



Cape Peninsula
University of Technology

**ENHANCEMENT OF MEMBRANE SURFACE CHARACTERISTICS TO IMPROVE
MEMBRANE PERFORMANCE AND DURABILITY IN THE TREATMENT OF MUNICIPAL MBR
EFFLUENT**

by

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ABSTRACT

Fresh, clean water has always been critical for the world's social development. Supply of water can be reinforced through recycling and reuse; and secondary treatment of municipal wastewater effluent with a membrane bioreactor (MBR) followed by a reverse osmosis (RO) process, has emerged as a crucial treatment process for water reuse. However, fouling of RO membranes in such process is unavoidable. This leads to poor performance, increase in operational cost and degradation of the membrane material, which reduces the membrane life span. Various researches have been conducted to provide an understanding of the mechanism of fouling, and methods have been developed to minimize it.

In this research, the effect of surface modification to minimise fouling on a thin film composite polyamide RO membrane was investigated. This study was divided into three parts, namely: membrane modification, biofouling and filtration using RO. Two modifying agents, PVA and DMAEMA, were used as grafting solutions. *Escherichia coli* (*E. coli*) were used as the biofoulant to study the ant-biofouling properties of the membranes. A make-up synthetic MBR secondary effluent feed was used in a bench scale RO process.

During the membrane modification process, the membrane was treated using two different approaches. Firstly, the covalent attachment of polyvinyl alcohol (PVA) through Glutaraldehyde (GA) onto the surface and secondly the redox initiated grafting of dimethyl amino ethyl methacrylate (DMAEMA PVA and DMAEMA grafting solutions were applied at four different concentrations).

The PVA and DMAEMA modifying agents were successfully grafted onto the membrane top layers and were confirmed by the functional groups, present, using the Attenuated Total Reflectance–Fourier Transform Infrared spectroscopy (ATR-FTIR) spectra. The morphology of the membrane surfaces was investigated using Scanning Electron Microscopy (SEM), before and after treatment. SEM analysis showed better membrane structures with PVA grafting compared to DMAEMA.

The cross-section images depicted a noticeable change in the thickness of the top layers of the modified membranes from both procedures. An increase in the concentration of the PVA aqueous solution caused an increase in the membrane surface roughness and a decrease of the pure water flux. Contrary, an increase in the concentration of the DMAEMA aqueous solution caused an increase of the pure water flux.

During the anti-biofouling test with *E. coli* as biological foulant the sterilization ratio for the unmodified, DMAEMA and PVA modified membranes was 33.8, 76.8 and 36.8 %, respectively. The DMAEMA modified membrane with the highest sterilization ratio shows better anti-microbial properties against microorganism tested, obstruct growth and multiplication. This was confirmed with the pure water flux test, where the unmodified, DMAEMA and PVA modified membranes declined by 46, 26 and 29 %, respectively. Again the modified membranes showed better anti-biofouling properties and prove to minimize *E. coli* bacteria adsorption on the membrane surface.

Anti-fouling properties and performance of membranes was tested using synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent using a lab scale RO process. The salt rejection for both PVA and DMAEMA modified membranes decreased as its concentration increased, due to the change in surface charge. The flux decline ratio for the unmodified membrane was the highest at 38.21%. As the modifying agent concentration of PVA and DMAEMA increased, the flux decline ratio (FDR) decreased to 21.78 and 25.54% respectively. The flux recovery ratio (FRR) for the unmodified membrane was the lowest at 68.61%. As the modifying agent concentration of PVA and DMAEMA increased so did the flux recovery ratio to 82.16 and 83.57%, respectively. It was clearly shown that the PVA and DMAEMA grafting solutions changed the structure of the membrane top layer, enhancing the resistance to fouling.

It can be confirmed that the membrane performance improved when applying modifications, using various modifying solution concentrations with an RO process.

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DEDICATION

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RESEARCH OUTPUTS

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TABLE OF CONTENTS

DECLARATION	ii
ABSTRACT	iii
ACKNOWLEDGMENTS	v
DEDICATION	vi
RESEARCH OUTPUTS.....	vii
TABLE OF CONTENTS.....	viii
LIST OF TABLES.....	xv
LIST OF FIGURES	xxii
LIST OF PHOTOS	xxvi
LIST OF SYMBOLS	xxvii
ABBREVIATIONS	xxviii
Chapter 1	1
1 Introduction	2
1.1 Background	2
1.2 Municipal wastewater treatment processes.....	4
1.2.1 Problem related to discharge of Municipal wastewater effluent	4
1.2.1 Reverse Osmosis Membranes	4
1.2.2 Fouling.....	5
1.2.3 Remediation of membrane fouling	5
1.3 Research Problem.....	7
1.4 Research topic.....	7
1.5 Research question.....	8
1.6 Objectives of the research.....	8
1.7 Delineation.....	9
1.8 Thesis Outline.....	10

Chapter 2	11
2 Literature review	12
2.1 Water shortages	12
2.2 Technologies for the treatment of municipal waste water	13
2.2.1 Oxidation ditch (OD) process	13
2.2.2 Ponds and constructed wetlands (PCW).....	13
2.2.3 Trickling/ biological filter (TBF) process	13
2.3 Conventional activated sludge (CAS).....	14
2.4 Membrane bioreactor process.....	15
2.4.1 Use of MBR in waste water process	16
2.5 Membrane Technology.....	18
2.6 Membrane Configuration	20
2.6.1 Hollow fine fibre.....	20
2.6.2 Plate and frame membranes	21
2.6.3 Tubular membranes	21
2.6.4 Spiral wound membranes.....	22
2.7 Membranes types based on pore size.....	23
2.7.1 Micro filtration	23
2.7.2 Ultrafiltration	23
2.7.3 Nanofiltration	23
2.7.4 Reverse osmosis.....	23
2.8 MBR-RO system in the treatment of municipal waste water treatment	25
2.9 RO Membrane fouling	27
2.9.1 Factors causing membrane fouling	27
2.9.2 Effects of membrane fouling on the filtration process	28
2.10 Type of foulants	29
2.10.1 Fouling by organics	29

2.10.2	Fouling by inorganics	29
2.10.3	Fouling by colloids	30
2.10.4	Fouling by microorganisms (Bacterial fouling)	30
2.11	RO Membrane fouling in the treatment of MWW secondary effluent	31
2.11.1	Fouling Mechanism	31
2.12	Membrane fouling tests	33
2.13	Minimizing membrane fouling	35
2.14	Membrane surface modification	36
2.14.1	Surface Modification by Additives (Surface adsorption)	36
2.14.2	Surface Modification by Coating	37
2.14.3	Surface Modification by Graft Polymerization	37
2.14.4	Grafting by UV irradiation	37
2.14.5.	Grafting by Chemical Reaction	38
2.15	Other surface modification methods	39
2.15.1	Modification by Molecular Imprinting	39
2.15.2	Modification by Enzyme immobilization	39
2.15.3	Surface Modification by Interfacial Polymerization or Copolymerization	40
2.15.4	Surface Modification by Plasma Treatment	40
2.15.5	Ion-beam Irradiation	40
2.15.6	Surface Modification by Heat Treatment	41
2.16	Modifying agents used in this study	42
2.16.1	Dimethyl Amino Ethyl Methacrylate (DMAEMA)	42
2.16.2	Poly vinyl alcohol (PVA)	43
2.17	RO process parameters	45
2.17.1	Salt rejection	45
2.17.2	Flux	45
2.17.1	Pressure	46

2.17.2	Recovery	47
2.17.3	Temperature	47
2.17.4	pH	47
2.18	Membrane surface characterization	48
2.18.1	Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR)	48
2.18.2	Atomic force microscopy	50
2.18.3	Nuclei Magnetic Resonance (NMR)	50
2.18.4	X-ray photoelectron spectroscopy	52
2.18.5	Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)	52
Chapter 3		55
3	Methodology	56
3.1	Introduction	56
3.2	Membrane surface modification	57
3.2.1	Introduction	57
3.2.2	Equipment	58
3.2.3	List of Chemicals	59
3.2.4	Experimental procedure for modification of membrane using PVA	60
	Modification steps in brief	60
3.2.5	Experimental procedure for modification of membrane using DMAEMA solution	62
	Modification steps in brief	62
3.3	Bio-fouling Experiments	63
3.3.1	Introduction	63
3.3.2	Apparatus for Biofouling test	65
3.3.3	E-coli culturing steps	68
3.3.4	Static adhesion test performed on membrane	68
3.3.5	Water flux tests experiments with contaminated membranes	69
3.4	RO system process description	70

3.4.1	Experimental Set-up	70
3.4.2	Making of the synthetic feed	73
3.4.3	RO system operation	74
3.4.4	RO cell start up procedure	74
3.4.5	Membrane cleaning	76
3.4.6	Membrane replacement	76
3.4.7	Equipment used during RO operation	78
3.5	Membrane characterization analysis	80
3.5.1	ATR-FTIR analysis	80
3.5.2	SEM analysis	80
Chapter 4		81
4	Results and discussion	82
4.1	Membrane surface modification using PVA: membrane characterization	82
4.1.1	ATR-FTIR analysis	82
4.1.2	SEM analysis	84
4.2	Membrane surface modification using DMAEMA: membrane characterization	87
4.2.1	ATR-FTIR analysis	87
4.2.2	SEM analysis	88
4.3	Pure water flux and % salt rejection of PVA modified membrane	91
4.4	Pure water flux and % salt rejection of DMAEMA modified membranes	93
4.5	Flux of PVA modified membranes during the fouling test	96
4.6	Flux of DMAEMA modified membranes during the fouling test	98
4.7	Antifouling properties of PVA modified membranes	100
4.7.1	Antifouling properties of PVA modified membranes model	102
4.8	Antifouling properties of DMAEMA modified membranes	104
4.8.1	Antifouling properties of DMAEMA modified membranes model	106
4.9	Membrane anti biofouling properties	108

Chapter 5	112
Conclusion	113
Recommendations	115
Bibliography	117
Appendix A	128
RO cell experimental runs with unmodified membrane	128
Appendix B	142
RO cell experimental runs with 0.2 g/L PVA modified membranes	142
Appendix C	156
RO cell experimental runs with 0.15 g/L PVA modified membranes	156
Appendix D	170
RO cell experimental runs with 0.1 g/L PVA modified membranes	170
Appendix E	183
RO cell experimental runs with 0.05 g/L PVA modified membranes	183
Appendix F	198
RO cell experimental runs with 0.1 mol/L DMAEMA modified membranes	198
Appendix G	212
RO cell experimental runs with 0.05 mol/L DMAEMA modified membranes	212
Appendix H	226
RO cell experimental runs with 0.02 mol/L DMAEMA modified membranes	226
Appendix I	239
Biofouling test: pure water flux of selected membranes for the test after 30 hours contact with E. coli bacterial solution	239
Appendix J	247
Sample calculations of RO parameters	247
Flux	248
Salt Rejection	248

Flux Decline Ratio (FDR)	248
Flux Recovery Ratio	249
Appendix K	250
Modifying agent solutions preparation (Sample calculation) & Design expert models reports of FDR	250
PVA polymer solution and GA solution preparations	251
DAMEMA monomer an initiators solutions preparation ($\text{Na}_2\text{S}_2\text{O}_5$ and $\text{K}_2\text{S}_2\text{O}_8$) GA solution	252
Design expert model report: Flux decline ratio of DMAEMA modified membranes.....	254
Design expert model report: Flux decline ratio of PVA modified membranes	257
Appendix L	261
Testing procedure of physical and chemical parameters of the RO process	261
Flux	262
Electrical Conductivity (EC)	262
Total Dissolved Solids (TDS).....	262
Turbidity	262
Temperature	262
Appendix K	263
Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR) data of PVA modified membranes.....	263
Appendix L	268
Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR) data of DMAEMA modified membranes	268

LIST OF TABLES

Table 2-1: Comparison of biological performances of the full-scale conventional activated sludge (CAS) and pilot-scale hollow-fiber (HF) and flat-sheet (FS) membrane bioreactor (MBR) (adapted from Radjenovic, et al., 2009).	15
Table 2-2: water quality requirement: case of irrigation (agriculture, landscape, turf grass) (adapted from Pedrero et al., 2010).	16
Table 3-1: Membrane surface modification-PVA	61
Table 3-2: Membrane surface modification-DMAEMA	62
Table 3-3: Experiments summary	69
Table 3-4: RO system equipment	71
Table 3-5: Synthetic feed solution composition and characteristics	73
Table 3-6: RO system operating conditions	77
Table 3-7: Experiments summary	79
Table 4-1: Reported values of membrane sterilization ratios obtained from the selected membranes	108
 Table A- 1: Membrane specification and initial operating conditions of experimental run:	129
 Table A-3. 1: Pure water Flow rate of the unmodified membrane before fouling experimental run 1	136
Table A-3. 2: Pure water Flow rate of the unmodified membrane before fouling experimental run 2	137
 Table A-4. 1: Pure water Flow rate of the unmodified membrane after fouling experimental run 1	138
Table A-4. 2: Pure water Flow rate of the unmodified membrane after fouling experimental run 2	138
 Table A-5. 1: Calculated values of the normalized flux and Flux decline ratio (FDR) of unmodified membranes	139
 Table A-6. 1: Summarized values of the calculated parameters of unmodified membranes after 42 hours fouling test using the synthetic feed	141

Table B- 1: PVA modifying solutions at various concentrations.....	143
Table B- 2: Membrane specification and initial operating conditions of experimental run:	143
Table B-3. 1: Measured and calculated process parameters of 0.2 g/L PVA modified membrane (Experimental run 1)	144
Table B-3. 2: Measured and calculated process parameters of 0.2 g/L PVA modified membrane (Experimental run 2)	146
Table B-4. 1: Pure water (DI water) flow rate of the 0.2 g/L PVA modified membrane before fouling experimental run 1	150
Table B-4. 2: Pure water (DI water) flow rate of the 0.2 g/L PVA modified membrane before fouling experimental run 2	151
Table B-5. 1: Pure water Flow rate of 0.2 g/L PVA modified membrane after fouling experimental run 1.....	152
Table B-5. 2: Pure water Flow rate of 0.2 g/L PVA modified membrane after fouling experimental run 2.....	152
Table B-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.2 g/L PVA modified membranes	153
Table B-7. 1: Summarized values of the calculated parameters of 0.2 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed.....	155
Table C- 1: PVA modifying solutions at various concentrations	157
Table C- 2: Membrane specification and initial operating conditions of experimental run:	157
Table C-3. 1: Measured and calculated process parameters of 0.15 g/L PVA modified membrane (Experimental run 1)	158
Table C-3. 2: Measured and calculated process parameters of 0.15 g/L PVA modified membrane (Experimental run 2)	160

Table C-4. 1: Pure water (DI water) flow rate of the 0.15 g/L PVA modified membrane before fouling experimental run 1.....	164
Table C-4. 2: Pure water (DI water) flow rate of the 0.15 g/L PVA modified membrane before fouling experimental run 2.....	165
Table C-5. 1: Pure water Flow rate of 0.15 g/L PVA modified membrane after fouling experimental run 1.....	166
Table C-5. 2: Pure water Flow rate of 0.15 g/L PVA modified membrane after fouling experimental run 2.....	166
Table C-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.15 g/L PVA modified membranes	167
Table C-7. 1: Summarized values of the calculated parameters of 0.15 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed.....	169
Table D- 1: PVA modifying solutions at various concentrations	171
Table D- 2: Membrane specification and initial operating conditions of experimental run:	171
Table D-3. 1: Measured and calculated process parameters of 0.1 g/L PVA modified membrane (Experimental run 1)	172
Table D-3. 2: Measured and calculated process parameters of 0.1 g/L PVA modified membrane (Experimental run 2)	174
Table D-4. 1: Pure water (DI water) flow rate of the 0.1 g/L PVA modified membrane before fouling experimental run 1	178
Table D-4. 2: Pure water (DI water) flow rate of the 0.1 g/L PVA modified membrane before fouling experimental run 2	178
Table D-5. 1: Pure water Flow rate of 0.1 g/L PVA modified membrane after fouling experimental run 1.....	179
Table D-5. 2: Pure water Flow rate of 0.1 g/L PVA modified membrane after fouling experimental run 2.....	179

Table D-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.1 g/L PVA modified membranes	180
Table D-7. 1: Summarized values of the calculated parameters of 0.1 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed.....	182
Table E- 1: PVA modifying solutions at various concentrations.....	184
Table E- 2: Membrane specification and initial operating conditions of experimental run:	184
Table E-3. 1: Measured and calculated process parameters of 0.05 g/L PVA modified membrane (Experimental run 1)	185
Table E-3. 2: Measured and calculated process parameters of 0.05 g/L PVA modified membrane (Experimental run 2)	187
Table E-4. 1: Pure water (DI water) flow rate of the 0.05 g/L PVA modified membrane before fouling experimental run 1.....	191
Table E-4. 2: Pure water (DI water) flow rate of the 0.05 g/L PVA modified membrane before fouling experimental run 2.....	192
Table E-5. 1: Pure water Flow rate of 0.05 g/L PVA modified membrane after fouling experimental run 1.....	193
Table E-5. 2: Pure water Flow rate of 0.05 g/L PVA modified membrane after fouling experimental run 2.....	194
Table E-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.05 g/L PVA modified membranes	195
Table E-7. 1: Summarized values of the calculated parameters of 0.05 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed.....	197
Table F- 1: DMAEMA modifying solutions at various concentrations	199
Table F- 2: Membrane specification and initial operating conditions of experimental run:.....	199

Table F-3. 1: Measured and calculated process parameters of 0.1 mol/L DMAEMA modified membrane (Experimental run 1)	200
Table F-3. 2: Measured and calculated process parameters of 0.1 mol/L DMEMA modified membrane (Experimental run 2)	202
Table F-4. 1: Pure water (DI water) flow rate of the 0.1 mol/L DMAEMA modified membrane before fouling experimental run 1.....	206
Table F-4. 2: Pure water (DI water) flow rate of the 0.1 mol/L DMAEMA modified membrane before fouling experimental run 2.....	207
Table F-5. 1: Pure water Flow rate of 0.1 mol/L DMAEMA modified membrane after fouling experimental run 1	208
Table F-5. 2: Pure water Flow rate of 0.1 mol/L DMAEMA modified membrane after fouling experimental run 2	208
Table F-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.1 mol/L DMAEMA modified membranes	209
Table F-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.1 mol/L DMAEMA modified membrane	211
Table G- 1: DMAEMA modifying solutions at various concentrations.....	213
Table G- 2: Membrane specification and initial operating conditions of experimental run:	213
Table G-3. 1: Measured and calculated process parameters of 0.05 mol/L DMAEMA modified membrane (Experimental run 1)	214
Table G-3. 2: Measured and calculated process parameters of 0.05 mol/L DMEMA modified membrane (Experimental run 2)	216
Table G-4. 1: Pure water (DI water) flow rate of the 0.05 mol/L DMAEMA modified membrane before fouling experimental run 1	220
Table G-4. 2: Pure water (DI water) flow rate of the 0.05 mol/L DMAEMA modified membrane before fouling experimental run 2	221

Table G-5. 1: Pure water Flow rate of 0.05 mol/L DMAEMA modified membrane after fouling experimental run 1	222
Table G-5. 2: Pure water Flow rate of 0.05 mol/L DMAEMA modified membrane after fouling experimental run 2	222
Table G-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.05 mol/L DMAEMA modified membranes	223
Table G-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.05 mol/L DMAEMA modified membrane	225
Table H- 1: DMAEMA modifying solutions at various concentrations	227
Table H- 2: Membrane specification and initial operating conditions of experimental run:	227
Table H-3. 1: Measured and calculated process parameters of 0.02 mol/L DMAEMA modified membrane (Experimental run 1)	228
Table H-3. 2: Measured and calculated process parameters of 0.02 mol/L DMEMA modified membrane (Experimental run 2)	230
Table H-4. 1: Pure water (DI water) flow rate of the 0.02 mol/L DMAEMA modified membrane before fouling experimental run 1	234
Table H-4. 2: Pure water (DI water) flow rate of the 0.02 mol/L DMAEMA modified membrane before fouling experimental run 2	234
Table H-5. 1: Pure water Flow rate of 0.02 mol/L DMAEMA modified membrane after fouling experimental run 1	235
Table H-5. 2: Pure water Flow rate of 0.02 mol/L DMAEMA modified membrane after fouling experimental run 2	235
Table H-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.02 mol/L DMAEMA modified membranes	236
Table H-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.02 mol/L DMAEMA modified membrane	238

Table I- 1: Number of E.coli colonies in solutions, determined by manual plate counting method	240
Table I- 2: Membrane specification and initial operating conditions of experimental run:	240
Table I-3. 1: Pure water flux of the unmodified membrane after 30 hours contact with E. coli (experimental run 1)	241
Table I-3. 2: Pure water flux of the unmodified membrane after 30 hours contact with E. coli (Experimental run 2)	242
Table I-4. 1: DI water flux of the 0.015 g/L PVA modified membrane after 30 hours contact with E. coli (Experimental run 1)	243
Table I-4. 2: DI water flux of the 0.015 g/L PVA modified membrane after 30 hours contact with E. coli (Experimental run 2)	244
Table I-5. 1: DI water flux of the 0.05 mol/L modified membrane after 30 hours contact with E. coli (Experimental run 1)	245
Table I-5. 2: DI water flux of the 0.05 mol/L modified membrane after 30 hours contact with E. coli (Experimental run 2)	246

LIST OF FIGURES

Figure 2-1: Conventional activated sludge system (adapted from Peinemann & Nunes, 2010).	14
Figure 2-2: Membrane bioreactor configurations: (a) side stream MBR (b) submerged MBR (Judd, 2015).	17
Figure 2-3: Diagram of a water treatment using a membrane (adapted from Kucera, 2011)	18
Figure 2-4: Deconstructed hollow fibre membrane module (Wang et al., 2008)	20
Figure 2-5: Plate and frame membrane module (Kucera, 2015)	21
Figure 2-6: Tubular membrane module (Porter, 1989)	22
Figure 2-7: Cutaway view of spiral wound module (Coulson, 1962)	22
Figure 2-8: Graphic illustration of concentration polarization and fouling occurring at the surface of a RO membrane (Asadollahi et al., 2017; Pabby et al., 2015)	32
Figure 2-9: Diagram showing the difference between grafting chains onto the surface of the membrane and coating onto the surface of the membrane (Shahkaramipour et al., 2017)	38
Figure 2-10: Chemical structure of 2N dimethyl aminoethyl methacrylate (Wang et al., 2015)	42
Figure 2-11: Chemical structure of membrane after modification (Wang et al., 2015)	43
Figure 2-12: Chemical structure of polyvinyl alcohol (Asadollahi et al., 2017)	43
Figure 2-13: Graphic illustration of grafting of PVA with GA as a initiator on a TFC PA membrane surface using (Yutao Hu et al., 2016)	44
Figure 2-14: Water flux of a reverse osmosis membrane Vs pressure	46
Figure 2-15: Characteristics of functional groups frequencies on FTIR spectra (Coates, 2006; Socrates, 2001)	49
Figure 2-16: Spin lattice relaxation time (T_1) and Spin-spin relaxation time (T_2) as function of the correlation time (T_C) for a particular sequence (Jonas & Gutowsky, 1968)	51
Figure 2-17: Illustration of an AFM apparatus (Xu et al., 2009)	52
Figure 2-18: Diagram of SEM apparatus (Xu et al., 2009)	53
Figure 2-19: Cross-sectional images of RO membranes (a) Polyamide composite membrane (b) Cellulose acetate membrane (Kucera, 2015)	54
Figure 3-1: Schematic representation of the RO system	72
Figure 3-2: Timeline during the fouling experiment using the RO cell	74
Figure 3-3: Chemical structure of a polyamide composite RO membrane (Kucera, 2015)	77
Figure 4-1: ATR-FTIR spectra of PVA modified membranes	83
Figure 4-2: SEM images of the unmodified membrane: (left) top view (right) cross-section	85

Figure 4-3: SEM images of the 0.05 g/L PVA modified membrane: (left) top view (right) cross-section.....	85
Figure 4-4: SEM images of the 0.1 g/L PVA modified membrane: (left) top view (right) cross-section.....	85
Figure 4-5: SEM images of the 0.15 g/L PVA modified membrane: (left) top view (right) cross-section.....	86
Figure 4-6: SEM images of the 0.2 g/L PVA modified membrane: (left) top view (right) cross-section.....	86
Figure 4-7: ATR-FTIR spectra of DMAEMA modified membranes	87
Figure 4-8: SEM images of the unmodified membrane: (left) top view (right) cross-section.....	89
Figure 4-9: SEM images of the 0.02mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section	89
Figure 4-10: SEM images of the 0.05mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section	89
Figure 4-11: SEM images of the 0.075 mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section.....	90
Figure 4-12: SEM images of the 0.1 mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section	90
Figure 4-13: Pure water flux of modified membranes and the observed salt rejection during filtration of the MSWWT MBR effluent synthetic feed solution- (grafting of PVA)	91
Figure 4-14: Membranes permeability in terms of pure (DI) water flux before and after fouling test	92
Figure 4-15: Pure water flux of modified membranes and the observed salt rejection during filtration of the MSWWT MBR effluent synthetic feed solution- (grafting of DMAEMA)	93
Figure 4-16 Membranes permeability in terms of pure (DI) water flux before and after fouling test	95
Figure 4-17: Time dependent flux of PVA modified membranes: treatment of the synthetic feed.	96
Figure 4-18: Time dependent flux of DMAEMA modified membranes during filtration of the synthetic feed	98
Figure 4-19: FDR during filtration of the synthetic feed and pure water FRR membranes (-PVA grafted membranes).....	100
Figure 4-20: Contour (left) and 3D (right) graphs portraying the effect of PVA concentration change on the flux decline during the filtration of the synthetic feed	102

Figure 4-21: Predicted values of the flux against actual values of flux obtained (PVA grafted membrane).....	103
Figure 4-22: FDR during filtration of the synthetic feed and pure water FRR membranes (DMAEMA grafted membranes).....	104
Figure 4-23: Contour (left) and 3D (right) graphs portraying the effect of PVA concentration change on the flux decline during the filtration of the synthetic feed	106
Figure 4-24: Predicted values of the flux against actual values of flux obtained (DMAEMA grafted membrane).....	107
Figure 4-25: Pure water flux of membranes before and after biofouling of E.coli bacteria	110
Figure B- 1: Permeate flux of 0.2 g/L PVA modified membranes at same operating conditions	149
Figure B- 2: average permeate flux of 0.2 g/L PVA modified membranes.....	149
Figure C- 1: Permeate flux of 0.15 g/L PVA modified membranes at same operating conditions	163
Figure C- 2: average permeate flux of 0.15 g/L PVA modified membranes	163
Figure D- 1: Permeate flux of 0.1 g/L PVA modified membranes at same operating conditions	177
Figure D- 2: average permeate flux of 0.1 g/L PVA modified membranes	177
Figure E- 1: Permeate flux of 0.05 g/L PVA modified membranes at same operating conditions	190
Figure E- 2: average permeate flux of 0.1 g/L PVA modified membranes.....	190
Figure F- 1: Permeate flux of 0.1 mol/L DMAEMA modified membranes at same operating conditions.....	205
Figure F- 2: average permeate flux of 0.1 mol/L DMAEMA modified membranes.....	205
Figure G- 1: Permeate flux of 0.05 mol/L DMAEMA modified membranes at same operating conditions.....	219
Figure G- 2: average permeate flux of 0.05 mol/L DMAEMA modified membranes	219

Figure H- 1: Permeate flux of 0.02 mol/L DMAEMA modified membranes at same operating conditions.....	233
Figure H- 2: average permeate flux of 0.02 mol/L DMAEMA modified membranes	233

LIST OF PHOTOS

Photo 3-1: A membrane fixed around the frame before modification	57
Photo 3-2: Rectangular frame with membrane fixed for modification	58
Photo 3-3: Hot plate magnetic stirrer (left) and Hg thermometer (right).....	58
Photo 3-4: Oven model used during modifications of membranes	59
Photo 3-5: Flasks and beakers types used for the preparation of E.Coli	65
Photo 3-6: petri dishes used during microbial growth	65
Photo 3-7: Incubator model used in the project	66
Photo 3-8: Lab Purifier (laminar flow) with UV light (Left), adjustable-volume micropipette (middle) and Bunsen burner (right)	66
Photo 3-9: Spectrophotometer model used in this project	67
Photo 3-10: Autoclave machine type used in the project.....	67
Photo 3-11: RO Cell system (lab 1.1, science building, CPUT, August 2017).....	70
Photo 3-12: Synthetic effluent.....	73
Photo 3-13: Pictures showing the two different spacers (left) and membrane placed with spacers in the cell (right) (lab 1.1, science building, CPUT, August 2017).....	74
Photo 3-14: Pictures illustrating the position of sealers on the module (left) and the correct placement of membrane on module (right) (lab 1.1, science building, CPUT, August 2017)	75
Photo 3-15: Cylindrical beaker (Left) and stop watch (right).....	78
Photo 3-16: YSI EcoSense EC300 conductivity meter model use during the experiments	78
Photo 3-17: COD RD125 thermo reactor (left) and spectrophotometer (right) models used in the project	79
Photo 4-1: Viable E.Coli colonies collected after contact with me membranes (From left to right: Unmodified membrane, PVA grafted membrane, DMAEMA modified membrane)	109

LIST OF SYMBOLS

A	Area (m^2)
EC	Conductivity (μS)
J	Water flux ($\text{L.m}^{-2} \text{ hr}^{-1}$)
M_w	Molecular weight (g/mol)
P	Pressure (bar)
R	Salt rejection (%)
T	Temperature ($^{\circ}\text{C}$)
t	Time (hours)
Δt	Time interval (min)
V	Volume (L)

Subscripts

f	Feed
p	Permeate
w^f	Time dependant
w^i	Initial water
w^t	Time dependant

ABBREVIATIONS

AA:	Acrylic acid (AA)
AC-HBPAE:	Acrylated hyper branched poly (amine ester)
AEMA:	Amino ethyl methacrylate
AFM:	Atomic force microscopy
ATR-FTR:	Attenuated total reflectance–Fourier transform infrared
BOD:	Biological oxygen demand
BSA:	Bovine serum albumin
DI:	Deionized
CA:	Cellulose acetate
CAS:	Conventional activated sludge process
CBMA:	Carboxybetaine methacrylate
COD:	Chemical oxygen demand
DMAEMA:	N, N-dimethylacetamide methacrylate
DTAB:	Dodecyltrimethyl ammonium bromide (DTAB)
EfOM:	Effluent organic matter
EMP:	Emerging micro-pollutants
FDR:	The flux decline ratio
FRR:	Water recovery ratio
GA:	Glutaraldehyde
HF:	Hollow fiber
HRT:	Hydraulic retention time
LPRO:	low pressure reverse osmosis membrane
MBR:	Membrane Bioreactor
NF:	Nanofiltration
NIPAm:	N-isopropyl acrylamide
NOM:	Natural organic matter
OD:	Oxidation ditch
P:	Pressure
PA:	Polyacrylic acid
PCW:	Ponds and constructed wetlands
PVA:	Polyvinyl alcohol

RO:	Reverse osmosis
SDS:	Sodium dodecyl sulphate
SEM:	Scanning Electron Microscopy
SRT:	Solid retention time
SS:	Suspended solids
TDS:	Total dissolved solids
T/BF:	Trickling Biological Filter
TFC:	Thin film composite
TFN:	Thin film Nano-composite
UF:	Ultra filtration
XPS:	X-ray photoelectron spectroscopy

Chapter 1

INTRODUCTION

1 Introduction

1.1 Background

Saqib & Aljundi, (2016) stated that improving the access to clean drinking water is a serious concern around the globe. According to Li et al., (2007), in the past few decades, water as a major source of living and production has become more and more critical due to excessive use and increasing contamination of natural water sources. As a result, secondary effluent from municipal wastewater treatment plants has been considered as an alternative source of quality water.

The application of membrane filtration has received much attention as it is been expanded to purification of water and wastewater treatment due to the standard of water quality that can be produced from this process. It also requires considerably less space and process time than other separation processes (Chennamsetty et al., 2006).

Li et al., (2007) says that the treatment of the secondary effluent before reuse often requires reverse osmosis (RO) to remove organic and inorganic contaminants.

However, Ponnusamy et al., (2013) indicated that a major concern associated with membrane processes in the treatment of wastewater is the degradation and poor performance, caused by fouling, which impedes membrane operation. Membrane fouling is caused by the deposition of unwanted materials on membrane surfaces such as inorganic compounds, dissolved organic matter, chemical reactants and biofilms by microorganisms. Fouling causes flux decline which leads to an increase in production cost due to an increase in energy demand. Pre-treatment of the feed solution and chemical cleaning of the fouled membranes also have a significant increase in the operational cost.

Saqib & Aljundi, (2016) confirm that membrane fouling, which still constitute a challenge in membrane technology can't be eradicated, but it can be minimized. Therefore, pre-treatment of the feed water or membrane modification is used to minimize fouling.

Sun et al., (2013) also point out the use of cleaning agents to minimize fouling and that pre-treatment measures have been used. Although problems of membrane fouling and flux decline in long-term operations, still persist. Cleaning the membrane regularly is likely to increase operation costs and decrease membrane module performance and operation efficiency. Membrane modification is the introduction of hydrophobic groups to the surface of the membrane.

1.2 Municipal wastewater treatment processes

According to Templeton & Butler, (2011), wastewater originates from domestic, commercial and industrial sources. Municipal wastewater treatment entails the treatment of domestic effluent into a cleaner product, which can be reused or discharged into local water surfaces.

In a conventional activated sludge (CAS) municipal wastewater treatment is divided into a primary and secondary treatment process. The primary process removes most of the solids from the effluent, but does not remove or degrade dissolved organic matter. Secondary treatment uses microorganisms to convert these organics to simple compounds and uses the energy of the sun to destroy pathogens. The effluent is then adequate to be treated with a RO system (Delgado, et al., 2011).

Melvin & Leusch, (2016) have specified five main treatment technologies for municipal wastewater treatment. These technologies include; conventional activated sludge (CAS), oxidation ditch (OD), ponds & constructed wetlands (PCW), trickling biological filter (TBF) and membrane bioreactor (MBR).

1.2.1 Problem related to discharge of Municipal wastewater effluent

Robinson et al., (2016) state that when secondary municipal wastewater effluent are discarded into local surface waters the risk of causing pervasive ecological responses includes the following; adverse effects on the physiology, growth, and survival of certain ecologically important aquatic plants; the reduction of water transparency and other disruptions to the normal ecological balance among vascular plants and algae as well as fish and invertebrate mortalities.

1.2.1 Reverse Osmosis Membranes

According to Cartagena et al., (2013), nanofiltration (NF) and reverse osmosis (RO) are the most promising technologies for the removal of emerging micro-pollutants (EMPs). Li et al., (2007) and Dolar et al., (2012) concur that the reverse osmosis (RO) process can be used to remove organic and inorganic contaminants present in secondary municipal effluent for reuse applications. The

nanofiltration and reverse osmosis membranes almost remove most of the EMPs that occur in the MBR effluent. NF membranes generally require less energy than the RO membranes, although many energy saving RO membranes are available. These RO membranes produce high flow rate rejections at low pressures (Cartagena et al., 2013).

1.2.2 Fouling

Xu et al., (2010) say that regardless of the improvement in membrane technologies, operating membranes in water and wastewater treatment plants, membrane fouling is a major challenge. Dissolved elements present in the secondary effluent can adsorb, accumulate or precipitate within or on the membrane surfaces, leading to membrane fouling.

Membrane declining performance and lifespan over extended time period is a foremost problem in the treatment of waste water due to fouling. Therefore, different methods have been developed to modify membrane surface characteristics to improve membrane performance and minimize fouling. Previous studies indicated that the fouling mechanism is related to membrane surface characteristics and interaction between membrane surfaces and foulants (Kang & Cao, 2011).

1.2.3 Remediation of membrane fouling

According to Sun et al., (2013) the aim of membrane modification is to handle the fouling effects when poly amide (PA) thin film composite (TFC) RO membranes. Membrane modification is classified into two groups namely: the modification of the membrane matrix (or bulk modification), which include blending and copolymerizing; and secondly membrane surface modification, which introduces polar groups or grafting hydrophilic monomers to the membrane surface.

Nguyen et al., (2012) confirm that membrane surface modification can efficiently inhibit the growth of microorganisms as it provides bacteriostatic properties to the membrane.

Saqib & Aljundi, (2016) indicate that membrane surface modification can be done through surface coating or surface grafting. However, it is pointed out that surface coating weakness is that the fragile interaction between the membrane and the coated layer ends up sweeping away that layer. Modification by surface grafting is one of the favourable methods to alter membrane surfaces and

minimize fouling. This involves covalent bonding among grafted chains with associated membrane.

1.3 Research Problem

The tertiary treatment of secondary MSWW MBR effluent with RO membranes provides an alternative source for the reuse of non-potable water in various applications and is beneficial for water resources and wastewater management. However, the major challenge associated with these treatment processes, is membrane fouling, which causes degradation and poor performance. Chemical grafting could minimise membrane fouling and possibly enhance the performance of a RO membrane.

1.4 Research topic

Li et al., (2007) motivates that to eliminate organic and inorganic contaminants present in secondary effluent from biological treatment using CAS-MBR process, RO could be used as a tertiary treatment.

Ishigami et al., (2012) indicates that there is a decline in water flux during the RO process and membrane deterioration, which occurs overtime, caused by membrane fouling. Consequently, there is an increase in cost as supplementary energy is required and membranes needs to be replaced. Surface roughness, morphology and other factors such as initial permeate flux; interactions between the membrane surface and some foulants are responsible for the mechanism of membrane fouling. Providing RO membranes with antifouling properties is a methodology in minimizing expenses. Various methods to modify RO membrane surfaces have been developed. This includes graft polymerization or surface coating. These processes inhibit the adhesion of foulant compounds and improve the antifouling properties of the membrane.

1.5 Research question

1. Can membrane modification using grafting improve membrane anti-biofouling properties?
2. What influence will membrane modification have on RO membranes when using synthetic or simulated municipal sewage waste water MBR secondary effluent feed?

1.6 Objectives of the research

The aim of this research is to improve membrane performance and resistance to fouling through chemical grafting in the treatment of a secondary MSWW MBR effluent with a lab scale RO process.

Secondary objectives is as follows:

1. To investigate the structure of membrane surfaces before and after surface grafting.
2. To assess the membrane resistance to biofouling using Escherichia coli (E. coli) bacteria solution.
3. To investigate the efficacy of two grafting polymers: DMAEMA & PVA on a low pressure RO polyamide membrane using a lab-scale flat cell with a simulated (synthetic) MSWW MBR secondary effluent as feed solution

1.7 Delineation

This study focused on surface modification of a TFC polyamide RO membrane through chemical grafting of two polymers: dimethyl amino ethyl methacrylate and Poly vinyl alcohol aqueous solution. E. coli bacteria solution was used to evaluate membrane anti-biofouling properties. Synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent was used in a lab-scale RO process, to evaluate membrane performance and resistance to fouling. ATR-FTIR and SEM analysis were used to study the structure of the membrane before and after surface grafting. This research focused on the effect of the variation of modifying agent concentrations on the performance of membranes. All other are delineated.

1.8 Thesis Outline

- Chapter 1** provides a detailed background of the entire study, calls attention to key points of this research such as the objectives, research question and significance of the study;
- Chapter 2** gives an in-depth detail of literature and theory in relation to the different topics linked to this research
- Chapter 3** gives details of the procedures, equipment and apparatus used for data acquisition
- Chapter 4** discusses different results obtained from experimental runs
- Chapter 5** concludes the research based on the results achieved and gives recommendations

Chapter 2

LITERATURE REVIEW

2 Literature review

2.1 Water shortages

Water resources as well as its quality degradation have become worldwide worries, which will intensify with increasing water demand, unexpected impacts of extreme events and climate change (Pedrero et al., 2010)

Gumbo et al., (2005) stated that with a population over 200 million people which are constantly increasing with time will results in fresh water shortages, thus intensifying in SADC countries.

South Africa is a semi-arid country due to geographic location where the volumes of rain are low at an average of 5mL per annum and evaporation rates are high with an average of 17mL per annum. This causes a depletion of the availability of fresh water to be supplied. Drinking water is of the highest quality and is frequently used for landscape irrigation; toilet & urinal flushing and industrial applications. This practice is not sustainable in context of water shortage Adewumi et al., (2010).

According to Adewumi et al., (2010), the potential of wastewater reuse for non-drinking water requirements is viewed as a viable alternative in the determination of overcoming the challenges of current and future water shortages in South Africa. A wide range of effective wastewater treatment technologies exist and successful wastewater reuse applications have been observed in many countries like Singapore, USA, Israel, Australia, Spain, Germany, United Kingdom and many more.

Waste water originates from different sources ranging from industrial to municipal. In South Africa municipal waste water reuse can be promoted due to the high volume of its population. The State of California in the USA are regarded as pioneers in efforts to promote water reclamation and reuse where residents reuse 656 million cubic meters from municipal effluent, overcoming challenges of fresh water shortages (Pedrero et al., 2010).

Lazarova & Bahri, (2004) indicate that wastewater treatment is essential for environmental safety and the reduction of wastewater discharge.

2.2 Technologies for the treatment of municipal waste water

The major treatment technologies for municipal wastewater are as follows: conventional activated sludge (CAS); oxidation ditch (OD); ponds & constructed wetlands (PCW); trickling biological filter (TBF) and membrane bioreactor (MBR) (Melvin & Leusch, 2016)

According to Hoinkis et al., (2012), CAS and MBR are the processes mostly used in the treatment of municipal wastewater, worldwide.

2.2.1 Oxidation ditch (OD) process

Oxidation ditch (OD) is a different activated sludge process, known as continuous loop reactor. It is preferred due to its high nitrogen and phosphorus removal characteristics (Lian-feng et al., 2011).

2.2.2 Ponds and constructed wetlands (PCW)

Mburu et al., (2013) stated that ponds and constructed wetlands (PCW) is a natural treatment system of sewage which presents some advantages over CAS and MBR process. It has low operation and maintenance costs since it does not require skill labour.

However, Chyan et al., (2016) indicated that constructed wetlands have a capacity and efficiency in nutrient removal, but remain far from satisfactory.

2.2.3 Trickling/ biological filter (TBF) process

According to Godoy-Olmos et al., (2016), trickling/ biological filter (TBF) processes uses fixed-film biological filters as biological treatment. Biological filters present some advantages which include low prices and simple design construction and operation.

2.3 Conventional activated sludge (CAS)

Radjenović et al., (2008) divide a conventional activated sludge (CAS) treatment process into the following stages:

1. Pre-treatment which includes screening and gridding;
2. Physical process of settling in a primary clarifier using a primary sedimentation unit;
3. Secondary biological treatment with an anaerobic and aerobic process.
4. The effluent of the biological treatment is then sent to secondary clarifiers.

Peinemann & Nunes, (2010) demonstrate the CAS system in the diagram in Figure 1, below:

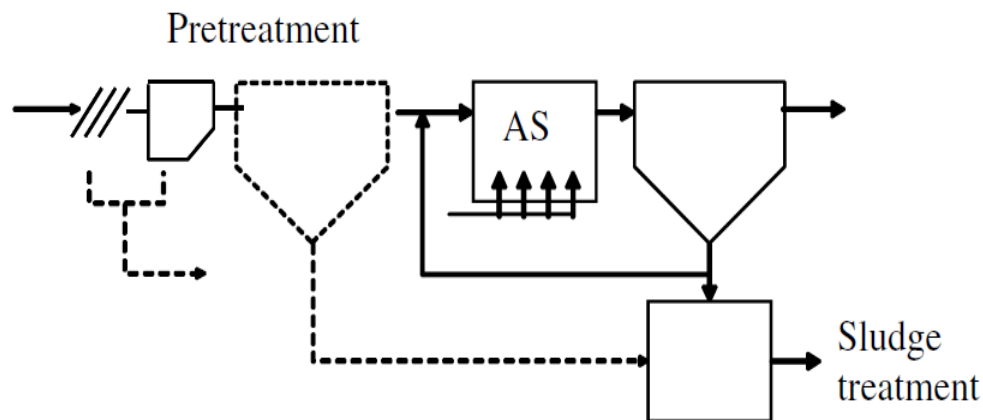


Figure 2-1: Conventional activated sludge system (adapted from Peinemann & Nunes, 2010)

According to Çeçen & Aktas, (2011) conventional activated sludge process stabilizes the wastewater aerobically or anaerobically where the growth of an activated mass of microorganisms is used. This process removes organic matter, mostly nutrients, nitrogen, phosphorus, as well as trace concentrations of inorganics.

2.4 Membrane bioreactor process

Judd, (2015) says that a membrane bioreactor (MBR) is a hybrid system of biological and filtration treatment, where micro or ultrafiltration membranes are used. MBR has received much attention as it produces clarified and largely disinfected effluent.

Lazarova & Bahri, (2004) indicated that MBR can be used as a final treatment process in water reuse if followed by disinfection of the effluent.

Radjenovic, et al., (2009) stated that for the past 25 years the MBR, one of the advanced technologies, has gained more attention over the CAS process due to high quality treated effluent for possible solutions for safe reclamation. This technology integrates biological degradation of organic matter present in wastewater with membrane filtration thus surpassing the limitations of the CAS treatment such as limited operational solids retention time (SRT) and sludge settling characteristics. Results comparing CAS with MBR follows in table 1.

Table 2-1: Comparison of biological performances of the full-scale conventional activated sludge (CAS) and pilot-scale hollow-fiber (HF) and flat-sheet (FS) membrane bioreactor (MBR) (adapted from Radjenovic, et al., 2009).

Parameter	Average concentration (mg/L)		
	CAS effluent	HF MBR	FS MBR
TSS	20	1.5	2
NH ₄	30	0.4	0.8
BOD	88	40.5	31
COD	15	4	4

Lazarova & Bahri, (2004) say that the MBR process is also referred to membrane activated sludge, as this later is used for the biological treatment of the sewage prior to membrane filtration. Some advantages include higher percentages removal; minimizing cost on water by recycling the treated water.

According to (Sabrina et al., 2013), the biological treatment is responsible for the conversion of particulates in wastewater which are transformed into end products before membrane filtration intervenes.

However, there is a need to make sure that the secondary treatment of the waste water provides water quality required for different reuse applications. Failure to properly treat and manage wastewater could results into adverse health effects (Pedrero et al., 2010).

Table 2-2: water quality requirement: case of irrigation (agriculture, landscape, turf grass) (adapted from Pedrero et al., 2010).

	Degree of restriction use			Unit
Salinity	Low	Moderate	severe	dS/m
EC	≤0.7	0.7–3.0	≥3.0	mg/l
TDS	450	450-2000	2000	
Sodium				
Surface irrigation	≤3	3–9	≥9	mg/L
Sprinkler irrigation	≤70		>70	mg/L
Chloride				
Surface irrigation	≤140	140–350	≥350	mg/L
Sprinkler irrigation	mg/l ≤100		>100	mg/L
Nitrogen (total)	≤5	5-30	>30	mg/L
Bicarbonate	≤90	90-500	>500	mg/L
Residual Chlorine	≤1	1-5	>5	mg/L
pH	Range from 6.5-8.			

Hoinkis et al., (2012) stated that the purpose of water reuse requires higher water quality. The removal of contaminants from water using MBR is only effective to a certain degree, thus this technology is used as pre-treatment process. If higher water quality water is desired, a consecutive additional membrane tertiary treatment step should follow.

2.4.1 Use of MBR in waste water process

According to Cartagena et al., (2013) the membrane bioreactor system is one of the best appropriate technologies for wastewater treatment. The MBR technology presents far more advantages over conventional activated sludge plants which include better effluent quality, good disinfection, smaller footprint and reactor volume, less sludge production and the possibility of operating at higher volumetric loading rates and biomass concentrations.

The configuration of MBR differs, from flat sheet to cylindrical shape, with the membrane positioned outside or inside the tank. Fenu et al., (2012) point out that the first MBRs were made in external configurations, in 1960s, thereafter; the development of immersed MBR enhanced the market of MBR, as it proved to be energetically higher than the first membrane configuration. Judd, (2015) says that when placed inside the tank, permeate is removed on the permeate side under suction pressure, or it is extracted on the brine side through the static head of pressure. And when operated outside the tank, water infiltrates the membrane under pressure, as shown in the figure below. The required pressure for an external MBR is generally higher than the one of a submerged MBR.

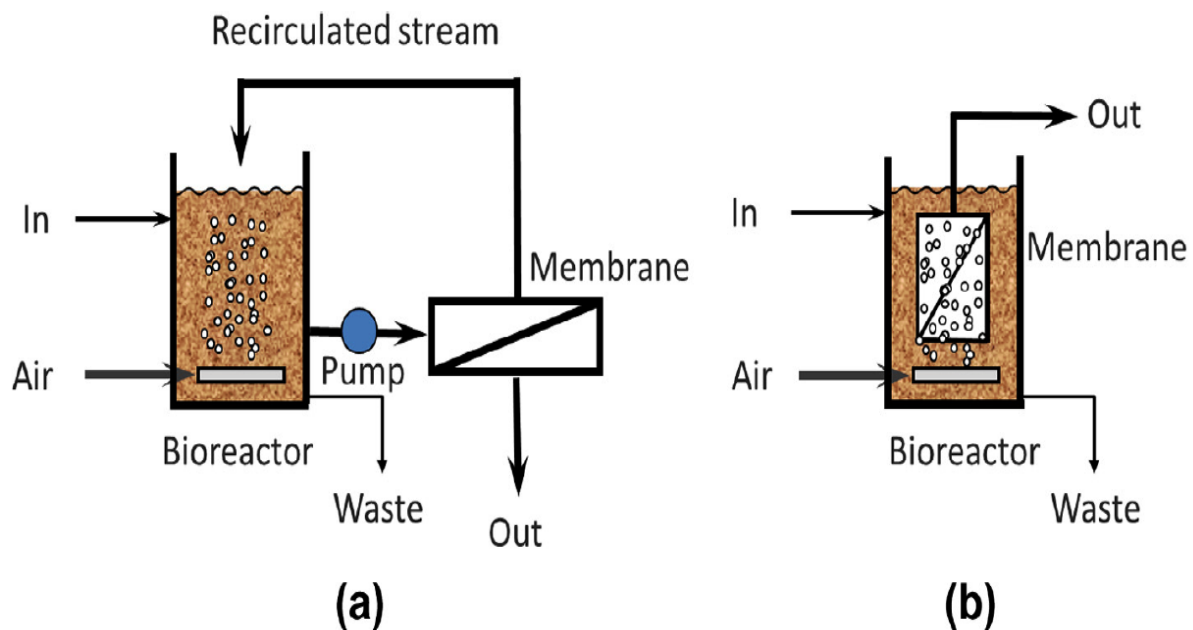


Figure 2-2: Membrane bioreactor configurations: (a) side stream MBR (b) submerged MBR (Judd, 2015).

2.5 Membrane Technology

A membrane filter is a thin porous film which blocks the path of materials bigger in size than its pores and results in cleaner water (Ponnusamy et al., 2013).

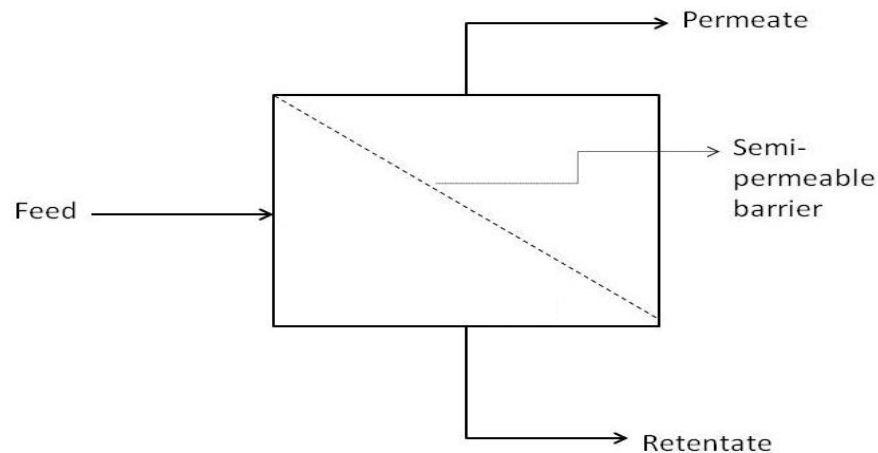


Figure 2-3: Diagram of a water treatment using a membrane (adapted from Kucera, 2011)

According to Childress & Elimelech, (1996) there are two membrane structures commercially available: asymmetric and thin-film composite (TFC). Asymmetric membranes are made by casting a polymer into a homogeneous film by a single-step phase inversion method. The result is a dense surface skin on a porous sub layer. The skin and the sub-layer have the same chemical composition. Thin film composite membranes, on the other hand, are made from a two-step procedure. Firstly, a thick, porous support layer is created, and secondly, an ultrathin barrier layer is coated on top of the supported layer. Unlike asymmetric membranes, the skin and the sub layer usually have different chemical compositions.

TFC membranes have many advantages which kept them competitive in the commercial market (Lau et al., 2012).

According to Saqib & Aljundi, (2016) the major advantage of TFC membranes over asymmetric membranes is that each particular layer in a TFC membrane can be adjusted for its individual application. At the thin barrier layer solvent flux and salt rejection are merged. The porous layer acts as a support and enhances the strength and providing compression resistance along with minimum flow resistance.

Childress & Elimelech, (1996) states that the TFC membranes have higher salt rejection than asymmetric membranes. It also includes a much wider feed pH range that is less susceptibility to microbiological attack, and better hydraulic stability than asymmetric membrane material.

A typical TFC RO membrane is made of three layers:

- Polyester (130 nm thick),
- Polysulfone (40 nm thick)
- Polyamide (0.3–3 nm thick).

The polyamide layer (active layer) is the layer accountable for salt rejection (Xu et al., 2010).

