$$
$$1\frac{mOsmole}{kg}H_2O = \ 0.001\frac{Osmole}{kg}H_2O$$
$$1\frac{mOsmole}{kg}H_2O = 2.48kPa$$

Reference: Physiological Plant Ecology: Ecophysiology & Stress Physiology of Functional Groups by Walter Larcher.2001.

2. 1 Osmolal solution = 2.48MPa at 25°C

Reference: Encyclopaedia of Plant Physiology: New Series Volume 12. Physiological Plant Ecology 3 by O.L. Lange, P.S. Nobel, C.B. Osmond & H.Zielger.1983.

3. 1 Osmol/kg water will develop a water potential of 2.48MPa at 25°C.

Reference: Advances Microbial Ecology Volume 5 by M. Alexander.1981.

4. Analytical Procedure for osmotic Pressure analysis

- Pipette a sample volume of 50µl into an unused and clean measuring vessel
  - The sample must be pipetted without air bubbles.
- Position measuring vessel on thermistor probe with cover facing front
  - NOTE : The measuring vessel is securely attached to the thermistor probe when it clicks into place
- Tap "Printer On" on the measurement menu to output the measurement results to a printer. Make sure that the printer is ready
- To start the measurement, tap "Single Sample"
- If necessary, enter the sample ID using the virtual keyboard.
- The sample ID can be pre-defined in the user preferences. In this case, the system assigns the sample ID automatically
- Move elevator DOWN for measurement to occur
  - Moving the elevator up during the measurement will abort the measurement.
- The sample measurement is performed automatically. Pay attention to the displays on the touchscreen
- The measurement result displays on the touchscreen (in mOsmol.kgH_20)and, if applicable, prints
- Move elevator up.
- Remove measuring vessel from thermistor probe.
- Dispose of measuring vessel and sample according to local regulations.
- Clean thermistor probe using a soft paper towel

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APPENDIX C: Data from duplicate experiments

