Water Reuse Using a Dual-Stage Membrane Bioreactor for Industrial Effluent Treatment

> W Edwards, MS Sheldon, PJ Zeelie, D de Jager, LG Dekker & CC Bezuidenhout

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# WATER REUSE USING A DUAL-STAGE MEMBRANE BIOREACTOR FOR INDUSTRIAL EFFLUENT TREATMENT

Report to the WATER RESEARCH COMMISSION

by

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#### **EXECUTIVE SUMMARY**

This report presents the results and findings of Water Research Commission (WRC) project K5/1900 "*Water Reuse using a Dual-Stage Membrane Bioreactor for Industrial Effluent Treatment*". In this study, the performance of membrane bioreactors (MBR) for the treatment of textile and paper mill effluent was assessed.

The aims of this research project were to:

- Design and construct a pilot scale dual-stage side-stream membrane bioreactor (dsMBR) plant (5-10 m<sup>3</sup>/d capacity).
- 2. Retrofit and commission dsMBR pilot plants to treat trade industry sector effluents.
- Conduct an economic viability assessment of the dsMBR technology in the context of the Western Cape trade industry sector, its existing infrastructure and current treatment practices and paradigms.
- Facilitate capacity building for industrial application of MBR technology at the Cape Peninsula University of Technology (CPUT) through the training of in-service trainees and postgraduate students.

Previous research described in WRC Report 1371/1/07 focused on the development of a novel operations strategy employing laboratory-scale MBRs for the treatment of wastewaters of industrial origin. This project investigated the application of this operations strategy in a pilot plant evaluation of a dsMBR for the on-site treatment and recovery of industrial trade effluent. The purpose of the evaluation was to determine if the use of membrane systems in combination with biological processes is a plausible method for wastewater treatment, recovery, and reuse in the trade industry sector. In addition, a primary component of the research was to assess the economic viability of using membrane technology for producing process water from industrial trade effluents, which traditionally are discharged without pre-treatment to the main municipal sewerage grid on a pay-to-pollute principle.

Two companies representative of the Western Cape trade industry sector were approached as potential industrial partners by Atl-Hydro with a proposal to enter into a joint piloting evaluation of an

MBR effluent treatment system as part of a technology assessment project funded by the WRC of South Africa. The purpose of the piloting evaluation was to optimise the effective and efficient on-site treatment of the industrial partner's trade effluent and, in conjunction with the industrial partner, propose and design a full-scale MBR plant to provide a complete solution to meet the current and future water needs of the industrial partner.

A textile manufacturer located in the Western Cape was chosen as one of the industrial partners for the on-site evaluation of the pilot plant. A 5-10 m<sup>3</sup>/day MBR pilot plant incorporating Norit's sidestream Airlift<sup>™</sup> membrane modules was designed and was operated on-site form March to December 2010. The design of the dsMBR process was geared towards optimal microbial community enrichment and was based on a pre-denitrification configuration coupled with enhanced biological phosphate removal (EBPR) (anaerobic-anoxic-aerobic with recycle loops). The anaerobicanoxic-aerobic process was designed to incorporate two primary functionalities: influent azo dye cleavage in a reducing environment followed by oxidation of the resultant aromatic amines; and biological nutrient removal through enrichment of associated microbial consortia using nitrification, denitrification, and phosphate removal process control. In terms of overall results, chemical oxygen demand (COD) removal fluctuated considerably during the 3-month start-up stage (~100 days). The effluent stream was characterised by a COD range of between 45 to 2,820 mg/L and an average biological oxygen demand (BOD) of 192.5 mg/L. The dsMBR achieved an average COD reduction of 75% with a maximum of 97% over the 9 month test period. The COD concentration obtained after dsMBR treatment averaged at 190 mg/L, which was well within the discharge standard. The average reduction in turbidity and total suspended solids (TSS) was 94% and 19.6%, respectively, during the ultrafiltration (UF)-MBR stage of the system. Subsequent treatment of the UF-permeate with nanofiltration (NF) and reverse osmosis (RO) removed both the residual colour and remaining salt. A consistent reduction in the colour of the incoming effluent was evident. The American dye manufacturing index (ADMI) was reduced from an average of 659 to below 20, a lower ADMI and colour compared to their potable water. An average conductivity rejection of 91% was achieved with conductivity being reduced from an average of 7,700 to 693 µS/cm and the total dissolved solids (TDS) reduced from an average of 5,700 to 473 mg/L, which facilitated an average TDS rejection of 92%.

Implementing a dsMBR system coupled with NF successfully removed colour from industrial textile effluent bringing all the parameters measured during the study to within the CCT wastewater discharge standards, thereby reducing their discharge costs financially. However, coupling the dsMBR system with RO not only successfully removed the residual colour from the effluent; RO also had the capability of reducing the salts present in the dsMBR product to within

potable water standards. By treating the effluent to within potable water standards the treated water can be re-used on-site within the textile dyeing processes, thereby reducing reduce the wastewater load sent to the municipal treatment works, reducing the volume of water used by the textile company thus decreasing their water dependence on the municipality, and assisting in reducing their impact on the environment (i.e. carbon footprint).

However, a dsMBR system would not be ideal for this particular textile company, since the industry does not operate continuously and has periods of down time over weekends and public holidays. Biological systems require continuous effluent feed in order to supply the activated sludge with nutrients and thus operate efficiently. With non-continuous effluent production by the textile company the system would have many periods of unstable treatment while the activated sludge stabilised after nutrient starvation. Therefore, the ideal wastewater treatment system for this textile company would include UF, NF and RO without the pre-treatment biological tanks as used in the pilot scale plant. The absence of the biological tanks would make it easy to start-up and shut down the wastewater treatment system in accordance with the effluent production of the textile company without being detrimental or affecting the efficiency of the effluent treatment.

A paper and pulp industry located in the Western Cape was also chosen as an industrial partner for the evaluation of a pilot-scale MBR plant for the treatment of paper mill effluent. A 45-65 L/day MBR pilot plant incorporating ceramic membranes in an external modular configuration (similar to Norit's sidestream Airlift<sup>™</sup> membrane modules) was designed and was operated in a laboratory from June to November 2010. The design of the dsMBR process was geared towards optimal microbial community enrichment and was based on a pre-treatment high rate anaerobic system (Expanded Granular Sludge Bed) coupled with a post-treatment denitrification/nitrifation configuration (anaerobic-anoxic-aerobic with recycle loops). The high rate anaerobic process was designed to reduce influent COD in an attempt to reduce the need for high volume dosing. In addition to the COD reduction, the potential for extracting methane as a potential energy source was also considered. The anoxic-aerobic processes were designed to incorporate two primary functionalities: further reduction of COD concentration; and biological nutrient removal through enrichment of associated microbial consortia using nitrification and denitrification process control. The paper mill effluent stream was characterized by a COD range of between 1,600 to 4,400 mg/L and an average BOD of 2,400 mg/L. In terms of effluent COD reduction efficiency, the anaerobic pre-treatment stage facilitated an average of 70% COD removal, thus lowering the MBR COD feed concentration to consistently below 750 mg/L. The

subsequent anaerobic product stream was the feed stream for the MLE-MBR which facilitated an average of 97% COD removal over the piloting trial period. Combining a high-rate anaerobic pre-treatment EGSB with a modified Ludzack-Ettinger (MLE) MBR process configuration produced a high quality permeate. Preliminary NF and RO results indicated an overall COD removal of around 97 and 98%, respectively.

#### CHALLENGES AND CONCLUSIONS

Projected savings on overall costs over a 10-year period are critical in determining whether fullscale implementation will meet financial ROC (Return On Capital) requirements. These projections are calculated based on the current method of municipal tariff determination and can be calculated on a conservative flat tariff rate escalation. Based on the above case studies, it is our recommendation that the following initiatives be considered when making decisions to implement full-scale interventions

- Onsite piloting trials must be conducted to provide long-term optimization and scalability data
- Cleaner production and waste minimization audits should be conducted in parallel to capitalize on increased long-term savings potential
- Stream segregation analysis should be implemented during the latter phases of pilot trials if a decision to implement a treatment strategy at full-scale is considered
- Full-scale implementation should be done using a modular approach to match expansion requirements when necessary.

Process designs for full-scale treatment facility should be conducted using a modular approach to accommodate potential production capacity increases in the short- to medium-term (3-5 years) – in terms of footprint requirements; the modular design is based on incremental capacity expansion.

Based on the calculated OPEX savings potential, overall savings taking into account full-scale CAPEX and OPEX should translate into an ROI/ROC period of approximately 5-7 years with an overall savings potential of 25-50% calculated on a cost-per-kL basis calculated over the 10-year operating period (NOTE: this excludes any additional savings related to implementing cleaner production and waste minimization audits which would optimize raw material usage, energy requirements, and production manufacturing.

# LIST OF PUBLICATIONS, CONFERENCE PROCEEDINGS AND STUDENT TRAINING ON WRC PROJECT K5/1900

#### Papers published

SHELDON MS, ZEELIE PJ and EDWARDS W (2012) Treatment of paper mill effluent using Membrane Bioreactors. *Water Science and Technology* **65**(7):1265-1272 [doi:10.2166/wst.2012.007].

DE JAGER D, SHELDON MS and EDWARDS W (2012) Membrane bioreactor application within the treatment of high-strength textile effluent. *Water Science and Technology* **65**(5):907-914 [doi:10.2166/wst.2012.920].

#### Paper submitted

DE JAGER D, SHELDON MS and EDWARDS W (2012) Colour removal from textile effluent using a pilot-scale UF-dsMBR and subsequent NF/RO system (Submitted to WISA 2012 for consideration for publication in Water SA – waiting on feedback).

#### Paper in progress

DE JAGER D, SHELDON MS, ZEELIE PJ and EDWARDS W (2012) Membrane Bioreactors (MBRs) in the treatment of textile effluent in South Africa. (In progress: To be submitted to Water Research by end of April 2012).

#### Presentations

EDWARDS W, SHELDON MS and WALL K (2010) A National Water Services Franchising Model for the Operation and Maintenance of Membrane Technology-based Trade Effluent Treatment Plants, WISA, Durban, 18-22 April 2010.

EDWARDS W, ZEELIE PJ and SHELDON MS (2010) Treatment of Recycled Paper Mill Effluent using Membrane Bioreactors – Nampak Tissue Case-Study. TAPPSA National Conference and Exhibition, Durban, 19-20 October 2010. EDWARDS W, ZEELIE, PJ, DE JAGER D and SHELDON MS (2010) Membrane Bioreactors in the Industrial Trade Sector. Joint Workshop on Environmental Controls in Trade Effluent Control. Paradise Valley, Pinetown, 24 May 2011.

DE JAGER D, SHELDON MS and EDWARDS W (2011) Application of a pilot-scale MBR system for the removal of colour from industrial textile effluent. WISA-MTC'11, 11-14 Sept 2011, Durban.

ZEELIE PJ, SHELDON MS and EDWARDS W (2011) A pilot-scale ultra-filtration membrane bioreactor application for the treatment of paper and pulp wastewater. WISA-MTC'11, 11-14 Sept 2011, Durban.

DE JAGER D, SHELDON, MS and EDWARDS W (2012) Colour removal from textile effluent using a pilot-scale UF-dsMBR and subsequent NF/RO system. WISA-Biennial conference, 6-10 May 2012, CTICC (paper number 342.00).

#### Presentations accepted for 2012 (international)

SHELDON MS, ZEELIE PJ, SCHOEMAN A and EDWARDS W (2012). Two case studies on the treatment of industrial wastewater in SA using a hybrid anaerobic/aerobic membrane bioreactor: Paper mill and potato-maize effluent. Singapore International Water Convention 2012, 1-5 July, Singapore, Sands Expo and Convention Center, Marina Bay Sands [Combined manuscript Numbers: IWA 9480 and IWA 9632 – accepted for presentation].

#### Posters

DE JAGER D, SCHOEMAN HA, SHELDON MS and EDWARDS W (2010) Membrane bioreactor application within the treatment of high-strength textile effluent. CPUT Research Day, 3 December 2010, Cape Town.

ZEELIE PJ, SHELDON MS and EDWARDS W (2010) Design, construction and operation of a membrane bioreactor for the treatment of paper and pulp wastewater. CPUT Research Day, 3 December 2010, Cape Town.

SHELDON MS, ZEELIE PJ and EDWARDS W (2011) Treatment of paper mill effluent using Membrane Bioreactors. 2<sup>nd</sup> Regional YWP Conference, CSIR, 2-5 July 2011, Pretoria.

DE JAGER D, SHELDON MS and EDWARDS W (2011) Membrane bioreactor application within the treatment of high-strength textile effluent. 2<sup>nd</sup> Regional YWP Conference, CSIR, 2-5 July 2011, Pretoria.

DE JAGER D, SHELDON MS and EDWARDS W (2012) Membrane bioreactor application within the treatment of high-strength textile effluent. WISA-Biennial conference, 6-10 May 2012, CTICC.

#### Poster accepted for 2012 conferences

DE JAGER D, SHELDON MS and EDWARDS W (2012) A case study on the treatability of industrial textile wastewater in South Africa using a combined MBR-NF/RO system for re-use. Water Convention 2012, 1-5 July, Singapore, Sands Expo and Convention Center, Marina Bay Sands [Manuscript No: IWA 9443].

#### **Capacity building**

From 2009 to 2011 a total of 10 students at different levels were trained within the wastewater treatment sector: 6 in-service training (IST) students, 3 BTech students and 1 postgraduate Doctoral student, . This includes 7 males and 2 females of which 4 were black, 4 white and 1 coloured student.

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	Year		2005	200	201(	201(	2010	201
	Nationality		South African	South African	South African	South African	South Africa	South African
	Race		Black	White	Black	Black	Black	Coloured
	Gender		Male	Male	Male	Male	Female	Male
	Degree obtained		ND Chemical Engineering	ND Chemical Engineering	ND Chemical Engineering	ND Chemical Engineering	ND: Analytical Chemistry	ND: Chemical Engineering
)	Student	number	206128320	207005311	207081182	208093524	209018712	210210613
5	Title		Mr	Mr	Mr	Mr	Miss	Mr
	Initials		Μ	ЬJ	A	Μ	Z	Y
þ	Student	Surname	Ratshefola	Zeelie	Buyana	Mashalaba	Sanda	Salie

In-service training students who graduated during WRC K5/1900 project: 2009-2011

BTech students who graduated during WRCK5/1900 project: 2009- 2011

Student Surname	Initials	Title	Student number	Degree obtained	Project title	Gender	Race	Nationality	Year
Angus	D	Mr	206080581	BTech Chemical Engineering	Effect of operating parameters on the gas production and product quality of an EGSB used for paper & pulp wastewater	Male	White	South African	2010
Schoeman	A	Mr	207035075	BTech Chemical Engineering	Residual dye removal from textile effluent by adsorption, using granular activated carbon	Male	White	South African	2010
Zeelie	ГЧ	Mr	207005311	BTech Chemical Engineering	Design, construction and operation of an MBR for the treatment of papermill effluent	Male	White	South African	2010
An additional 4 BT	echs worked	on MBR wa	istewater treatmer	nt projects during 2011					

n additional 4 B lechs worked on MBK wastewater treatment projects during 2011

Postgraduate students involved during WRCK5/1900 project: 2009-2011

Student Degree number
200679007 DTech: Chemical
Engineering

×

	Ger	nder		Race		Total
	Μ	F	Black	White	Coloured	
IST	5	1	4	1	1	6
BTech	3	-	-	3	-	3
Doctoral	-	1	-	1	-	1
	8	2	4	5	1	10

Breakdown of students trained by gender and race 2009-2011

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Cs	Saturation concentration of water	
CL	Designed dissolved oxygen concentration	kg O <sub>2</sub> /L
Con.N	Mass of oxygen required per mass of nitrogen oxidized	kg O <sub>2</sub> /kg N
N <sub>effective</sub>	Average ammonium in the effluent	kg/L
Q	Volumetric flow rate	m³/hr
Т	Inlet temperature of aerobic tank	°C
T <sub>ref</sub>	Ambient temperature	°C

#### Greek Symbols

α	Transfer coefficient for oxygen from potable water to wastewater	
β	wastewater factor that inhibits oxygen transfer	
θ	Arrhenius constant	
$ ho_{std}$	saturation water vapour pressure under standard conditions	Pa
$ ho_{air}$	density of air	kg/m <sup>3</sup>
т	temperature correction factor for saturation concentration of water	
ω	pressure correction factor for saturation concentration of water	

### LIST OF ABBREVIATIONS

AAR	Actual air flow rate required
AD	Anaerobic Digestion
ADMI	American Dye Manufacturing Index
AECI	African Explosives and Chemical Industries
AOMBR	Anaerobic-oxic Membrane Bioreactor
AOR	Actual oxygen mass flow rate required
AS	Activated Sludge
BBBEE	Broad Based Black Economic Empowerment.
BNR	Biological Nutrient Removal
BOD	Biological Oxygen Demand
BRIC	Biotechnology Regional Innovation Centre
BTech	Baccalaureus Technologiae
Ca	Calcium
CAPEX	Capital Expenditure
CAS	Conventional Activated Sludge
CBT	Cape Biotech Trust's
ССТ	City of Cape Town
CH <sub>3</sub> COONH <sub>4</sub>	Ammonium acetate
CIP	Cleaning-In-Place
C:N:P	Carbon:Nitrogen:Phosphate ratio
COD	Chemical Oxygen Demand
CO <sub>3</sub>	Carbonate
CPUT	Cape Peninsula University of Technology
DAF	Dissolved Air Flotation
DE	Adams Nickerson colour difference
DO	Dissolved Oxygen
dsMBR	Dual-stage membrane bioreactor
DTech	Doctor Technologiae
DWAF	Department of Water and Forestry
DWEA	Department of Water and Environmental Affairs
EBPR	Enhanced Biological Phosphate Removal
EGSB	Expanded Granular Sludge Bed reactor
F	Female
F/M	Feed-to-Microorganism ratio
FO	Forward Osmosis
GAC	Granular Activated Carbon

Gross Domestic Profit
Hydrogen Sulphide
Hydrocarbonate ions
Historically Disadvantaged Individuals
Hollow Fibre
Hydraulic Retention Time
Internal Circulation reactor
Intellectual Property
Potassium dihydrogen phosphate
Male
Membrane Bioreactor
Microfiltration-Membrane bioreactor
Modified Lutzack-Ettinger
Mixed Liquor Suspended Solids
Mixed Liquor Volatile Supended Solids
Azo groups
Sodium Hypochlorite
National Diploma
Nanofiltration
Ammonium
Nitrate
Organic Loading Rate
Operational Expenditure
Oxygen Transfer Rate
Patent Cooporation treaty
Piping and Instrumentation Diagram
Programmable Logic Controller
Phosphate
Polyvinyl Chloride
Qualifying Small Enterprises
Reverse Osmosis
South Africa
South African National Standard
Sequencing Batch Bioreactor
Small Medium and Micro Enterprises
Sulfonic electron withdrawing groups

SO <sub>4</sub>	Sulphate
SOR	Oxygen mass flow rate required under standard conditions
SRT	Sludge/Solid Retention Times
SS	Suspended Solids
TDS	Total Dissolved Solids
TFA	Technical Feasibility Assessment
TIA	Technology Innovation Agency
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Bed reactor
UCT	University of Cape Town
UF	Ultrafiltration
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solids
WCWSS	Western Cape Water Supply System
WDCS	Waste Discharge Charge System
WRC	Water Research Commission
WWTP	Waste Water Treatment Plant
ZLD	Zero Liquid Discharge

## CHAPTER 1

#### 1. INTRODUCTION AND BACKGROUND

#### 1.1 BACKGROUND TO THE PROJECT

Previous research focused on the development of a unique operations strategy employing laboratory-scale membrane bioreactors (MBRs) for the treatment of wastewaters of industrial origin (WRC Report 1371/1/07; PCT/IB2008/05033; SA National Patent 2009/00398). The process design facilitated a continuous development and acclimation strategy for generating consortia of microorganisms capable of degrading specific industrial wastewaters. These adapted consortia were then 'harvested' to be used in the continuous operation of 'hydrolysis' reactors. The 'hydrolysis' reactors were operated under similar conditions to conventional wastewater treatment facilities. However, the continuous addition of adapted microbial populations 'developed' within the 'seeding' reactor configuration facilitated, firstly, significantly decreased adaptation periods (decrease of 75%) associated with conventional treatment strategies, and secondly, an inherent robustness facilitated by obviating the requirement for adaptation within the hydrolysis reactor configuration.

In comparison to activated sludge systems, the long-term operation of this MBR process treating high-strength effluents was characterised by more stable microbial populations that are significantly less susceptible to deleterious shifts in the community dynamics resulting in enhanced process efficiency due to less process variability.

Due to the associated robustness of the dsMBR system, it is ideally suited to the treatment of a variety of industrial process wastewaters generated by diverse industries within the Western Cape area. However, variations in wastewater streams make it imperative to assess the performance of the system on site and at the pilot-scale level in order to accurately gauge the impact of real wastewater challenges on the robustness of the process technology.

This pilot project therefore aimed to address several challenges currently experienced by the water and wastewater sector in the Western Cape. Firstly, to develop on-site wastewater treatment solutions for industries monitored and tariffed by local municipalities as increases in monitoring and legislative framework capacity are realised. As legislative enforcement is addressed, increasingly, industrial offenders responsible for further burdening already

overloaded municipal waste water treatment plant (WWTP) infrastructure will be forced to implement on-site wastewater treatment and recycle solutions due to the ever increasing economic impact on operational expenditure (OPEX). This technology aimed to address these increasingly prevalent needs by providing a mobile, adaptable solution to specific industry needs. Secondly, a further challenge experienced by the wastewater treatment sector is the severe shortage of skilled labour.