Zhao et al., (2013) indicated that the final membrane structure is influenced by the composition such as concentration, solvent and additives, the non-solvent or the mixture of non-solvents and the environment.

Membrane fouling is a serious problem for hollow fiber membranes especially in applications of water treatment. When fouling takes place on membrane surfaces, it causes flux decline that results into the increase in production cost due to energy demand (Zhao et al., 2013).

2.6 Membrane Configuration

Based on the shape, according to Kucera, (2015), there are four types of membranes modules:

- Hollow fiber
- Plate-and-frame
- Spiral wound
- Tubular

2.6.1 Hollow fine fibre

De & Mondal, (2012) states that hollow fibres membranes are made up of extrudes cellulose acetate material and do not allow turbulent flow across the fibre surface. This characteristic makes them more susceptible to scaling and fouling. It is difficult to clean the fouling area due to its failure to reach. Hollow fibres are mostly used in seawater desalination, where the fouling potential is minimal.

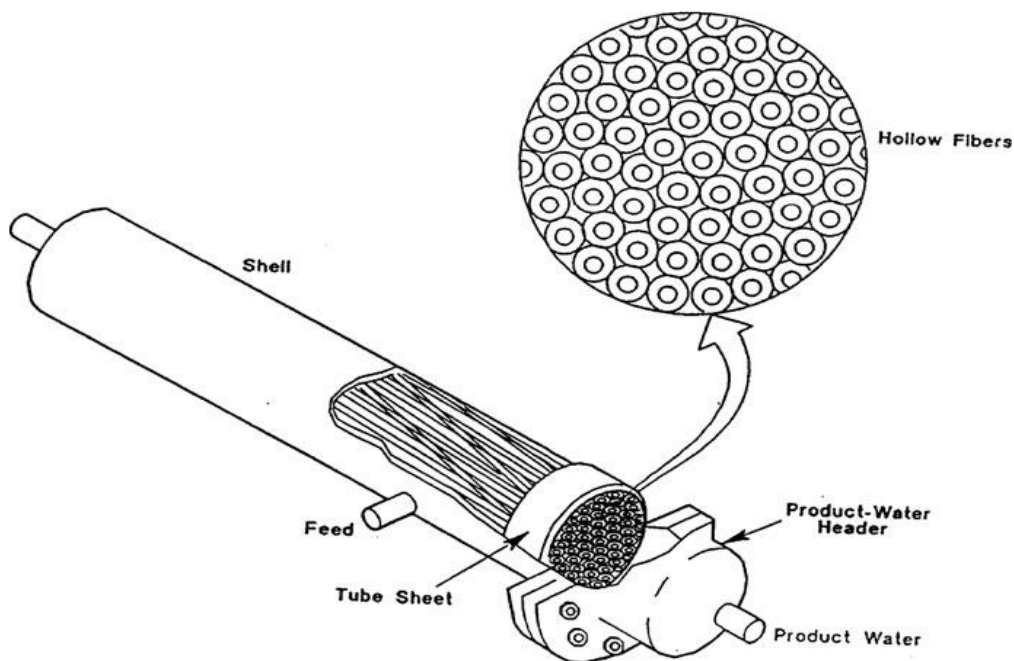


Figure 2-4: Deconstructed hollow fibre membrane module (Wang et al., 2008)

2.6.2 Plate and frame membranes

Plate and frame modules consist of flat sheet membranes sealed to a frame. This type of module operates easily when the waste streams contain high amounts of fouling agents. The plates provide a flow channel for permeate to be collected from a tube at the side of the plate through its pores (De & Mondal, 2012).

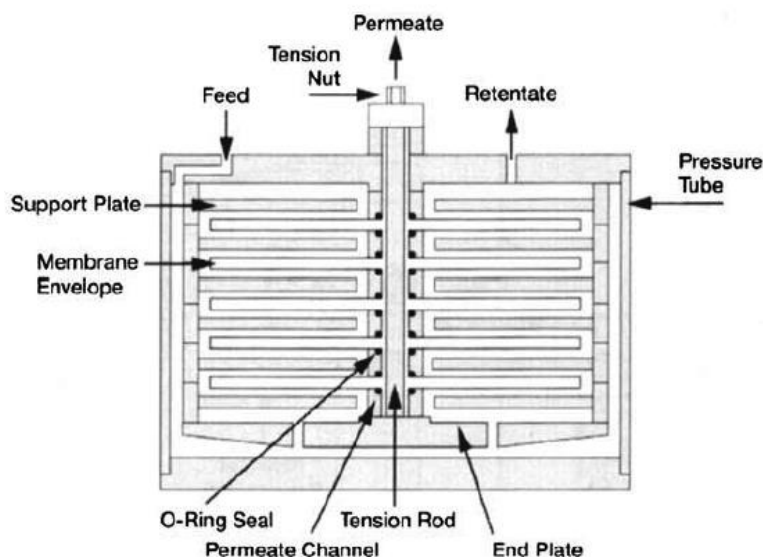


Figure 2-5: Plate and frame membrane module (Kucera, 2015)

Baker (2004), states that plate-and-frame module membranes are used for small-scale applications with reverse osmosis and ultrafiltration, when treating highly foulant effluent. This application is however expensive and leaks through the gaskets are identified as one of the main disadvantages. Their current applications are in electro dialysis and pervaporation.

2.6.3 Tubular membranes

Porter (1989) suggested that a tubular module may be the simplest configuration where a membrane is fixed inside the wall of the tube. Tubular membranes with diameters less than 2.54 cm which are exposed to fouling can easily be cleaned. However, they are too costly. Tubular structured membranes are mostly used to process feed with high dissolved and suspended solids which includes oil and grease.

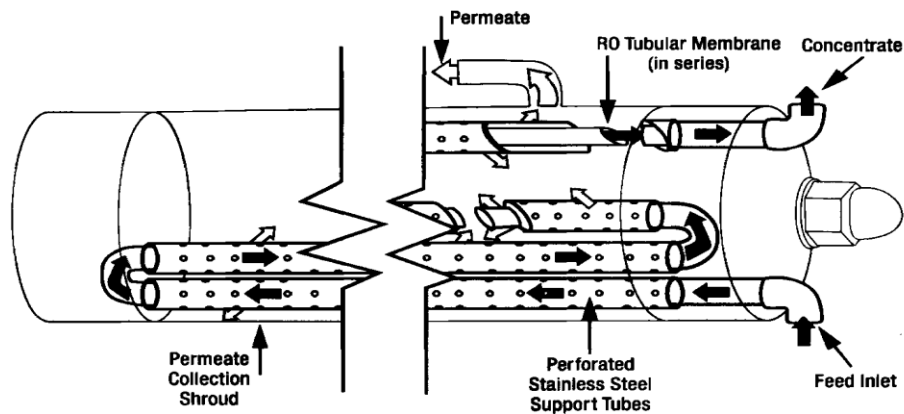


Figure 2-6: Tubular membrane module (Porter, 1989)

2.6.4 Spiral wound membranes

According to Radjenovic et al., (2009) spiral wound membranes are comprised of flat sheet membranes that are sealed together with feed spacers and permeate carriers. It can be used in brackish water treatment, protein separation, sea water desalination and more.

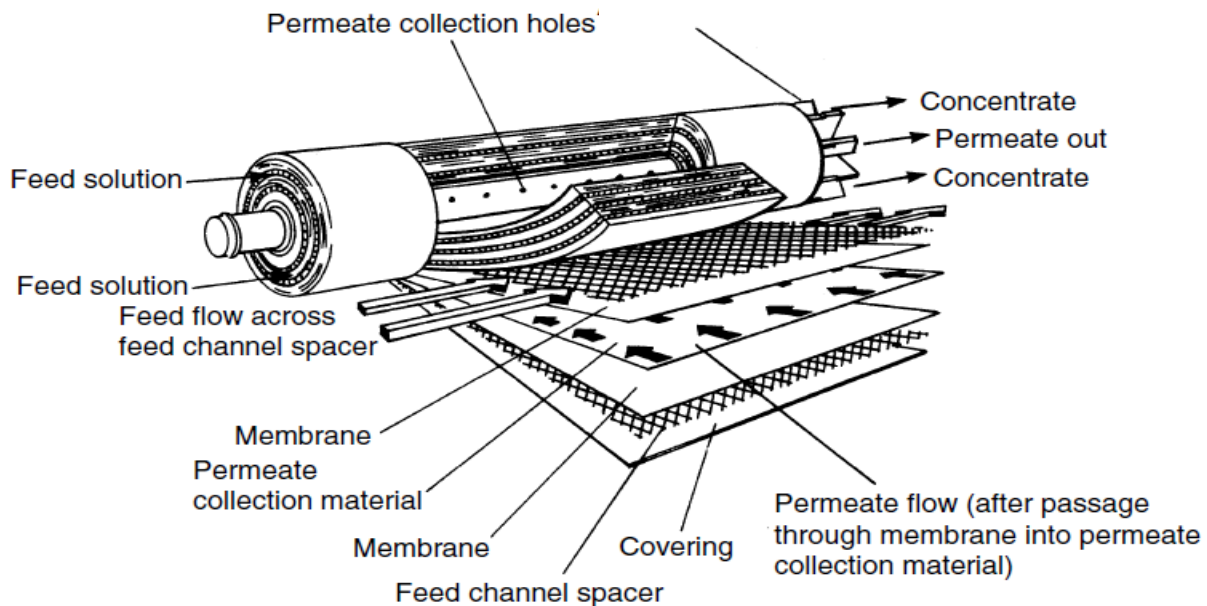


Figure 2-7: Cutaway view of spiral wound module (Coulson, 1962)

2.7 Membranes types based on pore size

Membrane filtration is divided into the following four types, depending on the size of the molecules to be filtered (Kucera, 2015):

- Micro filtration (MF)
- Ultra filtration (UF)
- Nano-filtration (NF), and
- Reverse Osmosis (RO) (Hyper filtration)

2.7.1 Micro filtration

Microfiltration (MF) membranes have the largest pore size of 0.1 micron. It is mostly used in the filtration of water as well as in the medication industry. MF membranes are also used in clarifiers and processes that require the removal of macromolecules. These types of membranes only remove microorganism from the solvents (Safe Drinking Water Foundation, 2009).

2.7.2 Ultrafiltration

Ultrafiltration (UF) membranes have a pore size of 0.01 microns. This membrane is used for the removal of suspended solids and some viruses. Similarly, to MF, UF cannot remove ions, except when used with activated carbon adsorption process (Safe Drinking Water Foundation, 2009).

2.7.3 Nanofiltration

Nanofiltration (NF) membranes are used for the removal of molecules of sizes bigger than 0.001 microns. Certain molecules such as organics and ions causes' water to be hard and NF are used to make it softer (Safe Drinking Water Foundation, 2009).

2.7.4 Reverse osmosis

A reverse osmosis membrane consists of a supporting layer with 50 μm and a barrier layer of 0.2 μm in thickness. RO processes do not include pore size, because it is function of diffusion which dictates the performance of the process. It is mostly used in food & pharmaceutical industries and the production of drinking water (Koch Chemical Technology Group, 2013).

According to Wang, et al., (2008), the phenomenon of osmosis, which is the diffusion of a liquid through a semi-permeable membrane, was discovered in 1748. The liquid diffuse from a channel with a low solute concentration to a channel with a higher solute concentration until an equilibrium is reached. When pressure is applied, water flows through a membrane from high solute concentration side to the low solute concentration side and thus, the separation of water from the solution is achieved. This is then called reverse osmosis (RO).

Table 2 Characteristics of composite polyamide RO membranes. (Kucera, 2010)

Property	Value for PA Membranes
Membrane Type	Homogenous asymmetric, thin-film composite
Pore size	~0.67 nm
Salt rejection (%)	~98+
Silica rejection (%)	~96+
pH range	2-12
Feed pressure (brackish membrane)	8.6 - 27.6 bar
Temperature tolerance	Up to 45°C
Surface charge	Negative (anionic)
Chlorine tolerance	< 0.02 ppm
Biological growth	Causes membrane fouling
Fouling tolerance	Fair
Surface roughness	Rough

2.8 MBR-RO system in the treatment of municipal waste water treatment

Dolar et al.,(2012) reported that a few studies conducted using a combined treatment system of MBR-NF or MBR-RO has focused on the removal of emerging micro-pollutants from wastewater. The authors reported that this treatment system can match each other very well to achieve an improved removal efficacy of a variety of trace organic contaminants. However, most of these studies were achieved at lab-scale level with either synthetic or real water spiked with target compounds.

Cartagena et al., (2013) conducted a study on a MBR pilot plant with FS and HF membranes coupled with another pilot plant that was equipped with NF/RO membranes to treat municipal wastewater from plant. The plant contained two submerged units with ten FS chloral polyethylene membranes of 0.8m² each, and four submerged HF polyamide modules 5m² each with a total surface area of 20m². The MBR permeates were treated by means of NF and RO installed parallel to each other and in line with the MBRs. The RO system consisted of one pressure vessel with a negative poly amide spiral wound membrane (FILMTEC,BW30-4040); and the NF system consisted of a polyamide spiral wound membrane (FILMTEC,NF90-4040).

The global removal efficiency of salinity (conductivity), organic matter (TOC) and nutrients (N-NO₃) for each permeate from the MBR after passing through the NF and RO membranes was presented. This study concluded a removal efficiency greater than 90% for all combined systems (MBR-NF and MBR-RO). The authors also pointed out that no differences in the concentrations of the target compounds were obtained when comparing NF and RO membranes used.

A study conducted by Dolar et al., (2012) on a MBR-RO pilot plant revealed that RO membranes can complement MBR treatment as the majority of compounds detected in the MBR effluent during this study, were completely removed and concentrations were very low after RO filtration. A removal efficiency of suspended solids (SS), turbidity and chemical oxygen demand (COD) of 99.99%, 99.72% and 97.3% was achieved, respectively.

The system consisted of a primary wastewater settler followed by a MBR with anaerobic, anoxic and aerobic tanks configuration and membrane compartment for biological nutrient removal. The membrane compartment holds 8 m² of flat sheet. A temperature of 16.1 °C was observed inside

the reactor. Sludge from WWTP was used as influent to the MBR. The MBR was operating with hydraulic retention time of 12.5 h and solid retention time was 45 days. The MBR provided feed water for the coupled RO system, which was composed of one pressure vessel housing, a double element with an automatic cleaning system. The RO membrane used was a high flow, crosslinked, aromatic polyamide, negative charge spiral wound module. The removal of selected emerging contaminants with RO membrane was higher than 99%. Although experimental results obtained revealed also that removal performance of pharmaceuticals present in the influent was significantly better in MBR–RO system, the authors point out that the long term implication concerning energy consumption, fouling, and waste treatment have not been considered, but would certainly affect the economic effectiveness of the technology.

2.9 RO Membrane fouling

According to Saqib & Aljundi, (2016) membrane fouling mechanism by which membrane is blocked or coated by some component present in the treated stream, which in the end results in declining of flux.

Sun et al., (2013) state that the reasons of membrane fouling include pore clogging, contaminants adsorption, the formation of the gel layer, concentration polarization (influenced by feed water composition and concentration), and cake layer formation.

Fouling at the surface and in the pores are the two mechanisms by which fouling membrane take place. However it is observed that surface fouling is more conspicuous in RO membranes, as these membranes don't have distinct pores and are considered to be dense (Saqib & Aljundi, 2016).

2.9.1 Factors causing membrane fouling

According to Saqib & Aljundi (2016) there are different types of foulants that attack RO membranes surfaces, which are categorized in four:

- Suspended particulate
- Dissolved organic substance
- Dissolved objects
- Bacterial material

Suspended solids include metal oxides in colloidal forms such as iron and silica. Non-biological (non-living organism with carbon based chemical structures) organic foulants include oil, cationic surfactants, plant materials and hydrocarbons. High concentrations of dissolved organic compounds in the secondary effluent can cause severe fouling of RO membranes (Li et al., 2007). Biological fouling cause's membrane decomposition and flux decline due to the formation of a layer on the membranes surface (Saqib & Aljundi, 2016).

Sun, et al., (2013) state that membrane surface parameters such as hydrophobicity, charge, morphology and roughness is critical to the mechanism of fouling which, will affect product quality and membrane performance

2.9.2 Effects of membrane fouling on the filtration process

According to Li et al., (2007) membrane fouling causes permeate flux and treated water quality, decline. As a solution, cleaning agents are used to minimize fouling. But frequent membrane cleaning causes shorten membrane life as well as increasing operational cost.

Nguyen et al., (2012) confirm that membrane fouling causes a rise in energy consumption as high pressure is needed to overcome the resistance of the layer formed on the surface of the membrane. The authors further indicate that acidic by-products which concentrate at the surface during the fouling mechanism causes membrane degradation.

2.10 Type of foulants

Baker, (2004) state that in reverse osmosis process membrane fouling remain the main cause of permeant flux decline and loss of product quality. Fouling can be devised in different categories which are discussed in below

2.10.1 Fouling by organics

Kucera, (2015) state that organics can adsorb to the surface of the and cause flux decline which cannot be recovered in some circumstances. The author further point out that at pH less than 9, poositve organics foulants easily adsorbe to the surface of the membrane. Most of organics foulants are nutrients to microbes and therefore favore bio-fouling, as many organics are nutrients for microbes. Based on the the total organic carbon (TOC) parameter, it is advised that the concentration be less than 3 ppm to minimize the possibility of fouling in RO process.

2.10.2 Fouling by inorganics

Dissolved metal salts (which are inorganics) that precipitate in the RO iffluent are the main cause of scale phenomenon on the membrane surface. As they are removed in the permeate, the concentration of ions in the feed increases until at some point the solubility limit is exceeded and the salt precipitates on the membrane surface (Baker, 2004)

The salts that usually cause scaling of the membrane are:

- calcium carbonate;
- calcium sulfate;
- silica complexes;
- barium sulfate;
- strontium sulfate;
- Calcium fluoride

2.10.3 Fouling by colloids

Wang et al., (2008) say that colloidal particles are major foulants in all kinds of membrane processes. The size of colloidal particles ranges from a few nanometers to a few micrometers. They are ubiquitous in natural waters and examples of inorganic colloids include metal oxides, clay minerals, colloidal silica, and silicon. There are also plenty of colloidal particles of organic and biological origins. Most colloids carry negative surface charge in pH range of natural waters. Under the drag force of permeate flux, these colloidal particles will accumulate on the RO membrane surface to form a cake layer. The formation of this cake layer of the deposited colloidal particles adds on an additional resistance to the membrane resistance. This type of fouling is known as colloidal fouling

2.10.4 Fouling by microorganisms (Bacterial fouling)

Wang et al., (2008) say that microorganisms present in the feed effluent cause biological fouling of the membrane. They adsorb to the surface of the membrane; once attached and multiplied, they can cause biodegradation of the membrane in long term operation.

Microscopies can be used for direct evaluation of fouling of microorganisms on the surface of the membrane, if not, the parameters such as solute rejection and permeate flux can be used measured and correlated to biofilm formation as this later influences them.

2.11 RO Membrane fouling in the treatment of MWW secondary effluent

The extent of RO membrane fouling also depends on the quality of the influent (Khan et al., 2014), Fouling during wastewater treatment is more complex than fouling that occurs in the treatment of sea water (Tang et al., 2016). Fouling in RO process mainly takes place due to scaling by inorganics, cake layer formed by colloids, interactions between organics and adhesion and growth of bacteria onto the surface of the membrane; and these mechanisms may take place concurrently (Liu et al., 2015; Tang et al., 2014)

Pandey et al., (2012) indicate the presence of large portion of colloidal, soluble impurities as well as suspended solids in UF treated effluent, and especially effluent organic matter (EfOM) which has been significantly involved in the RO fouling phenomenon. The authors further indicate that RO fouling in the treatment of wastewater biologically treated secondary effluent is also attributed to other foulants such as low-molecular weight dissolved organic components, sparingly soluble salts, metal oxides and hydroxides and biological agents.

2.11.1 Fouling Mechanism

Adsorption of feed solution contaminants, pores blockage, formation of gel, bacterial growth and interaction between solutes and membrane surface are considered to be the major mechanisms of membrane fouling (Pabby et al., 2015).

According to Zhao et al., (2010) in order to implement an appropriate fouling control strategy it is crucial to understand the fouling development during membrane operations and examine the fouled membrane surface and fouling layer structure as well analyze the feed water fouling potential.

Zhao et al., (2010) investigated the fouling behavior of a bench scale RO system by characterizing the fouling layer on the membrane. The RO system was fed with a secondary effluent from a full scale UF plant. At the start a flux decline which was caused by carbohydrates and proteins was observed which followed with a severe flux decline caused by organics and inorganics such as calcium phosphate and calcium carbonate.

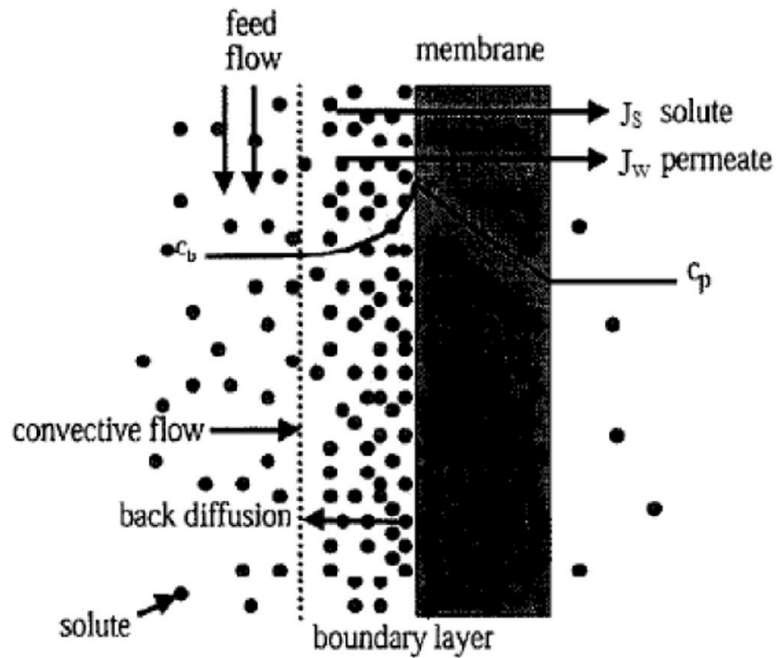


Figure 2-8: Graphic illustration of concentration polarization and fouling occurring at the surface of a RO membrane (Asadollahi et al., 2017; Pabby et al., 2015)

Concentration polarization affects the performance of RO membrane separation processes. Figure 2-7 above illustrates a convective transport of solute and water molecules to the surface of the membrane. Concentration at the surface of the membrane rises with time as most of solutes are retained while the solvent molecules cross the membrane. Although the solute molecules at the surface tend to diffuse back to the bulk solution due to diffusion phenomenon, the concentration of solutes progressively increases at the surface of the membrane as the diffusion is far slower than the convection. This consequently creates a boundary layer at the surface of the membrane (Asadollahi et al., 2017)

2.12 Membrane fouling tests

Zhao et al., (2013) say that it is necessary to have a membrane fouling testing method that is short in time, uses a minimum amount of test solution, and that involves a small membrane area, which is representative of the large-scale process.

Yisong Hu et al., (2016) evaluated membrane antifouling properties through cross- flow filtration tests with model foulants of BSA, SDS (Sodium dodecyl sulfate) and DTAB (Dodecyltrimethyl ammonium bromide). The concentrations of the model foulants in feed solutions varied. During the fouling experiments, time-dependent permeate flux was continuously monitored throughout the filtration period until a steady-state flux was obtained. After which, the membrane samples were flushed using de-ionized water for a certain duration to get rid of the foulants that loosely deposited on the membrane surface and re-evaluated for water flux under the same trans-membrane pressure of fouling experiment. The resulting flux profile was used to investigate the fouling behavior of the tested membrane. The flux decline ratio (FDR) and water recovery ratio (FRR) were thereafter calculated using the formulas below. A lower value of FDR value indicates better antifouling property, while higher FRR value shows the higher cleaning efficiency.

$$FDR\% = \frac{J_{w0} - J_{wt}}{J_{w0}} \times 100 \quad \dots \text{(Equation 1)}$$

$$FRR\% = \frac{J_{wc}}{J_{w0}} \times 100 \quad \dots \text{(Equation 2)}$$

J_{w0} : Initial water flux

J_{wt} : Time dependant permeate flux

J_{wc} : Re-evaluated water flux

Zhao, et al., (2013) further discuss previous studies where ESR spectroscopy was used to study fouling of a UF membrane and say that the fouling of the membrane was dependent on the size and shape of the macromolecular solute and the operating feed pressure. ESR spectroscopy provided a good method to study membrane fouling, by analyzing the ESR signal from the radical probe (added into the feed solution), the mobility of the macromolecular solute in the foulant layer, either on the membrane surface or in the membrane pore, could be investigated.

Another study mentioned by Zhao, et al., (2013) investigated the surface pore structure of a membrane using non-contact AFM. The performance of the membrane was linked with AFM analysis. AFM could then provide much information on the membrane fouling tests.

Cheng, et al. (2013) evaluated membrane fouling on a TFC RO membrane which was modified through redox initiated graft polymerization of N-isopropyl acrylamide followed by acrylic acid. Membrane fouling was assessed through cross-flow filtration using aqueous feed solution containing 200 mg/l BSA and 500 mg/l NaCl, at initial flux of 25.0 l/m² h. The permeate flux was constantly controlled over the experimental test period and the BSA fouling behavior was analyzed using the resultant flux profile. After fouling experiments, the fouled membrane was treated with deionized water by soaking for 3 hours at temperatures of 25 and 45 °C then flushing for 30 minutes. The water flux of the washed membrane was again evaluated with aqueous solution containing 500 mg/l NaCl.

Madhavi et. Al., (2017) investigated hyperbranched poly amine ester (A-HBPAE) on the surface of a poly amide nanofiltration membrane which was characterised by ATR-FTIR. Modified membranes were tested for performance using different types of synthetic feed such as BSA. Results revealed that the increase in membrane hydrophilicity and resistance to fouling was attributed to grafting of the modifying agent. It was concluded that a relationship existed between the concentration of the modifying solution and the resistance to fouling.

2.13 Minimizing membrane fouling

Membrane fouling is a fundamental problem when it comes to membrane processes. According to Shahkaramipour et al., (2017) an effective strategy to mitigate membrane fouling is to enhance antifouling properties through membrane modification

Sun, et al., (2013) indicated that the polymeric material of which most membranes are manufactured with such as cellulose, polysulfone, polyacrylonitrile, polyvinylidene fluoride, polyether ketone, polyamide, do not possess all the required properties. These properties include chemical durability, thermo stability, acid-base resistance property, good mechanical strength, to mention a few. Thus, researchers have applied the membrane modification methodology to improve performances and required membrane properties. Membrane modification is the introduction of grafting hydrophilic monomers to the surface.

Kang & Cao, (2011) observed that the methods used to minimize operational difficulty during membrane performance and expand membrane life time, can be pretreatment processes. And the design of new membrane modules and the development of antifouling RO membranes.

According to Zhao et al., (2013) the three important techniques of membrane modification : bulk modification of the material; surface modification of the membrane; and blending, which is also considered to be part of surface modification. Actions of membrane modification aim at conciliating hydrophobicity and hydrophilicity provide change to the material which then has a positive effect on flux and fouling reduction. The bulk modification of membrane material involves annealing of porous membranes by heat treatment.

Surface modification includes physical and chemical modification. These processes make the surface of the membrane more hydrophilic after the modification has been initiated. Techniques used to introduce or attach functional group to the surface of the membrane include graft polymerization, plasma treatment, physical pre-adsorption of hydrophilic components (Zhao et al., 2013).

2.14 Membrane surface modification

The demand for membrane technology in the field of wastewater treatment, medicine, pharmaceuticals, gas separation, and desalination has become significant worldwide. The properties of polymers are of primordial importance in many industrial applications.

Much attention has been paid to membrane modification as the performance of membranes are strongly influenced by their structures. Furthermore, the membrane surface can be contaminated, leading to the deterioration in membrane performance (Khulbe et al., 2004).

Thus, many studies have been devoted to the surface modification as a way of modifying the intrinsic properties of membranes and imparting improved anti-fouling property, easy-cleaning, lower flux decline and higher rejection (Wang et al., 2016).

According to Kang et al., (2011), membrane modification ranges from physical to chemical treatment. Both can be applied for the improvement of surface morphology and properties.

The treatments are classified as follows:

- Surface adsorption
- Surface coating
- Hydrophilization treatment
- **Surface grafting**

2.14.1 Surface Modification by Additives (Surface adsorption)

This method involves the blending with additive substances to change the chemical composition of the modified and thus imparting new properties to the membrane surface to improve its performance (Khulbe et al., 2010). Wang et al., (2006) modified the surface of phenolphthalein poly(ether sulfone) UF membranes by blending with acrylonitrile based copolymer containing ionic groups in order to modify surface electrical properties. Xu and Xu (2002) showed that adding polyvinyl pyrrolidone (PVP) or poly(ethylene glycol) (PEG) in the preparation of polyvinyl chloride (PVC) hollow-fibre UF membranes increased the membrane porosity and enhanced the permeation flux by changing the membrane morphology.

2.14.2 Surface Modification by Coating

This method involves modifying the membrane surface by contacting the surface of one side of the polymeric membrane (A) with a solution of a different polymer (B). A thin layer of polymer (B) remains on the membrane of polymer (A) after the solvent is evaporated Khulbe et al., (2010). Basheer et al., (2004) synthesized polyhydroxylated polyparaphenylene (PH-PPP) and coated on the surface of a porous polypropylene hollow-fibre membrane, thus imparting a higher sensitivity and selectivity in the extraction of fifteen organic chlorine pesticides from water.

2.14.3 Surface Modification by Graft Polymerization

Grafting involves the attachment of polymeric chains on the surface of a polymeric membrane. Although this method is used for any polymeric materials, it is mostly used for the surface modification of polyamide thin-film composite membranes or porous polypropylene membranes (Xu et al., 2009).

Saqib & Aljundi, (2016) states that surface grafting modification is an acceptable method to enhance membrane surface characteristics. It involves bonding monomer or mixture of monomers to the surface of the membrane. It is therefore initiated by chemical means, through UV-irradiation, by plasma induced techniques etc

Previous studies conducted by researchers such as Wang et al., (2015), Yutao Hu et al., (2016a), Cheng et al., (2013) have shown satisfactory effects in terms of membrane antifouling properties, as better results of membrane performance and resistance to fouling were obtained after membrane modification.

2.14.4 Grafting by UV irradiation

UV-ozone treatment have also been used to improve the permeability of poly(ethylene terephthalate) (PET), polyethylene (PE), polypropylene (PP) (Park et al., 2003).

Exposing PP to ozone in the presence of UV light is a simple and effective way of modifying its surface for imparting higher permeability and adhesion.

Nie et al., (1999) modified a polypropylene membrane by UV-ozone irradiation and studied the modified membrane using atomic force microscopy (AFM). They found that the modified membrane had a different surface morphology and increase adhesion (due to increased surface energy).

2.14.5. Grafting by Chemical Reaction

The membrane surface can also be modified by chemical reaction. Hydrophilic materials are grafted on the surface of the membrane to improve the hydrophilicity of the surface of the membrane thus reducing adsorption of foulants to the surface of the membrane. The hydration layer produced by hydrophilic material is accountable for the enhanced properties of the membrane surface (Shahkaramipour et al., 2017).

Freger et al., (2002) state that polymers attached to the surface of the membrane grow by propagation and factors such as modification time, polymer concentration and initiator concentration affect the coverage of the surface by polymers.

Modifying the surface via chemical bond formation also improve membrane chlorine resistances and anti-biofouling properties. High chlorine-resistance polymers such as poly(N,N-dimethylaminoethyl methacrylate and polyvinyl alcohol can be used for the treatment of membranes (Wei et al., 2010)

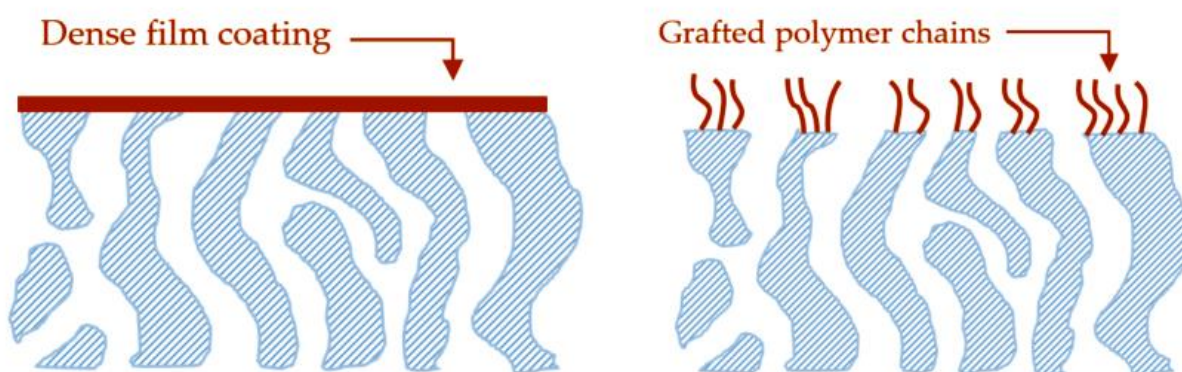


Figure 2-9: Diagram showing the difference between grafting chains onto the surface of the membrane and coating onto the surface of the membrane (Shahkaramipour et al., 2017)

2.15 Other surface modification methods

Other methods of modification applied to the surface of the membrane in order to improve the surface properties (such as hydrophilicity, hydrophobicity, biocompatibility, anti-fouling, surface roughness, antistatic and anti-bacterial properties) are discussed below:

2.15.1 Modification by Molecular Imprinting

Molecularly imprinted membranes add to conventional membrane separation technology (such as continuous operation, low energy consumption etc) the highly selective recognition of the molecular imprinting technology (MIT) (Xu et al., 2009). MIT allows the preparation of polymeric materials with selectivity towards specific molecules (Khulbe et al., 2009). There are several methods used in MIT among which the following can be cited:

- Surface photografting;
- Surface deposition;
- Emulsion polymerization of the membrane surface.

Molecularly imprinted membranes have excellent permeability, binding capability and good stability because of their high porosity and good mechanical properties (Xu et al., 2009).

2.15.2 Modification by Enzyme immobilization

An enzyme is a type of biocatalyst. Enzymes differ from conventional catalysts in that they have various advantageous features and have a high catalytic efficiency compared to chemical catalysts. In addition, enzymes generally operate under mild conditions of temperature, pressure and pH value. Therefore, introducing an enzyme to a membrane is beneficial in that it can impart the functions of catalyst to membrane, thus combining them with the conventional functions of a membrane (Xu et al., 2009). There are several methods used in enzyme immobilization among which the following can be cited:

- Physical absorption;
- Chemical binding;
- Entrapment.

2.15.3 Surface Modification by Interfacial Polymerization or Copolymerization

This technique involves allowing two reactive polymers to be dissolved in two different solvents and allowing them to come into contact. A reaction will occur at the interface between the two phases, and thus creating a thin polymeric film. This technique is well established in the synthesis of NF and RO membranes (Khulbe et al., 2009). Zhang et al., (2003) synthesized composite NF membranes subjected to concentration of antibiotics by interfacial polymerization of piperazine and trimesoyl chloride, some of which were coated with polyvinyl alcohol (PVA). It was found that this coated surfaces were smoother and more hydrophilic, which could improve the membrane anti-fouling ability.

2.15.4 Surface Modification by Plasma Treatment

Plasma is a highly unusual and reactive chemical environment because it contains highly excited atomic, molecular, ionic, and radical species. Plasma polymerization is a method that allows the synthesis of highly crosslinked polymers from non-functional monomers that are not used in conventional polymer synthesis. Plasma surface modification can impart higher biocompatibility and biofunctionality to the surface of the membrane without affecting the bulk properties of the membrane (Xu et al., 2009).

2.15.5 Ion-beam Irradiation

Chennamsetty et al., (2006) modified a commercial surfonated polysulfone water treatment membrane by ion-beam irradiation. During the irradiation process, cross-linking was induced by the breaking of sulfonic groups. This membrane modification resulted in decreasing the negative charge of the membrane and improving anti-fouling ability.

Good et al., (2002) also reported a positive impact on membrane performance and anti-fouling ability when they treated commercial water treatment membranes with ion-beam irradiation.

2.15.6 Surface Modification by Heat Treatment

This method involves treating membranes by applying heat to modify their surfaces. Preparation of polyethersulfone (PES) hollow-fibre membranes reported involved the dry-wet-spinning method and heating in an oven 120, 150 and 180 °C, which resulted in shrinking of the membrane and decreasing the pore size. This study indicated that increasing the temperature of the membrane resulted in a decrease of the pore size of the membrane (Ameri, et al., 2004).

2.16 Modifying agents used in this study

According to Rana & Matsuura, (2010), different studies have reported the use of Dimethyl amino ethyl (meth) acrylate (DMAEMA) for the graft polymerization of membrane surfaces where fouling tests were conducted using of *Escherichia coli* bacterial model foulant as well as BSA and lysozyme solutions. Authors pointed out a considerable improvement were observed with surface-modified membranes when fouling was eradicated. Polyvinyl alcohol has been used in the modification of NF and RO membrane surfaces for the treatment of aqueous solutions containing humic acid as model foulant as well as dyeing wastewater effluent. It was reported that the modified membrane considerably reduced fouling.

2.16.1 Dimethyl Amino Ethyl Methacrylate (DMAEMA)

Dimethyl aminoethyl methacrylate is a cationic monomer (Water soluble), containing a tertiary amine group (Zha et al., 2002)).

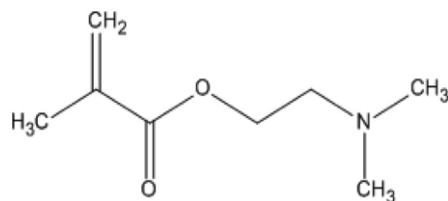


Figure 2-10: Chemical structure of 2N dimethyl aminoethyl methacrylate (Wang et al., 2015)

Research conducted on a polyamide TFC RO membrane involved the reaction of the polyamide selective surface with the monomer N, N-dimethyl aminoethyl methacrylate (DMAEMA). The grafted membrane was additionally treated with 3-bromopropionic acid (3-BPA). The modification aimed at enhancing membrane anti-biofouling properties and water flux (Wang et al., 2015). Chemical analyses of the membranes were conducted to characterize the structure of the membranes after modification. Fouling experimental runs used synthetic feed containing a known concentration of 2000 mg/L NaCl, then the model foulant BSA. Results obtained showed enhancement of membrane salt rejection and antifouling properties. Modified membrane also showed better resistance to microbial adhesion and anti-microbial properties than the unmodified membrane, when tested with both *E. coli* and *B. subtilis* bacterial solutions.

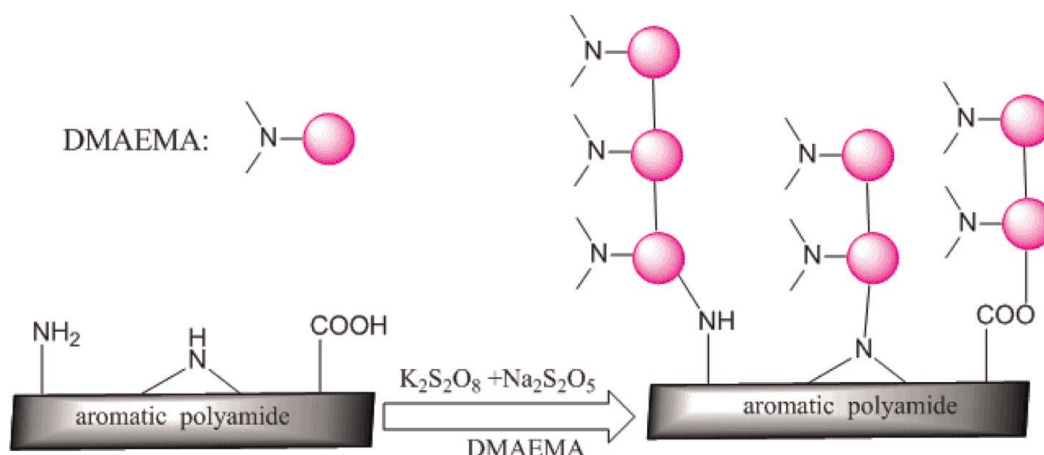


Figure 2-11: Chemical structure of membrane after modification (Wang et al., 2015)

2.16.2 Poly vinyl alcohol (PVA)

Polyvinyl alcohol is used in different applications as a binding and coating agent where moisture barrier and protection properties are required (Saxena, 2004)

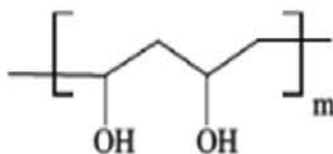


Figure 2-12: Chemical structure of polyvinyl alcohol (Asadollahi et al., 2017)

Introducing modifying agents by physical methods are found to be not sustainable as the agent is swept away from the surface of the membrane with time. Consequently, introducing PVA to the surface of the membrane via blending or physical means may not be sustainable with time during the RO operation as it may have impact on the performance stability and anti-fouling properties of the membrane. It is therefore useful to introduce PVA via chemical method (An et al., 2011).

Hu et al., (2016) used polyvinyl alcohol to improve membrane anti fouling properties and membrane resistance to chlorine exposure, on a TFC RO membrane. The membrane was treated with aqueous Glutaraldehyde (GA) followed by Poly vinyl alcohol (PVA) aqueous solution. Modification of the membrane was observed through the change of membrane physio-chemical properties. Fouling tests were conducted using BSA aqueous solution. PVA content of modifying solution was altered so as to improved salt rejection and water flux of the membrane. Results revealed that that PVA modified membranes presented resilient resistance to negative effects imposed by the chlorine disinfectants. Furthermore, the modified membrane was tested using an industrial effluent from a textile factory with a conductivity of 0.319 S/m; and COD of 135.4 mg/l. it is indicated that the modified membrane could improve rejection and resistance to fouling in tertiary treatment of industrial effluent

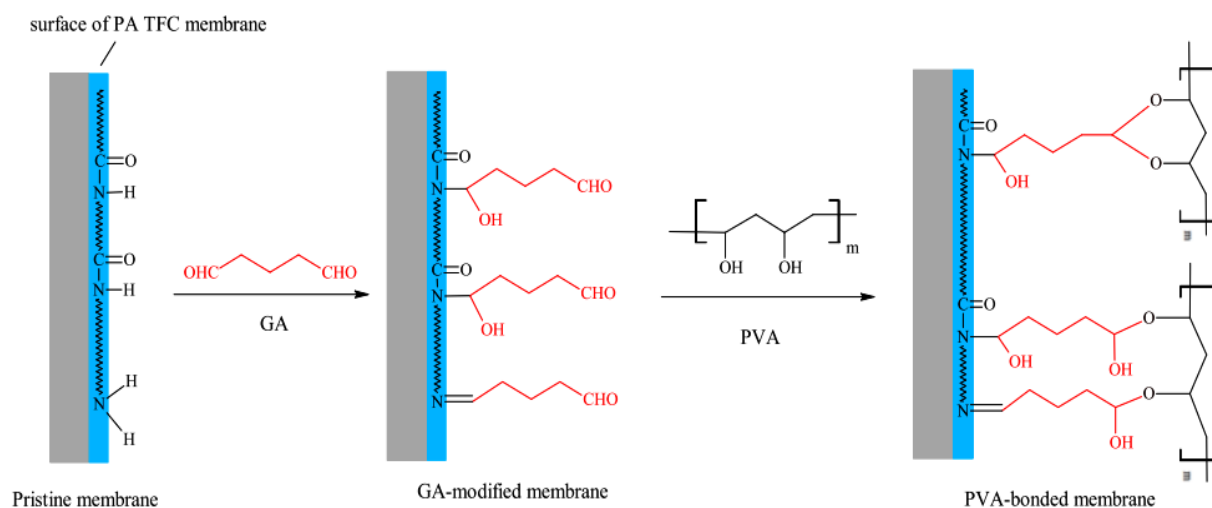


Figure 2-13: Graphic illustration of grafting of PVA with GA as a initiator on a TFC PA membrane surface using (Yutao Hu et al., 2016)

2.17 RO process parameters

2.17.1 Salt rejection

Reverse osmosis systems are used to remove dissolved salts; measuring salt rejection is therefore a direct way to monitor the performance of such systems.

Salt rejection describes the percentage of the feed water TDS that has been removed in the permeate water. The way to monitor the salt rejection is to measure permeate water conductivity. The permeate water conductivity should be measured for each pressure vessel daily. This helps to determine if a high salt passage problem is universal (indicating membrane damage); if it is isolated to a certain stage (possible fouling) or if it is isolated to an individual pressure vessel (indicating O-ring problems). Probing of individual pressure vessels can also be carried out to isolate a salt rejection problem to an individual membrane element (Kucera, 2011).

The flux observed salt rejection is calculated according to the following formula of Zhang et al., (2017):

$$R = \frac{C_f - C_p}{C_f} \times 100 \quad \dots \text{(Equation 3)}$$

C_f ($\mu\text{S/cm}$), C_p ($\mu\text{S/cm}$) and R (%) are the feed conductivity permeate conductivity and salt rejection respectively

2.17.2 Flux

Water flux is typically expressed as volume per area per unit of time. Flux is used to express the rate at which water passes through the surface of a reverse osmosis membrane. The flux of a RO membrane is directly proportional to temperature and pressure. The solute flux is the amount of total dissolved solids that has permeated a given area of the membrane per unit of time. Solute flux depends on the concentration gradient and not driving pressure. Therefore with increasing driving pressure, the concentration of solute in the permeate decreases due to constant salt leakage and increased water flux (Kucera, 2011).

The flux can be calculated according to the following formula of Hu et al., (2016):

$$J = \frac{V}{A \times \Delta t} \quad \text{(Equation 4)}$$

V , A , Δt and J are the volume of permeate (L), the effective area of the membrane (m^2), the interval time (hr) and the permeate water flux respectively

2.17.1 Pressure

Geankoplis, (2003) says that operating pressure in reverse osmosis is mostly in the range of 1035 Kpa to 10 350 Kpa. Kucera, (2015) states that operating pressure has a direct effect on the water flux and while its effect on the salt rejection is indirect.

When feed pressure increases, the permeation of water molecules through the membrane increases while solute molecules passage stays more or less unchanged, hence the permeate contains lower concentration of solutes (Geankoplis, 2003).

An increase in pressure drop generally results from a disruption in the flow pattern through the membrane, usually caused by the accumulation of material on the surface of the membrane (Kucera, 2011).

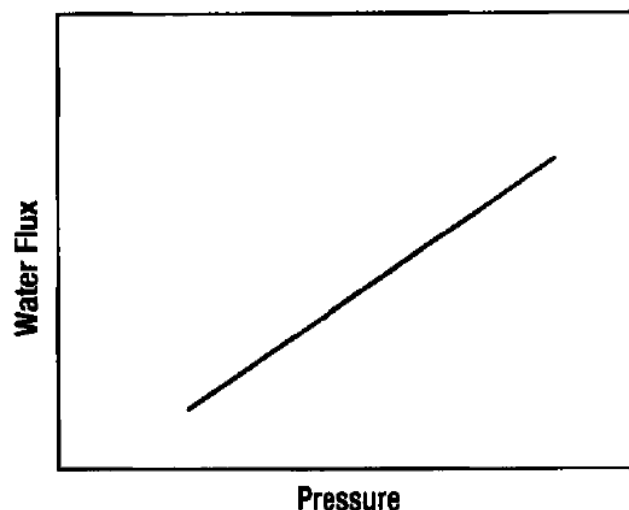


Figure 2-14: Water flux of a reverse osmosis membrane Vs pressure

2.17.2 Recovery

The percentage recovery is the fraction of the feed water which becomes permeate water. When the recovery rate is increased, there is less concentrate recycled but rather more collected as permeate. A high recovery rate can also cause soluble salts to precipitate. However, if the percentage recovery is too high for the RO design then it can lead to larger problems due to scaling and fouling (Kucera, 2015).

2.17.3 Temperature

Say that the temperature of the feed being treated is an essential parameter to observe in RO process. It is known that the effect of temperature on the salt rejection and water flux is complex. Passage of both solute and solvent (water) increases exponentially with increasing temperature. It has been reported that the water flux doubles as the temperature is increased by 30 °C; meanwhile the salt rejection declines slightly as the temperature increases (Baker, 2004).

2.17.4 pH

The stability of polyamide thin film composite membrane is susceptible to pH of the feed solution. However, the PA TFC membranes can operate within a pH ranging from 2 to 11. It should be noted that at higher temperature it is required to operate within narrowed ranges of pH. The pH also affects the rejection efficiency of the membrane. Highest rejections of most species are found to be in the pH range of 7 to 7.5. The reason of low salt rejection in the scenario of higher or lower pH operating condition is unfortunately not well explained in the literature; however, it can be attributed to stems from the ionic state of the rejected ions, as well as some changes on the molecular level with the membrane. On the other hand, the pH barely affects the water flux as this last stays somewhat constant over the range of pH (Kucera, 2011)

2.18 Membrane surface characterization

Zhao, et al., (2013) state that characterization of membrane after modification is critical to confirm whether the changes of composition (FTIR, NMR and XPS), morphological structure (AFM, SEM), and performance are desirable

Different analyses that most researchers use to study the structure of modified membrane include the following:

2.18.1 Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Fourier transform infrared spectroscopy is a quantitative and qualitative analysis method which allows the direct study of the chemical composition of material surfaces (Schmitt & Flemming, 1998). Shai, (2013) adds that Infrared spectroscopy is a very reliable technique to perform these duties.

FTIR uses measurements of vibrational spectra to identify the chemical structure of the material, after irradiation with H^+ ion beam (Chennamsetty, et al., 2006). Lin et al., (2016) indicated that ATR-FTIR is a simple and fast analytical technique with any special preparation necessary for quantitative measurements.

According to Chennamsetty, et al., (2006), ATR-FTIR can be used to study the advancement of chemical structure of membranes. Zhao et al., (2013) confirmed that ATR-FTIR can also be used to characterize chemical structure of membrane surfaces after surface modification. Cahill & Freger, (2017), stated that chemical changes occurring on the surface subsequent to chlorination can also be identified. The thickness of the thin layer can be determined when comparing intensities of the attached material bands as well as the polysulfone support layer or the attenuation of the support layer (Cahill & Freger, 2017).

Zularisam et al., (2006) stated that ATR-FTIR spectrometry also provides insight into the nature of foulants in the membrane texture. Functional groups of certain unknown foulants are also determined by ATR-FTIR by relating them to their vibrational energy of the atomic bonds.

Zularisam et al., (2006) continue: “Different functional groups absorb energy at different specific wavelengths that later can be translated into an intensity response”. However, this technique may be irrelevant in identifying certain functional groups when the absorption reading gives broad overlapping bands.

Adapted from Coates, (2006); Socrates, (2001), the figure 2-15 below, portrays a schematic representation of characteristic functional groups assigned to their frequencies.

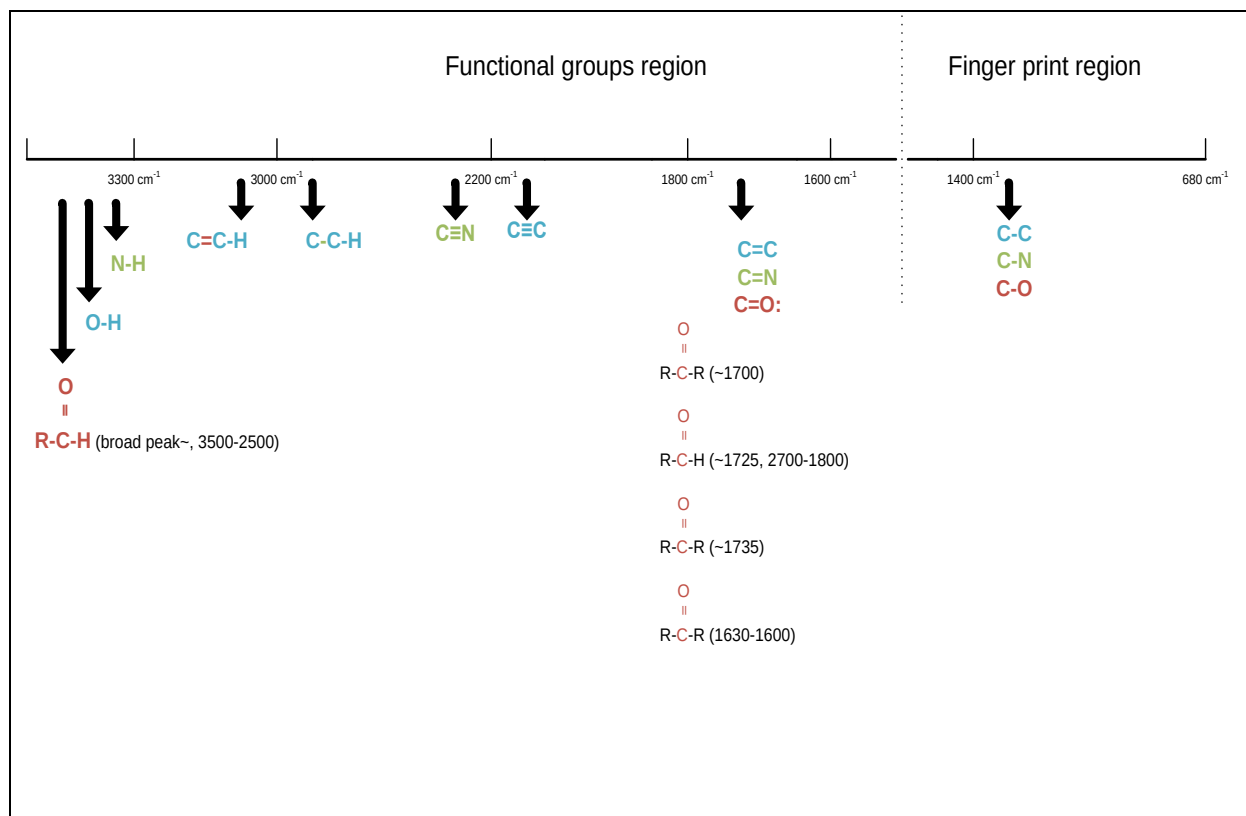


Figure 2-15: Characteristics of functional groups frequencies on FTIR spectra (Coates, 2006; Socrates, 2001)

Several researchers have estimated the extent of surface modification on membranes using the attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectroscopy to confirm grafting (Cheng et al., 2013); (Freger et al., 2002); (Wang et al., 2015).