1. Production of a dye solution using deionised water as feed solution

Table C1: Control experiments with Reactive Black as a DS

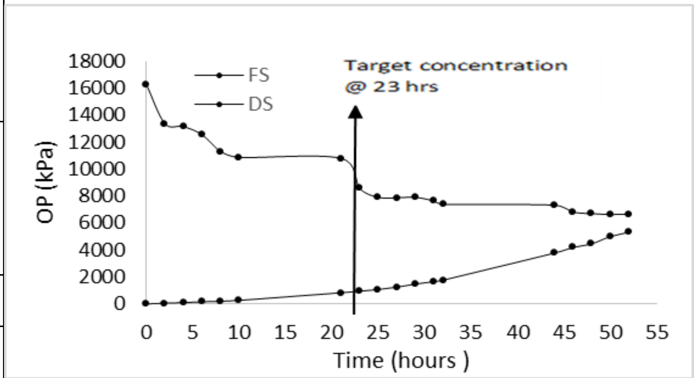
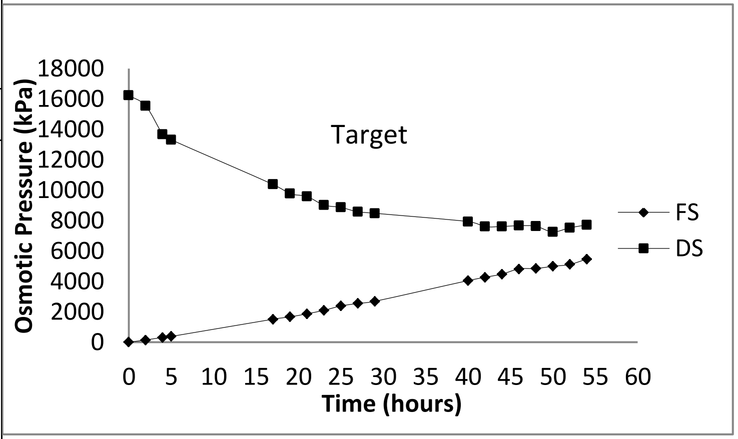
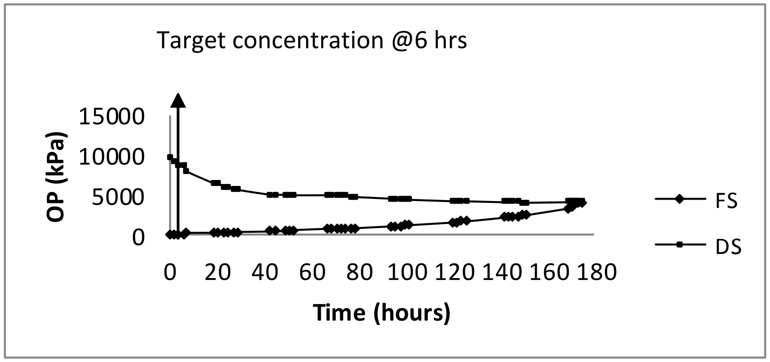
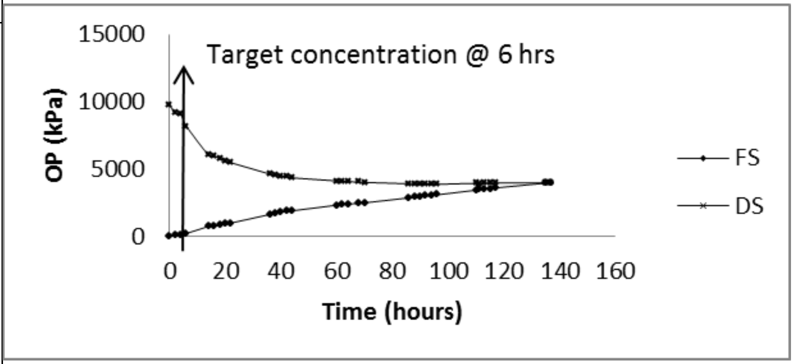
Feed	(a) DI OP : 0 kPa Volume : 2L	(b) DI OP : 0 kPa Volume : 2L	**Averaged**	 
Draw	0.02 M Black dye OP : 16306.6 kPa Volume 1L	0.02 M Black dye OP : 16231 kPa Volume 1L	16268.8 kPa	
Δ**OP**	16306.6 kPa	16230 kPa	16268.3 kPa	
Target concentration	0.002 M OP: 8667 kPa	0.002 M OP: 8667 kPa		
Initial Flux (J)	16.97 7.00	15.39 9.29	16.18 8.145	
Final Flux (Jf)	1.26	3.38	2.32	

Table C2: Control experiments with Basic Blue as a DS

Feed	(a) DI OP : 0 kPa Volume : 2L	(b) DI OP : 0 kPa Volume : 2L	**Averaged Results**	**OP GRAPH**
Draw	0.02 M Blue dye OP : 9773.68 kPa Volume 1L	0.02 M Blue dye OP : 9773.68 kPa Volume 1L	9773.68	
Δ**OP**	9773.68 kPa	9774.92 kPa	9774.3	
Target concentration	0.0041 M OP: 8853 kPa	0.0041 M OP: 8853 kPa		
Initial Flux (J)	20.45 6.75	19 4.7	19.73 5.73	
Final Flux (Jf)	2.61	0.61	1.61	
OP (kPa) @ equilibrium	FS = 3987.84 DS =4111.84	FS = 3968 DS =3979.16		
				