#### 1.2 AIMS

Following the approval of a provisional patent and subsequent patent cooperation treaty (PCT) application by the WRC, a proposal was submitted to further evaluate the technology in conjunction with an industrial partner through an on-site pilot plant study. To address the recommendations put forward at the conclusion of WRC Project 1371/1/07, the following aims and associated deliverables were formulated to explore the technology assessment in a commercial environment with an industrial partner. The commercial framework for the technology assessment was implemented in order to design and operate the piloting facility with the objective of scale up to full treatment capacity. This process would form the basis of the skills development initiative and knowledge generation by exposing historically disadvantaged students through the CPUT internship program to on-site training in MBR technology.

#### 1.2.1 OBJECTIVES

- 1. Design and construct a pilot scale side-stream dsMBR plant (5-10 m<sup>3</sup>/d capacity).
- 2. Retrofit and commission dsMBR pilot plants to treat trade industry sector effluent.
- Conduct and economic viability assessment of the dsMBR technology in the context of the Western Cape trade industry sector, its existing infrastructure and current treatment practices and paradigms.
- 4. Facilitate capacity building for industrial application of MBR technology at the CPUT through the training of in-service trainees and postgraduate students.

## CHAPTER 2

#### 2. LITERATURE REVIEW

#### 2.1 ECONOMIC EVALUATION OF WATER REUSE AND RECYCLE

#### 2.1.1 ECONOMIC DRIVERS – GLOBAL PERSPECTIVE

A 2009 McKinsey report forecast that the global water demand would increase from 4,500 to 6,900 billion m<sup>3</sup> by 2030. The supply-demand gap is 40% above the current accessible, reliable supply. Whilst, agriculture accounts for 71% of current global water withdrawal and demand will increase by 45%, this will have declined slightly to 65% as a percentage of the global water demand in 2030. Overall domestic withdrawal demand will also decrease as a percentage of total global demand from 14% today to 12% in 2030. In contrast, industrial water withdrawal which accounts for 16% of today's global water withdrawal will increase to 22% by 2030.

The report further identified China, India, South Africa and Brazil as the countries that will account for 40% of the world's population, 30% of the world gross domestic profit (GDP), and 42% of the global water demand by 2030 (Table 2.1).

Country	Current supply *	Demand (2030) *	Demand Gap (%)
China	618	818	32
Brazil 18.7		20.2	8
India	740	1500	102
South Africa	15	17.7	18

**Table 2.1** Projected Water consumption compared to current sustainable water supply(McKinsey, 2009)

\* billion cubic meters (m<sup>3</sup> or kL)

#### 2.1.2 ECONOMIC DRIVERS – NATIONAL PERSPECTIVE

In South Africa, demand is projected at 17.7 billion m<sup>3</sup> in 2030 with household demand accounting for 34% of the total. With the current supply of only 15 billion m<sup>3</sup> and severe constraints due to low rainfall, limited underground aquifers, and reliance on significant water transfers from neighbouring countries, South Africa will have to balance water usage between agriculture, key industrial activities, and increasing urbanisation. In addition, water resources

challenges have been projected based on the water resource availability and demand of historical climate conditions. Yet, South Africa is faced by increased uncertainty in water resource availability as a result of the impact of global climate change with an "average" expectation of climate change for South Africa by 2030 showing a slight decrease in supply and a more pronounced increase in crop demand, growing the 2030 demand-supply gap from 18% to 30%. In addition, a recent survey of 14 countries including Canada, USA, Australia, UK and 9 EU members, South Africa rated 13<sup>th</sup> in terms of the cost of water per kilolitre. However, from 2003 to 2008, South Africa rated 3<sup>rd</sup> in terms of the rate at which water costs are increasing, with a 70% increase in water costs over the 5 year period. Whilst, this represented a 9.2% increase during 2006/2007, announcements by Rand Water in 2008 of double digit rate increases have been indicative of a National trend (EMMT, 2008). A statement issued by the Department of Water and Environmental Affairs (DWEA) in February 2010, warned of a 6.1% increase in bulk raw water costs from two National dams and water imported from Lesotho. The affected dams supply over 12 million people in provinces of Gauteng (including Johannesburg), Mpumalanga, the Free State and North West. The immediate response of water utility, Johannesburg Water, was that it had no choice but to pass on the tariff increase to consumers at a significantly higher rate than the bulk water supply tariff rate increase (EMMT, 2008).

To close the demand-supply gap would require region-specific combinations of three fundamental solutions. Assuming economic activity remains constant, the first two focus primarily on technical improvements and increasing supply and productivity. The third option available involves a reduction in water withdrawals through changes in the underlying economic activities that fuel these withdrawals. Therefore, bridging the supply-demand gap requires that the specific regional water sector is well managed and has the technical and socio-economic framework in place to identify and implement the correct mix of solutions that is both sustainable and economically viable.

These frameworks, however, are severely constrained within South Africa. With over R2,5billion approved for National water projects in 2008/2009 and water services projects (renovations and additions only) worth R674-million being awarded in the Western Cape, followed by R620-million in Gauteng, R321-million in the Eastern Cape and R165-million in KwaZulu-Natal. Only 32 of South Africa's approximately 970 wastewater treatment works comply with requirements for safe discharge – a compliance level of just 3% according to the National 'Green Drop' initiative (Green Drop Report, 2010/2011) (Table 2.2). According to the National Budget Speech for 2011/2012, R3.6 billion will be spent on improving water infrastructure and services (South Africa, 2011).

Province	% non-compliant WWTWs	% WWTPs exceeding design flow	
Free State	99	77	
Northern Cape	96	87	
Eastern Cape	89	95	
Gauteng	67	84	
Limpopo	95	95	
North West	100	95	
Western Cape	19	29	
Mpumalanga	90	89	
Kwazulu-Natal	77	50	

 Table 2.2 National non-compliance levels of Wastewater Treatment plants (Green Drop Report, 2010/2011)

For all industries with process flow configurations designed around dual-stream reticulation, i.e. processes where both potable water and non-potable treated municipal wastewater is utilised, cost implications of this non-compliance is significant as this directly impacts water supply security. Industries that are reliant on lower cost non-potable water for certain process requirements are increasingly forced to use costly potable water for these applications due to the lack of non-potable water supply.

#### 2.1.3 ECONOMIC DRIVERS – LOCAL PERSPECTIVE

The Western Cape Water Supply System (WCWSS) supplies to a diverse and growing economy. The main user of the supplied water is agricultural, industrial and tourism industries and besides the industries, the WCWSS supplies drinkable water to more than 3 million people (South Africa, 2009c). The current usage from the WCWSS is 493 Mm<sup>3</sup>/annum, while the current supply is 556 Mm<sup>3</sup>/annum (South Africa, 2009c).

The water supply for the City of Cape Town (CCT) district is supplied by the Berg River catchment (South Africa, 2009c). However, this catchment does not have enough water to supply to this region. As a result a transfer scheme is in place to meet the demand (South Africa, 2009c). The current transfer scheme will be able to provide the CCT with enough water

until 2013 (South Africa, 2009c). From this time onward, new avenues of water reclamation needs to be investigated in order for the CCT municipality to provide water for the increasing demand (South Africa, 2009c).

Currently the CCT is investing in the Western Cape Water Reconciliation Strategy. The focus of the strategy is to investigate possible alternatives to help meet the future water demands of the region. The CCT water control and water demand management has implemented a strategy to divert more water to the CCT areas where needed. Even though this has proven successful, new interventions should be acquired before 2019 (South Africa, 2009c). As it takes a number of years to plan, approve, design and implement large new ventures, the research and development of possible water reclamation projects should begin now in order for the CCT to avoid an even bigger water crisis. In addition to the urgency is the fact that external factors such as climate change could bring forth the need for a new water source earlier than 2019.

#### 2.1.4 NATIONAL MARKET DRIVERS – LEGISLATIVE COMPLIANCE

Industrial water discharge compliance levels are governed by the National Water Act No. 36 of 1998 according to General Limits stipulated in the Wastewater Discharge Standards Guidelines (South Africa 1998). The purpose of these guidelines is to protect, manage, control, reduce, and prevent the pollution of South Africa's water resources. Within the context of the National Water Act (36 of 1998), the purpose of local government is to ensure that this legislation is adhered to in the interests of a sustainable environment through the enforcement of Wastewater and Industrial Effluent By-laws. This "polluter pays" principle involves the payment of penalty charges by industries for the discharge of industrial effluent that is non-compliant with the current General Limit discharge standards. However, the enforcement of the more stringent 2010 Wastewater Discharge Standards (see Table 2.3) will have a significant impact on penalties incurred by non-compliant industries forcing industries to adopt Cleaner Production systems in combination with water reuse and recycle processes and technology.

In addition, the new National Environmental Management: Waste Act came into force on July 3, 2009 (South Africa, 2009b). With the new amendments to the National Environmental Management Act (South Africa, 2009b) having also come into force, compliance and enforcement of various pieces of environmental legislation has been significantly strengthened including the increase in penalties for those who do not comply with specific environmental acts.

 Table 2.3 National Water Act (36 of 1998) Waste Discharge Standards: DWEA 2010 guidelines (South Africa, 1998)

Variables and Substances	Existing General	Future all
	Standards	discharge
Chemical Oxygen Demand	75 mg/L	65 mg/L
Colour, odour or taste	No substance capable of producing the variable listed	No substance capable of producing the variable listed
Cyanide (as Cn)	0.5 mg/L	0.006 mg/L
Ionised and unionised ammonia (free and saline ammonia as N)	10 mg/L	1 mg/L
Nitrate (as N)	-	15 mg/L
рН	Between 5.5 and 9.5	Between 5.5 and 7.5
Phenol index	0.1 mg/L	0.01 mg/L
Residual chlorine (as Cl)	0.1 mg/L	0.014 mg/L
Suspended solids	25 mg/L	18 mg/L
Total aluminium (as Al)	-	0.03 mg/L
Total arsenic (as As)	0.1 mg/L	0.03 mg/L
Total boron (as B)	1 mg/L	0.5 mg/L
Total cadmium (as Cd)	0.05 mg/L	0.001 mg/L
Total chromium III (as Cr <sub>III</sub> )	-	0.11 mg/L
Total chromium VI (as Cr <sub>VI</sub> )	0.5 mg/L	0.02 mg/L
Total copper (as Cu)	1 mg/L	0.002 mg/L
Total iron (as Fe)	-	0.3 mg/L
Total lead (as Pb)	0.1 mg/L	0.009 mg/L
Total mercury (as Hg)	0.02 mg/L	0.001 mg/L
Total selenium (as Ce)	0.05 mg/L	0.008 mg/L
Total zinc (as Zn)	5 mg/L	0.05 mg/L
Typical faecal coli per 100 ml	0 mg/L	0 mg/L

2009/2010 was to be a year of transition in the environmental compliance and enforcement sector, with the consolidation of the Department of Water and Environmental Affairs under a single ministry (DWEA; previously DWAF); as well as the commencement of a series of National environmental legislation acts, namely, the National Environmental Management: Waste Act 59 of 2008 (South Africa 2009b); the Air Quality Act 39 of 2004 (South Africa 2005); and Integrated Coastal Management Act 24 of 2008 (South Africa, 2009a). The bringing into effect of these laws will drive the need to have properly trained and designated Environmental Management Inspectors at national, provincial and local spheres of government. There is likely to be an increased expectation that environmental enforcement officials will utilize significantly increased

maximum penalties and jurisdiction of the magistrates' courts provided for in legislative amendments to achieve appropriate sentences in cases where there has been serious, irreparable harm to the environment.

#### 2.2 MEMBRANE BIOREACTORS – INTRODUCTION TO THE TECHNOLOGY

Traditional wastewater or effluent treatment primarily uses biological degradation in conventional activated sludge (CAS) reactors followed by a clarification step, which is typically a sedimentation process. These plants tend to have a large footprint and do not produce water that can be recycled back into the process stream unless specialized disinfection steps are included in the process design (Figure 2-1).



Figure 2.1: Schematic of a conventional activated sludge process (A); Sidestream MBR (B); and immersed MBR (C) (Adapted from Judd, 2008)

In contrast, MBRs represent a relatively new technology that combines several typical unit operations (primary sedimentation, activated sludge aeration, secondary sedimentation, and tertiary media filtration) into a single treatment step. In MBRs, solid/liquid separation is facilitated by the membrane component of the process, which acts as a barrier effectively removing or retaining particulates, including pathogenic protozoans, bacteria and viruses in the feed stream. The technology of membrane separation of activated sludge is the combination of an aerated bioreactor, where the organic components are oxidized by the activated sludge together with an integrated separation of the biological sludge by ultrafiltration membranes (Figure 2.2) to

produce a particle-free effluent. The filtration step replaces the final clarifiers used in conventional activated sludge treatment, which achieve solid separation by gravity only.

The physical barrier imposed by the membrane system provides complete retention of all mixed liquor suspended solids (MLSS) and therefore disinfection of the treated effluent. This unique character enables MBRs to be operated at very high biomass concentrations (up to 18g/L compared with 6g/L for CAS) with sludge ages approaching infinity. Although the viability of biomass decreases with an increase in the sludge age, the long sludge residence time (SRT) in MBRs allows the proliferation of microorganisms higher up in the food chain, which prey on bacterial cells thereby reducing excess biomass production. In combination with low feed/microorganism (F/M) ratios, high MLSS in MBRs promotes cell lysis and cryptic growth and a resultant low sludge production and therefore a reduced plant footprint.

#### 2.2.1 OPERATIONAL EVALUATION OF MBRs

The capital expenditure (CAPEX) and OPEX associated with the filtration component of the MBR process is driven by the value of the absolute permeate flux and the specific flux (permeability). Efficient cost comparisons between CAS and MBRs requires careful consideration of the type and strength of the wastewater and the degree of treatment required. The most significant advantages of the MBR process is that the membrane filters replace the need to install costly secondary clarifiers downstream of the CAS. In addition, MLSS values in the order of 12-18 g/L are common in MBRs as opposed to 3-6 g/L typical of CAS systems. A higher operating MLSS translates into a 50-75% reduction in plant footprint as well as longer SRT and lower F/M ratios. Long SRTs result in significantly less sludge production and disposal costs and low F/M ratios enables short Hydraulic Retention times (HRT) to be implemented.

#### 2.2.1.1 Membrane Bioreactor Configurations – Cost Considerations

The MBR process comprises a relatively simple flow configuration and is therefore ideally suited to industries that have effluents that are difficult to treat, requirements for high quality treated water, and footprint constraints. The key market drivers can therefore be separated by discharge requirements and reuse requirements (Table 2.4).

 
 Table 2.4 Key market drivers for membrane process applications in wastewater treatment (Adapted from Judd, 2006)

Discharge	Reuse			
Membrane costs have decreased 10-fold in the past 15 years				
	Mandatory for meeting standards in			
Meets regulatory standards	potable applications			
for discharge	Membrane filtration pre-treatment is			
	mandatory for NF and RO processes			
	Increased value for industrial			
Meets standards for	applications			
discharge to pristine	Permeate quality instrumental in			
environments	obtaining Greenfield development			
	permits			

In addition, significant cost reductions in terms of OPEX and CAPEX have been realised over the past 15 years (Figure 2.2). This has had a significant impact on the adoption of MBR processes at large scale for both industrial and domestic/municipal effluent treatment.



Figure 2.2: Global CAPEX and OPEX cost reduction trends for MBRs over the past 15 years (Kennedy & Churchouse,2005)

Comparativa Factor	External MBR Internal MBR		Economic		
Comparative Factor	Crossflow	ossflow Airlift Hollow Fibre Flat Sheet		implication	
	Higher flux th	nerefore lower	Lower flux but	greater packing	External 2.5x higher
Membrane area	membrane are	а	density (300 m <sup>2</sup> /m <sup>3</sup> for hollow		flux than internal
			fibre (HF); 100 m	n²/m³ for FS)	
Footprint	Higher flux 8	high volatile	Higher packing	density & high	Lower CAPEX
requirement	suspended	solids (VSS)	VSS results in co	ompact system	requirements
loquionon	results in comp	oact system			
Bioreactor and	Bioreactor & r	nembrane can	Design & operat	ion of bioreactor	Ease of optimization
membrane design &	be independe	ntly optimized.	& membrane	tank not	results in lower OPEX
operation	BNR possible.		independent. Hi	gh recycle ratio	
dependency			requirements to	limit VSS build-	
			up (4x recycle ra	tio).	
Membrane	Robust – less	susceptible to	Susceptible to	wastewater &	Lower OPEX for
performance	wastewater &	piomass	biomass chara	cteristics (CIP-	external MBR (CIP-
efficiency &	characteristics		frequency & strategy		related)
consistency			dependence)		
	Off-line cleanir	ng – 1-2 month	Off line recovery cleaning		Lower OPEX for
Membrane	intervals; Automated 4-hour intervals;		interval 2-6 m	onths; complex	external MBR
performance	procedure		and time consuming; membrane		
recovery			must be physically removed from		
			tank		
Membrane	Operating lifeti	me – 7 years	Operating lifetime 5 years		Lower CAPEX for
replacement					external MBR
Full scale application	Long track re	cord at large	Full scale appli	cations globally	Market-related cost
	SC	ale		cations globally	reduction
Flux values	85-135				Desired flux must be
(l.m <sup>-2</sup> .hr <sup>-1</sup> )	l m hr	40-80 L.m.hr	<35 L.m.hr	<35 L.m.hr	balanced energy
( )	<b>_</b>				requirements
	2540		0306	0306	Comparable energy
Energy requirements 2.5-4.0 0.4 kWh/m <sup>3</sup>		0.3-0.0	0.3-0.0	costs for Internal &	
			KVVI/III	KVVI/III	external
	Comparable c	apital costs at	Capital & power	External suitable for	
Overall economics	lower feed rat	es (4 Ml/day).	at high feed rate	s (>4 Ml/day)	industrial & municipal;
	Ideal for industrial effluents				internal suitable for
			municipal		

Table 2.5 Comparative Evaluation of External and Internal MBR Process (	Configurations (Ju	udd,2006)
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MBR systems are classified into two major categories based on the location of the filtration component of the MBR. 1<sup>st</sup> generation external MBR configurations use membrane modules that are located externally to the bioreactor – the bioreactor liquor is physically separated from the membrane component and requires pumping from the bioreactor to the modules to facilitate the filtration process. Conversely, 2<sup>nd</sup> generation or immersed MBRs are designed around an internal configuration based on the membranes being physically immersed within the bioreactor mixed liquor and aerated from below. 3<sup>rd</sup> generation systems combine the lower energy requirements and air scouring mechanisms employed in immersed MBRs with the advantages of external membrane module placement (Table 2.5).

#### 2.2.2 ADVANTAGES OF MBRs FOR INDUSTRIAL EFFLUENT TREATMENT

MBR applications are ideally suited to treating industrial wastewaters that are difficult to treat without long SRT and where settling or clarification problems are frequently encountered. The main advantages associated with MBRs in the treatment of industrial wastewaters are summarized in Table 2.6 below.

Physical advantages	Biological advantages
More compact, lower footprint	Unencumbered SRT control provides optimum
reactors due to high MLSS vs. CAS	control of microbial population
(low MLSS)	
SRT independent of HRT	Slow growing microorganisms such as nitrifiers are
	readily maintained
Independent of biomass settling	Rapid start-up due to complete retention of
characteristics	microbial inoculum
Attractive option for upgrades or	Readily configured for enhanced biological
expansions of existing CAS with	phosphates removal (EBNR) and nitrogen removal
clarifier problems, excessive	with denitrification processes.
operational needs, or where site	
footprint is constrained	
MBRs can be operated unattended	Particulate& high MW organics are retained
due to high levels of automation	according to the SRT and not the HRT providing
	maximum opportunity for degradation
Ideal pre-treatment for RO	Non-biodegradables discharged with sludge
applications	component

 Table 2.6 Physical and biological advantages of MBRs for industrial effluent treatment (adapted from Judd,2006)

## CHAPTER 3

#### 3. TRADE EFFLUENT SECTOR ANALYSIS

In the interim between proposal submission and approval by the WRC, the initial identified industrial partner, a food processing factory in Brackenfell, Cape Town, became unavailable for the on-site technology evaluation. An alternative industrial partner, SANS Fibres, was therefore successfully approached in August 2008. However, in November 2008, AECI announced that permanent closure of the plant would commence in March 2009. As a result, the lead organization, Atl-Hydro CC., conducted a detailed trade effluent industry market analysis with the goal of identifying several possible industrial partners who could be approached with the offer of a technology assessment partnership in conjunction with the WRC.

#### 3.1 TRADE EFFLUENT INDUSTRY MARKET ANALYSIS (CCT)

The trade effluent industry in the CCT comprises approximately 4,100 companies registered with the Metro municipality for the discharge of industrial and domestic effluents into the municipal sewerage grid. Approximately 6.5% of these companies are non-compliant with the Municipal effluent discharge By-laws and are therefore tariffed according to the discharge limits set out within the Municipal By-law. These are industries that operate on a pay-to-pollute principle and have either ineffective or no on-site treatment capacity for the effluents generated during daily operations.

Based on annual tariff revenues, companies that would derive the greatest economic benefit through implementing full-scale on-site effluent treatment plants within the textile, paper and pulp, beverage, dairy, and food sectors were therefore approached telephonically and then forwarded an electronic marketing brochure outlining the proposed collaborative project. These sectors were chosen because they generate 83% of the trade industry tariff and associated potable water revenue for the CCT.



