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HYBRID SUBMERGED MEMBRANE PHOTOCATALYTIC PROCESS

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ABSTRACT

A hybrid system combining low-pressure submerged membrane filtration and photocatalysis in a single module was developed and was used for removal of trace organics from water. A comprehensive membrane stability protocol was devised to identify the polymeric membranes that were most suitable for the photocatalytic-membrane process. Membrane stability was characterized by changes in pure water flux (PWF), release of total organic carbon (TOC), changes in hydrophobicity, morphology and surface groups. The results revealed that polytetrafluoroethylene (PTFE) and hydrophobic polyvinylidene fluoride (PVDF) membranes showed the greatest stability. The stability of the membranes and the mechanisms involved in the degradation under different filtration conditions, with and without a titanium dioxide (TiO_2) cake layer, were also investigated.

The feasibility of operation of the submerged membrane photocatalytic reactor (SMPR), with external ultraviolet (UV) lamp sources, in the degradation of Bisphenol-A (BPA) was investigated. The influences of pH, aeration rate, TiO_2 and initial BPA concentration were investigated in batch kinetic tests. In these studies, a combination of pH 4, 0.5g/L TiO_2 and 0.5L/min aeration rate were determined to be the optimized conditions for application of the continuous SMPR. The degradation of BPA fitted the Langmuir-Hinshelwood (L-H) kinetics well. At 100L/m².hr of permeate flux which resulted in 2 hours residence time, 97% degradation and more than 90% mineralization of 10ppm BPA were achieved after 90min and 120min, respectively. Different methods for controlling membrane fouling during the operation of the SMPR were compared.

A new SMPR with multiple submerged lamp sources was designed and built for better distribution of UV photons and better utilization of reactor volume. This reactor design was able to ensure uniform distribution of UV light, well-mixed conditions as well as better heat dissipation during the photoreaction. The efficiencies of the old and new photoreactor were compared using a new concept of

limiting photonic efficiency, ζ_{lim} . The new reactor was found to be 145% ($TOC_{resorcinol}$) and 132% (TOC_{BPA}) more efficient and less prone to fouling compared to the old reactor. Long-term operation of the SMPR was evaluated and the issues related to the lifetime of TiO_2 , fouling control and stability of the membrane were systematically addressed.

Finally, a modified continuous stirred-tank reactor (CSTR) model was used to predict the degradation of resorcinol in the new SMPR. Reaction surface coverage ratio, β , which was assumed to be a function of the bulk resorcinol concentration, was introduced to the classical CSTR model. The adequacy of the modified model in simulating steady-state concentrations for different feed concentrations and residence times was evaluated. The new SMPR design was effective and can achieve removals of low concentration organics in a compact, low energy system.

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TABLE OF CONTENTS

ABSTRACT	I
ACKNOWLEDGEMENTS	III
TABLE OF CONTENTS	IV
LIST OF PUBLICATION.....	IX
LIST OF FIGURES	X
LIST OF TABLES	XVI
ABBREVIATION.....	XVIII
LIST OF SYMBOLS.....	XXII
CHAPTER 1 INTRODUCTION.....	1
1.1 Background	1
CHAPTER 2 LITERATURE REVIEW	5
2.1 Membrane Separation	5
2.1.1 Overview	5
2.1.2 Ultrafiltration and Microfiltration.....	7
2.1.3 Membrane Process Configurations	7
2.1.3.1 Deadend versus Crossflow Filtration.....	7
2.1.3.2 Membrane Crossflow Modules.....	8
2.1.3.3 Submerged Membrane Modules.....	12
2.1.4 Bulk Mass Transport of Microfiltration / Ultrafiltration.....	12
2.1.4.1 Concentration Polarization	13
2.1.4.2 Adsorption and Pore Plugging.....	14

2.2	Semiconductor Photocatalysis	16
2.2.1	General.....	16
2.2.2	Mechanisms of Heterogeneous Photocatalysis	18
2.2.3	Dynamic Overview of Primary Processes in Photocatalysis	20
2.2.4	Factors Affecting Photoactivity of TiO ₂	22
2.2.4.1	Effect of pH	22
2.2.4.2	Effect of Light Sources and Light Intensity.....	23
2.2.4.3	Effect of Presence of Inorganic Anions.....	24
2.3	Membrane – Photocatalytic Reactor Configurations	25
2.3.1	Selected Reactor Design Considerations	25
2.3.2	Photocatalytic Immobilization System	25
2.3.2.1	Immobilization of TiO ₂ on Non – Porous Substrate.....	27
2.3.2.2	Immobilization of TiO ₂ on Porous Substrates	27
2.3.3	Coupling of Photocatalysis and Filtration (Individual System).....	29
2.3.4	Photocatalytic – Membrane Filtration Hybrid System.....	32

CHAPTER 3 INVESTIGATION OF STABILITY OF POLYMERIC MEMBRANES36

3.1	Introduction.....	36
3.1.1	Choice of Membranes	36
3.1.2	Stability of Polymeric Membranes	3X
3.1.2.1	Factors Affecting Stability.....	37
3.1.2.2	Oxidative / UV Stability of Polymeric Membranes.....	38
3.2	Experimental	40
3.2.1	Preliminary Screening of Membranes.....	40
3.2.1.1	Materials	40
3.2.1.2	Procedure and Analytical Measurements	41
3.2.2	Stability of Hollow Fibre Membrane	42
3.2.3	Experimental Runs with Different Filtration Conditions.....	43
3.2.3.1	Materials and Apparatus	43
3.2.3.2	Procedure	45
3.3	Results and Discussion	47
3.3.1	UV Screening of Membranes.....	47
3.3.1.1	One – Day Illumination	47
3.3.1.2	Three – Days Illumination	51

3.3.1.3	Thirty – Days Illumination Test	53
3.3.2	Oxidation Test for Membranes	56
3.3.3	Stability of Membranes under Different TiO ₂ Filtration Conditions	60
3.3.3.1	Non – Cake Situation.....	60
3.3.3.1	With Cake Situation.....	64
3.4	Summary	70

CHAPTER 4 FEASIBILITY STUDY OF A LOW - PRESSURE SUBMERGED MEMBRANE PHOTOCATALYTIC SYSTEM.....72

4.1	Introduction.....	72
4.2	Background.....	73
4.2.1	Adsorption of Organics on TiO ₂	74
4.2.2	Photodegradation of BPA	76
4.3	Experimental	79
4.3.1	Materials and Analytical Measurements.....	79
4.3.2	Dark Adsorption.....	80
4.3.3	Batch Photocatalytic Reactor	80
4.3.4	Submerged Membrane – Photocatalytic Reactor (SMPR).....	82
4.3.5	Membrane Adsorption and Critical Flux	83
4.3.6	Analytical Methods.....	83
4.4	Results and Discussion	84
4.4.1	Parameters Affecting the Photodegradation of BPA	84
4.4.1.1	Dark Adsorption of BPA on TiO ₂	84
4.4.1.2	Effect of Initial Suspension pH.....	86
4.4.1.3	Effect of TiO ₂ Concentration	87
4.4.1.4	Effect of Initial Concentration of BPA	88
4.4.1.5	Effect of Aeration	90
4.4.2	Microfiltration of TiO ₂	94
4.4.3	Degradation of BPA in a SMPR under a Continuous Mode of Operation	96
4.4.3.1	Permeate Delay Investigation	98
4.4.4	Variations in Feed Concentration	99
4.4.5	Fouling Control in the Operation of a SMPR	103
4.4.5.1	Critical Flux.....	103
4.4.5.2	Use of bubbling.....	104

4.4.5.3	Intermittent Permeation	106
4.5	Summary	110
 CHAPTER 5 DEVELOPMENT AND PERFORMANCE OF AN IMPROVED SUBMERGED MEMBRANE PHOTOCATALYTIC REACTOR.....111		
5.1	Introduction	111
5.2	Theoretical Background	113
5.2.1	UV Photoreactor Configuration	113
5.2.2	Process Efficiency of Photoreactors	114
5.3	Experimental Procedures	117
5.3.1	Materials	117
5.3.2	Improved Submerged Membrane Photoreactor	118
5.3.3	Light Distribution.....	119
5.3.3.1	Direct Sensor Measurement.....	119
5.3.3.2	Chemical Actinometry.....	120
5.3.4	Tracer Test	121
5.3.5	Analytical Methods.....	122
5.4	Results and Discussion	123
5.4.1	Design of Reactor	123
5.4.1.1	Radiation Field of UV Light Source.....	123
5.4.1.2	Completely – Mixed Condition – Tracer Test.....	126
5.4.1.3	Heat Concern	127
5.4.2	Parameters Affecting the Photodegradation of Resorcinol.....	129
5.4.2.1	Effect of Catalyst Concentration	129
5.4.2.2	Degradation Kinetics of Resorcinol.....	132
5.4.3	Process Efficiency of the Improved Submerged Light Photoreactor.....	133
5.4.4	Performance of the Submerged Light SMPR	140
5.4.4.1	Membrane Filtration Characteristics	144
5.4.5	Importance of Controlling Reaction Temperature	146
5.4.6	Long – term Operation.....	150
5.4.7	Practical Applicability of the Submerged Light SMPR.....	155
5.5	Summary	157

CHAPTER 6 KINETICS MODELING OF SUBMERGED MEMBRANE PHOTOCATALYTIC REACTOR (SMPR)	159
6.1 Introduction.....	159
6.2 Model Development.....	161
6.3 Results and Discussion	164
6.3.1 Determination of Kinetic Rate Constant.....	164
6.3.2 CSTR Model Evaluation.....	166
6.3.3 Modification of Classic Model and Verification	168
6.3.3.1 Model Improvements.....	168
6.3.3.2 Verification of the Modified Model	172
6.4 Summary	176
6.5 Nomenclature.....	177
CHAPTER 7 CONCLUSIONS & RECOMMENDATIONS	178
7.1 Conclusions.....	178
7.1.1 Investigation of Stability of Polymeric Membranes	178
7.1.2 Feasibility Study of a Low – Pressure Submerged Membrane Photocatalytic System.....	179
7.1.3 Development and Performance of a New Improved Submerged Membrane Photocatalytic Reactor	180
7.1.4 Submerged Membrane Photocatalytic Reactor Modeling	181
7.2 Recommendations for Future Research	181
7.2.1 Investigation of Stability of Polymeric Membranes	181
7.2.2 Feasibility Study of a Low – Pressure Submerged Membrane Photocatalytic System.....	182
7.2.3 Development and Performance of a New Improved Submerged Membrane Photocatalytic Reactor	183
7.2.4 Submerged Membrane Photocatalytic Modeling.....	183
REFERENCES.....	184
APPENDIX A	214
APPENDIX B	216
APPENDIX C	218
APPENDIX D.....	226

LIST OF PUBLICATIONS

Chin S. S., Chiang K. and Fane A. G., (2006), The Stability of Polymeric Membranes in a TiO₂ Photocatalysis Process, Journal of Membrane Science, v275, pp 201-211.

Chin S. S., Lim T.M., Chiang K. and Fane A. G., (2007), Hybrid Low-Pressure Submerged Membrane-Photoreactor for the Removal of Bisphenol A, Desalination, v202 (1-3), pp253 – 261.

Chin S. S., Lim T.M., Chiang K. and Fane A. G., (2007), Factors Affecting the Performance of a Low-pressure Submerged Membrane Photocatalytic Reactor, Chemical Engineering Journal, v130 (1), pp 53-63

Chin S. S., Lim T.M., Chiang K. and Fane A. G., A New Improved Submerged Membrane Photocatalytic Reactor, In preparation.

Chin S. S., Lim T.M., Chiang K., Phattaranawik J. and Fane A. G., Model Development for Predicting Efficiency of the Continuous Submerged Membrane Photocatalytic Process, In preparation.

LIST OF FIGURES

Figure 2.1	Filtration spectrum [Solvay Membranes, 2003]	6
Figure 2.2	Schematic diagram of (a) deadend and (b) crossflow filtration.....	8
Figure 2.3a	Schematic representations of (a) spiral wound (b) hollow fiber (c) tubular.....	9
Figure 2.3b	Schematic representation of plate-frame membrane configurations	10
Figure 2.4	Boundary layer model of crossflow filtration.....	13
Figure 2.5	Fouling schematics. D = diameter of particles, D_p = diameter of pores.....	15
Figure 2.6	An illustration of the photogeneration of electron-hole pairs, where ecb- is the electrons.....	18
Figure 2.7	A simplified diagram of processes occurring in a semiconductor particle	21
Figure 2.8	Radiation spectrum and transmittance of TiO_2 layer [Source: Otaki et al. (1996)].....	23
Figure 2.9	Patented design of photocatalytic membrane reactor [Source: Bischoff et al., 1999].....	29
Figure 2.10	Suspended catalyst in the recirculation tank with the irradiation of flat sheet membrane cell [S: recirculation tank, Rp: permeate tank, L: UV lamp, R: flat sheet membrane] [Molinari et al., 2000].....	33
Figure 2.11	Schematic diagram of membrane photocatalytic suspended system to treat E. Coli [Sun et al., 2003]	34
Figure 2.12	Schematic diagram of submerged membrane photoreactor [Fu et al., 2006a]	35
Figure 3.1	(a) Schematic diagram of setup used for flat-sheet membrane pure water permeate flux test and (b) side-stream configuration for hollow fibre membrane stability test.....	43
Figure 3.2	Schematic diagram of the flat-sheet membrane photoreactor.....	44
Figure 3.3	Spectral range of the UVA light source used	45

Figure 3.4	Change in resistances of different microfiltration membranes before and after UV illumination	48
Figure 3.5	UV absorption of several polymers [Hamid et al., 1992]	48
Figure 3.6	Formation of hydroperoxides from polypropylene intramolecular hydrogen atom abstraction process [Allen and Edge, 2002]	49
Figure 3.7	Change in resistance of different ultrafiltration membranes before and after the UV illumination (constant pressure: 100kPa)	49
Figure 3.8	Change in resistance of different membranes before and after the 3-days of UV illumination	52
Figure 3.9	Photodegradation of polycarbonate [Allen and Edge, 1992]	52
Figure 3.10	ATR-FTIR spectra of Millipore PVDF membrane before and after 17 days of UV exposure. Inset: Enlargement of spectra from 1500 to 1800cm ⁻¹	55
Figure 3.11	Change in resistance of membranes before and after the 30-days of UV illumination	55
Figure 3.12	Change in resistance ratio of the PTFE, PVDF (phobic), PVDF-Pall and PAN membranes under 200mM of H ₂ O ₂ and UV/H ₂ O ₂ for 10 days	57
Figure 3.13	Membrane on right: PAN exposed to H ₂ O ₂ for 10 days. Membrane on the left: PAN exposed to UV/H ₂ O ₂ for 10 days	59
Figure 3.14	Quantum energies associated with wavelength in the near UV region of the electromagnetic spectrum (Source: Allen and Edge, 1992) ...	59
Figure 3.15	Micrograph of the surface of the (a) before and (b) after crossflow non-cake filtration membrane	61
Figure 3.16	Percentage change in the resistance of membranes under crossflow conditions of UV light, TiO ₂ without light and UV/TiO ₂ (crossflow velocity: 0.83m/s, constant flux: 30L/m ² .hr, unadjusted pH)	62
Figure 3.17	Effect of pH on the percentage change of membrane resistance under similar crossflow conditions (crossflow velocity: 0.83m/s, constant flux: 30L/m ² .hr)	63
Figure 3.18	Effect of TiO ₂ cake thickness on the percentage change of the membrane resistance	64

Figure 3.19	SEM images of the a) cross-section and b) surface of the 5µm cake membrane.....	65
Figure 3.20	UV-Vis transmittance analysis of different thickness of TiO ₂ formed under dead-end filtration unit	67
Figure 3.21	ATR-FTIR spectra of the Millipore PES membrane after 150µm TiO ₂ UV-oxidation	68
Figure 3.22	Illustration of the mechanism for the photocatalytic degradation of polymeric membrane under dead-end filtration study. Note that activated TiO ₂ layer is where the oxidative radicals are produced...	69
Figure 3.23	Two-layers cakes formed for the study of the mechanism of the degradation of polymeric membrane by the TiO ₂	70
Figure 4.1	Chemical structure of bisphenol A (BPA).....	78
Figure 4.2	Schematic diagram of the batch photoreactor experimental setup (a) side view, (b) top view.....	81
Figure 4.3	Schematic diagram of the continuous submerged membrane photoreactor experimental setup.....	82
Figure 4.4	Establishment of Langmuir monolayer adsorption constants for the adsorption of BPA over TiO ₂ at different pH (unadjusted pH = pH 5.5)	85
Figure 4.5	Influence of initial concentration of BPA (TiO ₂ concentration = 0.5g/L, initial pH = 4, BPA feed concentration = 10ppm, 0.5L/min aeration rate)	88
Figure 4.6	Photodegradation of BPA as function of different aeration rate (0.5g/L TiO ₂ , initial pH = 4, initial BPA concentration = 10ppm)...	91
Figure 4.7	Bubbles resulting from a) 0.5L/min b) 4L/min of aeration rate	93
Figure 4.8	Comparison of the effects of aeration, TiO ₂ concentration and pH on the initial degradation rate of BPA	94
Figure 4.9	TiO ₂ size distributions after 10min of sonication and 3hrs of 0.5L/min aeration at pH 4	95
Figure 4.10	TiO ₂ size distribution in different pH suspension after 1hr of aeration at 0.5L/min.....	96

Figure 4.11	Degradation and mineralization of BPA (TiO ₂ concentration = 0.5g/L, initial pH = 4, BPA feed concentration = 10ppm, 0.5L/min aeration rate)	97
Figure 4.12	Pulse tracer tests for determination of permeate delay caused by adsorption of BPA on PVDF membrane (flux 100L/m ² .hr)	99
Figure 4.13	The mineralization of BPA for various initial concentrations of BPA in the permeate of SMPR (TiO ₂ loading: 0.5g/L, aeration rate: 0.5L/min, filtration flux: 100L/m ² .hr)	100
Figure 4.14	Amount of TOC removed at 40min of continuous operation of the SMPR under different feed concentration	101
Figure 4.15	Mineralization efficiency of 20ppm of BPA by different permeate flux (TiO ₂ concentration = 0.5g/L, initial pH = 4, BPA feed concentration = 20ppm, 0.5L/min aeration rate)	102
Figure 4.16	Effect of different filtration fluxes on the TMP development (TiO ₂ loading: 0.5g/L, aeration rate: 0.5L/min, BPA concentration: 20ppm)	103
Figure 4.17	The change in transmembrane pressure for different filtration flux (0.5g/L TiO ₂ , 0.5L/min bubbling)	104
Figure 4.18	Percentage increase in transmembrane pressure under different bubbling rates at TiO ₂ concentration of 0.5g/L and constant flux operation of 100 L/m ² .hr	105
Figure 4.19	TMP change for continuous 100L/m ² .hr and intermittent permeation operation (intermittency of 2min close/5min open)	107
Figure 4.20	Comparison of the TMP change, TOC degradation and production of water between continuous and intermittent permeation operation .	108
Figure 4.21	Comparison of air bubble and water flow hydrodynamics within a (a) U-shaped (b) curtain type hollow fibre modules	109
Figure 5.1	(a) Schematic diagram of the newly developed submerged membrane photoreactor (SMPR). (b) Arrangement of two UV lamps within a borosilicate glass tube. Left: side view, Right: Top view.....	119
Figure 5.2	Experimental radial light intensity profiles in water medium (0g/L) and different TiO ₂ concentrations at center of borosilicate glass tube (Conditions: without bubbling, UV range measured: 320 – 380nm).	124

Figure 5.3	Configuration of UV lamps in the new 15cm photoreactor (solid line represents borosilicate glass tubes, dotted line represents UV illumination area).....	125
Figure 5.4	Tracer test data obtained from the SMPR continuous operation at different bubbling rates.....	126
Figure 5.5	Temperature profile in the bulk and at the wall of the lamp tubes under controlled and uncontrolled temperature tests.....	128
Figure 5.6	Effect of photolysis and TiO ₂ concentration on the degradation of resorcinol: (◇) light only, (—) 0.002g/L, (□) 0.02g/L, (●) 0.2g/L, (x) 0.5g/L and (Δ) 1.0 g/L.	129
Figure 5.7	Effect of TiO ₂ concentration on (a) the degradation and (b) the mineralization rate of various concentrations of resorcinol.....	130
Figure 5.8	Linearisation of Langmuir-Hinshelwood isotherms: reciprocal of the initial rate as a function of the reciprocal of the initial concentration ([TiO ₂] = 0.5g/L, pH = unadjusted).	132
Figure 5.9	Dependent of resorcinol initial degradation on the initial concentration.....	136
Figure 5.10	Limiting quantum yield of degradation and mineralization of resorcinol and BPA.....	137
Figure 5.11	Degradation and mineralization of resorcinol in the new SMPR ([TiO ₂] = 0.5g/L, [Resorcinol] ₀ = 10ppm, residence time = 1hr). ..	140
Figure 5.12	Degradation and mineralization of resorcinol in the new SMPR. Conditions: (a) [TiO ₂] = 0.5g/L, [Resorcinol] ₀ = 30ppm, residence time = 2hr. (b) [TiO ₂] = 0.5g/L, [Resorcinol] ₀ = 50ppm, residence time = 3.5hr.....	142
Figure 5.13	Resorcinol (a) degradation and (b) mineralization profile with (■) and without (▲) control of temperature. Secondary axis in (a) shows dissolved oxygen of controlled temperature (□) and uncontrolled temperature (Δ) and in (b) shows temperature profile of controlled temperature (□) and uncontrolled temperature (Δ). Conditions: [TiO ₂] = 0.5g/L, [Resorcinol] ₀ = 50ppm, residence time = 1.5hr...	147
Figure 5.14	Effect of temperature on the transmembrane pressure change	149
Figure 5.15	(a) Degradation and mineralization profile of long-term operation of SMPR (b) Amplification of steady-state concentration region of (a). Conditions: [TiO ₂] = 0.5g/L, [Resorcinol] ₀ = 30ppm, residence time = 3.5hr, controlled temperature.....	151

Figure 5.16	Long-term transmembrane pressure ratio change for the new SMPR operating with a flux of $36\text{L/m}^2\cdot\text{hr}$153
Figure 5.17	EDX micrograph of the inner surface of the washed PVDF membrane.....155
Figure 5.18	Schematic diagram of a conventional drinking water treatment plant in United States of America (Source: Stackelberg et al., 2004).....156
Figure 6.1	Relationship between initial concentration of resorcinol and first-order kinetic rate constants.165
Figure 6.2	Experimental and calculated values of resorcinol concentration in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{ppm}$, residence time = 1hr.....166
Figure 6.3	Experimental and calculated values of resorcinol concentration in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 30\text{ppm}$, residence time = 2hr.....167
Figure 6.4	Experimental and calculated values of resorcinol concentration in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 50\text{ppm}$, residence time = 3.5hr.....167
Figure 6.5	Relationship between model parameter (a) and the initial concentration of resorcinol171
Figure 6.6	Comparison of the original and modified model in predicting the degradation of resorcinol in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{ppm}$, residence time = 1hr173
Figure 6.7	Comparison of the original and modified model in predicting the degradation of resorcinol in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 30\text{ppm}$, residence time = 2hrs.....173
Figure 6.8	Comparison of the original and modified model in predicting the degradation of resorcinol in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 50\text{ppm}$, residence time = 3.5hrs.....174
Figure 6.9	Effect of retention time in the degradation of resorcinol in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{ppm}$175
Figure 6.10	Effect of initial feed concentration in the degradation of resorcinol in the new SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, residence time = 3.5hrs176

LIST OF TABLES

Table 2.1	Suspended versus immobilized photocatalytic systems	30
Table 3.1	Types of membranes used in the UV exposure test.....	40
Table 3.2	Comparison of leakage of TOC (ppm) from the respective membranes after 24 hours of UV exposure.....	50
Table 3.3	Comparison of leakage of TOC (ppm) from the respective membranes [TOC values = membrane with UV exposure – membrane in dark (blank test)]	51
Table 3.4	Comparison of leakage of TOC from the respective membranes [TOC values = membrane with UV exposure – membrane in dark (blank test)]	53
Table 3.5	Oxidation power of respective oxidants (Source: US peroxide, 2003)	56
Table 3.6	Change in resistance of the membrane before and after 30days of UV/H ₂ O ₂ exposure.....	60
Table 4.1	Bisphenol - A characteristics	80
Table 4.2	Calculated Langmuir adsorption constants.....	84
Table 4.3	Initial rate of degradation of 10ppm of BPA at various pH conditions (TiO ₂ concentration = 0.5g/L, initial BPA concentration = 10ppm, aeration rate: 1L/min)	86
Table 4.4	The rate of degradation of 10ppm of BPA under different TiO ₂ concentration conditions (initial BPA concentration = 10ppm, pH = unadjusted, aeration rate = 1L/min)	87
Table 4.5	Initial degradation rates of BPA for different initial concentration of BPA (initial pH = 4, TiO ₂ concentration = 0.5g/L)	89
Table 4.6	Average particle size of TiO ₂ at different aeration rate (initial pH = 4, TiO ₂ concentration = 0.5g/L).....	92
Table 4.7	Intensities of transmitted light at different bubbling rates	93
Table 4.8	Experimental conditions with different filtration fluxes (0.5g/L TiO ₂ , initial pH = 4, initial BPA concentration = 20ppm, 0.5L/min aeration rate)	102

Table 4.9	Summary of intermittence frequency tests	107
Table 5.1	Resorcinol characteristics	118
Table 5.2	Summary of the observed mean residence time	126
Table 5.3	Langmuir-Hinshelwood adsorption constant (K_{LH}) and kinetic constants (k_{LH})	133
Table 5.4	Details of the two photoreactors	134
Table 5.5	Initial photonic efficiency of resorcinol degradation in old and new lamp photoreactor	135
Table 5.6	Increase in efficiency of new reactor over the old reactor.....	138
Table 5.7	Estimated values of UV utilization efficiency of photocatalytic reactors reported in the literature.....	144
Table 5.8	Critical flux determination of the old and new reactor under respective conditions.....	145
Table 6.1	First-order kinetic rate constants of resorcinol, conditions: $[TiO_2] = 0.5g/L$, unadjusted pH = 5.6, air bubbling rate = 0.5L/min, Temperature = 26°C	164
Table 6.2	Relationship between $C_A(t)$ and calculated reaction surface ratio, β .170	
Table 6.3	Comparison of $\beta(t)$ values obtained from general equation and the original equation	172