2. Production of dye solution using synthetic seawater as a feed solution

Table C3: Using SSW as a FS with Reactive Black as a DS

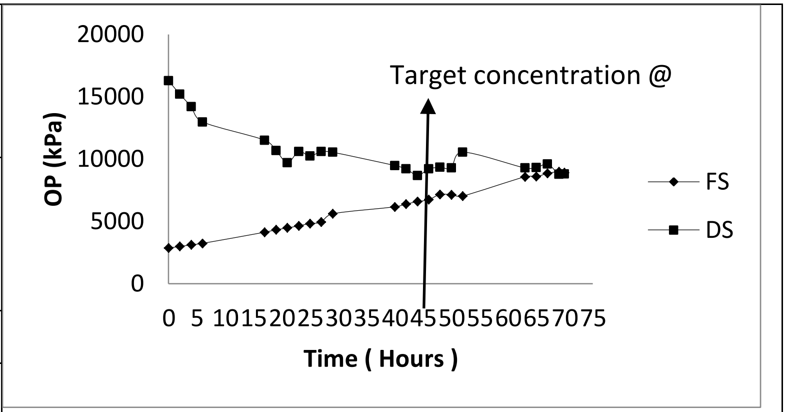
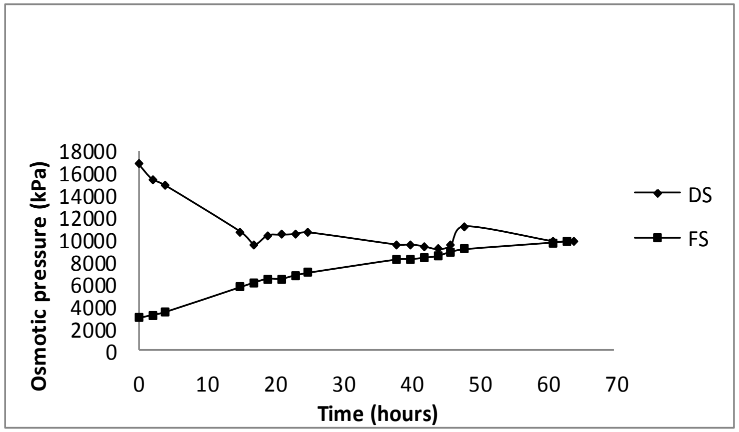
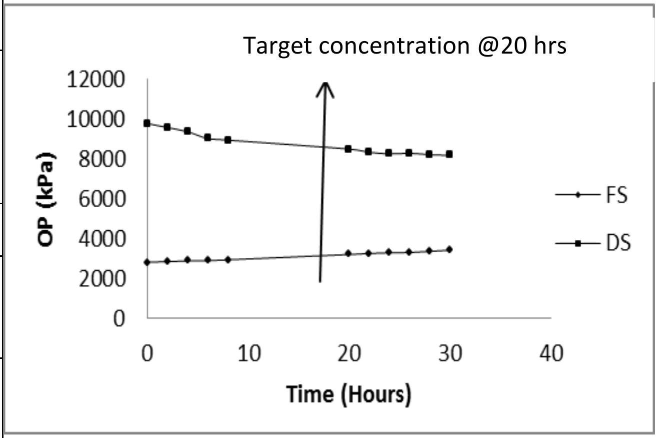
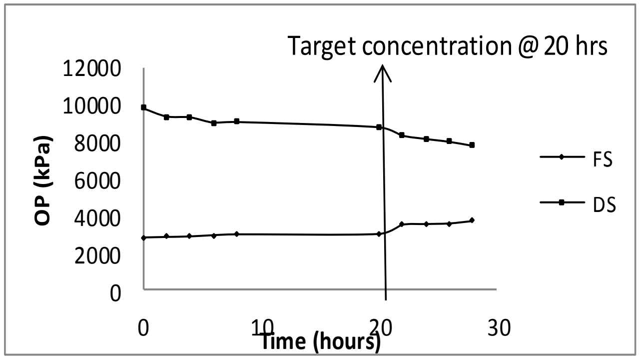
Feed	(a) SSW OP : 2870.5 kPa Volume : 2L	(b) SSW OP : 2832.5 kPa Volume : 2L	**Averaged results**	 
Draw	0.02 M **Black** dye OP : 16268.8 kPa Volume 1L	0.02 M **Black** dye OP : 16752 kPa Volume 1L	16510.4 kPa	
ΔOP	13398.3 kPa	13919.5 kPa	13658.9	
Target concentration	0.002 M OP: 8667 kPa	0.002 M OP: 8667 kPa		
Initial Flux (J)	20.31 7.50	20.17 9.71	20.24 8.61	
Final Flux (Jf)	0.07	0.00	0.035	