**Figure 3.1:** Tariffed trade industry sectors in the City of Cape Town Metro Municipality. Figures represent monthly effluent discharge volumes (kL/month). Adapted from: Water Service Development Plan – City of Cape Town (2008-2013)

#### 3.2 IDENTIFICATION OF COMMERCIAL INDUSTRY PARTNER

#### 3.2.1 SCREENING OF POTENTIAL INDUSTRIAL PARTNERS

Four of the companies that responded positively to the piloting proposal were chosen as potential industrial partners for this evaluation. Over a period of approximately four months, weekly grab samples were analysed from each company and the effluent composition monitored. Several effluent composition parameters were monitored in-house by in-service trainees and the remainder was outsourced to an ISO17025-certified laboratory in Cape Town. The results of this evaluation are shown in Table 3.1 below. To determine the most appropriate industrial partner for the pilot evaluation, several criteria were chosen as the basis for assessment and thus included amongst others: effluent volumes; composition variability; biological degradation potential; site location; economic risk analysis; scale-up potential; and most importantly; the enthusiasm and attitudes of the senior and operations management at each company. Of the four industrial candidates, based on these criteria, it was determined that 2 companies, the textile and the paper and pulp company were the most appropriate technology evaluation partners for this pilot plant. However, due to the scale of the paper and pulp company, a lab-scale pilot plant was chosen for this company.

**Table 3.1:** Effluent volumetric and compositional analyses of potential industry partner candidates monitored over a 4-month period

		Textile 1	Textile 2	Paper & Pulp 1	Textile 3
		Company 1	Company 2	Company 3	Company 4
		AVG (min-max)	AVG (min-max)	AVG (min-max)	AVG (min-max)
Potable water volume	kL/month	2,350	34,810	39,992	3,418
Effluent volume	kL/month	2,234	29,394	36,480	3,247
Effluent volume	kL/month	74	980	1,216	108
Effluent volume	m³/hour	3.1	40.83	50.67	3.61
Total volume water	kL/month	4,584	64,204	76,472	6,665
Location	-	Bellville, Cape Town	Paarl, Cape Town	Bellville, Cape Town	Bellville, Cape Town
n (sampling period)	weeks	17	16	8	13
рН	pH units	10.1 (7.4-11.5)	10.4 (6-11.8)	6.44 (4.4-6.8)	7 (4.7-2)
Temperature	°C	32.4	30.6	37.01	23.3
Conductivity	μS/cm	2,792 (471-10, 513)	1125.7 (257-3603)	1845.75 (1203- 2530)	639.7 (153-3260)
TDS	mg/L	1,039	700.9	1301.88	454.4
Turbidity	NTU	45 (17-116)	243.2 (28-700)	177.8 (151-283)	84 (1-484)
COD	mg/L	570 (155-823)	1119.3 (178-2683)	2760.21 (1362- 4105)	1590 (102-3637)
BOD	mg/L	192.5	720	2400	-
TSS	mg/L	19 (4-51)	36 (21-54)	124.8 (19-447)	-
NH <sub>4</sub> -N	mg/L	10 (4-42)	28.4 (9.7-88.2)	5.18 (3.9-7.1)	5.6 (2.6-8.4)
NO <sub>3</sub> -N	mg/L	6.24	8.58	5	-
Na	mg/L	189	98	162	-
к	mg/L	19	50	9	-
Са	mg/L	10	20	365	-
Mg	mg/L	3.4	9.55	15.14	-
		Textile 1	Textile 2	Paper & Pulp 1	Textile 3
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		Company 1	Company 2	Company 3	Company 4
		AVG (min-max)	AVG (min-max)	AVG (min-max)	AVG (min-max)
Fe	mg/L	0.14	0.255	0.264	-
CI	mg/L	147	49	141.56	-
CO <sub>3</sub>	mg/L	0	0	N/A	-
HCO <sub>3</sub>	mg/L	188	434	1,018	-
SO <sub>4</sub>	mg/L	87	19	454	-
В	mg/L	0	0.045	1.15	-
Mn	mg/L	0.03	0.05	0.06	-
Cu	mg/L	0.02	1.1	0.002	-
Zn	mg/L	0.05	0.105	0.154	-
Р	mg/L	7.97	27.685	2.336	-
F	mg/L	1.1	0	0	-
COD/BOD	-	2.96	1.55	1.15	-
BOD/COD	-	0.34	0.64	0.87	-

## 3.2.2 TREATMENT OF TEXTILE EFFLUENTS

The textile industry not only consumes large quantities of water (Brik *et al.*, 2006; Badani *et al.*, 2005; Chakraborty *et al.*, 2003; Barclay & Buckley, 2002) but, it also produces large volumes of toxic, low biodegradable, and highly coloured wastewater (You & Teng, 2009; Arnal *et al.*, 2008; You *et al.*, 2008; You *et al.*, 2007; Badani *et al.*, 2005; Kim *et al.*, 2004). Textile wastewater contains high concentrations of slow or nonbiodegradable organic substances, as well as inorganic chemicals (Badani *et al.*, 2005; Lubello & Gori, 2004) and is characterised by high COD and the presence of nonbiodegradable components such as dyes, pigments and often heavy metals (El Defrawy & Shaalan, 2007).

Conventional treatment processes used in the treatment of textile wastewater include physical and chemical methods (e.g. coagulation, activated carbon adsorption, ion exchange, reverse osmosis filtration, coagulation); chemical oxidation (e.g. UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub> Fenton's reagent); advanced oxidation processes (e.g. photocatalysis, electrochemical, sonolysis, ionising radiation), as well as biological (e.g. activated sludge, sequencing batch reactor) (You & Teng, 2009; González-Zafrilla *et al.*, 2008; Badani *et al.*, 2005; Chakraborty *et al.*, 2003; Kural *et al.*,2001; Gupta *et al.*, 2000).

Often biological processes are combined with physical and chemical treatments, such as flocculation, precipitation and chemical coagulation, in order to better decolourise the wastewater and treat the effluent of activated sludge (You *et al.*, 2008). However, these physical and chemical treatments result in excess sludge, which requires safe environmentally friendly disposal. Therefore, a demand exists for the development of natural alternative economic and environmentally friendly methods for the decolourisation of wastewater containing dyes (Pandey *et al.*, 2007; Chang *et al.*, 2001).

## 3.2.2.1 TEXTILE EFFLUENTS – DYE STRUCTURE AND DECOLOURATION

Azo dyes commonly utilised in the textile industry include reactive, acid and direct dyes (You & Teng, 2009). Azo dyes are the largest chemical class of synthetic dyes and therefore a major problem in the treatment of textile effluent. These dyes are electron deficient, xenobiotic compounds because they possess one or more azo (-N=N-) groups, as well as sulfonic (-SO<sub>3</sub>) electron withdrawing groups. This generates electron deficiency within the molecule, making the compound less susceptible to oxidative catabolism by bacteria. The reactive azo dyes contain one to four azo bonds (You & Teng, 2009), which are easily reduced under anaerobic conditions. Table 3.2 is a summary of the different classifications of dyes used in the textile industry.

<b>Dye Type</b>	Structural Formula	Commercially	Predominant Feature	Colour Range
		Available as		
Azo Dyes	$\bigcup_{SO_3H}^{SO_3H} \underset{H_3C}{\overset{N=N-}{\underset{N=}{\overset{N-}{\underset{N=}{\underset{N=}{\overset{N-}{\underset{N=}{\underset{N=}{\overset{N-}{\underset{N=}{\underset{N=}{\overset{N-}{\underset{N=}{\underset{N}{\underset{N=}{\underset{N}{\underset{N=}{\underset{N}{\overset{N-}{\underset{N}{N}}{\underset{N=}{\underset{N}{\underset{N=}{\underset{N=}{\underset{N}{N$	C.I. Reactive Yellow 4	Virtually every Hue in the spectrum can be achieved by mono- and di-azo dyes	Virtually every Hue in the spectrum can be achieved by mono- and di-azo
Metal-Complex Dyes	O SO HI	C.I. Reactive Red 23	Exceptionally lightfast dyes	Assorted colours; Yellow, Ruby, Violet, Blue, Brown, Olive, Black
Anthraquinone Dyes	O HN SO,H	C.I. Reactive Blue 19	Violet and Blue	Brilliance, good Light-fastness and chromophore - acidic and basic
Triphenodiaxazine Dyes	N/A	N/A	Brilliant blue dyes	Less expensive
Formazan Dyes	N/A	N/A	Red to greenish-blue shades	Alternatives to Anthraquinone dyes
Phthalocyanine Dyes	N/A	N/A	Brilliant turquoise and green shades	Contains Copper and Nickel as their central atom

 Table 3.2: Dye classification summary (Hunger and Herbst, 2003)

Biological decolourisation to transform, degrade or mineralize azo dyes requires a two stage bacterial process (refer to Figure 3.2) based on the observation that azo dyes can be anaerobically reduced into colourless aromatic amines, which can be degraded aerobically. Many bacterial consortia possess enzymes (azo-reductases) capable of disrupting the azo bonds under anaerobic conditions (negative redox potential) (Żyłła *et al.*, 2006). The product of this anaerobic degradation is colourless aromatic amines, which are carcinogenic. These colourless aromatic amines can be readily degraded via aerobic digestion. Figure 3.2 illustrates

the pathway of azo dye degradation via anaerobic digestion and the degradation of the resulting aromatic amine via aerobic digestion (Van Der Zee & Villavrede, 2005).



Figure 3.2: Anaerobic and aerobic degradation pathways of azo dyes and aromatic amines (Van Der Zee & Villavrede, 2005).

- Step 1: Under anaerobic conditions, reduction of azo dye to the corresponding amine. A reaction catalysed by an enzyme azoreductase and an electron donor (Dafale *et al.*, 2010).
- Step 2: Degradation of the resulting aromatic amine via a multi-step bioconversion under aerobic conditions (Dafale *et al.*, 2010).

The degradation of aromatic amines depends on their chemical structure, simple aromatic amines can be mineralised under methanogenic conditions, while sulphonated aromatic amines are resistant and require specialised aerobic microbial consortia in order to be mineralised (Pandey *et al.*, 2007). The use of bacterial strains to decolourise azo dyes is generally initiated by azoreductase-catalysed direct or indirect anaerobic reduction or cleavage of the azo bonds. The resulting aromatic amines are either aerobically or anoxically degraded by the use of a mixed or pure bacterial community. These operating conditions allow the reaction to be non-specific with respect the bacteria, as well as the dyes (Chang *et al.*, 2001; Libra *et al.*, 2004; Pandey *et al.*, 2007). Hu (1994) isolated and identified a bacterial strain of *Pseudomonas luteola* 

capable of efficiently decolourising a group of azo dyes, specifically, reactive red 22 (Chang *et al.*, 2001). Several genera of *Basidiomycetes* have also been identified as capable of mineralising azo dyes (Libra *et al.*, 2007).

## 3.2.2.2 TEXTILE EFFLUENTS AND MBRs

Membrane techniques show great promise in the treatment of textile wastewater (Marcucci *et al.*, 1970) as they either remove the dyestuff allowing reuse of the auxiliary chemicals used for dyeing or concentrate the dyestuffs and auxiliaries producing purified water (Chakrabarty *et al.*,2003). An important feature of MBRs is the possibility of facilitating the growth of specialised micro organisms due to the ability to employ high sludge ages, in this way promoting improved degradation of refractory organics (Brik *et al.*, 2006; Stephenson *et al.*, 2000). The advantage of a membrane reactor, as well as a flow reactor with recycle used to treat industrial wastewater and slurries is to allow operation at lower residence times, thus increasing the throughput of effluent (Nelson *et al.*, 2008). The recycle in the continuous flow bioreactor allows the retention of a higher concentration of micro organisms within the bioreactor, which results in the reactor operating at greater flow rates and increases its efficiency (Nelson *et al.*, 2008).

Generally, textile effluent is trademarked by its high COD. The COD is the measure of the oxygen required to oxidise both organic and inorganic compounds in wastewater. Large variations in the influent of MBRs treating textile effluent is a common occurrence (Yigit *et al.*, 2009; Zheng & Lui., 2006; Schoeberl *et al.*, 2004; Badani *et al.*, 2005). This is mainly due to the variations in the production programs of the textile industry and the shut downs for cleaning and maintenance during weekends (Yigit *et al.*, 2006).

Although there were large COD variations in the MBR influent, Banadi *et al* (2005) had an average COD removal of 96%. Lubello and Gori (2004) achieved an average COD removal of 93%, while Brik *et al.* (2006) observed a COD removal of greater than 90% (refer to Table 3.3 for the various MBR set-ups utilised).

Set-up	COD	COD	BOD	BOD	тос	Colour	TRUE	SS	SS (md/l )	Reference
	(mg/L)	removal	concentration (mg/L)	removal	removal	removal	colour (ADMI)	removal		
MBR (submerged hollow fibre membrane module in an aeration tank0	1411 (influent)		455 (influent)							You <i>et al.,</i> 2009
Anaerobic sequencing batch reactor (SBR)		92.30%				74.60%	264.2 ± 49.9			You & Teng,
Aerobic MBR		5.20%				9.10%	169.0 ± 22.4			2009
SBR	133 (effluent)		68 (effluent)				548		96	
Aerobic MBR	95 (effluent)		3 (effluent)				513		0	You <i>et al.</i>
Anaerobic-oxic Membrane Bioreactor (AOMBR)	37 (effluent)		3 (effluent)				196		0	2008
AOMBR/RO	38 (effluent)		0 (effluent)				32		0	
Aerobic MBR (activated sludge reactor connected to	1380-6033 (influent)									Brik <i>et al.</i> ,
an external cross-flow UF unit)	130-900 (effluent)	%08-00				00-88-00				2006
Submerged microfiltration MBR					95%	68.30%				Hai <i>et al.,</i> 2009
SBR	133 (effluent)	%02	6.8	%96		51%	548 (effluent )	%09	96	Voit of ol
MBR	95 (effluent)	%62	-	%66		54%	513 (effluent	100%	0	2007 et al.,
Aerobic MBR	1280-5600 (influent) 240 (effluent)	%96				72%				Badani <i>et al.</i> , 2005

Table 3.3: Summary of COD, BOD, total organic carbon (TOC), colour removal, true colour and suspended solids (SS) removal capabilities of the various MBR configurations

5

Set-up	COD	COD	BOD	BOD	TOC	Colour	TRUE	SS	SS	Reference
	concentration (mg/L)	removal	concentration	removal	removal	removal	colour	removal	(mg/L)	
			(IIIG/L)							
Aerobic MBR (external UF module with plate and frame	500-1700 (influent)	93%				70-80%				Lubello &
membranes)	40-60	(average)								Gon, 2004
MBR (activated sludge reactor connected to an external cross-flow UF unit)	280 (effluent)	91.80%								Schoeberl <i>et</i> al., 2004

Table 3.3: Summary of COD, BOD, TOC, colour removal, true colour and SS removal capabilities of the various MBR set-ups continue

When the influent COD values were at its maximum level (2,278 mg/L), Yigit *et al.* (2009) observed a COD removal that always exceeded 95%. Zheng and Lui (2006) and Schoeberl *et al.* (2004) both observed an average COD removal exceeding 90%. This indicates that the MBR system responds very well to variations in the influent and is also able to buffer the changing influent composition. Therefore, it can be stated that the MBR system is a very stable system and that the outlet values are substantially independent from the inlet loads. Yigit *et al.* (2009) had a BOD<sub>5</sub>/COD ratio of 0.32, which suggest the dominance of slowly biodegradable and/or biorecalcitrant organics in the textile wastewater. The stable and successful performance of Yigit *et al.* (2009) MBRs biological activity despite the low BOD<sub>5</sub>/COD ratio, demonstrates the presence of a robust and specialized biomass mixture in the MBR that could respond to the sudden variations within the influent and degrade synthetic chemicals such as dyes. Another key feature underlined by this constant COD removal is that within the MBR, the insoluble components are rejected until they are susceptible to biodegradation or drawn out with surplus sludge.

#### 3.2.3 TREATMENT OF PAPER AND PULP EFFLUENT

In the production of paper large volumes of high quality water needs to be readily available. The paper and pulp industry in South Africa is one of the industries with the largest consumption and discharge of water and wastewater, respectively. A single paper and pulp processing plant consumes approximately 130 million m<sup>3</sup> of water per annum (Steffen *et al.*, 1990; Christopher, 2007). The effluent from a paper and pulp is high in pollutants such as TSS, conductivity and sulphates. Also problematic with this type of effluent is the COD and BOD as well as carbonates and hydro carbonates (Christopher, 2007). Table 3.4 illustrates the typical composition of paper and pulp effluent.

The paper and pulp industry requires a variety of treatment processes, the two broad categories of which are physico-chemical and biological treatment. Physico-chemical includes; sedimentation/flotation, coagulation /precipitation, adsorption, chemical oxidation, membrane filtration, and ozonation (Pokhrel & Viraraghavan, 2004). Sedimentation/flotation is used when wastewater is high in fibrous particles. Sedimentation and flotation are the preferred methods when 60 to 75% removal TSS is desired. Coagulation is generally applied in the tertiary treatment phase to remove total organic carbon (TOC), and organic halides. Adsorption is mainly used in the paper industry when colour, such as dyes, require removal from the wastewater.

Table 3.4: Typical characteristics of wastewater (mg/l) for different paper and pulp processes (Bajpai, 2000; Rajeshwari et al., 2000)

				Paran	neters				
					Acetic				
Process	Hq	suspengeg Solids (mg/l)	BUD (mg/L)	COD (mg/l)	Acid (mg/l)	metnanol (mg/l)	N (mg/l)	P (mg/l)	S (mg/l)
TMP <sup>1</sup>	I	383	2800	7210	235	25	12	2.3	72
TMP <sup>1</sup>	4.2	810	2800	5600		ı			
CTMP <sup>2</sup>	ı	500	3000-4000	0006-0009	1500				167
Kraft Bleaching	10.1	37-74	128-184	1124-1738	0	40-76		ı	ı
Kraft foul (1)	8	16	568	1202		421		·	5.9
Kraft foul (2)	10.2	0	10,700	16,000		ı	306	-	91
Kraft foul (3)	9.5-10.5	0	5500-8500	10 000-13 000		7500-8500	350-600	0.02-1.55	120-375
Sulfite condensate (1)	2.5		2000-4000	4000-8000		250		·	800-850
Sulfite condensate (1)	2.8-5.9		3700-5110	9800-27 100	ı	ı			840-1270
NSSC <sup>3</sup> Pulping:									
Spent Liquor	ı	253	13,300	39,800	3200	06	55	10	868
Chip wash	ı	6095	12,000	20,600	820	70	86	36	315
Paper mill		800	1600	5020	54	6	11	0.6	97
<sup>1</sup> Th arm and a hand and Durkin a									

<sup>1</sup>Thermomechanical Pulping <sup>2</sup>Chemi-thermomechanical Pulping <sup>3</sup>Neutral Sulfide Semichemical

Ozonation is employed to remove COD, TOC and increase the biodegradability of the paper and pulp effluent (Pokhrel & Viraraghavan, 2004).

## 3.2.3.1 BIOLOGICAL TREATMENT

Both anaerobic and aerobic biological treatment stages are used in the paper industry. The most commonly used reactors are: anaerobic lagoons, anaerobic contact, fluidized bed, and UASB (Pokhrel & Viraraghavan, 2004). Table 3.5 compares the difference between aerobic and anaerobic treatment options.

Feature	Aerobic	Anaerobic
Organic removal efficiency	High	High
Effluent quality	Excellent	Moderate to poor
Organic loading rate	Moderate	High
Sludge production	High	Low
Nutrient requirement	High	Low
Alkolinity requirement	Low	High for certain industrial
Aikainity requirement	LOW	waste
Energy requirement	High	Low to moderate
Temperature sensitivity	Low	2-4 months
Start-up time	2-4 weeks	2-4 months
Odour	Less opportunity for	Dotontial adour problems
Odoui	odours	Potential odour problems
Nutrient recovery	No	Yes
Mode of treatment	Total	Essentially pre-treatment

 Table 3.5: Comparison of aerobic and anaerobic treatment (Pokhrel & Viraraghavan, 2004)

## 3.2.3.2 ANAEROBIC DIGESTION

Anaerobic digestion (AD) is a biological process whereby organic matter is decomposed under oxygen limited conditions (Salminen & Rintala, 2002) and is considered more suitable for high strength effluents with COD exceeding 1,000 mg/L (Pokhrel & Viraraghavan, 2004). Methane gas along with others gases is produced that can be used as an alternative energy source (Salminen & Rintala, 2002). The benefits of anaerobic digestion are odour reduction, pathogen control, minimizing sludge production, and conservation of nutrients (Wilkie, 2005).

The mechanism of AD requires strict anaerobic conditions to function correctly. The process of AD can be viewed as four distinct steps, and involves many types of microorganisms (Mutombo, 2004). The overall process is illustrated in Figure 3.3 (Appels *et al.*, 2008).



Figure 3.3: Subsequent steps in the anaerobic digestion process (Appels et al., 2008)

The complex organic matter (insoluble organics and high molecular weight compounds, i.e. proteins, lipids and carbohydrates), undergoes hydrolysis, to form simpler soluble organic compounds (amino acids, fatty acids, peptides and sugars) (Salminen & Rintala, 2002; Mutombo, 2004; Appels *et al.*, 2008). The soluble organic compounds are fermented to volatile fatty acids (VFA) by the acidogens in acidogenesis (Salminen & Rintala, 2002; Mutombo, 2004; Appels *et al.*, 2008). The higher organic acids and alcohols are subsequently converted to acetic acid and hydrogen gas by the acetogens (Salminen & Rintala, 2002; Mutombo, 2004; Appels *et al.*, 2008). Lastly the hydrogen and acetic acid is converted to methane and carbon dioxide by the methanogens (Salminen & Rintala, 2002; Mutombo, 2004; Appels *et al.*, 2008).