ABBREVIATION

μm	micrometer
AO7	Acid Orange dye
BPA	bisphenol-A
CA	cellulose acetate
CFST	continuous flow stirred tank
C_{pulse}	concentration of permeate pulse tracer test
CSTR	continuous stirred tank reactor
DBPs	disinfection by-products
EDCs	endocrine disruptors
EPS	extracellular polymers
FLR	flux loss ratio
FTIR-ATR	Fourier Transform Infrared-Attenuated Total Reflectance
g	gram
H_2O	water
H_2O_2	hydrogen peroxide
HCl	hydrochloric acid
HClO_4	perchloric acid
HPLC	high performance liquid chromatograph
hr	hour
hrs	hours
KCl	potassium chloride
KOH	potassium hydroxide
L	litre
L/D	length to diameter ratio
L-H	Langmuir-Hinshelwood
$\log K_{\text{ow}}$	octanol–water partitioning coefficients

m ³	cubic meter
MF	microfiltration
mg	milligram
min	minute
mM	millimolar
MQ	Millipore milliQ water
M _r	molecular weight
MWCO	molecular weight cutoff
NaOH	sodium hydroxide
NF	nanofiltration
nm	nanometer
NOM	natural organic matters
O ₃	ozone
PAC	powdered activated carbon
PAN	polyacrylonitrile
PC	polycarbonate from Millipore
PCO	photocatalytic oxidation
PES	polyethersulphone
PET	Poly(ethylene terephthalate)
PFR	plug flow reactor
PMMA	Polymethylmethacrylate
PP	polypropylene
ppm	parts per million, mg/L
ppt	parts per trillion, µg/L
PS	polysulphone
PS	polysulphone
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	polyvinylidene fluoride
PVDF-Pall	hydrophilic polyvinylidene fluoride from Pall corporation
PVDFphobic	hydrophobic polyvinylidene fluoride from Millipore
PVP	Polyvinylpyrrolidone

PWF	pure water flux
pzc	point of zero charge
RO	reverse osmosis
RTD	residence time distribution
s	seconds
SEM	scanning electron microscope
SMPR	submerged membrane photoreactor
T_{bulk}	temperatures in the bulk solution
THMs	trihalomethanes
TiO_2	titanium dioxide
TOC	total organic carbon
T_{wall}	temperatures next to the glass tube wall
UF	ultrafiltration
UV	ultraviolet
VOCs	volatile organic compounds
W	watts

LIST OF SYMBOLS

ΔTMP	transmembrane pressure drop
R_m	resistance of the membrane
R_{cp}	polarization resistance
R_g	gel layer resistance
R_a	adsorption resistance
δ	boundary layer
C_f	bulk feed concentration
C_w	membrane surface concentration
k	mass transfer coefficient
d	diameter of particles
d_p	diameter of pores
ΔE_{gap}	band-gap energy
V_b	valence band
C_b	conduction band
h^+	holes
e_{cb}^-	electrons at the conduction band
$\text{OH}^\bullet$	hydroxyl radicals
R_{mi}	initial resistance of the membrane
R_{mf}	final resistance of the membrane
J_i	initial permeate flux
J_f	final permeate flux
m_c	mass of TiO_2 per membrane area
C	feed concentration
V_p	volume of permeate
t_c	cake layer thickness
ρ	density of TiO_2 particles
ε	porosity of cake
μ	viscosity of the filtrate
$\text{HOO}^\bullet$	hydroperoxide radicals

q_A	amount of solute adsorbed per unit weight of TiO_2
K_f	adsorption capacity
C_e	equilibrium concentration
$1/n$	adsorption intensity
r_o	initial rate of disappearance of organic compound
C_o	initial concentration
K_{LH}	L-H equilibrium adsorption constant
k_{LH}	pseudo-first order initial reaction rate constant
K_{ads}	Langmuir adsorption equilibrium
θ	TiO_2 surface coverage
Q_{ads}	adsorbed quantity
Q_{max}	maximum adsorbable quantity
C_{eq}	Langmuir adsorption equilibrium
k_{app}	apparent first-order rate constant
t	time
$\Phi_{overall}$	overall quantum yield
η	refractive indices
I	scattered light intensity
ζ	photonic efficiency
ζ_r	relative photonic efficiency
$\Phi_{standard}$	standard quantum yield
$\mu E/s$	microEinstein/second
ζ_{lim}	limiting photonic efficiency
A_r	radiation area
β	reaction surface coverage ratio
V_R	reactor volume
Q_f	feed volumetric flow rate
Q	output volumetric flow rate
$C_{A,f}$	feed concentration
C_A	output concentration
r_A	rate of reaction
τ	residence time

a	model parameter
b	model parameter
c	model parameter
$d[C_A]/dt$	change in concentration of A with respect to time
k_i	kinetic constant at the resorcinol concentration, C_A ,
k_{ref}	kinetic constant of the initial resorcinol concentration, C_{AO}

CHAPTER 1

INTRODUCTION

1.1 Background

The ever-increasing demand for higher living standards has led to the presence of new pollutants in effluent which are not readily degradable by conventional treatment methods [Gogate and Pandit, 2004; Bauer and Fallmann, 1997]. In recent years, increased public awareness of the effect of these pollutants on human health and the environment has also contributed to more stringent environmental laws and regulations. Thus, there is an imperative need for the development of new technologies that can address the new emerging pollutants in water and wastewater.

Chlorination and ozonation are traditionally used to produce drinking water and to treat wastewater effluents. Despite chlorination effectiveness, the formation of toxic, carcinogenic trihalomethanes (THMs) and disinfection by-products (DBPs) has been a concern in its use [Watts et al., 1995]. Other methods of water purification such as ultraviolet (UV) disinfection system and phase separation techniques (adsorption process) have their own limitations. The latter technique merely transfers the contaminants from one phase to another [Kroschwitz et al, 1996]. An additional process is required to dispose these secondary forms of contaminants, thus incurring higher cost of purification.

Although reverse osmosis (RO) filtration is designed to reject 99% of colloids, organic deposits, bacteria and viruses, there is still a chance that low concentration of organics, as low as parts per trillion (ppt), will be able to pass through the membranes [Chin, 1996]. For example, ultrapure water is found to contain trace amounts of impurities such as organics, colloids and microorganisms and therefore needs further treatment [Matsuda et al., 1996].

The photocatalytic oxidation (PCO) process has been considered as an innovative and “green” alternative for water treatment, especially for the treatment of trace organics [Glaze et al, 1993]. PCO is defined as a catalytic process that generates hydroxyl radicals in the presence of photons of equal or higher than the band gap energy of the catalyst for the degradation of pollutants and microorganisms [Gogate and Pandit, 2004; Bhatkhande et al., 2001]. Titanium dioxide (TiO_2) is the most widely used and the most promising among the photocatalysts because it is cheap, inert and can work for a wide range of pH.

Regardless of the proven oxidative capability of TiO_2 , the recovery of fine colloidal photocatalysts is one of the main concerns that affects the engineering application on the large scale. Although several works have been done to immobilize TiO_2 powder on a suitable substrate [Matsunaga et al., 1988; Ireland et al., 1993; Choi et al., 2000], problems associated with reduced catalyst area to volume ratio will tend to restrict the mass transport [Butterfield et al., 1997]. For suspended photocatalyst systems, researchers have tried to improve the recovery by using TiO_2 pellets [Yamazaki et al, 2001a; Yamazaki et al, 2001b], adjusting the pH of the system to enhance aggregation of TiO_2 [Fernandez-Ibanez, 2003] and by the invention of a magnetic core TiO_2 [Beydoun, 2000]. These methods enhance sedimentation and thus facilitate the recovery of the catalysts. However, a limitation to these methods is that the treated water cannot be withdrawn immediately after treatment and a batch system has to be adopted. Another problem associated with the use of suspended photocatalyst systems is the difficulty of achieving uniform radiation in the entire system [Dijkstra et al., 2001]. This has been one of the biggest challenges for the large-scale application of TiO_2 photocatalysis.

Therefore, there is a need for the development of a novel photocatalytic reactor, which is not only capable of efficient photocatalysis but also allows continuous withdrawal of the treated water from the reactor. According to Molinari and co-workers [2000], the coupling of a photocatalytic reaction with a membrane separation may present an ideal solution, with the membrane supporting the task of retaining the catalyst as well as acting as a selective barrier for the species to be degraded. Individual systems such as a photocatalytic reactor followed by

separation of the TiO_2 using a filtration unit have been studied [Karakulski et al., 1998; Molinari et. al., 2001]. This type of separate system of filtration and photocatalytic reactor will require a relatively large footprint and therefore may face constraints in a country like Singapore, where land availability is limited. Molinari et al [2000], Higgins et al [2000] and Sun et al [2003] have also attempted to combine photocatalysis and membrane technologies into a single reactor and the details of their process configurations will be discussed later.

Though several papers have been published on the combined photocatalysis and membrane technologies in a single reactor, less effort has been placed on the use of low-pressure membrane for a more cost effective process. Therefore it becomes the challenge of the present work:

- (1) *to source for oxidation resistant membranes that are not rapidly degraded by UV/ TiO_2 ;*
- (2) *to incorporate low-pressure submerged membranes, photoreactor and light guide into a hybrid module;*
- (3) *to evaluate the effectiveness of the low pressure submerged membrane photoreactor (SMPR) using selected model organic compounds such as bisphenol - A (BPA) and resorcinol;*
- (4) *to model the photoefficiency of the chosen organics.*

A review of the titanium dioxide photocatalysis, membrane technologies and the combination of both processes will be given in Chapter 2. Chapter 3 presents a detailed stability study on the selection of polymeric membranes, which are stable under UV lights and oxidative environment. The effects on the stability of the membranes under different TiO_2 fouling mechanism, with cake and without cake, will also be discussed.

Chapter 4 evaluates the feasibility of the submerged membrane photoreactor (SMPR). The ability of the low- pressure membrane to retain the model organic

compound, Bisphenol-A, and TiO_2 will be presented. The effect of different parameters on the photoefficiency of the reactor will also be included in this chapter.

Chapter 5 focuses on the improvement of the SMPR configuration. Submerged light was used in the submerged reactor and comparison of this improved submerged light reactor to the previous external light reactor is provided in terms of fouling and photoefficiency.

Chapter 6 presents the development of a model that predicts the efficiency of the newly developed submerged light SMPR. A correction factor, reaction surface coverage ratio, was introduced to the classical CSTR model and the adequacies of the new model with respect to the degradation kinetics of resorcinol under different experimental conditions are evaluated.

Chapter 7 summarizes the major findings from this study. The recommendations for future work are also highlighted in this chapter.

CHAPTER 2

LITERATURE REVIEW

This chapter provides a review of the relevant literature. The first section deals with membrane separation technology. The second section introduces semiconductor photocatalysis and the final section reviews the state-of-the-art of membrane photocatalytic reactors.

2.1 Membrane Separation

2.1.1 Overview

A membrane process requires two bulk phases physically separated by a third phase, the membrane. The membrane acts as a control for the mass exchange between the two phases. In this case, the membrane allows selective and controlled transfer of one species from one bulk phase to another bulk phase separated by the membrane. A driving force such as pressure or temperature difference is necessary to initiate the mass transport across the membrane [Zeman and Zydney, 1996]. The stream that goes through the membrane is known as the permeate while the fraction of feed which remains is the retentate.

Membrane separation techniques have grown from a simple laboratory tool to an industrial process with more applications expected in the future. The introduction of membranes has resulted in a considerable technical and commercial impact in the industry of separation [Strathmann, 1992]. The more common commercialized separation processes include reverse osmosis, ultrafiltration, microfiltration, gas permeation, pervaporation, dialysis, electrodialysis, and emulsion liquid membranes.

The basis of membrane separation processes can be specified based on the following seven aspects [Kesting, 1985]:

- 1) Separation goal
- 2) Nature of species retained (size of the species)
- 3) Nature of species transported through membrane
- 4) Minor or major species of feed solution transported through membrane
- 5) Driving force
- 6) Phase of feed and permeate streams
- 7) Mechanism for transport/selectivity

Examples of how the processes can be classified based on the membrane retention ability are shown in Figure 2.1. Moving from the smallest to largest pore size, there are Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF) and Microfiltration (MF).

Detection Method	Scanning Tunnelling Electron Microscope	Scanning Electron Microscope		Optical Microscope	Naked Eye
Range	IONS	MOLECULES	MACRO MOLECULES	MICRO PARTICLES	MACRO PARTICLES
Size Microns (µm)	0.001	0.01	0.1	1	100
Angstrom Units	10	100	1,000	10,000	100,000
Approx. Molecular Weight	200	20,000	200,000	> 500,000	
Relative Size of Various Materials	Metal Ions Pesticides Herbicides Dissolved Salts	Sugars Viruses Album in Protein Humid Acids	Paint Pigment Colloids	Bacteria Red Blood Cells Human Hair	Algae and Protozoans Sands Granular Activated Carbon
Separation Process	REVERSE OSMOSIS (RO)	NANO FILTRATION	ULTRA FILTRATION (UF)	MICRO FILTRATION (MF)	PARTICLE FILTRATION

Figure 2.1 Filtration spectrum [Solvay Membranes, 2003]

2.1.2 Ultrafiltration and Microfiltration

Ultrafiltration is a size-exclusion-based separation process. Its retention capability is represented by a nominal molecular weight cutoff (MWCO) with reference to the molar mass of a retained macromolecule. UF membranes typically have pore size ranges from 1 to 100 nanometer (nm) and are capable of retaining species in the molar mass range of 300 to 500,000 g/mol (Daltons) [Kulkarni et al., 2001]. As illustrated in Figure 2.1, UF membranes are defined to include those membranes with pores small enough to reject viruses, larger dissolved and colloidal species.

Microfiltration membranes have pore sizes that are larger than ultrafiltration membranes. It is the “fine” end of particle filtration, with pores from 0.1 to 1 micrometer diameter. The transmembrane pressure drop, which drives the microfiltration process, is relatively small (typically 0.1 to 3.4bar). This is the reason why microfiltration is considered the most economical type of membrane separation in the separation of particles or microbes greater than 0.1 μm .

2.1.3 Membrane Process Configurations

2.1.3.1 Dead-end versus Cross-flow Filtration

Microfiltration or ultrafiltration is carried out in two types of configurations: dead-end or cross-flow filtration as shown in Figure 2.2 [Davis, 2001]. As shown in Figure 2.2 (a), the feed for the dead-end filtration flows perpendicular to the membrane whereas the feed flows parallel to the membrane surface in cross-flow filtration (Figure 2.2b).

Figure 2.2 Schematic diagram of (a) dead-end and (b) cross-flow filtration

For the former, all the particles are retained on the filter surface and a cake layer is formed during the filtration process. Cake build up results in increased filtration resistance and in turn causes a drop in permeate flux rate if the transmembrane pressure is held constant, or causes the transmembrane pressure to increase if flux is held constant. Dead-end filtration is by nature a batch process since it is necessary to periodically remove the particles from the membrane surface. On the other hand, the cross-flow filtration cake formation will depend on the shear forces and the flow pattern in the narrow feed channel to control the fouling effect. Compared to the dead-end filtration, the cake layer formed remains relatively thin. As such, the cross-flow configuration is effective in controlling fouling and maintaining high flux over prolonged time periods.

2.1.3.2 Membrane Cross-flow Modules

Several membrane modules are available commercially for pressure-driven liquid-phase applications. The more common ones include spiral-wound, hollow fiber, tubular and plate and frame modules as shown in Figure 2.3 (a) to (d) respectively [Zeman and Zydney, 1996].

Figure 2.3a Schematic representations of (1) spiral wound (2) hollow fiber (3) tubular configurations.

Figure 2.3b Schematic representation of plate-frame membrane configuration.

- (a) **Spiral wound modules:** The basic design consists of a membrane sandwich with the active sides facing away from each other and containing a permeate carrier. The membranes are separated by a thin mesh-like spacer and are wound as a spiral on a permeate tube. This module requires low capital cost but is relatively easily plugged. The feed channel is usually 0.5 – 1mm thick and requires feed turbidities to be less than 1 NTU (Nephelos turbidity unit). Various manufacturers offer modules for more turbid feeds based on increasing effective feed channel height [Kulkarni, 2001]. The RO spiral wound modules are the preferred geometry for RO desalination and reclamation.
- (b) **Hollow fiber modules:** The bore diameters of the hollow fibers (self-supporting) are usually in the range of 0.5 to 2.5mm and the fiber walls are microporous with a dense skin layer. The dense skin layer gives the membrane its permselectivity and these fibers are spun separately, bundled and potted into a cartridge housing, usually a shell-and-tube arrangement.

The skin layers of the membranes are either on the lumen side of the fiber (an inside-out filter) or on the outside of the fiber (an outside-in filter). The inside-out filters with the feed flowing into the fiber lumen and out radially allow the module to be operated at higher pressure due to the greater structural stability when the flow is directed out of the lumen. The cartridges typically have one feed inlet, a retentate outlet and two permeate exits. The hollow fiber can also be bundled in a U-shaped configuration in which two ends of the fibers are potted together and there is only one permeate exit. Hollow fiber modules have a high packing density and are relatively low in manufacturing cost. They are also useful for applications where frequent cleaning is required since the modules allow simple backflushing.

(c) **Tubular modules:** Tubular devices are essentially similar to hollow fiber modules but with two important differences: larger tubes are employed (typically 0.3-2.5cm diameter) and tubular membranes are not self-supporting, which means they are usually cast in place within porous support tube such as fiberglass or plastic. Several of these tubes can then be housed in a shell-and-tube arrangement and the flow is typically inside-out. The primary advantage of the tubular modules is that they are highly resistant to particulate plugging. The modules are usually designed to have the bore diameters ten times larger than the largest particles. Several disadvantages of tubular modules reported include low surface/volume ratio, high holdup volume and large energy consumption due to the high Reynolds number typically applied [Kulkarni, 2001].

(d) **Plate-frame modules:** The plate-frame membrane modules were among the earliest configurations on the market. The middle of the module is the support plate that is sandwiched between two flat-sheet membranes. The membranes are sealed to the plate by either gaskets with locking devices, glue or are directly bonded. Several of these plates are then stacked together to form a complete module. The permeate is manifolded separately from the feed stream and can be combined within or outside the module, depending

on the particular device design. An advantage of the plate-frame module is that though the membrane requires replacement when fouled, the rest of the materials and hardware can be reused. At times the membranes may be removed and carefully cleaned by hand.

2.1.3.3 Submerged Membrane Modules

A new membrane module concept, the submerged membrane, has been widely accepted for water and wastewater treatment, especially in the use of the membrane bioreactor (MBR) (Fane et al., 2002). The use of submerged membranes has reduced the energy consumption of membrane bioreactors significantly and hence increased the potential application of membranes in wastewater treatment. The membrane module is always in direct contact with the suspension medium in a submerged membrane configuration and permeate is removed by suction from the membrane so as to avoid pressurizing the bioreactor. Another key feature of submerged systems includes using bubbling as the primary fluid mechanical method to keep solids in suspension and to control deposition and fouling. The membranes are either hollow fiber, vertical or horizontal, or flat plate membranes aligned vertically. Submerged membrane systems are found to be relatively easy to operate if the air flow rates are sufficiently high and flux is sufficiently low. However, it was found that more than 80% of the energy consumption in a MBR system was for aeration (Howell et al., 2004).

2.1.4 Bulk Mass Transport of Microfiltration /Ultrafiltration

Understanding the mechanisms underlying the bulk transport of MF and UF is important in controlling the overall performance of the filtration processes. As filtration proceeds, a resistance to filtration builds up due to the accumulation of particulates at the membrane surface. This phenomenon is generally referred to as concentration polarization, which can eventually lead to fouling of the membrane [Cheryan, 1998].

2.1.4.1 Concentration Polarization

In membrane filtration, the flux is directly proportional to the pressure gradient across the membrane and inversely proportional to the viscosity as seen from Equation 2.1 [Mulder, 1989].

$$J = \frac{\Delta TMP}{\mu(R_m + R_{cp} + R_g + R_p + R_a)} \quad (2.1)$$

ΔTMP is the transmembrane pressure drop. R_m represents the resistance of the membrane which is a constant and can be calculated from the pure water flux. As molecules started to accumulate near the membrane surface, concentration polarization resistance, R_{cp} , may occur. This is commonly known as the cake resistance. The concentration of the accumulated solute molecules may increase to a point that a gel layer is formed that exerts a gel layer resistance, R_g . With porous membrane, it is possible for some solutes to penetrate into the pores and block the pores, leading to pore blocking resistance, R_p . R_a is the resistance that may be caused by adsorption of molecules.

As seen from Figure 2.4, there is a boundary layer, δ between the bulk feed concentration, C_f and membrane surface concentration, C_w . The thickness of this layer is controlled by the module flow regime and the diffusion conditions of retained species [Kulkarni et al., 2001].

Figure 2.4 Boundary layer model of cross-flow filtration

Initially, the transport of solute to the membrane surface is by convective flow of the permeate and the concentration buildup will cause a steep concentration gradient within the boundary layer. This is balanced by back-transport of the solute into the bulk solution by diffusion. This leads to Film Model, Equation 2.2 (Porter, 1992).

$$J = k \ln \left(\frac{C_w - C_p}{C_f - C_p} \right) \quad (2.2a)$$

Or, when complete solute retention (i.e. $C_p \rightarrow 0$)

$$J = k \ln \left(\frac{C_w}{C_f} \right) \quad (2.2b)$$

where k is the mass transfer coefficient, C_w is the concentration of the solute being accumulated at the membrane surface and C_f is the concentration of the solids in the bulk slurry. The mass transfer coefficient, k , is determined by nature of the fluid flow in the membrane module.

2.1.4.2 Adsorption and Pore Plugging

Besides the well-understood boundary layer and concentration polarization theory as discussed, other factors also contribute to the eventual fouling of the membranes. Refer to Figure 2.5 for a series of fouling mechanisms [Perry and Green. 1997]. Case A illustrates the pore narrowing by deposition of particles; Case B shows the total blockage of pores; Case C clearly shows the formation of a cake layer on the membrane surface while case D demonstrates the selective plugging of largest pores by the particles.

Figure 2.5 Fouling schematics, d = diameter of particles, d_p = diameter of pores [Perry and Green, 1997].

Fane [1986] has discussed the long-term flux decline of ultrafiltration in terms of factors such as pore plugging, deposition/adsorption and cake consolidation. Howell and Velicangil [1987] have also divided UF process into three main steps:

- 1 First few seconds: A quasi-steady state concentration polarization layer is set up.
- 2 1 to 10min: Solute adsorption.
- 3 Long-term: Gelation

Adsorption is determined by the membrane material and solute(s) interaction. Dal-Cin and co-workers [1995] illustrated the adsorptive fouling of pulp mill effluent using different membrane materials. They reported that the relatively hydrophobic materials such as polysulphones and polyether-imide exhibited severe adsorptive fouling when compared to hydrophilic membranes. The same conclusion was drawn by Choe et al. [1986] earlier for the filtration of bovine serum albumin (BSA). Dal-Cin et al [1995] suggested using the ratio of the number of pores (n) to the pore length (Δx) per unit area (A) to evaluate fouling mechanisms. An increased $n/\Delta x A$ ratio indicates that adsorption occurred on the membrane surface rather than in the pores.

Fouling was further investigated by Dal-Cin et al [1996] who suggested that flux loss ratio (FLR) was as an alternative way to present the individual resistances due to adsorption, pore plugging and concentration polarization. FLR's are based on the

ratio of the absolute flux decline for a given mechanism to the overall flux loss. They concluded that pore plugging was a more important factor with the open membranes while surface adsorption was more likely for lower MWCO membranes. Overall, adsorptive fouling has been recognized as a significant factor in flux decline [Brites and Pinho, 1993; Babu and Gaikar, 2001].

As mentioned earlier, adsorption is affected by the interactions between the solute and the membrane. All membranes and macro-solutes will eventually acquire a net surface charge either due to the adsorption of negative or positive ions from the solution and/or ionization of any acidic groups (e.g. $-\text{COOH} > -\text{COO}^-$) or an increase in deionization of any basic groups (e.g. $-\text{NH}_3^+ > -\text{NH}_2$). Most membranes possess net negative charge at neutral pH [Cheryan, 1998]. The magnitude of the electrostatic interactions between the membrane and the charged solutes depends on ionic concentration of the solution. The dissolved electrolytes will provide shielding and thus reduce the electrical interactions between the charged surfaces. The electrical double layer, measured as the Debye length, is formed when the membrane's charged surface attracts cations or anions, resulting in a more positive or more negative region immediately adjacent to the surface [Zeman and Zydney, 1996]. According to Zeman and Zydney [1996], the effect of electrical interactions becomes negligible when the membrane surfaces are separated by more than a few Debye lengths.

2.2 Semiconductor Photocatalysis

2.2.1 General

Photocatalysis is a reaction occurring in the presence of a catalyst and the energy of light. *A catalyst is a substance which either speeds up or slows down a chemical reaction, but which itself undergoes no permanent chemical change* [Michel, 1997]. There are basically two types of photocatalytic process, namely homogeneous and heterogeneous photocatalysis. Homogeneous process, which consists of only a

single phase, utilizes oxidizers such as ozone (O_3), hydrogen peroxide (H_2O_2) or fenton reagent for the degradation of organics. In the case of fenton reactions, hydrogen peroxide reacts with ferrous sulphate (fenton reagent) and UV light to produce hydroxyl radicals which are known to be powerful oxidants [Malato et al., 2002]. On the other hand, heterogeneous photocatalysis uses air or oxygen and semiconductors at low (ambient) temperature to photodegrade the targeted compounds. A good photocatalyst should be (i) photoactive, (ii) able to utilize visible/ to near UV light, (iii) biologically and chemically inert, (iv) not prone to photocorrosion, (v) inexpensive and (vi) nontoxic. Many semiconductors such as Si, ZnO, ZnS, TiO_2 and Fe_2O_3 can be used as photocatalysts. However, TiO_2 has been regarded as the most pertinent catalyst due to its superior properties with regard to chemical stability, high permittivity, non-toxicity and insolubility [Matthews, 1993]. It also has added advantages of being commercially available and inexpensive.

Heterogeneous photocatalysis in purification and sterilization of wastewater has several advantages over competing processes. These are,

- (1) complete mineralization,
- (2) no waste disposal problem
- (3) low cost since the oxidant is ambient oxygen
- (4) only mild temperature and pressure conditions are necessary
- (5) long wavelength UV such as the natural UV component of sunlight is able to activate TiO_2 and thus potentially no power sources are required

The drawbacks of photocatalytic processes include:

- (1) It is very difficult to achieve uniform light irradiation of the entire catalyst surface with the same incident intensity. The scale-up from laboratory to industrial scale is constrained by the phenomena of opacity, light scattering, depth of radiation penetration and local volumetric light absorption.
- (2) The ultrafine TiO_2 particle separation in a suspended form of reactor can be an inconvenient, time consuming and expensive process.

- (3) As will be discussed later, the presence of radical scavengers such as humic acid and the presence of anions and cations in real effluents affect the overall photoactivity of the system. The rates in real applications will thus be substantially lower to that observed in the model effluent studies.

2.2.2 Mechanisms of Heterogeneous Photocatalysis

TiO₂ particles act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an unfilled conduction band [Hoffmann et al., 1995]. The absorption of light energy ($h\nu$) equal or greater than the band-gap (ΔE_{gap}) energy of the semiconductor promotes electrons from the valence band (V_b) to the conduction band (C_b), creating positive holes (h^+) at the valence band and extra electrons at the conduction band (e_{cb}^-) as shown in Equation 2.3 and Figure 2.6. These electron-hole pairs have potential energies corresponding to the thermodynamic levels, E_{cb} for the electrons and E_{vb} for the hole, where $E_{cb} - E_{vb}$ is the band gap energy (ΔE_{gap}).