Table C4: Using SSW as a FS with Basic Blue as a DS

Feed	(a) SSW OP : 2819.76 kPa Volume : 2L	(b) SSW OP : 2802.4 kPa Volume : 2L	**Averaged results**	
Draw	0.02 M **Blue** dye OP : 9772.4 kPa Volume 1L	0.02 M **Blue** dye OP : 9774.48 kPa Volume 1L	9773.4	
$\Delta \mathbf{OP}$	6952.64 kPa	6972.08 kPa	6962.36	
Target concentration	0.0041 M OP: 8853 kPa	0.0041 M OP: 8853 kPa		
Initial Flux (J)	18.59 1.76	18.85 4.54	18.72 3.15	
Final Flux (Jf)	2.04	2.38	2.21	
OP (kPa) @ 30 hrs	FS = 3428.6 DS =8171.6	FS = 3697.68 DS =8198.88		

3. Production of a dye solution using reclaimed textile wastewater as a feed solution :Textile wastewater from Factory 1

Table C5: TWW (Factory 1) with Basic Blue as a DS

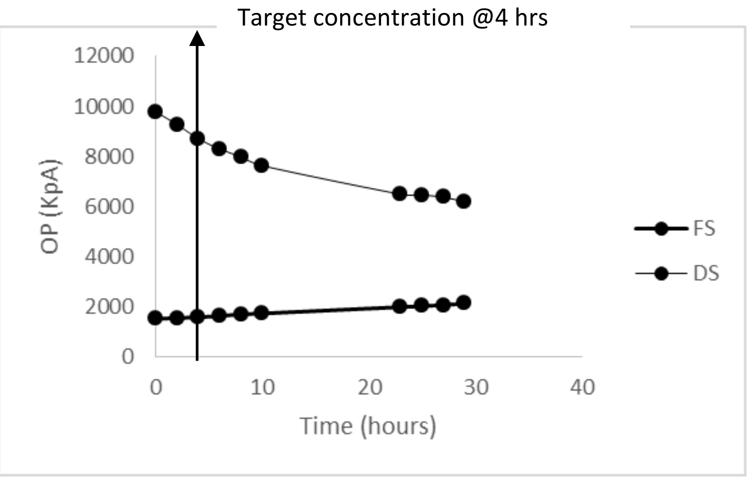
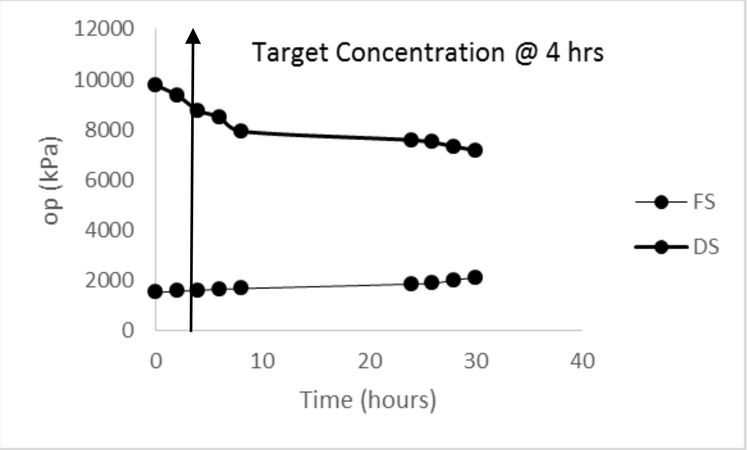
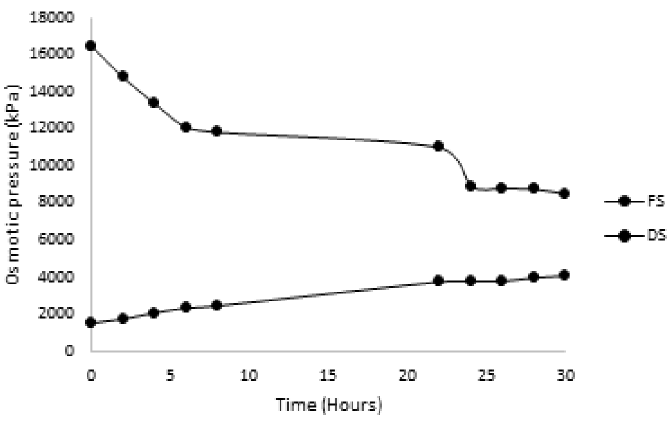
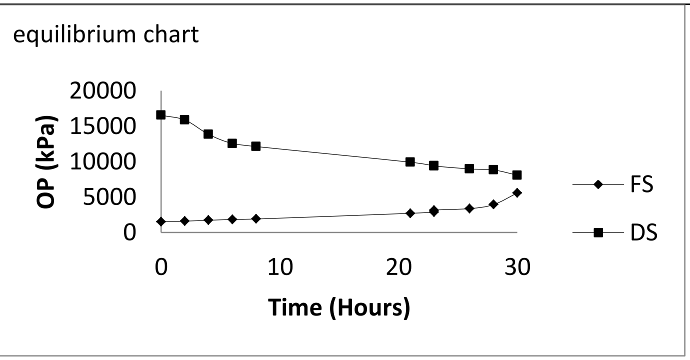
Feed	(a) TWW OP : 1515.26 kPa Volume : 1L	(b) TWW OP : 1511.56 kPa Volume : 1L	**Averaged results** **1513.41**	 
Draw	0.02 M **Blue** dye OP : 9773.68kPa Volume 0.5L	0.02 M **Blue** dye OP : 9774.92 kPa Volume 1L	9774.3	
ΔOP	8258.42 kPa	8263.36 kPa	8260.89	
Target concentration	0.0041 M OP: 8853 kPa	0.0041 M OP: 8853 kPa		
Initial Flux (J)	15.57 3.92	14.69 2.47	15.13 3.195	
Final Flux (Jf)	2.42	0.61	1.52	
OP (kPa) @ 30 hrs	FS = 2115.44 DS =6187.6	FS = 3697.68 DS =8198.88		