The three most commonly used anaerobic reactors are the Upflow Anaerobic Sludge Bed reactor (UASB), Expanded Granular Sludge Bed reactor (EGSB) and the Internal Circulation reactor (IC) (refer to Figure 3.4). The UASB reactor is used when a high OLR is applied (Driessen & Vereijken, 2003). Two key aspects of a UASB are granule formation (1 to 4 mm diameter) and the requirements for a 3-phase gas separator at the top of the system

(Figure 3.4 A) which retains the sludge and removes gas formed in the system (Driessen & Vereijken, 2003; Mutombo, 2004). The UASB achieves a high organic loading rate (OLR) by feeding wastewater from the base with the wastewater passing through suspended sludge/granular blanket allowing for maximum biomass/substrate contact (Mutombo, 2004).

The EGSB can be described as a modification of the UASB (Driessen & Vereijken, 2003; Mutombo, 2004; Yejian *et al.*, 2008) with much the same components (Figure 3.4 B), however, in the EGSB internal recirculation is applied to the effluent and this causes the sludge bed to be more fluidized than UASB sludge beds. The higher upflow velocity accompanied by the internal recycle provides greater contact time with the sludge bed and allows for a higher OLR (Driessen & Vereijken, 2003; Mutombo, 2004).



Figure 3.4: Schematic diagram of (A) Upflow Anaerobic Sludge Bed, (B) Expanded Granular Sludge Bed and (C) Internal Circulation reactors

The IC reactor design comprises two UASB reactors operated vertically in-series and the UASB uses a single-phase separator positioned at the top of the reactor, whereas the IC uses two-phase separators (Figure 3.4 C). In the IC reactor, the lower UASB has high mixing driven by its own gas production and product recycle, the second UASB turbulence is significantly reduced due to the first phase separator and allows the second separator to separate the anaerobic sludge from the wastewater (Driessen & Vereijken, 2003).

## 3.2.4 PAPER AND PULP EFFLUENT AND MBRs

The extent of the research done on the application of MBRs for the treatment of paper mill effluent is not extensive. The reason for this is attributed to the typical characteristics of paper mill effluent. Due to the high TSS and low nutrient levels, the paper industry is in need of further

research into the use of MBRs for the treatment of their specific effluent (Whyte & Swartz, 1997; Pokhrel & Viraraghavan, 2004; Lerner *et al.*, 2007). The research that has been done gives great insight into the challenges faced and possible successes that can be achieved with MBRs when used in the paper and pulp industry (Table 3.6). However, extensive research has been done in the application of different biological treatment options for the treatment of paper mill effluent (Steffen *et al.*, 1990; Whyte & Swartz, 1997; Mahmoud *et al.*, 2003; Bajpai, 2000; Christopher, 2007; Lerner *et al.*, 2007; Ali *et al.*, 2009).

Set-up	Scale of plant	Effluent	Effluent pre- treatment	Permeate Flux (L/(m2.h)	% COD removal	% TSS removal	% Conductivity removal	Reference
Submerged UF-MBR (Anoxic and 2 Aerobic stages) with RO system	Pilot (48 m <sup>3</sup> /day)	Black Liquor, paper bleaching and white water	Sedimentation tank	15	92	99	16	Zang et al., 2008
Submerged UF-MBR (membranes submerged in single aerobic tank)	Pilot	Paper mill effluent	None	10-60	95	34	36	Kay <i>et al.</i> , 2004
Submerged MBR with NF polishing stage/RO polishing stage	Laboratory	Thermochemical Pulp plant effluent	Flotation and 100 µm screen	N/A				Mantarri <i>et</i> <i>al.</i> , 2006
Submerged microfiltration (MF)-MBR with anaerobic and aerobic stages and a RO polishing stage	Laboratory	High cellulose waste water	None	2-40	43-99			You <i>et al.,</i> 2009

## Table 3.6: Application of MBRs in the treatment of paper and pulp effluent

# **CHAPTER 4**

## 4. TEXTILE EFFLUENT TREATMENT

The textile industry not only utilises large quantities of water, but produces highly coloured wastewaters, polluted with dyes, textile auxiliaries and other chemicals, that are generally toxic and resistant to biological treatment methods (Ledakowicz *et al.*, 2001; Barclay and Buckley, 2002; Chakraborty *et al.*, 2003; Badani *et al.*, 2005; Brik *et al.*, 2006; El-Gohary and Tawfik, 2009). Textile wastewater is characterised by significant fluctuations in the COD and BOD concentrations, pH, colour and salinity (Dos Santos *et al.*, 2007), due to the composition of the dye effluent varying with the textile produced (O'Neill *et al.*, 1999). The release of textile wastewater into the environment is undesirable since the dyes and their breakdown products affect the aesthetics of aquatic environments due to highly visible colour; have an acute and/or chronic effect on the organisms exposed to them depending on the length of exposure; interferes with the growth of bacteria that degrade water impurities due to the dyes adsorbing and reflecting the sunlight entering the water, which affects the transparency and gas solubility in water bodies; and are also toxic and mutagenic or carcinogenic to life (Slokar and Le Marechal, 1998; Dos Santos *et al.*, 2007; Firmino *et al.*, 2010).

## 4.1 TEXTILE PROCESSING PLANT

A textile company located in Bellville in the Western Cape was approached as a potential industrial partner on 26-06-2009 with a proposal to enter into a joint piloting evaluation of an MBR effluent treatment system. This textile company is an international clothing and lifestyle brand and legwear market leader. Headquartered in Germany, this textile group produces men's, ladies, and children's knitted socks, ladies fully fashioned stockings, tights and bodies, menswear and other textile products, which are exported to more than 30 countries. The company has 16 factories worldwide, achieved an annual turnover in 2008 of €195.5 million, and employs over 2,600 people worldwide.

The purpose of the piloting evaluation was to optimize the effective and efficient on-site treatment of the industrial partner's trade effluent and, in conjunction with the industrial partner, propose and design a full-scale MBR plant to provide a complete solution to meet their current and future water needs.

On 28 September 2009, a Technical Proposal was presented to their Senior and Middle management outlining a Technical Feasibility Assessment (TFA) for the proposed installation of the MBR wastewater treatment pilot plant and water recovery process in Bellville, Cape Town. The assessment followed a detailed sampling schedule which was initiated on the 17<sup>th</sup> July 2009 consisting of weekly effluent grab sampling and associated chemical and physical analyses. This data as well as several issues and concerns identified during this process were used to design the pilot plant and enable a preliminary design and cost analysis proposal of the full-scale treatment plant to be compiled. This was presented as part of a Technical Proposal presentation.

# 4.1.1 MOTIVATION FOR WASTEWATER TREATMENT AND WATER RECOVERY AT THE TEXTILE COMPANY

Wastewater is generated at the textile factory from water used in dyehouse processes, washing and drying of material, machine cleaning, and rain and wash water runoff from process areas. This wastewater is currently channelled to a primary effluent settling tank where it is transferred via gravity separation into an overflow sump before discharge into the municipal sewer line.

Their motivation for entering into the proposed evaluation of the pilot treatment process was based on the following:

- They are willing to explore opportunities to decrease annual operating expenditure by lowering effluent discharge tariffs and potable water intake costs through process wastewater treatment and recycle potentially aiming to achieve a status of Zero Liquid Discharge (ZLD).
- Being part of a large international group, they are committed to continually improving environmental performance in line with international best practice.
- The WRC-funded piloting project is a low-risk point-of-entry into the on-site wastewater treatment market for them.

The purpose of this section is to provide a: (1) detailed account of the client's requirements for this project; (2) detailed technical description of the activities involved; and (3) an overview of the technology offering considered for the proposed project.

# 4.2 DESCRIPTION OF THE CURRENT WATER AND WASTEWATER SITUATION AT THE TEXTILE PROCESSING PLANT

## 4.2.1 ECONOMIC FRAMEWORK AND MUNICIPAL WATER CHARGES

Currently the textile processing plant consumes an average of 2,500 kL/month of potable water and discharges approximately 95% of this as effluent to the municipal sewer. Between August and June 2009, their water consumption increased by 10%. Both municipal effluent discharge tariffs and potable water charges increased, between September 2008 and April 2011, by 7% (from R5.99/kL to R7.63/kL) and 10% (from R7.59/kL to R9.93/kL), respectively (South Africa, 2011). This translated into an overall cost-to-company increase in total water charges of 31% between May-2009 and April-2011. If these consumption and economic trends remain consistent on an annual basis, without wastewater treatment and recycle, the textile company's water consumption and effluent discharge will cost R4.79 million over the next 54-months.

Additionally, with the proposed advent of the WDCS by the DWEA and its expected rollout to municipalities, both municipalities and industries will be increasingly pressurized to seek innovative ways to deal with industrial wastewater at source rather than the current practice which is end-of-pipe, i.e. at wastewater treatment works (Mazema *et al.*, 2009; South Africa, 2003). The most likely pressurizing mechanism will be increasing water costs meaning annual rate increases in excess of 7% and 10% for effluent discharge and potable water consumption respectively (Mazema *et al.*, 2009; South Africa, 2003). The WDCS will also provide incentives to companies that move towards the efficient use of water and who implement water recycle systems. The aim of the WDCS is not only to financially pressurize companies into being environmentally conscious, but also to provide social protection to users of the natural water sources (Mazema *et al.*, 2009; South Africa, 2003).

#### 4.2.2 DESCRIPTION OF THE WASTEWATER STREAM COMPOSITION

The textile processing plant currently discharges a single combined waste stream generated by various processes in its textile processing train. The combined process streams were characterised by an average COD 1,260 mg/L and an average BOD of 195 mg/L. The effluent stream is alkaline with an average pH of 10.5 requiring neutralization to facilitate biological reduction of the COD concentration to acceptable levels. As is typical of textile industry effluents, the processing plant's effluent stream is also characterized by high conductivity and TDS concentration. A full compositional analysis of the effluent stream is given in Table 4.1.

		Feed Water Quality – Tex	tile Company 1	
		Company 1	<b>SANS 241</b>	<b>SANS 241</b>
		AVG (min-max)	Class I	Class II
нα	pH units	<b>10.1</b> (7.4-11.5)	5-9.5	4.0-10
Temperature	°C	32.4	not indicated	not indicated
Conductivity	uS/cm	<b>2,792</b> (471-10, 513)	<1.500	1.500-3700
TDS	ma/L	1,039	<1.00	1.000-2.400
Turbidity	NTU	<b>45</b> (17-116)	<1	1.0-5.0
COD	mg/L	<b>1,264</b> (45-2,820)	not indicated	not indicated
BOD	mg/L	192.5	not indicated	not indicated
TSS	mg/L	<b>19</b> (4-51)	not indicated	not indicated
NH4-N	mg/L	<b>10</b> (4-42)	<1.0	1.0-2.0
NO3-N	mg/L	6.24	<10	10-20
Na	mg/L	189	<200	200-400
к	mg/L	19	<50	50-100
Са	mg/L	10	<150	150-300
Mg	mg/L	3.4	<70	70-100
Fe	mg/L	0.14	<0.2	0.2-2
CI	mg/L	147	<200	200-600
CO <sub>3</sub>	mg/L	0	not indicated	not indicated
HCO <sub>3</sub>	mg/L	188	not indicated	not indicated
SO <sub>4</sub>	mg/L	87	<400 (200)	400-600
В	mg/L	0	not indicated	not indicated
Mn	mg/L	0.03	<0.1	0.1-1
Cu	mg/L	0.02	<1	1.0-2.0
Zn	mg/L	0.05	<5	5.0-10
Р	mg/L	7.97	not indicated	not indicated
F	mg/L	1.1	<1.0	<5.0-1.5
COD/BOD	-	2.96	not indicated	not indicated
BOD/COD	-	0.34	not indicated	not indicated

**Table 4.1:** Effluent water quality and composition of Textile processing plant stream compared with South

 African National Standard (SANS) 241 Class I & II drinking water quality standards.

Bold values: Key parameters used in design phase

#### 4.2.3 AVAILABILITY OF HISTORICAL EFFLUENT QUALITY DATA

No analytical laboratory facilities were available on-site to analyse the wastewater and the municipal sewerage charges are currently based on volume. Therefore, no historical effluent quality analysis data was available. To design all wastewater treatment processes, but especially those aimed at industrial trade effluents, an historical effluent compositional trend analysis is necessary. This facilitated identification of effluent composition variability and pollutant or chemical spikes and peaks that may deleteriously impact on the primary biological treatment phase or the secondary physical filtration processes of an MBR effluent treatment design.

An historical effluent compositional trend analysis is shown in Figure 4.1. Key effluent physicochemical parameters were measured on a weekly basis to determine the variability of the effluent composition. These parameters were integral to many aspects of the overall MBR design including headworks requirements, membrane choice, and process control and configuration.

#### 4.2.4 DYE COMPOSITION

This textile company uses a variety of different dye compounds during the production finishing processes including mono-azo, vinylsulphone, and anthraquinone-based dyes etc. Both the different chemical structures and the requirements to accommodate potential future use of different dye vendors or types were incorporated into the overall process design. These design criteria and considerations are detailed in Section 4.3.



Figure 4.1: Textile effluent composition trend analysis: (A) COD and ammonia; (B) conductivity and TDS; (C) pH and temperature; (D) TSS and turbidity

## 4.3 DESCRIPTION OF THE PROPOSED TECHNICAL SOLUTION

The proposed MBR wastewater treatment plant entailed the introduction of an equalization and neutralization facility as part of the existing effluent settling tank and overflow sump and provision of the dsMBR biological treatment process coupled with a downstream NF and reverse RO post-treatment polishing facility.

This section of the technical report provides an overview of the treatment technology offered as a solution to the effluent treatment and water recycle requirements of the textile company. The proposed treatment solution involves a two-step membrane filtration of the feed stream involving a primary biological treatment of the effluent using the dsMBR coupled with a tertiary NF/RO treatment process.

The proposed overall treatment process was based on the use of membrane filtration processes to accomplish the water recovery and waste stream volume reduction objectives of the project. Substantial pre-treatment systems have been included to provide suitable feed water to the NF/RO process and post-treatment chemical addition will be considered if it is necessary to condition the product water to meet compatibility and internal regulatory objectives for recycle into the dye house train.

A process flow schematic that illustrates the relationship between the existing headworks and proposed MBR and NF/RO treatment process components is shown in Figure 4.2.



Figure 4.2: Process flow schematic for the MBR wastewater treatment plant

A simplified process flow diagram of the proposed dsMBR compared with a traditional UCTconfigured biological nutrient removal (BNR) CAS system is shown in Figure 4.3. The layout of the MBR biological treatment aeration section relative to the primary anaerobic effluent inlet section, where phosphate removal and azo dye reduction processes dominate prior to the anoxic tank where denitrification occurred is indicated. Recycle of the mixed liquor containing the wastewater and microorganisms was facilitated by Norit Airlift<sup>™</sup> UF modules, which allowed treated and filtered UF product water to feed the polishing component of the final treatment process prior to water reuse and transfer of acclimated microbial consortia to the aerobic and anoxic tanks. Piping and instrumentation diagram (P&ID) process flow design drawings are included as Annexures detailing the MBR components, pumping systems, programmable logic controller (PLC), biological process etc. The headworks, equalisation and neutralization P&ID's are detailed in **Annexure A1**. The MBR, nitrification, and denitrification P&IDs are detailed in **Annexure A2**. The P&ID for the MBR modules, cleaning-in-place (CIP), and backflush is detailed in **Annexure A3**.



Figure 4.3: (A) UCT conventional activated sludge system and; (B) dsMBR process flow diagrams

## 4.3.1 EXISTING HEADWORKS

The existing headworks infrastructure consisted of a concrete outfall channel leading from the dye house into a settling tank connected to an overflow sump that emptied directly into the municipal sewer line. The overflow sump served as the feed stream source for the proposed treatment plant. A 1 mm screened inlet submerged pump was installed in the overflow sump just below the municipal overflow exit pipe.

## 4.3.2 FLOW EQUALISATION AND NEUTRALISATION VESSEL

An equalisation tank was installed to take feed from the screened inlet submerged pump in the overflow sump. The purpose of the equalisation tank was to eliminate contaminant spikes by providing sufficient residence time on the feed to the MBR via the neutralization tank. A submerged recirculation pump was provided to enable mixing of the tank and avoid stratification. The tank was connected to the existing headworks and the proposed treatment process with the installation of associated piping, instrumentation, electrics and civils where necessary. In addition, whilst biological processes such as the MBR operate optimally at near-neutral pH values, the effluent is alkaline with an average pH of 10.1. Therefore, the incorporation of acid dosing pumps with an integrated pH monitoring probe was used to facilitate the tank feed being neutralised prior to being fed to the MBR anaerobic tank.

## 4.3.3 MEMBRANE BIOREACTOR AND NORIT AIRLIFT™ ULTRAFILTRATION SYSTEM

MBRs are an advanced wastewater treatment process that combines an activated sludge biological oxidation process with membrane filtration. The process of combining wastewater and biological microorganisms coupled to a membrane filtration component produces an extremely high quality effluent suitable for reuse or discharge. This MBR design used energy efficient, airlift-assisted tubular membranes from Norit X-Flow (Figure 4.4). The membrane system was located outside the biological reactor enabling installation at the most convenient and accessible location at the plant site (refer to **Annexure A4** and **A5**). Unlike MBR technology offerings from Zenon, Kubota, and Koch, no membrane system components are submerged in the biological mixed liquor, which permitted independent operation and optimization of the biological and membrane systems. In addition, unlike submerged product offerings, Norit Airlift<sup>™</sup> modules facilitated the dsMBR operating process strategy.



Figure 4.4: Norit Airlift<sup>™</sup> MBR systems

The membrane system was independently optimised to provide the best performance for the specific application whilst the biological process was based on a long sludge age design, which provided excellent BOD removal and nitrification. Anoxic and anaerobic zones integrated within this process design enhanced phosphate removal, denitrification, and dye degradation. Increased mixed liquor concentrations mean more biological treatment capacity within the same footprint. Long sludge age treatment resulted in less waste sludge production, excellent process stability, low membrane fouling and lower overall operating costs. The MBR received feed from the existing settling tank and overflow sump via the 10 m<sup>3</sup> equalization/neutralization tank.

#### 4.3.4 NANOFILTRATION / REVERSE OSMOSIS (NF/RO) TERTIARY TREATMENT

To investigate the potential to reuse the treated UF-MBR permeate as feedwater for the dye house, a NF/RO treatment system was installed downstream of the UF-MBR step. The purpose of the piloting study was to investigate the possibility of residual dye removal with a NF/RO system instead of a granular activated carbon (GAC) system. The resulting permeate was evaluated and the system assessed to investigate the viability of utilizing the tertiary polishing stage product water for reuse in the dye house.

## 4.3.4.1 ALTERNATIVE POLISHING METHOD CONSIDERED

Forward osmosis (FO) is a concentration driven membrane process, utilising the osmotic pressure difference across a selectively permeable membrane as the driving force (Wang *et al.*, 2010). In RO the driving force which facilitates mass transport through the membrane is the applied pressure (Cath *et al.*, 2006). FO has applications in the separation processes for wastewater treatment, food processing and desalination (Cath *et al.*, 2006); and has been used at bench-scale to treat industrial wastewater (Cath *et al.*, 2006; Wang *et al.*, 2010), to treat liquid foods in the food industry; and to concentrate landfill leachate at pilot-scale. Research is currently occurring using FO to reclaim wastewater for potable re-use, desalinating seawater and for purifying water (Cath *et al.*, 2006; Wang *et al.*, 2010) in emergency relief situations (Cath *et al.*, 2006). Other unique research with regards to FO includes pressure-retarded osmosis for the generation of electricity from salt and fresh water (Cath *et al.*, 2006).

Advantages of FO include: 1) operating at low or no hydraulic pressures; 2) high rejection of a wide range of contaminants; 3) it may have a lower membrane fouling than pressure driven processes (Cath *et al.*, 2006); Wang *et al.*, 2010). However, a number of technical barriers exist that prevent the use of FO in industrial applications, including: 1) the lack of an optimised membrane capable of producing a high flux comparable to commercial RO membranes (Wang *et al.*, 2010); and 2) the lack of robust membranes and membrane modules for FO (Cath *et al.*, 2006).

## 4.3.5 MBR PROCESS CONTROL AND SYSTEM DESIGN

#### 4.3.5.1 ANAEROBIC AND AEROBIC TREATMENT REQUIREMENTS

Although resistant to aerobic degradation processes, the azo chromophore linkage can readily be reduced under anaerobic conditions producing aromatic amines that are susceptible to aerobic degradation and autoxidation (see Figure 3.2). In addition. the carbon:nitrogen:phosphate (C:N:P) ratio for the influent was determined to be 100:1.75:1.4, significantly lower in terms of nitrogen requirements for these systems where ratios of between 100:5:1 and 100:20:1 are necessary for optimal biological maintenance and growth (Russell, 2006). Thus additional nitrogen in the form of urea (1.7 molar) and phosphorus in the form of phosphoric acid (0.5 molar) was added to the inlet of the MBR train. The design of the MBR process therefore had to take into account nitrification and denitrification as well as phosphate removal in order to lower the overall pollutant load of the wastewater before recycle using RO.

## 4.3.5.2 EBPR AND PRE-DENITRIFICATION PROCESS DESIGN

The dsMBR was therefore designed to facilitate the reductive cleavage of the azo bond at the MBR train inlet along with EBPR. The nitrogen and resultant aromatic amines were then transferred via the anoxic tank to the aerobic tank, where oxidation and mineralization of the aromatic amines was facilitated, before being recycled back into the anoxic environment where denitrification of the nitrates occurred. The process is schematically represented in Figure 4.5, with the recycle and HRT operating modes indicated in Table 4.2. The HRT refers to the measure of the average length of time that a soluble compound remains in a reactor (Ryan, 2007) and is calculated by dividing the volumetric flow rate (L/hr) entering a tank by the volume (L) of that particular tank (Ryan, 2007).