Figure 2.6 An illustration of the photogeneration of electron-hole pairs.

The magnitude of the fixed band gap varies for different semiconductors and this determines the sensitivity of an individual semiconductor to irradiation. Anatase TiO₂ has a bandgap energy of 3.2 eV while rutile TiO₂ has a bandgap energy of 3.0 eV. TiO₂ in the anatase and rutile crystalline forms behave as classical semiconductors. Illumination of these forms of TiO₂ with light less than 385nm

promotes a redox environment. However, many researchers have concluded that rutile TiO_2 is much less active than anatase TiO_2 as a photocatalyst [Bhatkhande et al., 2001].

Redox reaction takes place on the TiO_2 surface due to the presence of the positive holes at the valence band and the negative electrons at the conduction band. These charge carriers can recombine or diffuse rapidly to the surface for reduction or oxidation processes [Kroschwitz et al, 1996]. From a thermodynamic point of view, any species can be oxidized if the reduction potential of the species is more negative than the valence band energy ($E_{\text{ox}} < E_{\text{vb}}$). The same applies to the reductive processes. Any species can be photoreduced provided that the reduction potential of the species is more positive than the potential of the conduction band ($E_{\text{red}} > E_{\text{cb}}$).

If a photogenerated hole reaches the surface of TiO_2 , it can oxidize an adsorbed substrate by accepting an electron from the substrate. Similarly, the negative electron donates an electron to the adsorbed substrate so as to photoreduce the substrate. Simplified Equations (2.4) and (2.5) represent oxidation and reduction processes respectively with the donor (D) and acceptor (A) being the adsorbed substrates.

For application of photocatalysis in an aqueous environment, D can either be water (H_2O) or an organic contaminant. The reaction of holes with H_2O will be far more likely since water is more abundant when compared to the contaminants present. Oxidation of H_2O or hydroxide ions (OH^-) produces hydroxyl radicals ($\text{OH}^\bullet$) which are known to be the most potent oxidizing agents [Bhatkhande et al., 2001]. These oxidizing agents will in turn oxidize the contaminants to carbon dioxide and water by a process known as mineralization.

Equations 2.6 and 2.7 illustrate the process of production of hydroxyl radicals when illuminated TiO₂ interacts with water.

Additionally, in the presence of oxygen (O₂), OH[•] radicals are produced at the conduction band as follows [Cai et. al, 1991]:

2.2.3 Dynamic Overview of Primary Processes in Photocatalysis

The photocatalytic reaction takes place on TiO₂ surface through a series of processes. The interfacial charge transfers as shown in Equations 2.4 and 2.5 are the ultimate reactions of the series of reactions involved in the oxidation or reduction of adsorbed substrates. The complex reaction can be illustrated using Equations 2.12 to 2.18 [Hoffmann et al., 1995].

Charge carrier generation

Charge carrier trapping

Charge-carrier recombination

Interfacial charge transfer

whereby $>\text{TiOH}$ represents the primary hydrated surface functionality of TiO_2 , e_{cb}^- represents a conduction band electron, e_{tr}^- represents a trapped conduction band electron, h^+ represents a valence band hole, Red is an electron donor (reductant), Ox is an electron acceptor (oxidant), $\{> \text{Ti}^{\text{IV}}\text{OH}^{\bullet}\}^+$ is the surface-trapped valence hole (i.e. the surface bound hydroxyl radical) and $\{> \text{Ti}^{\text{III}}\text{OH}^{\bullet}\}$ is the surface-trapped conduction band electron.

Both charge carriers in Equation (2.12) migrate to the surface of TiO_2 in picoseconds, where they are ultimately trapped in shallow traps or deep traps as shown in Figure 2.7 [Beydoun, 1999].

Beydoun [2000] defined shallow traps (represented by Equation 2.14a) as sites where charge carrier recombination will take place rapidly and deep traps (represented by Equation 2.14b) as sites where the charge carriers are long-lived.

Figure 2.7 A simplified diagram of processes occurring in a semiconductor particle [Source: Beydoun, 1999].

Since the recombination of e_{cb}^-/h_{vb}^+ is rapid, the rate of charge carrier trapping must be fast enough to account for this. It is important to recognize that recombination is detrimental to photoactivity of TiO_2 as suggested by Fox and Dulay [1993]. The competition between charge carrier recombination and trapping followed by competition between trapped carrier recombination and interfacial charge transfer (microseconds to milliseconds) determines the overall quantum efficiency of interfacial charge transfer [Hoffmann et al., 1995].

2.2.4 Factors Affecting Photoactivity of TiO_2

2.2.4.1 Effect of pH

The particle size, surface charge and band edge positions of TiO_2 are strongly influenced by pH [Fox and Dulay, 1993]. The flat band potential of TiO_2 particles exhibits Nernstian behavior which shifts 59mV more negative for one unit change in pH. In turn the redox potentials of the photogenerated holes and electrons in the valence bands and conduction bands are affected.

Also, pH of the medium affects the adsorption characteristics of TiO_2 . In order to have an effective carrier charge trapping, the adsorption-desorption equilibria which depend on pH is important. The point of zero charge (pzc) for TiO_2 in water is about $pH_{pzc} = 6.0$. At low pH ($pH < pH_{pzc}$), TiO_2 particles possess positive charge which should enhance adsorption of anions and polar substrates. On the other hand, TiO_2 surface has a negative charge in alkaline media ($pH > pH_{pzc}$) and would enhance adsorption of cations [Kroschwitz, 1996].

Korrmann et al., [1991] postulated that surface adsorption of electron donors on TiO_2 played a more important role than the shifting of the redox potentials of the band edges on the improved rates of oxidation.

2.2.4.2 Effect of Light Sources and Light Intensity

Light with wavelength less than 385nm excites TiO_2 and creates a redox environment. The energy of a photon is related to its wavelength while the overall energy input to a photocatalytic process is dependent upon the light intensity [Bhatkande et al., 2001]. Matthews and McEvoy [1992] showed that shorter wavelength (254nm) radiation was considerably more effective than radiation at 350nm. Furthermore, they reported that a lower catalyst dosage was needed for optimum degradation when using the 254nm light source. The same conclusion that shorter wavelength was more effective in the degradation of 4-chlorophenol was reported by Hofstadler et al. [1994]. This was attributed to the fact that shorter wavelengths carry higher energy.

Figure 2. 8 Radiation spectrum and transmittance of TiO_2 layer [Source: Otaki et al. (1996)].

On the other hand, the transmittance of light source plays an important role when the reactor design utilizes multilayers of immobilized TiO_2 to increase reaction surface. As shown in Figure 2.8, the transmittance of TiO_2 at 254nm (UV) is almost zero whilst at 360nm (black light), it is more than 80%. Thus, black light whose wavelength is 365nm is more useful in TiO_2 immobilized system since it is able to pass through the TiO_2 layers [Otaki et al., 1996].

Light intensity (I) is one of the important operational parameters that affect photocatalysis rate. Generally, degradation rate is proportional to $I^{0.5}$ and $I^{1.0}$ at high and low intensity respectively [Chen and Ray, 1999]. An increase in light intensity resulted in a decrease in survival ratio of *E. coli* [Horie et al., 1998] or an increase in the rate of degradation of chlorinated hydrocarbons [Crittenden et al., 1997]. Nonetheless, it should be noted that there is a limit to the advantage of having high light intensity because a high photon rate will lead to faster recombination of charge carriers, e_{cb}^- / h^+ [Litter, 1999]; thereby decreasing the overall photoactivity of the system.

2.2.4.3 Effect of Presence of Inorganic Anions

The efficiency of a photocatalytic process on titanium dioxide is dependent on the presence of inorganic anions. The presence of co-dissolved species can have a substantial influence on the rate of photocatalytic oxidation [Abdullah et al., 1990]. Abdullah and co-workers [1990] have investigated the effect of common inorganic anions on the rates of photocatalytic oxidation of salicylic acid, ethanol, 2-propanol, phenol and aniline. It was found that at pH 4.1, sulphate, chloride and phosphates reduced the rates of oxidation even in millimolar concentrations. They also reported that perchlorates and nitrates had little effect.

On the other hand, Kormann et al., [1991] proposed that the degree to which the anions inhibited degradation was correlated strongly with the extent to which they sorbed to the catalyst surface. In their study, they found that the attachment of carbonate ions reached a maximum at pH 5 while the attachment of chloride ions was only significant at low pH. Due to electrostatic repulsion between the anions and the photocatalyst, no inhibition was observed at higher pH. These results were supported by D' Oliveira et al., [1993] who found no change in the initial rate of photocatalytic transformation of 3-chlorophenol by addition of chloride, sulphate, nitrate and bicarbonate at pH 8, but did observe an interfering effect by chloride and sulphate at low pH.

Further work by Wang et al. [2000] showed similar results as that of Korrman et al., [1991]. Wang and co-workers [2000] observed that at pH 4, the presence of chloride and sulphate ions showed inhibitive effects on the photocatalytic degradation of o-methylbenzoic acid while at pH 11, the addition of chloride ions did not influence the reaction. They also reported that the presence of sulphate at pH 11 slightly promoted the reaction.

Overall, the effect of the inorganic anions on the photoactivity of TiO_2 varies with the type of organic solute, the pH of the solution and the concentration of the anions present.

2.3 Membrane-Photocatalytic Reactor Configurations

2.3.1 Selected Reactor Design Considerations

Since fouling is the main concern for the efficiency of a membrane system, the design of the membrane equipment should therefore aim to reduce concentration polarization. To reduce the solid concentration at the surface, good mixing should be the priority choice [Cheryan, 1998]. Mixing can be enhanced by paddle mixers in laboratory-scale apparatuses, static mixers in large-scale designs or mesh-spacer turbulence promoters in plate designs. The design of ‘thin channel’ is also favourable for maximizing the shear rate at the membrane surface.

In any design, there is always a trade-off between the amount of membrane area used and the numbers of supporting equipment such as the pumps and pipes. Perry and Green [1997] suggested three issues that would drive a design toward the use of more membranes and less mechanical equipment: 1) cheaper membranes, 2) very high flux, and 3) very low flux. Besides the design issue, optimization of operating conditions e.g. pressure, pH of solutions, flow rate, temperature and feed concentration, plays a vital role in creating an efficient membrane system.

The main challenge in the photoreactor design is to achieve uniform radiation of the entire catalyst surface at the incident light intensity [Dijkstra et al., 2001]. This is a major problem associated with large-scale designs. Efficient illumination of the catalyst will ensure high activity in the reactor. In a suspended system, the suspensions have to be well-mixed so that all particles are illuminated. Furthermore, a laminar thin film reactor such as those described by Turchi and Ollis (1990) as well as Li and Yue [2003] can be used to achieve a large illuminated surface area with minimal mass transfer limitations.

Another point that needs to be considered in large-scale photocatalysis design is the elimination of mass transfer resistances. This problem is less significant in a slurry type reactor and most likely to occur in an immobilized TiO_2 reactor [Gogate and Pandit, 2004]. A good reactor design must have a high density of immobilized catalyst illuminated by the light source as well as to be in close contact with the liquid to be treated. Thus, the thickness of the supported catalyst should be small enough to allow light to penetrate to all the catalyst [Dijkstra et al., 2001].

Reactor design accomplished with modeling and simulation would shorten the time needed for expensive lab-scale trials. The modeling done by Ray is worth mentioning in this field [Ray, 1998; Ray 1999]. Ray [1999] modeled reactor performance by incorporating the effects of intensity, incidence angle, tube diameter and wall thickness. He then constructed an immobilized reactor based on the modeling output and obtained results that were very promising. Li and Yue (2003) modeled the thin-film slurry system in terms of radiation source, light absorption, fluid dynamics and geometry. Detailed modeling studies of radiation extinction by the TiO_2 suspension were done by Cassano and Alfano (2000) and Pozzo et. al. (2002).

2.3.2 Photocatalytic Immobilization System

2.3.2.1 Immobilization of TiO₂ on Non-porous Substrate

With regard to the post-treatment issue of suspended TiO₂ systems, coating of TiO₂ on supports has been widely studied in the field of photocatalysis. Sunada et al [2003] evaluated the coating of TiO₂ on a thin glass film for the photokilling of bacteria. Tabatabaie-Raissi and co-workers [1997] invented the concept of coating of TiO₂ on wood such as wooden furniture to inhibit the emission of volatile organic compounds (VOC). The coating of TiO₂ acts as a chemical membrane possessing the photocatalytic ability to degrade the formaldehyde emitted from the wooden substrate.

One of the most common TiO₂ immobilization medium is the optical fiber [Peill and Hoffmann, 1995; Choi et al., 2001; Wang and Ku, 2003]. However, most of the applications involving optical fibers as the immobilizing medium are used for the treatment of air. Similar to those configurations described before, the photocatalyst is coated on a non-porous support whereby the treated contaminants are not able to flow through the support. With this type of configuration, the efficiency of the process is decreased [Bischoff et al., 1999] due to the large area to volume ratio of the immobilized system.

2.3.2.2 Immobilization of TiO₂ on Porous Substrates

Studies on immobilization of TiO₂ have also been extended to the use of porous supports. In this case, the contact frequency and time of the organic substrate and TiO₂ will be greatly enhanced since the organic substrate is allowed to pass through the porous support. Also, the area to volume ratio of the photoreactor will be increased as compared to a TiO₂ non-porous support reactor.

The decomposition of estrogens was demonstrated with the use of TiO₂ - Polytetrafluoroethylene (PTFE) mesh sheets. TiO₂ was immobilized on stacks of mesh sheets and immersed in a 5L photoreactor with the help of a rotating motor

[Nakashima et al., 2003]. It was found that the reaction rate was proportional to the square root of the rotation speed of the mesh sheet, which was mainly due to the mass-transfer limited condition in their system. Villacres et al. [2003] studied the immobilization of TiO_2 nano-particles on stainless steel mesh and fiberglass cloth for the decomposition of volatile organic compounds (VOCs). Attempts have also been made to immobilize TiO_2 photocatalysts on porous ceramics and fabricating a micro-channel reactor using these ceramics [Teekateerawej et al., 2006]. The effects of surface roughness and circulation velocities for methylene blue degradation were reported. A velocity above a critical value of 5mL/min, was found to increase the stagnation region around the TiO_2 laminar flow channel and thus inhibited the degradation of methylene blue.

Another popular porous support is the use of membranes. Photocatalytic membranes have been used successfully to photodegrade alkanoic acid [Rivas et al., 1998], phenol [Barbara et al, 1995] and dye [Zhang et al., 2006]. These membranes can be either ceramic or polymeric and many of the ceramic membranes include the combination of TiO_2 with other oxides such as aluminium oxide and zirconia to improve the properties of the membranes. Sekulic et al. [2004] reported that the zirconia/titania membrane permeability was eight times higher than the alumina membrane.

It is worth to mention the photocatalytic membrane patented by Bischoff and co-workers [1999] as shown in Figure 2.9.

Figure 2.9 Patented design of photocatalytic membrane reactor (7', optical fibre to transmit light to the catalytic membrane) [Source: Bischoff et al., 1999].

The design comprises the use of optical fiber transmission as the light source for direct illumination of the membrane surface. The group claimed that this design ensured that the chemically active TiO_2 surface would have constant contact with the selected reactants flowing through the membrane support. The invention could be used for removal of VOCs, metal stripping and recovery of metals and the preparation of Ultrapure water.

2.3.3 Coupling of Photocatalysis and Filtration (Individual System)

Many reports favour suspended systems in terms of photocatalytic efficiency of the organics when compared to an immobilized system [Sabate and Anderson, 1992], Geissen et al. [2001] and Kuo [2000]. A comparison between a suspended and an immobilized system is shown in Table 2.1 [Lasa et al., 2004].

Table 2.1 Suspended versus immobilized photocatalytic systems

Slurry reactors	Immobilized reactors
<i>Advantages</i> <ul style="list-style-type: none"> Fairly uniform catalyst distribution High photocatalytic surface area to reactor volume ratio Limited mass transfer problems Minimum catalyst fouling effects due to the possible continuous removal and catalyst replacement Well mixed particle suspension Low pressure drop through the reactor 	<i>Advantages</i> <ul style="list-style-type: none"> Continuous operation Improved removal of organic material from water phase while using a support with adsorption properties No need for an addition of catalyst separation operation
<i>Disadvantages</i> <ul style="list-style-type: none"> Requires post-process filtration Important light scattering and adsorption in the suspended particle medium 	<i>Disadvantages</i> <ul style="list-style-type: none"> Low light utilization efficiencies Restricted processing capacities due to possible mass transfer limitations Possible catalyst deactivation and catalyst wash out.

Although the suspended system offers a more intensive treatment, it requires post-treatment to separate TiO_2 particles from the photocatalytic treated water. Several attempts have been made to facilitate the recovery of particulate catalysts which include improving the aggregation of TiO_2 through pH adjustment [Fernande et al., 2003] and enhancing the separation of TiO_2 in a magnetic field by coating it onto magnetic particles [Beydoun et al., 2000]. These methods enhance sedimentation and thus facilitate the recovery of the catalysts in a batch process. Nevertheless a limitation to these methods is that the treated water cannot be withdrawn continuously during the oxidation process without losing any TiO_2 catalysts.

Membrane technology could improve the implementation of the photocatalytic oxidation (PCO) process by enhancing the separation of particulate TiO_2 from the treated water. In this case, a higher throughput of treated water may be achieved. According to Molinari and co-workers [2000], the coupling of a photocatalytic reaction with a membrane separation could result in a very powerful system, with

the membrane performing the task of retaining the catalyst as well as acting as a selective barrier for the species to be degraded. In a comparison of continuous membrane (NF-UF) photocatalysis processes, the membrane reactor with suspended photocatalysis was preferred to fixed-bed, either membrane entrapped or immobilized TiO_2 , due to higher photocatalytic activity [Molinari et al., 2002]. The suspended catalyst reactor was found to be 30% more effective than the TiO_2 immobilized membrane.

The membrane options for use with photocatalytic reaction include high - pressure NF as used by Molinari et al. [2002], or low-pressure membranes such as MF and UF [Fu et al., 2006]. Molinari et al. [2002] demonstrated the degradation of humic acid, organic dyes and 4-nitrophenol using a hybrid photocatalytic-nanofiltration unit operating at a system pressure of 6 bar. In their study, the use of nanofiltration (NF) membrane was to retain both the photocatalysts and the organics in the system during the photocatalytic reaction. Though it was reported that the parent organic compound could be retained till complete degradation, some of the smaller molecular size intermediates that formed during the photocatalytic process were still able to pass through the nanofiltration membrane, which lowered the overall efficiency in terms of mineralization. This group also discussed how the rejection of the NF membrane depends on the type of organics and their interactions with the NF membranes. The choice of NF membrane is thus important since the membrane will retain small molecules carrying the same membrane charge due to electrostatic repulsion. Molinari et al. [2004] extended their work to the degradation of dyes, Congo red and Patent blue, where they examined the influence of different operational parameters so as to obtain the highest reaction rates, operating stability and high membrane rejection. Recently they set up a solar photoreactor followed by a NF membrane flat-sheet pressurized module for the degradation of lincomycin, an antibiotic [Augugliaro et al., 2005]. The coupling of solar energy has indeed broadened the application of photocatalysis since sunlight is abundant in many countries

NF has the advantage of retaining low molecular weight species but low-pressure MF and UF have an energy benefit since they can be operated at a much lower transmembrane pressure. In the experimental setup of Sopajaree and co-workers [1999a], wastewater that had been treated in a photoreactor was pumped to a side-stream hollow-fiber ultrafiltration membrane unit so as to retain the TiO_2 in the system. In the presented work, ultrafiltration provided a complete separation of the TiO_2 particles. Fu et al. [2006b] degraded NOM (fulvic acid) in a suspended photoreactor and the spent TiO_2 was recycled back to the reactor after separation using a 50kg/mol UF membrane. Lee et al. [2001] studied the fouling phenomena and the effect of natural organic matters (NOM) on the filterability of the TiO_2 cake. They found that a denser TiO_2 cake was formed in the presence of humic acid. However, if the humic acid had undergone photodegradation before filtration, the flux was greatly enhanced due to the formation of less adsorbable intermediates. Thus, photocatalytic processes in some cases could help to decrease fouling problems of membranes.

Cross-flow MF with a nominal pore size of $0.2\mu\text{m}$ has been reported to be able to separate TiO_2 successfully [Xi and Geissen, 2000]. The medium particles size ($X_{50\%}$) of TiO_2 at pH 6 and 8 was found to be about $3.5\mu\text{m}$ which was much greater than the MF membranes used. In another report, a $0.22\mu\text{m}$ membrane was not only able to retain TiO_2 particles completely in a closed-system comprised of a photoreactor followed by a separate MF module; the membrane also removed 18% of the total organic carbon (TOC) [Le-Clech et al., 2006].

2.3.4 Photocatalytic-Membrane Filtration Hybrid System

Limited work has been reported on the possibility of combining photocatalytic and membrane processes into a single reactor though membrane filtration has been demonstrated to fulfill the task of retaining TiO_2 . The definition of single reactor refers to the design whereby photocatalysis and membrane filtration occur in the same module. Molinari et al. [2000] have been the pioneers for combining the two

processes into a single reactor. Their system (Figure 2.10) consisted of a flat sheet membrane module with a quartz opening in which UV light was illuminated directly onto the membrane.

Figure 2.10 Suspended catalyst in the recirculation tank with the irradiation of flat sheet membrane cell [S: recirculation tank, Rp: permeate tank, L: UV lamp, R: flat sheet membrane] [Molinari et al., 2000].

The UV light employed in the above setup was a 500W medium pressure mercury lamp, giving a light intensity of 6.4 mW cm^{-2} . A series of preliminary tests were done to obtain the best polymeric UF membrane, polyacrylonitrile (PAN), which was stable under UV irradiation. The group also compared results for two types of reactor configurations, suspended catalyst and deposited catalyst, both employing flat sheet membrane systems. They found that the suspended catalyst reactor achieved degradation of 80% of 4-nitrophenol in 5 hours (hrs) compared to 51% in an immobilized system.

Sun and co-workers [2003] attempted to combine photocatalysis and membrane technologies to deactivate *E. Coliform* (*E. coli*) in water. Their experimental setup as shown in Figure 2.11 comprised a low-pressure mercury lamp suspended vertically in the middle of the reactor. A cylindrical pyrex sheath was fitted with an air diffuser and the membrane employed, an inorganic-based ceramic membrane,

was incorporated into the system as shown. The use of a novel composite photocatalyst $\text{TiO}_2\text{-Fe}_2\text{O}_3$ removed the *E. coli* at a rate as high as 99% at a dissolved oxygen level of 21.34mg/L.

Figure 2.11 Schematic diagram of membrane photocatalytic suspended system to treat *E. Coli* [Sun et al., 2003].

Fu et al. [2006a] have described a submerged membrane photoreactor for the degradation of fulvic acid. The reactor consisted of two compartments, for filtration and photocatalytic oxidation, in a single reactor (Figure 2.12). As shown, though in the same reactor, the photocatalytic reaction and the membrane filtration occurred in different compartments of the reactor. An ‘in-house’ synthesized TiO_2 of 50 μm size was used and reported to enhance the separation of TiO_2 and to maintain high flux of filtrate due to the larger particle size compared to that of Degussa P25 (a commercial TiO_2). It was also shown that a removal of 73% of total organic carbon (TOC) could be achieved within 2 h of UV irradiation.

Figure 2.12 Schematic diagram of submerged membrane photoreactor [Fu et al., 2006a].

In summary, heterogeneous photocatalytic oxidation is an effective mean for removing trace organics from water. A suspended catalyst, such as TiO_2 , coupled with low pressure membranes holds promise as a low energy hybrid process. Based on the prior work, there is a need for further research to integrate photocatalytic oxidation and membrane filtration processes. Areas for optimization include membrane selection, reactor configurations, methods of light input, operating mode (batch vs continuous), aeration intensity and membrane fouling management. This thesis addresses these issues.

CHAPTER 3

INVESTIGATION OF STABILITY

OF POLYMERIC MEMBRANES*

3.1 Introduction

3.1.1 Choice of Membranes

The properties of membranes play a part in the efficiency of the separation process [Perry and Green, 1997]. Therefore, a good choice of membrane is important. For MF and UF membranes, there are basically two types of membranes used commercially, namely the polymeric and the ceramic membranes. The factors that affect the separation efficiency of the membrane include retention ability, hydrolytic stability, permeability, chemical and temperature resistance, adsorption ability and service life.

Ceramic membranes have emerged as a type of membrane to be considered when harsh conditions are encountered during the separation process. Ceramic membranes possess superior physical integrity as well as chemical and thermal resistances. Zhao et al [2002] investigated the recovery of fine TiO_2 particles from acid wastewater using tubular $\alpha\text{-Al}_2\text{O}_3$ membrane. They studied the fouling mechanism of the ceramic membrane and concluded that the regeneration of membrane was possible using a backpulsing technique. The same conclusion was drawn by Xu et al [2002]. They found that ceramic membranes had exceptional performance for cleaning and regeneration when compared to organic membranes. Regardless of the advantages associated with ceramic membranes, they are not as commonly applied on an industrial scale as the organic membranes because of their higher production cost. The production costs of ceramic membranes are many times

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higher than that of a polymeric type [Moritz et al., 2001]. Also ceramic membranes may be too rigid to be used in some applications, for example those whereby flexibility of the membrane is required.

Polymeric membranes on the other hand are widely used in all types of membrane separation processes. Many polymeric membranes available nowadays have excellent hydrolytic stability especially Polytetrafluoroethylene (PTFE), polysulphone (PS), polyvinylidene fluoride (PVDF), polyethersulphone (PES) and acrylic copolymers [Perry and Green, 1997]. Not all types of polymers can be made into membrane and different polymers actually form different types of membrane structures. The polymer chosen has to be a good membrane former i.e. compatible with selected membrane technology, easily available and affordable and suitable for the targeted application [Zeman and Zydney, 1996].

3.1.2 Stability of Polymeric Membranes

3.1.2.1 Factors Affecting Stability

Most polymers undergo photolytic, photooxidative, and thermo-oxidative reactions when exposed to UV radiation. These processes lead to the degradation of the material. The degradation suffered can range from mere surface discolouration to loss of mechanical properties of the polymers [Fechine et al., 2002]. Data regarding the photodegradation of some common polymeric materials are widely available [Zhang et al., 1996; Torikai and Hasegawa, 1997; Gesenhues, 2000; Fechine et al., 2002; Martin et al., 2003]. The polymers investigated include Polymethylmethacrylate (PMMA), Poly(vinyl chloride) (PVC), Polypropylene (PP), Poly(ethylene terephthalate) (PET) and some Polystyrene blends.

Besides understanding the mechanisms of degradation, knowing the wavelength sensitivity of certain materials is also important. Andrady [1998] has done a thorough study on the wavelength sensitivity of different polymers and found a linear relationship existed between the logarithm of the effectiveness of damage and the wavelength of exposure, with higher damage per incident photon obtained at the

shorter UV wavelength. It is worth noting that even with the same type of polymer, the effective wavelength region may not be the same depending on the irradiation time [Hu, 1997] and also on the amount and type of additives present [Torikai and Hasegawa, 1997].