Table C6: TWW (Factory 1) with Reactive Black as a DS

Feed	TWW OP : 1501.64 kPa Volume : 1L	TWW OP : 1505.36 kPa Volume : 1L	**Averaged Results** **1503.5**	
Draw	0.02 M Black dye OP : 16541.60 kPa Volume 0.5L	0.02 M Black dye OP : 16442.4 kPa Volume 0.5L	16492	
$\Delta\mathbf{OP}$	15039.96 kPa	14937.04 kPa	14988.5	
Target concentration	0.002 M OP: 8853 kPa	0.002 M OP: 8853kPa		
Initial Flux (J) Final Flux (Jf)	19.19 6.66	19.83 5.19	19.51 5.93	 equilibrium chart

Textile wastewater from Factory 2

Table C7: Using TWW (Factory 2) with Basic Blue as a DS

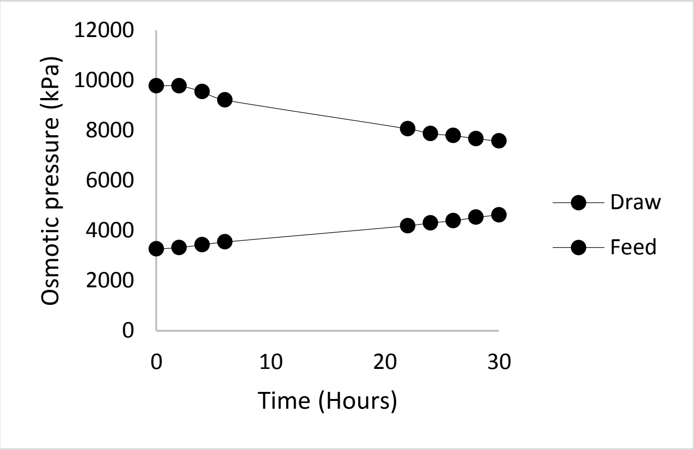
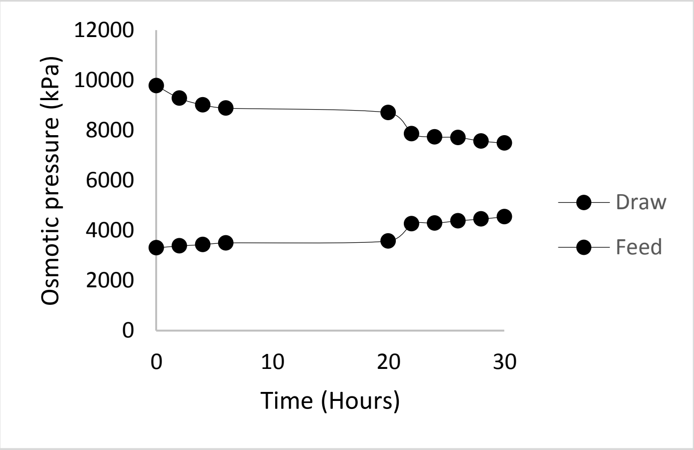
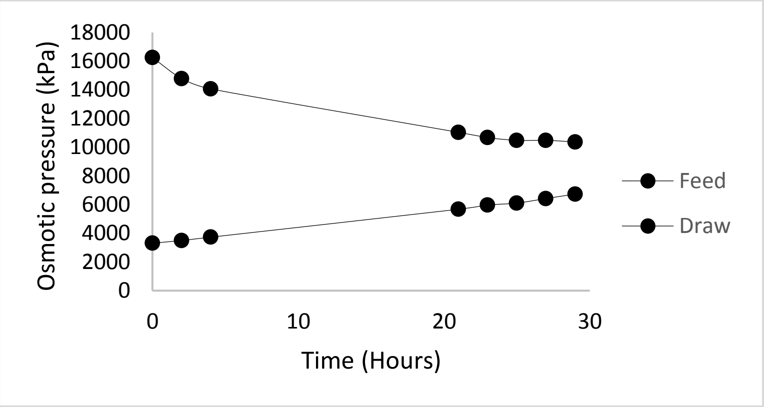
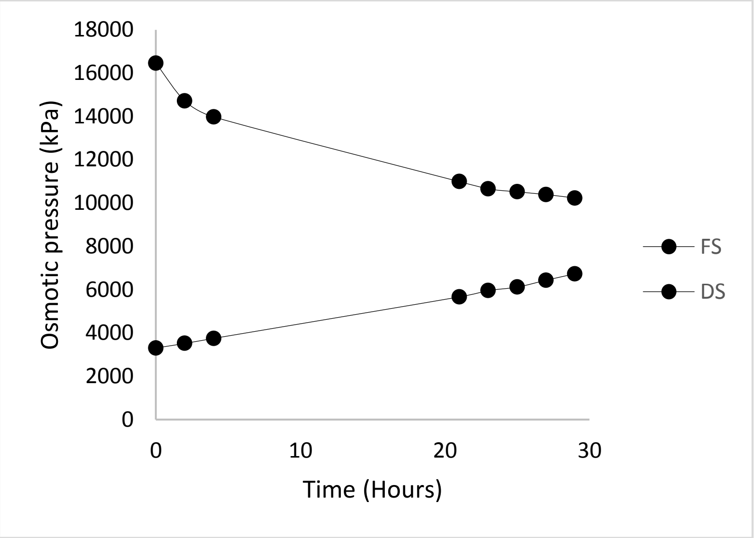
Feed	(a) TWW OP : 3261.2kPa Volume : 1L	(b) TWW OP : 3300.88kPa Volume : 1L	**Averaged results** **3281.04**	 
Draw	0.02 M **Blue** dye OP : 9773.68kPa Volume 0.5L	0.02 M **Blue** dye OP : 9778.64 kPa Volume 0.5 L	9776.16	
$\Delta \mathbf{OP}$	6512.48 kPa	6477.76 kPa	6495.12	
Target concentration	0.0041 M OP: 8853 kPa	0.0041 M OP: 8853 kPa		