2.18.2 Atomic force microscopy

According to Chennamsetty, et al., (2006) the AFM is used to investigate the surface morphology of the membrane. The analysis offers a simple and fast method to detect the surface structure of a wide range of materials. It allows obtaining 3D topographic data with a high vertical resolution. Moreover, AFM analysis also allows the calculation of average roughness's of the surface, the maximum peak-to-valley distances and the surface areas of the membranes (Cahill & Freger, 2017)

2.18.3 Nuclei Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is a technique that uses electromagnetic pulsations to evaluate the magnetic moment of a given NMR active nuclei such as ^1H , ^{13}C , ^{23}Na , etc. (Fridjonsson et al., 2015).

NMR was previously used to measure the magnetic shielding, electrical field gradient and coupling tensors in physics, and also to analyse structures in chemistry. However its applications since 1970 have extended to an imaging technique, to observe morphological variations in tissues, and as analytical aid medicine (Kuhn, 1990).

NMR analysis can be conducted on a solution state basis or solid state basis. Both methods are good in analysing chemical composition and they require signals from different chemical sites being analysed can be resolved from each other in some ways (Duer, 2008).

Cahill & Freger, (2017) state that solid state NMR spectroscopy allows studying molecular motion and molecular-level free-volume characteristics of the thin-film polymers.

Zhao, et al., (2013) also indicate that the NMR method is also commonly used for the configuration characterization of the chemically modified membrane materials. NMR is rarely used for direct characterization of the chemical compositions on the surface of membrane; but instead, it is often used to reflect the structure of the modifying agents.

NMR relaxation time analysis reveals the inflection actions of magnetic dipoles through which molecular motions in reverse osmosis and nanofiltration TFC membranes surface layer can be reflected. Relaxation analysis uses two different methods, namely pulsed wide line spectroscopy

and magic-angle spinning. Pulsed wide line spectroscopy allows determining the average local motion of the polymer surface layer by measuring the proton spin-lattice relaxation time T_1 and determining its correlation time T_C (Cahill & Freger, 2017).

The spin-lattice relaxation time T_1 describes the time taken by the system to reach thermal equilibrium. The spin-spin relaxation time T_2 is an easy accessible parameter and can also be used. It describes the time taken for the NMR signal to decay towards zero (loss of signal coherence) (Fridjonsson et al., 2015).

In the second method mentioned earlier, magic-angle spinning can be used detect the structure of ^{13}C and distinguish the mobility of specific sites within the thin-film membrane surface. ^1H T_1 of a thin-film polymer was measured and correlated to T_C after interfacial polymerization with the addition of dimethyl sulfoxide (DMSO). It was observed that chains within the thin-film layer were less mobile and had a higher number of amide linkages acting as hydrogen bonding sites, making easy the passage of water molecules and hence enhancing water flux without compromising much the salt rejection (Cahill & Freger, 2017).

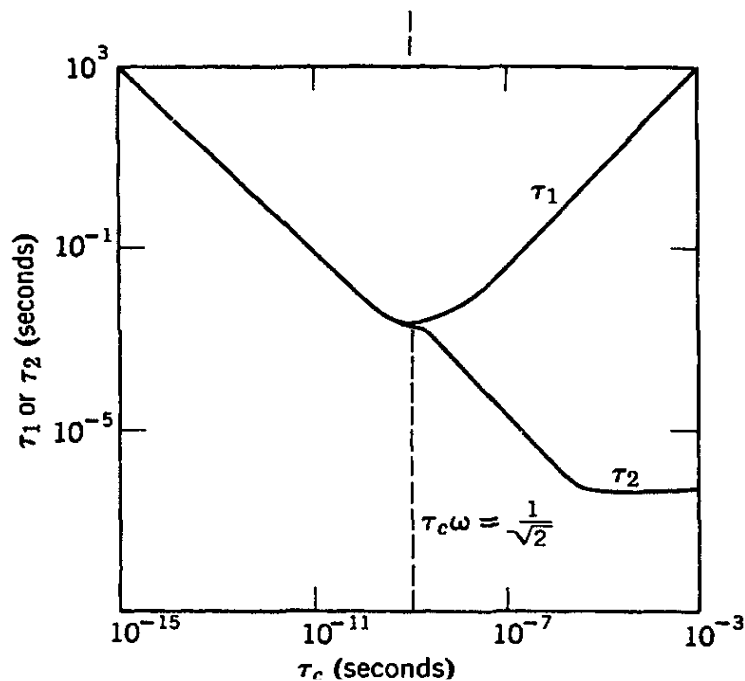


Figure 2-16: Spin lattice relaxation time (T_1) and Spin-spin relaxation time (T_2) as function of the correlation time (T_C) for a particular sequence (Jonas & Gutowsky, 1968)

2.18.4 X-ray photoelectron spectroscopy

The XPS technique is used to measure the elemental composition, chemical and electronic state of the elements present within a material. It is also used in the characterization of modified membranes by previous researchers (Zhao et al., 2013).

Cahill & Freger, (2017) conducted XPS analysis and studied C, N, and O core levels of aromatic rings, amide groups, and carboxylic acid groups. The results revealed an increase in the amide linkages relative to the pendant carboxylic acid groups in the thin film composite RO membrane formed through interfacial polymerization with the addition of dimethyl sulfoxide (DMSO)

2.18.5 Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

Micro-techniques often used in characterization of morphology and structure of modified membranes include SEM and AFM. Straight observation of the features of surfaces and cross-section of modified membranes with the assistance of micro-technique can directly reveal the difference of morphologies and structures before and after modification (Zhao, et al., 2013).

AFM is part of scanning force microscopes, which produce images by a force signal formed by the interaction of the tip-specimen. AFM is also preferred due to its great power to cope with macromolecules and perform at Nano-scale; reason why it is found to be a crucial instrument in nanotechnology (Xu et al., 2009).

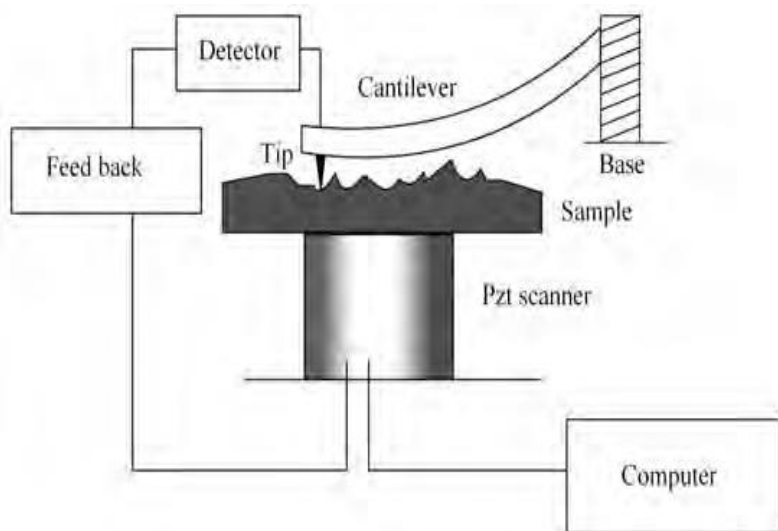


Figure 2-17: Illustration of an AFM apparatus (Xu et al., 2009)

Totten & Liang, (2004) say that AFM can be used to determine the Nano-mechanical properties of a the membrane surface layer; and, can also successfully evaluate membrane surface structure with the calculation of surface free energy by the measurement of the contact angle during wetting by the test liquid. However, Zhao et al., (2013) say that SEM is the most frequently used method for direct observation in the studies on modification of membranes.

Abdullah et al., (2014) say that only restricted information on sample preparation for SEM analysis has been reported despite its common use for membrane surface properties characteristics.

However, it is known that preparation of samples for SEM analysis needs to be done carefully. It usually requires metal coating since polymeric membranes are mostly nonconductive. Freeze-drying operation needs to be applied in order to dry wet membranes, otherwise water need to be replaced by a low surface tension liquid to prevent the damage by the capillary force. A freeze-fracturing treatment is advised for the preparation of a cross-section sample to avoid damaging the porous structure (Xu et al., 2009).

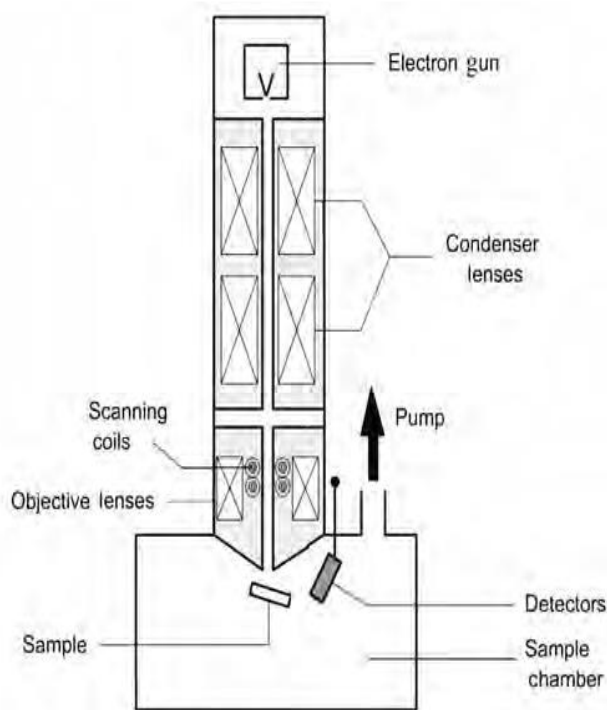


Figure 2-18:Diagram of SEM apparatus (Xu et al., 2009)

SEM analysis is known to present two disadvantages (Totten & Liang, 2004):

- The sample size is limited
- The analysis cannot quantify roughness.

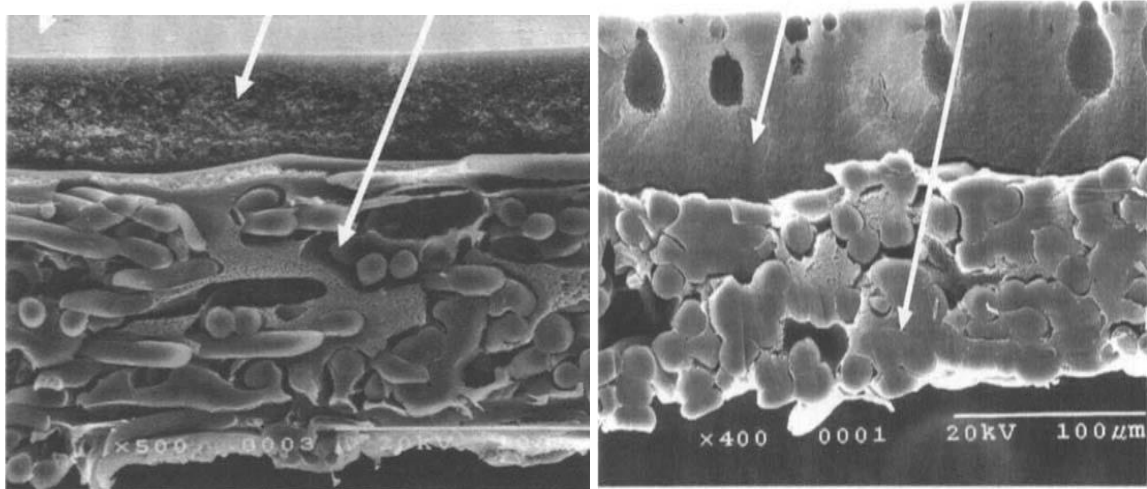


Figure 2-19: Cross-sectional images of RO membranes (a) Polyamide composite membrane
(b) Cellulose acetate membrane (Kucera, 2015)

In SEM analysis imaging parameters such as tilt angles, detectors are usually varied to acquire a finest quality of sample image (Abdullah et al., 2014).

Mittal, (2010) says that the maximum cross resolution in SEM analysis is done with a field emission gun and extents to 0.2 Am.

Chapter 3

RESEARCH METHODOLOGY

3 Methodology

3.1 Introduction

In this chapter the details are given regarding the use of equipment and materials, as well as experimental procedures followed during all experimental runs conducted. Descriptions of instruments used are also included. During this research, a quantitative experimental approach was used.

This project is divided into three sections namely:

1. Membrane surface modification;
2. Biofouling tests using E. coli bacterial solution;
3. Bench scale reverse osmosis process;

All experiments were conducted at the Cape Peninsula University of Technology in Chemical Engineering Environmental Research Laboratory 1.11.

3.2 Membrane surface modification

3.2.1 Introduction

A RO virgin membrane was cut to a specific size for membrane surface modification prior to fouling experiments. DMAEMA and PVA solutions were used as modification agents. Membranes were tested before and after membrane surface modification in a bench scale RO system. A static adhesion test was performed to study biofouling. All modifications were performed in duplicate and used for further experiments. Below, in Photo 3-1, a membrane is being fixed around a frame prior to modification.

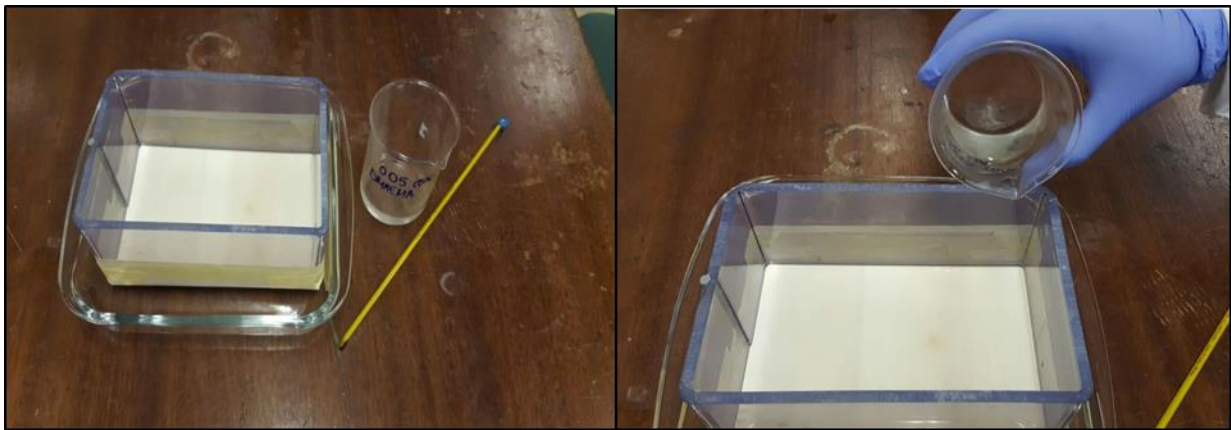


Photo 3-1: A membrane fixed around the frame before modification

3.2.2 Equipment

The apparatus and other chemicals involved in the modifications include the following:

- A Rectangular plastic frame was used where the membrane was fixed during modification procedures to allow exclusive contact of the membrane top layer with the modifying agents.



Photo 3-2: Rectangular frame with membrane fixed for modification

- A hot plate with magnetic stirrer was used for the preparation of solutions and a mercury thermometer was used to control the temperature in the modification procedure and preparation of modifying solutions.



Photo 3-3: Hot plate magnetic stirrer (left) and Hg thermometer (right)

- A oven was used in the modification procedure to maintain the temperature at desired condition during grafting



Photo 3-4: Oven model used during modifications of membranes

3.2.3 List of Chemicals

Ammonium phosphate and sodium sulphate ($\text{Na}_2\text{S}_2\text{O}_5$), Polyvinyl alcohol (PVA), Glutaraldehyde (GA), dimethyl amino ethyl methacrylate (DMAEMA), Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), Sodium chloride (NaCl), Potassium chloride (KCl), Sodium bicarbonate (Na_2CO_3), Magnesium sulphate (MgSO_4), Calcium sulphate (CaSO_4) and humic (CHOOH) acid Sulphuric acid (H_2SO_4) were all of analytical grade, used without further purification. Deionized (DI) water with a conductivity less than $12 \mu\text{s}/\text{cm}$ used for solutions preparation and rinsing of membranes was obtained from a laboratory water purification System.

3.2.4 Experimental procedure for modification of membrane using PVA

1. PVA was grafted onto the surface of the virgin membrane through covalent bonding initiated by GA. Modification procedure was similar to the one described by Hu et al., (2016).
2. A RO spiral wound TFC membrane was cut into flat sheets with dimensions of 18 cm length and 12 cm width. Giving a surface area of 0.216m²
3. Membrane sample was immersed in DI water over a period of 12 hours, manually replacing the water every hour to remove preservatives from the membrane sample. DI water was used to thoroughly rinse the membrane and allowed to dry at room temperature thereafter.
4. The membrane was then wrapped around a rectangular frame, in such a way that the layer faced the inner part of the frame to allow thorough contact with the modifying agent solution.
5. GA solution was prepared by diluting 25 wt.% GA solution to 0.05 wt.% with pH adjusted to 3.05 with diluted H₂SO₄. 100 mL of the prepared solution was added into the rectangular frame where the membrane has been fixed for 5 min and the excess solution removed.
6. The membrane was then manually rinsed with DI water and allowed to dry completely.
7. PVA solutions of different concentrations were then prepared (0.5 g.L⁻¹, 0.1 g.L⁻¹, 0.15 g.L⁻¹ and 0.2 g.L⁻¹).
8. A fix amount of PVA was added to 1L of DI water and placed on a heating element with a magnetic stirrer used to mix the solution for 30 min at 75 °C until the PVA was dissolved completely.
9. The PVA solution was allowed to cool and the pH was adjusted to about 3.05 using diluted sulphuric acid.
10. The prepared PVA solution was then poured on the coated membrane around the rectangular frame for 3 min and the solution was removed and placed in the oven at 50 °C for 6 min.
11. DI water was used to rinse the modified membrane, and the membrane was further placed in DI water at 45 °C for at least 10 hours, manually replacing the water every hour to remove unreacted molecules from the surface.
12. The membrane stored in DI water before experimental runs.

Modification steps in brief

1. Rinse the membrane with de-ionised water.
2. Allow the membrane to dry under room temperature conditions.

3. Once the membrane is dry, wrap the membrane to the frame.
4. Add 100 ml GA solution to the membrane and allow it to stand for 5 min.
5. After 5min, remove the GA solution and rinse the membrane thoroughly with DI water.
6. Let the membrane dry
7. Add 50ml of PVA solution to the frame and allow 3 min contact time with membrane. Rinse thereafter and place the membrane in the oven at 50 degrees Celsius for 6 min.

Table 3-1: Membrane surface modification-PVA

Experiment	PVA
	Concentration (g/L)
1	0.05
2	0.01
3	0.15
4	0.2

3.2.5 Experimental procedure for modification of membrane using DMAEMA solution

Pre-treatment of the membrane prior to modification was similar to the procedure described above from 1 - 4

5. Modifying solutions of fixed concentrations ($0.025 \text{ mol. L}^{-1}$, 0.05 mol. L^{-1} , $0.075 \text{ mol. L}^{-1}$ and 0.1 mol. L^{-1} DMAEMA) contained sodium sulphate (0.5 mol% of DMAEMA) and potassium persulfate (0.5 mol% of DMAEMA).
6. Modification was conducted by pouring DMAEMA solution on the surface of the membrane fixed around the rectangular frame and the membrane placed in the oven for an hour at 30°C .
7. The modified membrane was then rinsed thoroughly and preserved in DI water.

Modification steps in brief

1. Rinse the membrane with de-ionised water.
2. Allow the membrane to dry under room temperature conditions.
3. Once the membrane is dry, wrap the membrane to the frame.
4. Add 50ml of DMAEMA solution and allow the membrane to stand for 5min.
5. After 5 min, remove the solution of DMAEMA and place the membrane in the oven for 60 min at 30 degrees Celsius.

Table 3-2: Membrane surface modification-DMAEMA

Experiment	DMAEMA
	Concentration (mol/L)
1	0.02
2	0.05
3	0.75
4	0.1

3.3 Bio-fouling Experiments

3.3.1 Introduction

Bio-fouling experiments were conducted to evaluate membrane surface resistance to biofouling using the gram negative *E. coli* bacteria in solution.

Membranes with better permeations were selected and further studied in terms of resistance to bacterial growth and biofilm formation. *E. coli* bacterial solution was used as a model foulant. Bacterial growth measurement was similar to that described by Wang et al., (2015) with minor modifications.

1. The membrane was cut into small sizes (2 cm x 2 cm) and placed under UV for half hour.
2. The membrane was placed into a nutrient broth (NB) of ≈ 0.47 OD and for a period of 3 hours.
3. The membrane was removed and rinsed with fresh broth and the solution collected was diluted in series (2-10 folds).
4. 100 μ L of diluents were plated on LB Agar medium in and incubated overnight.
5. The plate count method was used to determine the number of *E. coli* bacteria in contact with the membrane.
6. The same NB of *E. coli* suspension, without being in contact with the membrane, was diluted in series (2-10 folds) and plated on LB agar medium and incubated at 37 °C for 20 hours.

The number of *E. coli* bacteria without being in contact with the membrane was also determined as mentioned above; and this allowed calculating the mortality ratio (R) according to the formula:

$$R = \left(\frac{B - A}{A} \right) \times 100 \quad \dots \text{(Equation 5)}$$

Where B is the number of viable bacteria not in contact with membrane surface and A is the number of viable bacteria in contact with membrane surface for a given contact time.

Biofouling effect was further investigated by measuring pure water flux of membranes before and after incubation of 2.1×10^8 CFU.mL⁻¹ E. coli bacteria suspension for 30 hours.

3.3.2 Apparatus for Biofouling test

- Sterilized Erlenmeyer flasks and beakers were used to prepare and grow the microorganisms (*E. coli*)



Photo 3-5: Flasks and beakers types used for the preparation of *E. coli*

- Petri dishes with Nutrient agar were used to grow bacteria in order to assess they shapes and mount them manually (plate counting method).



Photo 3-6: petri dishes used during microbial growth

- An Incubator was used to grow the bacteria (at 37 °C) for the biofouling and static adhesion tests.



Photo 3-7: Incubator model used in the project

A laminar flow with UV light was used during the preparation of bacterial solution. The UV light from the laminar flow was also used to sterilize them membrane prior to biofouling tests. Adjustable-volume pipette and Bunsen burner were used while sampling the bacterial solutions.



Photo 3-8: Lab Purifier (laminar flow) with UV light (Left), adjustable-volume micropipette (middle) and Bunsen burner (right)

- A spectrophotometer was used to measure the optical density of the bacterial solution used in biofouling tests.



Photo 3-9: Spectrophotometer model used in this project

- An autoclave machine was use to sterilize material and apparatus used for biofouling tests



Photo 3-10: Autoclave machine type used in the project

3.3.3 E-coli culturing steps

1. 31.5 g of nutrient broth powder was dissolved in 1L de-ionised water.
2. The nutrient broth and nutrient agar solutions were autoclaved at 121 °C and allowed to cool down.
3. The nutrient agar was allowed cool to 60 °C on a magnetic plate together with a magnetic stirrer to allow cooling without solidification.
4. The agar solution was poured into petri dishes once it has cooled and was allowed to solidify.
5. 5 µL of E. coli solution preserved in a glycerol stock at -80 °C was poured onto the petri dishes and incubated at 37 °C overnight.
6. A pure colony was streaked from the petri dishes and inoculated in 10 mL of nutrient broth overnight.
7. The 10ml nutrient broth with e-coli was then inoculated in a 250ml volumetric flask of nutrient broth.
8. The optical density (OD) of the broth was monitored to obtain an optical density of approximately $\pm 0.47\text{Abs}$ (at 590 nm).
9. 1mL from the solution was diluted in series (2-10 folds).
10. 100 µL of diluents were plated on nutrient Agar (NA) in petri dishes, labelled into a distinguishing pattern and incubated at 37 °C for 20 hours to determine the number of E. coli bacteria in the solution by plate count method.

3.3.4 Static adhesion test performed on membrane

1. Membrane was cut into small sizes (2 cm x 2 cm) and placed under UV for half hour.
2. The pieces of modified and unmodified membranes were placed for 3 hours in contact with Nutrient broth (NB) of approximately $\pm 0.47\text{Abs}$ (at 590 nm) containing E. coli suspension.
3. The membranes were then removed and rinsed with fresh broth and 1 mL of the solution collected was diluted in series (2-10 folds).
4. 100 µL of diluents were plated on nutrient Agar (NA) in petri dishes, labelled into a distinguishing pattern and incubated at 37 °C for 20 hours.
5. The petri dishes were removed and the number of E. coli bacteria in contact with each membrane was determined by the plate count method.

3.3.5 Water flux tests experiments with contaminated membranes

Two membranes each from the two modifications procedures investigated in this research were selected based on their permselectivity. These membranes together with the unmodified membranes were used to test water flux after exposure to E. coli cell suspension for 30h under 5 Bar and room temperature, using DI water

The following procedure was followed to water flux data collection:

- After exposure of membrane to bacteria cells, membranes were rinsed and placed into the RO cell.
- DI water was added to the system
- The operating conditions of the RO system were set to 5bar feed pressure, 19 cm/s cross velocity
- The flux of the contaminated membrane was recorded every 30min for a period of 6 hours.

Table 3-3: Experiments summary

Experimental run	Membrane
1	Unmodified membrane
2	Unmodified membrane (Duplication)
3	0.05 mol.L ⁻¹ DMAEMA membrane
4	0.05 mol.L ⁻¹ DMAEMA membrane (Dup)
5	0.15 g.L ⁻¹ PVA membrane
6	0.15 g.L ⁻¹ PVA membrane (Dup)

3.4 RO system process description

3.4.1 Experimental Set-up

Figure 3-1 below shows a schematic diagram of the experimental set up. The experiments are carried out on lab scale using a bench scale RO cell. Feed used was acquired from an existing MBR WWTP and make-up synthetic feed, made of specific identified foulants. A low pressure high flow rate hydra-cell pump is used to pump the water through the cell. Permeate is discharged into a holding flask and the brine is recycled to the feed tank. LabVIEW is used as the controller where the velocity of the system is controlled and the pressure around the cell is monitored using a hydraulic pump. The feed pressure is regulated in order to achieve a constant flux and readings are recorded.

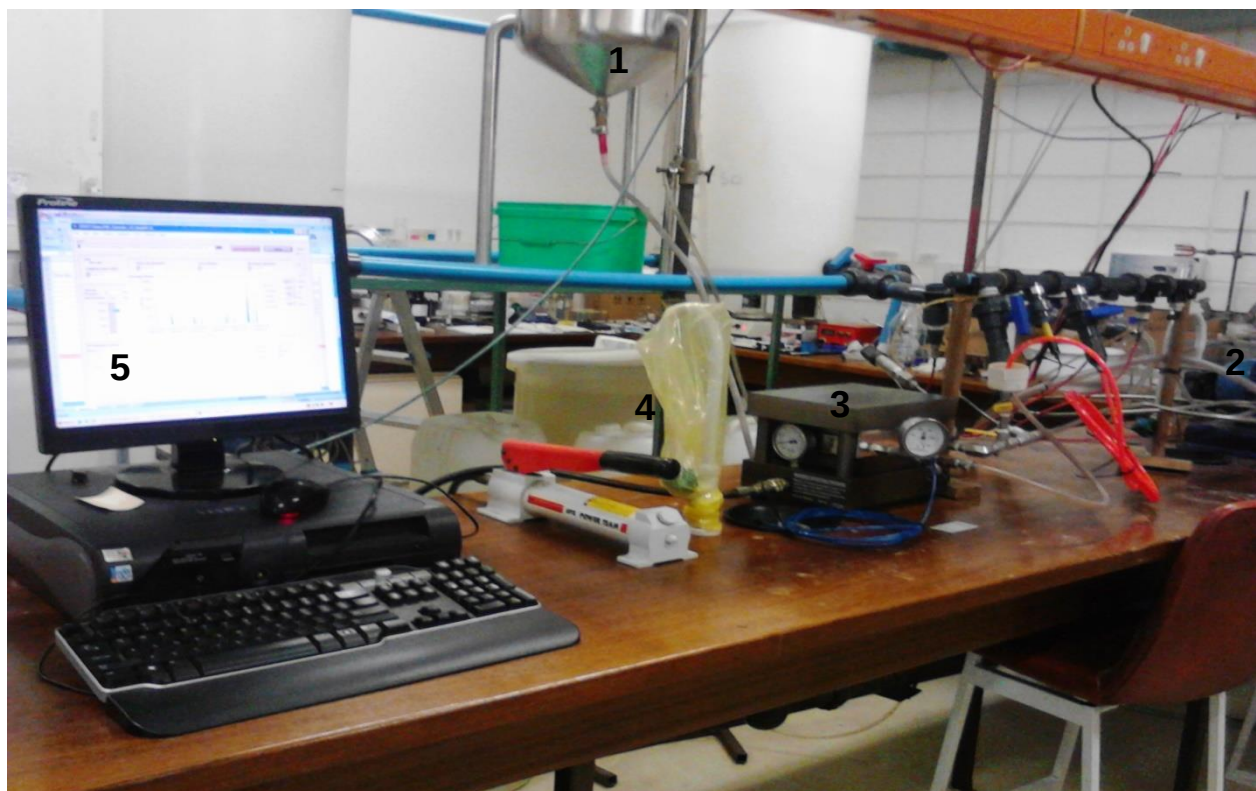


Photo 3-11: RO Cell system (lab 1.1, science building, CPUT, August 2017)

Table 3-4: RO system equipment

Feed Tank	1
Hydra cell Pump	2
Pipes	3
RO Sepia Cell	4
Computer with LabVIEW	5

Other equipment used during experiments with the RO system

- Bench scale RO cell
- 50 L MBR permeate as feed
- Hanna analytical equipment and reagents
- Portable EC and pH meters
- Lab view (Process Controller)
- Stop watch
- Measuring cylinder

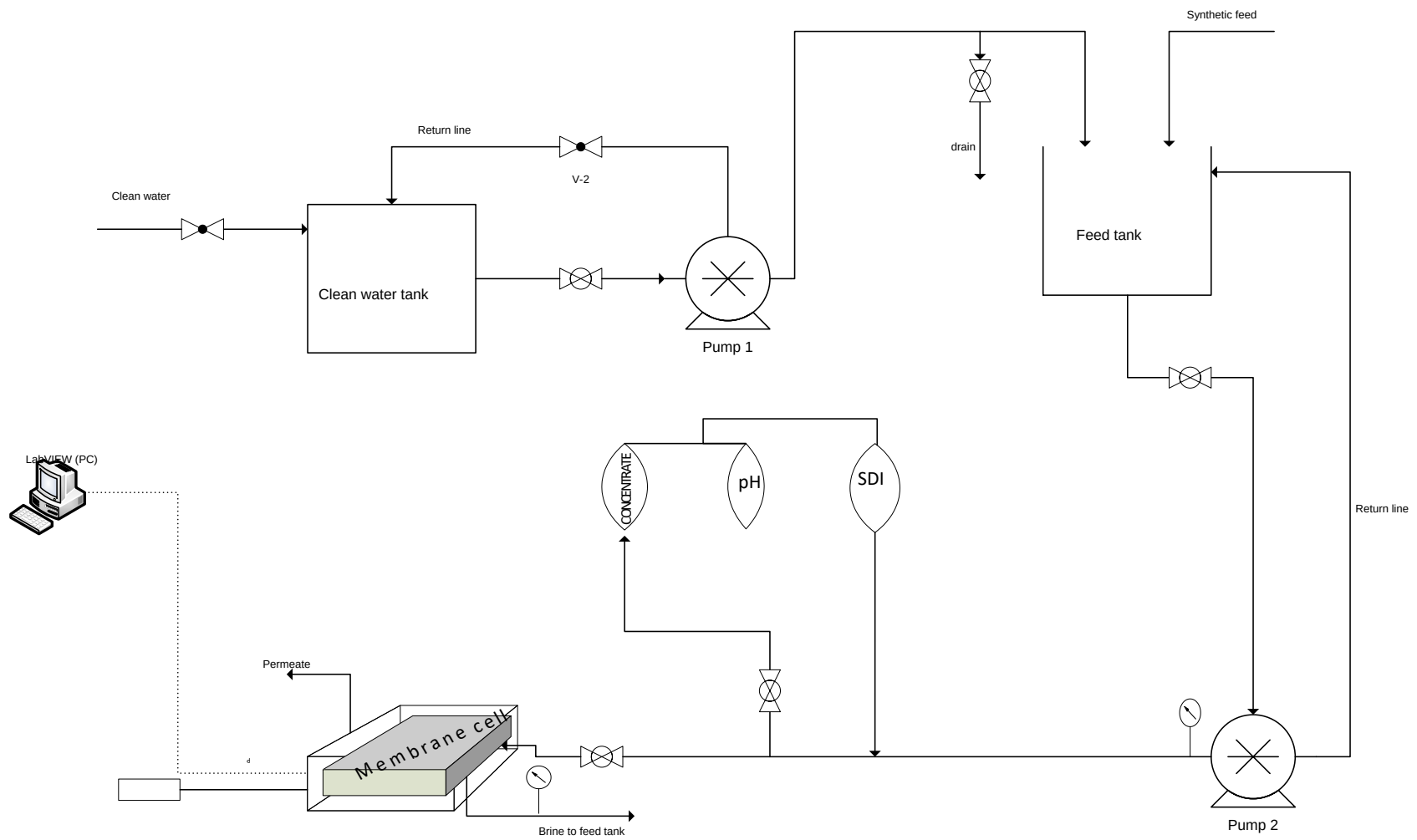


Figure 3-1: Schematic representation of the RO system

3.4.2 Making of the synthetic feed

Synthetic feed make-up was measured in terms of chemical mass, weighed on an analytical scale. Thereafter it is poured into a volumetric flask to be diluted with 1L of water. This is done individually for each chemical. As the chemicals dissolved, the solution is poured into the tank. The tank is filled with water to make a total feed volume of 15L synthetic feed.



Photo 3-12: Synthetic effluent

Table 3-5: Synthetic feed solution composition and characteristics

Chemical composition	Concentration
Potassium chloride	4mg/L
Sodium chloride	7mg/L
Sodium bicarbonate	93mg/L
Magnesium sulphate	60mg/L
Ammonium phosphate	60mg/L
Calcium sulphate	60mg/L
Humic acid	4.2mg/L
pH $\approx$ 5.64 at 18.1 °C Turbidity $\approx$ 1.155 Ntu Salinity $\approx$ 0.3 ppt	

3.4.3 RO system operation

LabVIEW was used to set-up the operating condition. Conductivity, TDS and temperatures of the feed, permeate and recycled brine was recorded every 45min for the 42 hours experimental run.

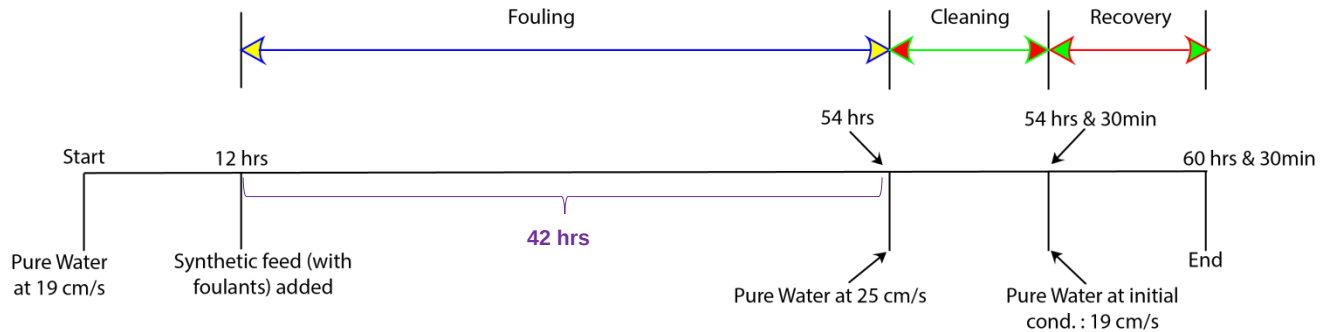


Figure 3-2: Timeline during the fouling experiment using the RO cell

3.4.4 RO cell start up procedure

- A screw driver is used to open the cell module due to hydraulic pressure.
- Two spacers are cut out in the same shape as the membrane active area surface as shown in fig. 3-15: the spacer with bigger holes is placed on the higher pressure side (feed side); the spacer with smaller holes is placed on the low pressure side (permeate side).



Photo 3-13: Pictures showing the two different spacers (left) and membrane placed with spacers in the cell (right) (lab 1.1, science building, CPUT, August 2017)

- The spacers are then wetted rinsed with deionised water

- The membrane is cut from an opened spiral wound FILMTEC (DOW) membrane (XLE-4040) in a rectangular shape with size 14.5 x 9.5 cm, giving an active surface area of 0.014m², so that it covers the inner sealer in the flat cell as shown in fig. 3-15 placed on it. It was very significant that the shiny side of the membrane faced down on the cell.



Photo 3-14: Pictures illustrating the position of sealers on the module (left) and the correct placement of membrane on module (right) (lab 1.1, science building, CPUT, August 2017)

- The cell is closed and placed back in its holder and compressed using the hydraulic pump.
- The hydraulic pump pressure is then set to 12-14 bars. After the cell is secured the pump is switched on and the feed valve is opened.
- Fresh de-ionised (DI) water is then transferred to the feeding tank.
- The LabVIEW programme was opened to control the operating conditions of system. The operating conditions and time were pre-set for the experimental runs as follows:
 - (1) starting time: 30sec
 - (2) shutdown time: 30sec
 - (3) experimental run time: 120 hours
 - (4) pressure: 5 bar
- The system was started and the velocity was increased slowly from zero to 19cm/sec.
- Once the standard conditions were achieved it was allowed to reach steady state by recording the flux in 30 min intervals until the flux remained constant. Once a steady flux

was achieved (mostly after 12 hours), the de-ionised water was drained and replaced with the synthetic feed.

- After the system reached stability again at the required system conditions, the conductivity, TDS and temperature of the feed, brine and permeate were recorded every 45 minutes throughout the experimental run.

3.4.5 Membrane cleaning

- The system was flushed before and after the experimental runs with de-ionised water. The conductivity of the water used to flush the system had an electro-conductivity of $10\mu\text{S}\cdot\text{cm}^{-1}$. Each experimental run started with a new membrane.
- After the cleaning time of 30 minutes with DI water at a velocity of 25 cm/s and 6 bar, the system was reset to initial conditions of pressure and velocity (5 bar and 19 cm/S) for a duration of 6 hours to allow comparisons of the water fluxes before and after experiments.

3.4.6 Membrane replacement

The membrane cell is opened and rinsed with DI water. Both spacers are removed and soaked in DI water to ensure all contaminants are washed away. The spacers are placed back into the cell together with a new membrane, closed up and ready for the next experimental run.

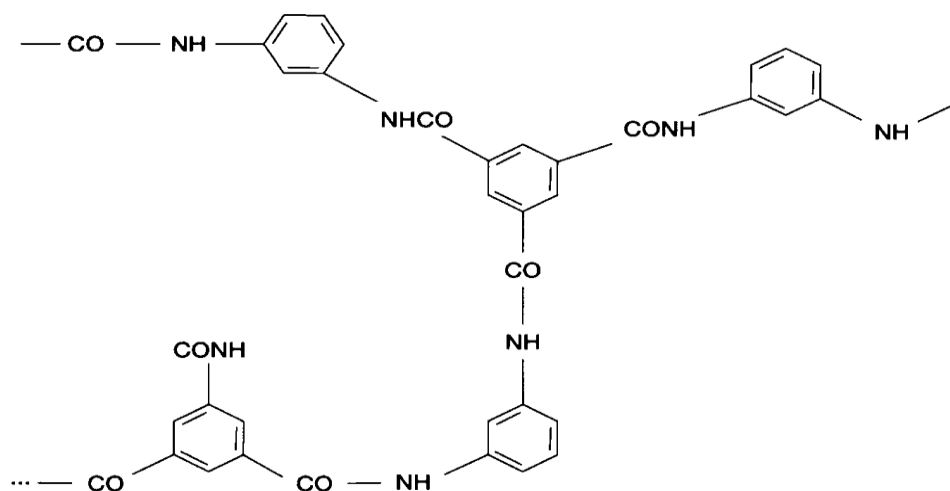


Figure 3-3: Chemical structure of a polyamide composite RO membrane(Kucera, 2015)

Table 3-6: RO system operating conditions

Initial Conditions	Feed solution
Flux: 60 L/m ² .hr	Synthetic
Pressure: 5 bar	Real effluent (membrane with best perm selectivity)
Cross velocity: 19 Cm/s	
Temperature: Ambient	

3.4.7 Equipment used during RO operation

- A 10mL graduated glass cylinder and stopwatch were used to manually measure the flow rates of the streams (feed, brine and permeate)



Photo 3-15: Cylindrical beaker (Left) and stop watch (right)

- The conductivity meter used in this project simultaneously measured conductivity from which the salt rejection (%) was calculated; the salinity (ppt), the total dissolved solids (mg/L) and the temperature (°C).



Photo 3-16: YSI Eco Sense EC300 conductivity meter model use during the experiments

- A COD reactor was used to prepare the MBR secondary effluent from MSWWTP samples for COD analysis using a water testing meter (spectrophotometer). The spectrophotometer was further used for the analysis of specific ions identified as contaminants in the effluent such as ammonia, phosphate, carbonate, nitrate, and nitrite.



Photo 3-17: COD RD125 thermo reactor (left) and spectrophotometer (right) models used in the project

Table 3-7: Experiments summary

Experiment	Membrane	Experiment	
1	Unmodified M	10	0.02 mol.L ⁻¹ DMAEMA mod. M (Dup)
2	Unmodified M (Dup)	11	0.05 g.L ⁻¹ PVA mod. M
3	0.05 mol.L ⁻¹ DMAEMA mod. M	12	0.05 g.L ⁻¹ PVA mod. M (Dup)
4	0.05 mol.L ⁻¹ DMAEMA mod. M (Dup)	13	0.1 g.L ⁻¹ PVA mod. M
5	0.075 mol.L ⁻¹ DMAEMA mod. M	14	0.1 g.L ⁻¹ PVA mod. M (Dup)
6	0.075 mol.L ⁻¹ DMAEMA mod. M (Dup)	15	0.15 g.L ⁻¹ PVA mod. M
7	0.1 mol.L ⁻¹ DMAEMA mod. M	16	0.15 g.L ⁻¹ PVA mod. M (Dup)
8	0.1 mol.L ⁻¹ DMAEMA mod. M (Dup)	17	0.2 g.L ⁻¹ PVA mod. M
9	0.02 mol.L ⁻¹ DMAEMA mod. M	18	0.2 g.L ⁻¹ PVA mod. M (Dup)

Dup: Duplicated experimental run

M: Membrane

mod. M: Modified membrane

3.5 Membrane characterization analysis

A qualitative analysis (SEM) and semi-quantitative analysis (ATR-FTIR) were used to characterize the membrane before and after modifications. Both analyses were done externally.

3.5.1 ATR-FTIR analysis

ATR-FTIR analysis was conducted to observe the chemical change after modification. The analysis was conducted using a Nicolet ATR with HOMNIC software. The ATR-FTIR spectra were recorded at a resolution of 2 cm^{-1} during 64 scans at a nominal incident angle of 45° with a wavenumbers ranging between 1950 and 650 cm^{-1}

3.5.2 SEM analysis

A scanning electron microscope (Nova NanoSEM) was used to observe changes in membrane morphology after modification of the membrane surface. Top view images were scanned at $40000\times$ magnifications and 5.00 keV landing electron for all samples, while cross-section images were at a $1000\times$ magnification and 5.00 keV landing electron.

Chapter 4

RESULTS AND DISCUSSION

4 Results and discussion

Results presented under this chapter are divided into three sections:

1. Membrane surface characteristics obtained from and ATR-FTIR and SEM analysis
2. RO process
3. Bio-fouling tests results

The second section is followed by a statistical analysis performed on experimental data using design expert 2010.

4.1 Membrane surface modification using PVA: membrane characterization

Modification of the of the polyamide thin-film composite reverse osmosis membrane was conducted by bonding PVA cross-linked with Glutaraldehyde, to the membrane top selective layer. ATR-FTIR analysis was used to study the physio-chemical structure of unmodified and PVA modified membranes.

4.1.1 ATR-FTIR analysis

ATR-FTIR was used to verify grafting of PVA chains onto the TFC membrane surface. The analysis provided a suitable method of identifying different chemical groups on the surface of the membrane, thus, differentiated the existing polymeric species on the surface. The ATR-FTIR spectra were recorded at a resolution of 2 cm^{-1} during 64 scans at a nominal incident angle of 45° with a wavenumbers ranging between 1950 and 650 cm^{-1} . The wavenumber intensities were normalized to allow accurate representations and easy comparisons between spectra. The identification of the functional groups at different peaks is presented in the chapter 2 in figure 2-15.

Below in figure 4-1, it was found that the peaks at 1240, 1482, 1510 and 1589 cm^{-1} are characteristics that identified the polysulfone support layer of the membrane, as described by Cheng et al., (2013) and Wei et al., (2010). The active layer on the TFC membrane was too thin, therefore the IR spectrum provided information of both the top layer as well as the polysulfone support layer of the membrane (Freger et al., 2002; Kang et al., 2007).

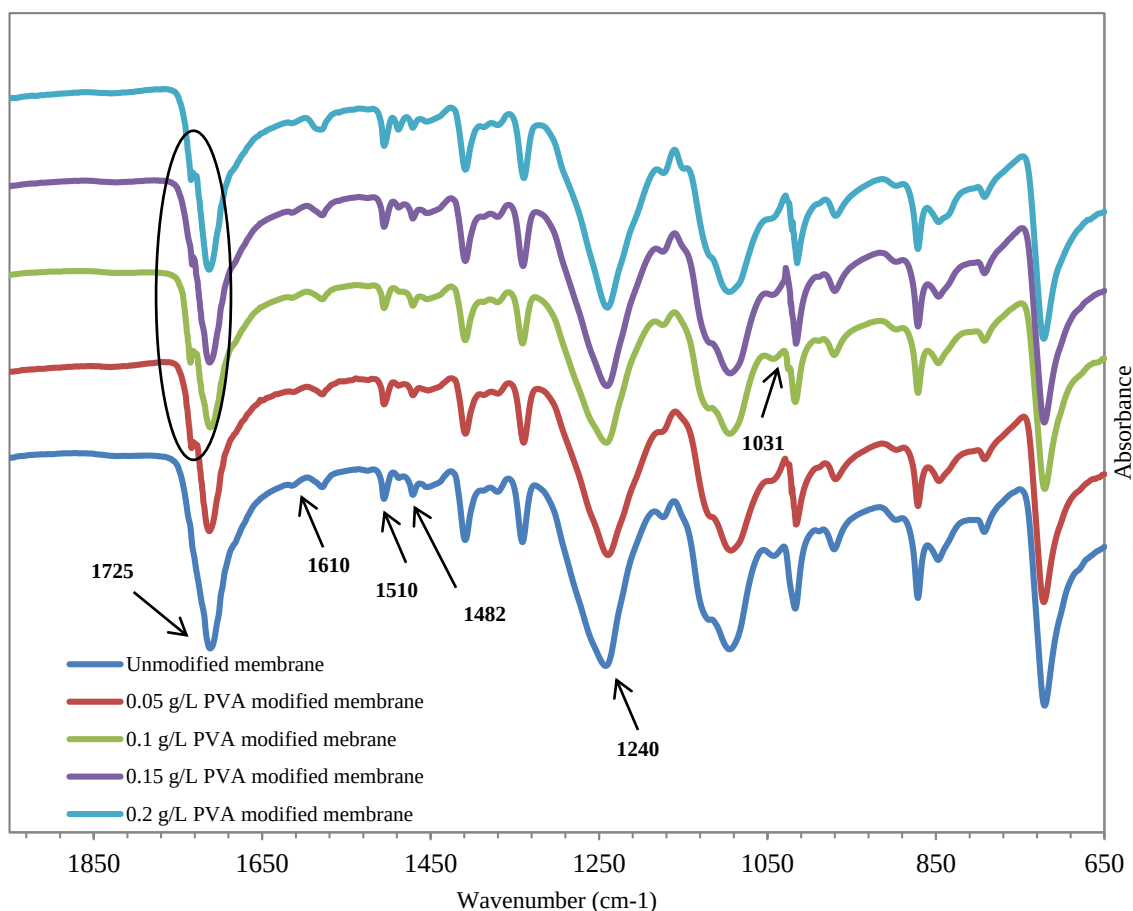


Figure 4-1: ATR-FTIR spectra of PVA modified membranes

The peak at 1725 cm^{-1} of the unmodified and modified membranes at different concentrations revealed the presence of carbonyl functional groups. Furthermore, the small but clear peaks at 1610 cm^{-1} presented the spectra corresponding to the amide I group ($\text{C}=\text{O}$ stretching), which was ascribed to the polyamide top layer of the membrane. Liu et al., (2015) concur to this, in their study. Lin et al., (2016) confirmed that the presence of these peaks showed that the structures of the membranes were not affected after modification.

The ester peak of 1730 cm^{-1} on the spectra of the modified membranes portrayed an adsorption band, that was absent on the unmodified membrane. Hu et al., (2015) attributed this to the presence of PVA molecules that was attached to the polyamide layer. An adsorption band of different intensities at about 1030 cm^{-1} could be noticed on the modified membranes spectra. According to Yutao Hu et al., (2016), this proved the cross-linkage of the PVA molecules and GA onto the surface of the membrane. It can be confirmed by the ATR-FTIR analysis that the PVA were successfully attached to the top layer of the membrane.

4.1.2 SEM analysis

SEM was used to qualitatively observe the structures of the membranes before and after grafting of PVA. SEM photographs of the top surface layer and cross-section of the membranes are shown in figs 4-2 to 4-6. The SEM analysis was conducted with a magnification of 40,000 for all samples. All membranes presented a ridge-and-valley structure as shown by the top views (Freger et al., 2002). However, the unevenness in the structure of the unmodified membranes differs from the modified membranes. PVA modified membranes portrayed a less fixed structure as compared to the unmodified membrane, which is less compact. The level of disproportion in the structure differs from one modified membrane to another. It can be observed when comparing the top views from the SEM, that the modified membranes become more compact as the concentration of PVA increases from 0.05 to 0.2 g/L. However, An et al., (2011), used a solution containing PVA with piperazine (PIP) reported that the decrease in density of surface and unevenness structure caused by stronger hydrogen molecular bonding between chains, and resulted in a smoother surface. Liu et al., (2015), concur with An et al., (2011) when using a solution containing PVA with potassium persulfate. In this study a solution containing PVA with GA, resulted in the decrease of surface smoothness when the PVA concentration were increased. Yutao Hu et al., (2016), used a solution containing PVA with GA and achieved rough surfaces as well. Both studies used GA prior to treatment with PVA and achieved similar observations.