Some laboratory tests on the degradation of polymeric materials were carried out under conditions of simulated weather conditions [Zhang et al., 1996]. The rates of degradation depend on the type of polymer, moisture content, temperature and on the UV flux. Reciprocity law with extrapolation of results from high radiant flux to low radiant flux has been successfully employed in the medical and biological fields [Martin et al., 2003]. However, there is a lack of acceptance for the aging test done using laboratory weathering tests. The reason is due partly to the knowledge that the spectral emissions from laboratory light sources are different from that of the solar emission. Thus, the type of light source plays a part in the degradation mechanism of the polymer.

3.1.2.2 Oxidative/UV Stability of Polymeric Membranes

In order for a polymeric membrane to be used in a TiO_2 /UV process, the membrane has to be stable under UV exposure as well as in an oxidative environment since photocatalysis produces oxidizing hydroxyl radicals. Ceramic membranes are attractive for this application, but are disadvantaged by their significantly higher costs than the polymeric types [Moritz et al., 2001]. In view of this economic concern, suitable polymeric membranes should be sought for this application. Many polymers are unstable in such environments. Hisao et al [1996] and Horikoshi et al. [1998; 2001] developed a series of tests to study the degradation of polymers in aqueous TiO_2 suspensions with the aim of solving the disposal problem associated with different types of polymer including Polyvinylpyrrolidone (PVP) and Poly(vinyl chloride) (PVC) by photocatalysis. Horikoshi and co-workers [2001] inferred that the break down of PVP involved three steps. The first step was the adsorption of water soluble PVP onto TiO_2 surfaces, followed by an attack of the polymer by $\text{OH}^\bullet$ and/or $\text{OOH}^\bullet$ radicals. The second step was the degradation which

causes the main chain of PVP to undergo cleavage and the final major step involved the very slow photomineralization of PVP to NH_4^+ and NO_3^- ions and carbon dioxide.

Although extensive data are available for the study of UV photodegradation of a wide variety of polymers, there is a limitation to the usage of these data. The extrapolation of research findings on UV-induced degradation of pure polymer resins to compounded and processed products of the same polymer is often unreliable [UNEP, 1998]. Photodegradation data generated on the actual polymer formulations offers the most useful data for assessment of damage. Therefore the effect of photocatalyzed TiO_2 degradation on polymeric membranes should be investigated before selecting suitable membranes for the photocatalytic reactor process that involves activated TiO_2 .

Only a few studies have reported the UV stability of polymeric membranes. The most relevant work to date is by Molinari et al [2000] who reported preliminary work on the effects of UV light on some polymeric membranes for their membrane photocatalytic reactor. This group found that commercial membranes made of PAN (Tech-Sep), Polysulphone (PS) + Polypropylene (PP) (GR 51-TechSep) and fluoride + PP (FS 50 PP-Dow) were the more stable membranes after 24 hours of UV exposure. They further concluded that polymeric membranes could be used for photocatalytic processes on the basis of these preliminary tests to select the suitable membranes. To date (to the best of the author's knowledge), no detailed works have been carried out to study the stability of polymeric membranes under photocatalytic oxidative environment.

In this chapter, a detailed stability study is reported with membrane exposure to UV and UV/ H_2O_2 conducted in order to evaluate the rate and mechanism of degradation of selected polymeric membranes that could be potentially used in a coupled membrane-photocatalytic application. Flat sheet membranes were used in this study since they are readily available commercially compared to hollow fiber membranes. The specific type of hollow fiber membrane to be used for future experiment was

then sourced and tested for stability after a suitable membrane material had been identified from the flat sheet membrane study. The oxidative effects of photocatalysis on the membranes under different filtration conditions, i.e. with and without TiO₂ deposition (cake formation) were investigated. Formation of a layer of powdered activated carbon (PAC) to separate the TiO₂ cake and the membrane surface was also done in order to investigate the degradation mechanism of TiO₂ on the polymeric membranes.

3.2 Experimental

3.2.1 Preliminary Screening of Membranes

3.2.1.1 Materials

Ten types of polymeric membrane (Table 3.1) were subjected to the stability test. The hydrogen peroxide used in the oxidation test was 30% by weight from Merck Co. All tests were performed using Millipore Co. MilliQ (MQ) water of 18.2MΩ cm resistivity unless otherwise stated.

Table 3.1 Types of membranes used in the UV exposure test.

	Suppliers	Type of membranes	*	Pore Size
1	Millipore	Polyvinylidene Fluoride (PVDFphobic)	HPO	0.22μm
2	Millipore	PVDF-MP	HPY	0.22μm
3	Pall Filtration	PVDF-Pall	HPO	0.1μm
4	Millipore	Polycarbonate (PC)	HPY	0.1μm
5	Osmonics	Polysulphone (PS)	HPY	600kDa
6	Cole Parmer	Polytetrafluoroethylene (PTFE)	HPO	0.2μm
7	Osmonics	Polypropylene (PP)	HPO	0.1μm
8	Cleanseas	Polyacrylonitrile (PAN)	HPY	≈40kg/mol
9	Millipore	Polyethersulphone (PES)	HPO	50kg/mol
10	MFS	Cellulose Acetate (CA)	HPY	0.2μm

* HPO = hydrophobic membrane, HPY = hydrophilic membrane

3.2.1.2 Procedure and Analytical Measurements

All hydrophilic and hydrophobic membranes (47mm diameter) were pre-treated before the stability test. MQ Water was passed through all the hydrophilic membranes for 30min to ensure the removal of membrane surface preservatives. The hydrophobic membranes were wetted for 15min with 80% w/w ethanol followed by 30min of MQ water permeation to remove all ethanol from the membrane surface and pores. The pre-treated flat sheet membranes were placed face down in covered and sealed Pyrex petri dishes filled with MQ water and were exposed, 1 day to 30 days, to two 20W NEC UV-A blacklight lamps (wavelength ranging from 300 to 430nm with peak at 365nm, refer to Figure 3.3) which were placed 7cm away from the bottom of the petri dish. The incident light intensity was 2.1mW/cm^2 as measured by a radiometer (International Light PMA 2200) equipped with an UV-A sensor (PMA2110). A pure water flux (PWF) test at constant pressure (100kPa for ultrafiltration membranes and 20kPa for microfiltration membranes) before and after UV irradiation was carried out using a laboratory dead-end cell setup (Figure 3.1a). The results are presented as the change in membrane resistance using Equation 3.1 to 3.3.

$$R = \frac{\Delta TMP}{J\mu} \quad (3.1)$$

$$\text{Ratio changes} = \frac{R_{mi} - R_{mf}}{R_{mi}} \quad (3.2)$$

$$\begin{aligned} \Delta R_m (\%) &= \left[\frac{R_{mi} - R_{mf}}{R_{mi}} \right] \times 100\% \\ &= \left[\left(\frac{1}{J_i} - \frac{1}{J_f} \right) \times J_i \right] \times 100\% \end{aligned} \quad (3.3)$$

where ΔTMP is the transmembrane pressure, μ is the viscosity of the filtrate, R_{mi} and R_{mf} are the initial and final resistances of the membrane, respectively while J_i and J_f are the initial and final permeate fluxes, respectively. A change in resistance

(typically a decrease) was assumed to arise from any damage caused by exposure to UV.

The UV stability of the membranes was also characterized by the amount of total organic carbon (TOC) present in the MQ water before and after a pre-defined time of UV exposure. The organic concentration was determined by a TOC analyzer (Shimadzu V CSH). All aqueous samples in which the membranes were immersed were diluted to 50ml as a base for TOC comparison. Scanning electron microscope (SEM) studies were also carried out with a Joel JSM-5310LV microscope to observe the surface morphology of the membranes before and after the exposure to UV light. The overall change in surface hydrophobicity or hydrophilicity of the membranes was determined with the contact angle test using a Dataphysics contact angle system (Model: OCA20).

The stability of membranes in the presence of 200mM H_2O_2 as the oxidant with and without UV illumination was also investigated through PWF and SEM studies.

3.2.2 Stability of Hollow Fibre Membrane

Figure 3.1b shows the side-stream module made of borosilicate glass where two strands of hollow fibre membranes (0.22 μm , PVDF, BlueStar China) were secured during the UV/ H_2O_2 stability tests. The membranes were soaked in 400mM of H_2O_2 during UV illumination and the outlets of the borosilicate glass tube were sealed. For 30 days of H_2O_2 /UV illumination, the membrane module was placed in a UV box with four pieces of 8W black light lamps surrounding it for illumination of the hollow fibres. The PWF test was carried out before and after UV/ H_2O_2 tests with the outlets of the glass tube connected to a pump. The permeate flux was recorded by a balance and the change in the weight of water filtered was logged by a data acquisition system.

Figure 3.1 (a) Schematic diagram of setup used for flat-sheet membrane pure water permeate flux test and (b) side-stream configuration for hollow fibre membrane stability test.

3.2.3 Experimental Runs with Different Filtration Conditions

3.2.3.1 Materials and Apparatus

In order to study the photocatalytic degradation of membranes under different filtration conditions, a 10kg/mol PES membrane (Biomax PBGC) supplied by Millipore Co. was used. This membrane was specifically chosen as it was found to be UV-sensitive in the preliminary tests. The TiO_2 (P25) used was kindly supplied by Degussa AG, Germany. It has a BET specific surface area of $50\text{m}^2/\text{g}$, crystal size of $\sim 21\text{nm}$ and density of about $3700\text{kg}/\text{m}^3$ [Degussa, 1989]. Figure 3.2 is a schematic diagram of the experimental set-up. A Masterflex peristaltic pump was used to feed the TiO_2 suspension to the stainless steel flat sheet membrane module of size $18 \times 9 \times 4.5\text{cm}$, which had a Pyrex window panel where the membrane was directly exposed to the UV light. The active membrane area was 48.6cm^2 . Two UV-A blacklight lamps ($2 \times 8\text{w}$) with identical emission spectra were used for illumination. The lamps were placed at a distance of 5cm away from the window panel and the measured power intensity was $1.35\text{mW}/\text{cm}^2$. The suspensions were prepared by subjecting the appropriate amounts of MQ water and TiO_2 at the desired pH to sonication for 10 minutes. The pH of the suspension was adjusted and

maintained using NaOH and HClO₄. The Norit SA2 PAC used for the two layers study was supplied by Norit Nederland and the average size of the PAC was reduced by grinding to about 8µm (d₅₀, as determined by Mastersizer Malvern 2000).

Figure 3.2 Schematic diagram of the flat-sheet membrane photoreactor.

SEM was also used to view the surface and cross-sections of the cakes formed on the membrane. A UV-Vis Spectrophotometer (Jasco-V550) with an integrating sphere attachment (ISV-469) was used to determine the transmittance of the different cake layers. The zeta potential of the PES membrane was measured using an electrokinetic analyzer (EKA) (Anton Paar). In this process, two active layers of membrane samples were placed facing each other in a flat-sheet cross-flow module. The streaming potential was then measured using Ag/AgCl electrodes with 0.01M KCl being the background electrolyte at pH range from 2 to 10 (pH was changed using HCl and KOH). The zeta potential and size distribution of the TiO₂ particles were measured using a ZetaPals (Brookhaven Instruments Corp). FTIR-ATR (Fourier Transform Infrared-Attenuated Total Reflectance) (Perkin-Elmer Spectrum One) was also used to examine the chemical changes to the membrane. The ATR accessory contained a diamond crystal at a nominal incident angle of 45°. All spectra were taken at 50 scans at 4.0cm⁻¹ resolution.

Figure 3.3 Spectral range of the UVA light source used

3.2.3.2 Procedure

Two protocols were used, one with TiO_2 suspension in cross-flow without TiO_2 deposit/cake layer formation, and the other with a TiO_2 cake formed in dead-end operation.

For the non-cake layer formation study, a cross-flow velocity of 0.83m/s (equivalent to $\text{Re} \approx 2500$ in the 1.5mm channel) and a 'sub-critical' flux of $30\text{L}/(\text{m}^2 \cdot \text{hr})$ were used to avoid the deposition of TiO_2 particles on the membrane. The critical flux (below which deposition does not occur and TMP remains constant) was determined empirically by step-fluxing tests whereby the permeate flux was increased in increments of $40\text{L}/(\text{m}^2 \cdot \text{hr})$ up to a flux of $160\text{L}/(\text{m}^2 \cdot \text{hr})$. The TMP of the system was adjusted by regulating the metering valve in the retentate line and the constant flux was measured gravimetrically by a balance (Mettler Toledo PG4002) [Figure 3.2]. A steady state flow of the TiO_2 suspension was achieved before the UV lights were turned on.

For the study in the presence of a TiO_2 cake layer, TiO_2 suspension was filtered in a dead-end (no cross-flow) operation to provide a specific cake loading on the membrane given by,

$$m_c = \frac{V_p C}{A_m} \quad (3.4)$$

where m_c = mass of TiO_2 per membrane area, C = feed concentration, and V_p = volume of permeate. The depth of the cake was approximately calculated by assuming a cake porosity using,

$$t_c = \frac{m_c}{[\rho(1 - \varepsilon)]} \quad (3.5)$$

where t_c = cake layer thickness, ρ = density of TiO_2 particles, ε = porosity of cake. The typical cake porosity was initially estimated by depositing a cake with known m_c and then analyzing the cake layer cross-section thickness under SEM. With the actual thickness obtained, the porosity of the cake was then estimated using Equation 3.5. This process was repeated for a range of m_c and at least three times for each experiment before the estimated porosity was used in the formation of the other required cake layer thicknesses.

For this dead-end protocol, the outlet of the cross-flow membrane module (Figure 3.2) was closed so as to change the system from cross-flow to dead-end. TiO_2 cakes were formed at 180kPa for 45min before the UV-A lights were switched on. The change in permeability of the membrane during light illumination was recorded with respect to time in the presence and absence of a cake layer. For selected runs, the cake layer and the membrane surfaces were examined by SEM at the end of the experiments. In order to measure the UV transmittance of a cake layer, the desired cake thickness was first formed at 180kPa in a dead-end cell. The cake layers together with the membrane were then carefully removed from the cell and placed on the integrating sphere attachment of the spectrophotometer. Transmittance data over the UV range of 300nm to 400nm were then measured and corrected with a clean membrane being used as the baseline.

3.3 Results and Discussion

3.3.1 UV Screening of Membranes

3.3.1.1 One-Day Illumination

The short-term UV stability tests were performed in order to select membranes that are potentially suitable for uses under UV exposure and to eliminate those that are clearly UV-sensitive. Control experiments under darkness were also carried out to ensure that the observed effects were solely due to UV exposure. Furthermore, all tests were run in duplicates or triplicates for statistical verification of changes.

Figure 3.4 shows the stability test results obtained from the microfiltration membranes selected in this study, it can be seen that no significant change in resistances was observed for the PTFE, PVDFphobic, PVDF-Pall and PC membranes. However, the resistances for the PP, CA and PVDF-MP membranes decreased after 24 hours of UV exposure. A change in resistance for a membrane reflects that the membrane has undergone alteration either physically or chemically which changes its flow properties upon the UV exposure. The decreases in PP (20%) and CA (20%) resistance were higher than that of the PVDF-MP membrane (6%).

As shown in Figure 3.5, PP should not theoretically absorb long UV light $> 300\text{nm}$. The observed drop in resistance was most probably due to the absorption of light by the impurity such as chromophores, carbonyl and hydroperoxides, which usually display maximum wavelength sensitivities at about 320 – 370nm [Hamid et al, 1992; Zhang et al, 1996; Fechine et al., 2002]. This range of wavelength coincides with the light spectrum of the UV-A fluorescent light used in the current setup (Figure 3.3), thus activating the photodegradation of PP. In PP, hydroperoxides are produced quite rapidly through an intramolecular hydrogen atom abstraction process as shown in Figure 3.6. Hydroperoxides formed can undergo bond dissociation to produce alkoxy and hydroxyl radicals as shown in Equation 3.6

which is detrimental to the chemical stability of polypropylene since the whole process becomes autocatalytic [Allen and Edge, 2002].

Figure 3.4 Resistances of different microfiltration membranes before and after UV illumination.

Figure 3.5 UV absorption of several polymers [Hamid et al., 1992].

Figure 3.6 Formation of hydroperoxides from polypropylene intramolecular hydrogen atom abstraction process [Allen and Edge, 2002].

Figure 3.7 Resistances of different ultrafiltration membranes before and after the UV illumination (constant pressure: 100kPa).

As shown in Figure 3.7, for ultrafiltration membranes, no significant change in resistance of the PAN membrane was observed. However, the resistances of the PS and PES membrane decreased by approximately 26% and 30% respectively after 24 hours of UV exposure. These changes were relatively higher compared to all the MF membranes. This can be attributed to the fact that PES and PS contain sulphur in their main chain that is highly susceptible to UV-irradiation [Allen and Edge,

1992]. The initiation step in the photodegradation of PS is believed to be the cleavage of the C-S bond and involves main chain scission [Kuroda et al., 1990]. The photodegradation effect of PS and PES membranes were further exemplified with the high TOC leakage of 19mg/L and 12mg/L respectively (Table 3.2). The TOC leakage indicates the presence of organic species released during the photodegradation of the polymeric membrane. It also indirectly shows that the membrane has undergone chemical changes, main chain scissions, that might have in turn affected the overall porosity of the membrane and thus the resistance.

Table 3.2 Comparison of leakage of TOC (mg/L) from the respective membranes after 24 hours of UV exposure.

Membrane	TOC (mg/L)	Membrane	TOC (mg/L)
PC	2.4	PVDF-MP	4.8
PTFE	0.8	PVDF-phobic	1.11
CA	1.1	PVDF-Pall	1.4
PES	11.6	PAN	2.43
PS	18.6	PP	1.45

It is worth noting that no direct relationship could be drawn between the resistance changes and the TOC release measurement results. Changes based on the TOC test (Table 3.2) follow the sequence:

PS > PES > PVDF-MP > PC = PAN > PP > PVDFphobic > CA > PVDF-Pall > PTFE while the changes based on the PWF (resistance) tests (Figure 3.4 and 3.7) follows the order:

PES > PS > PP = CA > PVDF-MP > PC > PVDF-Pall = PTFE = PAN = PVDFphobic.

This observation seems to be contradicting the PS and PES observation whereby high TOC leakage is accompanied by high resistance change as discussed earlier. This might be due to the type of photodegradation chemical change that occurred and the extent of damage that would result in detectable membrane resistance change. For example, the PP resistance change was higher than PC but the TOC detected was 2 times lower. The presence of hydroxyl radicals produced during

photodegradation of PP as shown in Equation 3.6 might have oxidized the TOC released thus resulting in a lower measurable TOC value. Molinari and co-workers [2000], who drew no conclusions between the effect of TOC and resistance results support the findings.

As resistance is closely related to membrane structure, it is probably a more direct measure of membrane damage. However, the TOC results can be seen as secondary indications of membrane damage. For example, as shown in Table 3.2, the amount of TOC released from the PS (19mg/L) and PES (12mg/L) membranes (which showed larger resistance changes) was a magnitude higher than the other membranes such as CA, PAN and PVDF-MP membranes. This confirms that these two membranes are particularly sensitive and not suitable to be used with applications that involve UV light.

3.3.1.2 Three-Days Illumination

The membranes that showed reasonable stability under 24 hours UV-A exposure were also subjected to a longer exposure of 3-days. The TOC results and changes in resistance are shown in Table 3.3 and Figure 3.8, respectively. The ratio changes as shown in Figure 3.8 are the relative percentage changes in the resistance of the membranes based on a new piece of membrane (ratio changes = 1). A value less than 1 would mean that the resistance of the membrane decreases leading to higher water flux after the UV exposure.

Table 3.3 Comparison of leakage of TOC (mg/L) from the respective membranes [TOC values = membrane with UV exposure – membrane in dark (blank test)]

	<i>PTFE</i>	<i>PC</i>	<i>Hydrophilic PVDF-MP</i>	<i>Hydrophobic PVDF</i>	<i>PAN</i>
24hours	0.82	2.43	4.80	1.11	2.43
72hours	6.70	3.98	10.00	4.18	11.00

A 7% increase in resistance of the PC membrane was observed after 72 hours of UV exposure. This finding is interesting and it is postulated that the membrane

morphology changes in a way that the overall pore volume of the membrane is reduced. A decrease in porosity would lead to higher resistance of the membrane after the UV exposure. PC can absorb light in the near UV region and scission of the main chains is the predominant photochemistry for this polymer with the production of benzophenone type products as shown in Figure 3.9. These products, polymeric benzophenone and phenyl esters, account in part for their greater stability to photodegradation when compared to PS and PES which also belong to the heterochain polymers [Allen and Edge, 1992]. This postulation fits well with the 24 hour experimental results whereby the decreases in resistance of PS and PES were 26% and 30%, respectively (Figure 3.7) compared to PC with a change of only 5% (Figure 3.4).

Figure 3.8 Change in resistance of different membranes before and after the 3-days of UV illumination.

Figure 3.9 Photodegradation of polycarbonate [Source: Allen and Edge, 1992]

As observed in Table 3.3 and Figure 3.8, the performance of the hydrophilic PVDF was worse than the hydrophobic PVDF. This could be attributed to the loss of surface coating of the PVDF (hydrophilic) membrane. PVDF membranes are naturally hydrophobic, however, they are modified to serve as low-protein binding hydrophilic membranes [Gabriels, 1999]. Under prolonged UV irradiation, the surface might tend to become unstable and thus alter the structure of the membrane, decreasing the resistance of the membrane after 3-days exposure by about 16%.

3.3.1.3 Thirty-Days Illumination Test

From the previous tests, PTFE, PAN and hydrophobic PVDF were selected and subjected to an even longer UV test. The conditions of the tests were kept constant except for a longer UV exposure time of 30 days. In order to confirm the postulation regarding the unstable coating of the hydrophilic PVDF-MP membrane, another hydrophilic PVDF membrane (from Pall Corporation; PVDF-Pall) was also used in the 30-days test.

Table 3.4 Comparison of leakage of TOC from the respective membranes
[TOC values = membrane with UV exposure – membrane in dark (blank test)]

	<i>PTFE</i>	<i>Hydrophilic PVDF-Pall</i>	<i>Hydrophobic PVDF</i>	<i>PAN</i>
24hours	0.82	-	1.11	2.43
3 days	6.70	2.30	4.18	11.00
10 days	7.63	15.97	4.89	23.48
30 days	13.07	108.96	3.62	28.96

An interesting observation was that the PVDF-Pall membrane released an extremely high amount of TOC of 109mg/L after 30-days of UV exposure (Table 3.4). This value was about 30 times greater than that of the hydrophobic PVDF membrane for which the TOC amount was only about 3.6mg/L. As mentioned before, it is probable that the high TOC detected was due to an unstable hydrophilic coating on the PVDF membrane.

The contact angle of the PVDF-Pall membrane before and after 30-days of UV illumination was measured using the continuous mode of the contact angle system. The continuous mode enables instantaneous recording of the contact angle starting from the time the water droplet touches the membrane till the disappearance of the drop of water. A new piece of PVDF-Pall membrane gave an initial contact angle of 65° and the value dropped to about 17° after 1 min 30 s. However, the UV-exposed membrane started with an almost similar initial contact angle but still had an angle of 37° at 3 min and 11s. This shows that the surface of the PVDF-Pall membrane had been modified by the UV making it less hydrophilic. Triplicates were carried out and the trends observed for the exposed membranes were similar.

ATR-FTIR analysis was performed on the hydrophilic PVDF membranes to identify chemical changes. Figure 3.10 presents typical ATR-FTIR spectra for a new PVDF-MP membrane and a PVDF-MP after 17 days of UV illumination. It can be seen that the peak at 1732cm^{-1} has disappeared from the UV illuminated membrane. According to the manufacturer, the peak at 1732cm^{-1} in the new membrane is associated with the carbonyl stretch of polyacrylate groups that are introduced into the PVDF membranes to make them hydrophilic [Singh et al., 2005]. The loss of this peak further confirmed that the surface of the PVDF membranes had undergone chemical surface changes.

Regardless of the high TOC detected after 30-days, the change in resistance of the PVDF-Pall membrane was within 10% (Figure 3.11). Compared to the PVDF-MP membrane for which the resistance dropped by 15% under the 3-days UV test (Figure 3.8), the PVDF-Pall membrane performance proved to be more robust.

Figure 3.10 ATR-FTIR spectra of Millipore PVDF membrane before and after 17 days of UV exposure. Inset: Enlargement of spectra from 1500 to 1800 cm^{-1} .

Figure 3.11 Change in resistance ratio of membranes before and after the 30-days of UV illumination.

As described in the contact angle study, water droplets on the membrane moved more slowly through the exposed membranes than through the unexposed membranes. This indicates that the exposed membrane had become less hydrophilic and the flux of water passing through the membrane should theoretically decrease which contradicted with the observed data (Figure 3.11). This contradiction may relate to changes in pores size. Mueller and Davis [1996] found that the water fluxes for hydrophilic surface modified PP and Polyethylene (PE) membranes were consistently lower than those of the unmodified membranes, presumably due to slight closure of the pores. Water flux loss after surface modification was also observed by Kim and co-workers [1994]. Therefore, the loss of a hydrophilic surface coating in this study could have opened up the pores slightly and thus increased the permeability of the modified membrane.

The UV resistance study was completed with the 30 days UV-A exposure at 2.1mW/cm^2 intensity. The membranes with acceptable UV resistance include PTFE, PAN and hydrophobic PVDF.

3.3.2 Oxidation Test for Membranes

H_2O_2 itself is a powerful oxidizer and has higher oxidation potential than chlorine, chlorine dioxide and potassium permanganate as shown in Table 3.5. Thus it was decided to use H_2O_2 to investigate the effect of oxidation on the membranes. The study was conducted by soaking the membranes in water containing 200mM of hydrogen peroxide (H_2O_2).

Table 3.5 Oxidation power of respective oxidants (Source: US peroxide, 2003)

	Oxidants					
	Fluorine	Hydroxyl Radical	Ozone	Hydrogen Peroxide	Potassium Permanganate	Chlorine
Oxidation Power, V	3.0	2.8	2.1	1.8	1.7	1.4

Figure 3.12 shows the effect of H_2O_2 on PTFE, PVDFphobic and PVDF-Pall, which does not show any significant changes. However, the PAN membranes performed less effectively in these oxidation tests. The resistance of the PAN membrane declined by approximately 22% after 10 days of exposure to 200mM of H_2O_2 . It is of interest that the PAN membrane was the membrane chosen to be used by Molinari et al [2000] for their study of the photocatalytic membrane reactor. Despite the fact that SEM analysis of the PAN membrane had revealed some damage and 3.7mg/L of TOC release was detected after 24hrs of UV illumination, it was still chosen as the membrane to be used in their photocatalytic reactor because its permeate flux was constant throughout the 24 hrs of UV illumination. The constant permeate flux after 24hrs of UV exposure agrees with the results in Figure 3.7. They also reported that a lower degradation was expected in the photocatalytic reactor due to the greater distance of the lamp from the membrane surface as compared to the stability test and the formation of a catalyst layer on the membrane which could act as a UV filter for the membrane. Their group chose the membrane based on the preliminary UV-stability test but did not carry out tests to investigate the effect of oxidation on this polymeric membrane. This is indeed a true concern since hydroxyl radicals are known to be powerful oxidants as shown in Table 3.5.