Initial Flux (J)	14.45 3.52	12.38 2.92	13.42 3.22	
Final Flux (Jf)	0.92	4.21	2.56	
OP (kPa) @ 30 hrs	FS =4625.2 DS = 7571.44	FS = 4543.36 DS = 7482.16	4584.28 7499.94	

Table C8: Using TWW (Factory 2) with Reactive Black as a DS

Feed	TWW COLORITE OP : 3309.56 kPa Volume : 1L	TWW COLORITE OP : 3308.32 kPa Volume : 1L	**Averaged results** 3308.94	
Draw	0.02 M **Black** dye OP : 16244 kPa Volume 1L	0.02 M **Black** dye OP : 16454.8 kPa Volume 1L	16349.9 kPa	
ΔOP	12935 kPa	13146.48 kPa	13040.74 kPa	
Initial Flux (J)	14.02 6.07	12.83 5.42	13.43 5.745	
Final Flux (Jf)	1.52	0.45		
				

APPENDIX D: Colour Hazen

True colour determination using Hazen Colour

The samples were at room temperature (±25 °C), and 5 ml of sample was filtered through a 0.45 µm Luer Lock syringe. The 2ml of the filtered sample was then transferred to a 50 mm glass cuvette using P5000 Gilson pipette. The 50mm glass cuvette was then placed into the cell compartment of Nova 60 and a method was selected, which is code 179.

