Table of Contents

List of Publications	ii
Abstract	iv
Abbreviations	xii
Contents	xvi
1 CHAPTER: INTRODUCTION	2
1.1 Background of the project	3
1.2 Motivation for work	8
1.3 Goal and research objectives	9
1.4 Outline (structure) of this study	10
1.5 References	
2 CHAPTER: LITERATURE REVIEW	20
2.1 Pulp-and-paper mill manufacturing	21
2.1.1 Pulp making	22
2.1.2 Pulp processing	23
2.1.3 Paper-making	23
2.2 Effluent characteristics from Paper i	ndustry 24
2.3 Wastewater treatment in paper indu	stry 25
2.3.1 Primary / physical treatment	26
2.3.2 Secondary treatment	26
2.3.2.1 Aerobic Treatment	27
2.3.2.2 Anaerobic Treatment	29
2.3.3 Tertiary treatment	32
2.4 Membrane filtration fundamentals	32
2.4.1 Ultrafiltration membrane process	35
2.4.2 Comparison between Dead - end	vs. cross-flow Ultrafiltration 37
2.4.3 Membrane Fouling	40
2.4.4 Internal and external fouling	41
2.4.5 Reversible and irreversible fouling] 42
2.4.6 Prevention and reduction of mem	brane fouling 42
2.5 Mathematical models for membrane	e fouling analysis 44

	2.5.1 Por	e blocking mechanisms	44
	2.5.1.1	Pore blocking models for dead-end filtration	46
	2.5.1.2	Pore blocking models adapted for cross-flow filtration	48
	2.5.2 Res	sistance-in-series model	51
	2.5.3 Cor	nstant-pressure filtration and cake formation	52
	2.6 Memb	brane foulants characterization and identification	54
	2.6.1 Mai	nly membrane foulants components	55
	2.6.1.1	Dissolved and colloidal substances	55
	2.6.1.2	Biofoulants y Organic Foulants	56
	2.6.1.3	Inorganic Foulants	58
	2.6.2 Spe	ecific ultraviolet absorbance (SUVA)	58
	2.6.3 Flu	prescence spectroscopy	59
	2.6.4 Atte	enuated total reflection-Fourier transform infrared (ATR-FTIR)	62
	2.6.5 Sca	Inning electron microscopy (FESEM)	66
	2.6.5.1	SEM-energy-dispersive spectrophotometry (EDX)	66
	2.6.6 Opt	ical coherence tomography (OCT)	67
	27 Refer	00000	69
	2.7 110101		
3	CHAPTER	Reverse and the second se	92
3	CHAPTER 3.1 Source	e and properties of treated effluent used as feed solution in th	92 e UF
3	CHAPTER 3.1 Source process	Reverse and properties of treated effluent used as feed solution in the	92 e UF 93
3	CHAPTER 3.1 Source process 3.2 Analy	R: GENERAL MATERIALS AND METHODS e and properties of treated effluent used as feed solution in th tical methods and apparatus	92 e UF 93 95
3	CHAPTER 3.1 Source process 3.2 Analy 3.2.1 Gen	R: GENERAL MATERIALS AND METHODS e and properties of treated effluent used as feed solution in th tical methods and apparatus	e UF 93 95
3	CHAPTER 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb	R: GENERAL MATERIALS AND METHODS e and properties of treated effluent used as feed solution in th tical methods and apparatus neral characteristics orane properties and characteristics	e UF 93 95 95 97
3	CHAPTER 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Membre 3.4 Pre-tr	R: GENERAL MATERIALS AND METHODS e and properties of treated effluent used as feed solution in th tical methods and apparatus heral characteristics orane properties and characteristics eatment before the UF processes	e UF 93 95 95 97 98
3	CHAPTER 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Membre 3.4 Pre-tr 3.5 Cross	R: GENERAL MATERIALS AND METHODS e and properties of treated effluent used as feed solution in th tical methods and apparatus heral characteristics orane properties and characteristics eatment before the UF processes	e UF 93 95 95 97 98 99
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb 3.4 Pre-tr 3.5 Cross 3.5.1 Cro	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 97 98 99 99
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb 3.4 Pre-tr 3.5 Cross 3.5.1 Cro 3.5.2 Member 3.5.2 Member 3.5.5.2 Member 3.5.5.2 Member 3.5.5.2 Member 3.5.5.5 Member 3.5	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 97 98 99 99 99 - 101
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb 3.4 Pre-tr 3.5 Cross 3.5.1 Cro 3.5.2 Men 3.5.3 Flux	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 97 98 99 99 99 - 101 - 102
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb 3.4 Pre-tr 3.5 Cross 3.5.1 Cro 3.5.2 Men 3.5.3 Flux 3.5.4 Cle	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 97 98 99 99 99 - 101 - 102 - 103
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Memb 3.4 Pre-tr 3.5 Cross 3.5.1 Cro 3.5.2 Men 3.5.3 Flux 3.5.3 Flux 3.5.4 Cle 3.6 Dead	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 97 98 99 99 99 - 101 - 102 - 103 - 104
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Membre 3.4 Pre-tr 3.5 Cross 3.5.1 Cross 3.5.2 Memretr 3.5.3 Flux 3.5.3 Flux 3.5.4 Cle 3.6 Deade 3.6.1 Deade	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 95 97 98 99 99 99 -101 - 102 - 103 - 104 - 104
3	CHAPTEF 3.1 Source process 3.2 Analy 3.2.1 Gen 3.3 Membre 3.4 Pre-tr 3.5 Cross 3.5.1 Cross 3.5.2 Memretr 3.5.3 Flux 3.5.3 Flux 3.5.4 Cle 3.6 Deade 3.6.1 Deade 3.6.2 Filtr	R: GENERAL MATERIALS AND METHODS the and properties of treated effluent used as feed solution in the tical methods and apparatus	e UF 93 95 95 95 95 97 98 99 99 99 101 - 102 - 103 - 104 - 104 - 106