Figure 3.12 Change in resistance ratio of the PTFE, PVDF (phobic), PVDF-Pall and PAN membranes under 200mM of H_2O_2 and UV/ H_2O_2 for 10 days.

Under UV illumination with $\lambda < 370\text{nm}$, H_2O_2 in aqueous solution is known to produce powerful hydroxyl radicals by photolysis [Pace et al., 1995]. These hydroxyl radicals lead to more efficient oxidation of many compounds such as dinitrobenzene, benzoic acid [El-Dein et al., 2003; Andreozzi and Marotta, 2004]. In order to evaluate further the stability of polymeric membranes against oxidative hydroxyl radical attack, they were soaked in a 200mM of H_2O_2 solution under UV irradiation ($2.1\text{mW}/\text{cm}^2$) for 10 days.

As shown in Figure 3.12, the changes in the resistances of the hydrophilic PVDF-Pall membrane, PVDFphobic and PTFE were small to negligible. However, the PAN membranes started to show cracks after 10 days of UV exposure. It was also noted that these membranes became hard and started to break into pieces when lifted from the dead-end cell. As a result it was not possible to measure the ratio change for PAN with UV/ H_2O_2 at 10 days for Figure 3.12. A damaged PAN membrane is shown in Figure 3.13. H_2O_2 is a source of free hydroxyl ($\text{HO}^\bullet$) and hydroperoxide ($\text{HOO}^\bullet$) radicals which accelerate degradation processes in polymers as discussed in section 3.3.1.1. Active free radicals are able to abstract hydrogen atoms from macromolecules and initiate efficient polymer degradation. Kaczmarek [1996] has observed similar embrittlement of poly(2-6-dimethyl-1,4-phenylene oxide (PPO) samples exposed to UV/ H_2O_2 environment. They attributed the initial microcracks of their sample to the presence of fragments from the breaking of polymer bonds which occupy more volume than the original macromolecules, leading to stresses and strains in the polymer film. In the case of PAN membranes, chemical change has led to the loss of mechanical properties of the membrane which further confirmed that the PAN membrane is not suitable for use in oxidizing environments although it is quite stable under UV light when compared to other membranes such as PS and PP.

Figure 3.13 Membrane on the right: PAN exposed to H_2O_2 for 10 days. Membrane on the left: PAN exposed to UV/ H_2O_2 for 10 days

Since the degradation and oxidation of polymers generally cause chain scission, one of the most important factors controlling polymer stability is the strength of their primary valence bonds. Thus, the stronger the chemical bond, the more stable the polymer will be. Among these four types of membranes, PAN with structures $(-\text{CH}_2\text{CHCN})_n$ contains the larger number of weaker $-\text{CH}-$ bonds compared to PTFE $(-\text{CF}_2\text{CF}_2-)_n$ and PVDF $(-\text{CH}_2\text{CF}_2-)_n$ [Allen and Edge, 1992]. This may be the reason why the PAN membrane broke down under the harsh environment of UV in the presence of the powerful hydroxyl radicals. Furthermore, the quantum energy associated with the near-UV region wavelength is sufficient to break the chemical bonds of $-\text{C}-\text{H}-$ as presented in Figure 3.14 [Allen and Edge, 1992].

Figure 3.14 Quantum energies associated with wavelength in the near UV region of the electromagnetic spectrum (Source: Allen and Edge, 1992)

Hollow fibre membranes provide higher surface filtration area per volume than flat-sheet membranes in terms of membrane module size. As a result it was decided to subject hollow fibre membranes to oxidation tests to ensure that only membranes which had undergone oxidation tests were to be used in the photocatalytic oxidation environment. Earlier UV and oxidation tests performed on flat-sheet membranes showed that non-modified PVDF is the most suitable membrane besides PTFE. Thus, a non-modified semi-hydrophilic PVDF microfiltration membrane (BlueStar China) was subjected to 30 days of 400mM (twice of that for flat-sheet membrane) H_2O_2 /UV exposure. Triplicates were done and the results are shown in Table 3.6. It can be seen that the chosen PVDF membrane was very stable; negligible change in resistance of the membrane after 30 days of harsh UV/oxidative exposure was observed.

Table 3.6 Resistance of the membrane before and after 30days of UV/ H_2O_2 exposure

Membrane	Average resistance (m^{-1})	Standard Deviation (m^{-1})	Change in resistance (%)
New	3.53×10^6	0.19×10^6	3.7
UV/ H_2O_2	3.40×10^6	0.14×10^6	

3.3.3 Stability of Membranes Under Different TiO_2 filtration Conditions

In the context of applying polymeric membranes under photocatalytic conditions, it is important to understand how different filtration conditions i.e. with and without a TiO_2 cake layer, will affect the stability of the membranes. Since the PES membrane showed the lowest stability under UV illuminated conditions, it was selected as the benchmark membrane in order to shorten the time necessary to investigate the effect of cake formation and photocatalysis on the stability of membranes. This membrane was expected to show the distinct effects of various filtration conditions due to its high sensitivity to photocatalytic oxidation.

3.3.3.1 Non-Cake Situation

In order to assess the stability of the membranes in the presence of a TiO_2 suspension with minimal cake formation, it was necessary to operate well below 'critical flux' (the flux above which deposition of particle deposition commences). After a series of measurements on the transmembrane pressure at different cross-flow velocities, a cross-flow velocity of 0.83m/s (equivalent to $\text{Re} \approx 2500$) was used with an imposed flux of $30\text{L}/(\text{m}^2\cdot\text{hr})$ and the critical flux at this cross-flow was estimated to be about $120\text{L}/(\text{m}^2\cdot\text{hr})$. SEM images taken of the used membrane at the above-mentioned conditions showed that a minimal amount of TiO_2 particles had deposited on the membrane (Figure 3.15) after 300min of operation.

Figure 3.15 Micrograph of the surface of the membrane (a) before and (b) after crossflow non-cake filtration.

The effect of TiO_2 photocatalytic oxidation on the membrane during the cross-flow filtration process is shown in Figure 3.16. The constant resistance observed in the experiment of un-illuminated TiO_2 further verified that the chosen cross-flow conditions prevented accumulation of TiO_2 on the membrane throughout the 7.5 hours. It was also observed that the applied UV light system alone had no effect on the stability of the PES membrane (constant resistance data – also top line in Figure 3.16). It should be noted that this is not in contradiction to the discussion of Figure 3.7 which showed PES degradation with UV exposure. In the case of Figure 3.16, the UV intensity was 1.5 times lower ($1.35\text{mW}/\text{cm}^2$ versus $2.1\text{mW}/\text{cm}^2$) and around 3 times shorter (7.5hours versus 24hours) than Figure 3.6. However, accelerated

degradation of the membrane was observed when TiO_2 was added to the UV system. The decrease in the resistance of the membrane by about 21% was assumed to be mainly due to the presence of the oxidative compounds produced during the photocatalytic reaction. These oxidative compounds were believed to be responsible for the degradation of the polymeric membrane.

Figure 3.16 Resistance of membrane as percentage of its original resistance under crossflow conditions of UV light, TiO_2 without light and UV/ TiO_2 (crossflow velocity: 0.83m/s, constant flux: 30L/(m².hr), unadjusted pH).

The solution pH was expected to affect the degradation process since pH affects the zeta potential of the TiO_2 [Fox et al., 1993] and the membranes [Kim et al., 1996] and thus the interaction between the two. Tests were performed to investigate the effect of pH and the results are depicted in Figure 3.17. It was found that the deterioration rate was slower when the pH of the TiO_2 suspension was maintained at pH 8. At the end of the UV exposure, the resistances of the membranes were about 88% and 78% for the pH 8 (control) and 5.5 (unadjusted), respectively. TiO_2 in water has a point of zero charge (pzc) at pH around 6.0-6.5. At low pHs (pH < pH_{pzc}), TiO_2 particles possess a positive charge while a negative charge is expected at higher pHs (pH > pH_{pzc}) [Fox et al., 1993]. Experiments conducted using the electrokinetic analyzer confirmed that TiO_2 particles and PES membrane

were both negatively charged at pH 8. With a repulsion force created by the similar charge between the membrane and the TiO_2 , the degradation rate was thus lower than the unadjusted pH situation.

Figure 3.17 Effect of pH on the resistance change of membrane as percentage of its original resistance under similar crossflow conditions (crossflow velocity: 0.83m/s, constant flux: 30L/(m².hr)).

For the system without pH adjustment, the pH decreased from an initial value of 5.5 to about 4 at the end of the test. The TiO_2 was found to be positively charged and had a greater chance to be attracted to the membrane surface in spite of the hydrodynamic back-transport for subcritical flux operation. As a result, there were more interactions between the membrane and the activated TiO_2 . As illustrated by Fujishima et al. [2000], close contact in the context of about micrometer was important for TiO_2 to be able to degrade certain organic compounds effectively and the reaction rate decreased with distance. This explains why the lower pH in the unadjusted pH situation resulted in a more damaging environment for the membrane than the high pH system.

3.3.3.1 With Cake Situation

In practice, filtration cake formation during filtration operations is unavoidable and thus it is of importance to understand the consequence of having a TiO_2 layer formed on the polymeric membrane during UV illumination. The total resistances of the filtration layers measured under UV illumination at different calculated cake thicknesses are compared and shown in Figure 3.18. The porosity of the cake was estimated to be about 0.85 ± 0.09 for all cake thicknesses. Consequently, all cakes were formed based on Equation 3.5 using a porosity of 0.85 and the thicknesses were confirmed ($\pm 13\%$) with SEM images [Figure 3.19a]. In accordance with the observation made in Figure 3.19b, the surface of the TiO_2 film seemed compact and aggregation of the particles was obvious. Figure 3.19b also indicates that the membrane was generally well covered by the compact TiO_2 film.

Figure 3.18 Effect of TiO_2 cake thickness on the change in membrane resistance as percentage of its original resistance.

Figure 3.19 SEM images of the membrane a) cross-section and b) surface of the 5μm cake.

With a 5μm thick layer of TiO₂ cake deposited on the membrane, the resistance of the membrane dropped by about 30% when exposed to 15hrs of photocatalytic environment (Figure 3.18). When the cake thickness was increased to 20μm, the change in resistance of the membrane was reduced to about 11%. Considering that TiO₂ layers absorbed UV light and the reaction varies with position within the layer due to light intensity gradients [Hertz, 2004], it is probable that the presence of more layers of photocatalyst would reduce the depth of penetration of the UV light. In the case of the 20μm cake formed, less of the light energy would be able to activate the bottom layers of the TiO₂ compared to the 5μm cake situation. This explains the observation that a thicker cake was less detrimental to the membrane. Despite the detrimental effect observed, it is of great interest that TiO₂ films have been used as a photo-protective coatings for the prevention of UV photodegradation of polymer films [Miyamae et al., 2001] or has been incorporated into the main polymer chain for the photocatalytic properties of TiO₂ [Losito et al., 2005; Klein et al., 2002]. Miyamae et al. [2001] characterized the buried interface of oxide/polymer system and they showed that C=O and C=C bonds were tilted from the surface plane for PET coated with a TiO₂ film (PET/TiO₂) as compared to the SiO₂-coated PET (SiO₂/PET) and the neat PET whereby the polymer chains were well aligned and parallel to the surface plane. This observation shows the possibility of structural modification of polymer surfaces with the deposition of TiO₂ film.

Furthermore, by irradiating UV pulses (355nm), it was reported that the presence of a TiO₂ film accelerates the photodegradation of PET while such photo-induced reactions were not observed for SiO₂/PET and PET surfaces. It is thus crucial to understand the physiochemical interactions between metals and polymers before the use of polymer/inorganic thin films can be established in any application.

The penetration depth of light has been previously estimated to be about 1.7 – 3.3μm for a TiO₂-coated fiber in aqueous solution [Peill and Hoffmann, 1995]. This is about 3 to 4 times more than what was reported by Danion et al. [2004], who estimated that a 0.6μm TiO₂ film was the penetration limit of the light from their designed optical fiber. It appears that the penetration depth of the 20μm cake formed in the present study was much larger than the previous values reported. This difference would be due to the porosity of our deposits and the way the other TiO₂ films were formed [Choi et al., 2001]. Films deposited by the alkoxide precursor sol-gel method as in Danion et al [2004] tended to be denser and more uniformly distributed [Negeshi et al., 1998; Balasubramanian et al., 2003]. For the porous cake of TiO₂ aggregates in the present case, it was expected that the photon would have a much larger penetration length in the TiO₂ filtration cake layer which has a porosity of about 0.85. This is supported by Finklea [1998] who reported that the penetration depth of 384nm photons was about 100μm in polycrystalline TiO₂ layers.

It was expected that the thicker the cake, the lesser would be the extent of damage to the TiO₂ on the membrane. However, the changes in resistance of the membrane for the 20μm and 150μm cake thicknesses were found to be almost similar [Figure 3.18]. As mentioned previously, the porosity of the cake formed was rather high regardless of the thickness of the cake layer. Thus it may be possible that the bottom layers of the 150μm cake were still able to receive a fraction of the UV light photons, causing production of oxidative radicals which were detrimental to the PES membrane. In order to confirm this postulation, the formed cakes were subjected to UV-Vis analysis so as to obtain the transmittance of the different cake layers. Figure 3.20 shows that as the TiO₂ cake thickness increased beyond 20μm,

the amount of light energy absorbed by the thicker layers was effectively the same at 360nm (peak of the current UV-A lights) which implies that the amount of the activated TiO_2 in the two cake thicknesses would have been comparable.

Figure 3.20 UV-Vis transmittance of different TiO_2 cake thicknesses.

The damage of the membrane caused by the light penetration through the 150 μm TiO_2 cake layer was further confirmed by the ATR-FTIR test. Figure 3.21 shows signs of chemical change in the PES membrane covered with a 150 μm thick of TiO_2 cake layer after 900min of UV illumination. The aromatic bands at 1578cm^{-1} and 1485cm^{-1} became weaker which showed that the aromatic bands had been degraded. A new band at 1027cm^{-1} was observed after 15hrs of oxidation and this is most probably the formation of sulfoxides ($\text{S}=\text{O}$) which are usually located in the $1070 - 1035\text{cm}^{-1}$ band [Socrates, 1994]. These sulfoxides might be the products of the breakage of the sulphones ($\text{O}=\text{S}=\text{O}$) during the photocatalytic oxidation (PCO) process as can be seen by the disappearance of the sulphones spectra at 1317cm^{-1} . All organic sulphones have two very strong bands due to asymmetric and symmetric stretching vibration at $1360\text{-}1290\text{cm}^{-1}$ and $1170\text{-}1120\text{cm}^{-1}$, respectively [Socrates, 1994].

Figure 3.21 ATR-FTIR spectra of the Millipore PES membrane after 150µm TiO₂ UV-oxidation.

The system studied, with permeate flowing through the TiO₂ film and the membrane, is illustrated in Figure 3.22a. With this arrangement, there could be two possible degradation mechanisms for the dead-end cake filtration test, namely the direct contact of photoexcited TiO₂ with the membrane or the transport of oxidizing species through the cake layer to the membrane surface by the moving permeate. The oxidative components may include short-lived hydroxyl and perhydroxyl radicals as well as the longer lifespan molecules of hydrogen peroxide [Ollis, 2000]. Based on an approximate calculation, which takes into account the tortuous path through the TiO₂ layer as approximately three times the cake thickness [Peill and Hoffmann, 1995]); it would take at least 1.8 sec for an oxidative species to get through a 5µm cake layer with the imposed flux of 30L/(m².hr) (refer to Appendix A for detailed calculation). However the estimated ‘lifetime’ of the oxidative species is of the order of ns to ms [Andreozzi and Marotta, 2004], consequently the latter mechanism proposed is probably less important and only applies when the distance between the point of production of these species and the membrane is very close. However it implies that if any UV photons reach the bottom layers of the

cake where it is in contact with the membrane, it could induce the production of oxidative species by the TiO_2 particle capable of degrading the membrane surface.

Figure 3.22 Illustration of the mechanism for the photocatalytic degradation of polymeric membrane under dead-end filtration. Note that the activated TiO_2 layer is where the oxidative radicals are produced.

In order to confirm that close proximity was indeed the main mechanism for the deterioration of the polymeric membrane by TiO_2 , a $60\mu\text{m}$ layer of PAC was first deposited onto the membrane before a TiO_2 layer was deposited on top of the layer (as depicted in Figure 3.22b). As shown in Figure 3.23, the drop in resistance of the membrane in the presence of the PAC was found to be only 12% and this value was much less than the value of 30% obtained from the system with a $5\mu\text{m}$ thick TiO_2 cake layer. The PAC layer reduced the direct contact of the TiO_2 and the membrane and thus reduced the extent of oxidation of the membrane. The fact that degradation was not totally eliminated could be due to some inhomogeneity in the formed double cake layers. This result also confirms the postulation that light penetration in the current TiO_2 cake study was much greater than that reported by others and explains why there was still degradation observed in the $150\mu\text{m}$ cake test.

Figure 3.23 Two-layer cakes formed (PAC-TiO₂) for the study of the mechanism of the degradation of polymeric membrane by the TiO₂.

3.4 Summary

In this study, polymeric membranes were subjected to UV and UV/oxidative environments to select membranes which can be used in photocatalytic oxidation processes. A total of 10 polymeric membrane materials were tested with PTFE, PVDFphobic, hydrophilic PVDF-Pall and PAN membranes found to be relatively stable after 30 days of UV illumination. Although the PAN membrane was stable under UV exposure, its resistance declined considerably when it was immersed in a 200mM H₂O₂ solution for over 10 days. The degradation of the membrane was accelerated when UV light was introduced to the system leading to the formation of cracks. Therefore, the PAN membrane is not a promising candidate for use in the photocatalytic reaction.

The hydrophobic PVDF membrane was found to be more stable, chemically (TOC release) and physically (membrane resistance), than the modified hydrophilic PVDF membranes in the UV and oxidative tests. High TOC leakage was detected for the hydrophilic PVDF membrane and the study of contact angle showed that the surface of the membrane had become more hydrophobic after UV illumination. This was

probably due to the degradation of the coating of the modified membrane under UV illumination. Even though the hydrophilic PVDF from Pall Co. and another from Millipore Co. are prepared from similar material with modification for hydrophilicity, the former was found to display smaller changes in resistance when compared to the latter after 24 hours of UV exposure. This demonstrates that the assessment of damage to the membranes has to be based on results generated on the actual polymer formulations used in practice rather than generalization from polymer materials. From the UV and oxidation stability tests, PTFE and hydrophobic PVDF are the preferred choice for photocatalytic applications.

A stability study of the polymeric membranes under different TiO_2 filtration conditions was performed using the PES membranes. The effect of pH on the stability of the membrane was also investigated and carried out under non-cake conditions. The extent of damage affected by the activated TiO_2 was less when the membrane and TiO_2 had similar charge resulting in charge repulsion and thus minimizing the deposition of 'active' TiO_2 onto the membrane. It is thus worthwhile to take the effects of pH into account if polymeric membranes are to be used with photocatalytic reactions. Having a very thin layer of TiO_2 cake formed on the membrane ($5\mu\text{m}$ in the current case) resulted in the fastest deterioration rate on the membrane, compared to thicker cake layers and the non-cake situation. It was found that $20\mu\text{m}$ and $150\mu\text{m}$ TiO_2 cake layers caused a similar but minor degree of damage to the PES membrane. This is attributed to the transmission of similar amounts of light by the two cake layers. Thus there is some evidence that as the TiO_2 layer became thicker, it acted as a protective layer for the membrane. However, this is not a very practical strategy because a TiO_2 film will reduce the permeability of the membrane, thus reducing the overall efficiency of the filtration system.

Nonetheless, a non-modified PVDF hollow fibre membrane has passed the stability test and is ready for use in the next phase of the work: the combination of a polymeric membrane with a photocatalytic process as described in Chapters 4 and 5.

CHAPTER 4

FEASIBILITY STUDY OF A LOW-PRESSURE SUBMERGED MEMBRANE PHOTOCATALYTIC SYSTEM*

4.1 Introduction

As revealed in Chapter 2, most of the prior work on the combination of photocatalysis and membrane filtration was done individually in which oxidation and filtration processes occurred in separate chambers. These process configurations required large footprints that might not be suitable for a land-scarce country like Singapore. In Singapore, a compact and energy-cost effective water treatment plant is of utmost importance.

The identification of a stable polymeric membrane material in Chapter 3 allows the integration of polymeric membranes and photocatalytic reactor into a single reactor module. The use of polymeric membranes will reduce the membrane cost as compared to the use of ceramic membranes. For the type of membrane, the low-pressure MF membrane is a good choice since it can be used in a submerged membrane module. Submerged membranes are now widely used in membrane bioreactors (MBR) owing to their recognized advantages of lower cost of fabrication and maintenance [Fane et al., 2002; Howell et al., 2004]. It is known that low-pressure membranes are not able to retain most of the organic compounds such as endocrine disruptors (EDCs), biocides and carcinogens. Therefore, the

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integration of photooxidation and microfilters can help to realize the removal of these compounds using low-pressure membrane operations.

In this chapter, the PVDF hollow fibre MF membranes as tested in the previous chapter are used in a submerged module in a photocatalytic reactor equipped with an external light source. The study of submerged membrane photocatalytic reactor (SMPR) for water purification is limited as discussed in Chapter 2. Hence, this chapter investigates the feasibility of applying the SMPR to the degradation of BPA. This investigation was carried out in 2 parts. The first part involved the study of a photoreactor system without a filtration unit and the aim was to gain a basic understanding on the effects of various operating parameters on the photocatalytic efficiency of TiO_2 in the degradation of BPA. This was then followed by the study of the combination of the two processes – oxidation and filtration. Different methods are also discussed for controlling membrane fouling involving TiO_2 particles.

4.2 Background

Phenol and phenolic compounds, which have been classified by the US EPA as priority pollutants, are used in many processes such as pharmaceuticals, petroleum refineries, resin and dye manufactures. Bisphenol A (BPA), also known as 2,2-bis-(4hydroxyphenyl) propane or 4,4'-isopropylidenediphenol, belongs to the family of phenolic compounds. It is an important monomer chemical used for the production of various polycarbonate and epoxy resins, unsaturated polyester styrene resins and flame-retardants. BPA is commonly found in compact disks, composite dental fillings and sealants, plastic drink bottles and food linings [Kaneco et al., 2004].

Due to its estrogenic activity, BPA was listed as an chemical EDC by the Japan Ministry of Environment and the European commission [Watanabe et al., 2003; Chiang et al., 2004]. EDCs exhibit biological behaviour that is similar to that of natural and synthetic estrogens with steroid structures and their metabolites. It is

also well documented that continuous exposure to low level of BPA could result in hormonal imbalance, male infertility and breast cancers in humans [Chiang et al., 2004].

4.2.1 Adsorption of Organics on TiO₂

Since the reactions involved in a heterogeneous photocatalytic process occur predominantly on the surface of the TiO₂, it is thus important to study the adsorption isotherm for the organic substrates and TiO₂. Two classical adsorption isotherm models, namely the Langmuir model and the Freundlich model, are usually used to describe the adsorption of organics on TiO₂ surfaces. The adsorption isotherm describes the relationship between the mass of dye adsorbed per unit weight of TiO₂ and the equilibrium concentration of the organics in solution.

Dionysios et al. [2000] and Bekbolet et al. [2004] fitted the adsorption of 4-chlorobenzoic acid and humic acid, respectively, using the Freundlich isotherm adsorption model (Equation 4.1).

$$q_A = K_f C_e^{1/n} \quad (4.1)$$

where q_A is the amount of solute adsorbed per unit weight of TiO₂ (mg/g); K_f is the adsorption capacity (L/mg); C_e is the equilibrium concentration (mg/L); $1/n$ is the adsorption intensity. By linearization (via plotting $\log q_A$ against $\log C_e$), the two Freundlich parameters, q_A and $1/n$ could be estimated from the intercept and the slope of the straight line respectively. The Freundlich isotherm was used to account for the heterogeneity of the surfaces assuming that the energy of adsorption depends on the degree of coverage.

The Langmuir adsorption model (Equation 4.2) is more commonly used compared to the Freundlich model [Kiriakidou et al., 1999; Xu and Langford, 2000; Vulliet et al., 2003; Tang and Chen, 2004]. It has been used for the adsorption study of many

organic compounds, including azo dyes, acetophenone, sulfonylurea herbicides, reactive black and reactive orange, on TiO₂ surfaces.

$$\theta = \frac{Q_{ads}}{Q_{max}} = \frac{K_{ads} C_{eq}}{1 + K_{ads} C_{eq}} \quad (4.2)$$

where θ , Q_{ads} , Q_{max} , K_{ads} and C_{eq} represent the TiO₂ surface coverage, the adsorbed quantity, the maximum adsorbable quantity, the Langmuir adsorption equilibrium (specific for the catalyst/organic) and the concentration of the organic in solution in equilibrium, respectively. K_{ads} and Q_{max} can be determined by the linear transformation of Equation 4.2

$$\frac{1}{Q_{ads}} = \frac{1}{Q_{max}} + \frac{1}{K_{ads} Q_{max}} \left(\frac{1}{C_{eq}} \right) \quad (4.3)$$

The pH of the solution is found to affect the adsorption of organic compounds since pH alters the surface charge of TiO₂ particles and affects the ionization of the organics. Kiriakidou et al. [1999] found that the adsorption of azo-dyes was enhanced significantly when the pH of solution was decreased from pH 12 to pH 2, which indicated that the adsorption of this dye was better at lower pH. The same applied to adsorption of another dye, eosin [Zhang et al., 1998]. However, some researchers found no trend in pH dependency of the adsorptions of certain organics on TiO₂. For the adsorption of reactive black 5 dye, the adsorption was better according to the following pH values: pH 2 > pH 10 > pH 6 [Tang and Chen, 2004] while the adsorption of reactive orange 4 was pH 5 > pH 3 > pH 7 [Muruganandham and Swaminathan, 2005]. According to the latter group, the adsorption of dye was favourable near to the pH_{pzc} (point of zero charge) of TiO₂ in the acidic pH range. It was explained that agglomeration of TiO₂ was enhanced at lower pH (pH < 3) thus reducing the surface area available for adsorption. Although significant adsorption of organic on catalyst could occur as a function of pH, there is not always a direct relationship between pH and the adsorption capacity.

Experiments have to be conducted to determine the relationship between pH and the specific catalyst/organic compound.