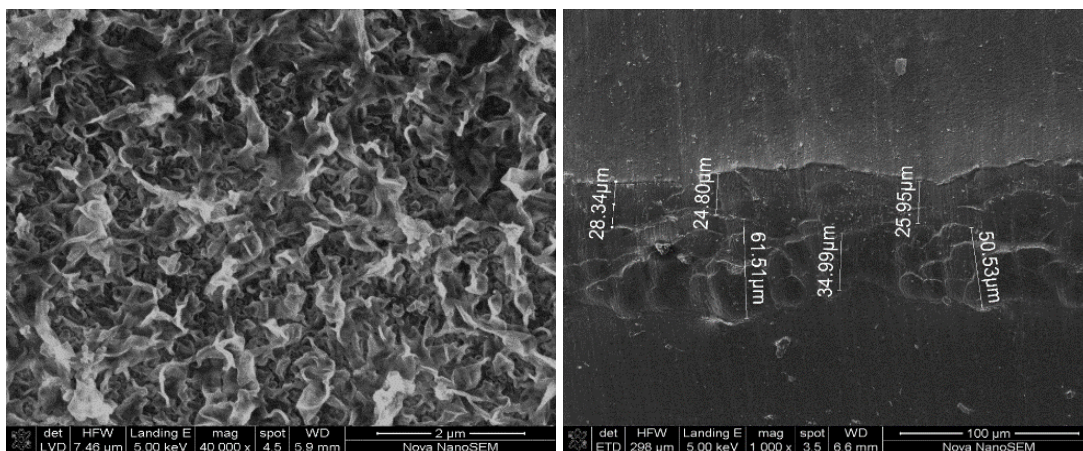


Figure 4-2: SEM images of the unmodified membrane: (left) top view (right) cross-section

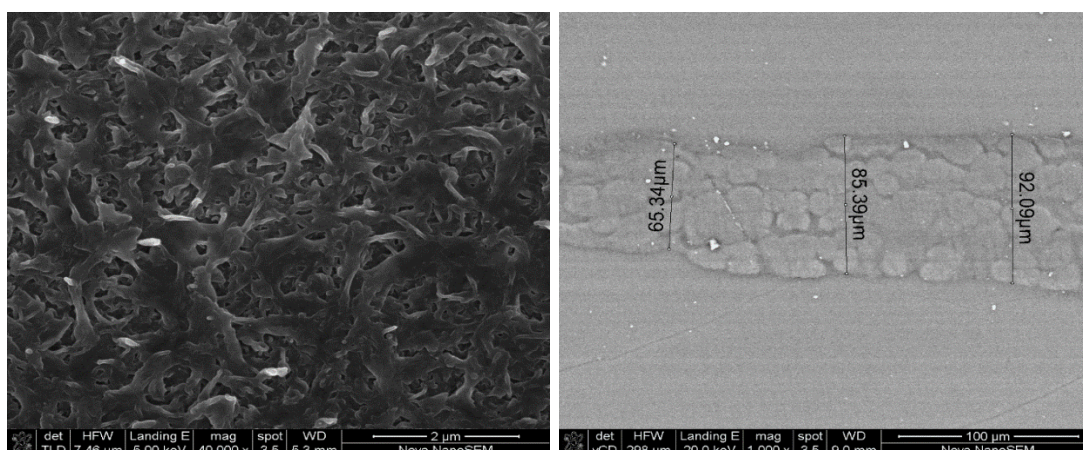


Figure 4-3: SEM images of the 0.05 g/L PVA modified membrane: (left) top view (right) cross-section

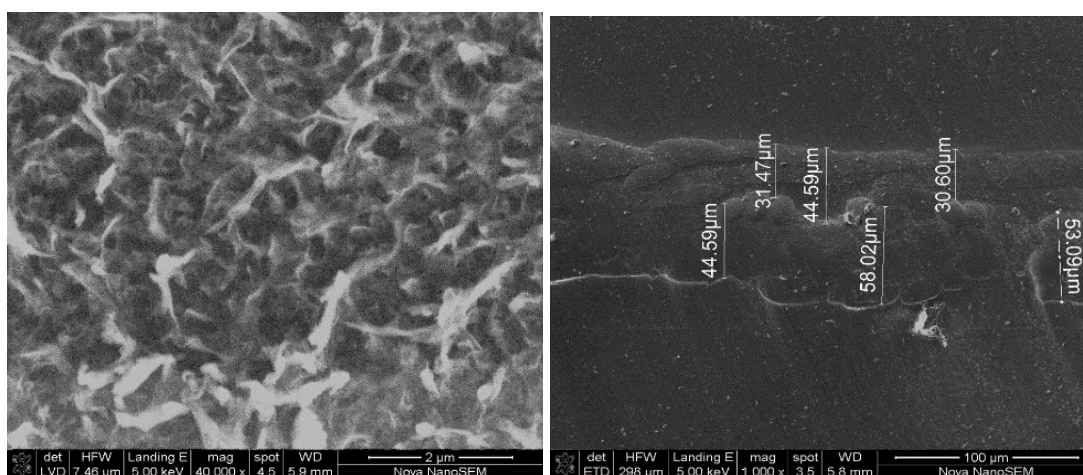


Figure 4-4: SEM images of the 0.1 g/L PVA modified membrane: (left) top view (right) cross-section

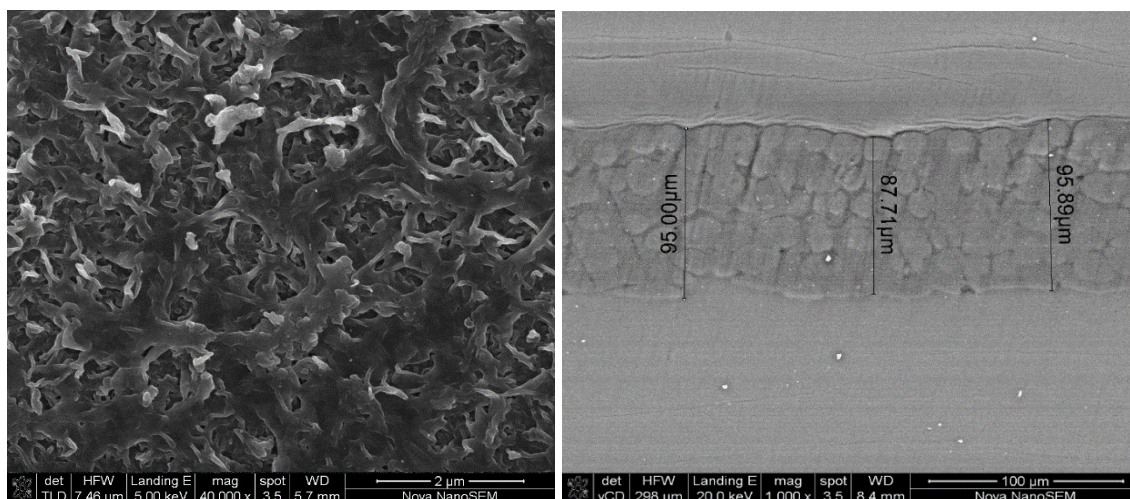


Figure 4-5: SEM images of the 0.15 g/L PVA modified membrane: (left) top view (right) cross-section

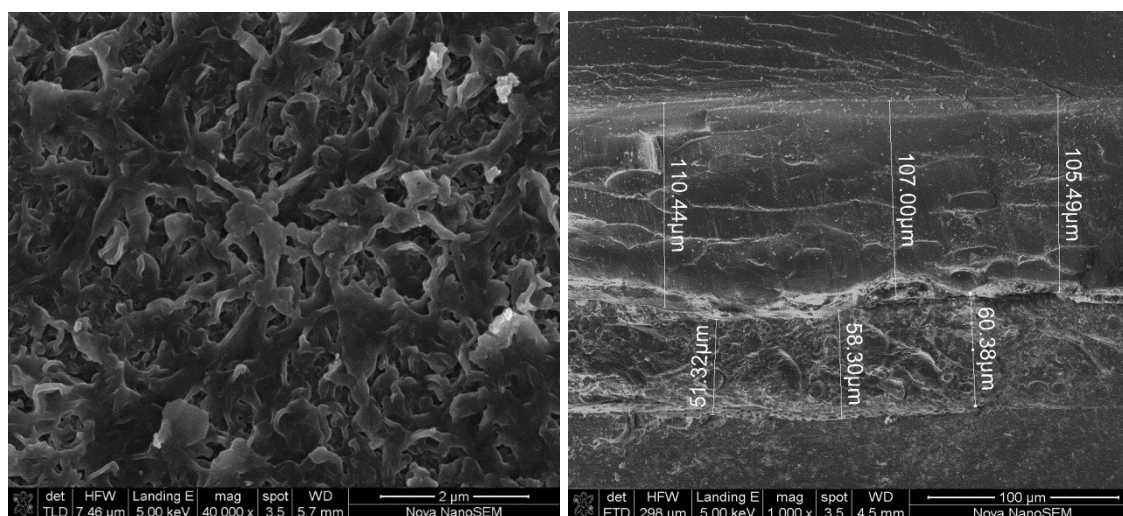


Figure 4-6: SEM images of the 0.2 g/L PVA modified membrane: (left) top view (right) cross-section

In figs 4-2 to 4-6, to the right, cross-sections are shown with the SEM for all membranes. The cross-section images were obtained at a magnification of 10,000. The thicknesses of the membrane samples were measured at different points and the average values were reported. It can be seen from the images above that the modification of membranes using PVA resulted in an increase of the thickness of the selective skin layer of the composite membrane as the PVA concentration increases from 0 to 0.20 g/L. Similar observations were concluded by Yutao Hu et al., (2016).

4.2 Membrane surface modification using DMAEMA: membrane characterization

DMAEMA was attached onto the surface of the polyamide layer through the graft polymerization procedure. According to Freger et al., (2002); Liu et al., (2015) and Wang et al., (2015) the monomer attacked the polymeric backbone of the membrane and grew by propagation.

4.2.1 ATR-FTIR analysis

ATR-FTIR analysis was conducted, similarly to the previous section to verify grafting of DMAEMA monomer onto the polyamide layer of the TFC RO membrane surface, after modification. The analysis was conducted at same conditions as described in the previous section.

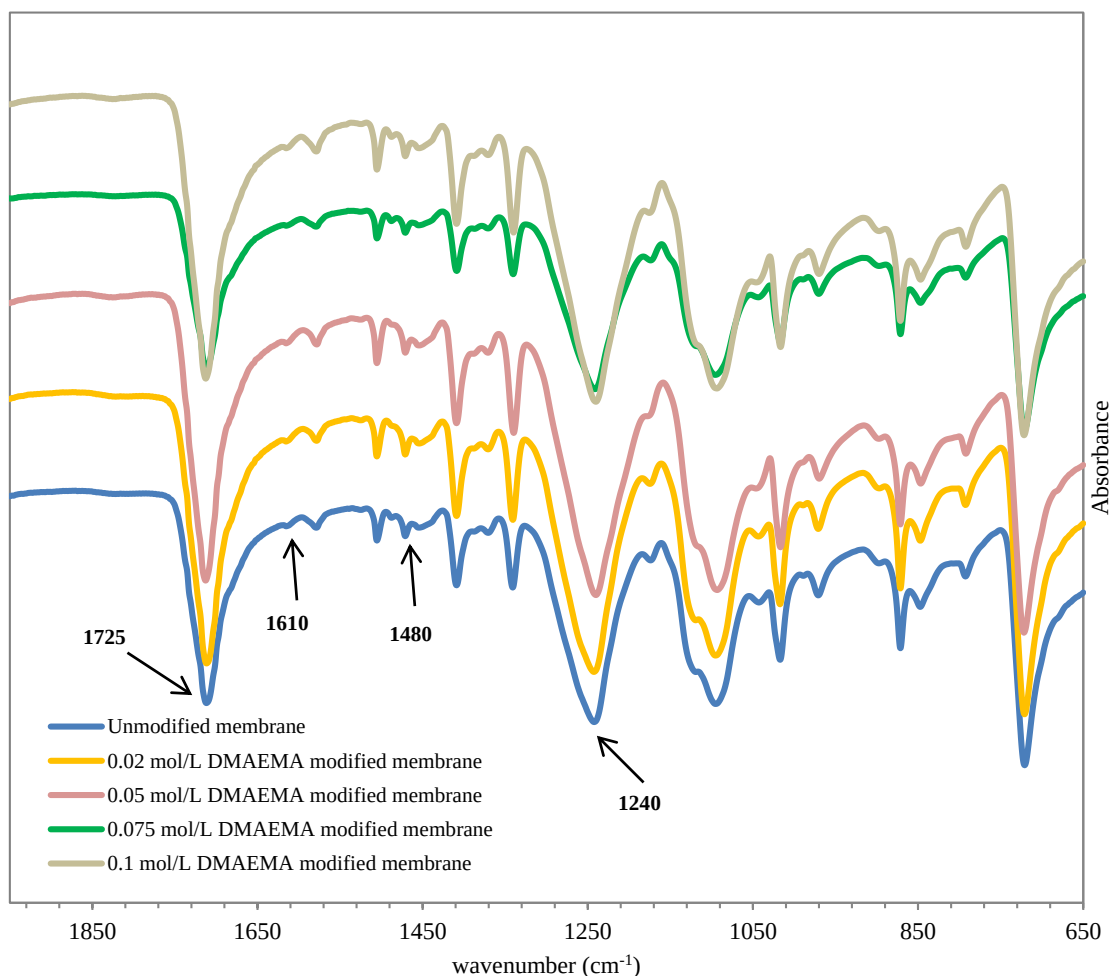


Figure 4-7: ATR-FTIR spectra of DMAEMA modified membranes

From the spectra the functional amide I group (hydrogen C=O) and the carbonyl group were identified at wavenumbers of 1610 cm^{-1} and 1725 cm^{-1} , respectively. This was attributed to the polyamide layer present. Small changes were observed for both unmodified and modified membranes. Similar observations were made at the adsorption bands at 1480, 1510, and 1585 cm^{-1} , which could be attributed to the polysulfone layer. Wang et al., (2015) suggested that at the peak at about 1240 cm^{-1} was ascribed to the aromatic structure of the membrane. According to Wei et al., (2010), the minute volume of aromatic polyamide layer grafting sites, may have caused the FTIR adsorption bands to amalgamate with other bands, limiting its observation.

It can be observed from the spectra, that the wavenumbers intensified with an increase of DMAEMA concentration on the modified membranes. Therefore, it could be deduced that the DMAEMA solution was effectively grafted on the membrane top layer. Cheng et al., (2013) investigated the graft polymerization of N-isopropyl acrylamide on a TFC membrane and also observed an increase in the intensities of the functional amide I group (hydrogen C=O) and the polysulfone layer, after modification. These results confirmed that the structure of the membranes was not affected after modification (Lin et al., 2016).

4.2.2 SEM analysis

Similarly to the previous modification, SEM images of the DMAEMA modified membranes were obtained at 40,000 magnifications. Top view images are shown on the left. It can be seen that both unmodified and modified membranes, present a rigid and valley structure as explained by Freger et al., 2002. The modified membranes showed a different morphology and the new structures appeared on the surfaces. These structures became more visible as the DMAEMA concentration increases and adjusted the densities, accordingly Mahdavi et al., (2017) investigated grafting using a TFC membrane and had similar observation.

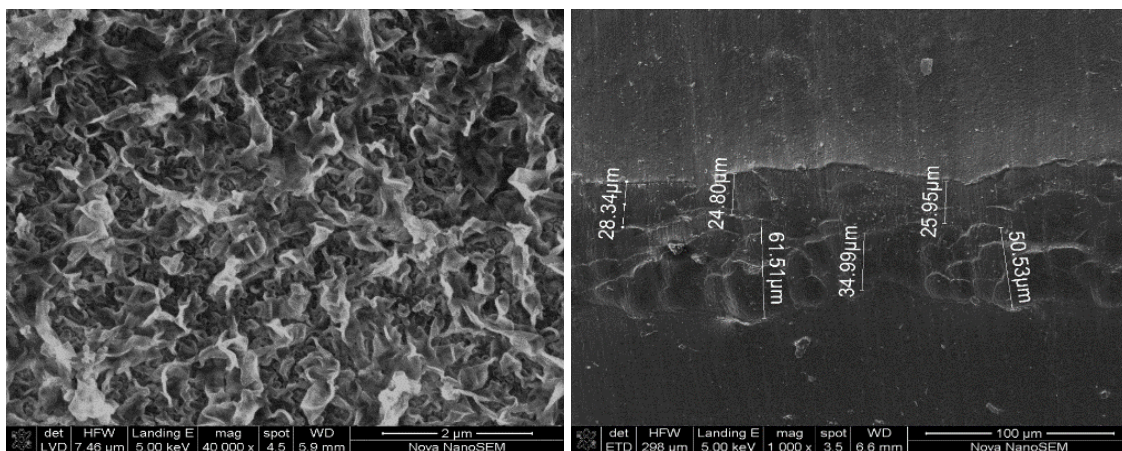


Figure 4-8: SEM images of the unmodified membrane: (left) top view (right) cross-section

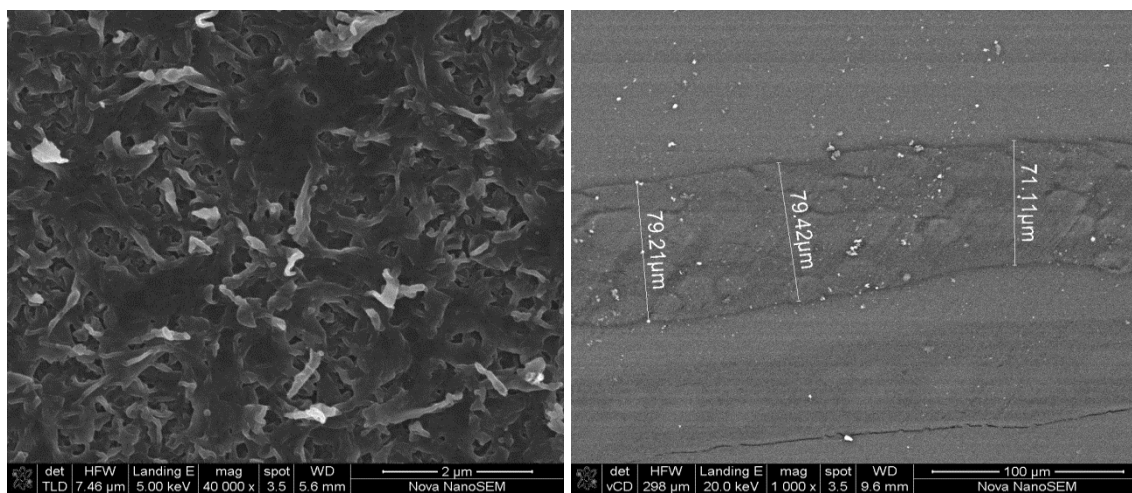


Figure 4-9: SEM images of the 0.02mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section

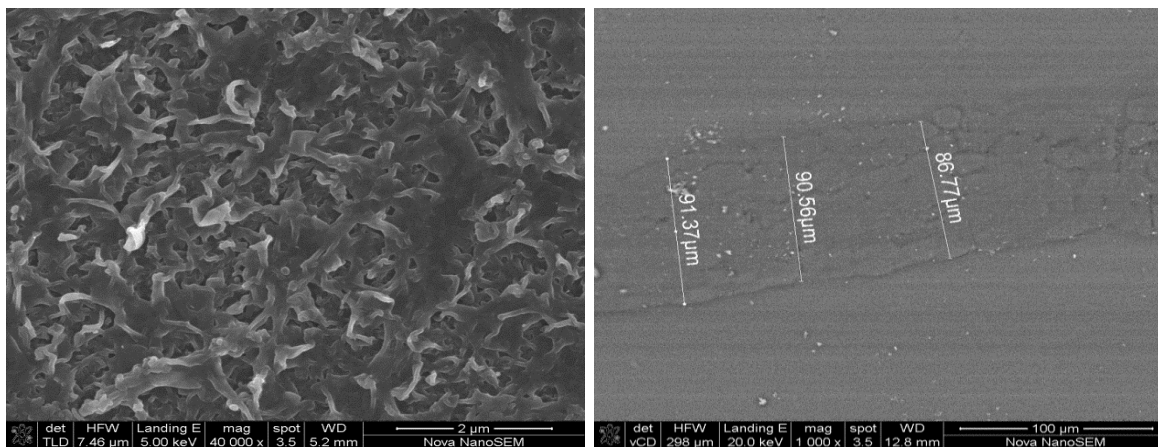


Figure 4-10: SEM images of the 0.05mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section

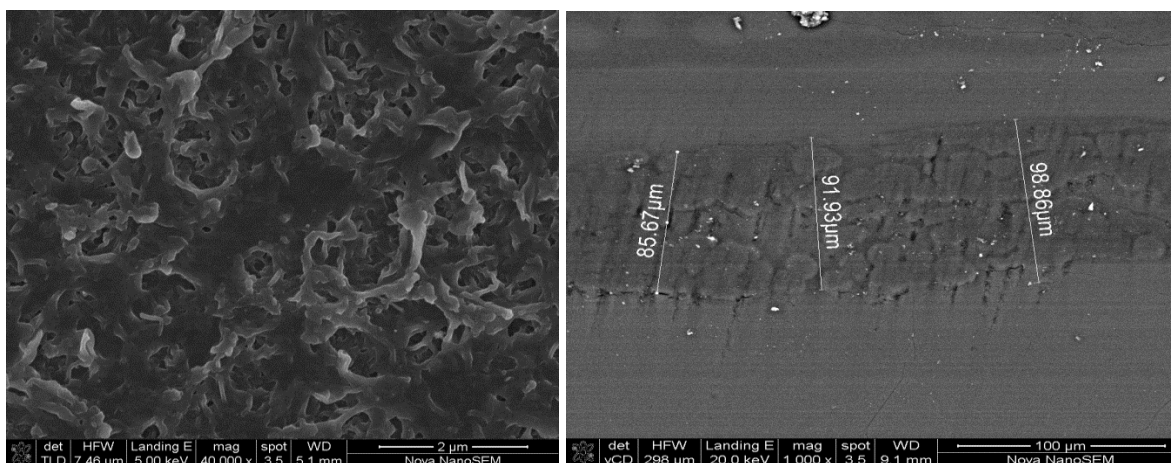


Figure 4-11: SEM images of the 0.075 mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section

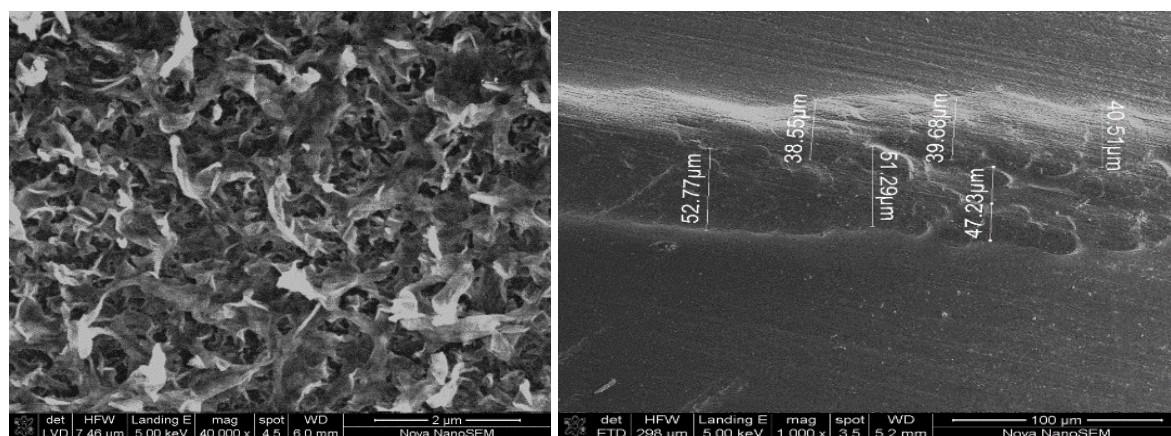


Figure 4-12: SEM images of the 0.1 mol/L DMAEMA modified membrane: (right) Top view (Left) Cross-section

In figures 4-6 to 4-12, the SEM images on the right, shows the cross-sectional morphology with a magnification of 10,000. The thickness of the unmodified membrane was measured at 75 µm. It seems that the selective skin layer of the composite membrane condenses with an increase in the concentration of the DMAEMA modifying solution. The newly formed skin layer showed a thickness of 77, 90, 92, and 93 µm as the DMAEMA solution increases from 0.02 to 0.1 mol/L, respectively. This is maybe be related to numerous functional groups on DMAEMA, which increased grafting yield and caused formation of agglomerated structures on the TFC membrane surface. Mahdavi et al., (2017) investigated the grafting of AC-HBPAE on a TFC membrane and had similar observations regarding the increase of membrane thickness when increasing the concentration of the modifying agent.

4.3 Pure water flux and % salt rejection of PVA modified membrane

The pure water flux of the unmodified membrane and PVA grafted membranes were evaluated in order to evaluate permeation properties of membranes. Experimental runs were conducted at a constant pressure of 5 bars, at room temperature. Results are shown in the figure below illustrating the water flux decline of $62 \text{ L.m}^{-2}.\text{hr}^{-1}$ for the unmodified membrane decreasing to $38 \text{ L.m}^{-2}.\text{hr}^{-1}$ for the modified membrane at the highest PVA concentration. Pure water flux of the modifying membranes decreased with increasing PVA concentration in the modifying solutions. A similar trend was observed by Liu et al., (2015), who attributed this to the increase of hydraulic resistance of the membranes. Previous modification attempts conducted, have reported a reduction of pure water flux, after modification, due to various factors (Louie et al., 2006; Yu et al., 2013; Liu et al., 2015). Azari & Zou, (2012) further described the reduction of pure water flux due to hydraulic resistance. This resistance hinders the normal hydrophilicity nature of the modified membrane.

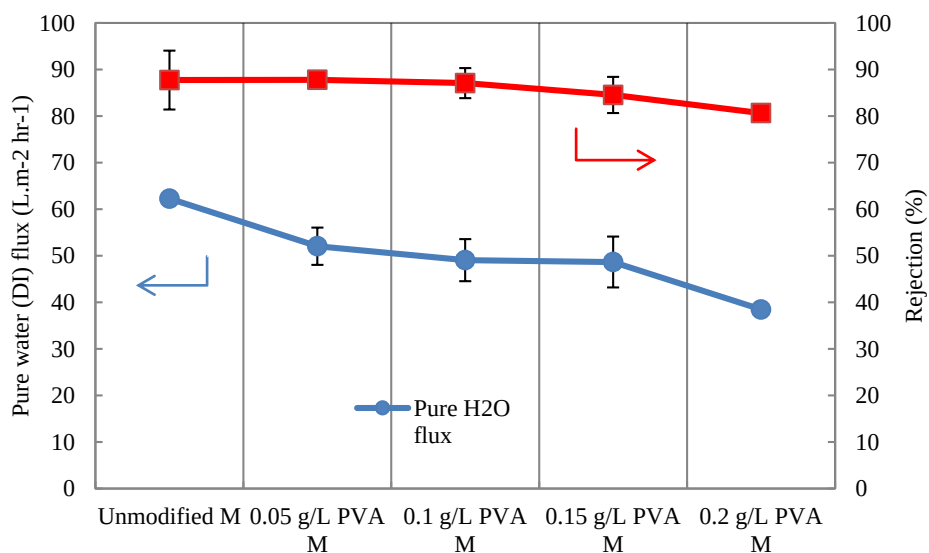


Figure 4-13: Pure water flux of modified membranes and the observed salt rejection during filtration of the MSWWT MBR effluent synthetic feed solution- (grafting of PVA)

Figure 4-13 shows the salt rejection trend during the RO fouling test using synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent. The salt rejection is constant and decreases slightly with an increase in PVA concentration. This could be due to the membrane surface charge and the ions interactions between membrane surface and the foulants after graft polymerization of PVA. (Wei et al., 2010; Yu et al., 2013). Kim et al., (2004) also observed a reduction in salt rejection after modification of a TFC RO membrane with PVA, while testing with solutions of MgSO_4 , CaCl_2 and NaCl . It was attributed to the reduction in the negative surface charge of the polyamide layer after attachment of the neutral polymer PVA.

The decrease in surface negativity is chemically explained by the covalent linkage of PVA molecules and the formation of hydrogen bonding between the carboxylic group of polyamide chains and hydroxyl groups of PVA (Yutao Hu et al., 2016). However, except for the highest concentration of PVA used in the modification, the differences in salt rejection of PVA grafted membranes and the unmodified membrane can be said to be within a margin of experimental error.

Pure water fluxes of the membranes were also compared to pure water flux after fouling experimental runs. Results are shown in the figure below, showing membrane cleaning properties (Zhao & Chen, 2015).

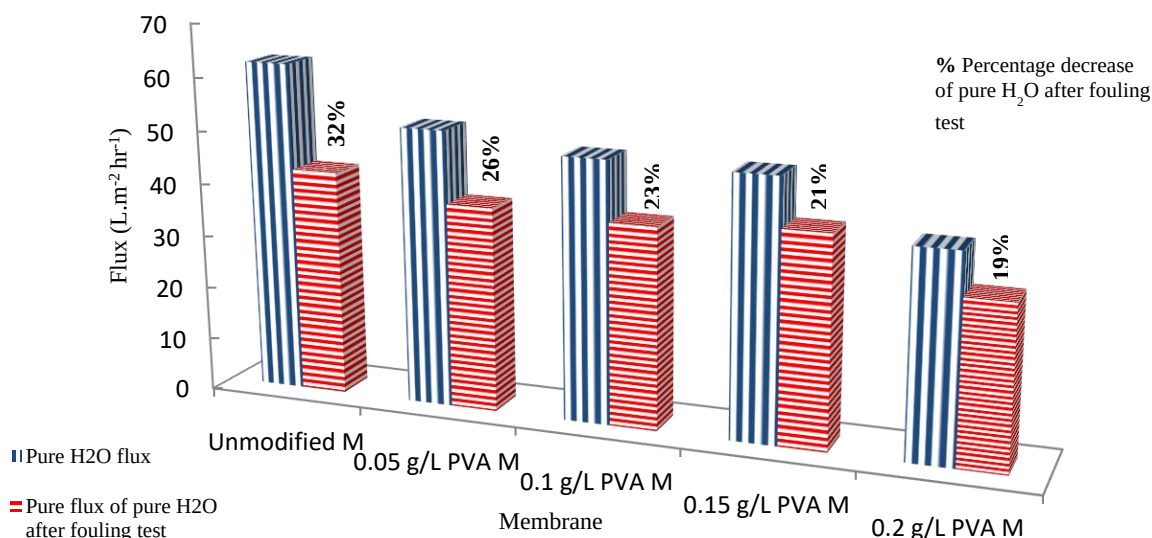


Figure 4-14: Membranes permeability in terms of pure (DI) water flux before and after fouling test (PVA grafted membranes)

The pure water flux of the unmodified membrane was reduced to by 32%. The same was observed for the modified membrane flux, that was reduced by a 26, 23, 21 and 19%, respectively, with increasing corresponding PVA concentration.

4.4 Pure water flux and % salt rejection of DMAEMA modified membranes

The pure water of DMAEMA modified membranes were evaluated and compared to the unmodified membrane, at the same operating conditions as above. In figure 4-14 it can be seen that DMAEMA modified membranes have higher pure water flux compared to the unmodified. This is contrary to the observation with the PVA modifying agent. According to Wei et al., (2010), this could be due to the increase in membrane surface hydrophilicity after grafting of the hydrophilic chains which enhance passage of water molecules. The pure water flux also increased along with DMAEMA concentration.

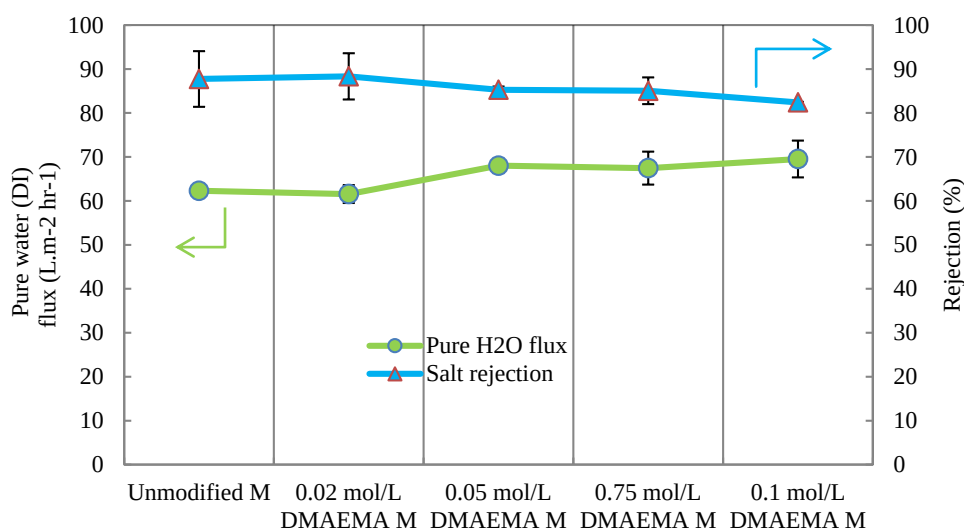


Figure 4-15: Pure water flux of modified membranes and the observed salt rejection during filtration of the MSWWT MBR effluent synthetic feed solution- (grafting of DMAEMA)

Wang et al., (2015) explained that by increasing the concentration of DMAEMA, more DMAEMA molecules attach to the polyamide surface through the Amide (II) groups. This causes a decrease in the inter-chain hydrogen bonds between carboxylic and amine groups of the polyamide layer of the membrane. Thus, resulting in a conformational change of polyamide chains and causes a

higher water flux. The grafted DMAEMA also increased the resistance to diffusion through the membrane selective layer. Hence the change of pure water flux observed was a result of effects explained above.

Figure 4-15 also shows the percentage salt rejection trend observed during the RO fouling test using synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent. Percentage salt rejections of the DMAEMA modified membranes are slightly lower than the unmodified membrane. Many researchers have attributed the decrease in percentage salt rejection after membrane surface modification, to the decrease of membrane surface negative charge. Salt rejection is partly determined by the Donnan exclusion effects.

Cheng et al., (2013) detected a decrease in salt rejection of NaCl aqueous solution after grafting of N-isopropyl acrylamide (NIPAm) to the surface of TFC polyamide RO membrane. Wei et al., (2010) observed similar trends after membrane surface modification when using 3-allyl-5,5-dimethylhydantoin. The decrease in salt rejection for both investigations was attributed to the Donnan exclusion effects.

The salt rejection investigated in this case, decreases with increased concentration of DMAEMA. The slight decrease in salt rejection also observed by Wang et al., (2015) in their research is attributed to the same reason observed for the increase in pure water flux as explained above: grafting causes decrease in the inter-chain hydrogen bonds between carboxylic and amine groups of the polyamide layer of the membrane, which causes a little decrease in salt rejection

Pure water fluxes of membranes were compared to pure water flux after fouling experiments, similarly to the previous section, as shown in figure 4-16 below.

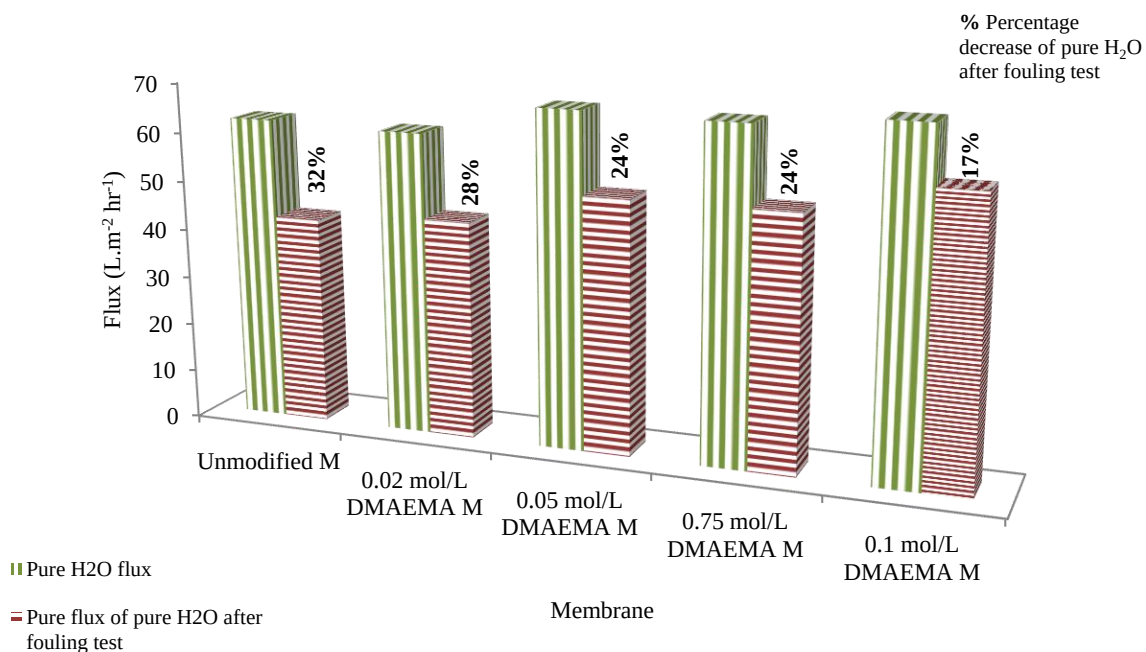


Figure 4-16 Membranes permeability in terms of pure (DI) water flux before and after fouling test (DMAEMA grafted membranes)

After fouling test and physical cleaning with DI water flux of pure water were at the same operating conditions as before fouling to make a comparison. It can be seen from the figure 4.16, that the DMAEMA modified membranes gives better cleaning properties then the unmodified membrane. The pure water flux declined by 28, 24, 24 and 17%, respectively, with increasing DMAEMA concentration.

4.5 Flux of PVA modified membranes during the fouling test

The figures below present the permeate normalized flux profile of the membranes during the filtration of a synthetic or simulated municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent with an average pH of 5.64. The initial permeate flux of $57.5 \text{ L.m}^{-2}.\text{h}^{-1}$ was used for all experimental runs. All experimental runs were duplicated and the average values were used to plot the data graphs. The empty spaces on the graphs were after hours when data was not collected. The starting time of each of the fouling experimental runs was preceded by a 12 hour of DI water flushing.

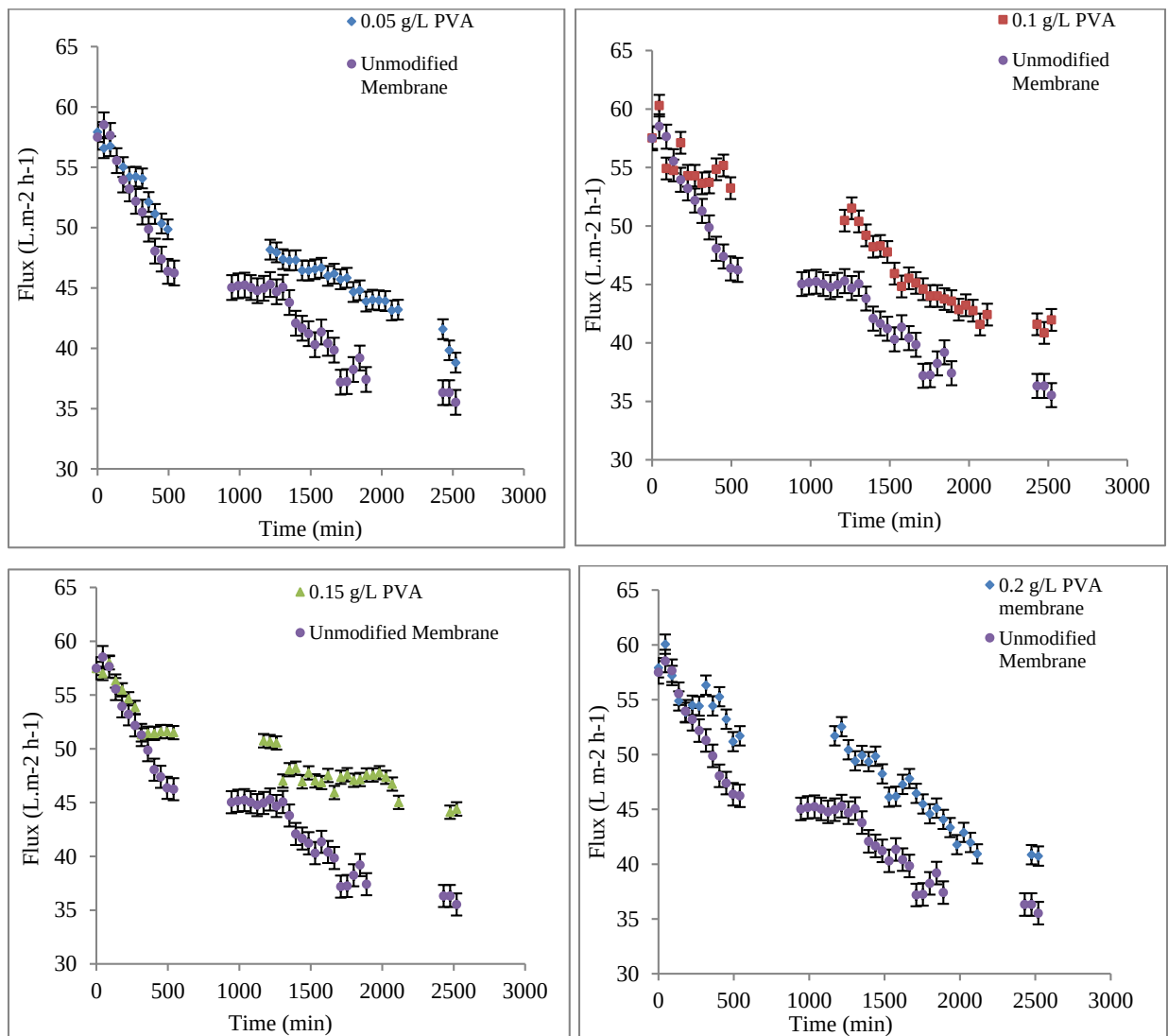


Figure 4-17: Time dependent flux of PVA modified membranes: treatment of the synthetic feed.

It can be seen that there is a persistent decrease in the flux, for all four graphs in figure 4-17, which proves the presence of fouling as confirmed by Cheng et al., (2013). Although the graphs reveal that a gradual decrease of the flux could not be totally eliminated, but the accumulation of fouling matter on the modified membranes was much lesser than the unmodified. It was also observed that the modified membrane flux after forty-two hours or 2520 minutes were higher than the unmodified.

The graphs show similar trends throughout the time period. It illustrates antifouling performance of membranes at similar conditions of 19 cm/s cross-velocity and 5 bars. The flux was normalized at a temperature of 25 °C to account for the variation of the feed temperature as it can be seen in Appendix C. In the first few minutes of filtration, the fouling seems not to be that significant. However, over time the flux decline is more noticeable, and the flux difference between the unmodified and the modified membranes, increases. The distance between fluxes curves on each plot, differ. The normalized flux decline of the 0.05 g/L PVA and the unmodified membrane seems to be similar in the first 500 min; thereafter it increases more for the unmodified. It can be seen that the flux decline ratio for the 0.15 g/L PVA membrane is the largest. These trends show that the flux decline is minimized when increasing the concentration of PVA in the modifying solution from 0.05 g/L to 0.15 g/L.

Wang, et al., (2015) used two different type of modification reagents, namely, DMAEMA and DMAEMA with 3-BPA on a polyamide TFC RO membrane. Although he did not investigate different concentrations of the modifying solutions, he observed similar trends when comparing modified and unmodified membrane flux.

Cheng, et al., (2013) also introduced hydrophilic chains N-isopropyl acrylamide with acrylic acid at different concentrations, to the surface of a polyamide TFC RO membrane and conducted fouling test using BSA solution. Similar trends were observed with the flux of the unmodified membrane declining by 45.3% against the modified membrane of 20.73%, after an experimental filtration run of 42 hours.

4.6 Flux of DMAEMA modified membranes during the fouling test

The figures below present the permeate normalized flux profile of membranes during the filtration of synthetic or simulated municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent with an average pH of 5.64. The same conditions were used in the RO process, as before, to evaluate fouling of DMAEMA modified membranes. The figures below show the flux profiles of all DMAEMA modified membranes.

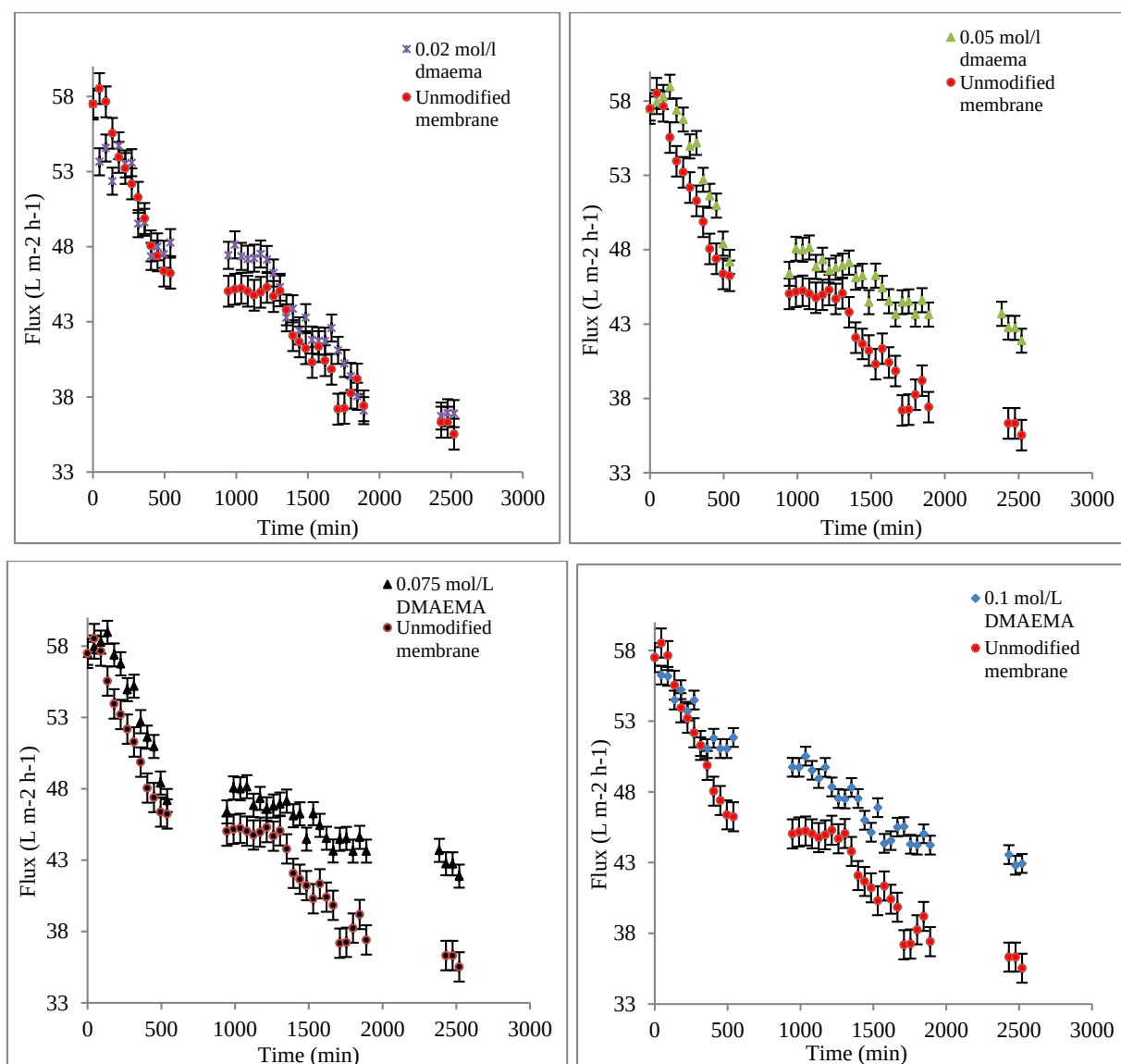


Figure 4-18: Time dependent flux of DMAEMA modified membranes during filtration of the synthetic feed

It is clear from graphs in figure 4-18, that there is a persistent decrease in the flux, which proves the presence of fouling. However, the trend of the flux decline differs between the unmodified and each of the individual modified membranes, as compared by each plot. Similarly to the previous modification, the flux decline of all the membranes is almost identical in the first 500 minutes of the fouling tests. It can be seen that the distance between the curves widens with time when comparing the unmodified with modified membranes. The flux profile of the 0.02 mol/L DMAEMA membrane is approximately the same as the unmodified membrane and after the 2520 minutes filtration time, the flux declined by 35.84 and 38.21% respectively. It can be said that 0.02 mol/L concentration is so low that only a slight change the structure of the membrane surface. This could be a reason why the results in membrane performance properties are similar to the unmodified ones.

The DMAEMA modified membrane with the highest concentration of 0.1 mol/L had the lowest flux decline. As mentioned before, the flux decline was minimized by adjusting the modifying solution concentration. Yutao Hu et al., (2016) noticed a similar trend in their investigation. They motivated that the flux decline was decrease when controlling the concentration of the modifying agent during modification of the membrane surface. Flux decline rate is an indication of fouling severity, thus higher flux decline indicates that sever fouling happens Yu et al., (2013). Thus it can be deduced that the fouling was more severe with the unmodified membrane and the least with the highest concentration of DMAEMA used.

4.7 Antifouling properties of PVA modified membranes

Antifouling properties of the membranes in the presence of synthetic feed foulants were evaluated using two ratios as reported by different researchers, namely: the flux decline ratio and the flux recovery ratio. (Shen et al., 2017; Zhao & Chen, 2015; Wang et al., 2015)

Figure 4-19 presents the flux decline ratio during filtration of the synthetic effluent alongside with the flux recovery ratio (FRR) which was obtained after the fouling experimental runs with unmodified and PVA modified membranes. The cleaning properties of membranes were evaluated by calculating the FRR the after fouling test and cleaning with DI water. Pure water fluxes of membranes were obtained before the fouling tests and compared to pure water fluxes of membranes after cleaning to calculate the flux recovered. The highest FDR and lowest FRR were obtained from the unmodified membrane.

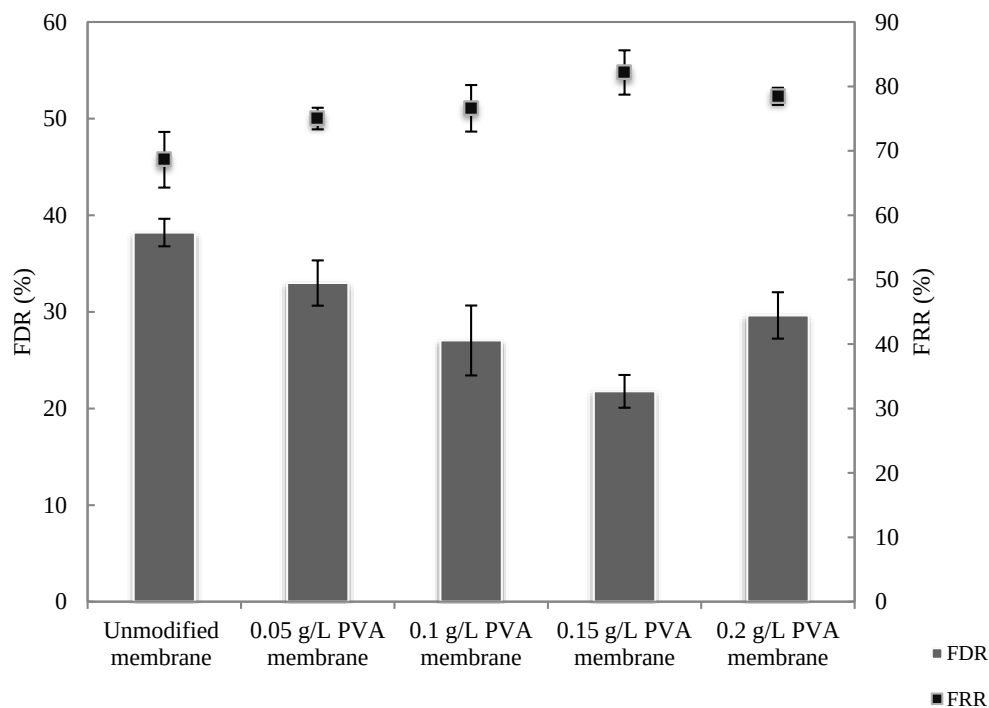


Figure 4-19: FDR during filtration of the synthetic feed and pure water FRR membranes (-PVA grafted membranes)

Figure 4-19 shows the flux decline ratio (FDR) for the unmodified and PVA modified membranes after a 42 hour (2520 minutes) fouling experimental run. For the unmodified membrane, FDR is 38.21%. The PVA modified membranes, the FDR is as follows: 32.99 % (0.05 g/L PVA); 27.05 % (0.1 g/L PVA); 21.66 % (0.15 g/L PVA) and 29.64 % (0.2 g/L PVA), respectively. The pure water flux of the unmodified membrane after fouling experiments was recovered only to 68.61%, while the FRR of the PVA modified membrane were 75.01%, 76.61%, 82.16% and 78.47% with increase concentration of PVA. According to Mahdavi et al., (2017), the higher flux recovery indicates that fouling occurring, is more reversible. Thus it can be said that fouling of modified membrane was more reversible with increasing concentration with the PVA.

4.7.1 Antifouling properties of PVA modified membranes model

Design expert was used to perform data analysis on the flux data obtained. The concentration of the modifying solutions and time were set as factors and the flux decline ratio as the response under “user defined”. Time as a factor was selected with 5 levels (0 hr, 21 hr, 32 hr, and 42h). The PVA concentrations were of 5 levels which corresponded to concentration of PVA used in the experiments.

The effect of modification of the membrane surface on membrane flux decline ratio could be predicted using the model as presented Appendix K.

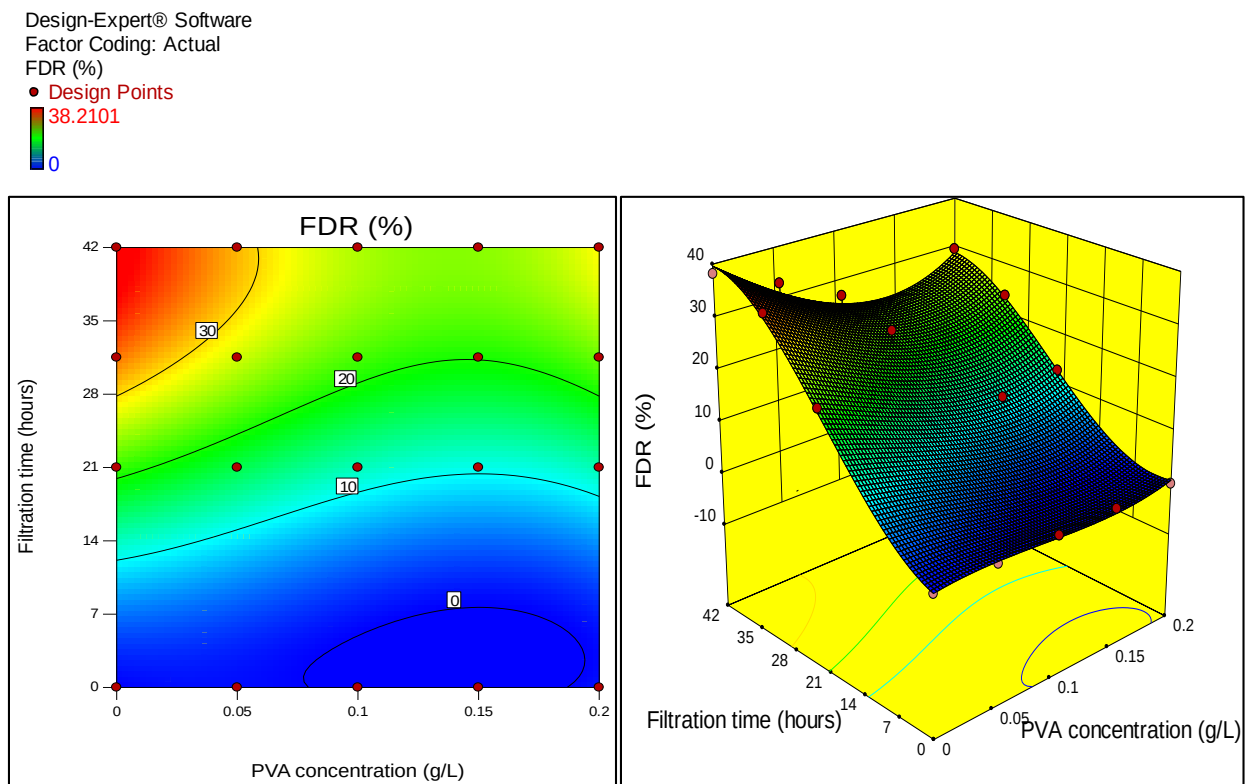


Figure 4-20: Contour (left) and 3D (right) graphs portraying the effect of PVA concentration change on the flux decline during the filtration of the synthetic feed

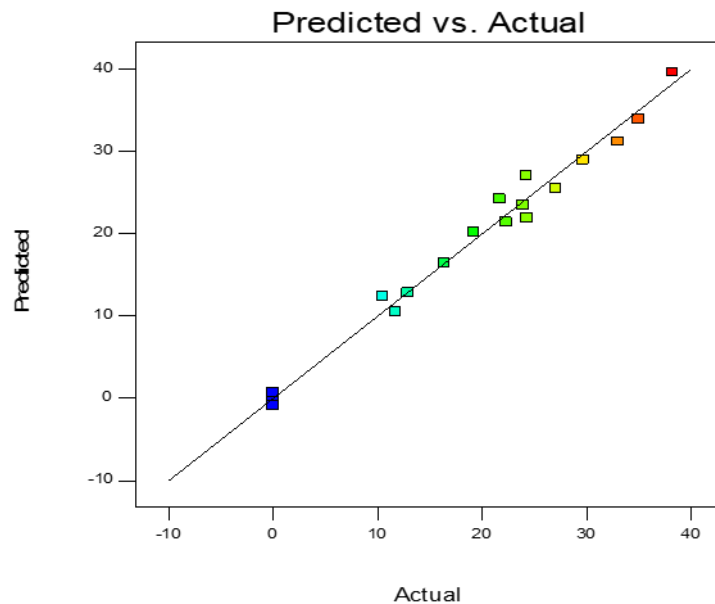


Figure 4-21: Predicted values of the flux against actual values of flux obtained (PVA grafted membrane)

Fig. 4-20 above shows clearly the effect of changing PVA concentration on the FDR. Furthermore, it can be seen that the lowest FDR is obtained around the concentration of 0.15 g/L PVA. Fig. 4-21 further displays predicted values of the FDR set against experimental values obtained. Points of experimental values are all scattered around the line as they all found to close to predict values. The minor difference between them is explained by the fact that experimental values represent the real behaviour of the FDR under conditions tested.