For the measuring range: 0 – 1000 Pt/Co (Hz)

1. Allow any samples stored in the refrigerator for preservation purposes to return to room temperature before testing for colour.
2. Filter 5 ml of the water sample through a membrane filter with a 0.45 µm pore size, using a Luer Lock syringe.
3. Transfer about 2 ml of the filtered sample into a 50 mm glass cuvette, using a P5000 Gilson pipette.
4. Place the 50 mm glass cuvette into the cell compartment of the NOVA 60 Spectroquant, and select the method (code no. **179**) on the menu.

For the measuring range: 0 – 500 Pt/Co (Hz)/0 – 250 Pt/Co (Hz)/0 – 100 Pt/Co (Hz)

1. Allow any samples stored in the refrigerator for preservation purposes to return to room temperature before testing for colour.
2. Filter 5 ml of the water sample through a membrane filter with a 0.45 µm pore size, using a Luer Lock syringe.
3. Transfer about 2 ml of the filtered sample into a 10 mm glass cuvette for the 0 – 500 Pt/Co (Hz) measuring range, a 20 mm glass cuvette for the 0 – 250 Pt/Co (Hz) measuring range and a 50 mm glass cuvette for the 0 – 100 Pt/Co (Hz) measuring range, using a P5000 Gilson pipette.
4. Place the corresponding glass cuvette into the cell compartment of the NOVA 60 Spectroquant, and select the method (code no. **032**) in the menu.

Notes:

Unfiltered sample = Apparent colour

Filtered sample = True colour

Ensure the glass cuvette is free of scratches and marks. Wipe the cuvette surface with a soft tissue before inserting into the NOVA 60 Spectroquant.

All samples are read in triplicate.

For the measuring range: 0 – 1000 Pt/Co (Hz), the code number 179 must be selected on the NOVA 60 Spectroquant menu

For the measuring ranges: 0 – 500 Pt/Co (Hz)/0 – 250 Pt/Co (Hz)/0 – 100 Pt/Co (Hz) the code number 032 must be selected on the NOVA 60 Spectroquant menu.

Hazen Colour analysis

Table D1: Reactive Black experiments Hazen Colour analysis

	DI colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 0 (b) 0	0	800 810	805
Final colour	(a) 8 (b) 5	7	500 500	500
	SSW colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 0 (b) 0	0	(a) 785 (b) 802	794
Final colour	(a) 500	496	(a) 500	500

	(b) 492		(b) 500	
	TWW Factory 1 colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 200		809	
	(b) 200	200	788	799
Final colour	(a) 500		682	694
	(b) 500	500	705	
	TWW Factory 2 colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 288		815	
	(b) 288	288	802	809
Final colour	(a) 500	500	715	712
	(b) 500		709	

Table D2: Basic Blue experiments Hazen Colour analysis

	DI colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Blue colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 0 (b) 0	0	(a) 550 (b) 547	549
Final colour	(a) 4 (b) 1	2.5	(a) 301 (b) 253	268
	SSW colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Blue colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 0 (b) 0	0	(a) 551 (b) 555	553
Final colour	(a) 23 (b) 24	24	(a)491 (b)312	402
	TWW Factory 1 colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 200 (b) 200	200	(a) 534 (b) 547	541
Final colour	(a) 267 (b) 244	256	(a) 491 (b) 312	402
	TWW Factory 2 colour (mg/L Pt)	**Averaged colour (mg/L Pt)**	**Black colour (mg/L Pt)**	**Averaged colour (mg/L Pt)**
Initial colour	(a) 288 (b) 288	200	(a) 548 (b) 532	540
Final colour	(a) 425 (b) 340	383	(a) 295 (b) 276	286