4.2.2 Photodegradation of BPA

It is found that BPA degradation follows a pseudo first order reaction [Fukahori et al., 2003] which can be represented by Equation 4.4.

$$\ln \frac{C}{C_o} = -k_{app} t \quad (4.4)$$

where k_{app} represents the apparent first-order rate constant, C represents organic substrate concentration at time t and C_o represents initial organic concentration

A modified equation that includes surface kinetics of a heterogeneous reaction, adsorption/desorption of the reactants, is obtained by introducing a driving force or displacement from the equilibrium constant to Equation 4.4 [Levenspiel, 1999]. For photocatalytic reaction, the Langmuir-Hinshelwood (L-H) kinetic model (Equation 4.5) is widely used because it enables one to correlate the degradation rate to the instantaneous concentration of the solution [Poulios et al., 2000; Vulliet et al., 2003]. This kinetic equation is shown as,

$$r_o = -\frac{dC}{dt} = \frac{k_{LH} K_{LH} C_o}{1 + K_{LH} C_o} \quad (4.5)$$

where r_o is the initial rate of disappearance of organic compound, C_o is the initial concentration, K_{LH} is the L-H equilibrium adsorption constant and k_{LH} is the pseudo-first order initial reaction rate constant at maximum coverage for the experimental conditions. This L-H equation was derived based on the assumptions that the oxygen and water vapour concentrations were constant throughout the photocatalytic process and the intermediates produced were weakly or noncompetitively adsorbed on the TiO_2 surface [Demeestere et al., 2004]. The experimental data can be fitted to the equation by plotting the inverse of the initial rate versus the inverse initial concentration (Equation 4.6):

$$\frac{1}{r_o} = \frac{1}{k_{LH}} + \frac{1}{k_{LH}K_{LH}} \times \frac{1}{C_0} \quad (4.6)$$

The rate constant can then be obtained from the intercept of the y-axis interception while the L-H constant is determined from the slope. In order to minimize the variations as a result of competitive effects of the intermediates or pH changes etc, the initial rates were usually calculated from the first 20 min of illumination [Poulios et al., 2000] or from 10-20% loss of the substrate [O' Shea and Cardona, 1995]. Xu et al. [2000] showed that different treatments of initial rate data might bring the different K_{LH} values. According to the their study, K_{LH} was found to depend on the light intensity and the initial time interval chosen for the rate calculation whereas the rate constant, k_{LH} , appeared to be less sensitive to the initial time interval.

Many studies have also showed that K_{LH} was different from the K_{ads} obtained from Equation 4.3 [Parra et al., 2004; Mills and Morris, 1993]. There have been several studies reporting that K_{LH} could be substantially larger than K_{ads} : 280 times for metobromuron [Parra et al., 2004], 220 times for 4-chlorophenol [Mills and Morris, 1993]. Reasons given includes: (i) the reaction would take place not only at the surface but also in the bulk solution [Cunningham et al., 1993] (ii) a photodesorption would happen [Lin et al., 2002] and (iii) UV illumination would change the electronic properties of TiO_2 surfaces [Xu and Langford, 2000]. In contrast, Vulliet et al., [2003] has found that K_{ads} was greater than K_{LH} during herbicides degradation. They accounted that the lower K_{LH} was most probably due to electron-hole recombination or thermodesorption, i.e. induced by an increase of surface temperature during UV illumination.

In most cases, L-H expressions are adequate to explain the basic initial kinetics of disappearance of the target compound but are not fundamental enough to reflect the consequences of changes in reaction parameters or reactor geometries. It has been pointed out that four possible mechanisms of reaction between hydroxyl radicals

and an organic substrate yield an expression in L-H form [Turchi and Ollis, 1990]. This may explain why L-H expressions can adequately account for the kinetics without having values for K_{LH} that can be related to adsorption as discussed before. This simple model does not provide detailed insight into the reaction mechanisms and modifications applied to L-H kinetic models will be discussed in greater details in Chapter 6.

The degradation mechanism and the intermediate products of BPA have also been studied in detail by Watanabe et al. [2003], Kaneco et al. [2004] and Fukahori et al. [2003]. Watanabe et al. [2003] estimated the first hydroxyl radical attack position of BPA by using point charge simulation and by calculating the frontier electron density. They reported that the initial degradation of BPA was initiated from the methyl groups, namely C14 and C15 in Figure 4.1. Although C3 and C8 were the most electron-rich atoms according to frontier electron calculations and theoretically hydroxyl radicals would preferentially attack these atoms, the point charge simulation showed that the negativity of C14 and C15 was higher than that of C3 and C8. Therefore, it would be easier for C14 and C15 to be attracted to the positively charged TiO_2 at pH 3.8 and thus initiate the degradation of BPA. In this case, the pH of the solution played an important role in enhancing adsorption of organic substrate onto the electronically charged TiO_2 as discussed before in Section 4.2.1.

Figure 4.1 Chemical structure of bisphenol A (BPA).

However, In contrast to the study above, the formation of 3-(4-hydroxyphenyl)-3-methyl-2-oxobutanoic acid during BPA degradation strongly suggested BPA

aromatic ring cleavage [Ohko et al., 2001]. This suggests that BPA degradation was initiated by the attack of electron-rich aromatic rings at C3 and C8.

Some intermediates detected during the degradation of BPA included p-isopropenylphenol, p-hydroxybenzaldehyde (p-HBA), p-hydroxy- α -methylstyrene (p-HMS) and p-hydroacetophenone (p-HAP) [Kaneco et al., 2004; Fukahori et al., 2003]. p-benzaldehyde was reduced to p-hydroquinone (p-HQ) and propenyl radicals by the hydroxyl radicals. The accumulation of p-HQ observed by Fukahori et al [2003] implied that a quinone separation pathway predominated instead of the reported ring-opening pathway. p-hydroxybenzoic acid (p-HBAcid) was also produced which was identified as an intermediate of p-HBA. These single aromatic intermediates were further oxidized through ring-rupturing reactions into aliphatic acids such as acetic acid, formic acid and acetaldehyde [Watanabe et al., 2003]. Finally, carbon dioxide was formed, indicating mineralization of BPA.

4.3 EXPERIMENTAL

4.3.1 Materials and Analytical Measurements

P25 TiO₂ used for the experiments was supplied by Degussa AG, Germany. High purity BPA (Merck-Schuchardt) was used and the physical and chemical characteristics of BPA are shown in Table 4.1. The pH of all suspensions was adjusted using sodium hydroxide and perchloric acid. Purified air was used as a source of oxygen in this study. Unless otherwise stated, all solutions were prepared using Millipore MilliQ (MQ) water with a resistivity of 18.2M Ω cm. Microfiltration (MF) hollow fiber membranes made of polyvinylidene fluoride (PVDF) were supplied by Bluestar China, with an average pore size of 0.2 μ m and an outer diameter of 1mm. The PVDF membranes were chosen based on the results from previous studies in Chapter 3.

Table 4.1 Bisphenol - A characteristics

Chemical Name	Bisphenol -A (BPA)
Molecular formula	C ₁₅ H ₁₆ O ₂
Molecular weight (g/mol)	228
Solubility at 22°C (mg/L)	120-300
Vapour pressure at 25°C (mmHg)	< 1
Density at 22°C (g/cm ³)	1.195
pKa	9.59-11.30
Log K _{ow}	3.40

4.3.2 Dark Adsorption

200ml of BPA aqueous solution of various initial concentrations (10 to 80mg/L) and at different pH values were mixed with 0.4g of TiO₂ (equivalent to 2g/L of TiO₂) in a capped glass bottle. The suspensions were then left to stir overnight at room temperature. In order to avoid the photoreaction of TiO₂, suspensions were kept in the dark for the entire period of the experiment. The samples were filtered at 0.22µm after adsorption before analysis of the concentration of BPA. The amount of BPA adsorbed on the catalyst was calculated by mass balance.

4.3.3 Batch Photocatalytic Reactor

Batch photocatalytic tests were carried out in a 800ml photoreactor made of borosilicate glass (Figure 4.2). UV-A irradiation was provided by four 8W black light fluorescent lamps (NEC FL8 BL-B) located on the four sides of the photoreactor. The lamps used had an emission with wavelengths from 300nm to 420nm and a peak at 355nm. 800ml of TiO₂ suspension was prepared by adding pre-determined amounts of TiO₂ and BPA followed by pH adjustment using perchloric acid and sodium hydroxide. The concentration of TiO₂ was varied from 0.2g/L to 2g/L and the concentration effect was studied at three different pH values of 4, 7 and 10. The solution, containing 10mg/L BPA, was sonicated for 10 minutes before charging into the photoreactor. The solution was also allowed to

equilibrate for 20min to attain TiO_2 -BPA adsorption equilibrium before illumination with light. In all experiments, the initial concentration of BPA was kept at 10mg/L unless otherwise stated. Aeration in the system was supplied by a purified air cylinder and distributed through a ceramic bubble diffuser. The effect of aeration rate was studied in the range of 0.2L/min to 4L/min (superficial gas velocities of 1.2×10^{-3} m/s to 2.4×10^{-2} m/s). For the study of bubble cloud effects, one of the 8W UV-BLB lamps was switched on. The incident light intensity, with or without aeration, was then measured using a radiometer (International Light PMA 2200) with an UV-A sensor (PMA2110) at the wall of the photoreactor (opposite to the lighted lamp). In this way, light transmission through the MQ water in the 65mm diameter photoreactor was measured. Samples at pre-defined time were taken, filtered through 0.22 μm filters and analyzed accordingly with different techniques (see 4.3.6). The TiO_2 particle size distributions at different aeration rates were measured at the end of each experiment.

Figure 4.2 Schematic diagram of the batch photoreactor experimental setup (a) side view, (b) top view.

4.3.4 Submerged Membrane Photocatalytic Reactor (SMPR)

A schematic diagram of the submerged hollow fiber microfiltration system is shown in Figure 4.3. It consisted of a 1L borosilicate glass photoreactor, similar to the one used in the batch kinetic tests, together with a portable hollow fiber membrane module having an effective filtration area of $4.107 \times 10^{-3} \text{ m}^2$ placed in the centre. During the experiments, a constant flux of $100 \text{ L}/(\text{m}^2 \cdot \text{hr})$ permeate was withdrawn from the system through the suction provided by a peristaltic pump. The transmembrane pressure in all experiments was measured by an online pressure gauge on the permeate line. A level sensor was used to control the feed rate of 10 mg/L BPA solution to the system in order to keep the total volume of the reactor constant. Samples at predefined times were taken from the permeate line and analyzed for BPA and total organic carbon (TOC) concentrations. The effect of permeate flux (40 , 60 and $100 \text{ L}/(\text{m}^2 \cdot \text{hr})$) on the degradation of 20 mg/L of BPA solution was conducted by changing the permeate pump settings accordingly. The effect of different constant feed concentrations of BPA at 10 , 20 and 50 mg/L was also studied.

Figure 4.3 Schematic diagram of the continuous submerged membrane photoreactor experimental setup.

4.3.5 Membrane Adsorption and Critical Flux

The determination of BPA adsorption on the membrane was performed using a pulse input tracer test in the SMPR reactor as shown in Figure 4.3, with or without the membrane module. Initially, MQ water was continuously drawn through the membrane module before a certain amount of BPA was injected to the reactor as a pulse input. The injected BPA was immediately mixed in the system by the 0.5L/min of bubbling provided. After the introduction of the BPA, the inlet of the MQ water to the system was stopped so that the concentration of the BPA in the system was fixed at 10mg/L after the dilution of the injection. The corresponding BPA concentration was then taken from the tank and at the permeate line after a predetermined time. For the critical flux determination, a step flux method was used whereby the SMPR permeate flux was increased in increments of 20L/(m².hr) up to a flux of 100L/(m².hr). Each flux increment was maintained for a duration of 25 minutes and the TMP was monitored.

4.3.6 Analytical Methods

The concentration of BPA in samples was measured using a high performance liquid chromatograph (HPLC, Waters Alliance) interfaced with a photodiode array detector. The separation was carried out by a Waters Xterra RP18 HPLC column (3.9mm x 150mm, 5µm) with a mobile phase consisting of 50% water and 50% acetonitrile. The TOC present in the samples was determined by a TOC analyzer (Shimadzu TOC-V_{CSH}). The particle size distribution of the sample was measured by a Brookhaven ZetaPals and Malvern particle sizer. The turbidity of samples was determined using a HACH 2100AN IS turbidity meter. The TOC contributed by BPA was calculated using Equation 4.7.

$$TOC_{organic\ substrate} = \left(\frac{Number\ of\ carbon \times M_r\ Carbon}{M_r\ organic\ substrate} \right) \times C_o \quad (4.7)$$

where M_r is the molecular weight, C_o is the initial concentration of the organic substrate, BPA in this case.

RESULTS AND DISCUSSION

4.4.1 Parameters Affecting the Photodegradation of BPA

The effects of different parameters on the photodegradation of BPA were first measured in the batch system to obtain the optimized conditions prior to the feasibility study of the integration of photocatalysis with submerged membrane filtration. The parameters investigated included adsorption of BPA on TiO_2 , the effect of initial pH, the effect of TiO_2 concentration, the effect of initial concentration of BPA and the effect of air bubbling rate.

Dark Adsorption of BPA on TiO_2

It has been shown in section 3.3.1 that close proximity of TiO_2 particles to the polymeric membrane was the main mechanism for the deterioration of the polymeric membrane due to the short-life of the oxidative species produced. In consideration of this finding, adsorption of BPA onto TiO_2 surfaces was expected to play a role in the photocatalytic oxidation process. Data obtained from dark adsorption experiments were fitted to the linear form of the rearranged Langmuir equation (Equation 4.3) and the results as shown in Table 4.2 and Figure 4.4.

Table 4.2 Calculated Langmuir adsorption constants.

	$Q_{\max}$ ($\mu\text{mol/g}$)	K_{ads} (L/mol)	R^2
pH 10	51.02	2.61×10^3	0.993
pH 7	129.87	4.51×10^3	0.999
pH 5.5	80.00	2.66×10^3	0.989
(unadjusted)			
pH 3	94.34	2.79×10^3	0.996

Figure 4.4 Establishment of Langmuir monolayer adsorption constants for the adsorption of BPA over TiO_2 at different pH (unadjusted pH = pH 5.5).

From Figure 4.4, the adsorption constants (Q_{max} and K_{ads}) of BPA were calculated with Q_{max} being the reciprocal of the ordinate at the origin and K_{ads} calculated from the slope. The adsorption data (Table 4.2) show that increasing pH from acidic to alkaline resulted in significant reduction in adsorption. The maximal adsorbable BPA (Q_{max}) per gram of TiO_2 decreased by 46% when pH increased from pH 3 to pH 10. The point of zero charge (pH_{pzc}) of Degussa P25 TiO_2 particles is around pH 6.3, hence the TiO_2 surface is positively charged under acidic media. From the simulation of molecular point charges of all the non-hydrogen atoms in BPA, BPA was found to possess two negative oxygen atoms at the hydroxyl groups (O16 and O17 in Figure 4.1) and four negative carbon atoms ortho to the phenolic group (C7, C8, C14, C15 in Figure 4.1) [Watanabe et al., 2003]. It was thus expected that attractive forces would be developed between the substrate and the TiO_2 surface, resulting in high adsorption in acidic medium. As the pH increased, the TiO_2 surface became progressively more negative which led to the development of greater repulsive forces between the TiO_2 surface and the adsorbate, and therefore resulting in less adsorption of BPA at pH 10.

4.4.1.2 Effect of Initial Suspension pH

The initial degradation rates obtained at different pH values are shown in Table 4.3. As observed, the degradation rate at pH 4 was about twice the rate at pH 10.

Table 4.3 Initial rate of degradation of 10mg/L of BPA at various pH conditions (TiO₂ concentration = 0.5g/L, initial BPA concentration = 10mg/L, aeration rate: 1L/min).

pH	Initial degradation of BPA (mg L ⁻¹ min ⁻¹)
pH 4	0.225 ± 0.008
pH 7	0.187 ± 0.010
pH 10	0.124 ± 0.005

Previous studies indicated that pH affected PCO in a number of ways. First, the mode of adsorption-desorption of organics on the TiO₂ surface since the TiO₂ surface charge was known to be pH dependent [Kroschwitz, 1996]. Second, hydroxyl radical generation was enhanced at high initial pH which came from the photooxidation of OH⁻ anions by holes forming on the TiO₂ surface (Equation 2.7). Third, acidic condition was reported to enhance agglomeration of TiO₂ particles and thus reduced the surface area available for dye adsorption and photon absorption [Fox and Dulay, 1993]. Fourth, different pH led to different photoreaction mechanisms [Kiriakidou et al., 1999; Chiang et al., 2004].

In this study, the acidic condition was found to favour the degradation of BPA and this could indicate that adsorption played a critical role in the initial degradation rate of BPA [Watanabe et al., 2003]. Dark adsorption results previously have shown that adsorption of BPA on TiO₂ was the strongest at pH 4. As depicted in Section 4.3.3, the TiO₂-BPA suspension was allowed to equilibrate for 20min before UV illumination. Hence when UV lights were switched on, the high amount of adsorbed BPA at pH 4 led to a rapid initial degradation rate as observed in Table 4.3. The estimated 'lifetime' of the oxidative species produced during photocatalytic oxidation was of the order of nano seconds to milli seconds [Andreozzi and

Marotta, 2004] and thus it could be envisaged that adsorption of BPA could increase the chance of interaction between the short-life powerful oxidative species and the substrate. Besides degradation by oxidative species, the organic substrate could also be degraded via direct electron transfer with trapped photogenerated holes on the surface of TiO_2 (Equation 2.4). Therefore, degradation of well-adsorbed BPA at low pH could also be enhanced via this mechanism.

4.4.1.3 Effect of TiO_2 Concentration

In the present study, it was found that the optimum TiO_2 concentration to be used for the degradation of 10mg/L BPA was 0.5g/L, as shown in Table 4.4. 0.2g/L of TiO_2 resulted in the slowest reaction rate, presumably owing to the fewer active sites available for the adsorption and degradation of BPA. Beyond 0.5g/L, adverse effects on the degradation rate of BPA were also noted. Although the total surface area available for reaction was higher in the 2g/L test compared to the 0.5g/L test, the initial reaction rate was found to be approximately 10% lower ($0.240 \text{ mgL}^{-1}\text{min}^{-1}$ compared to $0.264 \text{ mgL}^{-1}\text{min}^{-1}$). The decrease in efficiency could be attributed to light scattering of the UV light by the TiO_2 particles themselves [Wong and Chu, 2003].

Table 4.4 The rate of degradation of 10mg/L of BPA under different TiO_2 concentration conditions (initial BPA concentration = 10mg/L, pH = unadjusted, aeration rate = 1L/min)

TiO_2 concentration (g/L)	Initial degradation of BPA ($\text{mg L}^{-1} \text{ min}^{-1}$)
0.2	0.220 ± 0.013
0.5	0.264 ± 0.012
1.0	0.235 ± 0.007
2.0	0.240 ± 0.008

The optimum TiO_2 concentration found in this case was different from the study of Hermann [1999]. In their laboratory and solar pilot photoreactors, the optimum TiO_2 used was 2.5g/L and 0.2g/L, respectively. Also, Dionyniou et al. [2000] observed different effects of TiO_2 concentration when different types of photocatalysts were used. These studies suggest that the limit for TiO_2 concentration depends on the reactor geometry and also on the working parameters of the photoreactor.

4.4.1.4 Effect of Initial Concentration of BPA

Figure 4.5 shows the effect of initial concentration of BPA on the photodegradation rate of BPA. The quasi-exponential decay observed during the photodegradation indicates pseudo-first order kinetics, which is strongly dependent on the initial concentration of BPA [Parra et al., 2004]. Pseudo-first order kinetics of BPA was also confirmed with the use of Equation 4.4 whereby the experimental data in Figure 4.5 fitted plots of $\ln C_A/C_{A0}$ vs t well with regressions greater than 0.97. Table 4.5 shows the initial degradation rate under different initial concentration of BPA. It can be seen that the degradation rate increased with increasing concentration of BPA.

Figure 4.5 Influence of initial concentration of BPA (TiO_2 concentration = 0.5g/L, initial pH = 4, BPA feed concentration = 10mg/L, 0.5L/min aeration rate).

Table 4.5 Initial degradation rates of BPA for different initial concentration of BPA (initial pH = 4, TiO₂ concentration = 0.5g/L)

Initial concentration of BPA	Initial degradation of BPA (mg L ⁻¹ min ⁻¹)
10	0.265 ± 0.008
20	0.368 ± 0.013
30	0.382 ± 0.008
50	0.507 ± 0.011

Section 4.4.1.2 (effects of pH) has shown that adsorption was a crucial step in the initial photocatalytic degradation rate of BPA and this finding was further investigated in this section. The Langmuir-Hinshelwood model (Equation 4.6) has been used successfully to describe the influence of the initial concentration of organic substrate on the initial photocatalytic degradation rate [Cunningham et al., 1994; Parra et al., 2004; Vulliet et al., 2003]. In this case, the BPA concentration in the range of 10mg/L to 50mg/L fitted the L-H model well with $R^2 = 0.983$, $k_{LH} = 2.09 \text{ mol L}^{-1} \text{ min}^{-1}$ and $K_{LH} = 1 \times 10^4 \text{ L mol}^{-1}$. The good fit of data suggests that adsorption plays a key role in the photocatalytic degradation mechanism [Parra et al., 2004] which agreed with the mechanism suggested previously in Section 4.4.1.2. However so, it was arguable that this simple L-H model did not provide detailed insight into the reaction mechanisms [Turchi and Ollis, 1990] and modifications have to be applied to the basic L-H kinetic models. Further details regarding modeling work will be discussed in Chapter 6

It is worth noting that the K_{LH} ($1 \times 10^4 \text{ L mol}^{-1}$) obtained was different from the K_{ads} ($2.79 \times 10^4 \text{ L mol}^{-1}$) obtained from the dark adsorption study at pH 3. This difference is interesting because if the empirical parameter K_{LH} reflects the adsorption affinity of BPA for TiO₂ surface, K_{ads} and K_{LH} should be identical. The value determined from the dark adsorption study (section 4.4.1.1) was about 1.8 times higher than the K_{LH} determined from the L-H equation. In contrast to this finding, a few studies have been reported that $K_{LH} > K_{ads}$: 280 times for

metobromuron [Parra et al., 2001] and 220 times for 4-chlorophenol [Mills and Morris, 1993]. A possible explanation for this difference could be because of the irradiation induced changes on the electronic properties of TiO_2 , resulting in modified adsorptive sites in which BPA molecules were adsorbed. Also, photoadsorption and photodesorption during photoreaction might affect the overall adsorption capability of TiO_2 as compared to a dark reaction. In addition, the photodegradation products might compete with parent compound for reactive catalyst sites which thus resulted in a lower L-H adsorption constant [Kusvuran et al., 2005]. Similar observations, where $K_{\text{ads}} > K_{\text{LH}}$ have also been reported by Vulliet et al. [2003].

4.4.1.5 Effect of Aeration

Aeration is important for both the separation process by submerged membranes and the oxidation reaction in the photocatalytic processes. The former process requires mechanical agitation from aeration in order to reduce the fouling of the membrane surface as well as to keep the TiO_2 well-suspended in the solution; whereas the latter process requires dissolved oxygen to act as an oxidant and to slow down the electron-hole recombination reaction.

Figure 4.6 shows that the initial photodegradation rate increased with increasing bubbling rate and reached a maximum value at a bubbling rate of 0.5L/min, beyond which an insignificant change in the degradation rate was observed. This trend of results was reproducible. A similar finding has been reported by Lee et al. [2003] who performed their experiment in a fluidized photocatalytic reactor. In their experiment, bubbling enhanced the photodestruction of methyl orange and its effect reached a plateau above 2L/min.

Figure 4.6 Photodegradation of BPA as function of different aeration rate (0.5g/L TiO_2 , initial pH = 4, initial BPA concentration = 10mg/L).

In a bubbling system, aeration can affect the size of catalyst aggregates. The effect of aeration on the size distribution of the TiO_2 particles is shown in Table 4.6. It can be seen that after 1.5 hours of aeration at 0.2L/min and 4L/min, the average diameters (d_{50}) of TiO_2 were $0.75 \pm 0.15\mu\text{m}$ and $0.31 \pm 0.03\mu\text{m}$, respectively. Higher aeration rates produced greater shear rates which disintegrated the aggregated particles. Additionally, with lesser agglomeration occurring, a higher surface area on the smaller particles might be available for the degradation of BPA. This explains why 0.2L/min resulted in the slowest degradation rate as observed in Figure 4.5. A negative effect of TiO_2 particle agglomeration on the photocatalytic activity was also observed by Soparajee et al. [1999a]. In their system, TiO_2 particles recovered from the UF membrane system were sent back to the photocatalytic reactor and it was found that the performance of photocatalyst decreased after each repeat cycle. Caking and redispersing of the TiO_2 from the membrane surface after each cycle promoted the agglomeration of the TiO_2 particles in which there was an obvious shift of particles towards a coarser range after the tenth cycle.

Table 4.6 Average particle size of TiO₂ at different aeration rate (initial pH = 4, TiO₂ concentration = 0.5g/L).

Aeration rate (L/min)	Mean particle size (nm)
0.2	757 ± 147
0.5	477 ± 49
1.0	491 ± 52
4.0	309 ± 32

Increasing bubbling not only results in smaller particles as discussed before, but it also increases the liquid film mass transfer coefficient around the aggregates [Jia et al., 2006]. It should then be expected that increasing bubbling rate would increase the photodegradation rate. However, no enhancement of photodegradation rate was observed beyond 0.5L/min in this study. This was probably due to the presence of bubble clouds that could attenuate UV light transmission in the photoreactor. As illustrated in Figure 4.7, dense bubble clouds were formed during 4L/min bubbling. The light intensity through the 65mm outer diameter photoreactor was measured and found to decrease as bubbling rate increased (Table 4.7). Light intensity at 4L/min was only 55% of that at 0.5L/min. Though this measurement does not show the absolute value of the light intensity in the system, it confirms the possibility of light attenuation by bubble clouds. This explains the plateau in degradation rate observed as the aeration rate increased. The possibility of light scattering by bubbles was also studied by Emets et al. [1996] and Szymanski [1996]. The interplay of the competing mass transfer and light attenuation effects led to an optimal bubbling rate at 0.5L/min in this study.

Figure 4.7 Bubbles resulting from a) 0.5L/min b) 4L/min of aeration rate.

Table 4.7 Intensities of transmitted light at different bubbling rates.

Aeration rate (L/min)	Light intensity (mW/cm ²)
No bubbling	1.22
0.2	1.20
0.5	1.08
1.0	0.89
4.0	0.60

Figure 4.8 summarizes and compares the effects of different parameters (pH, aeration rate and TiO₂ concentration) on the initial degradation rate of BPA. The fastest and slowest rates obtained previously for each parameter were plotted. It is important to note that pH played the most prominent role among the three parameters investigated; an improvement of 45% in degradation rate was observed when pH was lowered from 10 to 4. The above parameter investigations have led to the optimized conditions of 0.5L/min aeration rate, 0.5g/L TiO₂ dosage and pH 4 for the continuous photodegradation of BPA using membranes in the subsequent sections of the feasibility study.

Figure 4.8 Comparison of the effects of aeration, TiO₂ concentration and pH on the initial degradation rate of BPA.