4.8 Antifouling properties of DMAEMA modified membranes

Figure 4-22 shows antifouling properties of the DMAEMA modified membranes. After the fouling test, the flux declines ratios (FDR) varied from 38.21 % for the unmodified membrane to 25.5 %, for the highest concentration of DMAEMA modified membrane. Yutao Hu et al., (2016) mentioned that lower flux decline rate shows that the membrane possesses better resistance to fouling. Thus it can be said that the modified membranes had better resistance to fouling than the unmodified membrane when exposed to the synthetic MSWW MBR secondary effluent.

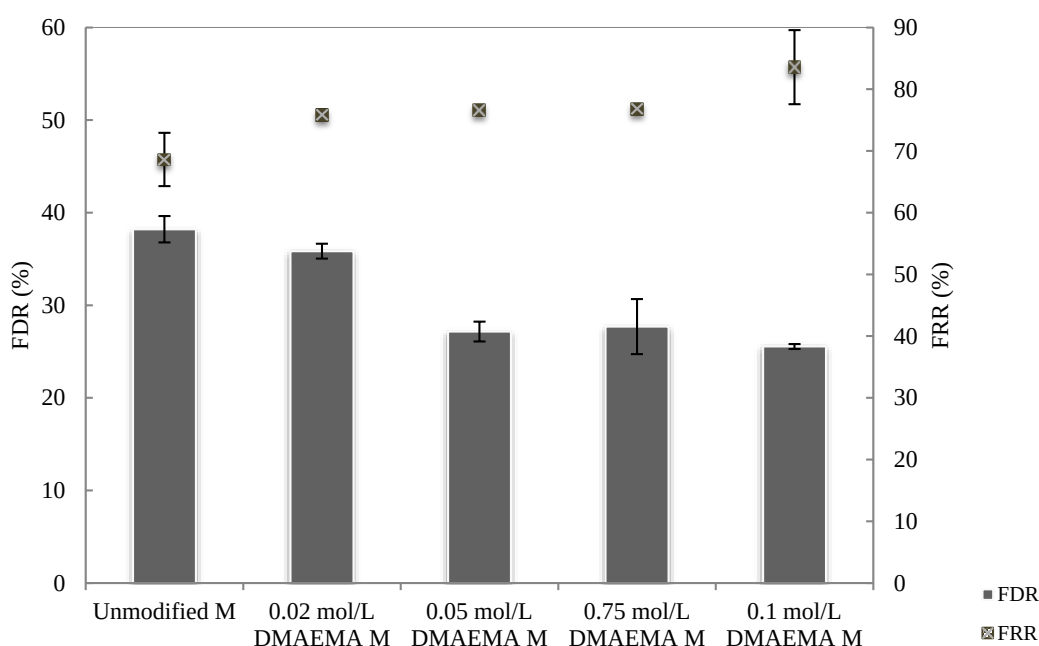


Figure 4-22: FDR during filtration of the synthetic feed and pure water FRR membranes (DMAEMA grafted membranes)

After fouling, membranes were cleaned with DI water for 30 min, and the operating conditions were set at same initial conditions for pure water flux measurement to calculate the FRR. In figure 4-22, it can be seen that flux recovery ratio (FRR) for modified membranes are higher than the unmodified. This suggests that the pure water flux of DMAEMA membranes could be recovered to a high value after the fouling test and cleaning process with DI water.

The FRR increases with an increasing concentration of DMAEMA in the modifying solutions. The FRR of the 0.1 mol. L⁻¹ modified membrane was the highest (83.57%), while the unmodified membrane had the lowest FRR (68.61%). The results show that fouling on the DMAEMA membrane caused by synthetic solution could be removed effortlessly compared to the unmodified membrane, thus showing an improvement in the membrane cleaning properties and membrane performance as stated by Zhao & Chen (2015).

4.8.1 Antifouling properties of DMAEMA modified membranes model

Design expert software was used to perform data analysis on the flux decline ratio data obtained, similarly to the previous section. The impact of the modifying solution concentration and fouling test time on the FDR were simultaneously analysed. The concentration of the modifying solutions and time were set as factors and the flux decline ratio as the response under “user defined”. Time as a factor was selected with 5 levels (0 hr, 21 hr, 32 hr, and 42h). The DMAEMA concentrations were of 5 levels which corresponded to concentration of PVA used in the experiments.

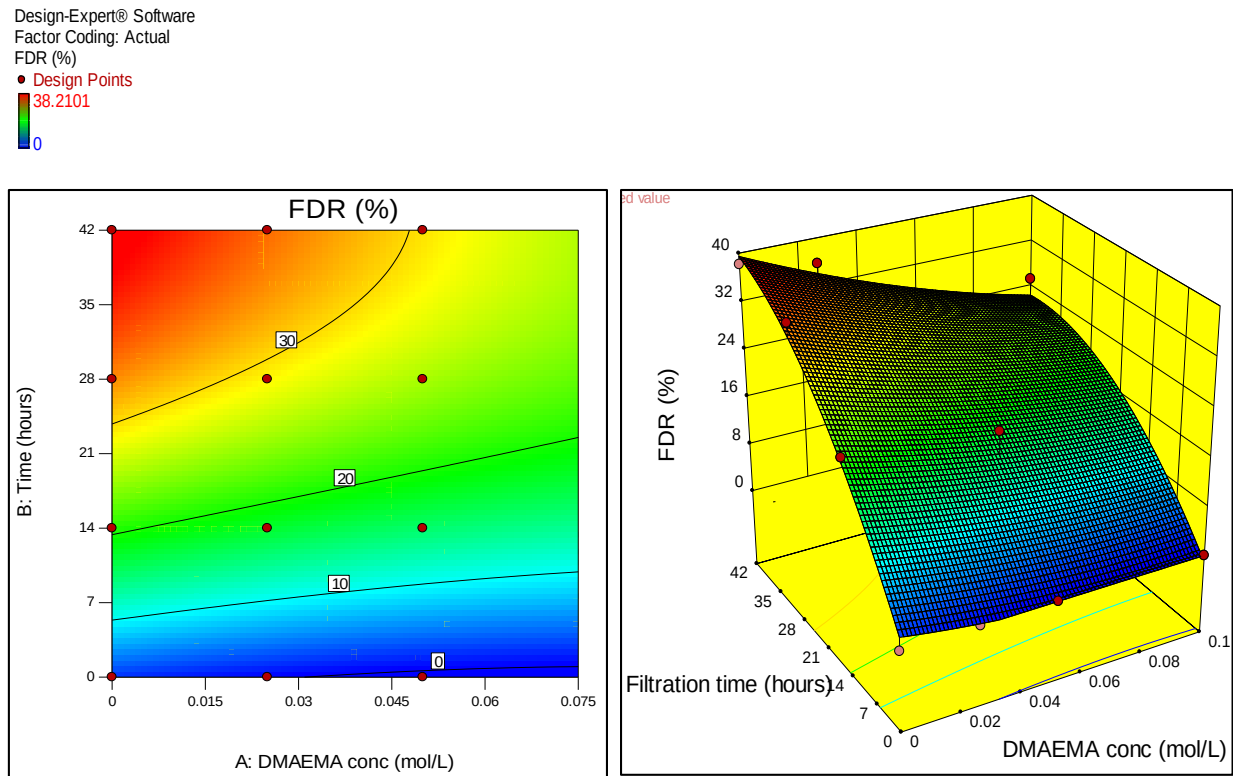


Figure 4-23: Contour (left) and 3D (right) graphs portraying the effect of PVA concentration change on the flux decline during the filtration of the synthetic feed

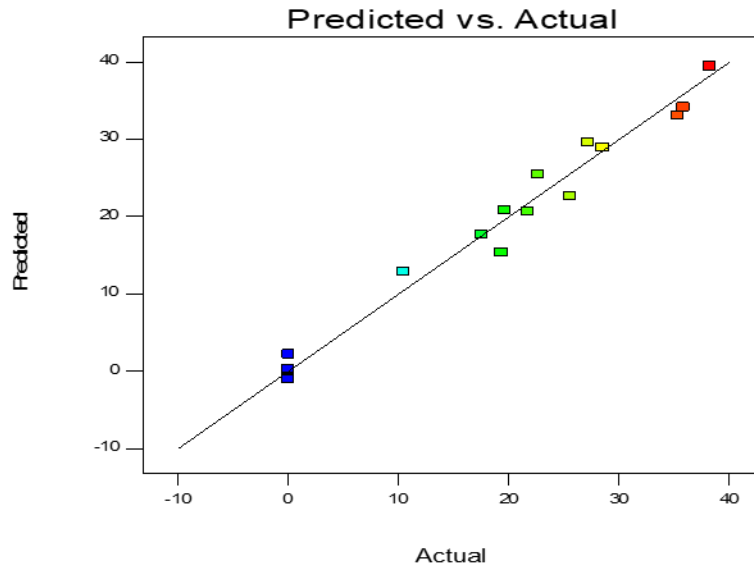


Figure 4-24: Predicted values of the flux against actual values of flux obtained (DMAEMA grafted membrane)

The plot above shows how the model predicts over the range of data. ANOVA report is provided in appendix K. it can be seen in figure 4-24 that points are scattered randomly about the 450 line in the middle of data. The points below the line shows issues of under predicting while points above the line shows problems of over predicting. Although all points are closed to the line, the plot indicates that the response of cannot be predicted very precisely.

4.9 Membrane anti biofouling properties

Three membranes were selected to perform biofouling test and evaluate membrane anti-biofouling properties: unmodified membrane, PVA and DMAEMA unmodified membranes. *Escherichia coli* (E.coli) which is seen as a crucial target microorganism by researchers (Wei et al., 2010) , was used as a model bio-foulant in this investigation. E.coli bacterial solution was prepared, with a concentration of 16×10^7 CFU/mL; (B : Number of viable bacteria in the solution not in contact with the membrane); and placed in contact with the membrane of a surface area 4cm^2 (2 cm x 2 cm), for a duration of 3 hours. In table 4-2, below, the number of viable bacteria in contact with the membrane (A) and sterilization ratio (R) of each of the selected membranes are reported. Experiments were conducted in duplication and average values are reported as follows:

Table 4-1: Reported values of membrane sterilization ratios obtained from the selected membranes

Membrane	A ($\times 10^6$ CFU/mL)	B (CFU/mL)	Sterilization ratio, R (%)
Unmodified M	106	16×10^7	33.8
0.1 DMAEMA mol/L M M	37	16×10^7	76.8
0.1 g/L PVA M M	100	16×10^7	36.8

The highest R value of 76.8% was obtained from the 0.1 mol/L DMAEMA modified membrane whilst the lowest value of 33.8%, for the unmodified. The R value of the 0.1 g/L PVA modified membrane was 36.8% compared to the unmodified of 33.8%. The PVA modified membrane R value is much lower compared to the DMAEMA modified membrane. A higher sterilization ratio shows that the membrane possesses high anti-microbial property against the microorganism tested which hinders the growth and multiplication of these microbial cells according to Xu et al., (2013) and Wang et al., (2013). It would be inaccurate to compare the two concentrations of the modified membranes selected in this section due to the different concentration units applied to investigate anti-biofouling properties.

Photo 4-1 shows the number of living colonies of *E. coli* bacteria, after contact with membranes for 3 hours. Number of cells was determined by dilution and inoculation of cells suspension on nutrient agar in petri dish followed by overnight incubation. (Plate of 10^6 mL diluted solution).

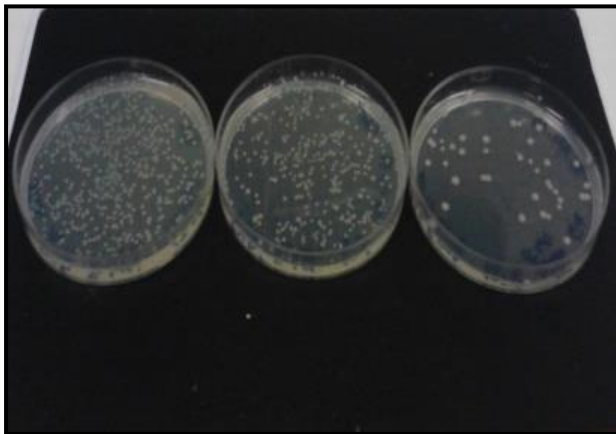


Photo 4-1: Viable *E. coli* colonies collected after contact with membranes (From left to right: Unmodified membrane, PVA grafted membrane, DMAEMA modified membrane)

Manual counting revealed that the number of living bacteria colonies on the DMAEMA modified membrane surface was less, while the unmodified membrane had the most number of colonies. According to Wang et al., (2015) the improved resistance to bacterial growth of the DMAEMA modified membrane is a result of the higher presence of tertiary amine groups on the surface. The PVA modified membrane had a low mortality ratio, similar to the unmodified membrane, and this can also be seen from the number of colonies obtained from cell suspension in contact with the PVA modified membrane as shown below.

The three membranes selected were further tested for water flux in the RO process after exposure to *E. coli* bacteria cell suspension for 30 hours. This followed the same methodology implemented by Zhang et al., (2017). Values of flux before and after exposure time were reported in the table below.

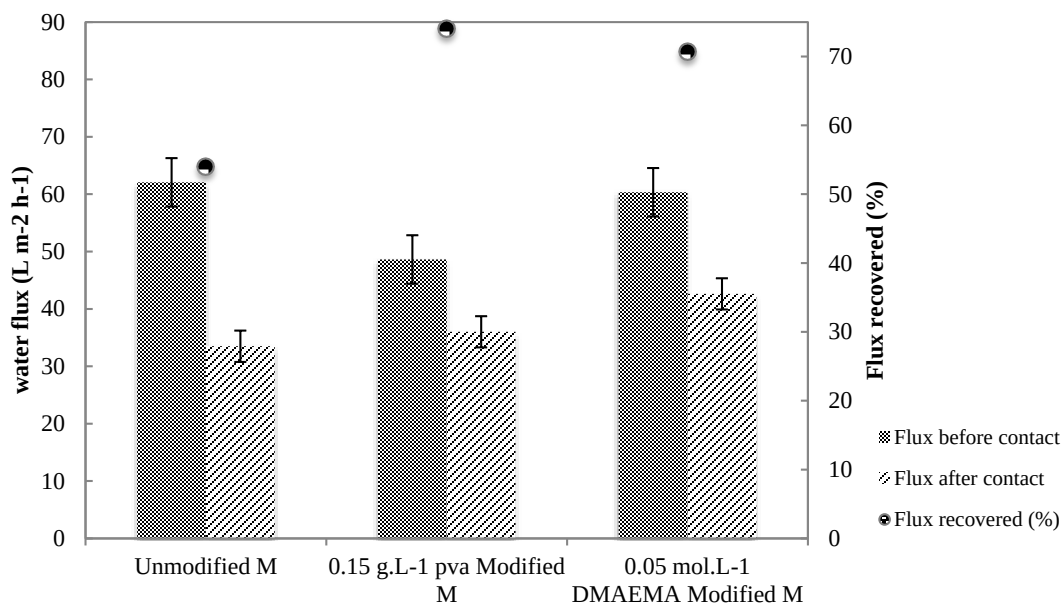


Figure 4-25: Pure water flux of membranes before and after biofouling of *E. coli* bacteria

After physical cleaning, the pure water flux of the membranes was measured at the same initial conditions and compared. The water flux of the unmodified membrane decreased from 62.07 L.m⁻²h⁻¹ to 33.49 L.m⁻²h⁻¹ after biofouling, which was caused by the adhesion of *E. coli* cells to the surface of the membrane. In contrast, water flux of the PVA and DMAMEMA modified membranes respectively decreased from 48.62 L.m⁻²h⁻¹ to 36.00 L.m⁻²h⁻¹, and 60.33 L.m⁻²h⁻¹ to 42.62 L.m⁻²h⁻¹ under the same fouling conditions. This mean, pure water flux of the unmodified membrane could be recovered to only 54%, while the flux of the PVA and DMAEMA modified membranes could be recovered to 74% and 70 %.

Mahdavi et al., (2017) stated that the flux recovery ratio after grafting of Acrylated hyper branched poly (amine ester) to a polyamide membrane and tested with BSA solution, can be said that fouling is more reversible with a modified membrane.

These observation, according to Zhang et al., (2017) further suggests that the modified membranes used, enhanced anti-biofouling properties with reduced adhesion of microorganism, improved contact-killing abilities, and decrease water flux decline after biofouling.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

Conclusion

The decrease in membrane performance over long periods in the treatment of waste water is one of the major problems caused by fouling. Fouling mechanisms are related to membrane surface characteristics and the interaction between membrane surfaces and foulants.

The chemical grafting on a polyamide TFC membrane was investigated with two different types of modifying agents. This was done to improve the membrane characteristics such as the resistance to fouling in a bench scale RO process. The first type of modifying agent was GA and PVA solution who were grafted to the surface of the membrane at four different PVA concentrations. The second modifying agent, DMAEMA with four different concentrations was attached to the surface of the membrane through redox initiated grafting.

The PVA and DMAEMA modifying agents were successfully grafted onto the membrane top layers and confirmed by the functional groups, present. The chemical composition of the modified membranes observed through the ATR-FTIR spectra, revealed an increase in the intensities of the peaks for all the modified membranes, when the concentration was increased.

A morphological change of the membranes was observed using SEM analysis. An increase in the concentration of the PVA aqueous solution caused an increase in the membrane surface roughness and a decrease of the pure water flux. Contrary, an increase in the concentration of the DMAEMA aqueous solution caused an increase of the pure water flux.

During the anti-biofouling test with *E. coli* as biological foulant the sterilization ratio for the unmodified, DMAEMA and PVA modified membranes was 33.8, 76.8 and 36.8 %, respectively. The DMAEMA modified membrane with the highest sterilization ratio shows better anti-microbial properties against microorganism tested, obstruct growth and multiplication. This was confirmed with the pure water flux test, where the unmodified, DMAEMA and PVA modified membranes declined by 46, 26 and 29 %, respectively. Again the modified membranes showed better anti-biofouling properties and prove to minimize *E. coli* bacteria adsorption on the membrane surface.

Anti-fouling properties and performance of membranes was tested using synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent using a lab scale RO process. The salt rejection for both PVA and DMAEMA modified membranes decreased as its concentration increased, due to the change in surface charge. The flux decline ratio for the unmodified membrane was the highest at 38.21%. As the modifying agent concentration of PVA and DMAEMA increased, the flux decline ratio (FDR) decreased to 21.78 and 25.54% respectively,

The flux recovery ratio (FRR) for the unmodified membrane was the lowest at 68.61%. As the modifying agent concentration of PVA and DMAEMA increased so did the flux recovery ratio to 82.16 and 83.57%, respectively.

It was clearly shown that the PVA and DMAEMA grafting solutions changed the structure of the membrane top layer, enhancing the resistance to fouling. A statistical analysis using Design expert 10 also revealed the impact of the modifying solutions concentration on the FDR.

It can be confirmed that the membrane performance investigated using synthetic municipal sewage waste water (MSWW) membrane bioreactor (MBR) secondary effluent could improve when applying modifications using various modifying solution concentration.

Recommendations

In order to improve the viability of this membrane surface modification process, the following should be considered:

- A thorough analysis of the main constituents of the effluent identified as foulants should be conducted to understand their interaction and repulsion effects with the surface of the modified membranes.
- A direct measurement and study through analysis on the fouling layer formed during the filtration of the effluent should be conducted to acquire in-depth characteristics of the layer composition. (AFM, XPS)
- Further investigations should be carried using a real MBR effluent from municipal waste water treatment plant
- A feasibility study for full scale application.

BIBLIOGRAPHY

Bibliography

- Abdullah, S.Z., Bérubé, P.R. & Horne, D.J. 2014. SEM imaging of membranes: Importance of sample preparation and imaging parameters. *Journal of Membrane Science*, 463: 113–125. <http://dx.doi.org/10.1016/j.memsci.2014.03.048>.
- Adewumi, J.R., Ilemobade, A.A. & Zyl, J.E. Van. 2010. Resources , Conservation and Recycling Treated wastewater reuse in South Africa : Overview , potential and challenges. '*Resources, Conservation & Recycling*', 55(2): 221–231. <http://dx.doi.org/10.1016/j.resconrec.2010.09.012>.
- An, Q., Li, F., Ji, Y. & Chen, H. 2011. Influence of polyvinyl alcohol on the surface morphology, separation and anti-fouling performance of the composite polyamide nanofiltration membranes. *Journal of Membrane Science*, 367(1–2): 158–165. <http://dx.doi.org/10.1016/j.memsci.2010.10.060>.
- Asadollahi, M., Bastani, D. & Musavi, S.A. 2017. Enhancement of surface properties and performance of reverse osmosis membranes after surface modification : A review. *Desalination*, 420(June): 330–383. <http://dx.doi.org/10.1016/j.desal.2017.05.027>.
- Azari, S. & Zou, L. 2012. Using zwitterionic amino acid L-DOPA to modify the surface of thin film composite polyamide reverse osmosis membranes to increase their fouling resistance. *Journal of membrane science*, 401: 68–75.
- Baker, R.W. 2004. Membrane technology and applications. *John Wiley & Sons, Ltd*: 96–103.
- Basheer, C., Suresh, V., Renu, R. & Lee, H.K. 2004. Development and application of polymer-coated hollow fiber membrane microextraction to the determination of organochlorine pesticides in water. *Journal of Chromatography A*, 1033(2): 213–220.
- Cahill, D.G. & Freger, V. 2017. Microscopy and Microanalysis of Reverse-Osmosis and Nanofiltration membranes. *MRS Bulletin*, 33(January 2008): 27–32. <https://www.cambridge.org/core/terms>. <https://doi.org/10.1557/mrs2008.11>

- Cartagena, P., Kaddouri, M. El, Cases, V., Trapote, A. & Prats, D. 2013. Reduction of emerging micropollutants , organic matter , nutrients and salinity from real wastewater by combined MBR – NF / RO treatment. *Separation and Purification Technology*, 110: 132–143. <http://dx.doi.org/10.1016/j.seppur.2013.03.024>.
- Çeçen, F. & Aktas, Ö. 2011. *Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment*. John Wiley & Sons.
- Cheng, Q., Zheng, Y., Yu, S., Zhu, H., Peng, X., Liu, J., Liu, J., Liu, M. & Gao, C. 2013. Surface modification of a commercial thin-film composite polyamide reverse osmosis membrane through graft polymerization of N-isopropylacrylamide followed by acrylic acid. *Journal of Membrane Science*, 447: 236–245. <http://dx.doi.org/10.1016/j.memsci.2013.07.025>.
- Chennamsetty, R., Escobar, I. & Xu, X. 2006. Characterization of commercial water treatment membranes modified via ion beam irradiation. *Desalination*, 188(1–3): 203–212.
- Childress, A.E. & Elimelech, M. 1996. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, 119: 253–268.
- Chyan, J.M., Jhu, Y.X., Chen, I.M. & Shiu, R.F. 2016. Improvement of nitrogen removal by external aeration and intermittent circulation in a subsurface flow constructed wetland of landscape garden ponds. *Process Safety and Environmental Protection*, 104: 587–597.
- Coates, J. 2006. Interpretation of Infrared Spectra, A Practical Approach. *Encyclopedia of Analytical Chemistry*: 1–23. <http://doi.wiley.com/10.1002/9780470027318.a5606>.
- Coulson, J.M. 1962. Coulson And Richardsons Chemical Engineering, Volume 2. *disp*, 10: 32.
- De, S. & Mondal, S. 2012. *Micellar Enhanced Ultrafiltration: Fundamentals & Applications*. CRC press.
- Dolar, D., Gros, M., Rodriguez-mozaz, S., Moreno, J. & Comas, J. 2012. Removal of emerging contaminants from municipal wastewater with an integrated membrane system , MBR – RO. *Journal of Hazardous Materials*, 239–240: 64–69. <http://dx.doi.org/10.1016/j.jhazmat.2012.03.029>.

- Duer, M.J. 2008. *Solid state NMR spectroscopy: principles and applications*. John Wiley & Sons.
- Fenu, A., Wilde, W. De, Gaertner, M., Weemaes, M., Gueldre, G. De & Steene, B. Van De. 2012. Elaborating the membrane life concept in a full scale hollow-fibers MBR. *Journal of Membrane Science*, 421–422: 349–354. <http://dx.doi.org/10.1016/j.memsci.2012.08.001>.
- Freger, V., Gilron, J. & Belfer, S. 2002. TFC polyamide membranes modified by grafting of hydrophilic polymers : an FT-IR / AFM / TEM study. , 209: 283–292.
- Fridjonsson, E.O., Vogt, S.J., Vrouwenvelder, J.S. & Johns, M.L. 2015. Accepted Manuscript. *Journal of Membrane Science*. <http://dx.doi.org/10.1016/j.memsci.2015.03.088>.
- Geankoplis, C.J. 2003. *Transport processes and separation process principles: (includes unit operations)*. Prentice Hall Professional Technical Reference.
- Godoy-Olmos, S., Martínez-Llorens, S., Tomás-Vidal, A. & Jover-Cerdá, M. 2016. Influence of filter medium type, temperature and ammonia production on nitrifying trickling filters performance. *Journal of Environmental Chemical Engineering*, 4(1): 328–340.
- Good, K., Escobar, I., Xu, X., Coleman, M. & Ponting, M. 2002. Modification of commercial water treatment membranes by ion beamGood, K., Escobar, I., Xu, X., Coleman, M. & Ponting, M. 2002. Modification of commercial water treatment membranes by ion beam irradiation. *Desalination*, 146(1–3): 259–264. irradiation. *Desalination*, 146(1–3): 259–264.
- Gumbo, B., Forster, L. & Arntzen, J. 2005. Capacity building in water demand management as a key component for attaining millennium development goals. , 30: 984–992.
- Hoinkis, J., Deowan, S.A., Panten, V., Figoli, A. & Rong, R. 2012. Procedia Engineering Membrane Bioreactor (MBR) Technology – a Promising Approach for Industrial Water Reuse. , 33(2009): 234–241. <http://dx.doi.org/10.1016/j.proeng.2012.01.1199>.
- Hu, Y., Lu, K., Yan, F., Shi, Y., Yu, P., Yu, S. & Li, S. 2016. Enhancing the performance of aromatic polyamide reverse osmosis membrane by surface modification via covalent attachment of polyvinyl alcohol (PVA). *Journal of Membrane Science*, 501: 209–219. <http://dx.doi.org/10.1016/j.memsci.2015.12.003>.
- Hu, Y., Wang, X.C., Yu, Z., Hao, H. & Sun, Q. 2016. New insight into fouling behavior and foulants

- accumulation property of cake sludge in a full-scale membrane bioreactor. *Journal of Membrane Science*, 510: 10–17. <http://dx.doi.org/10.1016/j.memsci.2016.02.058>.
- Ishigami, T., Amano, K., Fujii, A., Ohmukai, Y., Kamio, E., Maruyama, T. & Matsuyama, H. 2012. Fouling reduction of reverse osmosis membrane by surface modification via layer-by-layer assembly. *Separation and purification technology*, 99: 1–7.
- Jonas, J. & Gutowsky, H.S. 1968. Nuclear Magnetic Resonance. *Annual Review of Physical Chemistry*, 19(1): 447–476.
<http://www.annualreviews.org/doi/abs/10.1146/annurev.pc.19.100168.002311>.
- Judd, S.J. 2015. The status of industrial and municipal effluent treatment with membrane bioreactor technology. *CHEMICAL ENGINEERING JOURNAL*.
<http://dx.doi.org/10.1016/j.cej.2015.08.141>.
- Kang, G. & Cao, Y. 2011. Development of antifouling reverse osmosis membranes for water treatment: A review. *Water Research*, 46(3): 584–600.
<http://dx.doi.org/10.1016/j.watres.2011.11.041>.
- Kang, G., Liu, M., Lin, B., Cao, Y. & Yuan, Q. 2007. A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting poly (ethylene glycol). , 48: 1165–1170.
- Kang, G., Yu, H., Liu, Z. & Cao, Y. 2011. Surface modification of a commercial thin film composite polyamide reverse osmosis membrane by carbodiimide-induced grafting with poly (ethylene glycol) derivatives. *DES*, 275(1–3): 252–259.
<http://dx.doi.org/10.1016/j.desal.2011.03.007>.
- Khan, M.T., Busch, M., Molina, V.G., Emwas, A.H., Aubry, C. & Croue, J.P. 2014. How different is the composition of the fouling layer of wastewater reuse and seawater desalination RO membranes. *Water Research*, 59: 271–282. <http://dx.doi.org/10.1016/j.watres.2014.04.020>.
- Khulbe, K.C., Feng, C. & Matsuura, T. 2010. The art of surface modification of synthetic polymeric membranes. *Journal of Applied Polymer Science*, 115(2): 855–895.
- Khulbe, K.C., Hamad, F., Feng, C., Matsuura, T. & Khayetb, M. 2004. Study of the surface of the water treated cellulose acetate membrane by atomic force microscopy. , 161: 259–262.

- Kim, I.-C., Ka, Y.-H., Park, J., Lee, K.-H. & others. 2004. Preparation of fouling resistant nanofiltration and reverse osmosis membranes and their use for dyeing wastewater effluent. *Journal of Industrial and Engineering Chemistry*, 10(1): 115–121.
- Kucera, J. 2015. *Reverse osmosis: design, processes, and applications for engineers*. John Wiley & Sons.
- Kucera, J. 2011. *Reverse Osmosis: Industrial applications and processes*. Wiley.
- Kuhn, W. 1990. NMR Microscopy—Fundamentals, Limits and Possible Applications. *Angewandte Chemie International Edition in English*, 29(1): 1–19.
- Lau, W.J., Ismail, A.F., Misdan, N. & Kassim, M.A. 2012. A recent progress in thin fi lm composite membrane : A review. *DESALINATION*, 287: 190–199. <http://dx.doi.org/10.1016/j.desal.2011.04.004>.
- Lazarova, V. & Bahri, A. 2004. *Water reuse for irrigation: agriculture, landscapes, and turf grass*. CRC Press.
- Li, Q., Xu, Z. & Pinnau, I. 2007. Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent : Role of membrane surface properties and initial permeate flux. , 290: 173–181.
- Lian-feng, S., Rong-ping, C., Fa-wen, Z. & You, Y.J.L. 2011. Procedia Environmental Sciences Discussion on Nitrogen and Phosphorus Removal Process Characteristics of Improved Oxidation Ditch. , 11: 1291–1295. <http://dx.doi.org/10.1016/j.proenv.2011.12.193>.
- Lin, S., Huang, H., Zeng, Y. & Zhang, L. 2016. Facile surface modi fi cation by aldehydes to enhance chlorine resistance of polyamide thin fi lm composite membranes. *Journal of Membrane Science*, 518: 40–49. <http://dx.doi.org/10.1016/j.memsci.2016.06.032>.
- Liu, M., Chen, Q., Wang, L., Yu, S. & Gao, C. 2015a. Improving fouling resistance and chlorine stability of aromatic polyamide thin- fi lm composite RO membrane by surface grafting of polyvinyl alcohol (PVA). , 367: 11–20.
- Liu, M., Chen, Q., Wang, L., Yu, S. & Gao, C. 2015b. Improving fouling resistance and chlorine stability of aromatic polyamide thin- fi lm composite RO membrane by surface grafting of polyvinyl alcohol (PVA). *DES*, 367: 11–20. <http://dx.doi.org/10.1016/j.desal.2015.03.028>.

- Louie, J.S., Pinnau, I., Ciobanu, I., Ishida, K.P., Ng, A. & Reinhard, M. 2006. Effects of polyether-polyamide block copolymer coating on performance and fouling of reverse osmosis membranes. *Journal of Membrane Science*, 280(1–2): 762–770.
- Mahdavi, H., Hosseinzade, M.T. & Shahalizade, T. 2017. A polyamide thin-film composite membrane modified by Michael addition grafting of hyperbranched poly (amine ester). : 1–11.
- Mburu, N., Tebitendwa, S.M., Van Bruggen, J.J.A., Rousseau, D.P.L. & Lens, P.N.L. 2013. Performance comparison and economics analysis of waste stabilization ponds and horizontal subsurface flow constructed wetlands treating domestic wastewater: A case study of the Juja sewage treatment works. *Journal of environmental management*, 128: 220–225.
- Melvin, S.D. & Leusch, F.D.L. 2016. Removal of trace organic contaminants from domestic wastewater : A meta-analysis comparison of sewage treatment technologies. *Environment International*, 92–93: 183–188. <http://dx.doi.org/10.1016/j.envint.2016.03.031>.
- Mittal, V. 2010. *Advanced polymer nanoparticles: synthesis and surface modifications*. CRC Press.
- Nguyen, T., Roddick, F.A. & Fan, L. 2012. Biofouling of Water Treatment Membranes: A Review of the Underlying Causes, Monitoring Techniques and Control Measures. : 804–840.
- Nie, H.-Y., Walzak, M.J., Berno, B. & McIntyre, N.S. 1999. Atomic force microscopy study of polypropylene surfaces treated by UV and ozone exposure: modification of morphology and adhesion force. *Applied Surface Science*, 144: 627–632.
- Pabby, A.K., Rizvi, S.S.H. & Requena, A.M.S. 2015. *Handbook of membrane separations: chemical, pharmaceutical, food, and biotechnological applications*. CRC press.
- Pandey, S.R., Jegatheesan, V., Baskaran, K. & Shu, L. 2012. Fouling in reverse osmosis (RO) membrane in water recovery from secondary effluent: A review Pandey, S. R. et al. (2012) 'Fouling in reverse osmosis (RO) membrane in water recovery from secondary effluent: A review', *Reviews in Environmental Science and B. Reviews in Environmental Science and Biotechnology*, 11(2): 125–145.

- Park, H.B., Han, D.W. & Lee, Y.M. 2003. Effect of a UV/ozone treatment on siloxane-containing copolyimides: surface modification and gas transport characteristics. *Chemistry of materials*, 15(12): 2346–2353.
- Pedrero, F., Kalavrouziotis, I., José, J., Koukoulakis, P. & Asano, T. 2010. Use of treated municipal wastewater in irrigated agriculture — Review of some practices in Spain and Greece. , 97: 1233–1241.
- Peinemann, K.-V. & Nunes, S.P. 2010. *Membrane Technology, Volume 4: Membranes for Water Treatment*. John Wiley & Sons.
- Ponnusamy, K., Kappachery, S., Thekeettle, M., Song, J.H. & Kweon, J.H. 2013. Anti-biofouling property of vanillin on *Aeromonas hydrophila* initial biofilm on various membrane surfaces. *World Journal of Microbiology and Biotechnology*, 29(9): 1695–1703.
- Porter, M.C. 1989. Handbook of industrial membrane technology.
- Radjenović, J., Matošić, M., Mijatović, I., Petrović, M. & Barceló, D. 2008. Membrane bioreactor (MBR) as an advanced wastewater treatment technology. In *Emerging Contaminants from Industrial and Municipal Waste*. Springer: 37–101.
- Rana, D. & Matsuura, T. 2010. Surface Modifications for Antifouling Membranes. : 2448–2471.
- Robinson, S., Zaki, S., Bérubé, P. & Le-clech, P. 2016. Ageing of membranes for water treatment : Linking changes to performance. *Journal of Membrane Science*, 503: 177–187. <http://dx.doi.org/10.1016/j.memsci.2015.12.033>.
- Sabrina, N., Mutamim, A., Zainon, Z., Ariffin, M., Hassan, A., Yuniarto, A. & Olsson, G. 2013. Membrane bioreactor : Applications and limitations in treating high strength industrial wastewater. *CHEMICAL ENGINEERING JOURNAL*, 225: 109–119. <http://dx.doi.org/10.1016/j.cej.2013.02.131>.
- Saqib, J. & Aljundi, I.H. 2016. Journal of Water Process Engineering Membrane fouling and modification using surface treatment and layer-by-layer assembly of polyelectrolytes : State-of-the-art review. *Journal of Water Process Engineering*, 11: 68–87. <http://dx.doi.org/10.1016/j.jwpe.2016.03.009>.

- Schmitt, J. & Flemming, H. 1998. FTIR-spectroscopy in microbial and material analysis. , 41.
- Shahkaramipour, N., Tran, T.N., Ramanan, S. & Lin, H. 2017. Membranes with Surface-Enhanced Antifouling Properties for Water Purification. : 1–18.
- Shai, Y. 2013. ATR-FTIR studies in pore forming and membrane induced fusion peptides. *Biochimica et Biophysica Acta - Biomembranes*, 1828(10): 2306–2313. <http://dx.doi.org/10.1016/j.bbamem.2012.11.027>.
- Shen, L., Zuo, J. & Wang, Y. 2017. Tris(2-aminoethyl)amine in-situ modified thin-film composite membranes for forward osmosis applications. *Journal of Membrane Science*, 537(March): 186–201. <http://dx.doi.org/10.1016/j.memsci.2017.05.035>.
- Socrates, G. 2001. *Infrared and Raman characteristic group frequencies: tables and charts*. John Wiley & Sons.
- Sun, W., Liu, J., Chu, H. & Dong, B. 2013. Pretreatment and Membrane Hydrophilic Modification to Reduce Membrane Fouling. : 226–241.
- Tang, F., Hu, H.-Y., Sun, L.-J., Sun, Y.-X., Shi, N. & Crittenden, J.C. 2016. Fouling characteristics of reverse osmosis membranes at different positions of a full-scale plant for municipal wastewater reclamation. *Water Research*, 90.
- Tang, F., Hu, H., Sun, L., Wu, Q. & Jiang, Y. 2014. Fouling of reverse osmosis membrane for municipal wastewater reclamation : Autopsy results from a full-scale plant. *DES*, 349: 73–79. <http://dx.doi.org/10.1016/j.desal.2014.06.018>.
- Templeton, M.R. & Butler, D. 2011. *Introduction to wastewater treatment*. Bookboon.
- Totten, G.E. & Liang, H. 2004. *Surface modification and mechanisms: friction, stress, and reaction engineering*. CRC Press.
- Wang, J., Wang, Z., Liu, Y., Wang, J. & Wang, S. 2016. Surface modification of NF membrane with zwitterionic polymer to improve anti-biofouling property. *Journal of Membrane Science*, 514: 407–417.

- Wang, J., Wang, Z., Wang, J. & Wang, S. 2015. Improving the water flux and bio-fouling resistance of reverse osmosis (RO) membrane through surface modification by zwitterionic polymer. *Journal of Membrane Science*, 493: 188–199. <http://dx.doi.org/10.1016/j.memsci.2015.06.036>.
- Wang, L.K., Chen, J.P., Hung, Y.-T. & Shammash, N.K. 2008. *Membrane and desalination technologies*. Springer.
- Wang, M., Wu, L.-G., Zheng, X.-C., Mo, J.-X. & Gao, C.-J. 2006. Surface modification of phenolphthalein poly (ether sulfone) ultrafiltration membranes by blending with acrylonitrile-based copolymer containing ionic groups for imparting surface electrical properties. *Journal of colloid and interface science*, 300(1): 286–292.
- Wei, X., Wang, Z., Zhang, Z., Wang, J. & Wang, S. 2010. Surface modification of commercial aromatic polyamide reverse osmosis membranes by graft polymerization of 3-allyl-5, 5-dimethylhydantoin. *Journal of Membrane Science*, 351(1–2): 222–233. <http://dx.doi.org/10.1016/j.memsci.2010.01.054>.
- Xu, J., Wang, Z., Yu, L., Wang, J. & Wang, S. 2013. A novel reverse osmosis membrane with regenerable anti-biofouling and chlorine resistant properties. *Journal of Membrane Science*, 435: 80–91. <http://dx.doi.org/10.1016/j.memsci.2013.02.010>.
- Xu, P., Bellona, C. & Drewes, J.E. 2010. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation : Membrane autopsy results from pilot-scale investigations. *Journal of Membrane Science*, 353(1–2): 111–121. <http://dx.doi.org/10.1016/j.memsci.2010.02.037>.
- Xu, Z.-K., Huang, X.-J. & Wan, L.-S. 2009. *Surface engineering of polymer membranes*. Springer Science & Business Media.
- Yu, S., Yao, G., Dong, B., Zhu, H., Peng, X. & Liu, J. 2013. Improving fouling resistance of thin-film composite polyamide reverse osmosis membrane by coating natural hydrophilic polymer sericin. *Separation and Purification Technology*, 118: 285–293. <http://dx.doi.org/10.1016/j.seppur.2013.07.018>.

- Zha, L., Hu, J., Wang, C., Fu, S., Elaissari, A. & Zhang, Y. 2002. Preparation and characterization of poly (N-isopropylacrylamide-co-dimethylaminoethyl methacrylate) microgel latexes. *Colloid and polymer science*, 280(1): 1–6.
- Zhang, T., Zhang, K., Li, J. & Yue, X. 2017. Simultaneously enhancing hydrophilicity , chlorine resistance and anti- biofouling of APA-TFC membrane surface by densely grafting quaternary ammonium cations and salicylaldehydes. *Journal of Membrane Science*, 528(January): 296–302. <http://dx.doi.org/10.1016/j.memsci.2017.01.013>.
- Zhang, W., He, G., Gao, P. & Chen, G. 2003. Development and characterization of composite nanofiltration membranes and their application in concentration of antibiotics. *Separation and purification technology*, 30(1): 27–35.
- Zhao, C., Xue, J., Ran, F. & Sun, S. 2013. Progress in Materials Science Modification of polyethersulfone membranes – A review of methods. *Progress in Materials Science*, 58(1): 76–150. <http://dx.doi.org/10.1016/j.pmatsci.2012.07.002>.
- Zhao, G. & Chen, W. 2015. Enhanced PVDF membrane performance via surface modification by functional polymer poly (N-isopropylacrylamide) to control protein adsorption and bacterial adhesion. *REACT*, 97: 19–29. <http://dx.doi.org/10.1016/j.reactfunctpolym.2015.10.001>.
- Zhao, Y., Song, L. & Leong, S. 2010. Fouling behavior and foulant characteristics of reverse osmosis membranes for treated secondary effluent reclamation. , 349: 65–74.
- Zularisam, A.W., Ismail, A.F. & Salim, R. 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment — a review. , 194: 211–231.

APPENDICES

Appendix A

DATA FROM BATCH EXPERIMENTS

RO cell experimental runs with unmodified membrane

Kinetic data for the RO cell experimental runs with **unmodified membranes**, measuring operation parameters in the feed, brine and permeate.

Below in table A-1 the operating conditions is illustrated for the RO process and included are the membrane specification:

Table A- 1: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m ²)	0.013775
Nomination	XLE-4040
Feed P ₀ (bar):	5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table A-2. 1: Measured and calculated process parameters of unmodified membrane (experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R. (L/h)	Flux (L/h m ²)
0	341	174	24.3	343	174	151	77	25.0	0.004	0.003	0.79	57.5
45	347	175	24.5	348	175	130	67	24.2	0.004	0.003	0.79	57.5
90	350	176	24.9	350	176	132	68	24.2	0.004	0.003	0.79	57.5
135	353	177	25	355	177	123	63	24.2	0.004	0.003	0.77	55.8
180	357	178	25.1	358	178	113	58	24.0	0.004	0.003	0.74	54.0
225	360	179	25.2	359	180	106	55	23.9	0.004	0.003	0.72	52.3
270	363	180	25.3	365	181	97	50	24.0	0.004	0.003	0.72	52.3
315	364	181	25.3	368	181	96	49	24.0	0.004	0.003	0.70	50.5
360	370	182	25.5	371	183	94	48	24.9	0.004	0.003	0.70	50.5
405	375	183	25.7	377	184	93	46	24.9	0.004	0.003	0.65	47.0
450	379	184	25.9	380	185	90	45	24.7	0.004	0.003	0.65	47.0
495	383	185	26.1	382	185	90	45	24.9	0.004	0.003	0.65	47.0
540	386	187	26.2	387	187	89	45	24.8	0.004	0.003	0.64	46.2
945	389	188	26.3	390	189	89	44	25.1	0.004	0.003	0.62	45.3
990	394	189	26.4	392	190	87	44	24.9	0.004	0.003	0.62	45.3
1035	396	191	26.4	396	191	86	43	24.7	0.004	0.003	0.62	45.3
1080	399	192	26.4	399	192	83	42	25.0	0.004	0.003	0.62	45.3
1125	423	201	26.7	420	199	94	47	25.2	0.004	0.003	0.62	45.3

1170	425	203	26.8	429	204	94	47	25.3	0.004	0.003	0.62	45.3
1215	433	205	26.9	432	205	91	46	24.8	0.004	0.003	0.60	43.6
1260	436	207	26.7	433	207	93	47	24.5	0.004	0.003	0.60	43.6
1305	438	209	26.5	438	210	95	52	24.0	0.004	0.002	0.58	41.8
1350	439	212	26.4	438	212	81	40	24.2	0.004	0.002	0.58	41.8
1395	443	214	26.2	443	214	74	38	24.3	0.004	0.002	0.53	38.3
1440	449	217	26.2	449	218	69	35	24.8	0.004	0.002	0.53	38.3
1485	451	218	26.1	450	218	69	35	24.3	0.004	0.002	0.53	38.3
1530	461	223	26.1	462	224	71	36	24.6	0.004	0.002	0.53	38.3
1575	463	224	26.1	460	224	71	36	24.3	0.004	0.002	0.53	38.3
1620	465	225	26.1	462	226	72	37	24.3	0.004	0.002	0.53	38.3
1665	468	226	26.1	467	227	73	37	24.4	0.004	0.002	0.50	36.6
1710	471	229	26	468	227	72	36	24.3	0.004	0.002	0.50	36.6
1755	473	230	26	475	230	74	38	24.5	0.004	0.002	0.50	36.6
1800	476	231	26	476	231	78	40	24.4	0.004	0.002	0.50	36.6
1845	479	233	26	478	232	78	40	24.3	0.004	0.002	0.50	36.6
1890	481	234	26	482	234	81	42	24.4	0.004	0.002	0.50	36.6
2385	484	235	26	485	236	82	43	24.3	0.004	0.002	0.50	36.6
2430	577	273	26.8	575	274	97	48	24.9	0.004	0.002	0.48	34.6
2475	579	275	26.8	586	279	97	49	24.9	0.004	0.002	0.48	34.9
2520	585	277	26.8	589	280	97	49	24.9	0.004	0.002	0.48	34.9

Table A-2. 2: Measured and calculated process parameters of unmodified membrane (Experimental run 2)

	Feed		Brine		Permeate							
Time (min)	EC (μS)	TDS (mg/L)	Temp ($^{\circ}\text{C}$)	EC (μS)	TDS (mg/L)	EC (μS)	TDS (mg/L)	Temp ($^{\circ}\text{C}$)	Time (h)	Volume (L)	Flow R (l/h)	Flux ($\text{L}\cdot\text{h}^{-1}\text{m}^{-2}$)
0	350	171	25.8	353	173	112	55	25.0	0.004	0.003	0.792	57.5
45	351	172	25.8	354	174	87	44	24.6	0.004	0.003	0.792	57.5
90	356	173	26.0	356	174	86	44	24.6	0.004	0.003	0.768	55.8
135	360	174	26.0	359	174	83	42	25.0	0.004	0.003	0.744	54.0
180	361	176	26.0	360	177	86	44	25.0	0.004	0.003	0.720	52.3
225	364	176	26.1	365	178	69	35	24.9	0.004	0.003	0.720	52.3
270	367	178	26.0	367	178	56	28	25.0	0.004	0.003	0.696	50.5
315	366	176	26.2	367	177	54	27	25.0	0.004	0.003	0.696	50.5
360	367	178	26.4	368	176	53	26	24.8	0.004	0.003	0.672	48.8
405	367	176	26.5	368	176	31	16	24.9	0.004	0.003	0.672	48.8
450	366	177	26.4	371	178	25	13	24.8	0.004	0.003	0.648	47.0
495	377	181	26.4	380	182	28	14	24.8	0.004	0.003	0.624	45.3
540	383	182	26.4	386	185	28	14	25.1	0.004	0.003	0.636	46.2
945	391	187	26.4	387	188	34	17	25.3	0.004	0.003	0.624	45.3
990	399	192	26.5	400	192	37	18	25.3	0.004	0.003	0.624	45.3
1035	407	194	26.5	402	192	38	19	25.4	0.004	0.003	0.624	45.3
1080	410	195	26.6	406	193	35	18	25.4	0.004	0.003	0.624	45.3
1125	422	200	26.7	423	201	34	17	25.6	0.004	0.003	0.624	45.3

1170	426	204	26.6	427	203	33	16	25.2	0.004	0.003	0.624	45.3
1215	428	204	26.8	428	204	38	19	25.2	0.004	0.003	0.648	47.0
1260	378	172	25.6	381	181	31	15	25.1	0.004	0.003	0.624	45.3
1305	378	181	25.6	378	182	35	18	25.0	0.004	0.003	0.648	47.0
1350	383	183	25.6	380	183	29	15	25.4	0.004	0.003	0.624	45.3
1395	379	182	26.4	383	186	21	11	25.2	0.004	0.003	0.624	45.3
1440	380	182	26.5	382	182	22	11	25.4	0.004	0.003	0.624	45.3
1485	387	186	26.4	388	187	24	12	25.2	0.004	0.003	0.600	43.6
1530	386	186	26.3	384	182	24	12	25.0	0.004	0.002	0.576	41.8
1575	388	191	26.4	390	189	24	12	25.0	0.004	0.003	0.600	43.6
1620	387	190	26.4	389	181	24	12	25.1	0.004	0.002	0.576	41.8
1665	354	176	24.9	356	179	25	13	24.5	0.004	0.002	0.576	41.8
1710	357	178	25.0	355	178	29	15	24.6	0.004	0.002	0.504	36.6
1755	358	179	25.0	354	177	29	15	24.3	0.004	0.002	0.504	36.6
1800	361	182	24.8	363	182	31	16	24.2	0.004	0.002	0.528	38.3
1845	366	185	24.6	361	185	31	17	24.2	0.004	0.002	0.552	40.1
1890	370	187	24.5	371	188	30	16	24.1	0.004	0.002	0.504	36.6
2430	374	190	24.5	366	187	32	17	24.3	0.004	0.002	0.504	36.6
2475	380	194	24.4	374	191	29	15	24.0	0.004	0.002	0.504	36.6
2520	385	197	24.3	387	198	29	15	23.8	0.004	0.002	0.480	34.8

Data analysis report on the two ranges of data of unmodified membranes

Data analysis using Microsoft Excel was performed to assess the significance of data of an experimental run and the 'duplicate run' has a significant difference or not.