**Figure 4.5:** EPBR and pre-denitrification configurations adapted to dsMBR for azo dye-containing textile effluent treatment

Parameter	Recycle	Recycle	Recycle	Recycle	Recycle	Recycle
	mode 1	mode 2	mode 3	mode 4	mode 5	mode 6
Membrane area (m²)	10.2	10.2	10.2	10.2	10.2	10.2
J (flux (L/m²/h)	18	20	25	30	35	40
Volumetric flux (L/h)	4,405	4,895	6,120	7,344	8,568	9,792
Influent flow rate Q (L/d)	4,405	4,895	6,120	7,344	8,568	9,792
COD (mg/L)	570	570	570	570	570	570
Organic loading rate (kg COD/m <sup>3</sup> /day)	0.57	0.57	0.57	0.57	0.57	0.57
Loading rate (kg COD/day)	2.51	2.79	3.49	4.19	4.88	5.58
NH4 mg/L (average)	10	10	10	10	10	10
PO4 mg/L (average)	8	8	8	8	8	8
C:N:P (additional N required)	100:1.75:1.4	100:1.75:1.4	100:1.75:1.4	100:1.75:1.4	100:1.75:1.4	100:1.75:1.4
Volume Anaerobic Tank (L)	1,000	1,000	1,000	1,000	1,000	1,000
HRT (h) An	5.45	4.9	3.92	3.27	2.8	2.45
Voluem Anoxic tank (L)	1,500	1,500	1,500	1,500	1,500	1,500
HRT (h) Ax	8.17	7.35	5.88	4.9	4.2	3.68
Volume Aerobic tank (L)	1,500	1,500	1,500	1,500	1,500	1,500
HRT (h) Ae	8.17	7.35	5.88	4.9	4.2	3.68
HRT (h) (total)	21.86	19.67	15.72	13.1	11.22	9.82
AX/AN ratio (%)	100	100	100	100	100	100
AE/AX ratio (%)	100	150	200	250	300	400
MBR/AE ratio	500	500	500	500	500	500

Table 4.2 HRT and recycle operating modes at flux rates of 18-40 L.m<sup>-2</sup>.hr<sup>-1</sup>.

#### 4.3.5.3 MATERIALS AND METHODS

A pilot-scale MBR using two 5.1 m<sup>2</sup> Norit Airlift<sup>™</sup> membrane modules, as shown in Figure 4.6, was designed, constructed, commissioned and operated on site from March to December 2010. The anaerobic and aerobic tanks were inoculated with 9,000 mg/L mixed liquor volatile suspended solids (MLVSS) activated sludge obtained from the Bellville municipal wastewater treatment works. The system was robust and non-sterile with the sole purpose of the anaerobic tank the cleavage of the azo bonds. Denitrification occurred within the anoxic tank, while nitrification and mineralisation of the aromatic amines occurred within in the aerobic tank. The pilot plant was operated at ambient temperature with an adjusted C:N:P ratio of 100:10:1 (Russell, 2006), which was achieved by dosing the system with urea. The pH of the textile effluent was adjusted to ~7 before entering the treatment system using phosphoric acid. Depending on the flow rate of the permeate exiting the UF membranes the system was operated in 1 of 6 recycle modes (Table 4.2).

The effluent was pumped from the sump to the 10,000 L equalisation tank where treatment started. The equalisation tank was a buffer tank; therefore the colour of the effluent in the sump was not the same as the colour of the effluent stored in the equalisation tank. After the UF-MBR secondary treatment it was observed that there was still residual colour in the UF permeate. The tertiary polishing phase was to treat the permeate from the UF-MBR modules using NF/RO to remove residual colour present in the UF-permeate and facilitate desalination allowing re-use of the water.



Figure 4.6: Schematic diagram of the pilot plant located at the textile company

Flow rates for each tank were measured three times daily. Grab samples collected from the effluent, anaerobic-, anoxic-, aerobic-tanks and UF permeate, were analysed daily for pH,

conductivity and TDS and every second day for turbidity, COD, ammonium (NH<sub>4</sub>), nitrate (NO<sub>3</sub>), TSS and phosphate (PO<sub>4</sub>).

## 4.3.5.4 SUBSEQUENT NF/RO TREATMENT

Subsequent to the UF-MBR treatment the permeate still contained residual dye (colour) and salt. The removal of the residual dye and salt was imperative for successful reclamation of the effluent for re-use in dyeing processes. The UF-MBR permeate was therefore treated in a pilot-scale NF/RO system, as shown in Figure 4.7.



Figure 4.7: Pilot scale NF/RO system

Table 4.3: NF/RC	membrane specifications
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Membrane type	Model	Active area (m²)	Permeate flow rate (m <sup>3</sup> /d)	Maximum pressure drop (bar)	% MgSO₄ rejection
NF	DK2540	2.51	2.27	0.6	98
RO	DK2540	2.80	2.6	1.0	99.4

The NF process (refer to Table 4.3 for membrane specifications) was operated at a feed pressure of 13 bar, 0.609 bar differential pressure and a cross flow velocity of 950 L/hr. Although the NF process facilitated complete residual colour removal, conductivity and TDS reduction was nominal as expected (Table 4.6 and Figure 4.14C); the NF module was then replaced with an RO membrane (specifications indicated in Table 4.3) and operated with a feed pressure of 10 bar, 0.609 bar differential pressure and a cross flow velocity of 900 L/hr.

## 4.3.5.5 ULTRAFILTRATION (UF) MBR DESIGN

A photographic progress timeline during the manufacture and commissioning of the dsMBR is shown in Figures 4.8 to 4.12. The following photos depict the manufacture and commissioning progress during completion of the Norit Airlift<sup>™</sup> MBR pilot plant and the layout of the proposed plant relative to the effluent discharge sump on site.



**Figure 4.8:** (A) EPBR and pre-denitrification MBR configuration: 1. Equalisation; 2. anaerobic; 3. anoxic; 4. aerobic. (B) Reticulation to the sump and MBR UF unit; sump distance 50 m; MBR unit distance 36 m



**Figure 4.9** (A) Reticulation for 10,000 L equalization tank. (B) Recycle configuration between anaerobic and anoxic tanks.



**Figure 4.10** Aerobic tank reticulation entry point into dye house (the CAS tank system was located outside, whilst the UF-MBR unit is located within the dye house building.



**Figure 4.11:** (A) Reticulation entry point into sump and municipal drain (overflow design); (B) aerobic tank reticulation entry point into dye house – the MBR unit was connected to these pipes.



**Figure 4.12:** MBR pilot plant ultrafiltration unit indicating Norit X-Flow Airlift<sup>™</sup> pilot modules relative to pumps and pre-filter.

#### 4.3.5.6 ANALYTICAL METHODS

Representative samples of each biological treatment stage were analysed for colour via the spectrophotometric and American Dye Manufacturing Index (ADMI) tristimulus methods, as well as the colour Hazen method. Spectrophotometric analysis was utilised to quantify the colour of the combination of residual dyes remaining in the discharged effluent. There are a number of sub divisions for the ADMI tristimulus filter method used for the analysis of true colour in coloured aqueous effluents, namely: (1) the weighted ordinate method; (2) the 10 ordinate method; (3) the 4/6 wavelength method; and (4) the 3/31 wavelength method.

For this study the 10 ordinate method was used for determination of ADMI true colour values. The samples were filtered in order to remove excess quantities of suspended solids using a glass gooch filtering crucible, fitted to a flask connected to a vacuum pump. Glass fibre filter paper was used as the filtration medium since polymer membranes absorb the dye. Once filtered, the sample was analysed using a Cary 300 Bio UV/VIS spectrophotometer.

The photometric scan was used to determine the absorbance of each sample, at 10 different predetermined wavelengths (indicated in Table 4.4) for the columns X, Y and Z. From the absorbance values obtained the % transmittance, Adams Nickerson colour difference (DE) and ADMI were calculated.

Wavelength No.	X	Y	Z
1	435.5	498.5	422.2
2	461.2	515.2	432.0
3	544.3	529.8	438.6
4	564.1	541.4	444.4
5	577.4	551.8	450.1
6	588.7	561.9	455.9
7	599.6	572.5	462.0
8	610.9	584.8	468.7
9	624.2	600.8	468.7
10	645.9	627.3	495.2

Table 4.4: Selected ordinates for spectrophotometric colour determinations (Greenberg et al., 1985).

For the colour Hazen method the representative samples from the respective treatment phases were first filtered through a 0.22  $\mu$ m syringe filter, before using a NOVA 60 Spectroquant to read

the true colour of the samples. All true colour readings were measured using a 10 mm quartz cuvette.

## 4.4 RESULTS AND DISCUSSION

## 4.4.1 UF-MBR PERMEATE AND WATER DISCHARGE STANDARDS

As seen in Figure 4.13 the amount of COD removed from the textile effluent remained relatively stable after the system had operated for ~100 days. The minimum amount of COD removed was 19% and the maximum 97%, with an average of 75% (indicated in Table 4.4). When compared to the South African (SA) government discharge standard for COD (≤5000 mg/L), the COD value for the treated textile effluent (20 mg/L) was well within this standard.



Figure 4.13: Chemical Oxygen Demand removal.

As indicated in Table 4.5 negative percentage removal values were obtained for  $NH_4$  (-181.1%) and  $NO_3$  (-6.7%). This was due to incorrect dosing with urea, which influenced the C:N:P ratio and had a negative effect on the denitrification and nitrification processes occurring in the anoxic and aerobic tanks, respectively. Correcting the C:N:P ratio, improved denitrification, which in turn caused the percentage removal to increase. The percentage removal for conductivity (-66.7%) and TDS (-85.4%) showed negative values (refer to Table 4.5) after treatment with UF. These negative values occurred due to the addition of urea, phosphoric

Table 4.5: Average water quality during the different treatment stages compared to the SA water discharge standards.	
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Parameter	Units	Process plant effluent fed into the pilot plant	Anaerobic tank	Anoxic tank	Aerobic tank	UF-MBR Permeate	CCT Water discharge standards*
Temperature	D <sub>0</sub>	22.8	21.7	21.3	21.5	22.2	0-40
Hd		9.8	7.9	8.0	8.2	8.4	5.5-12
Conductivity	µS/cm	2715.8	3778.9	4520.9	4786.7	4527.9	≤5000
TDS	mqq	1972.7	3911.8	3625.8	3612.0	3656.7	4004.6
COD	mg/L	763.4	766.8	792.8	901.2	190.8	≤5000
Ammonium	mg/L	0.0	21.5	28.0	31.0	25.3	Not indicated
TSS	mg/L	54.9	82.8	259.8	1382.2	45.3	1000.0
Turbidity	NTU	45.1	87.8	203.0	333.8	2.7	Not indicated
Phosphate	mg/L	1.5	1.8	1.6	1.4	1.3	25.0
Nitrate	mg/L	3.0	3.0	3.9	3.9	3.2	Not indicated
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\*City of Cape Town: Wastewater and industrial effluent by-law (2006)

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Table 4.6: Average water quality of the permeate during the different treatment stages (and percentage removal) compared to the CCT water discharge standards

Parameter	Units	Process plant effluent fed into the pilot plant	UF-MBR Permeate	% Removal	Average effluent while NF/RO system was running	NF Permeate (NF membrane)	% Removal (NF membrane)	RO Permeate (RO membrane)	% Removal	CCT Water discharge standards*
Temperature	D <sub>0</sub>	22.8	22.2	N/A	23.6	22.6	N/A	24.7	N/A	0-40
Hd	I	9.8	8.4	N/A	9.7	9.2	N/A 20.4	9.3	N/A	5.5-12
Conductivity	µS/cm	2715.8	4527.9		1583	6077.3	Removal by NF only)	693	48.3	≤5000
TDS	mqq	1972.7	3656.7	·	1119	4076.8	, 82.3 (Removal by NF only)	473	51.9	4004.6
COD	mg/L	763.4	190.8	75.0	802	113.3	85.7	81.6	90.3	≤5000
Ammonium	mg/L	9.0	25.3		11	7.8	22.5	10.6	18.6	Not indicated
TSS	mg/L	54.9	45.3	20	30	4.5	82.4	1.7	94.9	1000.0
Turbidity	NTU	45.1	2.7	94.0	22.9	0.1	9.66	0.4	98.1	Not indicated
Phosphate	mg/L	1.5	1.3	15	0.9	0.4	70	1.6		25.0
Nitrate	mg/L	3.0	3.2		1.8	2.4		1.7	8.0	Not indicated
*City of	Cape Town	i: Wastewater and ir	ndustrial efflue	int by-law (2006)						

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acid and the retentate being recycled to the aerobic and anoxic tanks, which caused increased TDS values and therefore increased conductivity.

However, the percentage removal became positive once the UF-MBR permeate was treated with RO during the second phase of treatment due to the decrease in pore size from UF (0.2 to 0.02  $\mu$ m) and RO (<0.002  $\mu$ m) (Wagner, 2001). Subsequent treatment with RO removed any salts remaining in the UF-MBR permeate (indicated in Table 4.5) and the percentage conductivity and TDS rejection increased to an average of 48.3% and 51.9%, respectively (refer to Table 4.6). The average reduction in turbidity and TSS was 94% and 20% (refer to Table 4.5), respectively during the UF-MBR stage of the system. These percentage reductions increased to 98.1% and 94.9%, respectively after treatment with RO.

Following further treatment with the RO system (second phase) all measured parameters were below or close to the values obtained for the potable water (refer to Table 4.6) utilised by the textile company.

The conductivity and TDS values for both the holding tank and brine were higher than the UF-MBR permeate entering the NF/RO system, seen in Figures 4.14A and B. This is due to the concentrate (i.e. brine) that was removed by the NF or RO membrane being recycled to the holding tank. The brine being recycled to the holding tank, therefore contains a high concentration of removed salts and chemicals resulting in the holding tank and brine having the almost the same concentration of salts and chemicals.

As seen in Figure 4.14C the maximum percentage conductivity and TDS rejection with the NF membrane was 54% and 53%, respectively. The minimum rejection rate was 33% for both conductivity and TDS. The average rejection rate for conductivity and TDS for the NF membrane for the 4 days that it was in use was 43% and 40%, respectively. The maximum percentage conductivity and TDS rejection with the RO membrane was 98.3% and 98.3%, respectively. The minimum rejection rate was 82% for both conductivity and TDS. The average rejection rate for both conductivity and TDS for the RO membrane was 94.2%. It can be concluded from Figures 4.12A and B and from the percentage rejection that higher salt removal was achieved with the RO membrane than the NF membrane.


**Figure 4.14:** (A) Trend of TDS through the NF/RO system; (B) Trend of TDS through the NF/RO system; and (C) Trend of percentage conductivity and TDS removal in the NF/RO system

#### 4.4.2 COLOUR REMOVAL

The effluent discharged into the sump was continually changing depending on the process being utilised by the dye house of the textile company. The average sump effluent composition is indicated in Table 4.8. The discharged effluent varies from "light" to "medium" to "dark" in colour due to the erratic trends in dye consumption, which is mainly dependent on trends in the supply and demand of the textile fabric. The colour of the effluent being fed from the equalisation tank to the anaerobic tank via gravity was classified based on ADMI values (refer to Table 4.7). Effluent fed to the anaerobic tank with an ADMI value below 500 ADMI units (<500) was classified as light in colour, 500 to 1500 ADMI units (500-1500) was classified as medium in colour and above 1500 ADMI units (>1500) was classified as dark in colour. The ADMI of 5 sample sets (i.e. anaerobic feed, anaerobic tank, anoxic tank, aerobic tank, UF-MBR permeate and RO permeate), taking the HRT into consideration (refer to Table 4.8), was determined. No RO sample was taken for the HRT1 set of samples, since the NF/RO system was not installed and operating when the HRT1 samples were collected.

Samples	ADMI of anaerobic feed (ADMI units)	Colour classification
HRT1	1027.2	Medium colour
HRT2	1649.3	Dark colour
HRT3	1829.4	Dark colour
HRT4	2388.2	Dark colour
HRT5	289.9	Light colour

 Table 4.7: Colour classification based on the ADMI values of the effluent fed from the equalisation tank to the aerobic tank

Table	4.8:	Hydraulic	retention	time	of	the	5	sample	sets	in	the	different	biological	treatment
stages														

Treatment stage	HRT1 (hr)	HRT2 (hr)	HRT3 (hr)	HRT4 (hr)	HRT5 (hr)
Anaerobic tank	10	10	10	10	10
Anoxic tank	19.23	19.23	17.86	18.52	14.71
Aerobic tank	15.71	5.86	13.71	12.35	8.51





**Figure 4.15:** ADMI and colour Hazen values for : (A) HRT1 (medium colour); (B) HRT2 (dark colour); (C) HRT3 (dark colour); (D) HRT4 (dark colour) and (E) HRT5 (light colour)

**Table 4.9:** ADMI values for the respective treatment stages of: (A) HRT1 (medium colour); (B)HRT2 (dark colour); (C) HRT3 (dark colour); (D) HRT4 (dark colour); and (E) HRT5 (light colour)

Α	Operating tank		(ADMI <sub>s</sub>	/ADMI <sub>i</sub> )	% Reduction efficiency		
			Individual	Overall	Individual	Overall	
	Anaerobic feed	1027	-	-	-	-	
	Anaerobic tank	372	0.36	0.36	64	64	
	Anoxic tank	tank 484 1.3		0.47	-	53	
	Aerobic tank	409	0.84	0.40	16	60	
	UF-MBR Permeate	463	1.13	0.45	-	55	

в	Operating tank		(ADMI <sub>s</sub> /	ADMI <sub>i</sub> )	% Reduction	% Reduction efficiency	
			Individual	Overall	Individual	Overall	
	Anaerobic feed	1649	-	-	-	-	
	Anaerobic tank	1279	0.78	0.78	-	23	
	Anoxic tank	516	0.40	0.31	60	69	
	Aerobic tank	439	0.85	0.27	15	73	
	UF-MBR Permeate	507	1.15	0.31	-	69	
	RO Permeate	39	0.08	0.02	92	98	

С	Operating tank		(ADMI <sub>s</sub> /	ADMI <sub>i</sub> )	% Reduction efficiency	
			Individual	Overall	Individual	Overall
	Anaerobic feed	1829	-	-	-	-
	Anaerobic tank	797	0.44	0.44	56	56
	Anoxic tank	642	0.81	0.35	20	65
	Aerobic tank	613	0.95	0.33	5	67
	UF-MBR Permeate	613	1.00	0.34	-	67
	RO Permeate	10	0.02	0.01	98	99

D	Operating tank		(ADMI <sub>s</sub> /	ADMI <sub>i</sub> )	% Reduction efficiency		
			Individual	Overall	Individual	Overall	
	Anaerobic feed	2388	-	-	-	-	
	Anaerobic tank	966	0.40	0.40	60	60	
	Anoxic tank	649	0.67	0.27	33	73	
	Aerobic tank	920	1.42	0.39	-	62	
	UF-MBR Permeate	595	0.65	0.25	35	75	
	RO Permeate	6	0.01	0.00	99	100	

Е	Operating tank		(ADMI <sub>t</sub> /	ADMI。)	% Reduction efficiency		
_			Individual	Overall	Individual	Overall	
	Anaerobic feed	290	-	-	-	-	
	Anaerobic tank	581	2.01	2.01	-	-	
	Anoxic tank	406	0.70	1.40	30	-	
	Aerobic tank	387	0.95	1.33	-5	-	
	UF-MBR Permeate	423	1.09	1.46	-	-	
	RO Permeate	28	0.07	0.10	93	90	

It should be noted that the percent reduction (efficiency of colour removal) was divided into two; (1) the individual reduction, based on the percent decrease in ADMI from stage to stage  $(ADMI_{s1}/ADMI_{s2})$ , and (2) the overall reduction, based on the percent decrease with regards to the initial ADMI ( $ADMI_{s}/ADMI_{s}$ ) of the effluent fed from the equalisation tank to the anaerobic tank (i.e. the anaerobic feed).



Figure 4.16: HRT1 starting with a medium coloured discharge effluent fed to the anaerobic tank

The anaerobic feed of HRT1 was classified as a medium colour; since the ADMI value was 1027 ADMI units (refer to Table 4.7). The largest colour removal during the biological stages occurred during the anaerobic stage with 64 % reduction in colour (refer to Table 4.9A). Further colour reduction of 60 % was observed during the aerobic stage. During the anaerobic stage cleavage of the azo bonds occurred that resulted in aromatic amines. The colour removal noticed during the aerobic stage was a combination of the removal of dyes that did not contain azo bonds and the mineralisation of the aromatic amines formed during the anaerobic stage. The least amount of colour removal, 53 %, was observed during the anoxic phase. Colour removal of 55 % was also observed during the UF-MBR stage. In order to obtain a better visual representation of the above mentioned, the measured ADMI and true colour values obtained using the colour Hazen method were plotted graphically with respect to the various treatment stages (shown in Figure 4.15A). Even though two different methods were utilised to determine the colour during the different treatment stages, the same trend for colour reduction was observed in Figure 4.15A. Figure 4.16 provides a visual indication of how the colour changed during the various treatment stages. The final treated colour was compared to the SANS drinking water standards is discussed under section 4.4.3.



Figure 4.17: HRT2 starting with a dark coloured discharge effluent fed to the anaerobic tank

The anaerobic feed of HRT2 was classified as a dark colour; since the ADMI value was 1649 ADMI units (refer to Table 4.7) and therefore above 1500 ADMI units. The largest colour removal during the biological stages occurred during the aerobic stage with 73 % reduction in colour (refer to Table 4.9B). Colour reduction of 69 % was observed during the anoxic stage. The least amount of colour removal, 23 %, was observed during the anaerobic phase. Colour removal of 69 % was observed during the UF-MBR stage. However, the largest overall colour removal during the treatment process was observed during the last RO stage of the system, 98 %. In order to obtain a better visual representation of the above mentioned, the measured ADMI and true colour values obtained using the colour Hazen method were plotted graphically with respect to the various treatment stages (shown in Figure 4.15B). Even though two different methods were utilised to determine the colour during the different treatment stages, the same trend for colour reduction was observed in Figure 4.15B. Figure 4.17 provides a visual indication of how the colour changed during the various treatment stages. The sample representing the aerobic stage in Figure 4.17 appears to be darker than both the anaerobic and anoxic samples; however this can be attributed to the suspension of the micro organisms within the aerobic sample. The final treated colour was compared to the SANS drinking water standards is discussed under section 4.4.3.