4.4.2 Microfiltration of TiO₂

Microfiltration experiments were conducted to confirm that the chosen PVDF hollow fiber membrane of 0.2µm nominal pore size was able to retain all particles under different conditions. The particle size distribution of TiO₂ after 10min of sonication and after 1.5 hrs of 0.5L/min optimum bubbling rate are shown in Figure 4.9.

The size of the TiO₂ particles ranged from 0.3 to 2.0 µm after 10min of sonication, which was supposed to loosen and break up the agglomerates and evenly distribute the TiO₂ particles. 10min of sonication was introduced to all samples of the TiO₂ suspension before photocatalytic reaction so as to ensure that the initial particle size range was comparable in all cases. Although the crystal size of TiO₂ (P25) was reported to be approximately 20 to 30 nm [Degussa, 1989], these particles form agglomerates within the micron range in the aqueous phase.

Figure 4.9 TiO_2 size distributions after 10min of sonication and 3hrs of 0.5L/min aeration at pH 4.

There was a noticeable shift of the size distribution towards bigger particle size after 0.5L/min of bubbling as indicated in Figure 4.9. The average particle sizes for the 10min sonication and 3hrs aeration were $0.35\mu\text{m}$ and $0.45\mu\text{m}$, respectively. According to Figure 4.9, the smallest particles present during the continuous degradation of BPA were the ones immediately after sonication and since all particles were greater than the pore size of the membrane, $0.2\mu\text{m}$, it was expected that a complete separation of TiO_2 particles could be achieved. Membranes with similar pore size were also employed by Le-Clech [2006] and Fu et al. [2006a] in their separation of TiO_2 particles from the treated water.

pH is known to affect the zeta potential of TiO_2 and thus the agglomeration of the particles. Therefore, the permeate quality during membrane filtration at different pH condition was examined for the possible presence of particles. No particles could be detected when the permeate was measured using turbidity and the laser scattering method, indicating that the membrane was able to retain the TiO_2 particles completely in the system for pH ranges from 4-10. Figure 4.10 shows the effect of pH on the size of TiO_2 after one hour of in-situ 0.5L/min aeration. The largest particles were observed to form at pH 7 condition. This was attributed to the fact that pH 7 was close to the point of zero charge of TiO_2 ($\text{pH} = 6.3$) in which the

particles were uncharged, therefore the particles would agglomerate more easily than those charged particles at pH further away from the pHpzc. Although the average particles at pH 4, pH 5.5 and pH 10 were smaller than at pH 7, the particles at these pHs were still greater than the pore size of the membrane, $0.2\mu\text{m}$. These results thus provide further evidence to the absence of particles in the permeate as discussed previously.

Figure 4.10 TiO_2 size distributions in different pH suspension after 1 hr of aeration at 0.5L/min.

4.4.3 Degradation of BPA in a SMPR under a Continuous Mode of Operation

The feasibility of the submerged membrane photoreactor (SMPR) in the removal of small molecular organics was investigated using 10mg/L of BPA. It should be noted that in this system, the membrane module was submerged in the photoreactor and not in a separate chamber, unlike Fu et al [2006a]. This proposed approach should provide a more compact system, but requires careful selection of the membrane material as presented in Chapter 3.

Figure 4.11 shows the degradation and mineralization of BPA under continuous operation of the SMPR. The pH, TiO_2 concentration and aeration rate were fixed at the optimum values of 4, 0.5g/L and 0.5L/min, respectively. The permeate flux was

kept at $100\text{L}/(\text{m}^2\cdot\text{hr})$ which was equivalent to a BPA residence time of 2 hrs. This flux was chosen based on 95% mineralization of 10mg/L of BPA (1.5 hr) in the batch degradation study. A difference between the initial values of BPA and TOC in Figure 4.11 was due to the fact that 79% by weight of BPA was organic carbon, i.e. 10mg/L of BPA consists of only 7.9mg/L of organic carbon according to Equation 4.7.

Figure 4.11 Degradation and mineralization of BPA (TiO_2 concentration = 0.5g/L , initial pH = 4, BPA feed concentration = 10mg/L , 0.5L/min aeration rate, residence time = 2 hrs).

The concentration of BPA was reduced by 97% after 90 min of illumination and remained at this value until the end of the experiment. It was noted that the permeate and the bulk concentration in the tank during the continuous photocatalysis process differed at the initial stage. The permeate BPA concentration was always higher than the bulk concentration until about 90min. This could be due to adsorption/desorption of BPA on the membrane [Kim et al., 1996].

As can be seen, the concentration of TOC at 40min was about 3mg/L while the concentration of BPA at the permeate was about 1.6mg/L (equivalent to TOC of 1.26mg/L). The difference between the concentration of TOC and BPA concentrations indicates the presence of intermediates during the PCO reaction. One

of the potential advantages of applying photocatalysis for the decontamination of water is the ability of this process to photomineralize all organic components, including target substrates and any intermediates formed. The destruction of intermediates is critical since some of the intermediates generated during the degradation of BPA could be more toxic than the parent compound, especially at low pHs [Chiang et al., 2004]. Figure 4.11 shows that the SMPR process achieved 97% removal of BPA and 93% removal of all TOC at steady state conditions (at about 120min).

4.4.3.1 Permeate Delay Investigation

In order to verify the postulation concerning the difference of BPA concentration between the tank and permeate concentrations shown in Figure 4.11, separate pulse input tracer tests using BPA were conducted to confirm the possible adsorption of BPA on the membrane and the results are presented in Figure 4.12.

In the absence of a membrane filter, it took about 2 minutes for BPA to reach the same concentrations as the tank concentrations (Figure 4.12). The 2 min delay was calculated, using the permeate flow rate (6.7mL/min) and permeate dead volume (13ml), to be the time necessary for BPA to travel from the tank to the end of the sampling tube. However, when the membrane module was added, it took about 22min for BPA to reach the tank concentration, verifying that adsorption and saturation of BPA on the membrane surface and pores took place during the additional 20 min delay.

Before the start of any photocatalytic reaction, the continuous system was operated for one hour in the dark to ensure the system was in a steady-state condition (inlet = tank = outlet BPA concentration). During this period of time, BPA would have been adsorbed on the membrane surface and filled up the pores within the membrane. When the UV lights were switched on, the BPA concentrations in the bulk decreased steadily. In order to reach equilibrium state, BPA already adsorbed on the membrane would be released and eluted from the membrane when the lower

concentration of the bulk solution permeated through the membrane. This transfer of BPA from the membrane surface to the permeate resulted in a higher permeate concentration as observed in Figure 4.11. The discrepancy between the tank and permeate concentration ceased when the reaction reached steady-state at about 90min where adsorption/desorption equilibrium on the membrane system was achieved. Kim et al. [1996] observed competitive adsorption of o-dichlorobenzene (o-DCB) between the membrane and the PAC particles in their PAC-UF system. Investigation of the effect of different membrane materials revealed that hydrophobic polysulphone (PS) membranes adsorbed o-DCB 10 times higher than that of hydrophilic cellulose acetate and this was attributed to the stronger hydrophobic π -bonding interactions between DCB compounds and the benzene rings in the polysulfone chain.

Figure 4.12 Pulse tracer tests for determination of permeate delay caused by adsorption of BPA on PVDF membrane (flux = 100L/(m².hr))

4.4.4 Variations in Feed Concentration

Figure 4.13 shows the efficiency of the SMPR in removing BPA at various concentrations. It was observed that the steady-state mineralization efficiency of BPA decreased with increasing concentration of BPA feed. For a continuous feed of 50mg/L BPA, only 20% of TOC was removed at steady-state compared to 93%

removal at 10mg/L of BPA. One of the presumed reasons for the difference was due to the saturation of the TiO₂ surface active sites at high concentrations of BPA. TiO₂ particles would degrade the BPA which was initially at equilibrium on the surface and thus did not have active sites for the fresh BPA which was being sent to the SMPR. The BPA or intermediates which were not degraded were being drawn out of the system immediately as permeate and this effect was magnified at a higher feed concentration of 50mg/L.

Figure 4.13 The mineralization of BPA for various initial concentrations of BPA in the permeate of SMPR (TiO₂ loading = 0.5g/L, aeration rate = 0.5L/min, filtration flux = 100L/(m².hr)).

Figure 4.14 Amount of TOC removed at 40min of continuous operation of the SMPR under different feed concentration.

Although the steady-state mineralization efficiency of the SMPR decreased with increasing feed concentration, it was worth to note that the amount of TOC removed at higher feed concentration was indeed greater (Figure 4.14). The total organics removed after 40min of SMPR operation were 0.8mg, 3.3mg and 10.7mg for 10mg/L, 20mg/L and 50mg/L of feed, respectively. This observation is in agreement with the finding in Table 4.5 in which the rate of reaction increased with the increase in initial concentration of BPA during the batch photocatalytic study. In this case, the SMPR operating at higher feed concentration was more effective in the removal of TOC, in terms of the total mass of TOC removed. It is thus important to note the difference between the two reported efficiencies. For the practical application of the SMPR in the treatment of drinking water or wastewater, the former efficiency becomes more appropriate because it was important to achieve targeted organic removal (in terms of percentage removal) continuously before the drinking water can be used or wastewater can be discharged.

Control of residence time enables efficient degradation of different initial concentrations of organic substrate. Table 4.8 shows the relationship between the

filtration flux and the residence time. It is shown in Figure 4.15 that longer residence times, i.e. slower permeate flux, resulted in better TOC removal efficiency. This is logical since the longer residence time had allowed more contacts between BPA and TiO_2 for oxidation to take place in the SMPR. A flux of $60\text{L}/(\text{m}^2\cdot\text{hr})$ was a better choice for achieving a high TOC removal (90%) of 20mg/L of BPA.

Table 4.8 Experimental conditions with different filtration fluxes (0.5g/L TiO_2 , initial pH = 4, initial BPA concentration = 20mg/L , $0.5\text{L}/\text{min}$ aeration rate).

Filtration Flux ($\text{L m}^{-2}\cdot\text{hr}^{-1}$)	Residence time (min)
40	292
60	195
100	117

Figure 4.15 Mineralization efficiency of 20mg/L of BPA by different permeate flux (TiO_2 concentration = 0.5g/L , initial pH = 4, BPA feed concentration = 20mg/L , $0.5\text{L}/\text{min}$ aeration rate).

As expected, the lower filtration flux also led to a lower transmembrane pressure (TMP) rise (Figure 4.16). An increase in TMP indicates loss of active membrane area in a constant flux operation. When the flux rate was maintained at $40\text{L}/(\text{m}^2\cdot\text{hr})$ or $60\text{L}/(\text{m}^2\cdot\text{hr})$, the amount of TiO_2 particles retained on the membrane surface per unit time was lower than that seen at $100\text{L}/(\text{m}^2\cdot\text{hr})$. In addition, the applied aeration rate of $0.5\text{L}/\text{min}$ was able to exert adequate shear rate on the membrane and to facilitate the detachment of any TiO_2 particles from the membrane surface at lower permeate fluxes thus resulting in smaller TMP changes.

Figure 4.16 Effect of different filtration fluxes on the TMP development (TiO_2 concentration = $0.5\text{g}/\text{L}$, aeration rate = $0.5\text{L}/\text{min}$, BPA concentration = 20ppm).

4.4.5 Fouling Control in the Operation of a SMPR

4.4.5.1 Critical Flux

Critical flux is a common term used in membrane filtration fouling studies and is defined as the flux below which fouling of the membrane does not occur [Howell, 1995]. At this flux, the forces of convection are just balanced by back-transport mechanisms such as shear-induced diffusion. In practice, it is possible to run without particle deposition on the membrane if it is operated at controlled sub-critical flux. Figure 4.17 shows the results of the step-flux experiments which were

used to determine the critical flux for the SMPR TiO_2 suspension. The transmembrane pressure (TMP) was constant for filtration fluxes below $80\text{L}/(\text{m}^2\cdot\text{hr})$ and thus $80\text{L}/(\text{m}^2\cdot\text{hr})$ was taken as the critical flux found in this study. Above this value, the TMP became unsteady. The operation of the SMPR at a flux of $100\text{L}/(\text{m}^2\cdot\text{hr})$ resulted in fouling where the TMP steadily increased to about 12.5kPa from the initial 10kPa (Figure 4.16). As long as the membrane filtration was operated below critical flux, fouling could be minimized.

Figure 4.17 The change in transmembrane pressure for different filtration flux (TiO_2 concentration = $0.5\text{g}/\text{L}$, bubbling = $0.5\text{L}/\text{min}$)

4.4.5.2 Use of Bubbling

Figure 4.18 shows the effect of bubbling rate on membrane fouling. The benefit of bubbling in reducing TMP was observed at lower aeration intensity from $0.001\text{m}^3/\text{m}^2\cdot\text{s}$ ($0.2\text{L}/\text{min}$ bubbling) to $0.006\text{m}^3/\text{m}^2\cdot\text{s}$ ($1\text{L}/\text{min}$ bubbling). Aeration intensity is defined as the volume of bubbles per unit reactor cross-sectional area per unit time. In a submerged membrane system, bubbling helps to exert shear forces on the membrane and thereby reduce fouling [Hong et al., 2002; Sofia et al., 2004 and Liu et al., 2000]. However, when bubbling was increased four times from $0.006\text{m}^3/\text{m}^2\cdot\text{s}$ to $0.024\text{m}^3/\text{m}^2\cdot\text{s}$, the fouling tendency of the membrane at a flux of

100L/(m².hr) showed no significant improvement. The TMP increased by about 20% for both cases after about 300 min of filtration.

Figure 4.18 Percentage increase in transmembrane pressure under different bubbling rates at a TiO₂ concentration of 0.5g/L and constant flux operation of 100L/(m².hr).

When bubble aeration was increased, bubble collision would lead to larger bubbles and diminishing gas hold-up, which thus resulted in cross-flow velocities plateauing [Sofia et al., 2004]. In this case, the cross-flow velocities of the system might increase till 0.006m³/(m².s) and reaching the saturation point thereafter. As a consequence, negligible aid in reducing fouling was observed when the aeration rate was increased beyond 0.006 m³/(m².s).

The limiting effect of air bubbling was also observed by Sofia et al [2004] and Hong et al [2002] but at a different range of bubbling rates. It is worth noting that the aeration intensity employed in this case was about ten times lower than those typically used in a MBR system. This was believed to be closely associated to the nature of the suspended particles involved in filtration. In an MBR system, fouling is mainly affected by the formation of a concentrated biomass sludge cake layer, mainly consisting of bacterial cells and bacterically produced substances such as extracellular polymers (EPS) [Nagoka et al., 1996]. These sticky and viscous EPS

are believed to deposit on the membrane surface and are responsible for the drastic decrease in the membrane permeability. On the other hand, TiO_2 is expected to create lesser problems as a foulant since colloidal cake layers are not so compact and would have higher probability of detachment as compared to a sludge cake [Lee et al., 2001]. Therefore, airflow requirements in submerged MBRs are expected to be higher than in the SMPR system.

It is important to recognize that aeration incurs a major part in the operating cost of a submerged membrane system [Gillot et al., 1999] and minimizing unnecessary airflow is definitely attractive in the long term operation of a submerged system.

4.4.5.3 Intermittent Permeation

As noted above, increasing aeration would result in higher energy consumption and could also attenuate UV transmission (see section 4.4.1.5). Therefore, in an attempt to maintain high flux operation at low aeration rate, the effect of intermittent permeation was investigated and the results are shown in Figure 4.19. In this case, the permeation was closed for 2 min for every 5 min operation (open position). When the suction was stopped and no permeate was collected, there was a period for the aeration to exert shear on the membrane surface to facilitate the detachment of TiO_2 particles. This prevented an accumulation of TiO_2 particles on the membrane surface. The advantages of intermittent permeation to control fouling have also been reported by Howell et al. [2004] and Hong et al. [2002] during the operation of MBR systems.

Figure 4.19 TMP change for continuous 100L/m².hr and intermittent permeation operation (intermittency of 2min close/5min open)

The intermittence frequency (IF) is defined as the ratio of the time when the valve remained at close position (off) to the time when the valve remained at the open position (on). From a practical point of view, a lower IF would mean a higher production of treated water. Although the intermittent operation of 2min off and 5min on was shown to reduce the fouling tendency of the membrane as indicated in Figures 4.19, it resulted in a decrease in water production by about 30%. Therefore, optimization experiments with different IFs were carried out and the results are shown in Table 4.9 and Figure 4.20.

Table 4.9 Summary of intermittence frequency tests

IF	0.00	0.03	0.1	0.4	0.6
	Constant opening	Close for 9 sec, open for 5 min	Close for 1 min, open for 5 min	Close for 2 min, open for 5min	Close for 3 min, open for 5min

Figure 4.20 Comparison of the TMP change, TOC degradation and production of water between continuous and intermittent permeation operation. Change in TMP (%) = $100 \times (\text{steady-state TMP} - \text{initial TMP}) / \text{steady-state TMP}$ of continuous operation; Efficiency of TOC degradation (%) = $100 \times (\text{initial TOC} - \text{final TOC}) / \text{initial TOC}$; Production of water (%) = $100 \times (\text{volume of water at the designated IF} / \text{volume of water at continuous operation})$.

It is worth to note that the extent of mineralization was slightly enhanced by intermittent operation, possibly due to the increase in BPA residence time in the system as a consequence of the intermittent operation. The water production rate with an IF of 0.4 and 0.1 were approximately 70% and 84% with respect to continuous production rate. Reducing the intermittence frequency from 0.4 to 0.1 has increased the water production rate by about 14%. Most importantly, it was found that the change in TMP of the system was decreased by 20% with an IF of 0.1 compared to the continuous operation. Further reducing the IF to 0.03 helped to increase the production of water by another 13% whereas a 5% rise in TMP was compromised when compared to an IF of 0.1. Since the intermittent operation did not affect the extent of mineralization much, therefore it can be concluded that the advantages of employing intermittent operation was on the water production followed by reduction in TMP rise. However, the enhancement in preventing fouling was observed to be limited as seen in Figure 4.20, leveling off at IF 0.1. In

this case, IF 0.03 was chosen to be the best option for the experimental conditions, striking a balance between water production and fouling control.

Comparing intermittent permeation and the use of bubbling in controlling fouling in a SMPR system, the intermittent permeation seemed to be a better option though an enhancement limitation was observed for both methods. The usefulness of the bubbling option may depend on the membrane configuration. In this case, the membrane employed was a “U-shaped” type whereby both ends of the hollow fibre were fixed at one end to collect filtrate. The bubbling in this case might not be fully utilized as depicted in Figure 4.21. The bubbles were not able to service all the membrane surface compared to those with flat sheet, bundles or curtains of straight hollow fibres where contacts of bubbles with membrane surface are potentially much greater. Also, the choice of bubbling rate in this application was constrained by the possibility of UV light attenuation by the bubble clouds leading to the preferred method of using low, optimized IF to minimize fouling for long term operation of the SMPR. Further optimization of bubbling and module design are beyond the scope of this thesis.

Figure 4.21 Comparison of air bubble and water flow hydrodynamics within a (a) U-shaped (b) curtain type hollow fibre module.

4.5 Summary

This chapter has established the feasibility and various factors affecting the performance of the SMPR. The photocatalytic process was first optimized before combining the membrane separation with the degradation process. pH was found to affect the degradation of BPA most significantly compared to the effect of TiO_2 concentration and aeration rate. Lowering pH enhanced the degradation of BPA due to better adsorption of the solute on the catalyst. Increasing the aeration rate, up to 0.5L/min, increased the photocatalytic efficiency which leveled off at higher aeration rate. The limit to the improved effect of the aeration was most probably due to the competing effects between the enhancement of mass transfer and the light attenuation by bubble clouds which were formed at high aeration rates. The continuous SMPR was able to photodegrade 97% of the BPA and photomineralize 93% of the TOC after 90min and 120min of UV illumination, respectively. BPA adsorptions on the PVDF membrane was observed which caused a difference in the tank and permeate concentrations during the transition state of the SMPR. However, this difference diminished when the SMPR reached a steady-state owing to the fact that adsorption equilibrium was achieved between the membrane and the bulk solution at steady-state. Intermittent permeation is preferred over bubbling to control fouling in the SMPR. The possibility of operating the SMPR at a high flux ($100\text{L}/(\text{m}^2\cdot\text{hr})$) with low membrane fouling using an intermittent permeation method was demonstrated. Residence time control in the SMPR by varying the permeate filtration flux was verified to be vital with varying feed concentrations. For an efficient SMPR, factors influencing both photocatalytic degradation and membrane filtration, including fouling control, have to be taken into consideration. The compact and low-pressure SMPR has shown to be effective and attractive for the photodegradation of low concentrations of organics in water.

CHAPTER 5

DEVELOPMENT AND

PERFORMANCE OF AN

IMPROVED SUBMERGED

MEMBRANE

PHOTOCATALYTIC REACTOR

5.1 Introduction

In a good photoreactor design, the effective use of the UV light available plays an important role due to the inevitable attenuation or refraction of radiation within the TiO₂ photocatalyst suspension [Ray, 1999]. Many studies have been done on understanding the absorption and scattering effect of TiO₂ and thus the radiation field of a photoreactor [Martin et al., 1996; Salaices et al., 2002; Sellami et al., 2003; Cassano and Alfano, 2000]. One crucial piece of information obtained from these studies was that the maximum number of incident photons absorbable by TiO₂ is limited. This finding led to the urgency for maximizing the distribution of light in the reactor so as to compensate for the limitation of TiO₂ dispersion in absorbing UV photons. Ensuing maximum distribution of UV in a reactor would not only optimize photon efficiency, but it should also be accompanied by the advantage of better reactor volume exploitation. Higher rates of reaction would be achieved throughout most parts of the reactor and thus fully utilize the reactor space.

The selection of the radiation source is a critical step for optimal reactor design. In a photocatalytic reactor, a higher efficiency of photon utilization would be obtained using dilute artificial sources of UV irradiation such as fluorescent [Puma and Yue, 2003] which was similar to that used in Chapter 4. Chapter 4 has presented a feasibility study of the proposed SMPR configuration, where coupled photocatalysis and filtration processes occur in a single reactor, in the degradation of BPA. High conversion of BPA was continuously achieved with a residence time of 2 hrs. In the previous design, the photoreactor was operated using an external fluorescent UV light source which was built specially within a box for the containment of the UV light. Maximum utilization of UV light energy was not expected with this type of external light source configuration as a consequence of possible loss of UV light to the environment [Ray, 1999]. A TiO₂ slurry reactor with immersed UV lamps was reported to be more effective than the external UV reactor by Molinari et al. [2002]. In a slurry reactor, the depth of UV penetration is limited because of the strong absorption by catalyst and dissolved pollutants. As a result, reactor geometry and spatial arrangement of photon source(s) become critical during the design of a photoreactor.

With the objective of attaining better UV photon distribution and volume space utilization, an improved SMPR design with several submerged light sources and its performance are presented. This chapter reviews the development of the reactor design with regard to ensuring even distribution of UV light, well-mixed conditions as well as better heat dissipation during the photoreaction. The photonic efficiency of the design reported in Chapter 4 and the improved design are compared in terms of their performance in batch for BPA and resorcinol degradations. The importance of temperature control during the operation of a SMPR is also demonstrated. Finally, a long-term operation of the SMPR is presented and the issues related to the lifetime of TiO₂, fouling control and stability of the membrane are systematically addressed.

5.2 Theoretical Background

5.2.1 UV Photoreactor Configuration

The thin-film slurry reactor is one of the most common types of photoreactor used in photocatalytic degradation studies [Soparajee et al., 1999 b; Sellami et al., 2003; Puma and Yue, 2003]. Common thin film reactor configurations include an annular reactor in which two concentric tubes made up a channel for TiO_2 suspension to flow through. The lamp is placed inside the inner tube that is transparent to UV illumination. This reactor configuration has the advantage of providing symmetrical irradiation field and results in a large illuminated catalyst surface per unit volume of reactor. A thin-film reactor requires the use of a single lamp and thus occupies minimum floor space [Puma and Yue, 2003].

The concept of working with a thin-film slurry reactor advanced to the invention of a novel fountain photocatalytic reactor where a special nozzle provided a thin liquid film in the form of a TiO_2 suspension fountain exposed to a UV source. The photoreactor was opened to the atmosphere and was illuminated from the above by either artificial UV lamps or solar energy [Puma and Yue, 2001]. It was reported that this reactor configuration allowed for very high photocatalyst activation and high oxygen transfer rates and was able to utilize both direct and diffuse radiation from the UV energy source. However, due to the basic concept of a thin-film slurry reactor i.e. working with a small length of illuminated pathway, this type of configuration is, therefore, not suitable for incorporating with a submerged membrane filtration process due to the limited reactor space available for the membrane module.

For larger slurry photoreactor dimensions, effective UV utilization was expected to be more difficult because of the limitation in which UV light was able to penetrate through the TiO_2 particles [Pareek et al., 2003]. Molinari et al. [2002] reported that the immersion type of reactor with a UV lamp immersed within the reactor was more efficient than the external type where the UV lamp was placed outside the

reactor. A similar conclusion was also drawn by Ray [1999] in the comparison of his immobilized TiO₂ system. A common immersed UV lamp reactor involves the immersion of a single UV lamp in the TiO₂ slurry in which the UV lamp is contained in a quartz or borosilicate glass tube with cooling water circulating the immersed glass tube [Pareek et al., 2003; Molinari et al., 2002; Sauer et al., 2002]. Besides single UV configuration, a distributive immersed UV type, with the light distributed from the source to the reactor by optical means such as optical fibre, was studied [Lee et al., 2004]. The UV light was transmitted by an optical fiber bundle into the thin glass tubes of 20mm in the reactor where TiO₂ particles were immobilized on the external surface of these glass tubes. A similar design concept of employing TiO₂ coated hollow tubes as light guides to the reactor was also reported by Ray [1999]. The immersed distributive UV configuration ensures a better UV photon distribution within a photoreactor.

5.2.2 Process Efficiency of Photoreactors

The overall quantum yield, Φ_{overall} , is expressed as the number of reactant molecules that react for each photon absorbed (Equation 5.1) [Calvert and Pitts 1966].

$$\begin{aligned}\Phi_{\text{overall}} &= \frac{N_{\text{molecules}} (\text{mol s}^{-1})}{N_{\text{photon}} (\text{einstein s}^{-1})} \\ &= \frac{\text{rate of reaction}}{\text{rate of absorption of photons}}\end{aligned}\tag{5.1}$$

Owing to the absorption and scattering effects of particulate TiO₂, the determination of quantum yield is complicate in heterogeneous photocatalysis due to the difficulties in determining the efficiency of photon absorption. The extent of light scattering can reach 13 - 76% (depending on the type of semiconductors or insulators) of the total incident photon flux of an artificial UV_{300-400nm} lamp source [Schiavello et al., 1991]. Differences in the refractive indices of the components that make up a photocatalytic system, namely the type of TiO₂ ($\eta_{\text{1, anatase TiO}_2} = 2.5 - 3$ at 365nm), reactor wall material ($\eta_{\text{glass}} = 1.5-1.7$) and solution composition ($\eta_{\text{o, water}}$

= 1.33), explain why TiO_2 can never absorb all the photon fluxes from a designated light source. The intensity of scattered light depends on the refractive indices as

$$\frac{I}{I_o} = (\cos \theta)^2 \frac{\eta_1}{\eta_o} \quad (5.2)$$

where I is the scattered light intensity, I_o is the incident light, η_o is the refractive index of the medium and η_1 is the refractive index of the photocatalyst [Serpone et al., 1993]. When $\eta_1 \approx \eta_o$, the extent of scattered light is negligible whereas when $\eta_1 > \eta_o$, the light is highly scattered. In the above system, light is expected to be highly scattered since $\eta_1 > \eta_o$ [Rosenberg et al., 1992].