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized flux2</i>
Mean	45.4566285	44.40643013
Variance	32.40224722	52.49888764
Observations	38	39
df	37	38
F	0.617198738	
P(F<=f) one-tail	0.072472498	
F Critical one-tail	0.579685487	

t-Test: Two-Sample Assuming Unequal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	45.45663	44.40643013
Variance	32.40225	52.49888764
Observations	38	39
Hypothesized Mean Difference	0	
df	72	
t Stat	0.708234	
P(T<=t) one-tail	0.240543	
t Critical one-tail	1.666294	
P(T<=t) two-tail	0.481086	
t Critical two-tail	1.993464	

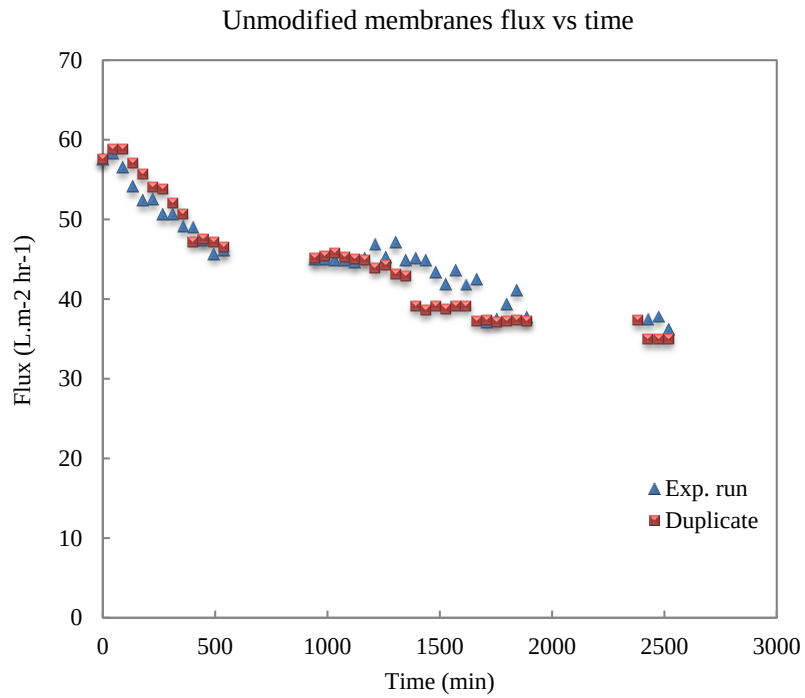


Figure A 1: Permeate flux of unmodified membranes at same operating conditions

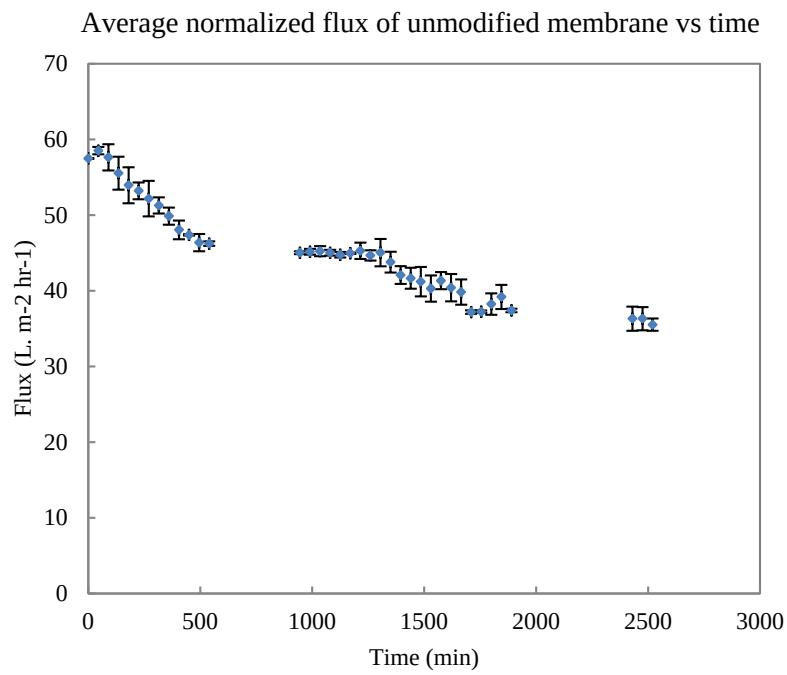


Figure A- 2: average permeate flux of unmodified membranes

Table A-3. 1: Pure water Flow rate of the unmodified membrane before fouling experimental run 1

Time (h)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (l/h)	Flux (L. m²h⁻¹)
0	15	0.004	0.003	0.72	52.3
30	15	0.004	0.0033	0.792	57.5
60	15	0.004	0.0034	0.816	59.2
90	15	0.004	0.0036	0.864	62.7
120	15	0.004	0.0036	0.864	62.7
150	15	0.004	0.0036	0.864	62.7
180	15	0.004	0.0036	0.864	62.7
210	15	0.004	0.0036	0.864	62.7
240	15	0.004	0.0036	0.864	62.7
270	15	0.004	0.0036	0.864	62.7

Table A-3. 2: Pure water Flow rate of the unmodified membrane before fouling experimental run 2

Time (min)	Flow measuring time (sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (l/h)	Flux (L. m⁻²h⁻¹)
0					
30					
60					
90					
120	15	0.004	0.0029	0.696	50.5
150	15	0.004	0.0030	0.720	52.3
180	15	0.004	0.0035	0.840	61.0
210	15	0.004	0.0035	0.840	61.0
240	15	0.004	0.0038	0.912	66.2
270	15	0.004	0.0036	0.864	62.7

Table A-4. 1: Pure water Flow rate of the unmodified membrane after fouling experimental run 1

Time (min)	Flow measuring time (sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (l/h)	Flux (L. m²h⁻¹)
0	15	0.004	0.0025	0.600	43.6
30	15	0.004	0.0024	0.576	41.8
60	15	0.004	0.0025	0.600	43.6
90	15	0.004	0.0026	0.624	45.3
120	15	0.004	0.0026	0.624	45.3

Table A-4. 2: Pure water Flow rate of the unmodified membrane after fouling experimental run 2

Time (min)	Flow measuring time (sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (l/h)	Flux (L. m²h⁻¹)
0	15	0.004	0.0022	0.528	38.3
30	15	0.004	0.0022	0.528	38.3
60	15	0.004	0.0023	0.552	40.1
90	15	0.004	0.0025	0.600	43.6
120	15	0.004	0.0026	0.624	45.3

Table A-5. 1: Calculated values of the normalized flux and Flux decline ratio (FDR) of unmodified membranes

Unmodified membranes						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux ($L \cdot m^{-2} h^{-1}$)	FDR (%)	Flux ($L \cdot m^{-2} h^{-1}$)	Time (Min)	Norm flux ($L \cdot m^{-2} h^{-1}$)	FDR (%)
0	57.50	0.00	57.50	0	57.50	0.00
45	58.18	-1.19	58.53	45	58.87	-2.39
90	56.42	1.88	57.64	90	58.87	-2.39
135	54.01	6.06	55.55	135	57.09	0.71
180	52.27	9.09	53.95	180	55.63	3.24
225	52.42	8.82	53.21	225	54.00	6.09
270	50.53	12.12	52.18	270	53.84	6.36
315	50.53	12.12	51.28	315	52.04	9.48
360	49.07	14.65	49.87	360	50.68	11.86
405	48.93	14.90	48.05	405	47.18	17.94
450	47.32	17.70	47.39	450	47.46	17.45
495	45.57	20.74	46.37	495	47.18	17.94
540	46.03	19.93	46.24	540	46.44	19.22
945	44.90	21.91	45.03	945	45.17	21.44
990	44.90	21.91	45.17	990	45.43	20.98
1035	44.77	22.14	45.23	1035	45.70	20.51
1080	44.77	22.14	45.03	1080	45.30	21.21

1125	44.50	22.60	44.77	1125	45.03	21.68
1170	45.03	21.68	44.97	1170	44.90	21.91
1215	46.76	18.66	45.29	1215	43.82	23.79
1260	45.17	21.44	44.69	1260	44.21	23.11
1305	47.04	18.18	45.06	1305	43.07	25.09
1350	44.77	22.14	43.79	1350	42.82	25.53
1395	45.03	21.68	42.08	1395	39.13	31.94
1440	44.77	22.14	41.66	1440	38.56	32.94
1485	43.30	24.69	41.22	1485	39.13	31.94
1530	41.81	27.27	40.30	1530	38.79	32.54
1575	43.56	24.24	41.34	1575	39.13	31.94
1620	41.69	27.49	40.41	1620	39.13	31.94
1665	42.44	26.19	39.84	1665	37.24	35.22
1710	37.02	35.61	37.19	1710	37.35	35.03
1755	37.35	35.03	37.24	1755	37.13	35.42
1800	39.25	31.74	38.25	1800	37.24	35.22
1845	41.03	28.64	39.19	1845	37.35	35.03
1890	37.57	34.65	37.41	1890	37.24	35.22
2385			37.35	2385	37.35	35.03
2430	37.35	35.03	36.32	2430	34.95	39.21
2475	37.69	34.45	36.32	2475	34.95	39.21
2520	36.10	37.21	35.53	2520	34.95	39.21

Table A-6. 1: Summarized values of the calculated parameters of unmodified membranes after 42 hours fouling test using the synthetic feed

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
62.72	62.29	61.85
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
43.91	42.51	41.12
Average salt rejection (%)		Average salt rejection (%)
92.21	87.74	83.26
FRR (%)		FRR (%)
71.67	68.61	65.56
FDR (%)		FDR (%)
37.21	38.21	39.21

Appendix B

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.2 g/L PVA modified
membranes**

Table B- 1: PVA modifying solutions at various concentrations

	PVA Concentrations	Units
1	0.20	g.L^{-1}
2	0.15	g.L^{-1}
3	0.10	g.L^{-1}
4	0.05	g.L^{-1}

Kinetic data for the RO cell experimental runs with **PVA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.2 PVA** concentration.

Below in table B- 2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table B- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m^2)	0.013775
Nomination	XLE-4040
Feed P_0 (bar):	6
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table B-3. 1: Measured and calculated process parameters of 0.2 g/L PVA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	349	209	19.5	351	210	155	94	18.9	0.004	0.0028	0.672	48.8
45	352	209	19.7	353	210	153	93	18.9	0.004	0.0029	0.696	50.5
90	354	210	19.9	355	210	151	92	19.0	0.004	0.0028	0.672	48.8
135	355	210	20.0	357	210	149	92	19.1	0.004	0.0026	0.624	45.3
180	357	210	20.1	359	210	146	91	18.9	0.004	0.0026	0.624	45.3
225	359	211	20.1	360	211	145	90	19.1	0.004	0.0027	0.648	47.0
270	361	211	20.2	362	211	143	89	19.1	0.004	0.0027	0.648	47.0
315	364	212	20.3	364	212	141	89	19.3	0.004	0.003	0.72	52.3
360	364	212	20.4	365	212	141	87	19.1	0.004	0.0028	0.672	48.8
405	367	213	20.4	368	213	139	86	19.1	0.004	0.0027	0.648	47.0
450	367	213	20.4	368	213	139	84	19.1	0.004	0.0026	0.624	45.3
495	370	214	20.4	371	215	177	107	19.1	0.004	0.0025	0.6	43.6
1215	341	202	19.9	342	202	160	99	18.9	0.004	0.0025	0.6	43.6
1260	342	202	19.9	343	202	165	103	18.9	0.004	0.0025	0.6	43.6
1305	343	202	20.0	343	202	152	94	19.0	0.004	0.0027	0.648	47.0
1350	344	202	20.0	344	202	159	99	19.0	0.004	0.0024	0.576	41.8
1395	344	202	20.0	344	202	143	89	19.0	0.004	0.0024	0.576	41.8
1440	345	202	20.2	345	202	127	80	19.1	0.004	0.00235	0.564	40.9

1485	345	202	20.1	346	203	108	67	19.0	0.004	0.0024	0.576	41.8
1530	346	202	20.2	347	203	100	62	19.0	0.004	0.00235	0.564	40.9
1575	347	202	20.3	348	203	87	57	19.1	0.004	0.0023	0.552	40.1
1620	348	202	20.3	348	204	75	51	19.1	0.004	0.0022	0.528	38.3
1665	348	202	20.4	350	204	69	47	19.2	0.004	0.0022	0.528	38.3
1710	352	203	20.4	354	204	81	54	19.2	0.004	0.0022	0.528	38.3
1755	352	205	20.5	354	205	67	46	19.2	0.004	0.00235	0.564	40.9
1800	356	206	20.5	355	205	67	46	19.0	0.004	0.0022	0.528	38.3
1845	357	206	20.6	359	207	68	47	19.0	0.004	0.0021	0.504	36.6
1890	359	207	20.6	360	207	71	48	19.0	0.004	0.0021	0.504	36.6
1935	361	208	20.6	363	209	71	48	18.9	0.004	0.00215	0.516	37.5
1980	363	209	20.6	364	210	71	48	18.9	0.004	0.00215	0.516	37.5
2025	365	211	20.6	366	211	71	48	18.7	0.004	0.002	0.48	34.8
2070	365	211	20.5	367	212	71	48	18.6	0.004	0.0019	0.456	33.1
2115	367	212	20.5	369	214	73	49	18.6	0.004	0.002	0.48	34.8
2430	357	208	19.6	360	211	69	47	18.5	0.004	0.002	0.48	34.8
2475	360	211	19.6	364	216	71	48	18.4	0.004	0.002	0.48	34.8
2520	369	218	19.9	372	219	72	48	18.5	0.004	0.0019	0.456	33.1
2565	372	220	19.8	375	221	72	49	18.5	0.004	0.0019	0.456	33.1

Table B-3. 2: Measured and calculated process parameters of 0.2 g/L PVA modified membrane (Experimental run 2)

	Feed			Brine		Permeate							
Time (min)	EC (μ S)	TDS (mg/L)	Temp ($^{\circ}$ C)	EC (μ S)	TDS (mg/L)	EC (μ S)	TDS (mg/L)	Temp ($^{\circ}$ C)	Time (s)	Time (h)	Volume (L)	Flow R (l/h)	Flux (L/h m ²)
0	338	208	19.9	341	208	186	116	19.5	15	0.004	0.0028	0.672	48.8
45	345	209	19.2	346	208	187	116	19.4	15	0.004	0.0029	0.696	50.5
90	348	208	19.6	350	208	182	113	19.0	15	0.004	0.0027	0.648	47.0
135	351	208	19.9	355	207	180	112	19.2	15	0.004	0.0027	0.648	47.0
180	359	207	20.5	360	207	181	113	19.4	15	0.004	0.0026	0.624	45.3
225	363	208	20.8	364	207	175	108	19.7	15	0.004	0.0026	0.624	45.3
270	365	208	21.0	366	207	185	115	19.8	15	0.004	0.0026	0.624	45.3
315	378	208	21.3	369	208	176	109	19.8	15	0.004	0.0025	0.600	43.6
360	372	208	21.4	372	210	166	103	19.8	15	0.004	0.0025	0.600	43.6
405	371	209	21.3	371	209	173	107	20.0	15	0.004	0.0027	0.648	47.0
450	372	209	21.4	373	210	178	110	20.0	15	0.004	0.0026	0.624	45.3
495	374	210	21.3	375	210	166	103	20.0	15	0.004	0.0025	0.600	43.6
1215	365	216	20.0	366	216	139	87	19.5	15	0.004	0.0025	0.600	43.6
1260	366	216	20.0	368	216	153	93	19.5	15	0.004	0.0025	0.600	43.6
1305	369	218	20.1	370	217	164	101	19.7	15	0.004	0.0024	0.576	41.8
1350	374	218	20.2	373	218	166	104	19.7	15	0.004	0.0025	0.600	43.6
1395	376	219	20.3	374	219	151	94	19.7	15	0.004	0.0024	0.576	41.8
1440	378	220	20.3	378	220	147	91	19.6	15	0.004	0.0025	0.600	43.6

1485	378	221	20.4	380	221	145	90	19.8	15	0.004	0.0024	0.576	41.8
1530	379	221	20.4	380	223	143	89	19.8	15	0.004	0.0025	0.600	43.6
1575	379	223	20.5	381	223	115	79	19.8	15	0.004	0.0024	0.576	41.8
1620	382	225	20.6	385	227	96	61	19.9	15	0.004	0.0023	0.552	40.1
1665	384	226	20.5	386	228	94	60	19.7	15	0.004	0.0023	0.552	40.1
1710	387	228	20.6	387	230	91	59	19.6	15	0.004	0.0024	0.576	41.8
1755	389	231	20.5	390	232	88	58	19.6	15	0.004	0.0023	0.552	40.1
1800	391	233	20.4	394	234	81	55	19.5	15	0.004	0.0023	0.552	40.1
1845	375	219	20.4	376	219	78	53	19.4	15	0.004	0.0023	0.552	40.1
1890	376	220	20.4	377	220	76	52	19.2	15	0.004	0.0022	0.528	38.3
1935	379	222	20.3	381	223	75	50	19.3	15	0.004	0.0022	0.528	38.3
1980	380	223	20.3	382	224	74	50	19.3	15	0.004	0.0021	0.504	36.6
2025	381	223	20.2	384	225	74	49	19.8	15	0.004	0.0022	0.528	38.3
2070	382	225	20.2	385	227	74	50	19.1	15	0.004	0.0021	0.504	36.6
2115	383	226	20.3	386	228	76	50	19.0	15	0.004	0.0021	0.504	36.6
2385	375	219	20.2	376	220	73	49	18.9	15	0.004	0.0020	0.480	34.8
2430	375	219	20.3	378	220	71	47	19.0	15	0.004	0.0019	0.456	33.1
2475	379	221	20.3	381	223	73	49	19.0	15	0.004	0.0020	0.480	34.8
2520	381	222	20.4	385	223	69	46	19.2	15	0.004	0.0020	0.480	34.8

Data analysis report on the two ranges of data of 0.2 g/L PVA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	49.50580168	48.98322
Variance	39.31932341	22.65542
Observations	37	37
df	36	36
F	1.73553681	
P(F<=f) one-tail	0.051302786	
F Critical one-tail	1.742973165	

t-Test: Two-Sample Assuming Unequal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	48.98322462	49.50580168
Variance	22.65542465	39.31932341
Observations	37	37
Hypothesized Mean Difference	0	
df	67	
t Stat	-0.403779086	
P(T<=t) one-tail	0.343830527	
t Critical one-tail	1.667916114	
P(T<=t) two-tail	0.687661054	
t Critical two-tail	1.996008354	

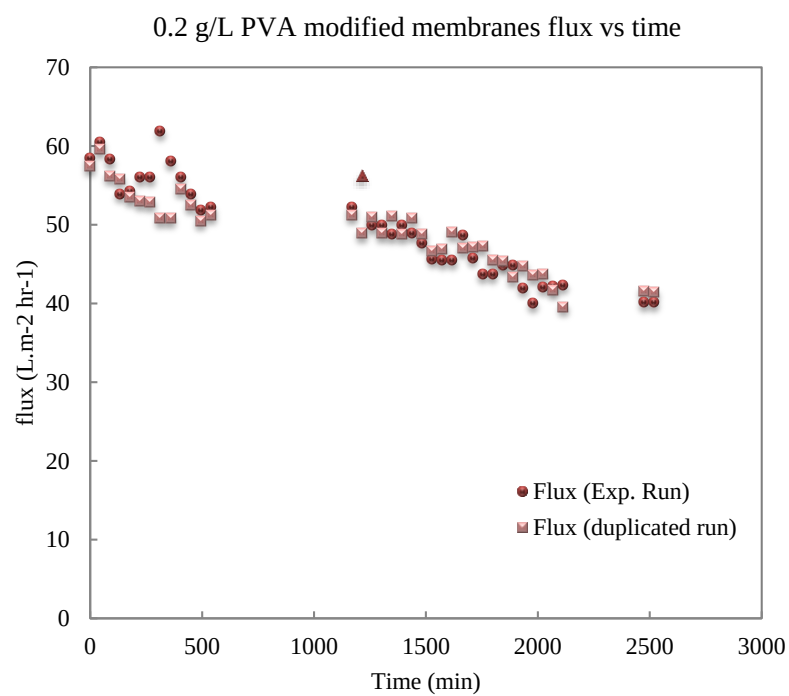


Figure B- 1: Permeate flux of 0.2 g/L PVA modified membranes at same operating conditions

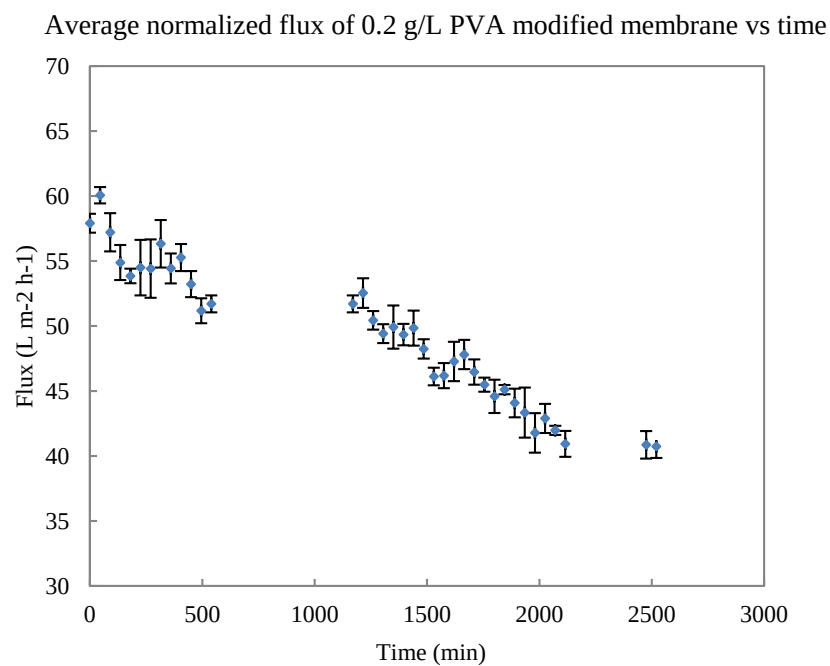


Figure B- 2: average permeate flux of 0.2 g/L PVA modified membranes

Table B-4. 1: Pure water (DI water) flow rate of the 0.2 g/L PVA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0					
30					
60	15	0.0042	0.002	0.48	34.846
90	15	0.0042	0.002	0.48	34.846
120	15	0.0042	0.0019	0.456	33.103
150	15	0.0042	0.002	0.48	34.846
180	15	0.0042	0.0019	0.456	33.103
210	15	0.0042	0.0021	0.504	36.588
240	15	0.0042	0.0022	0.528	38.33
270	15	0.0042	0.0021	0.504	36.588
300	15	0.0042	0.0022	0.528	38.33

Table B-4. 2: Pure water (DI water) flow rate of the 0.2 g/L PVA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0013	0.312	22.6
30	15	0.004	0.0014	0.336	24.4
60	15	0.004	0.0014	0.336	24.4
90	15	0.004	0.0015	0.360	26.1
120	15	0.004	0.0015	0.360	26.1
150	15	0.004	0.0015	0.360	26.1
180	15	0.004	0.0014	0.336	24.4
210	15	0.004	0.0013	0.312	22.6
240	15	0.004	0.002	0.480	34.8
270	15	0.004	0.0024	0.576	41.8
300	15	0.004	0.0024	0.576	41.8

Table B-5. 1: Pure water Flow rate of 0.2 g/L PVA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0009	0.216	15.7
30	15	0.004	0.0014	0.336	24.4
60	15	0.004	0.0016	0.384	27.9
90	15	0.004	0.0017	0.408	29.6
120	15	0.004	0.0016	0.384	27.9
150	15	0.004	0.0017	0.408	29.6
180	15	0.004	0.0017	0.408	29.6
210	15	0.004	0.0017	0.408	29.6

Table B-5. 2: Pure water Flow rate of 0.2 g/L PVA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0008	0.192	13.9
30	15	0.004	0.0008	0.192	13.9
60	15	0.004	0.0009	0.216	15.7
90	15	0.004	0.0008	0.192	13.9
120	15	0.004	0.0007	0.168	12.2
150	15	0.004	0.0017	0.408	29.6
180	15	0.004	0.0018	0.432	31.4
210	15	0.004	0.0019	0.456	33.1

Table B-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.2 g/L PVA modified membranes

0.2 g/L PVA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	58.42	0.00	57.91	0	57.40	0.00
45	60.51	-3.57	60.07	45	59.62	-3.88
90	58.25	0.30	57.21	90	56.17	2.14
135	53.93	7.69	54.88	135	55.84	2.71
180	54.25	7.14	53.85	180	53.45	6.87
225	56.00	4.14	54.49	225	52.98	7.69
270	56.00	4.14	54.42	270	52.83	7.96
315	61.86	-5.88	56.33	315	50.79	11.50
360	58.08	0.59	54.44	360	50.79	11.50
405	56.00	4.14	55.27	405	54.53	4.99
450	53.93	7.69	53.22	450	52.51	8.51
495	51.86	11.24	51.18	495	50.49	12.02
540	52.16	10.71	51.71	540	51.25	10.71
1170	52.16	10.71	51.71	1170	51.25	10.71
1215	56.17	3.86	52.54	1215	48.91	14.79
1260	49.93	14.54	50.44	1260	50.94	11.24
1305	49.93	14.54	49.42	1305	48.91	14.79

1350	48.74	16.57	49.92	1350	51.10	10.98
1395	49.93	14.54	49.35	1395	48.76	15.04
1440	48.89	16.32	49.84	1440	50.79	11.50
1485	47.71	18.34	48.23	1485	48.76	15.04
1530	45.63	21.89	46.11	1530	46.59	18.82
1575	45.50	22.12	46.18	1575	46.87	18.34
1620	45.50	22.12	47.28	1620	49.05	14.54
1665	48.60	16.81	47.80	1665	47.01	18.10
1710	45.77	21.66	46.46	1710	47.15	17.86
1755	43.69	25.22	45.49	1755	47.29	17.61
1800	43.69	25.22	44.59	1800	45.50	20.73
1845	44.86	23.21	45.11	1845	45.36	20.96
1890	44.86	23.21	44.08	1890	43.30	24.56
1935	41.98	28.15	43.34	1935	44.70	22.12
1980	40.00	31.54	41.78	1980	43.56	24.11
2025	42.10	27.94	42.90	2025	43.69	23.88
2070	42.23	27.72	41.98	2070	41.73	27.29
2115	42.35	27.51	40.94	2115	39.53	31.13
2475	40.12	31.34	40.86	2475	41.61	27.51
2520	40.12	31.34	40.74	2520	41.36	27.94

Table B-7. 1: Summarized values of the calculated parameters of 0.2 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
37.46	38.48	39.49
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
29.04	30.49	31.94
Average salt rejection (%)		Average Salt rejection (%)
80.56	80.65	80.75
FRR (%)		FRR (%)
77.52	78.47	79.41
FDR (%)		FDR (%)
31.34	29.64	27.94

Appendix C

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.15 g/L PVA modified
membranes**

Table C- 1: PVA modifying solutions at various concentrations

	PVA Concentrations	Units
1	0.20	g.L^{-1}
2	0.15	g.L^{-1}
3	0.10	g.L^{-1}
4	0.05	g.L^{-1}

Kinetic data for the RO cell experimental runs with **PVA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.15 g/L PVA** concentration.

Below in table C-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table C- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m^2)	0.013775
Nomination	XLE-4040
Feed P_0 (bar):	6
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table C-3. 1: Measured and calculated process parameters of 0.15 g/L PVA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	342	205	25.1	343	205	97	60	25.0	0.004	0.0033	0.792	57.5
45	349	210	24.7	354	210	125	77	24.6	0.004	0.0032	0.768	55.8
90	361	214	24.9	363	215	97	60	24.7	0.004	0.0032	0.768	55.8
135	369	218	24.9	371	219	98	61	24.7	0.004	0.0031	0.744	54.0
180	377	223	24.9	380	223	102	63	24.8	0.004	0.0031	0.744	54.0
225	386	238	24.9	389	228	91	56	24.8	0.004	0.0031	0.744	54.0
270	390	227	24.7	389	226	78	46	24.8	0.004	0.003	0.72	52.3
315	391	227	24.7	394	229	76	47	24.6	0.004	0.0029	0.696	50.5
360	394	230	24.7	399	232	75	47	24.5	0.004	0.0029	0.696	50.5
405	400	232	24.5	401	233	76	47	24.4	0.004	0.0029	0.696	50.5
450	404	235	24.5	405	236	76	47	24.4	0.004	0.0029	0.696	50.5
495	405	236	24.4	407	236	77	47	24.2	0.004	0.003	0.72	52.3
540	405	236	24.3	406	236	77	47	24.0	0.004	0.0029	0.696	50.5
1170	378	221	24.2	376	220	61	37	23.8	0.004	0.0028	0.672	48.8
1215	386	226	24.2	389	226	56	35	23.7	0.004	0.0028	0.672	48.8
1260	396	230	24.3	399	232	54	33	23.8	0.004	0.0028	0.672	48.8
1305	406	236	24.3	411	238	53	32	23.7	0.004	0.0026	0.624	45.3

1350	418	244	24.2	420	245	55	34	23.7	0.004	0.0026	0.624	45.3
1395	427	253	23.9	431	253	54	34	23.3	0.004	0.0027	0.648	47.0
1440	441	261	23.9	442	262	55	35	23.3	0.004	0.0026	0.624	45.3
1485	453	268	23.8	457	270	54	34	23.3	0.004	0.0026	0.624	45.3
1530	477	288	23.4	482	289	58	37	23.0	0.004	0.0026	0.624	45.3
1575	487	293	23.4	490	294	57	36	23.0	0.004	0.0025	0.6	43.6
1620	495	297	23.4	498	299	57	36	23.0	0.004	0.0026	0.624	45.3
1665	511	302	23.6	513	303	62	39	23.2	0.004	0.0025	0.600	43.6
1710	521	306	23.7	524	307	64	40	23.5	0.004	0.0026	0.624	45.3
1755	523	206	23.7	525	307	64	40	23.6	0.004	0.0025	0.6	43.6
1800	504	295	23.6	507	296	61	38	23.5	0.004	0.0026	0.624	45.3
1845	509	297	23.8	511	299	63	39	23.7	0.004	0.0026	0.624	45.3
1890	523	304	23.8	526	308	65	40	23.7	0.004	0.0026	0.624	45.3
1935	525	306	23.7	527	308	65	40	23.6	0.004	0.0026	0.624	45.3
1980	506	295	23.5	507	295	61	38	23.4	0.004	0.0026	0.624	45.3
2025	512	302	23.5	515	300	64	39	23.5	0.004	0.0026	0.624	45.3
2070	519	308	23.5	524	311	62	38	23.4	0.004	0.0025	0.600	43.6
2115	517	303	23.5	521	306	65	40	23.4	0.004	0.0025	0.600	43.6
2475	524	311	23.4	526	313	63	39	23.3	0.004	0.0024	0.576	41.8
2520	526	314	23.5	526	316	67	41	23.4	0.004	0.0025	0.600	43.6
2565	527	316	23.7	528	317	70	44	23.5	0.004	0.0025	0.600	43.6

Table C-3. 2: Measured and calculated process parameters of 0.15 g/L PVA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	342	198	24.5	344	198	164	100	24.0	0.004	0.0032	0.768	55.8
45	345	198	24.8	345	197	159	97	23.9	0.004	0.0032	0.768	55.8
90	345	198	24.8	346	198	158	96	23.7	0.004	0.0033	0.792	57.5
135	347	199	24.9	347	199	150	93	23.6	0.004	0.0032	0.768	55.8
180	348	199	24.0	349	199	148	93	23.4	0.004	0.0031	0.744	54.0
225	352	199	24.1	354	200	145	91	23.3	0.004	0.003	0.720	52.3
270	350	198	24.2	351	199	143	91	23.2	0.004	0.003	0.720	52.3
315	352	199	24.0	355	199	140	87	23.2	0.004	0.0028	0.672	48.8
360	354	199	24.0	354	200	142	89	23.1	0.004	0.0028	0.672	48.8
405	354	200	24.0	356	200	138	86	23.0	0.004	0.0039	0.936	67.9
450	355	200	23.9	356	200	141	87	23.0	0.004	0.0028	0.672	48.8
495	356	205	24.0	359	206	139	86	23.1	0.004	0.0028	0.672	48.8
1170	352	202	23.5	353	203	138	85	22.3	0.004	0.0027	0.648	47.0
1215	354	203	23.7	355	204	138	84	22.3	0.004	0.0027	0.648	47.0
1260	355	204	23.7	355	204	136	83	22.5	0.004	0.0027	0.648	47.0
1305	353	203	23.4	356	205	136	84	22.2	0.004	0.0028	0.672	48.8
1350	361	206	23.9	363	206	134	83	23.8	0.004	0.0026	0.624	45.3

1395	370	207	24.1	372	207	130	82	23.6	0.004	0.0027	0.648	47.0
1440	374	206	23.9	376	207	130	81	23.8	0.004	0.0026	0.624	45.3
1485	377	206	24.2	378	206	128	79	24.3	0.004	0.0026	0.624	45.3
1530	379	206	24.4	382	206	103	62	24.4	0.004	0.0027	0.648	47.0
1575	381	206	24.5	381	206	96	58	24.5	0.004	0.0026	0.624	45.3
1620	378	207	24.1	381	208	85	53	24.1	0.004	0.0026	0.624	45.3
1665	378	207	24.1	377	207	70	43	23.9	0.004	0.0025	0.600	43.6
1710	382	211	23.8	382	212	69	43	23.3	0.004	0.0025	0.600	43.6
1755	382	212	23.8	383	213	68	42	23.3	0.004	0.0027	0.648	47.0
1800	384	213	23.7	386	213	84	52	23.2	0.004	0.0026	0.624	45.3
1845	391	218	23.6	391	218	83	50	23.3	0.004	0.0025	0.600	43.6
1890	392	219	23.6	394	219	81	50	23.0	0.004	0.0025	0.600	43.6
1935	394	220	23.5	395	220	78	46	23.0	0.004	0.0026	0.624	45.3
1980	399	223	23.5	399	224	79	48	23.1	0.004	0.0026	0.624	45.3
2025	399	223	23.5	400	224	77	46	23.0	0.004	0.0026	0.624	45.3
2070	402	230	23.9	404	231	76	46	23.4	0.004	0.0028	0.672	48.8
2115	405	233	23.8	408	233	74	45	23.2	0.004	0.0026	0.624	45.3
2430	410	236	23.8	414	236	70	43	23.0	0.004	0.0024	0.576	41.8
2475	418	238	23.0	418	237	90	55	23.1	0.004	0.0024	0.576	41.8
2520	419	238	23.0	424	240	68	41	22.5	0.004	0.0023	0.552	40.1

Data analysis report on the two ranges of data of 0.15 g/L PVA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	49.48597968	50.37072843
Variance	12.26987338	15.48092559
Observations	38	38
df	37	37
F	0.792580089	
P(F<=f) one-tail	0.241507514	
F Critical one-tail	0.578199441	

t-Test: Two-Sample Assuming Equal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	49.48597968	50.37072843
Variance	12.26987338	15.48092559
Observations	38	38
Pooled Variance	13.87539948	
Hypothesized Mean Difference	0	
df	74	
t Stat	-1.035318576	
P(T<=t) one-tail	0.151945839	
t Critical one-tail	1.665706893	
P(T<=t) two-tail	0.303891679	
t Critical two-tail	1.992543495	

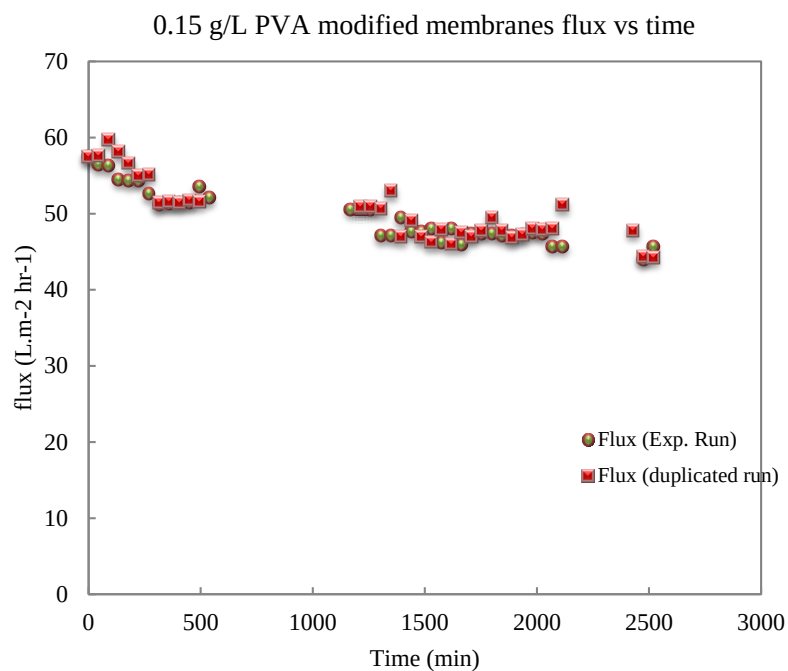


Figure C- 1: Permeate flux of 0.15 g/L PVA modified membranes at same operating conditions

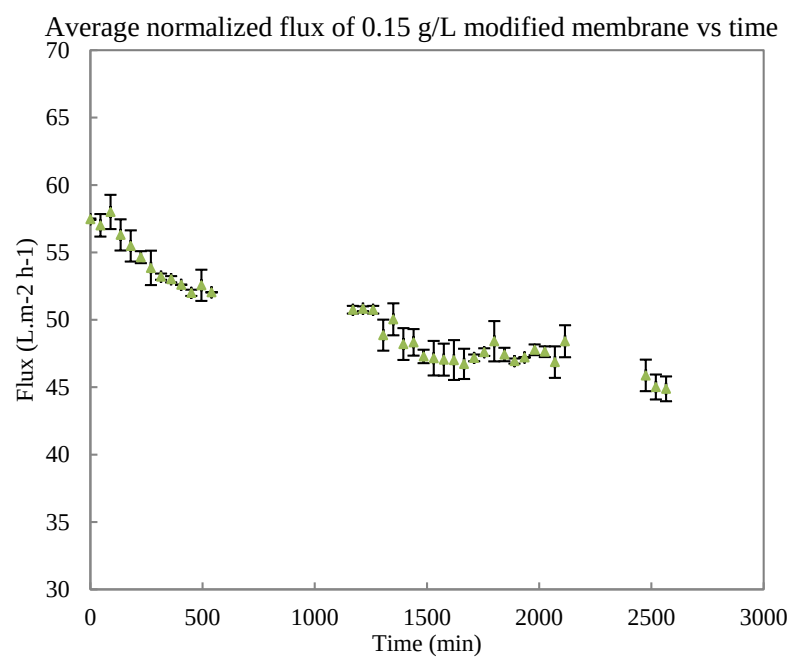


Figure C- 2: average permeate flux of 0.15 g/L PVA modified membranes

Table C-4. 1: Pure water (DI water) flow rate of the 0.15 g/L PVA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30					
60					
90	15	0.004	0.0029	0.696	50.5
120	15	0.004	0.0030	0.720	52.3
150	15	0.004	0.0030	0.720	52.3
180	15	0.004	0.0031	0.744	54.0
210	15	0.004	0.0030	0.720	52.3
240	15	0.004	0.0030	0.720	52.3
270	15	0.004	0.0031	0.744	54.0

Table C-4. 2: Pure water (DI water) flow rate of the 0.15 g/L PVA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0023	0.552	40.1
30	15	0.004	0.0023	0.552	40.1
60	15	0.004	0.0024	0.576	41.8
90	15	0.004	0.0026	0.624	45.3
120	15	0.004	0.0025	0.600	43.6
150	15	0.004	0.0026	0.624	45.3
180	15	0.004	0.0026	0.624	45.3
210	15	0.004	0.0026	0.624	45.3
240	15	0.004	0.0025	0.600	43.6
270	15	0.004	0.0026	0.624	45.3

Table C-5. 1: Pure water Flow rate of 0.15 g/L PVA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0023	0.552	40.1
30	15	0.004	0.0023	0.552	40.1
60	15	0.004	0.0026	0.624	45.3
90	15	0.004	0.0025	0.600	43.6
120	15	0.004	0.0025	0.600	43.6
150	15	0.004	0.0026	0.624	45.3
180	15	0.004	0.0025	0.600	43.6

Table C-5. 2: Pure water Flow rate of 0.15 g/L PVA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0019	0.456	33.1
30	15	0.004	0.0020	0.480	34.8
60	15	0.004	0.0020	0.480	34.8
90	15	0.004	0.0021	0.504	36.6
120	15	0.004	0.0020	0.480	34.8
150	15	0.004	0.0021	0.504	36.6
180	15	0.004	0.0021	0.504	36.6

Table C-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.15 g/L PVA modified membranes

0.15 g/L PVA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	57.50	0.00	57.46	0	57.43	0.00
45	56.42	1.88	57.01	45	57.60	-0.30
90	56.25	2.17	58.00	90	59.75	-4.04
135	54.49	5.22	56.30	135	58.11	-1.19
180	54.33	5.50	55.48	180	56.63	1.39
225	54.33	5.50	54.65	225	54.96	4.29
270	52.58	8.55	53.85	270	55.12	4.01
315	51.13	11.08	53.20	315	51.45	10.41
360	51.28	10.81	53.01	360	51.60	10.14
405	51.43	10.55	52.60	405	51.43	10.13
450	51.43	10.55	52.00	450	51.75	9.88
495	53.52	6.92	52.56	495	51.60	10.14
540	52.04	9.48	52.04	540	52.04	10.41
1170	50.55	12.09	50.75	1170	50.95	10.67
1215	50.70	11.83	50.82	1215	50.95	11.28
1260	50.55	12.09	50.75	1260	50.95	11.28
1305	47.07	18.13	48.86	1305	50.65	11.80

1350	47.07	18.13	50.03	1350	52.99	7.72
1395	49.47	13.97	48.20	1395	46.94	18.27
1440	47.63	17.15	48.33	1440	49.03	14.62
1485	47.63	17.15	47.28	1485	46.94	18.27
1530	48.06	16.41	47.15	1530	46.25	19.47
1575	46.21	19.63	47.05	1575	47.88	16.62
1620	48.06	16.41	47.02	1620	45.97	19.94
1665	45.94	20.10	46.73	1665	47.52	18.99
1710	47.35	17.64	47.17	1710	47.00	21.64
1755	47.40	21.04	47.60	1755	47.80	20.24
1800	47.35	17.64	48.41	1800	49.47	13.86
1845	47.07	18.13	47.42	1845	47.77	16.81
1890	47.07	18.13	46.94	1890	46.80	20.24
1935	47.21	17.88	47.21	1935	47.21	19.53
1980	47.49	17.40	47.78	1980	48.06	16.31
2025	47.35	17.64	47.63	2025	47.92	16.56
2070	45.67	20.57	46.86	2070	48.06	16.31
2115	45.67	20.57	48.41	2115	51.15	10.93
2430	47.77	16.81	47.77	2430	47.77	16.81
2475	43.97	23.52	45.01	2475	44.36	22.75
2520	45.67	20.57	44.88	2520	44.23	22.98
2565	45.53	20.81				

Table C-7. 1: Summarized values of the calculated parameters of 0.15 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
52.52	48.66	44.80
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
43.56	39.45	35.34
Average salt rejection (%)		Average Salt rejection (%)
87.29	84.54	81.79
FRR (%)		FRR (%)
84.60	82.16	79.72
FDR (%)		FDR (%)
20.57	21.78	22.98

Appendix D

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.1 g/L PVA modified
membranes**

Table D- 1: PVA modifying solutions at various concentrations

	PVA Concentrations	Units
1	0.20	g.L^{-1}
2	0.15	g.L^{-1}
3	0.10	g.L^{-1}
4	0.05	g.L^{-1}

Kinetic data for the RO cell experimental runs with **PVA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.1 g/L PVA** concentration.

Below in table D-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table D- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m^2)	0.013775
Nomination	XLE-4040
Feed P_0 (bar):	5.5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table D-3. 1: Measured and calculated process parameters of 0.1 g/L PVA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (μS)	TDS (mg/L)	Temp (°C)	EC (μS)	TDS (mg/L)	EC (μS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	331	196	19.8	335	197	133	89	19.4	0.004	0.0028	0.672	48.8
45	335	197	20.1	336	196	129	86	19.3	0.004	0.0028	0.672	48.8
90	335	196	20.2	338	196	127	85	19.4	0.004	0.0027	0.648	47.0
135	339	196	20.5	340	196	124	83	19.7	0.004	0.0027	0.648	47.0
180	340	196	20.7	342	196	123	83	19.6	0.004	0.0027	0.648	47.0
225	352	197	20.6	344	196	122	82	19.4	0.004	0.0026	0.624	45.3
270	344	197	20.8	345	197	121	81	19.4	0.004	0.0026	0.624	45.3
315	344	197	20.8	344	197	118	79	18.9	0.004	0.0025	0.600	43.6
360	344	197	20.8	344	197	117	78	18.9	0.004	0.0026	0.624	45.3
405	346	198	20.7	346	198	121	80	18.7	0.004	0.0026	0.624	45.3
450	347	199	20.7	348	199	120	80	18.7	0.004	0.0027	0.648	47.0
495	350	199	20.6	350	200	121	81	18.6	0.004	0.0025	0.600	43.6
540	351	200	20.6	352	201	119	79	18.5	0.004	0.0025	0.600	43.6
1215	334	196	20.6	334	197	115	78	18.6	0.004	0.0024	0.576	41.8
1260	334	194	20.7	337	195	108	73	18.7	0.004	0.0025	0.600	43.6
1305	336	195	20.6	338	195	92	66	18.7	0.004	0.0024	0.576	41.8
1350	336	195	20.5	339	195	90	64	18.8	0.004	0.0024	0.576	41.8
1395	335	194	20.5	337	195	81	78	18.8	0.004	0.0023	0.552	40.1

1440	337	195	20.4	338	195	79	75	19.0	0.004	0.0023	0.552	40.1
1485	337	194	20.7	340	194	75	74	19.9	0.004	0.0024	0.576	41.8
1530	342	195	20.5	344	194	73	72	19.9	0.004	0.0023	0.552	40.1
1575	346	194	20.5	346	194	74	74	20.1	0.004	0.0023	0.552	40.1
1620	347	194	20.5	348	194	72	71	20.4	0.004	0.0023	0.552	40.1
1665	348	194	24.6	349	194	68	53		0.004	0.0023	0.552	40.1
1710	348	194	20.7	351	194	69	53	20.4	0.004	0.0022	0.528	38.3
1755	352	195	20.7	352	194	65	51	20.5	0.004	0.0022	0.528	38.3
1800	350	193	20.8	352	195	63	49	20.4	0.004	0.0022	0.528	38.3
1845	350	194	20.8	349	195	60	48	19.4	0.004	0.0022	0.528	38.3
1890	351	195	20.8	349	195	59	47	19.5	0.004	0.0021	0.504	36.6
1935	349	196	20.7	348	196	58	47	19.2	0.004	0.0021	0.504	36.6
1980	349	197	20.6	347	197	58	47	19.0	0.004	0.0021	0.504	36.6
2025	348	197	20.5	347	197	58	47	19.1	0.004	0.0021	0.504	36.6
2070	348	197	20.4	347	198	58	47	19.0	0.004	0.0020	0.480	34.8
2115	349	196	20.4	348	196	59	47	19.0	0.004	0.0021	0.504	36.6
2475	350	196	20.2	351	198	56	45	18.7	0.004	0.0020	0.468	34.0
2520	351	196	20.2	352	199	54	44	18.6	0.004	0.0020	0.468	34.0
2565	352	197	20.2	353	199	50	42	18.6	0.004	0.0019	0.456	33.1

Table D-3. 2: Measured and calculated process parameters of 0.1 g/L PVA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	341	197	24.6	342	198	145	86	22.8	0.004	0.0033	0.792	57.5
45	357	201	24.7	360	202	182	107	23.0	0.004	0.0034	0.816	59.2
90	367	197	25.2	363	205	145	86	23.7	0.004	0.0030	0.720	52.3
135	380	212	25.2	374	210	140	84	23.6	0.004	0.0030	0.720	52.3
180	395	220	25.3	397	220	152	89	24.1	0.004	0.0033	0.792	57.5
225	412	229	25.3	414	229	176	103	24.3	0.004	0.0031	0.744	54.0
270	415	231	25.3	415	232	165	95	24.3	0.004	0.0031	0.744	54.0
315	416	232	25.4	416	233	169	97	24.3	0.004	0.0031	0.744	54.0
360	417	232	25.4	417	233	163	95	24.4	0.004	0.0030	0.720	52.3
405	416	231	25.2	416	233	167	97	24.3	0.004	0.0031	0.744	54.0
450	418	233	25.1	419	235	162	94	24.1	0.004	0.0030	0.720	52.3
495	420	235	24.8	421	236	160	94	24.0	0.004	0.0030	0.720	52.3
1215	430	241	24.2	435	243	156	93	23.9	0.004	0.0028	0.672	48.8
1260	434	243	24.2	434	245	157	93	23.8	0.004	0.0028	0.672	48.8
1305	446	251	24.3	448	252	188	111	23.9	0.004	0.0028	0.672	48.8
1350	364	210	24.2	369	209	158	94	24.2	0.004	0.0027	0.648	47.0
1395	372	211	24.3	374	211	151	88	24.1	0.004	0.0027	0.648	47.0
1440	379	213	24.3	378	213	160	95	23.8	0.004	0.0027	0.648	47.0

1485	382	216	24.4	382	215	107	64	23.8	0.004	0.0026	0.624	45.3
1530	388	218	24.5	391	219	86	51	23.7	0.004	0.0025	0.600	43.6
1575	396	221	24.6	398	222	71	42	23.8	0.004	0.0024	0.576	41.8
1620	402	224	24.6	404	225	83	49	23.8	0.004	0.0025	0.600	43.6
1665	409	228	24.6	411	228	59	35	23.8	0.004	0.0025	0.600	43.6
1710	408	229	24.7	410	229	47	29	23.7	0.004	0.0025	0.600	43.6
1755	414	230	24.6	415	232	45	28	23.1	0.004	0.0024	0.576	41.8
1800	417	234	24.5	417	234	45	27	23.2	0.004	0.0024	0.576	41.8
1845	420	236	24.5	420	236	44	27	23.2	0.004	0.0023	0.552	40.1
1890	420	236	24.5	421	237	44	27	23.2	0.004	0.0024	0.576	41.8
1935	417	234	24.4	418	235	42	25	23.2	0.004	0.0023	0.552	40.1
2430	401	230	24.2	402	231	32	20	22.8	0.004	0.0023	0.552	40.1
2475	402	230	24.1	403	232	33	20	22.9	0.004	0.0022	0.528	38.3
2520	406	232	24.2	407	233	43	29	22.7	0.004	0.0023	0.552	40.1
2565	410	234	24.2	410	235	44	27	22.7	0.004	0.0023	0.552	40.1

Data analysis report on the two ranges of data of 0.1 g/L PVA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	48.37238908	48.55568679
Variance	29.2889923	35.45273911
Observations	37	36
df	36	35
F	0.826141873	
P(F<=f) one-tail	0.285583399	
F Critical one-tail	0.57213539	

t-Test: Two-Sample Assuming Unequal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	48.37238908	48.55568679
Variance	29.2889923	35.45273911
Observations	37	36
Hypothesized Mean Difference	0	
df	70	
t Stat	-0.137526867	
P(T<=t) one-tail	0.445504589	
t Critical one-tail	1.666914479	
P(T<=t) two-tail	0.891009178	
t Critical two-tail	1.994437112	

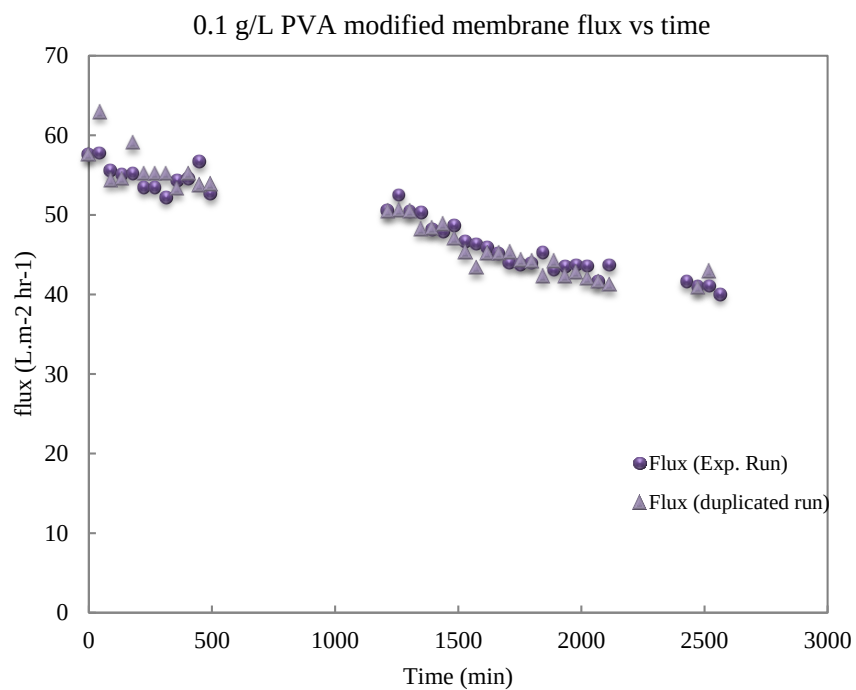


Figure D- 1: Permeate flux of 0.1 g/L PVA modified membranes at same operating conditions

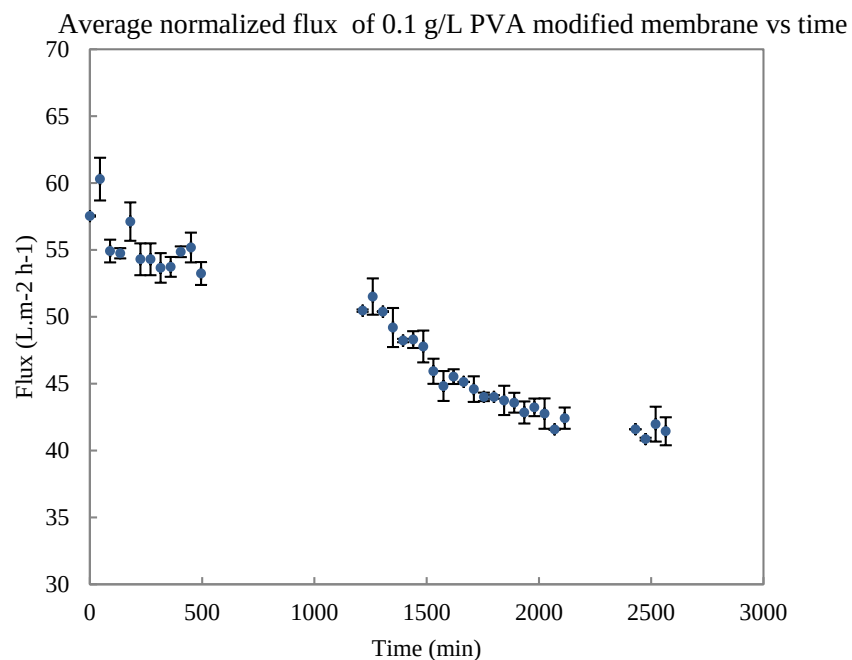


Figure D- 2: average permeate flux of 0.1 g/L PVA modified membranes

Table D-4. 1: Pure water (DI water) flow rate of the 0.1 g/L PVA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0027	0.648	47.0
30	15	0.004	0.0030	0.720	52.3
60	15	0.004	0.0030	0.720	52.3
90	15	0.004	0.0030	0.720	52.3
120	15	0.004	0.0030	0.720	52.3
150	15	0.004	0.0030	0.720	52.3
180	15	0.004	0.0030	0.720	52.3

Table D-4. 2: Pure water (DI water) flow rate of the 0.1 g/L PVA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0023	0.552	40.1
30	15	0.004	0.0027	0.648	47.0
60	15	0.004	0.0027	0.648	47.0
90	15	0.004	0.0027	0.648	47.0
120	15	0.004	0.0025	0.600	43.6
150	15	0.004	0.0026	0.624	45.3
180	15	0.004	0.0026	0.624	45.3

Table D-5. 1: Pure water Flow rate of 0.1 g/L PVA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30	15	0.004	0.0019	0.456	33.1
60	15	0.004	0.0023	0.552	40.1
90	15	0.004	0.0024	0.576	41.8
120	15	0.004	0.0024	0.576	41.8
150	15	0.004	0.0024	0.576	41.8
180	15	0.004	0.0024	0.564	40.9

Table D-5. 2: Pure water Flow rate of 0.1 g/L PVA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.384	0.0016	27.9
30	15	0.004	0.408	0.0017	29.6
60	15	0.004	0.456	0.0019	33.1
90	15	0.004	0.480	0.0020	34.8
120	15	0.004	0.456	0.0019	33.1
150	15	0.004	0.480	0.0020	34.8
180	15	0.004	0.480	0.0020	34.8

Table D-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.1 g/L PVA modified membranes

0.1 g/L PVA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	57.57	0.00	57.53	0	57.50	0.00
45	57.74	-0.30	60.29	45	62.85	-9.30
90	55.51	3.57	54.91	90	54.32	5.53
135	55.02	4.42	54.75	135	54.48	5.25
180	55.18	4.14	57.11	180	59.05	-2.70
225	53.45	7.14	54.30	225	55.14	4.10
270	53.45	7.14	54.30	270	55.14	4.10
315	52.16	9.38	53.65	315	55.14	4.10
360	54.25	5.76	53.73	360	53.20	7.46
405	54.57	5.20	54.86	405	55.14	4.10
450	56.67	1.56	55.17	450	53.68	6.64
495	52.63	8.58	53.23	495	53.84	6.36
1215	50.52	12.23	50.46	1215	50.40	12.35
1260	52.47	8.85	51.51	1260	50.55	12.09
1305	50.37	12.49	50.39	1305	50.40	12.35
1350	50.23	12.75	49.20	1350	48.17	16.22
1395	48.13	16.39	48.22	1395	48.31	15.98

1440	47.85	16.88	48.29	1440	48.74	15.23
1485	48.62	15.54	47.78	1485	46.94	18.37
1530	46.59	19.06	45.93	1530	45.26	21.27
1575	46.32	19.54	44.82	1575	43.32	24.65
1620	45.91	20.25	45.52	1620	45.13	21.51
1665	83.90	-45.75	45.13	1665	45.13	21.51
1710	43.91	23.72	44.59	1710	45.26	21.27
1755	43.78	23.94	44.01	1755	44.23	23.07
1800	43.91	23.72	44.01	1800	44.10	23.30
1845	45.23	21.43	43.75	1845	42.26	26.49
1890	43.05	25.22	43.57	1890	44.10	23.30
1935	43.43	24.56	42.85	1935	42.26	26.49
1980	43.69	24.11	43.23	1980	42.77	25.62
2025	43.56	24.33	42.76	2025	41.95	27.03
2070	41.61	27.72	41.58	2070	41.55	27.73
2115	43.69	24.11	42.42	2115	41.15	28.43
2430	41.59	27.75	41.59	2430	41.59	27.75
2475	40.93	28.90	40.86	2475	40.79	29.06
2520	41.05	28.69	41.97	2520	42.89	25.40
2565	40.00	30.52	41.44	2565	42.89	25.40

Table D-7. 1: Summarized values of the calculated parameters of 0.1 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
52.27	49.07	45.88
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
41.38	37.76	34.15
Average salt rejection		Average Salt rejection
84.80	87.09	89.37694542
FRR		FRR
79.17	76.61	74.05
FDR		FDR
30.52	27.05	25.40

Appendix E

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.05 g/L PVA modified
membranes**

Table E- 1: PVA modifying solutions at various concentrations

	PVA Concentrations	Units
1	0.20	g.L^{-1}
2	0.15	g.L^{-1}
3	0.10	g.L^{-1}
4	0.05	g.L^{-1}

Kinetic data for the RO cell experimental runs with **PVA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.05 g/L PVA** concentration.