Figure 4.18: HRT3 starting with a dark coloured discharge effluent fed to the anaerobic tank

The anaerobic feed of HRT3 was classified as a dark colour; since the ADMI value was 1829 ADMI units (refer to Table 4.7) and therefore above 1500 ADMI units. The largest colour removal during the biological stages occurred during the aerobic stage with 67 % reduction in colour (refer to Table 4.9C). Colour reduction of 65 % was observed during the anoxic stage. The least amount of colour removal, 56 %, was observed during the anaerobic phase. Colour removal of 67 % was observed during the UF-MBR stage. However, the largest overall colour removal during the treatment process was observed during the last RO stage of the system, 99 %. In order to obtain a better visual representation of the above mentioned, the measured ADMI and true colour values obtained using the colour Hazen method were plotted graphically with respect to the various treatment stages (shown in Figure 4.15C). Even though two different methods were utilised to determine the colour during the different treatment stages, the same trend for colour reduction was observed in Figure 4.15C. Figure 4.18 provides a visual indication of how the colour changed during the various treatment stages. The final treated colour was compared to the SANS drinking water standards is discussed under section 4.4.3.



Figure 4.19: HRT4 starting with a dark coloured discharge effluent fed to the anaerobic tank

The anaerobic feed of HRT4 was classified as a dark colour; since the ADMI value was 2388 ADMI units (refer to Table 4.7). The largest colour removal during the biological stages occurred during the anoxic stage with 73 % reduction in colour (refer to Table 4.9D). Colour reduction of 62 % was observed during the aerobic stage. The least amount of colour removal, 60 %, was observed during the anaerobic phase. Colour removal of 75 % was observed during the UF-MBR stage. However, the largest overall colour removal during the treatment process was observed during the last RO stage of the system, 100 %. In order to obtain a better visual representation of the above mentioned, the measured ADMI and true colour values obtained using the colour Hazen method were plotted graphically with respect to the various treatment stages (shown in Figure 4.15D). Even though two different methods were utilised to determine the colour during the different treatment stages, a similar trend for colour reduction was observed in Figure 4.19 provides a visual indication of how the colour changed during the various treatment stages. The final treated colour was compared to the SANS drinking water standards is discussed under section 4.4.3.



Figure 4.20: HRT5 starting with a light coloured discharge effluent fed to the anaerobic tank

The anaerobic feed of HRT5 was classified as a light colour; since the ADMI value was 230 ADMI units (refer to Table 4.7) and therefore below 500 ADMI units. An increase in ADMI value was observed between the anaerobic feed and the anaerobic tank, therefore the percentage removal was negative (refer to Table 4.9E). The increase in colour observed (see Figure 4.15E) was attributed to the presence of a dark colour (i.e. HRT4) in the anaerobic tank prior to the light colour being discharged and light colours taking longer to dilute dark colours. Therefore, with the exception of the RO stage, all the treatment stages showed a negative overall colour reduction. The largest colour removal, 90 %, was observed during the RO last stage, of the system. However, the individual stage with the largest colour reduction was the anoxic stage, during which a colour reduction of 30 % was observed. In order to obtain a better visual representation of the above mentioned, the measured ADMI and true colour values obtained using the colour

Hazen method were plotted graphically with respect to the various treatment stages (shown in Figure 4.15E). Even though two different methods were utilised to determine the colour during the different treatment stages, with the exception of the colour Hazen value obtained for the anaerobic stage, a similar trend for colour reduction was observed in Figure 4.15E. Figure 4.20 provides a visual indication of how the colour changed during the various treatment stages. The final treated colour was compared to the SANS drinking water standards is discussed under section 4.4.3.

From Figures 4.15A to 4.15E it was observed that the respective biological treatment stages, exhibit some degree of dye removal and hence, a reduction in colour, with the exception of a light coloured effluent being discharged after a dark coloured effluent. From the ADMI results obtained for medium (refer to Table 4.9A), dark (refer to Tables 4.9B – D) and light (refer to Table 4.8E) coloured discharged effluents it can be concluded that: (1) colour removal occurred during the UF-stage of the treatment system; (2) however, in the treatment system the largest overall colour reduction occurred during the RO treatment stage which removed any residual colour within the UF-MBR permeate; (3) for medium coloured discharged effluent the maximum colour removal during the biological stages, occurred during the anaerobic stage and the minimum colour removal occurred during the anoxic phase; (4) for dark coloured discharged effluent the largest coloured in both the aerobic and anoxic stages with the least amount of colour removal in the anaerobic stage.

# 4.4.3 UF, NF AND RO PERMEATE COMPARISON TO WATER DISCHARGE STANDARDS

Table 4.10 compares the analysed parameters of the UF, NF and RO permeate to the potable water and discharged effluent of the industrial partner, as well as the water discharge standards and the potable water standards.

After treatment with the biological system followed by the UF-membrane system the UF permeate obtained was within the South African discharge standards, but not all the parameters of the potable water standards. The UF permeate exceeded the potable water standards for conductivity (4527.9  $\mu$ S/cm), TDS (3656.7 ppm), ammonium (25.3 mg/L), turbidity (2.7 NTU) and colour Hazen (130.8 mg Pt/L). Therefore, the UF

permeate could not be re-used for dyeing purposes by the industrial partner. The UF permeate was subsequently treated with NF and RO. When comparing the NF permeate results to the RO permeate results (see Table 4.10) it was observed that the RO system provided permeate with lower conductivity (1462 µS/cm), TDS (987.8 ppm), COD (86.1 mg/L), TSS (0.0 mg/L), nitrate (1.8 mg/L) and ADMI (9.3 ADMI units). Therefore, it was concluded that the permeate from the RO system was preferred to the permeate from the NF system. With the exception of conductivity and ammonium (10.6 mg/L) all other parameters analysed within the RO permeate were within the potable drinking water standards. When compared to the potable water of the industrial partner with the exception of conductivity and TDS all the other parameters analysed were in the same range as the potable water. Optimising the efficiency of the RO system by adjusting the cross flow velocity to increase the HRT of the UF-permeate in the RO system, would decrease the conductivity and TDS of the RO permeate. A decrease in conductivity and TDS would bring all the parameters analysed to within range of the potable water of the industrial client and therefore make the RO permeate re-usable by the industrial partner. However, when solely examining the colour removal efficiency of the NF and RO membranes, the NF membrane would be the membrane of choice since colour removal of 93.5 and 98.7%, for true colour and ADMI, respectively was obtained with the NF membrane in comparison to 90.7 and 97.7% colour removal obtained with the RO membrane. Therefore if colour removal from textile wastewater is the primary objective, then an MBR coupled with NF is the treatment method to utilise. However, treatment of the UF-permeate with RO successfully removed both the residual colour and salts, which was imperative for successful reclamation of the effluent for re-use of the water, especially in dyeing processes. Treatment with RO brought all the parameters analysed to within range of the potable water of the industrial partner.

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Table 4.10: Average water quality of the textile company

Parameter	Units	Textile company potable water	Process plant effluent fed into the pilot plant	UF Permeate	NF Permeate	RO Permeate	CCT Water discharge standards*	Potable water standard**
Temperature	°	22.2	22.8	22.2	22.6	24.4	0-40	Not indicated
Hd		8.7	9.8	8.4	9.2	9.3	5.5-12	≤5 to ≥9.7
Conductivity	µS/cm	92.6	2715.8	4527.9	6077.3	1462.2	≤5000	≤1700
TDS	mqq	66.3	1972.7	3656.7	4076.8	987.8	4004.6	≤1200
COD	mg/L	58.9	763.4	190.8	113.3	86.1	≤5000	Not indicated
Ammonium	mg/L	11.2	9.0	25.3	7.8	10.6	Not indicated	≤1.5
TSS	mg/L	1.5	54.9	45.3	4.5	0.0	1000	Not indicated
Turbidity	NTU	1.5	45.1	2.7	0.1	0.4	Not indicated	<u>ام</u>
Phosphate	mg/L	1.3	1.5	1.3	0.4	1.5	25	Not indicated
Nitrate	mg/L	2.3	3.0	3.2	2.4	1.8	Not indicated	≤11
Colour Hazen	mg Pt/L	22.7	130.8	141.5	13.0	24.4	Not indicated	≤10
ADMI	ADMI units	16.8	659.2	471.0	11.9	9.3	Not indicated	Not indicated

<sup>\*</sup>City of Cape Town: Wastewater and industrial effluent by-law (2006) \*\*SANS 241 Drinking water specification (2011)

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#### 4.5 SUMMARY

The effluent stream was characterised by a COD range of between 45 to 2,820 mg/L and an average BOD of 192.5 mg/L. The dsMBR achieved an average COD reduction of 75% with a maximum of 97% over the 9 month test period. The COD concentration obtained after dsMBR treatment averaged at 190 mg/L, which was well within the discharge standard. The average reduction in turbidity and TSS were 94% and 19.6%, respectively, during the UF-MBR stage of the system. Subsequent treatment of the UF-permeate with NF and RO removed both the residual colour and remaining salt. A consistent reduction in the colour of the incoming effluent was evident. The ADMI was reduced from an average of 659 to below 20, a lower ADMI and colour compared to the received potable water. An average conductivity rejection of 91% was achieved with conductivity being reduced from an average of 7,700 to 693  $\mu$ S/cm and the TDS reduced from an average of 5,700 to 473 mg/L, which facilitated an average TDS rejection of 92%. Therefore if colour removal from textile wastewater is the primary objective, then an MBR coupled with NF is the treatment method to utilise. However, treatment of the UF-permeate with RO successfully removed both the residual colour and salts which was imperative for successful reclamation of the effluent for re-use of the water, especially in dyeing processes

# **CHAPTER 5**

## 5. PAPER AND PULP EFFLUENT TREATMENT

The paper and pulp industry in SA is one of the industries with the largest consumption and discharge of water and wastewater, respectively (Reddy *et al.*, 2005) with a consumption of approximately 130 million m<sup>3</sup> of water per annum (Steffen, Robertson and Kirsten Inc. 1990), whereas wastewater generated is up to 60 m<sup>3</sup>/ton of paper produced (Reddy *et al.*, 2005). Paper and pulp effluent is characterized by high TSS; COD and BOD; TDS; turbidity; colour and as a result poses a great threat to the environment (Steffen, Robertson and Kirsten Inc. 1990; Pokhrel & Viraraghavan, 2004; Christopher, 2007). The increasingly stringent local and national legislation, coupled with water supply security and eminent water scarcity issues in SA, is forcing this industry towards advanced treatment of their effluent.

# 5.1 PAPER AND PULP PROCESSING PLANT

The paper and pulp company is an international packaging company with processing plants throughout Africa and Europe. The company is currently the largest packaging company in Africa with a number of processing plants in South Africa. This company produces a wide range of corrugated packaging, bags, cartons and tissue products. The processing plant approached for this pilot research was a tissue processing plant situated in the Western Cape.

The company was approached on the 29<sup>th</sup> July 2009 with a proposal to enter into a joint piloting evaluation of a MBR effluent treatment system. The purpose of the piloting evaluation was to optimise the effective and efficient on-site treatment of the processing plants trade effluent and propose and design a full-scale MBR plant to provide a complete solution to meet their current and future water needs.

This proposed technical solution presents the outcome of a TFA for the proposed installation of a MBR wastewater treatment plant and water recovery process. The assessment followed a three-month detailed sampling schedule which was initiated on the 16<sup>th</sup> September 2009, consisting of weekly effluent grab sampling and associated chemical and physical analyses. These data as well as several issues and concerns, identified during this process, were used to design the pilot plant and enable a preliminary design and cost analysis proposal of the full-scale treatment plant to be compiled. One of the key design considerations identified was

implementing an anaerobic pre-treatment step into the process to reduce the effluent organic loading prior to aerobic treatment and integrated polishing via membrane filtration.

# 5.1.1 MOTIVATION FOR WASTEWATER TREATMENT AND WATER RECOVERY

Wastewater is generated at the processing plant from water in the pulping and paper making process; washing and drying of pulp; machine cleaning; and rain and wash water runoff from process areas. This wastewater is currently channelled to a back water tank, from where it is pumped to a Dissolved Air Flotation (DAF) unit. From the DAF unit the wastewater is fed through a centrifuge, two de-aeration tanks and then to a clarifier. The clarified wastewater is then fed either to a water buffer tank or sent to an effluent sump which feeds to the municipal sewage system.

The paper and pulp companies' motivation for entering into the proposed evaluation of the pilot treatment process was based on the following:

- They are willing to explore opportunities to decrease annual operating expenditure by lowering effluent discharge tariffs and potable water intake costs through process wastewater treatment and recycle potentially aiming to achieve a status of ZLD.
- Being part of a large international group, the company is committed to continually improving environmental performance in line with international best practice.
- The WRC-funded piloting project is a low-risk point-of-entry into the on-site wastewater treatment market for this company.

# 5.2 DESCRIPTION OF THE CURRENT WATER AND WASTEWATER SITUATION AT THE PAPER AND PULP PROCESSING PLANT

## 5.2.1 ECONOMIC FRAMEWORK AND MUNICIPAL WATER CHARGES

The paper processing plant currently consumes an average of 1,200kL/day of potable water and discharges approximately 95% of this as effluent to the municipal sewer. Between November 2007 and January 2011, water consumption of the plant increased by over 25% whilst both municipal potable water costs and effluent discharge tariffs increased by 31% (from R6.95/kL to R9.93/kL) and 14% (from R5.65/kL to R7.63/kL), respectively (Figure 5.1).



Figure 5.1: Current cost increase trends for municipal water supply and effluent discharge tariffs

This translated into an overall cost-to-company increase of 30% between November 2007 and January 2010 (refer to Figure 5.2). If these consumption and economic trends remain consistent on an annual basis, without wastewater treatment and recycle, their water consumption and effluent discharge will carry a cost-to-company in excess of R23.2 million over the next 36 months.



Figure 5.2: Water consumption and effluent discharge at paper and pulp company and associated cost increases

Additionally, with the proposed advent of the WDCS by the DWEA and its expected rollout to municipalities, both municipalities and industries may be increasingly pressurised to seek innovative ways to deal with industrial wastewater at source rather than the current practice which is end-of-pipe, i.e. at wastewater treatment works (Mazema *et al.* 2008; South Africa, 2003) . The most likely pressurizing mechanism will be increasing water costs meaning annual rate increases in excess of 7% and 10% for effluent discharge and potable water consumption, respectively (Mazema *et al.* 2008).

#### 5.2.2 DESCRIPTION OF THE WASTEWATER STREAM COMPOSITION

This paper and pulp processing plant currently discharges a single combined waste stream generated by its paper mill processing activities. The combined process streams have a COD range of between 1,300-4,500 mg/L and an average BOD of 2,400 mg/L, resulting in a BOD/COD ratio of 0.7-0.87. The effluent stream is neutral with a pH range of 6.5-6.8, requiring no further neutralization to facilitate biological reduction of the COD concentration to acceptable levels. As is typical of paper mill industry effluents, the effluent stream from the processing plant is also characterized by high conductivity and TDS concentration. A full compositional analysis of the effluent stream is given in Table 5.1.

#### 5.2.3 AVAILABILITY OF HISTORICAL EFFLUENT QUALITY DATA

Limited analytical laboratory facilities are available on-site and therefore no historical effluent quality analysis data was available. To design all wastewater treatment processes, but especially those aimed at industrial trade effluents, a historical effluent compositional trend analysis was necessary. This facilitated identifying effluent composition variability and pollutant or chemical spikes and peaks that may deleteriously impact on the primary biological treatment phase or the secondary physical filtration processes of an MBR effluent treatment design.

A historical effluent compositional trend analysis was conducted over a 12-week period, beginning on the 16-September-2009. Key effluent physico-chemical parameters were measured by Atl-Hydro personnel on a weekly basis to determine the variability of the effluent composition, as shown in Table 5.1 and Figure 5.3. These parameters were integral to many aspects of the overall wastewater treatment design including headworks, pre-treatment requirements, membrane choice, process control and AS process configuration.

PHYSIC	D-CHEMICA	L PARA	METERS		INORGANIC	COMPC	SITION	DESIGN PAR	RAMETERS
Parameter	units	AVG.	Min	Max	Parameter	units	AVG.	Parameter	value
pН	pH/units	6.3	5.2	7.1	Na	mg/L	112.2	Q (flow Rate)	1.2 ML/day
Conductivity	µS/cm	1587	1080	2100	К	mg/L	4.6	BOD/COD ratio	0.7-0.87
TDS	mg/L	1199	817	1587	Са	mg/L	307.1	COD/BOD ratio	1.15
Turbidity	NTU	287	55	779	Mg	mg/L	10.8	OLR	3000 kg BOD/day
COD	mg/L	2133	1655	2365	Fe	mg/L	3.2	SO₄/COD ratio	0.15
TSS	mg/L	112	25	362	CI	mg/L	75.5	C:N:P ratio	100:0.3:0.08
NH4-N	mg/L	12	4	21	CO <sub>3</sub>	mg/L	0		
NO3-N	mg/L	5	0.5	8	HCO <sub>3</sub>	mg/L	990.7		
PO <sub>4</sub>	mg/L	2	0.5	4.5	SO <sub>4</sub>	mg/L	345.1		
					В	mg/L	1.4		
					Mn	mg/L	0.09		
					Cu	mg/L	0.06		
					Zn	mg/L	0.1		
					Р	mg/L	0.9		
					F	mg/L	0.1		

Table 5.1: Effluent water quality and composition of paper and pulp company's discharge stream



**Figure 5.3:** Paper and pulp company's effluent composition trend analysis – (A) COD and ammonia; (B) Conductivity and TDS; (C) pH and temperature; (D) Turbidity and TSS

## 5.3 DESCRIPTION OF THE PROPOSED TECHNICAL SOLUTION

The proposed treatment solution involved a two-phase process comprising of primary biological treatment of the effluent coupled with membrane filtration of the treated wastewater. The high COD and low nutrient values are ideal for anaerobic pre-treatment of the effluent to reduce the organic load through conversion into biogas, followed by aerobic MBR treatment. Following anaerobic pre-treatment, the effluent is treated aerobically using an AS process coupled with an integrated membrane filtration polishing step.

A pilot plant was designed, constructed and commissioned based on the proposed technical solution described in Figures 5.4 and 5.5. Due to the high COD and low nutrient values of the paper mill effluent, a high rate anaerobic pre-treatment step in the form of an Expanded EGSB reactor was incorporated to facilitate a reduction in the organic load of the effluent prior to aerobic treatment. An EGSB system was used due to its increased contact time induced by the high upflow velocity in the column and it capacity to handle high OLR. In order to lower the requirement for N and P supplementation to maintain a C:N:P ratio approximating 100:10:1 in the aerobic step of the MBR. This would have significant bearing on the OPEX of a full-scale aerobic MBR without anaerobic organic load reduction pre-treatment.

Due to the absence of significant phosphate in the EGSB exit effluent, the system design did not require any biological phosphate removal capacity such as a modified UCT or 5-stage Bardenpho process and therefore a MLE process configuration was adopted for the biological AS component.



**Figure 5.4:** Pilot plant configuration – Anaerobic Expanded Granular Sludge Bed (EGSB) pre-treatment with downstream MLE AS external MBR

#### 5.3.1 REVERSE OSMOSIS TREATMENT SYSTEM

To investigate the potential for reuse of the treated MBR permeate as feed water, permeate was treated with a RO system to facilitate recovery and treatment of the UF permeate to potable water standards for reuse in the paper mill process. The purpose of the piloting study was therefore to optimize the pre-treatment systems and process control in order to limit the process fouling potential.

#### 5.3.2 MBR DESIGN AND OPERATION

# 5.3.2.1 ANAEROBIC PRE-TREATMENT: EXPANDED GRANULAR SLUDGE BED REACTOR SETUP

The EGSB reactor consisted of three parts: the lower distribution area; the middle biochemical reaction zone and the upper three-phase gas-liquid-solids separator. The gas-liquid-solids separator at the top of the column allowed for separation of the solids and biogas from the liquid phase. The liquid phase (product effluent) discharged at the top of the column was split into two streams: (i) EGSB product and (ii) effluent recirculation. Before the fresh feed effluent entered the EGSB, it passed through a settling tank fitted with a 1 mm mesh size, fine mesh filter operating under a vacuum of between -100 to 100 kPa, after which it was passed through an inline 0.5 mm cartridge filter (Effast, SA). This removed some of the insoluble COD and the larger fibrous material in the effluent to prevent it from entering the EGSB. The effluent recirculation from the top of the column was mixed with this filtered fresh feed in a mixing tank to ensure a homogenous feed into the EGSB. From the mixing tank the feed entered at the bottom of the EGSB at a liquid upflow velocity (V<sub>up</sub>) ranging between 1.1 and 10 m/hr depending on the expansion state of the internal sludge blanket. The EGSB product effluent was discharged from the top of the column to the anoxic tank.