4 CHAPTER: PROCESS OPTIMIZATION VIA TAGUCHI N	IETHOD TO REMOVE
COLLOIDAL SUBSTANCES FROM RECYCLED PAPER	AND CARDBOARD
PRODUCTION WASTEWATER	109
4.1 Abstract	110
4.2 Introduction	111
4.3 Materials and methods	113
4.3.1 Paper mill treated effluent feedstock	113
4.3.2 Membranes and experimental setup	113
4.3.3 Analytical methods	114
4.3.4 Field emission scanning electron microscopy (FESE	EM) 114
4.3.5 Experimental procedure	114
4.3.5.1 Ultrafiltration experiments	114
4.3.5.2 Average permeate flux, COD rejection and c	cumulative flux decline
analysis 115	
4.3.6 Experimental design based on the Taguchi method	116
4.3.7 Utility concept	119
4.3.8 Optimum performance prediction	121
4.3.9 Analysis of variance (ANOVA)	122
4.4 Results and discussion	123
4.4.1 Design of experiments and experimental results	123
4.4.2 Taguchi results	127
4.4.3 ANOVA results	131
4.4.4 Optimum results obtained from the Taguchi method	and utility concept134
4.4.4.1 Analysis of individual response optimization	134
4.4.4.2 Analysis of multi- response optimization	134
4.4.5 Confirmation experiment under optimum conditions	137
4.5 Conclusion	141
4.6 References	

5 CHAPTER: MODELLING APPROACH TO AN ULTRAFILTRATION	PROCESS
FOR THE REMOVAL OF DISSOLVED AND COLLOIDAL SUBSTANC	CES FROM
TREATED EFFLUENT FOR REUSE IN RECYCLED	PAPER
MANUFACTURING	147
5.1 Abstract	148
5.2 Introduction	148
5.3 Materials and methods	150
5.3.1 Effluent sample used as feed solution	150
5.3.2 Membrane fouling experiments	150
5.3.3 Fouling models for cross-flow filtration	150
5.3.3.1 Pore blocking description	150
5.3.3.2 Determination of the sum of squared deviations and aver	age relative
error	152
5.4 Results and discussion	154
5.4.1 Membrane characterisation	154
5.4.2 Physical and chemical aspects of PMTE after the ι	ultrafiltration
process	154
5.4.3 Pore Blocking Mechanism	155
5.4.4 Estimation of the Pore Blocking resistance (<i>Rpb</i>)	160
5.4.5 Predicting performance of constant-pressure filtration	(membrane
fouling)	165
5.4.6 Determination of membrane cleaning efficiency	16/
5.5 Conclusion	1/1
5.6 References	1/2
6 CHAPTER: IDENTIFICATION OF FOULANTS ON POLYETHER	RSULFONE
(PES) MEMBRANES USED TO REMOVE COLLOIDS AND DISSOLVE	D MATTER
FROM A PAPER MILL TREATED EFFLUENT	177
6.1 Abstract	178
6.2 Introduction	178
6.3 Materials and methods	181
6.3.1 Membrane filtration tests	181
6.3.2 Ultrafiltration fouling models	182
6.3.3 Mass Balance Analysis	184