Below in table E-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table E- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m^2)	0.013775
Nomination	XLE-4040
Feed P_0 (bar):	5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table E-3. 1: Measured and calculated process parameters of 0.05 g/L PVA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (μS)	TDS (mg/L)	Temp (°C)	EC (μS)	TDS (mg/L)	EC (μS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	343	201	25.1	345	200	196	119	24.5	0	0.004	0.0033	0.792
45	347	200	25.2	347	200	178	72	24.5	45	0.004	0.0032	0.768
90	350	201	24.7	350	201	186	93	24.4	90	0.004	0.0032	0.768
135									135			
180	357	202	24.7	358	202	190	98	24.2	180	0.004	0.0030	0.720
225	358	204	24.7	360	204	196	120	24.2	225	0.004	0.0029	0.696
270	363	204	24.6	364	204	106	87	24.5	270	0.004	0.0028	0.672
315	368	204	24.8	370	204	102	86	24.8	315	0.004	0.0028	0.672
360	373	205	24.8	373	207	85	64	24.3	360	0.004	0.0027	0.648
405	373	209	24.5	374	210	75	57	24.3	405	0.004	0.0028	0.672
450	374	219	24.5	375	211	78	59	24.0	450	0.004	0.0027	0.648
495	376	211	24.3	376	221	74	57	24.1	495	0.004	0.0028	0.672
1215	373	205	24.3	370	218	74	57	23.8	1215	0.004	0.0027	0.648
1260	373	219	24.3	373	219	73	56	24.1	1260	0.004	0.0028	0.672
1305	376	220	24.2	378	220	73	56	23.9	1305	0.004	0.0026	0.624
1350	375	218	24.3	377	219	72	56	24.0	1350	0.004	0.0026	0.624
1395	378	220	24.4	379	220	71	55	23.9	1395	0.004	0.0026	0.624

1440	380	220	24.5	383	221	70	55	23.8	1440	0.004	0.0026	0.624
1485	386	222	24.6	387	223	73	56	23.8	1485	0.004	0.0025	0.600
1530	381	220	24.6	380	220	74	57	23.8	1530	0.004	0.0027	0.648
1575	383	222	24.6	384	221	77	58	23.8	1575	0.004	0.0027	0.648
1620	384	221	24.7	380	222	77	58	23.9	1620	0.004	0.0028	0.672
1665	385	222	24.7	388	223	77	58	24.0	1665	0.004	0.0026	0.624
1710	384	221	24.6	389	223	82	62	23.9	1710	0.004	0.0027	0.648
1755	389	223	24.7	391	224	73	56	23.8	1755	0.004	0.0026	0.624
1800	396	226	24.6	397	228	71	55	23.8	1800	0.004	0.0025	0.600
1845	398	229	24.4	399	229	76	59	23.7	1845	0.004	0.0025	0.600
1890	399	230	24.3	400	229	89	66	23.7	1890	0.004	0.0023	0.552
1935	398	229	24.4	399	229	80	60	23.6	1935	0.004	0.0024	0.576
1980	399	230	24.4	401	231	70	53	23.6	1980	0.004	0.0025	0.588
2025	402	232	24.3	405	234	63	51	23.6	2025	0.004	0.0024	0.576
2070	405	236	24.3	409	237	60	50	23.5	2070	0.004	0.0024	0.576
2115	408	237	24.2	410	237	53	49	23.5	2115	0.004	0.0024	0.576
2430	400	230	23.9	404	233	52	48	23.5	2430	0.004	0.0023	0.552
2475	395	226	24.0	397	227	53	49	23.5	2475	0.004	0.0022	0.528
2520	397	226	24.1	398	228	44	38	23.6	2520	0.004	0.0021	0.504

Table E-3. 2: Measured and calculated process parameters of 0.05 g/L PVA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	342	197	25.2	344	197	189	110.1	25.0	0.004	0.0033	0.792	57.5
45	344	196	25.0	347	195	213	123.6	24.4	0.004	0.0040	0.960	69.7
90	351	196	25.1	354	196	201	115.3	24.7	0.004	0.0040	0.960	69.7
135	356	198	25.1	359	198	209	118.6	25.1	0.004	0.0036	0.864	62.7
180	362	199	25.2	363	199	164	93.3	25.0	0.004	0.0029	0.696	50.5
225	366	200	25.3	367	200	150	85.6	24.9	0.004	0.0029	0.696	50.5
270	362	197	25.2	363	197	147	84.4	24.9	0.004	0.0028	0.672	48.8
315	365	197	25.2	365	197	146	83.9	24.8	0.004	0.0028	0.672	48.8
360	365	197	25.3	367	198	141	82.2	24.7	0.004	0.0028	0.672	48.8
405	367	197	25.2	368	198	135	77.6	24.7	0.004	0.0027	0.648	47.0
1215	368	198	25.0	369	199	128	71.7	24.6	0.004	0.0027	0.648	47.0
1260	339	188	24.8	342	189	54	31.5	23.9	0.004	0.0026	0.624	45.3
1305	344	190	24.9	346	190	59	34.2	24.5	0.004	0.0026	0.624	45.3
1350	349	192	24.8	351	192	79	45.7	24.4	0.004	0.0027	0.648	47.0
1395	352	194	24.8	354	194	64	37.1	24.3	0.004	0.0028	0.672	48.8
1440	355	196	24.8	361	197	66	37.9	24.5	0.004	0.0026	0.624	45.3
1485	358	196	24.9	364	198	61	36.2	24.5	0.004	0.0027	0.648	47.0
1530	361	197	24.8	364	198	60	34.6	24.6	0.004	0.0028	0.672	48.8

1575	363	198	24.9	366	200	58	33.8	24.6	0.004	0.0027	0.648	47.0
1620	365	199	24.9	368	200	56	32.3	24.6	0.004	0.0027	0.648	47.0
1665	370	201	24.9	371	204	52	30.7	24.7	0.004	0.0026	0.624	45.3
1710	372	203	24.8	375	205	50	28.7	24.6	0.004	0.0026	0.624	45.3
1755	374	205	24.8	375	206	49	27.3	24.5	0.004	0.0027	0.648	47.0
1800	375	205	24.7	378	208	48	27.2	24.5	0.004	0.0025	0.600	43.6
1845	377	206	24.7	379	208	49	27.3	24.4	0.004	0.0025	0.600	43.6
1890	377	207	24.7	381	210	48	26.7	24.4	0.004	0.0026	0.624	45.3
1935	379	208	24.8	382	212	47	26.1	24.3	0.004	0.0025	0.600	43.6
1980	382	211	24.7	385	212	44	25.2	24.3	0.004	0.0025	0.600	43.6
2025	385	212	24.6	387	215	44	24.7	24.3	0.004	0.0026	0.624	45.3
2070	386	214	24.6	389	215	44	25	24.4	0.004	0.0024	0.576	41.8
2115	389	216	24.6	390	217	45	25.6	24.3	0.004	0.0024	0.576	41.8
2430	379	209	24.5	382	211	45	25.8	24.0	0.004	0.0023	0.552	40.1
2475	383	212	24.4	383	213	47	26.5	23.9	0.004	0.0022	0.528	38.3
2520	385	214	24.5	388	215	45	25.3	24.0	0.004	0.0022	0.528	38.3

Data analysis report on the two ranges of data of 0.05 g/L PVA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized Flux 2</i>
Mean	47.35226	48.43020305
Variance	19.73476	34.10343648
Observations	35	36
df	34	35
F	0.578674	
P(F<=f) one-tail	0.056902	
F Critical one-tail	0.565931	

t-Test: Two-Sample Assuming Unequal Variances

	<i>Normalized flux 1</i>	<i>Normalized Flux 2</i>
Mean	47.35226	48.43020305
Variance	19.73476	34.10343648
Observations	35	36
Hypothesized Mean Difference	0	
df	65	
t Stat	-0.876876	
P(T<=t) one-tail	0.191892	
t Critical one-tail	1.668636	
P(T<=t) two-tail	0.383783	
t Critical two-tail	1.997138	

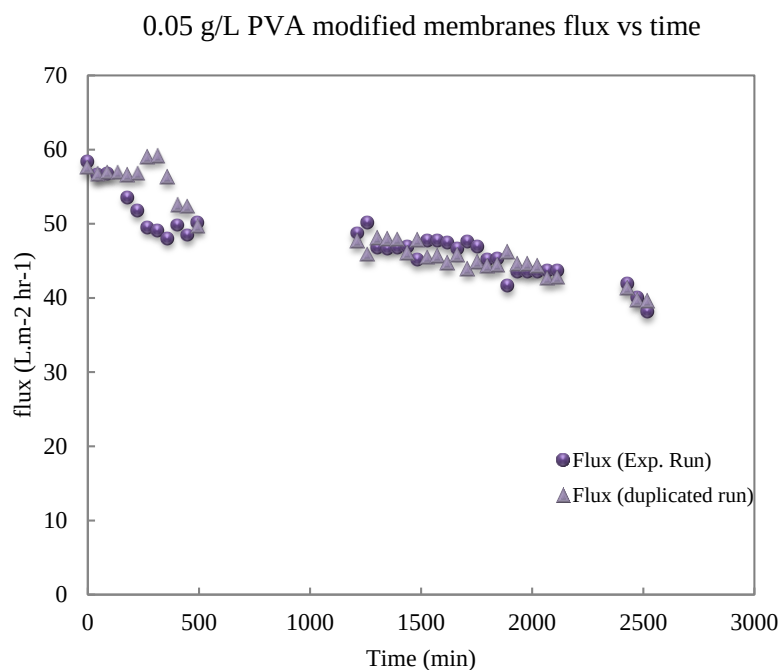


Figure E- 1: Permeate flux of 0.05 g/L PVA modified membranes at same operating conditions

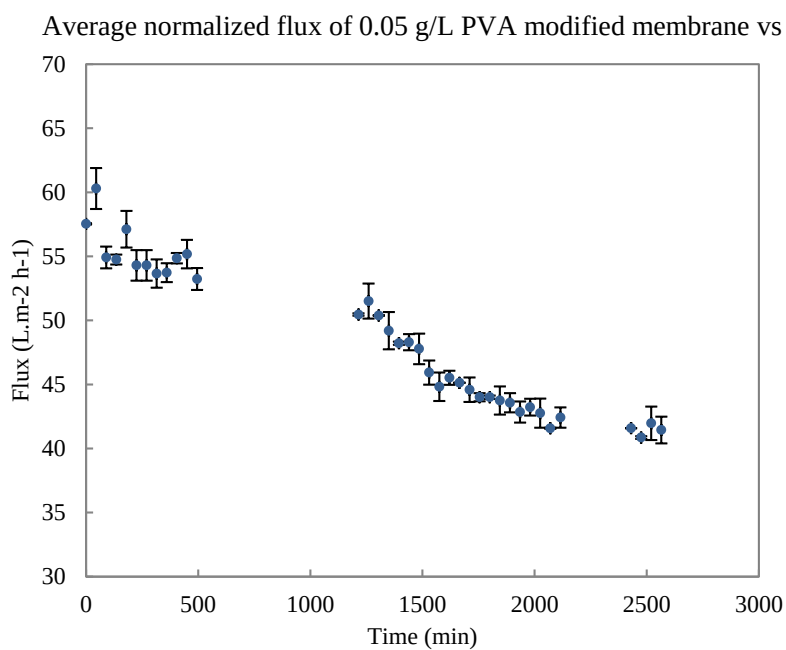


Figure E- 2: average permeate flux of 0.1 g/L PVA modified membranes

Table E-4. 1: Pure water (DI water) flow rate of the 0.05 g/L PVA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30					
60	15	0.004	0.0022	0.528	38.3
90	15	0.004	0.0020	0.480	34.8
120	15	0.004	0.0027	0.648	47.0
150	15	0.004	0.0028	0.672	48.8
180	15	0.004	0.0029	0.696	50.5
210	15	0.004	0.0028	0.672	48.8
240	15	0.004	0.0028	0.672	48.8

Table E-4. 2: Pure water (DI water) flow rate of the 0.05 g/L PVA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0026	0.624	45.3
30	15	0.004	0.0027	0.648	47.0
60	15	0.004	0.0028	0.672	48.8
90	15	0.004	0.0028	0.672	48.8
120	15	0.004	0.0029	0.696	50.5
150	15	0.004	0.0030	0.720	52.3
180	15	0.004	0.0032	0.768	55.8
210	15	0.004	0.0032	0.768	55.8
240	15	0.004	0.0032	0.768	55.8

Table E-5. 1: Pure water Flow rate of 0.05 g/L PVA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30					
60	15	0.004	0.0018	0.432	31.4
90	15	0.004	0.0021	0.504	36.6
120	15	0.004	0.0022	0.528	38.3
150	15	0.004	0.0021	0.504	36.6
180	15	0.004	0.0022	0.528	38.3
210	15	0.004	0.0021	0.504	36.6
240	15	0.004	0.0021	0.504	36.6

Table E-5. 2: Pure water Flow rate of 0.05 g/L PVA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0018	0.432	31.4
30	15	0.004	0.0019	0.456	33.1
60	15	0.004	0.0020	0.480	34.8
90	15	0.004	0.0022	0.528	38.3
120	15	0.004	0.0022	0.528	38.3
150	15	0.004	0.0023	0.552	40.1
180	15	0.004	0.0025	0.600	43.6
210	15	0.004	0.0024	0.576	41.8
240	15	0.004	0.0024	0.576	41.8

Table E-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.05 g/L PVA modified membranes

0.05 g/L PVA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	58.35	0.00	57.92	0	57.50	0.00
45	56.58	3.03	56.58	45	70.94	-23.38
90	56.75	2.74	56.75	90	70.31	-22.29
135			62.54	135	62.54	-8.77
180	53.52	8.28	55.02	180	56.53	12.12
225	51.74	11.34	54.21	225	56.68	11.86
270	49.51	15.15	54.22	270	58.93	14.90
315	49.07	15.90	54.07	315	59.07	14.65
360	48.03	17.70	52.12	360	56.22	14.40
405	49.80	14.65	51.13	405	52.46	17.45
450	48.45	16.96	50.34	450	52.23	17.86
495	50.10	14.14	49.86	495	49.62	18.92
1215	48.74	16.47	48.17	1215	47.60	17.21
1260	50.10	14.14	47.95	1260	45.80	18.61
1305	46.80	19.80	47.39	1305	47.97	20.04
1350	46.66	20.04	47.27	1350	47.88	16.72
1395	46.80	19.80	47.30	1395	47.80	13.38

1440	46.94	19.56	46.45	1440	45.97	20.04
1485	45.13	22.66	46.44	1485	47.74	16.96
1530	47.74	16.47	46.55	1530	45.36	14.14
1575	47.74	16.47	46.67	1575	45.60	17.21
1620	47.40	13.63	46.00	1620	44.60	17.21
1665	46.66	20.04	46.18	1665	45.70	20.51
1710	47.60	16.72	45.72	1710	43.84	20.28
1755	46.94	19.56	45.84	1755	44.74	16.96
1800	45.13	22.66	44.67	1800	44.21	23.11
1845	45.26	22.43	44.80	1845	44.34	22.89
1890	41.64	28.64	43.88	1890	46.11	19.80
1935	43.58	25.31	44.02	1935	44.47	22.66
1980	43.49	23.76	43.98	1980	44.47	22.66
2025	43.58	25.31	43.91	2025	44.25	19.56
2070	43.71	25.09	43.14	2070	42.56	25.97
2115	43.71	25.09	43.20	2115	42.69	25.75
2430	41.89	28.21	41.58	2430	41.27	28.21
2475	40.07	31.33	39.83	2475	39.60	31.13
2520	38.13	34.65	38.81	2520	39.48	31.33

Table E-7. 1: Summarized values of the calculated parameters of 0.05 g/L PVA modified membranes after 42 hours fouling test using the synthetic feed

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
49.22	52.05	54.88
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
36.34	38.50	40.65
Average salt rejection (%)		Average Salt rejection (%)
87.54	87.79	88.05049851
FRR (%)		FRR (%)
73.83	75.01	76.19
FDR (%)		FDR (%)
34.65	32.99	31.33

Appendix F

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.1 mol/L DMAEMA modified
membranes**

Table F- 1: DMAEMA modifying solutions at various concentrations

	DMAEMA Concentrations	Units
1	0.1	mol.L ⁻¹
2	0.075	mol.L ⁻¹
3	0.05	mol.L ⁻¹
4	0.02	mol.L ⁻¹

Kinetic data for the RO cell experimental runs with **DMAEMA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.1 mol/L DMAEMA** concentration.

Below in table F-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table F- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m ²)	0.013775
Nomination	XLE-4040
Feed P ₀ (bar):	4.5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table F-3. 1: Measured and calculated process parameters of 0.1 mol/L DMAEMA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	320	157	25.6	322	160	145	73	25.1	0.004	0.0033	0.792	57.5
45	327	161	25.6	329	161	164	83	25.1	0.004	0.0033	0.792	57.5
90	337	164	25.8	340	167	150	75	24.9	0.004	0.0033	0.792	57.5
135	345	168	25.8	348	169	157	79	25.0	0.004	0.0032	0.768	55.8
180	354	172	25.9	357	173	160	80	25.2	0.004	0.0033	0.792	57.5
225	362	175	26.0	366	176	162	81	25.2	0.004	0.0032	0.768	55.8
270	371	179	26.1	375	179	164	83	25.1	0.004	0.0033	0.792	57.5
315	371	179	26.1	383	182	164	83	25.0	0.004	0.0032	0.768	55.8
360	372	179	26.1	393	186	166	84	25.0	0.004	0.0030	0.744	54.0
405	375	181	26.1	402	189	164	83	24.9	0.004	0.0030	0.720	52.3
450	376	181	26.2	411	192	163	82	24.8	0.004	0.0030	0.720	52.3
495	377	182	26.2	420	196	165	83	24.7	0.004	0.0030	0.720	52.3
540	378	183	26.1	429	199	164	83	24.6	0.004	0.0031	0.744	54.0
945	380	183	26.2	437	202	164	83	24.6	0.004	0.0030	0.720	52.3
990	381	185	26.1	447	206	165	83	24.5	0.004	0.0030	0.720	52.3
1035	383	185	26.2	455	209	164	83	24.5	0.004	0.0031	0.744	54.0
1080	384	186	26.3	464	212	164	83	24.5	0.004	0.0030	0.720	52.3

1125	385	187	26.3	474	215	165	83	24.4	0.004	0.0030	0.696	50.5
1170	387	187	26.3	482	219	164	83	24.4	0.004	0.0030	0.720	52.3
1215	388	188	26.3	491	222	164	83	24.3	0.004	0.0029	0.696	50.5
1260	389	189	26.3	501	225	167	85	24.3	0.004	0.0029	0.696	50.5
1305	391	189	26.4	509	229	165	83	24.3	0.004	0.0028	0.672	48.8
1350	392	190	26.4	519	232	166	85	24.2	0.004	0.0030	0.720	52.3
1395	394	191	26.4	527	235	165	83	24.3	0.004	0.0029	0.696	50.5
1440	395	192	26.4	536	239	164	83	24.3	0.004	0.0028	0.672	48.8
1485	396	192	26.5	545	242	165	84	24.3	0.004	0.0027	0.648	47.0
1530	398	193	26.5	554	245	165	84	24.4	0.004	0.0028	0.672	48.8
1575	399	194	26.5	563	248	165	84	24.5	0.004	0.0026	0.624	45.3
1620	400	195	26.6	571	252	165	84	24.7	0.004	0.0026	0.624	45.3
1665	402	195	26.6	580	255	167	84	24.8	0.004	0.0026	0.624	45.3
1710	403	196	26.6	590	258	165	84	24.7	0.004	0.0027	0.600	47.0
1755	405	197	26.6	598	262	166	84	24.8	0.004	0.0026	0.624	45.3
1800	406	198	26.6	608	265	167	84	24.9	0.004	0.0025	0.600	43.6
1845	407	198	26.7	617	268	166	84	24.8	0.004	0.0026	0.624	45.3
1890	409	199	26.7	636	272	166	84	24.9	0.004	0.0025	0.600	43.6
2430	412	200	26.7	643	278	72	39	24.6	0.004	0.0025	0.600	43.6
2475	413	201	26.8	652	281	72	39	24.5	0.004	0.0025	0.600	43.6
2520	414	202	26.8	661	285	76	41	24.6	0.004	0.0025	0.600	43.6

Table F-3. 2: Measured and calculated process parameters of 0.1 mol/L DMEA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (μS)	TDS (mg/L)	Temp (°C)	EC (μS)	TDS (mg/L)	EC (μS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	344	182	23.0	346	184	154	83	22.0	0.004	0.0033	0.792	57.5
45	346	182	23.3	349	183	141	78	22.4	0.004	0.0034	0.816	59.2
90	350	183	23.6	353	184	134	73	22.5	0.004	0.0034	0.816	59.2
135	357	184	24.0	358	184	128	70	22.4	0.004	0.0033	0.792	57.5
180	359	184	24.2	358	184	131	72	22.0	0.004	0.0033	0.792	57.5
225	361	184	24.3	360	184	115	63	22.2	0.004	0.0032	0.768	55.8
270	363	185	24.3	363	187	106	58	22.2	0.004	0.0032	0.768	55.8
315	366	186	24.4	364	188	97	53	22.3	0.004	0.0029	0.696	50.5
360	367	186	24.4	368	188	88	48	22.2	0.004	0.0030	0.720	52.3
405	368	187	24.4	369	189	83	46	22.3	0.004	0.0032	0.768	55.8
450	369	188	24.5	370	189	78	42	22.5	0.004	0.0031	0.744	54.0
495	370	189	24.6	373	190	74	40	22.6	0.004	0.0031	0.744	54.0
540	372	189	24.5	373	191	68	36	22.6	0.004	0.0031	0.744	54.0
990	361	191	23.2	363	193	68	37	22.0	0.004	0.0030	0.720	52.3
1035	364	194	22.9	367	195	68	36	22.1	0.004	0.0030	0.720	52.3
1080	374	199	23.0	378	201	70	38	22.0	0.004	0.0030	0.720	52.3
1125	386	205	23.1	389	206	72	39	21.8	0.004	0.0030	0.720	52.3

1170	396	209	43.0	401	210	73	39	22.3	0.004	0.0030	0.700	52.3
1215	412	216	23.4	417	218	99	53	22.2	0.004	0.0030	0.720	52.3
1260	427	223	23.5	428	225	98	53	22.7	0.004	0.0029	0.696	50.5
1305	440	229	23.7	446	232	103	56	22.7	0.004	0.0028	0.672	48.8
1350	460	238	23.9	466	240	100	53	22.7	0.004	0.0029	0.696	50.5
1395	479	247	24.0	484	249	109	60	22.7	0.004	0.0028	0.700	48.8
1440	480	247	24.0	485	250	107	58	22.7	0.004	0.0028	0.672	48.8
1485	479	246	24.1	484	249	105	57	22.9	0.004	0.0027	0.600	47.0
1530	481	247	24.3	486	250	102	56	22.9	0.004	0.0027	0.600	47.0
1575	481	247	24.2	486	250	99	54	22.9	0.004	0.0028	0.672	48.8
1620	482	248	24.3	487	251	97	53	22.8	0.004	0.0027	0.600	47.0
1665	482	248	24.4	487	250	98	53	22.9	0.004	0.0027	0.600	47.0
1710	493	255	24.4	496	257	93	50	23.0	0.004	0.0028	0.672	48.8
1755	498	260	24.6	501	263	91	49	23.1	0.004	0.0027	0.600	47.0
1800	504	264	23.5	506	265	89	48	22.4	0.004	0.0027	0.648	47.0
1845	510	266	23.5	511	268	87	46	22.3	0.004	0.0028	0.700	48.8
1890	520	272	23.4	527	275	90	48	22.3	0.004	0.0028	0.700	48.8
1935	542	282	23.6	547	284	88	47	22.5	0.004	0.0028	0.700	48.8
2430	565	293	23.9	570	294	67	36	22.5	0.004	0.0027	0.648	47.0
2475	594	306	24.0	599	309	68	36	22.8	0.004	0.0027	0.600	47.0
2520	622	320	24.0	629	323	69	37	23.0	0.004	0.0026	0.600	45.3

Data analysis report on the two ranges of data of 0.1 mol/L DMAEMA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	50.10797718	47.67309766
Variance	23.17793386	13.71213371
Observations	38	38
df	37	37
F	1.690322917	
P(F<=f) one-tail	0.057417535	
F Critical one-tail	1.729507032	

t-Test: Two-Sample Assuming Unequal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	50.10797718	47.67309766
Variance	23.17793386	13.71213371
Observations	38	38
Hypothesized Mean Difference	0	
df	69	
t Stat	-0.573559026	
P(T<=t) one-tail	0.284065523	
t Critical one-tail	1.667238549	
P(T<=t) two-tail	0.568131046	
t Critical two-tail	1.994945415	

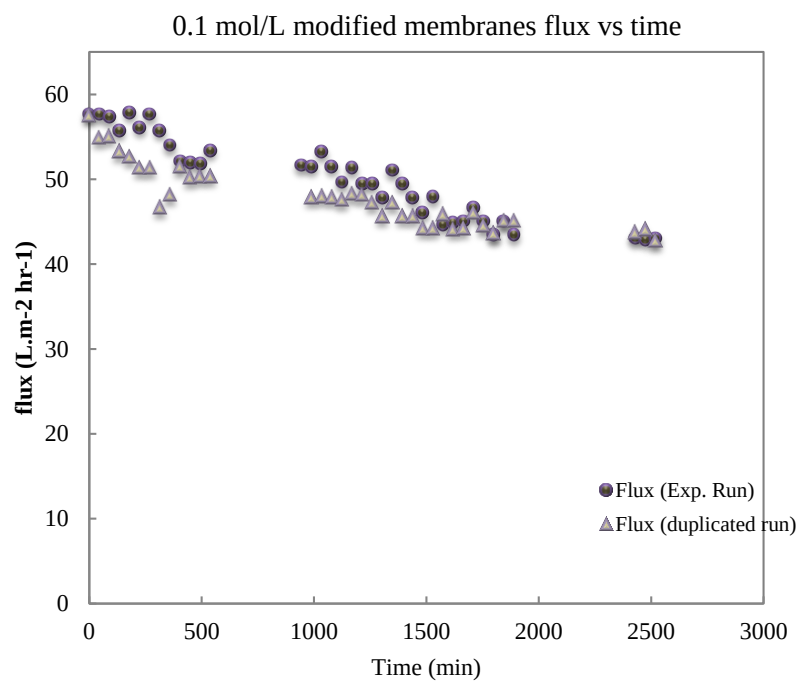


Figure F- 1: Permeate flux of 0.1 mol/L DMAEMA modified membranes at same operating conditions

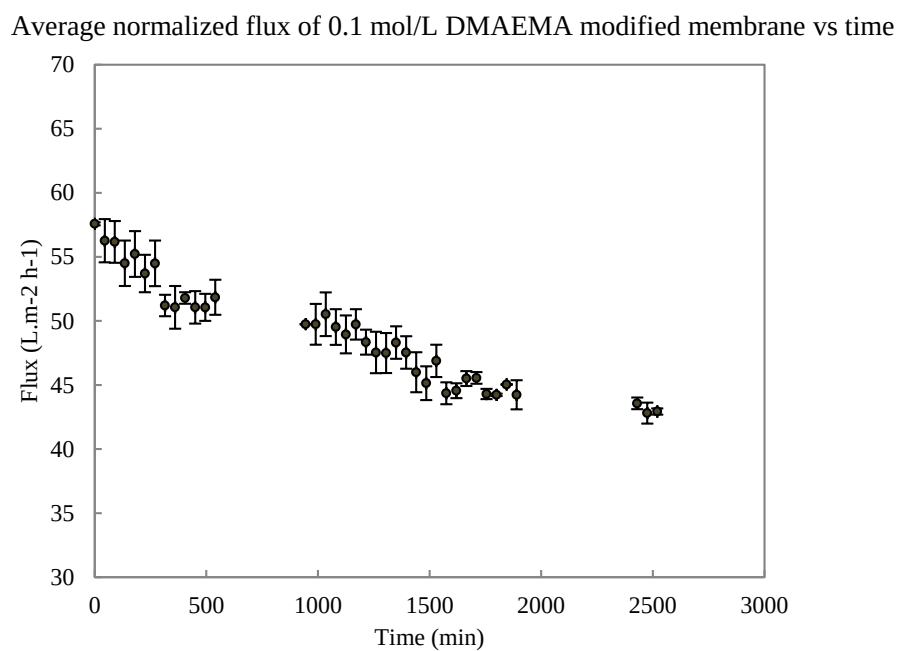


Figure F- 2: average permeate flux of 0.1 mol/L DMAEMA modified membranes

Table F-4. 1: Pure water (DI water) flow rate of the 0.1 mol/L DMAEMA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0039	0.936	67.9
30	15	0.004	0.0040	0.960	69.7
60	15	0.004	0.0042	1.008	73.2
90	15	0.004	0.0050	1.200	87.1
120	15	0.004	0.0046	1.104	80.1
150	15	0.004	0.0042	1.008	73.2
180	15	0.004	0.0042	1.008	73.2
210	15	0.004	0.0042	1.008	73.2
240	15	0.004	0.0040	0.960	69.7
270	15	0.004	0.0042	1.008	73.2

Table F-4. 2: Pure water (DI water) flow rate of the 0.1 mol/L DMAEMA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0039	0.936	67.9
30	15	0.004	0.0037	0.888	64.5
60	15	0.004	0.0039	0.936	67.9
90	15	0.004	0.0038	0.912	66.2
120	15	0.004	0.0038	0.912	66.2
150	15	0.004	0.0037	0.888	64.5
180	15	0.004	0.0038	0.912	66.2
210	15	0.004	0.0038	0.912	66.2
240	15	0.004	0.0039	0.936	67.9
270	15	0.004	0.0039	0.936	67.9

Table F-5. 1: Pure water Flow rate of 0.1 mol/L DMAEMA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0025	0.600	43.6
30	15	0.004	0.0030	0.720	52.3
60	15	0.004	0.0033	0.792	57.5
90	15	0.004	0.0033	0.792	57.5
120	15	0.004	0.0033	0.792	57.5
150	15	0.004	0.0033	0.792	56.2

Table F-5. 2: Pure water Flow rate of 0.1 mol/L DMAEMA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0030	0.720	52.3
30	15	0.004	0.0034	0.816	59.2
60	15	0.004	0.0035	0.840	61.0
90	15	0.004	0.0034	0.816	59.2
120	15	0.004	0.0034	0.816	59.2
150	15	0.004	0.0034	0.820	59.7

Table F-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.1 mol/L DMAEMA modified membranes

0.1 mol/L DMAEMA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	57.67	0.00	57.58	0	57.50	0.00
45	57.67	0.00	56.26	45	54.86	4.59
90	57.33	0.59	56.17	90	55.02	4.31
135	55.75	3.32	54.50	135	53.24	7.40
180	57.84	-0.30	55.23	180	52.62	8.49
225	56.08	2.74	53.70	225	51.32	10.73
270	57.67	0.00	54.50	270	51.32	10.73
315	55.75	3.32	51.20	315	46.65	18.86
360	54.01	6.34	51.06	360	48.12	16.31
405	52.11	9.63	51.80	405	51.48	10.47
450	51.96	9.89	51.06	450	50.16	12.75
495	51.81	10.16	51.06	495	50.31	12.49
540	53.38	7.44	51.84	540	50.31	12.49
945	51.65	10.42	51.65	945		
990	51.50	10.69	49.74	990	47.83	16.81
1035	53.22	7.71	50.53	1035	47.97	16.56
1080	51.50	10.69	49.53	1080	47.83	16.81

1125	49.64	13.92	48.95	1125	47.55	17.30
1170	51.35	10.95	49.73	1170	48.26	16.06
1215	49.49	14.17	48.35	1215	48.12	16.31
1260	49.49	14.17	47.53	1260	47.21	17.90
1305	47.79	17.13	47.50	1305	45.58	20.73
1350	51.05	11.48	48.31	1350	47.21	17.90
1395	49.49	14.17	47.53	1395	45.58	20.73
1440	47.79	17.13	46.00	1440	45.58	20.73
1485	46.08	20.09	45.14	1485	44.21	23.11
1530	47.93	16.89	46.89	1530	44.21	23.11
1575	44.63	22.60	44.36	1575	45.85	20.26
1620	44.90	22.14	44.56	1620	44.08	23.33
1665	45.03	21.91	45.51	1665	44.21	23.11
1710	46.63	19.14	45.55	1710	45.98	20.02
1755	45.03	21.91	44.30	1755	44.47	22.65
1800	43.43	24.69	44.24	1800	43.56	24.23
1845	45.03	21.91	45.04	1845	45.04	21.66
1890	43.43	24.69	44.24	1890	45.04	21.66
2430	43.05	25.35	43.56	2430	43.69	24.01
2475	42.92	25.57	42.81	2475	44.08	23.33
2520	43.05	25.35	42.94	2520	42.70	25.73

Table F-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.1 mol/L DMAEMA modified membrane

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
72.48	69.52	66.56
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
56.19	57.93	59.67
Average salt rejection (%)		Average Salt rejection (%)
82.3	84.30	82.5
FRR (%)		FRR (%)
79.33	83.57	87.82
FDR (%)		FDR (%)
25.35	25.54	25.73

Appendix G

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.05 mol/L DMAEMA modified
membranes**

Table G- 1: DMAEMA modifying solutions at various concentrations

	DMAEMA Concentrations	Units
1	0.1	mol.L ⁻¹
2	0.075	mol.L ⁻¹
3	0.05	mol.L ⁻¹
4	0.02	mol.L ⁻¹

Kinetic data for the RO cell experimental runs with **DMAEMA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.05 mol/L DMAEMA** concentration.

Below in table G-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table G- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m ²)	0.013775
Nomination	XLE-4040
Feed P ₀ (bar):	5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table G-3. 1: Measured and calculated process parameters of 0.05 mol/L DMAEMA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	320	152	27	319	152	160	85	26	0.004	0.0033	0.792	57.5
45	319	152	27	321	152	159	78	26	0.004	0.0033	0.792	57.5
90	319	151	27	321	152	148	71	26	0.004	0.0033	0.792	57.5
135	319	151	27	321	152	117	57	26	0.004	0.0033	0.792	57.5
180	319	151	27	320	152	112	54	26	0.004	0.0032	0.768	55.8
225	320	152	27	321	152	106	52	26	0.004	0.0032	0.768	55.8
270	320	153	27	322	153	101	49	26	0.004	0.0030	0.720	52.3
315	306	145	27	308	147	49	24	26	0.004	0.0030	0.720	52.3
360	308	146	27	309	148	47	23	26	0.004	0.0028	0.672	48.8
405	310	148	27	313	149	46	23	25	0.004	0.0028	0.672	48.8
450	315	150	27	318	151	46	23	26	0.004	0.0028	0.672	48.8
495	318	151	27	320	152	44	22	26	0.004	0.0027	0.648	47.0
540	322	153	27	323	155	42	21	25	0.004	0.0027	0.648	47.0
945	323	155	26	322	155	41	21	25	0.004	0.0026	0.624	45.3
990	325	157	26	326	158	45	22	25	0.004	0.0027	0.648	47.0
1035	327	160	26	328	160	40	21	25	0.004	0.0027	0.648	47.0
1080	328	161	26	328	161	42	21	25	0.004	0.0026	0.624	45.3
1125	333	162	26	334	163	41	21	24	0.004	0.0027	0.648	47.0
1170	336	163	26	337	164	44	22	25	0.004	0.0027	0.648	47.0

1215	338	163	26	339	165	44	22	25	0.004	0.0026	0.624	45.3
1260	338	163	26	338	163	46	23	25	0.004	0.0026	0.624	45.3
1305	340	164	26	341	165	48	23	25	0.004	0.0026	0.624	45.3
1350	342	164	26	342	165	49	24	26	0.004	0.0025	0.600	43.6
1395	341	164	26	342	164	50	24	25	0.004	0.0026	0.624	45.3
1440	340	162	27	341	165	49	24	26	0.004	0.0026	0.624	45.3
1485	341	164	27	341	164	47	23	26	0.004	0.0024	0.576	41.8
1530	341	164	27	342	164	47	23	26	0.004	0.0025	0.600	43.6
1575	342	164	27	342	163	46	23	26	0.004	0.0024	0.576	41.8
1620	343	165	26	343	163	45	23	26	0.004	0.0025	0.600	43.6
1665	344	165	26	343	163	44	23	26	0.004	0.0025	0.600	43.6
1710	344	166	27	344	162	44	22	26	0.004	0.0026	0.624	45.3
1755	345	166	26	344	162	43	22	26	0.004	0.0026	0.624	45.3
1800	346	166	26	344	162	45	22	26	0.004	0.0025	0.600	43.6
1845	347	167	26	345	161	46	22	26	0.004	0.0025	0.600	43.6
1890	348	167	26	345	161	45	22	25	0.004	0.0025	0.600	43.6
2385	348	168	26	346	161	43	21	25	0.004	0.0025	0.600	43.6
2430	349	168	26	346	160	44	21	25	0.004	0.0025	0.600	43.6
2475	350	169	26	347	160	43	21	25	0.004	0.0024	0.576	41.8
2520	351	169	26	347	160	43	21	25	0.004	0.0024	0.576	41.8
2565												

Table G-3. 2: Measured and calculated process parameters of 0.05 mol/L DMEMA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	315	154	25	316	148	169	89	25	0.00416667	0.0033	0.792	57.5
45	317	149	25	317	147	145	72	25	0.004	0.0033	0.792	57.5
90	315	150	26	316	147	118	56	25	0.004	0.0033	0.792	57.5
135	316	150	26	315	147	115	56	25	0.004	0.0034	0.816	59.2
180	316	147	27	315	146	116	56	25	0.004	0.0033	0.792	57.5
225	316	146	26	316	146	114	55	25	0.004	0.0032	0.768	55.8
270	316	144	26	316	146	113	54	25	0.004	0.0032	0.768	55.8
315	313	143	26	314	143	86	47	25	0.004	0.0033	0.792	57.5
360	310	141	26	318	145	68	41	25	0.004	0.0032	0.768	55.8
405	312	142	26	316	145	67	40	25	0.004	0.0031	0.744	54.0
450	314	142	26	318	145	69	42	25	0.004	0.0030	0.720	52.3
495	320	143	26	317	144	67	40	25	0.004	0.0028	0.672	48.8
540	321	143	26	323	144	60	37	25	0.004	0.0027	0.648	47.0
945	325	144	26	326	145	61	38	25	0.004	0.0027	0.648	47.0
990	327	144	26	327	146	61	38	25	0.004	0.0028	0.672	48.8
1035	332	145	26	330	147	61	39	26	0.004	0.0028	0.672	48.8
1080	330	145	26	333	147	62	40	25	0.004	0.0029	0.696	50.5
1125	332	146	26	335	148	61	40	26	0.004	0.0027	0.648	47.0
1170	338	146	26	337	149	60	39	26	0.004	0.0027	0.648	47.0

1215	339	147	26	340	150	60	39	26	0.004	0.0027	0.648	47.0
1260	340	147	26	342	151	59	38	26	0.004	0.0027	0.648	47.0
1305	336	148	26	345	152	60	39	26	0.004	0.0027	0.648	47.0
1350	338	149	26	347	153	58	38	26	0.004	0.0028	0.672	48.8
1395	345	149	26	349	153	56	36	26	0.004	0.0026	0.624	45.3
1440	343	150	26	352	154	59	38	26	0.004	0.0026	0.624	45.3
1485	345	150	26	354	155	59	38	26	0.004	0.0026	0.624	45.3
1530	347	151	26	347	156	55	36	26	0.004	0.0027	0.648	47.0
1575	350	151	26	350	157	60	39	26	0.004	0.0027	0.648	47.0
1620	347	152	26	351	158	62	40	26	0.004	0.0025	0.600	43.6
1665	347	152	26	364	159	68	42	26	0.004	0.0024	0.576	41.8
1710	348	153	26	376	159	69	43	26	0.004	0.0024	0.576	41.8
1755	349	153	26	359	160	63	40	26	0.004	0.0024	0.576	41.8
1800	349	154	26	351	161	63	41	26	0.004	0.0024	0.576	41.8
1845	350	154	26	353	162	66	42	26	0.004	0.0025	0.600	43.6
1890	350	155	26	356	163	66	42	26	0.004	0.0024	0.576	41.8
2385	351	155	26	358	164	64	41	25	0.004	0.0025	0.600	43.6
2430	351	156	26	361	164	61	38	25	0.004	0.0024	0.576	41.8
2475	352	157	26	363	165	57	37	25	0.004	0.0025	0.600	43.6
2520	352	157	26	365	166	55	35	25	0.004	0.0024	0.576	41.8
2565	351	158	27	368	167	56	36	25	0.004	0.0024	0.576	41.8

Data analysis report on the two ranges of data of 0.05 mol/L DMAEMA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 1</i>	<i>Normalized Flux 2</i>
Mean	48.82748	47.68527078
Variance	27.90303	27.71743926
Observations	40	40
df	39	39
F	1.006696	
P(F<=f) one-tail	0.49174	
F Critical one-tail	1.704465	

t-Test: Two-Sample Assuming Equal Variances

	<i>Normalized flux 1</i>	<i>Normalized Flux 2</i>
Mean	48.82748	47.68527078
Variance	27.90303	27.71743926
Observations	40	40
Pooled Variance	27.81024	
Hypothesized Mean Difference	0	
df	78	
t Stat	0.968634	
P(T<=t) one-tail	0.167861	
t Critical one-tail	1.664625	
P(T<=t) two-tail	0.335722	
t Critical two-tail	1.990847	

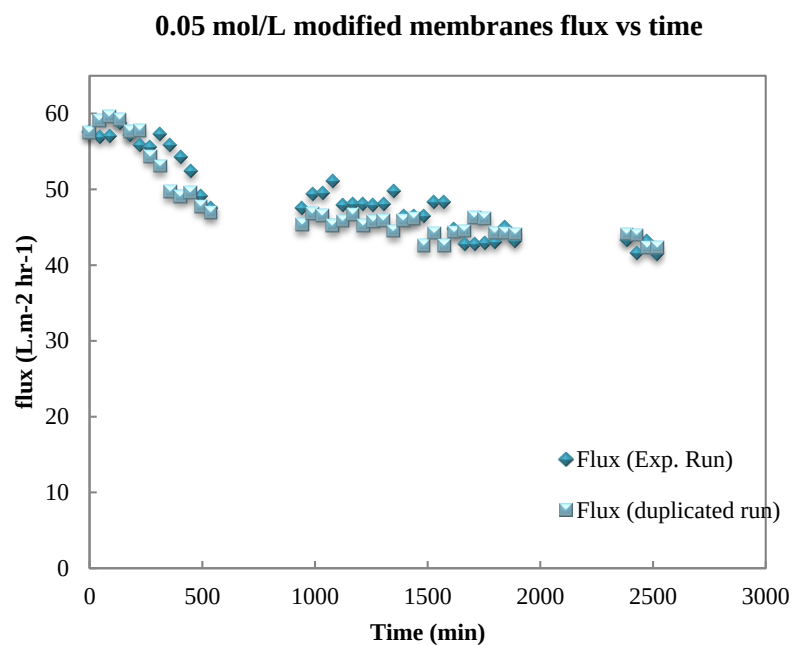


Figure G- 1: Permeate flux of 0.05 mol/L DMAEMA modified membranes at same operating conditions

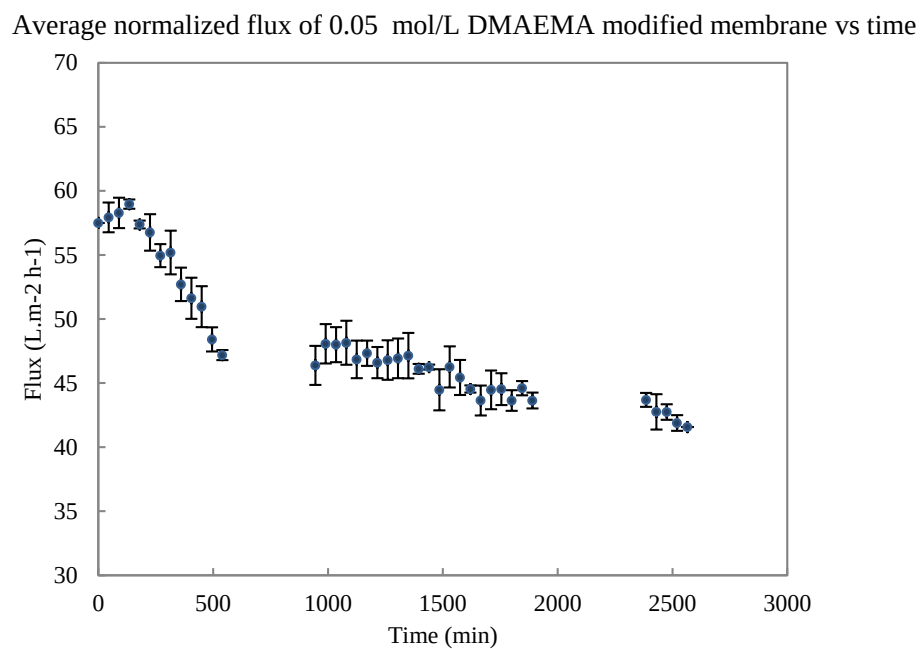


Figure G- 2: average permeate flux of 0.05 mol/L DMAEMA modified membranes

Table G-4. 1: Pure water (DI water) flow rate of the 0.05 mol/L DMAEMA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0039	0.936	67.9
30	15	0.004	0.0040	0.960	69.7
60	15	0.004	0.0040	0.960	69.7
90	15	0.004	0.0038	0.912	66.2
120	15	0.004	0.0039	0.936	67.9
150	15	0.004	0.0038	0.912	66.2
180	15	0.004	0.0039	0.936	67.9
210	15	0.004	0.0039	0.936	67.9
240	15	0.004	0.0038	0.912	66.2
270	15	0.004	0.0038	0.912	66.2

Table G-4. 2: Pure water (DI water) flow rate of the 0.05 mol/L DMAEMA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15				
30	15				
60	15	15	0.004	0.0039	0.936
90	15	15	0.004	0.0040	0.960
120	15	15	0.004	0.0041	0.984
150	15	15	0.004	0.0040	0.960
180	15	15	0.004	0.0040	0.960
210	15	15	0.004	0.0039	0.936
240	15	15	0.004	0.0040	0.960
270	15	15	0.004	0.0039	0.936

Table G-5. 1: Pure water Flow rate of 0.05 mol/L DMAEMA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0029	0.696	50.5
30	15	0.004	0.0029	0.696	50.5
60	15	0.004	0.0030	0.720	52.3
90	15	0.004	0.0029	0.696	50.5
120	15	0.004	0.0031	0.744	54.0
150	15	0.004	0.0031	0.744	54.0

Table G-5. 2: Pure water Flow rate of 0.05 mol/L DMAEMA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0026	0.624	45.3
30	15	0.004	0.0034	0.816	59.2
60	15	0.004	0.0029	0.696	50.5
90	15	0.004	0.0030	0.720	52.3
120	15	0.004	0.0030	0.720	52.3
150	15	0.004	0.0030	0.720	52.3

Table G-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.05 mol/L DMAEMA modified membranes

0.05 mol/L DMAEMA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	57.50	0.00	57.50	0	57.50	0.00
45	56.82	1.18	57.93	45	59.05	0.00
90	56.99	0.88	58.28	90	59.57	-3.61
135	58.71	-2.12	58.97	135	59.22	-3.00
180	57.16	0.59	57.38	180	57.60	-0.17
225	55.75	3.03	56.76	225	57.77	-0.47
270	55.59	3.32	54.95	270	54.32	5.53
315	57.33	0.30	55.19	315	53.05	7.74
360	55.75	3.03	52.71	360	49.66	13.63
405	54.17	5.78	51.62	405	49.07	14.65
450	52.42	8.82	50.97	450	49.51	13.89
495	49.07	14.65	48.41	495	47.74	16.96
540	47.46	17.45	47.18	540	46.90	18.42
945	47.46	17.45	46.38	945	45.30	21.21
990	49.36	14.14	48.06	990	46.76	18.66
1035	49.51	13.89	48.00	1035	46.49	19.14
1080	51.13	11.08	48.15	1080	45.17	21.44
1125	47.88	16.72	46.85	1125	45.81	20.33

1170	48.03	16.47	47.33	1170	46.63	18.90
1215	48.03	16.47	46.60	1215	45.17	21.44
1260	47.88	16.72	46.79	1260	45.70	20.51
1305	48.03	16.47	46.93	1305	45.84	20.28
1350	49.80	13.38	47.14	1350	44.47	22.66
1395	46.38	19.33	46.11	1395	45.84	20.28
1440	46.38	19.33	46.25	1440	46.11	19.80
1485	46.38	19.33	44.47	1485	42.56	25.97
1530	48.31	15.98	46.26	1530	44.21	23.11
1575	48.31	15.98	45.44	1575	42.56	25.97
1620	44.73	22.20	44.53	1620	44.34	22.89
1665	42.82	25.53	43.64	1665	44.47	22.66
1710	42.69	25.75	44.47	1710	46.25	19.56
1755	42.94	25.31	44.53	1755	46.11	19.80
1800	43.07	25.09	43.64	1800	44.21	23.11
1845	45.00	21.74	44.60	1845	44.21	23.11
1890	43.20	24.87	43.64	1890	44.08	23.34
2385	43.30	24.69	43.69	2385	44.08	23.34
2430	41.57	27.70	42.76	2430	43.95	23.57
2475	43.17	24.91	42.74	2475	42.31	26.41
2520	41.45	27.91	41.88	2520	42.31	26.41
2565	41.57	27.70	41.57	2565	41.57	27.70

Table G-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.05 mol/L DMAEMA modified membrane

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
69.11	68.01	66.90
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
51.69	51.63	51.57
Average salt rejection (%)		Average Salt rejection (%)
86.88	85.29	83.71
FRR (%)		FRR (%)
76.07	76.58	77.08
FDR (%)		FDR (%)
27.91	27.16	26.41

Appendix H

DATA FROM BATCH EXPERIMENTS

**RO cell experimental runs with 0.02 mol/L DMAEMA modified
membranes**

Table H- 1: DMAEMA modifying solutions at various concentrations

	DMAEMA Concentrations	Units
1	0.1	mol.L ⁻¹
2	0.075	mol.L ⁻¹
3	0.05	mol.L ⁻¹
4	0.02	mol.L ⁻¹

Kinetic data for the RO cell experimental runs with **DMAEMA modified membranes**, measuring operation parameters in the feed, brine and permeate at a **0.02 mol/L DMAEMA** concentration.