*Inoculum, substrates and nutrients:* The inoculum for seeding the EGSB was a mixture of granular sludge and sewage sludge. The anaerobic granular sludge, which contained 6240 mg/L SS and 3465 mg/L volatile suspended solids (VSS) was taken from a full-scale UASB reactor treating brewery effluent (SAB-Miller, Newlands). The digested sewage sludge was obtained from an anaerobic digester treating municipal waste (City of Cape Town WWTP, Athlone). The operation of the EGSB started immediately after inoculation with the paper mill effluent used as the carbon source. Nutrients needed for the optimal growth of the biomass were nitrogen (N) and phosphorus (P) and these were in short supply in paper and pulp

effluents (Christopher, 2007). During the start-up period nitrogen and phosphate were supplemented to facilitate a C:N:P ratio of 650:7:1 (Ali *et al.*, 2009) based on the feed COD concentration. This supplementary N and P dosing was terminated after 116 days, to determine the effect of dosing on the EGSB product quality.

*Operating conditions of the EGSB:* During the initial start-up period, the EGSB was operated at 25°C for 60-days and later operated continuously under mesophilic conditions of  $35^{\circ}$ C. During the start-up period the EGSB was operated at a HRT of 10.3 hr and OLR of 4.1 kg COD/m<sup>3</sup>.d. The HRT was decreased stepwise from 10.3 to 8.8 and 7.7 hr and the OLR was increased from 4.1 to 4.8 and 5.5 kg COD/(m<sup>3</sup>·d) during operation.



Figure 5.5: Expanded Granular Sludge Bed reactor (Anaerobic stage) P&ID

# 5.3.2.2 AEROBIC POST TREATMENT: MODIFIED LUDZACK-ETTINGER (MLE) PROCESS COUPLED WITH UF MEMBRANE (MLE-UF)

In addition to lowering the OLR, the anaerobic pre-treatment decreased the nitrogen and phosphorus supplementation requirements for the aerobic process, which operates optimally at a C:N:P ratio of 100:10:1 (Russell, 2006). Due to the absence of significant phosphate in the EGSB exit effluent, the system design did not require any biological phosphate removal such as a modified UCT or 5-stage Bardenpho process and therefore a MLE process configuration was adopted for the biological activated sludge component.

The modified MLE process was a dual process that incorporated biological denitrification and nitrification. What separates this process from the conventional Ludzack Ettinger process is the inclusion of an internal recycle, as shown in Figure 5.6. The denitrification/nitrification was achieved with an initial anoxic zone followed by an aerobic zone. Denitrification occurred in the anoxic environment, and converted the nitrates into gaseous N<sub>2</sub>. In the aerobic tank the organic-N and NH<sub>4</sub> were oxidized to nitrite/nitrate. The MLE process was coupled to two Airlift<sup>TM</sup> configuration vertically-orientated tubular UF membrane separation modules, to facilitate complete solids retention in the MLE-MBR.

The aerobic product was pumped through the lumen of the tubular membranes, and permeate was extracted on the shell side of the membrane modules, while the high nitrate-concentration retentate was recycled back to the anoxic and aerobic tanks. A recycle rate of 5 times the volumetric flow rate (Q) back to the anoxic stage facilitated optimal denitrification (Hatch Mott MacDonald, 2010). Membrane fouling was preventively controlled through the continuous air scouring on the membrane lumen side of each module. In addition, a continuous backwash system was implemented. The system was configured to forward feed for 5 min and then back pulse for 10s, using reverse permeate flow, controlled via a PLC. When the backwash pressure reached 55-60 kPa, the membranes were chemically CIP using 1% sodium hypochlorite (NaCIO) remove any bio-fouling and 10% citric acid solution to remove any chemical scaling.

*Inoculum, substrate and nutrients:* The anoxic and aerobic tanks were inoculated with 10 L of activated sludge. The sludge that contained 7200 mg/L SS was obtained from Bellville wastewater treatment (City of Cape Town, South Africa). The EGSB product feed was used as the carbon source for the anoxic and aerobic tanks. After 33 d nitrogen and phosphate were added to the anoxic tank in the form of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) and potassium

dihydrogen phosphate ( $KH_2PO_4$ ) to maintain an aerobic C:N:P ratio of 100:10:1, based on the EGSB product COD concentration.

*MLE Operating conditions:* The MLE-MBR was introduced to the EGSB system after 80 days. The overall HRT for the anaerobic/aerobic hybrid treatment process was decreased stepwise from 36, 31 to 26 hr. The MLE-MBR OLR was increased stepwise from 8.9 to 9.3 and then 9.7 kg COD/( $m^3$ ·d). The combined system was operated for 112 days and the flux was increased step wise from 20 to 24 and finally to 28 L/m<sup>2</sup>.hr. In the design of an aerobic digester, the rate of aeration is a critical component to the effectiveness of the aerobic system (Shammas & Wang, 2000). Aerobic conditions in the treatment of wastewater are needed for the oxidation of ammonium to nitrate (nitrification) (Christopher, 2007). The conversion of ammonia to nitrate is an oxygen intensive process (4.57 mg O<sub>2</sub>/mg NH<sup>+</sup>-H oxidized) and therefore the process requires large quantities of process air (Christopher, 2007). The required dissolved oxygen (DO) for optimal biological activity within an aerobic system is between 1.5 and 2 mg/L (Christopher, 2007). Table 5.2 indicates the constants needed to calculate the flow of air required for an aerobic system.

Constants	Value	Reference
Α	0.8	Bolles, n.d.
Θ	1.024	Bolles, n.d.
Р	23.69	Shammas & Wang, 2000
ρ <sub>std</sub>	17.51	Shammas & Wang, 2000
Cs	9.02	Bolles, n.d.
CL	2	Bolles, n.d.
В	0.95	Bolles, n.d.
т	0.91	Sinnott, 1999
Ω	0.98	Ryan, 2007
Pair	1.205	Sinnott, 1999
Oxygen % in air (23%)	0.23	Sinnott, 1999
Con.N	2.1	Bolles, n.d.

Table 5.2: Constants for required air rate calculations

These constants are based on a course bubble diffuser. The reason for this assumption is because of the design of the diffuser. The diffuser was constructed out of 32 mm polyvinyl chloride (PVC) pipe with 1 mm holes drilled in at the top. Therefore the assumption of course bubble diffuser is appropriate.

The concentration of nitrogen in the effluent that needs to be oxidized to nitrate is determined from analysis of the effluent. The oxidizable nitrogen in the effluent is  $NH_4$  (Table 5.3). The oxygen transfer rate (OTR) for 60% nitrification was determined using the average daily effluent flow rate (2.5 L/h), the universal gas constant (8.43), the average ammonium in the effluent ( $N_{effective}$ ) and the volumetric flow rate (Q). This is determined by Equation 5.1 (Bolles, n.d.).

$$OTR_{nitrification} = Con. N \times 8.43 \times N_{effective} \times Q$$
(Eq 5.1)

The ratio of actual oxygen required (AOR) to oxygen required under standard condition (SOR) was determined by utilizing Equation 5.2 (Bolles, n.d.). The reference temperature was taken as 20°C and the temperature of the feed to the MBR was used (25°C).

$$\frac{AOR}{SOR} = \frac{\alpha \times \theta \times (T - T_{ref})}{C_s \times \tau \times \beta \times \omega \times (C_s - C_L)}$$
(Eq 5.2)

Where,  $\alpha$  is the transfer coefficient for oxygen from potable water to wastewater;  $\theta$  is the Arrhenius constant; T is the inlet temperature of aerobic tank (°C); T<sub>ref</sub> is the ambient temperature (°C); C<sub>S</sub> is the saturation concentration of water;  $\tau$  is the temperature correction factor for saturation concentration of water;  $\beta$  is the wastewater factor that inhibits oxygen transfer;  $\omega$  is the pressure correction factor for saturation concentration of water and C<sub>L</sub> is the designed dissolved oxygen concentration (kg O<sub>2</sub>/L) (Bolles, n.d.).

The AOR (kg O<sub>2</sub>/hr) for the aerobic system was determined by Equation 5.3 (Bolles, n.d.).

$$AOR = \frac{\frac{AOR}{SOR}}{OTR_{nitrification}}$$
(Eq 5.3)

In order to determine the flow rate of air into the aerobic system to deliver the required oxygen for nitrification, Equation 5.4 was utilised. This equation was determined by manipulating the units of the different parameters and using the ratio of oxygen present in air.

$$AAR = \frac{\frac{AOR}{\rho_{air}} \times 0.23}{60}$$
(Eq 5.4)

The designed air flow rate for the aerobic tank was determined to be 12.7 L/min; the system was however operated at approximately 14 L/min for the increasing flow rates in the different operating conditions.

Determined Parameters	Units	Value
Effective Nitrogen to be oxidized to nitrate	kg/L	0.007
OTR <sub>nitrification</sub> for 60% nitrification	kg/hr	0.3
AOR/SOR		0.08
Actual Oxygen required	kg O₂/hr	4
Actual air required (AAR)	L/min	12.7

Table 5.3: Designed oxygen requirement



Figure 5.6: Membrane Bioreactor (Anoxic and Aerobic stage) P&ID

*Dosing:* The C:N:P ratio needed for optimal biological growth in the Anoxic and Aerobic stages must be in an range of 100:20:1 to 100:5:1 (Russell, 2006). If the C:N:P ratio is too strong in carbon, very poor biological growth will occur (Russell, 2006). Because of this ratio, a dosing system was considered to increase the ratio to within the optimal range (100:10:1). After further consideration, the dosing option was moved to the anaerobic stage due to the fact that the ratio for optimal growth in the anaerobic stage is obtained with a C:N:P ratio of 650:7:1 (Ali *et al.*, 2009). This ratio is much more cost effective, because much less nitrogen and phosphorus needs to be added through the dosing solution to maintain the proper ratio. Even with the dosing at a more cost effective range, the COD levels are still very high for the biological stages after the anaerobic stage.

## 5.4 RESULTS AND DISCUSSION

#### 5.4.1 ANAEROBIC PRE-TREATMENT: EGSB

As shown in Figure 5.7, the effluent received from the paper and pulp company had considerable variations in COD concentrations over the test period. The effluent stream was neutral with an average pH of 6.3, requiring no further neutralization to facilitate biological reduction of the COD concentration. In comparison to literature (Table 3.3), it was observed that the paper and pulp company is a typical paper mill in terms of their effluent composition. A compositional analysis of the effluent and the effluent after anaerobic treatment is given in Table 5.4. The COD concentration from the effluent received from the processing plant was between 1778 to 3428 mg/L, with an average concentration of 2132 mg/L. The average COD concentration in the EGSB product that was fed to the aerobic MBR was 697 mg/L. According to the national discharge standards (Table 5.7), the COD concentration after just anaerobic treatment is still too high for discharged into a natural reservoir. The company will therefore still have to pay a municipal penalty, if the water from the EGSB reactor is discharged into the municipal sewage system. Therefore, it is clear that further treatment is needed to reach the goal of helping to reduce the company's municipal penalty expenses as well as to preserve the natural resources.

		PHYSI	ICO-CHE	MICAL P	ARAMET	rers							INORGANIC COMPC	<b>DSITION</b>	
		P/ E	APER MI	Ⅎ⊢	EGS	B PROD	UCT	UF	Permea	te			PAPER MILL EFFLUENT	EGSB PRODUCT	UF Permeate
Parameter	Units	AVG.	Min	Мах	AVG.	Min	Мах	AVG.	Min	Мах	Parameter	Units	AVG.	AVG.	AVG.
На	pH units	6.3	5.2	7.1	7.2	5.2	8.2	8.2	7.5	9.0	Na	ma/L	112	105	114
Conductivity	µS/cm	1586	1080	2100	1329	761	2197	791	649	968	Ca	mg/L	307	291	88.2
TDS	mg/L	1199	817	1587	1049	603	2510	561	460	695	C	mg/L	75	75	77.6
Turbidity	NTU	286	54.5	778	100	9.5	474	1.4	0.4	5.7	CO3	mg/L	0	0	42.1
COD	mg/L	2132	1655	2365	697	10.0	1810	20	43	100	HCO3	mg/L	066	1338	394
TSS	mg/L	112	25	362	248			37	4	06	S04	mg/L	345	170	109
NH4-N	mg/L	11.6	4.4	20.6	3.71	2.92	4.5	3.6	0.3	6.8		I			
NO3-N	mg/L	4.9	0.5	8.4	2.1	0.0	4.2	6.9	2.3	9.7					
PO4	ma/L	2.0	0.5	4.5	2.8	0.6	5.1	0.9	0.3	2.8					

Table 5.4: Summary of Paper mill effluent, EGSB Product and UF-MBR permeate





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#### 5.4.2 GAS PRODUCTION



Figure 5.8: Gas production over test period



Figure 5.9 Temperature and pH of EGSB over test period

The rate of gas production was measured on a daily bases using a custom gas flow meter. The relationship between the gas production and COD removal is shown in Figure 5.8 and it is clear that large variations in the gas production rate were observed over the test period. The average gas production rate was found to be 29 L/d. The peak in gas production on day 134 was due to a failure in the mixing tank level control, which resulted in air being pumped through the system for an extended period of time. However, this had little impact on the COD removal, indicating that the anaerobic biological system was robust enough to cope with air. The low points in gas production were due to the system being off or on recycle; also the system showed an almost immediate response (10 min) to the lack of fresh feed being fed (Zang, *et.al*, 2008). The pH and

temperature were monitored throughout the project and is shown in Figure 5.9, the pH and temperature was very reasonable constant and the pH ranged from 6.2 to 8.2 and averaged at 7.2, well within the correct pH range for the methanogens, this showed that the system has enough alkalinity through all the HRT's to neutralise the feed acidity and to offset the acidity from the VFA produced during AD (Zang *et al*, 2008).

When dosing was applied to the system the gas production was 28.5 L/d. When the nutrient dosing was moved to the Anoxic stage, there were no significant changes in the gas production. Because the proportionality between COD removed and COD converted to biogas is approximately 90%, the removal of the additional nutrients had little effect on the gas production and COD removal. At an HRT of 10.9, 9.1, 7.8 hr and OLR of 4.3, 5.2 and 4.8 kg COD/m<sup>3</sup>.d, respectively. The observed gas production was 29, 33.6 and 34.5 L/d respectively for the different HRT's. An upward trend was noticed when the HRT was decreased and the OLR was increased. In literature, the general trend is as the OLR is increased the gas production will increase, because more organic matter is being fed with similar or increased COD reductions, Figure 5.8 confirms this statement. Two gas samples were taken for gas chromatography (J. Muller Laboratories), at HRT 9.1 and 7.8 hr, the results are shown below in Table 5.5. Both samples showed traces of hydrogen sulphide  $(H_2S)$  which means that if the methane is to be recovered for energy, the biogas will have to be stripped of the hydrogen sulphide before use. Further there was a very low percentage of hydrogen gas, showing the AD cycle (methanogens section) was operating correctly. At the HRT of 9.1 the methane % was 75, which compares well with literature.

HRT	9.1 hr %	7.8 hr V/V
O <sub>2</sub>	3.0	1.6
N <sub>2</sub>	13.7	6.9
CH <sub>4</sub>	75.5	83
со	0	<0.01
CO <sub>2</sub>	7.8	7.9
$H_2S$	0.3	0.58
H <sub>2</sub>	<0.01	0

 Table 5.5: Gas chromatography analysis

## 5.4.3 AEROBIC MBR POST-TREATMENT: MLE PROCESS WITH UF MEMBRANE

The EGSB was operated for 82 days before the MLE-MBR stage was introduced. The EGSB product effluent was fed directly into the anoxic tank to facilitate sufficient carbon availability to drive the denitrification process. The influent COD concentration to the MBR system varied with the introduction of new effluent. This is illustrated by sudden peaks in the effluent COD (Figure 5.7). However, the average COD concentration into the MBR system was fairly constant and averaged at around 697 mg/L.

The temperature and pH were checked on a daily basis and the results were consistent with literature. According to literature, pH is temperature dependant and figure 5.10, shows that with a change in the temperature the pH also changed. No significant changes in either the pH or temperature occurred during the test period. However, on day 19 of operation a peak in the aerobic pH was experienced. This was due to the method in which the sample was taken. After this incident, corrective measure was taken to improve the consistency of data through proper sampling. The average pH of the permeate over the test period was 8.2 pH units. This is within the range set out by the Water Act No. 36 of 1998 (Table 5.7)





According to literature, TDS and conductivity is directly related to one another (Whipker & Cavis, 2000). The relationship between conductivity and TDS can be represented by the following equation:

$$TDS = 900 \times EC$$

(Eq 3.5)

Figure 5.11 illustrates that with an increase in the TDS an increase in conductivity will also be experienced. A sudden spike in the aerobic conductivity and TDS was observed on day 19. This was due to the method of sampling on that specific day. The permeate conductivity and TDS were much lower than that of the anoxic and aerobic tanks. This is due to the effectiveness of the membranes to remove dissolved solids and to reduce conductivity. The average TDS for the permeate over the test period was 561.2 mg/L. According to the SANS 241 drinking water standards, the allowed TDS concentration must be less than 1000 mg/L. The main component that contributes to the TDS in the permeate is hydrocarbonate ions (HCO<sub>3</sub><sup>-</sup>). This was apparent during the operation of the MBR due to the high scaling levels observed. However, for the paper and pulp company to discharge their effluent without receiving penalties, the TDS is within range of the national standards. Because TDS and conductivity are directly related to one another, the conductivity is also within the national discharge standards.

The turbidity is the measure of the "cloudiness" of the water and TSS is the measure of the total suspended solids present in a sample of water. Therefore, these two parameters are interrelated to one another. From Figure 5.13, with an increase in the turbidity of a specific tank, there was an increase in the TSS. The suspended solids in the MBR system consist of biomass. During the first 10 days of operation, there was a sharp decrease in the aerobic turbidity and TSS. This was due to overflows that flushed out the biomass of the tanks and into the overflow tank and the aeration rate that was too low (10 L/min). After day 10, a steady increase in both parameters was observed due to increasing biological activity in the system. This increase can be contributed to the aeration rate that was adjusted to the design flow rate and the proper operation of the plant. From day 48 to 57, very low TSS and turbidity readings were observed in both anoxic and aerobic tanks. In an attempt to increase the biomass, 50 bio-balls were added to both the bioreactor tanks (Figure 5.12). This was to provide a surface area for the biomass to immobilise on and this in effect increased the amount of biomass in both tanks. From day 57, the levels in both the anoxic and aerobic tanks were maintained at 25 L each. It is clear that these measures helped to increase the amount of biomass in both tanks because a clear



Figure 5.11: Anoxic, Aerobic and Permeate TDS and Conductivity over test period



Figure 5.12: Bio-ball with biological growth



Figure 5.13: Anoxic, Aerobic and Permeate Turbidity and TSS over test period

increase in both parameters was noted. During the end of the test period, an increase in the turbidity and TSS of one tank and a decrease in these parameters in the other tank were observed. This was due to overflows from one tank into the other, while no biomass was lost to the overflow tank. The turbidity and TSS for the permeate was significantly lower than that of the aerobic and anoxic tanks. This indicates the effectiveness of a membrane as a solid liquid separation medium. The overall reduction in turbidity for the entire system was 99%. The turbidity was decreased from an average of 100 to 1.4 NTU. A 67% overall reduction in TSS was observed over the test period. The TSS was reduced from an average of 112 to 37 mg/L. The turbidity of the permeate is well within the national drinking water standards of between 1 and 5 NTU. The TSS however, was slightly more than the national discharge standards require (25 mg/L). This can be improved by improving the operation of the MBR system and the addition of a tertiary polishing stage (RO or NF membranes) to the existing UF membrane system.

The NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub> concentration of the EGSB product, aerobic and anoxic tanks were measured every second day. These parameters were an indication of whether denitrification occurred in the anoxic tank and nitrification occurred in the aerobic tank. From literature, ammonium is oxidized to produce nitrates and the nitrates, along with a carbon source is reduced to nitrogen gas. In Figure 5.14, the  $NO_3$  in the aerobic tank was consistently higher than the NO<sub>3</sub> in the anoxic tank. This indicated that nitrification was successful in the aerobic tank. To further investigate if nitrification occurred in the aerobic tank, the  $NH_4^+$  concentration in the aerobic and anoxic tanks were considered. Figure 5.14 illustrates that the concentration of NH<sub>4</sub><sup>+</sup> was predominantly higher in the anoxic tank but, this was not always the case. The fact that  $NH_4^+$  was dosed in the anoxic tank, through the addition of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>), can explain the higher levels of NH<sub>4</sub><sup>+</sup> in the aerobic tank. Because the NH<sub>4</sub><sup>+</sup> is not utilized in the anoxic stage, it is pumped over to the aerobic stage which increased the NH<sub>4</sub><sup>+</sup> concentration. To assess if denitrification occurred in the anoxic stage of the system, the NO<sub>3</sub> concentration of the EGSB product stream and the anoxic tank were considered. It was expected that the NO<sub>3</sub> concentration in the anoxic tank must be lower than that of the EGSB product stream. This was however not the case. Because the MBR system was based on the MLE process a constant stream of nitrified water was fed to the anoxic tank via a recycle stream. This increased the NO<sub>3</sub> concentration in the anoxic tank and made it much higher than that of the EGSB product stream. If there was no denitrification in the anoxic tank, it would be expected that the NO<sub>3</sub> concentration of both the anoxic and aerobic tanks be similar. However,

the  $NO_3$  concentration in the anoxic tank was consistently lower than that of the aerobic tank, which indicated that the  $NO_3$  was reduced to nitrogen gas, carbon dioxide and water.