6.3.4 Identification and characterization of foulants 185
6.3.4.1 Field emission scanning electron microscopy (FESEM) and energy
dispersive spectrophotometry (EDS) 185
6.3.4.2 Attenuated total reflection-Fourier transform infrared (ATR-FTIR)
spectroscopy analysis 186
6.3.4.3 Foulant extraction 187
6.3.4.4 3DEEM fluorescence spectra analysis 188
6.4 Results and discussion 191
6.4.1 Analysis of the influence of membrane MWCO on permeate flux and fouling
mechanism 191
6.4.2 Resistance-in-series and pore blocking model analysis 192
6.4.3 Mass balance analysis 198
6.4.4 Aromatic carbon (SUVA) removal by UF membrane 198
6.4.5 3DEEM fluorescence analysis 199
6.4.6 ATR-FTIR analysis 208
6.4.7 SEM and EDS analysis 212
6.5 conclusions 219
6.6 References 221
7 CHAPTER : CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS 228
7.1 Conclusions 228
7.2 Recommendations and future work 230
Appendix A: Factorial Design Calculations 232
Appendix B: The Matlab modelling programmes 235

List of Figures

Figure 2-1 - Schematic illustration of the pulp and paper process
Figure 2-2 - Typical layout of paper mill effluent treatment plant (Thompson et al., 2001)
Figure 2-3 - Basic principle of the active sludge process
Figure 2-4 - IC (anaerobic reactor @ Paques) for treatment of papermill effluent31
Figure 2-5 - Biobed EGSB anaerobic reactor (@Veolia Water Technologies) for treatment of paper mill effluent
Figure 2-6 - membrane separation by size exclusion
Figure 2-7 - Spectrum of membrane filtration. Addapted from Graff, 2012)35
Figure 2-8 - PES composite membrane used in UF- (a) Scheme - (b) FESEM pictures (magnification = 200 x, 100µm, 799V) highlighting the 3 layers
Figure 2-9 - Common commercial polymers used for production UF membranes36
Figure 2-10 - Principle of dead - end filtration: (a) schematic diagram setup;(b) separation mode
Figure 2-11 - Principle of cross flow filtration: (a) Schematic diagram of CFF system; (b) separation process
Figure 2-12 - Configuration of a) hollow fiber cartridges and b) plate and flat sheet.39
Figure 2-13 - A schematic diagram of the various fouling mechanisms on membrane.
Figure 2-14 - Different fouling mechanisms happening in porous membranes (Hermia, 1982)45
Figure 2-15 - Excitation and emission wavelength boundaries for natural organicmatter (Chen et al., 2003b)
Figure 2-16- Locations of fluorescence Peaks A, B, C, T and M.(adopted from Hudson et al., 2007)
Figure 2-17 - Spectra of PES UF membrane and fouled membrane by paper mill treated effluent

Figure 2-18 - Illustration of the membrane interfacing with the ATR crystal (successively fouling layer/active layer of membrane and support layer of membrane).65 Figure 3-1 - Aerial view of the wastewater treatment plant (WWTP) in a papermaking Figure 3-2 - Photograph of the setup for TOC-VCSN Shimadzu Analyzer used in the Figure 3-3 - Photograph of the setup for Zetasizer Nano ZS instrument (Malvern Instruments) used in the ISIRYM......97 Figure 3-4 - Schematic image of the setup with a membrane cell used for pre-filtration Figure 3-5 - Schematic image of the setup with a conventional filtration used for pre-Figure 3-6 - Photographs of the experimental system. UF pilot plant with flat-sheet Figure 3-7 - Schematic diagram for the cross-flow ultrafiltration membrane process. Figure 3-8 - Lab-scale of the dead-end membrane filtration system with stirred cell (a) Figure 4-1 Flow diagram of Taguchi method steps to optimize a UF process to remove DCS from paperboard mill treated effluent (Kumar and Singh, 2014; Roy, 1990)...119 Figure 4-2 - Volumetric flux as a function of transmembrane pressure for PES **Figure 4-3** - Profile of the permeate flux through the operating time for each MWCO: **Figure 4-4** - Mean effect curves for S/N ratios for a) the average permeate flux, b) Figure 4-5 - ANOVA results for the percentage contribution of each factor to the response processes......133

Figure 4-7 - Permeate flux as a function of time under optimized conditions during UF of PMTE: PES 100 kDa membrane at TMP= 2.0 bar, CFV = 0.752 m/s, and T = 15 °C.

Figure 5-3 - Hermia's pore blocking models fitting for recycled paper wastewater 10 kDa PES membrane filtration experiments, at 3 bar......156

Figure 5-5 -Hermia's pore blocking models fitting for recycled paper wastewater 10 kDa PES membrane filtration experiments, at 1 bar......157

Figure 5-7 - Experimental and predicted pore blocking resistance distribution for PMTE at 10 kDa PES membrane and different TMPs. Averaged values of resistance was used and the data was modeled using Matlab[@] modelling programmes (Appendix B).