Below in table H-2 the operating conditions is illustrated for the RO process and included are the membrane specifications:

Table H- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m ²)	0.013775
Nomination	XLE-4040
Feed P ₀ (bar):	5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table H-3. 1: Measured and calculated process parameters of 0.02 mol/L DMAEMA modified membrane (Experimental run 1)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m ²)
0	336	183	22	336	183	226	125	25	0.004	0.0033	0.792	57.5
45	336	183	22.1	337	184	221	121	24	0.004	0.0032	0.768	55.8
90	338	185	22.2	339	185	213	117	23.8	0.004	0.0032	0.768	55.8
135	340	186	22.2	340	186	211	115	24	0.004	0.0030	0.720	52.3
180	340	186	22.2	341	186	228	127	24	0.004	0.0031	0.744	54.0
225	342	187	22.2	340	186	264	148	23.4	0.004	0.0030	0.720	52.3
270	342	187	22.2	343	187	239	136	23	0.004	0.0029	0.696	50.5
315	347	187	22.7	347	187	336	132	22.4	0.004	0.0029	0.696	50.5
360	349	187	22.8	349	187	249	139	22.6	0.004	0.0028	0.672	48.8
405	350	188	22.9	353	187	236	131	21.6	0.004	0.0028	0.672	48.8
450	352	190	22.8	352	190	198	110	22.5	0.004	0.0029	0.696	50.5
495	352	190	22.7	355	192	123	75	23	0.004	0.0029	0.696	50.5
540	354	192	22.7	356	193	74	41	22.8	0.004	0.0029	0.696	50.5
945	333	184	21.8	334	185	31	19	22.8	0.004	0.0029	0.696	50.5
990	336	185	21.9	335	186	28	17	23	0.004	0.0029	0.696	50.5
1035	336	186	21.8	339	187	38	22	23	0.004	0.0029	0.696	50.5
1080	340	187	21.9	340	188	34	20	22.7	0.004	0.0028	0.672	48.8
1125	341	189	21.8	343	190	39	24	22.8	0.004	0.0028	0.672	48.8
1170	342	190	21.9	343	190	44	26	23.1	0.004	0.0028	0.672	48.8

1215	345	191	21.9	345	191	52	28	23.3	0.004	0.0029	0.696	50.5
1260	345	191	22	346	191	64	36	23	0.004	0.0028	0.672	48.8
1305	347	191	22.1	348	192	70	39	22.7	0.004	0.0027	0.648	47.0
1350	348	192	22.2	349	193	61	35	21.9	0.004	0.0025	0.600	43.6
1395	349	192	22.2	350	193	56	32	21.7	0.004	0.0026	0.624	45.3
1440	350	193	22.2	351	194	57	32	21.9	0.004	0.0024	0.576	41.8
1485	351	194	22.3	354	195	60	34	21.8	0.004	0.0025	0.600	43.6
1530	353	194	22.4	354	195	55	31	22	0.004	0.0024	0.576	41.8
1575	356	195	22.4	357	195	56	31	21.9	0.004	0.0024	0.576	41.8
1620	357	196	22.4	359	197	55	30	22	0.004	0.0025	0.600	43.6
1665	358	196	22.4	360	197	57	32	22	0.004	0.0025	0.600	43.6
1710	359	197	22.5	360	198	54	30	22.1	0.004	0.0024	0.576	41.8
1755	358	196	22.4	359	197	54	30	22.1	0.004	0.0024	0.576	41.8
1800	360	197	22.4	360	198	55	31	22.1	0.004	0.0023	0.552	40.1
1845	361	197	22.3	363	199	56	32	22	0.004	0.0024	0.576	41.8
1890	362	198	22.3	363	199	55	31	21.8	0.004	0.0024	0.576	41.8
1935	365	199	22.2	366	199	57	32	21.8	0.004	0.0023	0.552	40.1
1980	366	199	22.2	368	201	59	33	21.9	0.004	0.0023	0.552	40.1
2475	355	195	21.9	358	197	50	28	21.9	0.004	0.0023	0.552	40.1
2520	357	196	21.8	360	198	49	27	21.7	0.004	0.0022	0.528	38.3
2565	359	198	21.8	361	199	49	27	21.6	0.004	0.0023	0.552	40.1

Table H-3. 2: Measured and calculated process parameters of 0.02 mol/L DMEMA modified membrane (Experimental run 2)

	Feed			Brine		Permeate						
Time (min)	EC (µS)	TDS (mg/L)	Temp (°C)	EC (µS)	TDS (mg/L)	EC (µS)	TDS (mg/L)	Temp (°C)	Time (h)	Volume (L)	Flow R (L/h)	Flux (L/h m²)
0	347	190	22.1	351	193	70	39	23.6	0.004	0.0033	0.792	57.5
45	354	192	22.3	356	193	61	34	23.4	0.004	0.0032	0.768	55.8
90	357	194	22.4	362	195	55	31	23.7	0.004	0.0033	0.792	57.5
135	363	197	22.5	367	198	57	31	23.9	0.004	0.0032	0.768	55.8
180	373	200	22.7	376	202	59	33	23.7	0.004	0.0034	0.816	59.2
225	380	204	22.8	383	204	55	30	23.8	0.004	0.0034	0.816	59.2
270	388	207	22.9	393	209	51	28	24.2	0.004	0.0035	0.840	61.0
315	392	208	23.0	395	210	38	21	23.9	0.004	0.0031	0.744	54.0
360	394	210	23.1	395	211	37	20	23.8	0.004	0.0032	0.768	55.8
405	398	212	23.0	400	213	35	20	23.9	0.004	0.0030	0.720	52.3
450	400	215	23.1	401	216	34	19	24.0	0.004	0.0029	0.696	50.5
495	403	218	23.0	404	219	35	19	24.0	0.004	0.0028	0.672	48.8
540	408	220	23.0	409	220	34	19	24.1	0.004	0.0029	0.696	50.5
945	414	220	23.1	414	221	34	18	24.1	0.004	0.0029	0.672	48.8
990	421	222	22.9	424	224	30	17	23.7	0.004	0.0029	0.696	50.5
1035	422	222	22.9	425	225	30	16	23.8	0.004	0.0028	0.672	48.8
1080	422	223	23.0	426	226	29	16	23.8	0.004			
1125	424	224	23.1	431	227	29	16	23.8	0.004	0.0029	0.696	50.5

1170	423	224	23.1	428	226	28	16	23.9	0.004	0.0029	0.696	50.5
1215	433	229	23.2	436	230	36	20	22.0	0.004	0.0029	0.696	50.5
1260	443	233	23.3	446	234	39	21	22.2	0.004	0.0029	0.696	50.5
1305	450	236	23.4	455	238	41	22	22.3	0.004	0.0029	0.696	50.5
1350	458	242	23.4	465	243	36	20	22.4	0.004	0.0029	0.696	50.5
1395	473	247	23.5	476	248	32	18	22.3	0.004	0.0029	0.696	50.5
1440	482	252	23.5	487	253	41	22	22.3	0.004	0.0029	0.696	50.5
1485	494	257	23.7	498	258	46	25	22.5	0.004	0.0029	0.696	50.5
1530	495	258	23.6	498	262	47	25	22.5	0.004	0.0028	0.672	48.8
1575	497	258	23.7	501	267	48	26	22.5	0.004	0.0028	0.672	48.8
1620	499	264	23.7	501	267	49	27	22.4	0.004	0.0027	0.648	47.0
1665	501	267	23.8	502	268	51	28	22.5	0.004	0.0028	0.672	48.8
1710	500	265	23.8	502	267	48	26	22.6	0.004	0.0027	0.648	47.0
1755	501	268	23.7	504	270	49	28	22.5	0.004	0.0026	0.624	45.3
1800	502	268	23.8	504	270	47	25	22.4	0.004	0.0026	0.624	45.3
1845	490	261	23.0	493	263	27	15	21.6	0.004	0.0024	0.576	41.8
1890	492	262	23.0	493	264	28	16	21.5	0.004	0.0023	0.552	40.1
2430	498	266	22.9	496	267	29	16	22.3	0.004	0.0023	0.552	40.1
2475	500	267	22.9	503	269	28	16	22.6	0.004	0.0023	0.552	40.1
2520	509	272	22.8	512	274	28	15	22.5	0.004	0.0023	0.552	40.1
2565												

Data analysis report on the two ranges of data of 0.02 mol/L DMAEMA modified membranes

F-Test Two-Sample for Variances

	<i>Normalized flux 2</i>	<i>Normalized flux 1</i>
Mean	47.49753906	43.68835693
Variance	35.14705695	34.0913
Observations	38	40
df	37	39
F	1.030968516	
P(F<=f) one-tail	0.461671794	
F Critical one-tail	1.713211604	

t-Test: Two-Sample Assuming Equal Variances

	<i>Normalized flux 1</i>	<i>Normalized flux 2</i>
Mean	43.68835693	47.49753906
Variance	34.0913	35.14705695
Observations	40	38
Pooled Variance	34.60528694	
Hypothesized Mean Difference	0	
df	76	
t Stat	-2.858478985	
P(T<=t) one-tail	0.002745245	
t Critical one-tail	1.665151353	
P(T<=t) two-tail	0.005490489	
t Critical two-tail	1.99167261	

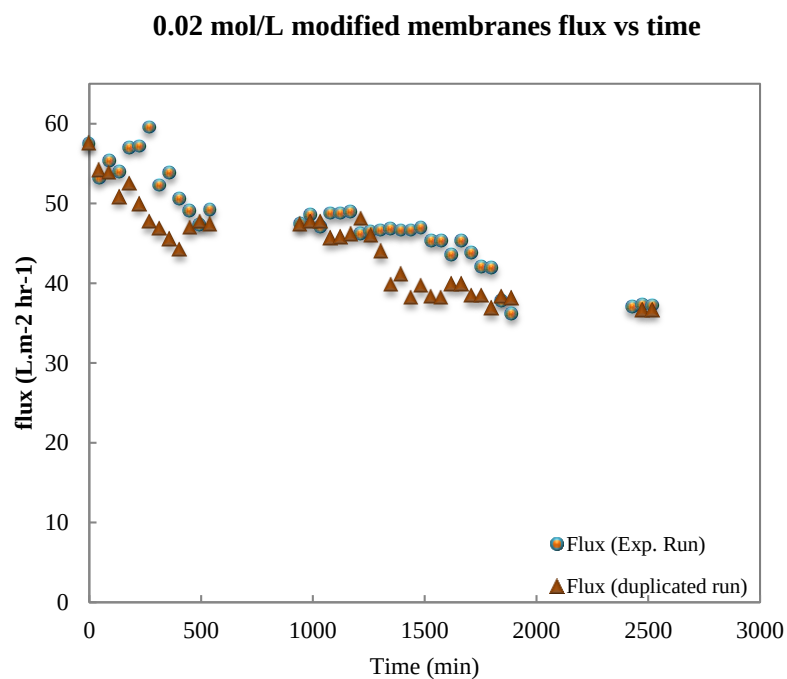


Figure H- 1: Permeate flux of 0.02 mol/L DMAEMA modified membranes at same operating conditions

Average normalized flux of 0.02 mol/L DMAEMA modified membrane vs time

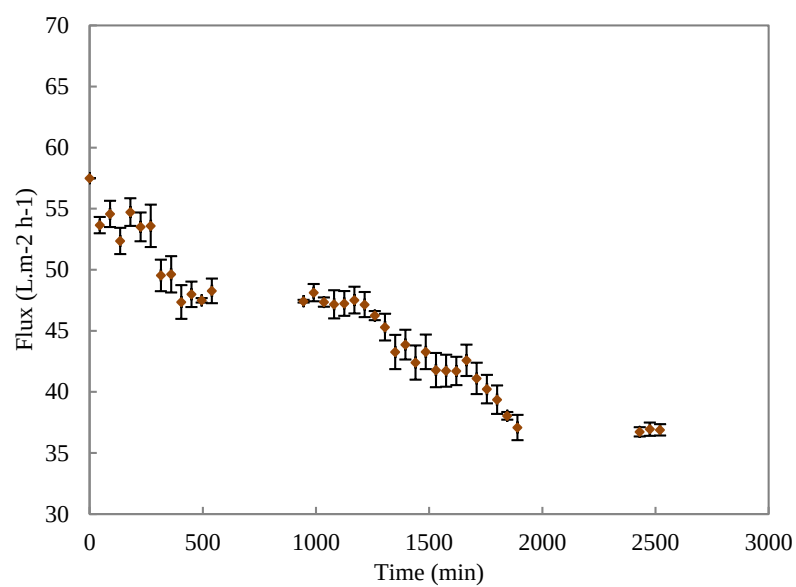


Figure H- 2: average permeate flux of 0.02 mol/L DMAEMA modified membranes

Table H-4. 1: Pure water (DI water) flow rate of the 0.02 mol/L DMAEMA modified membrane before fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0033	0.792	57.49546
30	15	0.004	0.0037	0.888	64.5
60	15	0.004	0.0036	0.864	62.7
90	15	0.004	0.0038	0.912	66.2
120	15	0.004	0.0036	0.864	62.7
150	15	0.004	0.0037	0.888	64.5

Table H-4. 2: Pure water (DI water) flow rate of the 0.02 mol/L DMAEMA modified membrane before fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.0029	0.696	50.5	0.0029
30	15	0.0033	0.792	57.5	0.0033
60	15	0.0037	0.888	64.5	0.0037
90	15	0.0035	0.840	61.0	0.0035
120	15	0.0036	0.864	62.7	0.0036
150	15	0.0037	0.888	64.5	0.0037

Table H-5. 1: Pure water Flow rate of 0.02 mol/L DMAEMA modified membrane after fouling experimental run 1

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.004	0.0021	0.504	36.6
30	15	0.004	0.0021	0.504	36.6
60	15	0.004	0.0023	0.552	40.1
90	15	0.004	0.0023	0.552	40.1
120	15	0.004	0.0024	0.576	41.8
150	15	0.004	0.0024	0.569	40.7

Table H-5. 2: Pure water Flow rate of 0.02 mol/L DMAEMA modified membrane after fouling experimental run 2

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L/h m²)
0	15	0.004	0.0025	0.600	43.6
30	15	0.004	0.0024	0.576	41.8
60	15	0.004	0.0024	0.576	41.8
90	15	0.004	0.0024	0.576	41.8
120	15	0.004	0.0025	0.600	43.6
150	15	0.004	0.0025	0.595	42.5

Table H-6. 1: Calculated values of the normalized flux (Norm flux) and Flux decline ratio (FDR) of 0.02 mol/L DMAEMA modified membranes

0.02 mol/L DMAEMA modified membrane						
Experimental run 1			Average	Experimental run 2		
Time (min)	Norm flux (L/m ² h ¹)	FDR (%)	Flux (L/m ² h ¹)	Time (min)	Norm flux (L/m ² h ¹)	FDR (%)
0	57.50	0.00	57.50	0	57.50	0.00
45	53.18	7.51	53.65	45	54.13	5.85
90	55.33	3.77	54.57	90	53.81	6.41
135	53.97	6.13	52.36	135	50.75	11.74
180	57.00	0.85	54.72	180	52.44	8.80
225	57.17	0.56	53.51	225	49.85	13.29
270	59.55	-3.58	53.59	270	47.63	17.17
315	52.28	9.07	49.54	315	46.79	18.62
360	53.81	6.41	49.63	360	45.44	20.96
405	50.60	12.00	47.36	405	44.12	23.26
450	49.05	14.68	47.99	450	46.93	18.38
495	47.36	17.62	47.49	495	47.63	17.17
540	49.20	14.43	48.27	540	47.35	17.65
945	47.50	17.38	47.42	945	47.35	17.65
990	48.62	15.43	48.12	990	47.63	17.17
1035	47.08	18.11	47.35	1035	47.63	17.17
1080	48.77	15.18	47.17	1080	45.58	20.73
1125	48.77	15.18	47.24	1125	45.71	20.49

1170	48.91	14.93	47.51	1170	46.12	19.79
1215	46.24	19.58	47.14	1215	48.05	16.43
1260	46.51	19.10	46.25	1260	45.98	20.02
1305	46.65	18.86	45.30	1305	43.95	23.56
1350	46.79	18.62	43.27	1350	39.74	30.88
1395	46.65	18.86	43.87	1395	41.09	28.53
1440	46.65	18.86	42.40	1440	38.15	33.64
1485	46.93	18.38	43.28	1485	39.63	31.08
1530	45.31	21.20	41.79	1530	38.27	33.44
1575	45.31	21.20	41.73	1575	38.15	33.64
1620	43.56	24.23	41.71	1620	39.86	30.67
1665	45.31	21.20	42.58	1665	39.86	30.67
1710	43.82	23.78	41.10	1710	38.38	33.25
1755	42.07	26.82	40.23	1755	38.38	33.25
1800	41.95	27.04	39.36	1800	36.78	36.03
1845	37.82	34.23	38.04	1845	38.27	33.44
1890	36.13	37.15	37.09	1890	38.04	33.84
2430	37.00	35.65	36.73	2430	36.46	36.59
2475	37.33	35.08	36.95	2475	36.56	36.41
2520	37.22	35.27	36.89	2520	36.56	36.41
				2565	34.77	39.53
				2610	36.24	36.97

Table H-7. 1: Calculated values of the deionized water fluxes before and after fouling experiment, flux recovery ratio (FRR) of 0.02 mol/L DMAEMA modified membrane

Experimental run 1	Averages	Experimental run 2
Initial DI flux (L/m ² h)		Initial DI flux (L/m ² h)
63.01	61.56	60.11
Final DI flux (L/m ² h)		Final DI flux (L/m ² h)
46.46	44.49	42.51
Average salt rejection (%)		Average Salt rejection (%)
84.63	88.34	92.06
FRR (%)		FRR (%)
72.07	71.40	70.72
FDR (%)		FDR (%)
35.27	35.84	36.41

Appendix I

DATA FROM BATCH EXPERIMENTS

Biofouling test: pure water flux of selected membranes for the test after 30 hours contact with E. coli bacterial solution

The following membranes were selected for biofouling tests:

- Unmodified membrane
- 0.05 mol/L DMAEMA modified membrane
- 0.15 PVA g/L PVA modified membrane

The Water flux of membranes was recorded over a period of 6 hours after contact time with E. coli bacteria. Values of pure water flux were compared to initial pure water flux for each of the above membranes as reported in **Appendices A, C and G** respectively.

Table I- 1: Number of E.coli colonies in solutions, determined by manual plate counting method

	Solution 1		solution 2	
Optical Density (Abs)	0.745		0.785	
Number of colonies (Plate x 10 ⁶)	Plate	Duplication	Plate	Duplication
	74	70	29	41
Colonies/mL	7.2 x 10 ⁺⁷		3.5 x10 ⁺⁸	

Table I- 2: Membrane specification and initial operating conditions of experimental run:

Dimensions	14.5 cm x 9.5 cm
Active Area (m ²)	0.013775
Nomination	XLE-4040
Feed P ₀ (bar):	5
Piston P (bar):	14
Feed velocity (Cm/s):	19
Brine p (Kpa):	100

Table I-3. 1: Pure water flux of the unmodified membrane after 30 hours contact with E. coli (experimental run 1)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	34	0.0094	0.0010	0.240	17.42
30	15	0.0042	0.0010	0.240	17.42
60	15	0.0042	0.0010	0.240	17.42
90	15	0.0042	0.0010	0.240	17.42
120	15	0.0042	0.0018	0.432	31.36
150	15	0.0042	0.0016	0.384	27.88
180	15	0.0042	0.0017	0.408	29.62
210	15	0.0042	0.0017	0.408	29.62
240	15	0.0042	0.0018	0.432	31.36
270	15	0.0042	0.0019	0.456	33.10
300	15	0.0042	0.0018	0.432	31.36
330	15	0.0042	0.0017	0.408	29.62
360	15	0.0042	0.0017	0.408	29.62

Table I-3. 2: Pure water flux of the unmodified membrane after 30 hours contact with E. coli (Experimental run 2)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30					
60	34	0.0094	0.0005	0.053	3.84
90	15	0.0042	0.0019	0.456	33.10
120	15	0.0042	0.0023	0.552	40.07
150	15	0.0042	0.0023	0.552	40.07
180	15	0.0042	0.0023	0.552	40.07
210	15	0.0042	0.0021	0.504	36.59
240	15	0.0042	0.0020	0.480	34.85
270	15	0.0042	0.0020	0.480	34.85
300	15	0.0042	0.0020	0.480	34.85
330	15	0.0042	0.0020	0.480	34.85
360	15	0.0042	0.0020	0.480	34.85

Table I-4. 1: DI water flux of the 0.015 g/L PVA modified membrane after 30 hours contact with E. coli (Experimental run 1)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.0042	0.0005	0.120	8.71
30	5	0.0042	0.0007	0.168	12.20
60					
90	15	0.0042	0.0016	0.384	27.88
120	15	0.0042	0.0022	0.528	38.33
150	15	0.0042	0.0019	0.456	33.10
180	15	0.0042	0.0019	0.451	32.75
210	15	0.0042	0.0018	0.432	31.36
240	15	0.0042	0.0017	0.408	29.62
270	15	0.0042	0.0017	0.408	29.62
300	15	0.0042	0.0017	0.408	29.62
330	15	0.0042	0.0018	0.432	31.36
360	15	0.0042	0.0018	0.432	31.36

Table I-4. 2: DI water flux of the 0.015 g/L PVA modified membrane after 30 hours contact with E. coli (Experimental run 2)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30	15	0.0042	0.0010	0.240	17.42
60	15	0.0042	0.0013	0.312	22.65
90	15	0.0042	0.0026	0.624	45.30
120	15	0.0042	0.0025	0.600	43.56
150	15	0.0042	0.0024	0.576	41.81
180	15	0.0042	0.0024	0.576	41.81
210	15	0.0042	0.0023	0.552	40.07
240	15	0.0042	0.0023	0.552	40.07
270	15	0.0042	0.0023	0.552	40.07
300	15	0.0042	0.0023	0.552	40.07
330	15	0.0042	0.0023	0.552	40.07
360	15	0.0042	0.0023	0.552	40.07

Table I-5. 1: DI water flux of the 0.05 mol/L modified membrane after 30 hours contact with E. coli (Experimental run 1)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0					
30					
60	15	0.0042	0.0080	0.192	13.94
90	15	0.0042	0.0011	0.264	19.17
120	15	0.0042	0.0020	0.480	34.85
150	15	0.0042	0.0025	0.600	43.56
180	15	0.0042	0.0026	0.624	45.30
210	15	0.0042	0.0025	0.600	43.56
240	15	0.0042	0.0026	0.624	45.30
270	15	0.0042	0.0026	0.612	44.43
300	15	0.0042	0.0026	0.624	45.30
330	15	0.0042	0.0027	0.648	47.04
360	15	0.0042	0.0026	0.624	45.30

Table I-5. 2: DI water flux of the 0.05 mol/L modified membrane after 30 hours contact with E. coli (Experimental run 2)

Time (min)	Flow measuring time(sec)	Flow measuring time (h)	Measured volume (L)	Flow Rate (L/h)	Flux (L h⁻¹m⁻²)
0	15	0.0042	0.0018	0.432	31.36
30	5	0.0042	0.0018	0.432	31.36
60	15	0.0042	0.0020	0.480	34.85
90	15	0.0042	0.0020	0.480	34.85
120	15	0.0042	0.0023	0.552	40.07
150	15	0.0042	0.0023	0.552	40.07
180	15	0.0042	0.0022	0.528	38.33
210	15	0.0042	0.0023	0.552	40.07
240	15	0.0042	0.0023	0.552	40.07
270	15	0.0042	0.0023	0.552	40.07
300	15	0.0042	0.0024	0.576	41.81
330	15	0.0042	0.0024	0.576	41.81
360	15	0.0042	0.0018	0.432	31.36

Appendix J

Sample calculations of RO parameters

Sample calculations are based on Unmodified Membrane data obtained

Flux

The permeate flux was calculated using the following formula (Hu et al., 2016):

$$J = \frac{V}{A \times \Delta t}$$

$$\frac{0.033L}{0.00416hr \times 0.013775m^2} = 57.5 L.m^{-2} hr^{-1}$$

The flux was then normalized to account for the change in temperature using the following formula (Water Environment Federation, 2006):

$$Normalized \quad flux = \frac{Actual \quad flux}{1.03^{(T-25)}}$$

$$Normalized \quad flux = \frac{57.5}{1.03^{(24.6-25)}} = 58.2 L.m^{-2} hr^{-1}$$

Salt Rejection

The observed salt rejection was calculated using the conductivities of the feed ($EC_{(F)}$) and the permeate ($EC_{(P)}$), according to (Kucera, 2015):

$$Salt \quad rejection = \left(1 - \frac{EC_{(P)}}{EC_{(F)}} \right) \times 100$$

$$Salt \quad rejection = \left(1 - \frac{28.7}{380.1} \right) \times 100 = 92.45$$

Flux Decline Ratio (FDR)

The flux decline ratio (in %) was recorded to evaluate the severity of fouling using the initial flux of water (J_i) and time dependent flux of water (J_t) all in in $L.m^{-2} h^{-1}$ in the following formula (Yutao Hu et al., 2016b):

$$\left(\frac{J_i - J_t}{J_i} \right) \times 100 \quad \dots \text{(Equation 6)}$$

$$\left(\frac{57.5 - 55.75}{57.5} \right) \times 100 = 3.03\%$$

Flux Recovery Ratio

The flux recovery ratio (FRR) was evaluated after 42 hours RO cell process experiments using the flux of pure water before experiment and the pure water flux after flushing (physical cleaning) of the membrane in the following formula:

$$FRR = \left(\frac{J_{wi}}{J_{wf}} \right) \times 100 \quad \dots \text{(Equation 7)}$$

$$FRR = \left(\frac{43.91}{62.29} \right) \times 100 = 70.49\%$$

Appendix K

Modifying agent solutions preparation (Sample calculation) & Design expert models reports of FDR

PVA polymer solution and GA solution preparations

Preparation of 0.05 % wt. GA and 0.1 g/L PVA solution

Dilution to a 500 mL solution of 0.05% wt. GA:

GA stock concentration: 25% wt.

Density: 1.06 g/mL

$$V_{\text{required}} = \frac{\% \text{required}}{\text{Actual}\%} \times \text{Volume}_{\text{solution}}$$

$$V_{\text{required}} = \frac{0.05}{25} \times 500\text{mL} = 1\text{mL}$$

Volume of water:

$$V_{\text{water}} = 500\text{mL} - 1\text{mL} = 499\text{mL}$$

Therefore, to prepare a 0.05 % wt. of GA 500mL solution, 1 mL from the stock solution has to be added to 499 mL of DI water.

- Adjusting the pH of the solution:

A diluted solution of H_2SO_4 is prepared by adding 2 drops of 98% H_2SO_4 to 100 mL of DI water. Then droplets of the prepared solution are slowly added to the GA solution to obtain a solution of pH 3.

- 0.1 g/L PVA solution:

0.1 g of PVA was measured on a weighing balance and added to 1 L of DI water. The solution was then placed on a magnetic stirrer plate and heated to about 70 °C until the PVA is completely dissolved. Then add an amount of DI water to compensate for the evaporated water.

DAMEMA monomer and initiators solutions preparation ($\text{Na}_2\text{S}_2\text{O}_5$ and $\text{K}_2\text{S}_2\text{O}_8$) GA solution

[] DMAEMA to be prepared: 0.1 mol/L

Finding the DMAEMA solution stock []:

Stock solution: 250 mL

0.93 kg = 1 L

Mw = 157.21 g/mol

$$0.93 \text{ kg} \rightarrow \left| \frac{930 \text{ g}}{\quad} \right| \left| \frac{\text{mol}}{157.21 \text{ g}} \right| \Rightarrow 5.916 \text{ mol / L}$$

Making a 200 mL DMAEMA solution:

$$C_1 V_1 = C_2 V_2$$

$$V_1 \times 5.916 = 0.1 \times 0.2$$

$$V_1 = 3.5 \text{ mL}$$

Volume of DI water required to make the solution:

$$V_{\text{H}_2\text{O}} = V_{\text{Solution}} - V_1$$

$$V_{\text{H}_2\text{O}} = 200 - 3.5 = 196.5 \text{ mL}$$

Masses $\text{Na}_2\text{S}_2\text{O}_5$ and $\text{K}_2\text{S}_2\text{O}_8$ required in the solution:

$\text{Na}_2\text{S}_2\text{O}_5 = 0.5 \text{ \% mol DMEMA}$

$$\frac{[\cdot]_{\text{Na}_2\text{S}_2\text{O}_5}}{0.1 \text{ mol}} \times 100 = 0.5$$

$$[\cdot]_{\text{Na}_2\text{S}_2\text{O}_5} = 5 \times 10^{-4} \text{ mol}$$

Mw $_{\text{Na}_2\text{S}_2\text{O}_5} = 190.1 \text{ g/mol}$

$$\text{mass}_{\text{Na}_2\text{S}_2\text{O}_5} = 5 \times 10^{-4} \text{ mol} \times 190.1 \text{ g / mol}$$

$$\text{mass}_{\text{Na}_2\text{S}_2\text{O}_5} = 0.0951 \text{ g}$$

$K_2S_2O_8 = 0.5 \% \text{ mol DMEMA}$

$$\frac{[.]_{K_2S_2O_8}}{0.1mol} \times 100 = 0.5$$

$$[.]_{Na_2S_2O_5} = 5 \times 10^{-4} \text{ mol}$$

$$Mw_{K_2S_2O_8} = 270.308 \text{ g/mol}$$

$$mass_{K_2S_2O_8} = 5 \times 10^{-4} \text{ mol} \times 270.308 \text{ g/mol}$$

$$mass_{Na_2S_2O_5} = 0.13516 \text{ g}$$

Hence the masses of $Na_2S_2O_5$ and $K_2S_2O_8$ to be added to the solution are 0.0951g and 0.13516g respectively.

Design expert model report: Flux decline ratio of DMAEMA modified membranes

Response	FDR					
ANOVA for Response Surface Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	2595.99	5	519.20	82.05	< 0.0001	significant
A-DMAEMA conc	150.16	1	150.16	23.73	0.0007	
B-Time	2233.63	1	2233.63	352.99	< 0.0001	
AB	56.15	1	56.15	8.87	0.0138	
A ²	6.55	1	6.55	1.03	0.3330	
B ²	145.65	1	145.65	23.02	0.0007	
Residual	63.28	10	6.33			
Cor Total	2659.26	15				

The Model F-value of 82.05 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, AB, B² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	2.52		R-Squared	0.9762
Mean	18.86		Adj R-Squared	0.9643
C.V. %	13.34		Pred R-Squared	0.9168
PRESS	221.20		Adeq Precision	26.265
-2 Log Likelihood	67.41		BIC	84.04
			AICc	88.74

The "Pred R-Squared" of 0.9168 is in reasonable agreement with the "Adj R-Squared" of 0.9643; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 26.265 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	df	Error	Low	High	VIF
Intercept	22.54	1	1.23	19.80	25.27	
A-DMAEMA conc	-4.29	1	0.88	-6.26	-2.33	1.91
B-Time	16.08	1	0.86	14.17	17.98	1.03
AB	-2.55	1	0.86	-4.46	-0.64	1.03
A ²	0.81	1	0.80	-0.97	2.59	1.91
B ²	-6.79	1	1.41	-9.94	-3.64	1.00

Final Equation in Terms of Coded Factors:	
FDR	=
+22.54	
-4.29	* A
+16.08	* B
-2.55	* AB
+0.81	* A ²
-6.79	* B ²

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors:	
FDR	=
+2.22658	
-89.80141	* DMAEMA conc
+1.53348	* Time
-3.23686	* DMAEMA conc * Time
+577.32636	* DMAEMA conc ²
-0.015394	* Time ²

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space. Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Externally Studentized Residuals to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Design expert model report: Flux decline ratio of PVA modified membranes

Response: FDR

ANOVA for Response Surface Cubic model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	2985.55	9	331.73	88.71	< 0.0001	significant
A-PVA concentration	38.81	1	38.81	10.38	0.0091	
B-Time	183.64	1	183.64	49.11	< 0.0001	
AB	42.71	1	42.71	11.42	0.0070	
A ²	78.00	1	78.00	20.86	0.0010	
B ²	0.15	1	0.15	0.041	0.8429	
A ² B	30.49	1	30.49	8.15	0.0171	
AB ²	6.11	1	6.11	1.63	0.2301	
A ³	4.29	1	4.29	1.15	0.3094	
B ³	26.65	1	26.65	7.13	0.0235	
Residual	37.40	10	3.74			
Cor Total	3022.95	19				

The Model F-value of 88.71 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, AB, A², A²B, B³ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	1.93	R-Squared	0.9876
Mean	17.49	Adj R-Squared	0.9765
C.V. %	11.06	Pred R-Squared	0.9469
PRESS	160.56	Adeq Precision	29.602
-2 Log Likelihood	69.27	BIC	99.23
		AICc	113.72

The "Pred R-Squared" of 0.9469 is in reasonable agreement with the "Adj R-Squared" of 0.9765; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 29.602 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	df	Error	Low	High	VIF
Intercept	12.35	1	1.01	10.09	14.60	
A-PVA concentration	-6.45	1	2.00	-10.91	-1.99	10.72
B-Time	21.03	1	3.00	14.34	27.72	26.34
AB	-2.81	1	0.83	-4.67	-0.96	1.04
A ²	4.79	1	1.05	2.45	7.12	1.03
B ²	0.22	1	1.06	-2.14	2.58	1.20
A ² B	3.99	1	1.40	0.88	7.11	2.46
AB ²	1.76	1	1.38	-1.31	4.84	2.62
A ³	2.18	1	2.04	-2.36	6.72	9.03
B ³	-8.07	1	3.02	-14.81	-1.33	24.59

Final Equation in Terms of Coded Factors:	
FDR	=
+12.35	
-6.45	* A
+21.03	* B
-2.81	* AB
+4.79	* A ²
+0.22	* B ²
+3.99	* A ² B
+1.76	* AB ²
+2.18	* A ³
-8.07	* B ³

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final Equation in Terms of Actual Factors:	
FDR	=
+0.087585	
+30.83253	* PVA concentration
+0.31988	* Time
-6.82073	* PVA concentration * Time
-575.21831	* PVA concentration ²
+0.051397	* Time ²
+19.00510	* PVA concentration ² * Time
+0.039988	* PVA concentration * Time ²
+2182.97486	* PVA concentration ³
-8.71552E-004	* Time ³

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space. Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Externally Studentized Residuals to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Appendix L

Testing procedure of physical and chemical parameters of the RO process

Flux

Permeate was collected in a small cylinder for a 15 second and the volume was noted. This value was used to determine the flux as shown in appendix C. Note that this was taken every 45 min during the experimental runs.

Electrical Conductivity (EC)

The EC was read off the EC meters (feed or permeate meter) when the probe of the EC meter was placed inside the feed tank or the permeate samples. This was also taken every 45 minutes during the experimental runs.

Total Dissolved Solids (TDS)

Again the TDS was read off the EC meters as well at the same time as the EC.

Turbidity

Ten millilitres (10 ml) sample of permeate was collected in a vile. The vile was dried with a dry cloth and placed in the sample holder of the Turbidity meter. The meter was then switched on and the “read” button was pressed. After a few seconds the turbidity value was displayed on the screen.

Temperature

The temperature was read off the EC meters as well.

Appendix K

Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR) data of PVA modified membranes

Data of FTIR analysis presented below are the first 10 points obtained for each experimental run. The spectra were recorded at a resolution of 2 cm^{-1} during 64 scans at a nominal incident angle of 45° with a wavenumbers ranging between 1950 and 650 cm^{-1} . The wavenumber intensities were normalized by dividing the intensity originally obtained by the maximum number of the axis, and a step increase of 0.2 was additionally added for each concentration.

Table K 1: first 10 points FTIR data of unmodified and 0.05 g/L PVA modified membranes

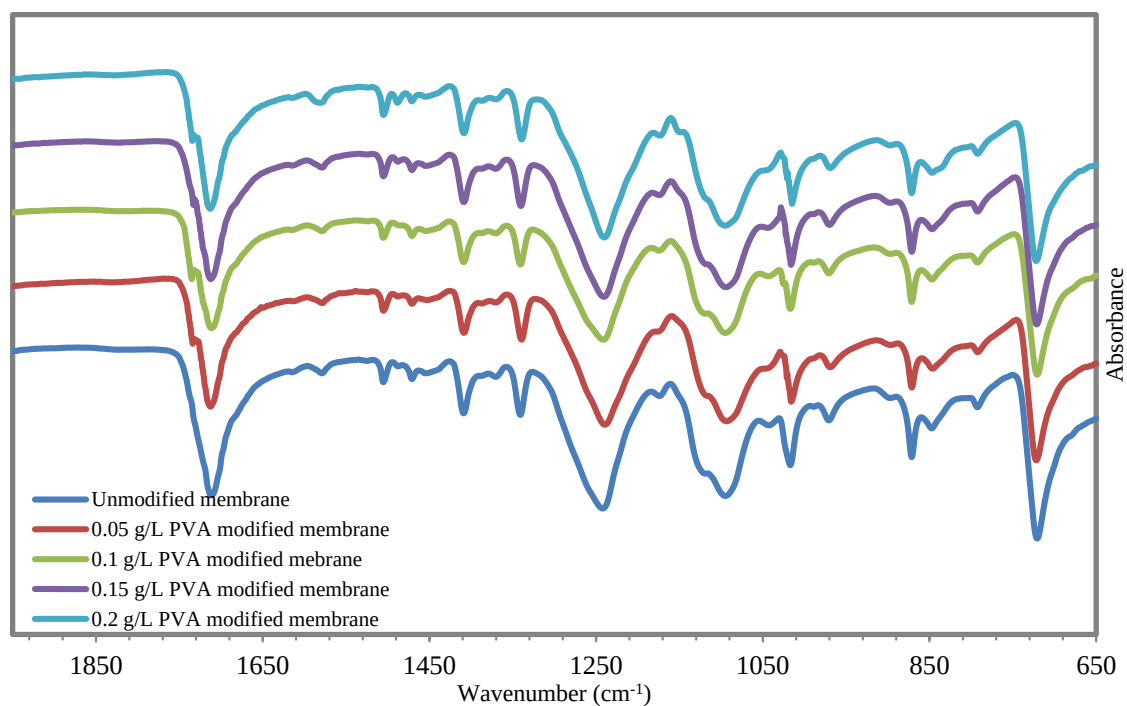
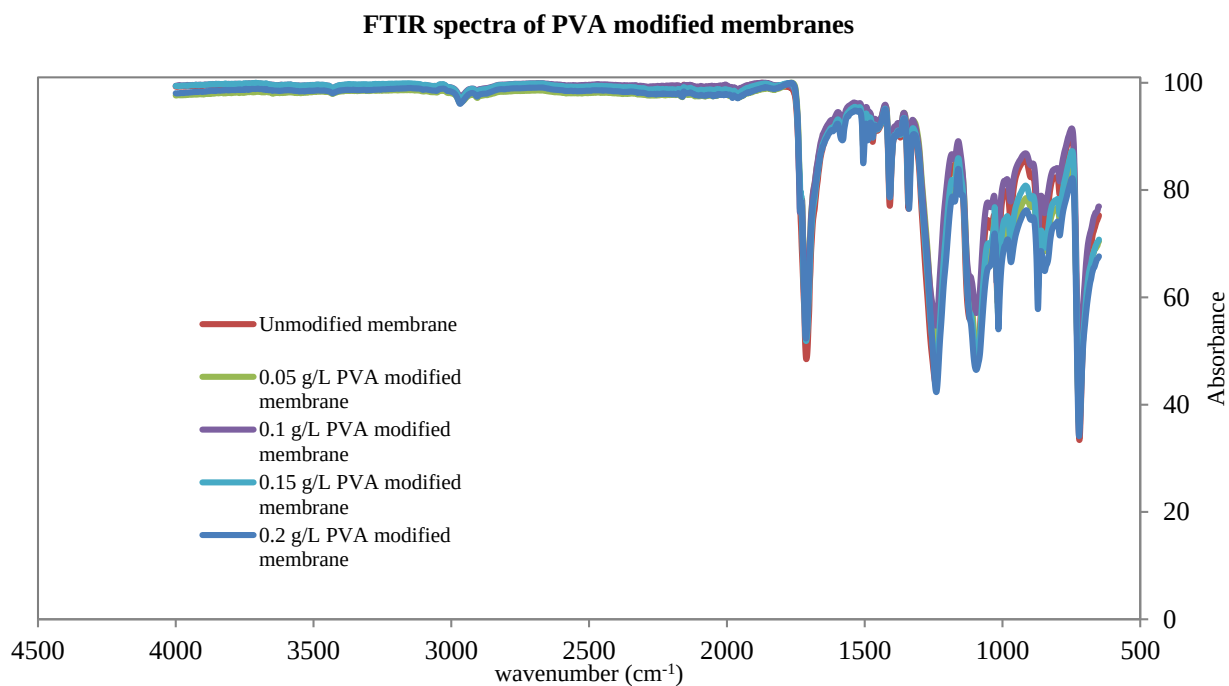
Unmodified membrane			0.05 g/L PVA modified membrane		
Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs	Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs
649.893	75.289	0.627	649.893	70.418	0.787
650.375	75.191	0.627	650.375	70.391	0.787
650.858	75.094	0.626	650.858	70.364	0.786
651.340	75.006	0.625	651.340	70.332	0.786
651.822	74.931	0.624	651.822	70.289	0.786
652.304	74.868	0.624	652.304	70.231	0.785
652.786	74.814	0.623	652.786	70.160	0.785
653.268	74.762	0.623	653.268	70.075	0.784
653.750	74.706	0.623	653.750	69.980	0.783
654.232	74.642	0.622	654.232	69.880	0.782
654.715	74.571	0.621	654.715	69.782	0.782
655.197	74.497	0.621	655.197	69.694	0.781
655.679	74.425	0.620	655.679	69.626	0.780
656.161	74.362	0.620	656.161	69.580	0.780
656.643	74.308	0.619	656.643	69.556	0.780
657.125	74.263	0.619	657.125	69.545	0.780

Table K 2: first 10 points FTIR data of the 0.1 and 0.15 g/L PVA modified membranes

0.1 g/L PVA modified membrane			0.15 g/L PVA modified membrane		
Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs	Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs
649.893	76.940	1.041	649.893	70.766	1.190
650.375	76.937	1.041	650.375	70.705	1.189
650.858	76.929	1.041	650.858	70.646	1.189
651.340	76.906	1.041	651.340	70.588	1.188
651.822	76.861	1.041	651.822	70.531	1.188
652.304	76.791	1.040	652.304	70.476	1.187
652.786	76.699	1.039	652.786	70.430	1.187
653.268	76.591	1.038	653.268	70.396	1.187
653.750	76.474	1.037	653.750	70.373	1.186
654.232	76.358	1.036	654.232	70.358	1.186
654.715	76.251	1.035	654.715	70.345	1.186
655.197	76.157	1.035	655.197	70.327	1.186
655.679	76.083	1.034	655.679	70.298	1.186
656.161	76.028	1.034	656.161	70.259	1.185
656.643	75.990	1.033	656.643	70.209	1.185
657.125	75.964	1.033	657.125	70.154	1.185

Table K 3: first 10 points FTIR data of the 0.2 g/L PVA modified membranes

0.2 g/L PVA modified membrane		
Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs
649.893	67.640	1.364
650.375	67.577	1.363
650.858	67.528	1.363
651.340	67.485	1.362
651.822	67.443	1.362
652.304	67.398	1.362
652.786	67.352	1.361
653.268	67.308	1.361
653.750	67.267	1.361
654.232	67.234	1.360
654.715	67.206	1.360
655.197	67.185	1.360
655.679	67.168	1.360
656.161	67.152	1.360
656.643	67.135	1.359
657.125	67.111	1.359



Appendix L

Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR) data of DMAEMA modified membranes

Data of FTIR analysis presented below are the first 10 points obtained for each run. The spectra were recorded at a resolution of 2 cm^{-1} during 64 scans at a nominal incident angle of 45° with a wavenumbers ranging between 1950 and 650 cm^{-1} . The wavenumber intensities were normalized by dividing the intensity originally obtained by the maximum number of the axis, and a step increase of 0.2 was additionally added for each concentration.

Table L- 1: first 10 points FTIR data of 0.02 and 0.05 mol/L DMAEMA modified membranes

0.02 mol/L DMAEMA modified membrane			0.05 mol/L DMAEMA modified membrane		
Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs	Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs
649.893	68.067	0.767	649.893	58.226	649.893
650.375	67.991	0.767	650.375	58.155	650.375
650.858	67.911	0.766	650.858	58.084	650.858
651.340	67.825	0.765	651.340	58.013	651.340
651.822	67.735	0.764	651.822	57.942	651.822
652.304	67.640	0.764	652.304	57.874	652.304
652.786	67.542	0.763	652.786	57.811	652.786
653.268	67.443	0.762	653.268	57.753	653.268
653.750	67.346	0.761	653.750	57.698	653.750
654.232	67.255	0.760	654.232	57.644	654.232
654.715	67.173	0.760	654.715	57.588	654.715
655.197	67.103	0.759	655.197	57.528	655.197
655.679	67.046	0.759	655.679	57.468	655.679
656.161	67.001	0.758	656.161	57.411	656.161
656.643	66.964	0.758	656.643	57.360	656.643
657.125	66.929	0.758	657.125	57.317	657.125

Table L- 2: first 10 points FTIR data of 0.075 and 0.1 mol/L DMAEMA modified membranes

0.075 mol/L DMAEMA modified membrane			0.1 mol/L DMAEMA modified membrane		
Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs	Wave Number (cm ⁻¹)	intensity (Abs)	Normalized Abs
649.893	75.183	1.227	649.893	59.622	1.297
650.375	75.175	1.226	650.375	59.570	1.296
650.858	75.160	1.226	650.858	59.524	1.296
651.340	75.134	1.226	651.340	59.476	1.296
651.822	75.095	1.226	651.822	59.425	1.295
652.304	75.045	1.225	652.304	59.367	1.295
652.786	74.987	1.225	652.786	59.305	1.294
653.268	74.926	1.224	653.268	59.239	1.294
653.750	74.863	1.224	653.750	59.170	1.293
654.232	74.801	1.223	654.232	59.098	1.292
654.715	74.740	1.223	654.715	59.020	1.292
655.197	74.683	1.222	655.197	58.938	1.291
655.679	74.631	1.222	655.679	58.851	1.290
656.161	74.583	1.222	656.161	58.762	1.290
656.643	74.540	1.221	656.643	58.672	1.289
657.125	74.498	1.221	657.125	58.584	1.288

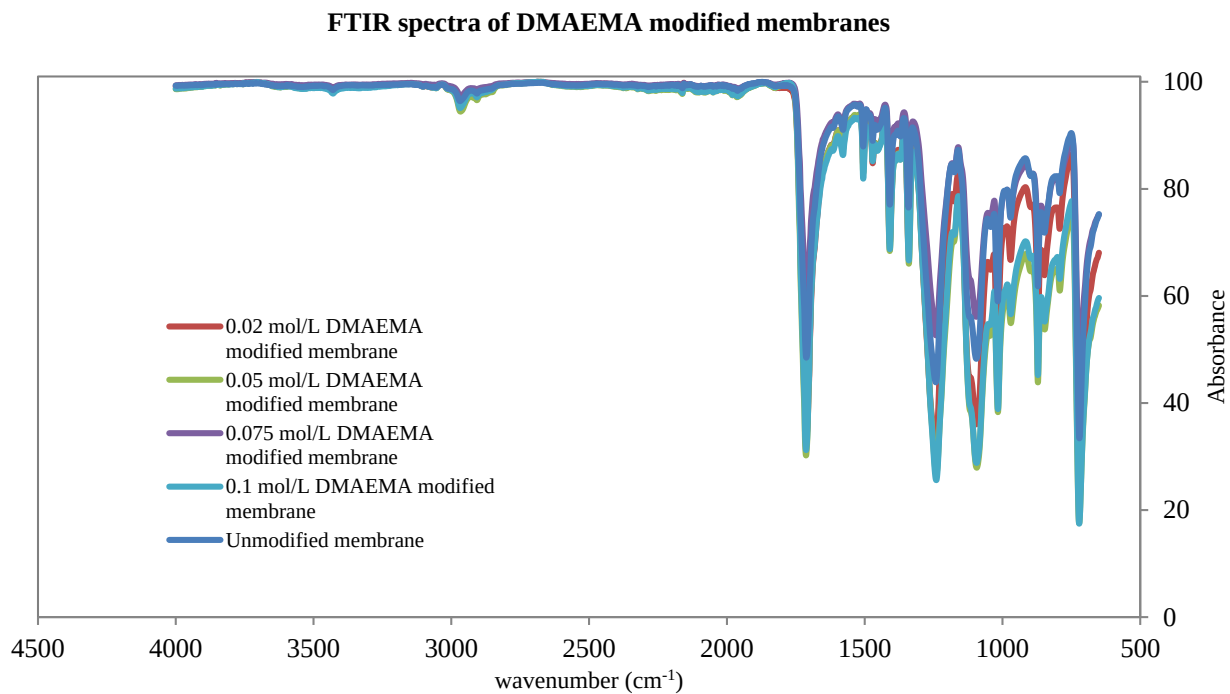


Figure L- 1: FTIR spectra of DMAEMA modified membranes originally obtained

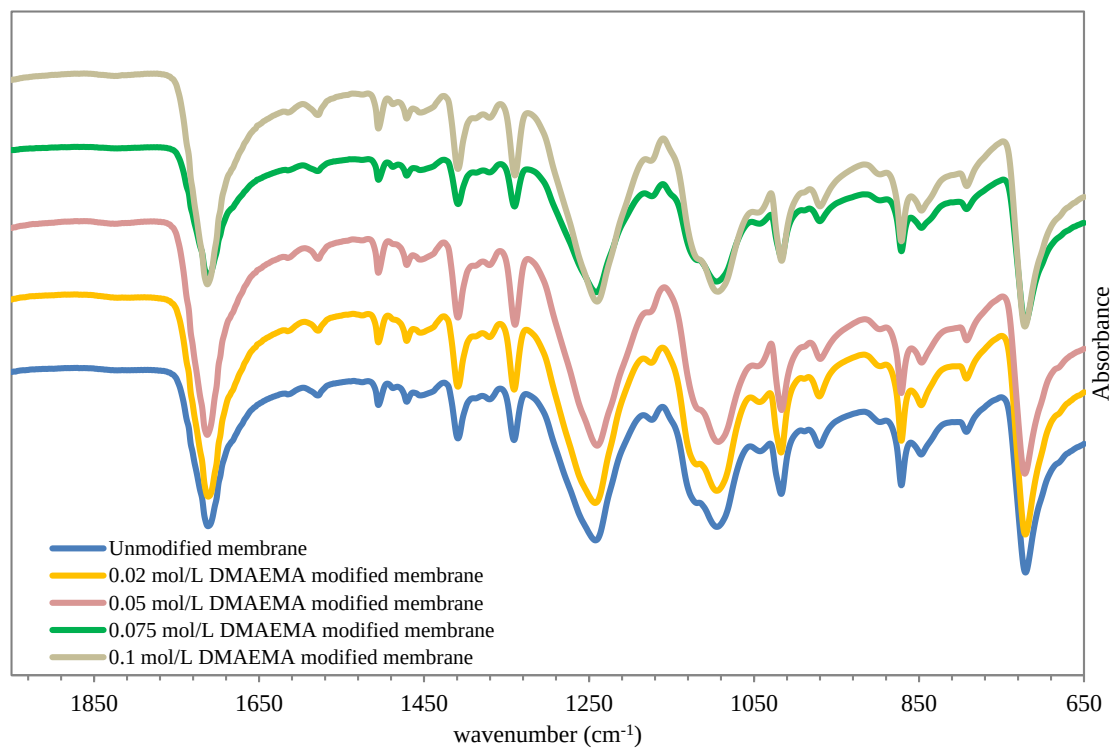


Figure L- 2: FTIR spectra of membranes after normalising and zooming into the functional groups region