Another factor considered when determining if nitrification and denitrification occurred was the pH. If the pH in the aerobic system shifts to the acid side, low nitrification will occur and vice versa for the denitrification process (Cheremisinoff, 1996). In Figure 5.10, it was noted that the pH of the aerobic tank was consistently higher than that of the anoxic tank. Therefore, it was confirmed that nitrification and denitrification was achieved in the biological stages of the MBR. The average concentration of NO<sub>3</sub> and  $NH_4^+$  in the permeate was 6.9 and 3.6 mg/L respectively. The NO<sub>3</sub> concentration did adhere to the national drinking water standards (Table 5.7). However, the NH<sub>4</sub><sup>+</sup> concentration was higher than the required maximum set out by the national drinking water standards of between 1 and 2 mg/L. The high levels of NH<sub>4</sub><sup>+</sup> in the permeate can be contributed to the dosing flow rate that was not always adjusted according to the inlet COD concentration, this caused overdosing and increased the levels of unused NH<sub>4</sub><sup>+</sup>. Another factor that could have caused the high NH<sub>4</sub><sup>+</sup> levels in the permeate is that the anoxic recycle was set at too high a flow rate. This decreased the HRT of both the anoxic and aerobic stages. With a decreased HRT, the nitrifying microbes did not have enough time to reduce the NH<sub>4</sub><sup>+</sup>. If the recycle flow rate should be reduced, higher denitrification and nitrification levels will be experienced and lower NO<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations will be present in the permeate.



Figure 5.14: Anoxic, Aerobic and Permeate Nitrate and Ammonium concentration over test period

The effluent received from the paper processing plant had a very low PO<sub>4</sub> concentration in comparison to the COD concentration. Because of this, the designed MBR system did not include a phosphate removal stage. The low PO<sub>4</sub> concentration also emphasizes the reason for choosing a MLE system over the UCT process. However, PO<sub>4</sub> was needed for optimal biological growth. Therefore, additional PO4 was introduced to the system via dosing of potassium dihydrogen phosphate ( $KH_2PO_4$ ). The dosing was introduced using a low speed dosing pump and the volume added to the anoxic stage was calculated based on a C:N:P ratio of 100:10:1. It would be expected that the  $PO_4$  concentration would be highest in the anoxic stage. On day 2, there was a peak in the PO<sub>4</sub> concentration in the anoxic tank (Figure 5.15). The dosing originally occurred in the EGSB mixing tank and was calculated based on a C:N:P ratio of 650:7:1. On day 2, the dosing was moved to the anoxic tank. The COD concentration on was 710 mg/L, which is lower than the COD concentration in the effluent tank. The dosing was never adjusted to the new COD concentration and therefore over dosing occurred on that specific day. A peak in the PO<sub>4</sub> concentration is again observed on day 70. This was due to the system being put on recycle without switching of the dosing pump. However, the overall  $PO_4$  concentrations were similar throughout the system over the test period (Table 5.6). PO<sub>4</sub> concentration in the permeate was noticeably lower, due to the membranes removing some of the PO<sub>4</sub>. According to Table 5.7, the phosphate concentration of the permeate was below the national discharge standards of 10 mg/L.



Figure 5.15: Effluent, anoxic, aerobic and permeate phosphate concentration over test period

Table 5.6: Average phosphate concentration for test period

		Anaerobi	c Pre-treatment		MBR	
		Feed	Product	Anoxic	Aerobic	Permeate
Parameter	Units					
PO <sub>4</sub> concentration	mg/L	2	2.8	2.8	2.5	1.0

Table 5.7: National Standards vs. Permeate Quality after test period

		CCT Wastewater By- Law (May 2006)	Sans 241:2011	Water Act No. 36 of 1998	Perm	eate
		Discharge to Wastewater treatment facility	Drinking Water specification	General Limit	Concentration	% Removal
Determinant	Units	Not Exceed				
Physical, Organoleptic Requirements:						
Conductivity at 25 °C (aesthetic)	mS/m	500	≤170	150	7.92	50.1
Dissolved solids (aesthetic)	l/gm	4000	≤1200	ni	561	53.2
pH at 25 °C (operational)	pH units	12	≥5 to ≤9.7	5.5-9.5	8.2	Increased
Turbidity (operational/aesthetic)	NTU	ni	≤1 / ≤5	ni	1.4	99.5
Chemical Oxygen Demand (COD)	mg/l	1000	ni	75	71	96.7
Suspended Solids	l/gm	1000	ni	25	37	67
Chemical requirements macro-determinant:						
Ammonium as N (operational)	mg/l	ni	ni	ni	4.5	62
Calcium as Ca (aesthetic/operational)	mg/l	ni	ni	ni	88	11
Chloride as Cl (aesthetic)	l/ɓm	1500	00€≥	0.25	78	Increased
Nitrites and Nitrates as N (acute health)	l/gm	ni	≥11 (Nitrites) ≤0.9 (Nitrates)	n	5.9	Increased
Sulfide as S	mg/l	ni	ni	ni	N/A	N/A
Sulfate as SO4 <sup>7</sup> (acute health/aesthetic)	mg/l	50	≤500 / ≤250	ic	110	68

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		CCT Wastewater By-		Water Act No. 36 of		
		Law (May 2006)	Sans 241:2011	1998	Perm	eate
		Discharge to Wastewater	Drinking Water specification			
		treatment facility		<b>General Limit</b>	Concentration	% Removal
Determinant	Units	Not Exceed				
Phosphates	mg/l	1500	ni	10	1.0	49
Ortho-Phosphate as phosphorous	mg/l	25	ni	10	1.0	49

ni – not indicated

One of the main parameters in determining the degree of water pollution is COD. From Figure 5.16, it was noted that the effluent received from the paper and pulp processing plant did not comply with national discharge or drinking water standards. After anaerobic pretreatment, the COD concentration was reduced with an average of 62% over the test period. Therefore the COD concentration entering the MBR system was much lower than that of the raw effluent (Table 5.4). With the introduction of a new batch of effluent to the system, a peak in the COD concentration of the effluent and the EGSB product was experienced. However, the COD concentration of the permeate was not affected by these peaks. When considering the national standards, the required COD concentration for industrial wastewater discharged into a water resource (river, dam, etc.) is 75 mg/L after the removal of algae. The average COD concentration obtained from the MBR system after the test period was 70.7 mg/L. This is well within the national standards. Regardless of the effluent COD concentration and the performance of the EGSB, an average COD reduction of 96% was obtained. When comparing the COD removal to MBRs operated with paper mill effluent, we see that the removal of the system is more than that of Zhang et al., 2004 (92%), Kay et al., 2004 (95%) and Mantarri et al., 1997 (75-90%).



Figure 5.16: Overall COD removal of MLE-MBR over test period

#### 5.4.4 EFFECTS OF HRT AND OLR ON PERMEATE QUALITY

The MBR system was operated under three different fluxes during the test period. The average, minimum and maximum COD concentration for the different flux periods were used to determine the HRT and OLR of the MBR system (Table 5.8 and Table 5.9). In order to change the OLR, the flow rate was changed. This was done because the COD concentration from the EGSB product was fixed and could not be varied. When the total daily flow rate was altered, the HRT was changed. These parameters were varied in order to determine the robustness of the system. Figure 5.17 illustrates that even with an increase in the OLR and a decrease in the HRT, the overall COD removal stayed constant at an average of 96%. Comparing this data to literature, we see that Zang *et al.*, 2008 obtained similar results. Even though the test period was longer (500 days), Zang *et al.*, 2008 had three changes in HRT and OLR over a period of 100 days.

Flux (L/m².h)	20	24	28
OLR (kg COD/m <sup>3</sup> .d)			
Minimum	0.3	0.5	0.6
Maximum	1.5	1.3	1.1
Average	0.6	0.7	1.1
COD (mg/L)			
Minimum	298	483	445
Maximum	1673	1190	823
Average	676	626	579

Table 5.8: Different operating conditions with OLR's

	0		
Flux (L/m².hr)	20	24	28
HRT (hr)	22	19	16
Average		10	10
HRT (d)	0.9	0.8	07
Average	0.0	0.0	0.1
Flow Rate (L/hr)	2.3	2.7	3.2
Average			0.2

	Table 5.9:	Different	operating	conditions	with	HRT's
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Figure 5.17: Effect of HRT and OLR on Overall COD removal

#### 5.4.5 OPERATION OF MLE-MBR PILOT PLANT

Daily operation of the MBR system included monitoring of pressures (feed, back pulse, permeate), setting and monitoring of flow rates between tanks and monitoring the levels in the different tanks. During the test period some operational challenges were encountered. The system was not designed to be an automated, therefore continues monitoring was required. The valves used on the MBR pilot plant were mainly ball valves and due to the characteristics of the valve it was not an ideal choice for throttling low flow rates. Constant resetting of flow rates was required due to the high TSS in the system. When the TSS increased to 3 g/L, the problem increased as the valves blocked more frequently when the flow of the recycle to the anoxic was set to a value of 25 L/hr. To overcome this problem, the recycle flow was increased (40-50 L/hr) to more than the original design to try and reduce the occurrence of blocking in the valves.

#### 5.4.6 FOULING

Fouling of the membranes was monitored through monitoring of the back pulse pressure. If the pressure increased, it illustrated that there were less pores for the permeate to move through and this was then the indication that fouling is occurring. During the test period it was observed that not only does the back pulse pressure increase when fouling is present, but the feed pressure also shows an increase. Figures 5.19 illustrate the feed, back pulse and permeate pressure for the test period. The feed pressure is however misleading when identifying fouling. To keep the shell side full of permeate at the different fluxes, a feed pressure was induced by partially closing BV 11 (Figure 5.3). When the back pulse

pressure reached a value of between 55 and 70 kPa, a CIP sequence was initiated. When the flux was moved up from 20 to 24, an increase in the fouling rate was observed. The increasing TSS levels of the system also contributed to the increasing rate of fouling. When the Flux was increased from 24 to 28, a significant increase in the fouling rate was observed. This increase in flux occurred from day 81 to day 112. During this period a spike in the TSS was also observed and the TSS maintained a high concentration of 3 g/L until the end of the test period. Two types of fouling were noticed during the test period, namely biological fouling (due to microbiological flocs) and chemical fouling. The three main components that made up the chemical fouling were calcium, carbonate and hydrocarbonate ions. These components are partially insoluble in water and were present throughout the system (Table 5.10). From Table 5.10, a significant increase in carbonate ( $CO_3$ ) is observed and a decrease in hydrocarbonate ( $HCO_3$ <sup>-</sup>). The  $CO_3$  and calcium (Ca) combine to form a virtually insoluble compound that precipitates out of the water and adheres to the membranes and causes chemical fouling.

A source of concern for the reuse of the treated wastewater in the company's papermaking process is the high levels of inorganic salts present after MBR treatment. The quality of water needed to operate equipment properly is in line with potable water standards. Table 5.4 indicates the average concentration of inorganic components in the permeate. If the permeate is utilized as process water, without further treatment, accumulation of these compounds will occur and cause problems in the process equipment.

Parameter	Units	Effluent	EGSB Product	MBR
Са	mg/L	307.1	249.1	100.3
CO <sub>3</sub>	mg/L	0.0	6.5	29.0
HCO <sub>3</sub>	mg/L	990.7	1053.3	458.6

 Table 5.10:
 Chemical Fouling composition



Figure 5.18: Back pulse, Feed and Permeate pressure

Figure 5.19 illustrates the content of each stage (feed, EGSB product, anoxic, aerobic, permeate). The biomass is clearly visible in Figure 5.12 and even from visual inspection, increasing fouling would have been expected



Figure 5.19: Samples from different stages of combined EGSB and MLE-MBR system

### 5.4.7 EFFECT OF CIP

The CIP sequence was initiated when the back pulse pressure reached a value of between 50 and 55 kPa. A 10% solution of Citric Acid and a 100 ppm solution of NaOCI were used to clean the membranes. The citric acid was used to remove all traces of

chemical fouling and the sodium hypochloride was used to remove all traces of biological fouling. Initially the system was operated for 30 days before a CIP sequence was needed. After the first CIP sequence, cleaning was needed at more regular intervals (Figure 5.20). This can be contributed to the increase in flux during the operational test period.



Figure 5.20: Back pulse pressure with CIP intervals

#### 5.4.8 TERTIARY POLISHING PROCESS: RO AND NF

In order for the paper and pulp company to use the treated effluent as process water, further treatment options were investigated. Samples of the permeate was sent for treatment with low pressure RO and NF membranes. After treatment with low pressure RO membranes, Ca, Na,  $HCO_3^-$  and  $SO_4$  was reduced by, 99%, 91%, 98% and 99% respectively. When the permeate was treated with low pressure NF membranes, Ca, Na,  $HCO_3^-$  and  $SO_4$  was reduced by, 99% respectively. These results showed promise for the complete recycling of effluent as process water, but a tertiary polishing stage is needed.

#### 5.5 SUMMARY

The paper mill effluent stream was characterized by a chemical oxygen demand (COD) range of between 1,600 to 4,400 mg/L and an average BOD of 2,400 mg/L. In terms of effluent COD reduction efficiency, the anaerobic pre-treatment stage facilitated an average of 70% COD removal, thus lowering the MBR COD feed concentration to consistently below 750 mg/L. The subsequent anaerobic product stream was the feed stream for the MLE-MBR which facilitated an average of 97% COD removal over the piloting trial period. Combining a high-

rate anaerobic pre-treatment EGSB with a MLE-MBR process configuration produced a high quality permeate. Preliminary NF and RO results indicated an overall COD removal of around 97 and 98%, respectively.

# **CHAPTER 6**

### **6.** TANDEM FRANCHISE MODEL

One of the challenges experienced by the wastewater treatment sector is the severe shortage of skilled labour. Part of the aims for this project were capacity building, knowledge generation and technology transfer within the wastewater treatment industry and to facilitate a skills development initiative by exposing historically disadvantaged students through the Cape University of Technology internship programme to on-site training specifically in MBR technology.

#### 6.1 SCARCE SKILLS

The severe shortage of skills in South Africa is being addressed through the Skills Development Act (No. 97 of 1998). This Act provides a framework for addressing, and aims to make the learning system more responsive to the skills requirements of industry. The Scarce Skills Development Fund strives to address the severe shortage of various critical skills in South Africa.

The fields that have been identified by the Department of Labour and the National Research Foundation where there is a scarcity of skills in South Africa are accounting, auditing, actuarial sciences, agricultural sciences, bioinformatics, biotechnology, chemistry, computer science, demography, **engineering**, geology, information systems, mathematical sciences, physics, statistics, tourism and transportation studies. With a particular **lack of skills of Engineers within the wastewater treatment industry**.

#### 6.2 CAPACITY BUILDING INITIATIVES

As part of the WRC capacity building initiative of this project, in-depth training of Cape University of Technology in-service trainees (ISTs) was an ongoing process. In addition to skills development training, the ISTs were encouraged to pursue their BTech degrees under the supervision of Atl-Hydro's directors. Furthermore, promising IST candidates were going to be exposed to commercial aspects of industrial wastewater treatment through enrolment in the Cape Biotech Trust annual Bioentrepreneurship programme. This programme was designed to transfer business skills to scientists and engineers working within South Africa's biotechnology sector. The outcome of this initiative would have been that each participant is trained and mentored through the process of writing a comprehensive business plan geared toward the commercialization of the technology that they were involved with through their IST programme. Whilst this was not the mandate of the WRC project, the technical skills gained through the pilot plant design, manufacture, operation, and optimization as part of the capacity building initiative, coupled with business skills development is part of Atl-Hydro's company growth strategy. However, due to the formation of the Technology Innovation Agency (TIA) this bioentrepreneurship programme through Cape Biotech Trust was terminated.

#### 6.2.1 CAPACITY BUILDING

Atl-Hydro's growth strategy is to develop a national franchise network of Atl-Hydrobranded MBR technology operations across the trade effluent landscape. Each franchise will be owned and run by Atl-Hydro in-service trainee 'graduates'. To achieve 'graduate' status, in-service trainees follow a 24-month phased training process geared toward the in-service trainees using their first 12-months mandatory in-service training as a hands-on introduction to all aspects of MBR operations, maintenance, and optimisation. Thereafter, trainees that demonstrate initiative and potential will be offered permanent employment, as well as an opportunity to complete their BTech degrees using plant operating data for their research projects during the second 12-month period. In addition, through the Cape Biotech Trust's (CBT) bioentrepreneurship programme, these employees will be given the opportunity to attend courses specifically geared toward small medium and micro enterprises (SMME) startups in the biotechnology field. CBT is the Biotechnology Regional Innovation Centre (BRIC) for the Western Cape and is one of the four centres established around the country to implement the national biotechnology strategy.

#### 6.2.2 TANDEM FRANCHISING MODEL

The success of Atl-Hydro's franchising strategy will be built around the implementation of a tandem franchising model which addresses the challenges of skills transfer to the franchisee via an ongoing mentoring process incentivised through real participation in equity. Once 'graduated' as described above, Atl-Hydro would enter into a Joint Venture agreement with the prospective franchisee with one of Atl-Hydro's Senior Management members serving as the franchisor-appointed mentor. The franchisee then purchases a minority stake in the franchise which initially is company-owned, through the in (IDC-SBU)

which offers funding for franchising to entrepreneurs with limited access to capital. By retaining the initial majority share, Atl-Hydro reduces the risk associated with funding this franchise structure. The franchisee effectively acts as an assistant manager for a predetermined period (12 months) until the appropriate knowledge and experience is gained through running the business in 'tandem' with the company-appointed mentor. During this first year of operation, the franchisee is a salaried employee of the Joint Venture and profits are accumulated in a separate fund and used to purchase more equity. The rate at which 100% equity is accrued becomes a function of the entrepreneurship skills of the franchisee and is the motivational driving force in keeping with Atl-Hydro's Quality Management System. Our goal is to ensure that at least 50% of our franchisees are classified as HDI (Historically Disadvantaged Individuals) so that as QSEs (Qualifying Small Enterprises) they automatically qualify as Level 3 contributors in terms of BBBEE (Broad Based Black Economic Empowerment).

## **CHAPTER 7**

#### 7. CONCLUSIONS

The following conclusions are presented for consideration in this final report:

#### 7.1 TEXTILE EFFLUENT TREATMENT

A pilot scale dual-stage side stream MBR plant was successfully designed, constructed, commissioned, operated and utilized in the treatment of textile processing effluent at a textile company in the Western Cape. After treatment with the UF-MBR system the UF permeate obtained was within the South African discharge standards, but not all the parameters of the potable water standards. NF and RO were subsequently used to treat the UF permeate, optimising the overall treatment efficiency. The RO system reduced all the parameters to within range of the potable water of the industrial client and therefore made the RO permeate re-usable.

Implementing a dsMBR system coupled with NF successfully removes colour from industrial textile effluent bringing all the parameters measured during the study to within the CCT wastewater discharge standards, thereby reducing their discharge costs financially. However, coupling the dsMBR system with RO not only successfully removed the residual colour from the effluent; RO also had the capability of reducing the salts present in the dsMBR product to within potable water standards. By treating the effluent to within potable water standards the treated water can be re-used on-site within the textile dyeing processes, thereby reducing reduce the wastewater load sent to the municipal treatment works, reducing the volume of water used by the textile company thus decreasing their water dependence on the municipality, and assisting in reducing their impact on the environment (i.e. carbon footprint).

However, a dsMBR system would not be ideal for this particular textile company, since the industry does not operate continuously and has periods of down time over weekends and public holidays. Biological systems require continuous effluent feed in order to supply the activated sludge with nutrients and thus operate efficiently. With non-continuous effluent production by the textile company the system would have many periods of unstable

treatment while the activated sludge stabilised after nutrient starvation. Therefore, the ideal wastewater treatment system for this textile company would include UF, NF and RO without the pre-treatment biological tanks as used in the pilot scale plant. The absence of the biological tanks would make it easy to start-up and shut down the wastewater treatment system in accordance with the effluent production of the textile company without being detrimental or affecting the efficiency of the effluent treatment.

#### 7.2 PAPER AND PULP EFFLUENT TREATMENT

A pilot scale dual-stage side stream MBR plant was successfully designed, constructed, commissioned, operated and utilized in the treatment of paper mill effluent. The pilot-scale MBR-MLE had good nitrification and denitrification capacity, but this can be even further improved by decreasing the recycle flow rate. The system achieved an average overall reduction of 99% in turbidity and a 96% reduction in the COD concentration. The COD removal achieved by the overall system was greater than that of similar systems operated in the past. Results showed that the changes in HRT's and OLR had little to no effect on the overall COD reduction of the effluent. The objectives of the project were achieved and Nampak effluent treated by the designed system could be discharged without any penalties. After treatment with RO and NF membranes systems an average of 90% removal of inorganic compounds were achieved. With the implication of stringent governmental laws with regards to effluent discharge, this research proved that an alternative is available as opposed to discharging untreated effluent into natural reservoirs or municipal sewage systems.

#### 7.3 OVERALL ENVIRONMENTAL, COST, AND ENERGY BENEFITS

Projected savings on overall costs over a 10-year period are critical in determining whether full-scale implementation will meet financial ROC (Return On Capital) requirements. These projections are calculated based on the current method of municipal tariff determination and can be calculated on a conservative flat tariff rate escalation. Based on the above case studies, it is our recommendation that the following initiatives be considered when making decisions to implement full-scale interventions

• Onsite piloting trials must be conducted to provide long-term optimization and scalability data

- Cleaner production and waste minimization audits should be conducted in parallel to capitalize on increased long-term savings potential
- Stream segregation analysis should be implemented during latter phase of pilot trials if decision to implement treatment strategy at full-scale is considered
- Full-scale implementation should be done using a modular approach to match expansion requirements when necessary

Process designs for full-scale treatment facility should be conducted using a modular approach to accommodate potential production capacity increases in the short- to medium-term (3-5 years) – in terms of footprint requirements, the modular design is based on incremental capacity expansion.

Based on the calculated OPEX savings potential, overall savings taking into account fullscale CAPEX and OPEX should translate into an ROI/ROC period of approximately 5-7 years with an overall savings potential of 25-50% calculated on a cost-per-kL basis calculated over the 10-year operating period (NOTE: this excludes any additional savings related to implementing cleaner production and waste minimization audits which would optimize raw material usage, energy requirements, and production manufacturing.

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