Figure 5-9 - Resistance of the cake layer and cake thickness as a function of UF time (8 h) in flat-sheet, crossflow filtration at constant pressure . Conditions TMP= 3.0 bar, Cg= 0.7, ϵ = 0.3, C₀ = 0.2 g/L, ap= 158 nm, Rm = 1.65× 10¹² m^{-1,} rc =3.01 × 10¹² (m⁻²).

List of Tables

Table 1-1 Physical-chemical characterization of recycled paper wastewater from Zwain et al. (2013)
Table 2-1 - Removal efficiency of different aerobic treatment processes applied in pulp-and-paper wastewaters. Adopted from (Ashrafi et al., 2015)
Table 2-2 - Removal efficiency of different anaerobic treatment processes applied inpulp-and-paper wastewaters. Adopted from (Ashrafi et al., 2015)
Table 2-3 -Classification of membrane Mulder processes with pore size and pressure-drive (adapted from Mulder, 1996)
Table 2-4 - Classification of membrane resistances. 52
Table 2-5 - Sources of DCS in various pulp and paper Process Waters adapted fromHubbe et al. (2012)
Table 2-5 - Guidelines on the nature of DOM according to SUVA. Addapted from(Cunha, 2014; Edzwald and Tobiason, 1999)
Table 2-6 - Commonly identified PARAFAC components and their correspondingpeaks identified in Coble. (1996). Adapted from B. Fellman et al., 2010 and Hudson etal., 2007
Table 2-7 - The most common peaks from PES and the residual fouling found in theIR spectrum.64
Table 2-8 - Summary comparing analytical techniques for foulant identification andcharacterization of membrane fouling. Addapted from (Chen et al., 2018).68
Table 3-1 - Average compositions of the paper mill treated effluent (anaerobic and aerobic treatment) used in the experiments
Table 3-2 - Technical data on the membranes used in this study
Table 4-1 - Average compositions of the paperboard mill treated effluent (biologicallytreated wastewater) used in the experiments.113
Table 4-2 - Process parameters and their levels
Table 4-3 - Experimental layout using L9 (34) orthogonal array in accordance with theTaguchi method

Table 4-4 - Taguchi orthogonal array L_9 (3 ⁴) for the operating parameters andexperimental response parameters.125
Table 4-5 - Signal-to-noise results (mean ± standard deviation (SD), three repetitionsfor each experimental condition).128
Table 4-6 - Analysis of variance (ANOVA) results for average permeate flux, CODrejection, and SFD for each factor
Table 4-7 - Individual Taguchi predictions for average permeate flux, COD rejectionrate and SFD.134
Table 4-8 - Pairwise comparison matrix. 135
Table 4-9 - Utility value based on UF responses (JP, COD rejection, SFD)
Table 4-10 - ANOVA analysis results for multi-response UF (overall utilityfunction)
Table 4-11 - Optimum conditions for multi–response UF predicted using the utility concept. 137
Table 4-12 - Permeate quality (process performance) under optimum conditions, at theend of 2 hours operating.140
Table 4-13 - Summary and comparison of experimental and predicted optimal conditions for PMTE. 140
Table 5-1 - Fouling mechanism for constant flow rate in cross-flow UF (Field et al.,1995)
Table 5-2 - Physical-chemical parameters of the effluent treated by conversionalfiltration and ultrafiltration separation
Table 5-3 - Pore blocking R ² , fitting of Hermia's models. Values for recycled paperwastewater 10 kDa MWCO PES membrane, ultrafiltration experiments.159
Table 5-4 - Pore blocking standard error of the estimate and coefficient of residualvariation between experimental data and Hermia's models against TMP.164
Table 5-5 - Membrane flux recovery after each cleaning step with DI water in backwashand NaOH. Initial permeate flux $55.5 \pm 1.0 \text{ L/m}^2\text{h}$.

Table 6-1 - Summary of the fouling mechanisms by blocking models during dead-endfiltration184Table 6-2 - Characteristics of the associated fluorophores detected by 3DEEMaccording to W. Chen et al. (2003b)189Table 6-3 - Permeate flux, flux reduction and total flux recovery after cleaning steps(relaxation and backwashing) from different MWCO membranes.192Table 6-4 - Values of pore blocking parameters, comparison between the experimentaland predicted average permeate flux and the model fitting accuracy (R²).194Table 6-5 - Aromatic carbon (SUVA) in the PMTE and permeates, at 2.0 bar anddifferent MWCO.199Table 6-6 - Volume of fluorescence Φi and the reduction in the concentration offluorescent compounds after UF.203Table 6-7- Peaks and assignments of infrared spectra for clean and fouledmembranes.211Table 6-8 - Inorganic composition of fresh and fouled membranes.218