To circumvent the problem of quantifying the number of photons absorbed, “photonic efficiency (ζ)” (Equation 5.3) can be used to represent the efficiency of a photoreactor for the degradation of the organic compounds [Serpone et al., 1993]. It describes the number of reactant molecules transformed or product molecules formed divided by the number of incident photons that fall on the front window of the cell at a given wavelength.

$$\zeta = \frac{\text{rate of reaction}}{\text{incident photon flux entering the photoreactor}} \quad (5.3)$$

For any given reaction, Φ_{overall} is always greater than, if not equal to, ζ owing to light scattering and reflective losses. Even so, photonic efficiency is directly proportional to the quantum yield and thus provides some idea of the photocatalytic light efficiency. It should be noted that photocatalysis depends on other parameters including reactor geometry, intensity of irradiation, concentration of catalysts, dissolved oxygen and reactant concentration, pH, competitive interfering species and also mixing of the system. As a result, the values of Φ_{overall} or ζ reported by one research group might be different from those obtained by another. It is thus important to stipulate the reactor geometry, light source and properties of the catalysts when reporting any light efficiency.

Theurich et al. [1996] has reported a range of ζ between 0.1% to 0.8% for the degradation of 4-Chlorophenol under different pH conditions. An equally low efficiency was obtained by Kaniou et al. [2006] who found a photonic efficiency of 1.25% for the degradation of sulfamethazine in a TiO₂ suspension. The ζ increased from 7.68% to 20.65% when TiO₂ was doped with silver and platinum [Sakthivel et al., 2004]. Muneer and Bahnemann [2002] obtained an even higher efficiency of 20.9% for the degradation of 2,4,5-tribormoimidazole compared to 4.7% for the degradation of Terbacil under identical conditions. In general, comparison among research groups is not straightforward since the reaction conditions used in each study would be different.

For comparison between different research groups, Serpone et al. [1996] has introduced the use of relative photonic efficiency, ζ_r , which is related to an acceptable standard process, a standard photocatalyst (Degussa P25) and a “standard secondary actinometer” in a photocatalyzed process. When the ζ for any test substrate and for the standard actinometer (usually phenol) are obtained under identical experimental conditions, ζ_r is then defined as in Equation 5.4.

$$\zeta_r = \frac{\text{initial rate of disappearance of substrate}}{\text{initial rate of disappearance of phenol}} \quad (5.4)$$

ζ_r is found to be independent of light intensity, reactor geometry and TiO₂ concentration but it depends on factors which influence the adsorption-desorption characteristics of TiO₂ particles (e.g. concentration of organic substrate, pH and temperature of solution). The comparison of ζ_r between research groups is made possible with the only constraint that phenol is the standard substrate against all ζ_r reported. Once ζ_r is known, Φ_{overall} of any process can be determined by $\zeta_r \cdot \Phi_{\text{standard}}$ where Φ_{standard} is the quantum yield of the disappearance of phenol under exactly the same reaction conditions.

The disadvantage of ζ_r is that it does not indicate the light efficiency with respect to light photons [Mills and Hunte, 1997]. It merely reports the degradation rate of an

organic compound with regard to a standard compound. For example, a value of 2 simply means that the degradation of the designated compound is twice as fast as the degradation of phenol under identical conditions; the value reported does not reveal light efficiency. Furthermore, in order to get Φ_{standard} , one still has to determine the quantum efficiency of phenol under certain conditions which is tedious. Since Φ_{standard} has to be determined whenever a reaction condition has changed, this presents no advantage to the measurement of Φ_{overall} directly [Gorges et al. 2004; Mills and Hunte 1997].

5.3 Experimental Procedures

5.3.1 Materials

The P25 TiO_2 used for the experiments was supplied by Degussa AG, Germany. High purity BPA (Merck-Schuchardt, similar to that used in Chapter 4) and resorcinol (Aldrich, 98%) were used and the physical and chemical characteristics of resorcinol are shown in Table 5.1. The pH of all suspensions was adjusted using sodium hydroxide and perchloric acid. Purified air was used as a source of oxygen in this study. Unless otherwise stated, all solutions were prepared using Millipore MilliQ (MQ) water with a resistivity of $18.2\text{M}\Omega\text{cm}$. Microfiltration (MF) hollow fibre membranes made of polyvinylidene fluoride (PVDF) were supplied by Bluestar China, with an average pore size of $0.2\mu\text{m}$ and were potted into an U-shaped module with an active filtration area of 0.0088m^2 . All chemicals used in the tracer and chemical actinometry tests were of analytical reagent grade.

Table 5.1 Resorcinol characteristics

Chemical Name	Resorcinol
Molecular formula	C ₆ H ₆ O ₂
Molecular weights (g/mol)	110.1
Solubility at 22 ^o C (g/L)	1400
Density at 22 ^o C (g/cm ³)	1.27
pKa	9.30
Log Kow	0.8

5.3.2 Improved Submerged Membrane Photoreactor

Figure 5.1(a) shows a schematic diagram of the 1200mL improved submerged light SMPR. Eight lamps of 4W UV-A (Japan NEC) were submerged in the system, two in each borosilicate glass tube (Figure 5.2 (b)). The four borosilicate glass tubes were then spaced accordingly in the reactor surrounding the submerged U-shaped membrane which was placed right in the middle of the SMPR. The borosilicate glass tubes were positioned based on the results obtained from a light distribution test study (section 5.4.1.1) to optimize light distribution in the submerged reactor. A cooling water jacket maintained the reaction at the required temperature. An aeration diffuser which was about the same diameter as the reactor provided an uplift circulation to maintain the TiO₂ particles in suspension and provided dissolved oxygen. In a typical experiment, a pre-set permeate flux was withdrawn from the system through the suction provided by a peristaltic pump. The transmembrane pressure (TMP) in all experiments was measured by an online pressure gauge on the permeate line. Samples at pre-defined times were taken from the permeate line for different analyses. The effect of permeate flux on organic degradation was conducted by changing the permeate pump settings accordingly.

Figure 5.1 (a) Schematic diagram of the newly developed submerged membrane photoreactor (SMPR). (b) Arrangement of two UV lamps within a borosilicate glass tube. Left: side view, Right: Top view.

5.3.3 Light Distribution

5.3.3.1 Direct Sensor Measurement

A UV radiometer equipped with a stainless steel waterproof probe was designed and custom made (HANDI, Beijing Normal University). The rigid probe was 30cm long with a 3mm sensing area at the end of the probe. The small size of the detector minimized the perturbation of the radiation field. The UV light extinctions at

different TiO₂ concentration suspensions were measured using a borosilicate glass tube containing two 4W UV-A fluorescent lamps, with lamp power and configuration similar to those used in the photoreactor as shown in Figure 5.1 (b). The probe was placed parallel to the glass tube and the light distribution profile was measured axially with increments of 1cm from the mid length of the borosilicate glass tube. This measurement was carried out for position (I), (II), (III) and (IV) and the average intensities for each increment point were reported; for example there would be 4 intensities measured for the point 1cm from the borosilicate glass tube, each from position (I), (II), (III) and (IV). Different concentrations of TiO₂ suspension were studied which included 0.02g/L, 0.2g/L, 0.5g/L and 1g/L.

5.3.3.2 Chemical Actinometry

The potassium ferrioxalate actinometry test was used to determine the incident photon flux of the submerged and external light photoreactors using 1200mL and 800mL of actinometric solutions, respectively. The conditions for the actinometry test were kept similar to those employed in typical photocatalytic experiments. 1200mL of actinometric reagent was prepared by dissolving 3.44g of iron (III) chloride (FeCl₃·6H₂O), 6.63g potassium oxalate (K₂C₂O₄) and 100mL of 1M sulphuric acid (H₂SO₄) in 2000mL of MQ water. 1200mL of this solution was then poured into the photoreactor and the UV lamps were switched on. Aliquots of 0.5mL were withdrawn at pre-determined time intervals and added into the 50mL of volumetric flask containing 2mL of 6.08mM ferrozine and 2mL of 2M sodium acetate buffer (pH 5.5). MQ water was added to fill the 50mL volumetric flask and the purple ferrous complex solutions were then analyzed with the spectrophotometer at 562nm after 30 minutes with a 1cm quartz cell.

To prepare the calibration curve for analysis of the Fe²⁺ complex, a standard solution of 1.79mM of ammonium ferrous sulphate (Fe(NH₃)₂(SO₄)₂·6H₂O) was prepared, making the ferrous (Fe²⁺) content to be 100mg/L (1.79mM). The standard solution was then diluted accordingly to different concentrations of ferrous content by adding the required amount to the 50mL volumetric flasks containing 2mL of

6.08mM ferrozine and 2mL of 2M sodium acetate buffer (pH 5.5). These solutions were left to stand for at least 30min before measuring the absorbance at 562nm by using a spectrophotometer. From the measurement, a linear relationship between the absorbance of the solutions versus the concentration of the ferrous ions was obtained. The relationship was then used as a calibration curve for the determination of the ferrous ion concentration. The intensity of the irradiating source was then calculated using Equation 5.5 [Calvert and Pitts, 1966].

$$I(einstein / s) = \frac{\Delta A V_2 V_3}{\phi \epsilon d V_1 t} \quad (5.5)$$

where ΔA is the absorbance (at 562nm) of irradiated actinometer solution corrected for absorption of blank, d is the path length of the absorption cell, ϵ is the extinction coefficient of the ferrozine complex at 562nm, Φ is the quantum yield of ferrous production at the wavelength of the light used [$\Phi = 1.15 - 1.26$ at 366nm], V_1 is the volume of irradiated actinometer solution withdrawn, V_2 is the volume of actinometer irradiated, V_3 refers to the volume of the volumetric flask used for dilution of irradiated aliquot, t is the irradiated time in seconds.

5.3.4 Tracer Test

Tracer tests with the use of an inert (conserved) material is a common test used to determine the mixing conditions of an aqueous reactor since it is evident that elements of fluid pass through the reactor using different routes and thus taking different lengths of time to exit the reactor [Levenspiel., 1999]. The determination of residence time distribution (RTD) of the SMPR was performed using a pulse input tracer test. Initially, MQ water was continuously fed and drawn through the membrane module before a certain amount of sodium chloride was injected to the reactor as a pulse input. The injected sodium chloride was immediately mixed in the system by the bubbling provided. Samples were taken from the tank and the permeate line after specific time intervals and measured for NaCl concentration. The concentrations of NaCl were then plotted against time in a C_{pulse} curve. To find

the observed mean residence time, Equation 5.6 was used where t_i is the specific time (min), C_i is the concentration of NaCl at the specific time and Δt_i is the time difference between samples. Note that the denominator represents the area under the C_{pulse} curve.

$$\bar{t}_{\text{obs}} = \frac{\int t C dt}{\int C dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (5.6)$$

The observed mean residence time was compared with the theoretical residence time as shown in Equation 5.7,

$$\bar{t}_t = \frac{V}{v} \quad (5.7)$$

where V is the active volume of the reactor and v is the volumetric flow rate.

5.3.5 Analytical Methods

The measurement of the BPA concentration by HPLC was similar to that described in Section 4.3.6 whereas the measurement for resorcinol was done by a Waters Atlantis dC₁₈ HPLC column (4.6mm x 150mm, 5 μ m) with a mobile phase consisting of 80% of 10mM ammonium formate buffer (pH 3) and 20% methanol. The TOC present in the samples was determined by a TOC analyzer (Shimadzu TOC-V_{CSH}). The ferrous formation in the light distribution test was measured with a UV-VIS spectrophotometer (Jasco V-550). The concentration of sodium chloride was determined using ion chromatography (Shimadzu LC-10Ai).

5.4 Results and Discussion

5.4.1 Design of Reactor

5.4.1.1 Radiation Field of UV Light Source

As mentioned in Section 2.3.1, the main challenge with the use of a slurry photocatalytic reactor is to obtain a homogeneous light distribution in turbid TiO_2 suspension [Dijkstra et al., 2001]. UV source configuration, in terms of spatial arrangement in a photoreactor, is thus important which in turn requires understanding of the light penetration lengths in different systems. Though extensive experimental and modeling works have been done in determining the absorption and scattering effect of TiO_2 and thus the radiation field of a photoreactor (Martin et al., 1996; Salaices et al., 2002; Sellami et al., 2003; Cassano et al., 2000), the general applications of these models remain limited. The total amount of absorbed photons was found not only to be a function of TiO_2 concentration but it also depended on the agglomerated TiO_2 size, mixing conditions, radiation wavelength and reactor geometry. Furthermore, several of the current methods for the measurement of radiation absorption lead to complex approaches that tend to underestimate the radiation absorption while giving local information about the energy absorbed, reported as the local volumetric rate of energy absorption. The use of the radiation transfer equation is a good example of the more complex method that employs the Beer-Lambert equation with true absorption and scattering coefficients and a radiation model to estimate the total light absorbed [Lasa et al., 2004].

With the approach of light to the TiO_2 particles, the light can be absorbed, scattered or transmitted. In simplification, light intensity at any point in the reactor = total incident ray – amount absorbed – amount scattered – amount transmitted. However, it is not within the scope of this study to determine the individual effects of the above-mentioned parameters because the main aim of this study was to determine the UV penetration length so that the spatial arrangement of multiple UV sources

could be optimized in the photoreactor. Thus a direct measurement of the light intensity, using a waterproof radiometer, at any radial point from the UV sources was adopted.

The average light intensity profiles as a function of TiO_2 concentration for the submerged light SMPR UV sources, which were contained in a borosilicate glass tube, are shown in Figure 5.2.

Figure 5.2 Experimental radial light intensity profiles in water medium (0g/L) and different TiO_2 concentrations at center of one borosilicate glass tube (Conditions: without bubbling, UV range measured: 320 – 380nm).

From Figure 5.2, water being a non-participating medium caused a 17% drop in UV intensity as the radial distance moved from 1cm to 5cm away from the lamp source. All light extinctions in Figure 5.2 followed an exponential profile which is consistent to the finding as reported by Pareek et al. [2003]. UV penetration decreased dramatically with increasing TiO_2 concentration. Even with a low concentration of TiO_2 , 0.02g/L, the UV intensity at the 5cm position decreased by 48% compared to that of water. For the commonly used catalyst loading of 0.5g/L, the light intensity at 1cm from the lamp was only 13% of the value in the water. Moving away from 1cm to 2cm further reduced the lamp intensity to 7.33 W/m^2 .

Based on the optimum catalyst concentration of 0.5g/L obtained in Chapter 4, the lamps were arranged in the reactor as shown in Figure 5.3.

Figure 5.3 Configuration of UV lamps in the submerged light 15cm photoreactor (solid line represents borosilicate glass tubes, dotted line represents UV illumination area).

The glass tubes were spaced 2cm from each other (measured from outer circumference) in a circular pattern whereas a distance of 4.7cm was measured diagonally between two glass tubes. The 2cm space ensured adequate maximum local light intensity for the reaction to occur (note that 2cm is the maximum distance for effective illumination based on 0.5g/L of TiO_2 concentration). It must be noted that the light distribution as shown in Figure 5.2 was done in the presence of one borosilicate glass tube (2 lamps of 4W UV). Hence a particular point in the submerged reactor configuration would receive photon illumination from one or more glass tubes. The overlapping circles as shown in Figure 5.3 illustrate the overlapping illuminated regions. The shaded region which made up approximately 11.5% of the total reactor volume represents the volume which might not be getting effective UV intensity. However, it was expected that a well-mixed condition would be able to compensate for the loss of this dark volume by mixing constantly the TiO_2 particles in the dark regions with those in the illuminated regions.

5.4.1.2 Completely-Mixed Condition – Tracer Test

The experimental pulse tracer test determined for the submerged light reactor is presented in Figure 5.4 (C_{pulse} curve). The observed mean residence time (Table 5.2) for each bubbling rate was obtained from Equation 5.6 with the use of the area under the C_{pulse} curve.

Figure 5.4 Tracer test data obtained from the SMPR continuous operation at different bubbling rates.

Table 5.2 Summary of the observed mean residence time

Bubbling rate	Observed mean residence time (min), t_{obs}	Theoretical residence time (min), t_t	Difference (%)
1L/min	47.7 ± 0.5	50	4.6%
2L/min	49.2 ± 0.3	50	1.6%
3L/min	49.0 ± 0.6	50	2.0%

As discussed in Section 4.4.1.5, mixing in the submerged light membrane system was solely provided by aeration which also kept the TiO_2 well dispersed in the suspension. It is also important to note that the continuous feed was immediately mixed with the reaction medium as soon as it entered the reactor based on the fact that the feed inlet was placed on top of the bubble diffuser [Figure 5.1 a]. Table 5.2

shows that aeration at the lowest value of 1L/min resulted in a greater deviation from the theoretical residence time. The theoretical residence time was calculated using Equation 5.7 and it represents the residence time if there is no by-pass and the reactor is in a state of ideal well-mixed condition. Therefore, the discrepancy between the observed and the theoretical residence times indicates deviation of the mixing condition from a well - mixed reactor. The mean residence time did improve slightly, by 3%, when doubling the bubbling rate to 2L/min. However, when bubbling rate was increased further from 2L/min to 3L/min, t_{obs} remained fairly constant.

Theoretically the mean residence time would decrease if the active volume became smaller, according to Equation 5.7, as a result of improper fluid dynamics in the reactor or insufficient mixing. A comparison of the C_{pulse} curve with the theoretical expected curve would pinpoint non-ideal flow in the reactor [Levenspiel, 1999]. For example, a sharp early peak would indicate a shortcircuiting of tracer from the inlet to the outlet without going through proper mixing. The exponential decays of NaCl concentration (Figure 5.4) observed for the three bubbling rates indicated that a reasonably good flow was achieved in all the three bubbling conditions. The slightly earlier observed mean residence time for 1L/min (Table 5.2) could mean that a small stagnant zone or dead spaces were present in the reactor.

As reported in the preceding Section 4.4.1.5, bubbling was postulated to attenuate light intensity and might be competing with the beneficial effect of mass transfer at high bubbling rate. Thus a 2L/min bubbling rate was fixed for subsequent experiments so as to ensure adequate mixing and, at the same time, minimizing the possibility of light attenuation by bubble clouds.

5.4.1.3 Heat Concern

In the submerged light photoreactor, two lamps of 4W UV were contained in each of the four borosilicate glass tubes and the heat energy given out by these eight fluorescent lamps had to be investigated. If the temperature increased substantially during a photocatalytic reaction, the reaction rate would be different from that

taking place at room temperature. A greater reaction rate was observed at higher temperature in which the degradation half times of chlorofenapyr at 25°C and 40°C were 16.2min and 11.7min, respectively [Cao et al., 2005]. The increase in reaction rate was attributed to increasing collision frequency of molecules in solution from 20°C to 50°C. Measures should thus be taken during the design of a reactor to minimize temperature effects for direct comparison of experimental results. The importance of controlling the temperature in the operation of the SMPR is further discussed in Section 5.4.5.

Figure 5.5 Temperature profile in the bulk and at the wall of the lamp tubes under controlled and uncontrolled temperature tests.

The temperatures next to the wall (T_{wall}) of the borosilicate glass tube where the lamps were contained and those in the bulk solution (T_{bulk}) were measured (Figure 5.5). Under the uncontrolled situation, the temperature increments were 15.7°C and 15.8°C for the bulk solution and the wall, respectively after irradiation for five hrs. T_{wall} was observed to be always close to T_{bulk} and this indicated that the heat dissipation in the reactor was satisfactory. Solution heated near the wall of the glass tube was immediately mixed with the bulk solution by the continuous aeration thus preventing localized heating concerns. Cooling water was used to maintain and control the temperature of the reaction medium by circulating it through the water jacket (Figure 5.5 - controlled temperature situation). When cooling water (set at

25.3°C) was passed through the water jacket of the stainless steel reactor, the average temperatures in the reactor (bulk and wall) were able to remain constant between 26.1°C to 26.3°C. The cooling system would be used in all future experiments unless otherwise stated.

5.4.2 Parameters Affecting the Photodegradation of Resorcinol

5.4.2.1 Effect of Catalyst Concentration

The effects of photolysis and photocatalytic oxidation are presented in Figure 5.6. It was evident that the addition of photocatalyst accelerated the degradation of resorcinol significantly. In the absence of catalyst, 8% degradation of resorcinol was achieved after 30min whereas 30% and 93% of resorcinol were degraded with the addition of 0.002g/L and 0.2g/L of TiO_2 , respectively. However, only a slight enhancement was observed with further increments in TiO_2 concentration beyond 0.2g/L. The rates of degradation were fairly close for TiO_2 concentrations between 0.5g/L to 1g/L.

Figure 5.6 Effect of photolysis and TiO_2 concentration on the degradation of resorcinol: (◇) light only, (—) 0.002g/L, (□) 0.02g/L, (●) 0.2g/L, (x) 0.5g/L and (Δ) 1.0 g/L.

(a)

(b)

Figure 5.7 Effect of TiO₂ concentration on (a) the degradation and (b) the mineralization rate of various concentrations of resorcinol.

Figure 5.7 summarizes the effect of TiO_2 concentration on the degradation and mineralization of resorcinol at different initial concentrations namely, 10mg/L, 30mg/L and 50mg/L. The effect of increasing catalyst loading from 0.2g/L to 1.0 g/L was more prominent at higher concentrations of resorcinol [Figure 5.7 a]. As the concentration increased from 0.2g/L to 1.0 g/L, the initial rate increased sharply from 0.83mg/L.min to 1.13 mg/L.min for 30mg/L of resorcinol. The same applied for the 50mg/L test where the initial degradation rate increased from 0.99mg/L.min to 1.33mg/L.min whereas the initial degradation rate of 10mg/L resorcinol remained constant when the TiO_2 concentration increased. The observed enhancement at higher resorcinol concentration of 30mg/L and 50mg/L could be explained in terms of TiO_2 surface saturation. At low TiO_2 concentration, the particle surfaces were most probably saturated with resorcinol leading to strong competition for the remaining non-adsorbed resorcinol. When more TiO_2 was added, an increased number of available adsorption and catalyst sites were expected together with a greater number of photons being absorbed which thus led to a higher degradation rate as observed.

It is noteworthy that an increase of TiO_2 from 0.2g/L to 0.5g/L doubled the 10mg/L mineralization rate (Figure 5.7 b) while its effect for the degradation rate was negligible as mentioned above. This suggests that 0.2g/L was sufficient for the degradation of the parent compound but not for the intermediates formed which were expected to be competing for the surface of TiO_2 . However, when the TiO_2 concentration was increased from 0.2g/L to 0.5g/L, the additional TiO_2 surfaces were available for the intermediates leading to the enhanced mineralization rate for the 10mg/L test. With this in mind, it was observed that the overall enhancement in the mineralization rate was greater compared to the degradation rate. Stafford [1994] presented a similar observation that whilst the removal rate of 4-chlorophenol increased little with increased TiO_2 , the rate of mineralization increased considerably.

Further increase in catalyst concentration beyond 1.0 g/L resulted in an insignificant change in initial rates of degradation and mineralization processes. Overloading of

TiO₂ caused light scattering and screening effects which thus reduced the specific activity of the catalyst as discussed before in Section 4.4.1.3 [Wong and Chu, 2003; Kiriakidou et al., 1999].

5.4.2.2 Degradation Kinetics of Resorcinol

The quasi-exponential decay observed during the photodegradation of resorcinol in Figure 5.6 indicates pseudo-first order kinetics [Ksibi et al., 2003]. Fitting of initial rate and concentration data from Figure 5.7 (a) into the Langmuir-Hinshelwood equation (Equation 4.6) yields a straight line as shown in Figure 5.8.

Figure 5.8 Linearisation of Langmuir-Hinshelwood isotherms: reciprocal of the initial rate as a function of the reciprocal of the initial concentration ([TiO₂] = 0.5g/L, pH = unadjusted).

The linear plot confirms the L-H relationship and indicates that adsorption represented the initial step in the photocatalytic process which was similar to BPA degradation. Table 5.3 summarizes the L-H adsorption constants and the initial reaction rate constant for BPA and resorcinol.

Table 5.3 Langmuir-Hinshelwood adsorption constant (K_{LH}) and kinetic constants (k_{LH})

	Resorcinol	BPA
K_{LH} (L mol ⁻¹)	3.90×10^3	1.00×10^4
k_{LH} (mol L ⁻¹ min ⁻¹)	1.71×10^{-5}	2.09×10^{-6}

The L-H kinetic constant for resorcinol was an order of magnitude higher than that for BPA indicating that the resorcinol initial reaction rate at maximum coverage was faster than for BPA under the conditions investigated. However, it was observed that the BPA L-H adsorption constant value was higher than the resorcinol value contradicting the discussion in Section 4.4.1.2 that better adsorption would lead to a higher reaction rate. This discrepancy could most probably be due to the different nature of the organic compounds in terms of adsorptive character and sensitivity to oxidation due to different molecular structure [Serrano and Lasa, 1999]. Vulliet et al. [2003] presented L-H constants for six different compounds and concluded that there was no possible direct comparison between different compound values. According to Yatmaz et al., [2001] the L-H adsorption parameter is related to the organic's affinity with TiO₂. Therefore, the parameters in Table 5.3 are specific to individual substrate/catalyst pairs with resorcinol $K_{LH} = 3.90 \times 10^3$ and $k_{LH} = 1.71 \times 10^{-5}$ and regression close to 0.99.

5.4.3 Process Efficiency of the Improved Submerged Light Photoreactor

The output of the fluorescent UV lamps used in the submerged light SMPR was mostly long-UV with a peak at 360 nm (refer to Figure 3.3 for spectra range of blacklight). Photon flux entering the external light reactor and the submerged light reactor was determined using potassium ferrioxalate actinometry and the incident photon flux was calculated using Equation 5.5.

Table 5.4 summarizes the differences between the two photoreactors and the calculated incident photon flux values.

Table 5.4 Details of the two photoreactors

	Submerged Light Photoreactor	External Light Photoreactor
Reactor Volume (ml)	1200	800
Norminal Light Intensity (Watts*)	8 x 4 W = 32W	4 x 8W = 32W
Total Incident Photon Flux ($\mu\text{E/s}$)**	3.910	1.763

*Lamps are rated in Watts to indicate power consumption.

** $\mu\text{E/s} = \mu\text{Einstein/s}$

With the same amount of electrical energy consumption of 32W, the photon flux produced by the submerged lamps was 2.2 times higher than the external UV source. This was because more of the UV photons were lost to the surroundings in the external lamp photoreactor compared to the submerged lamps whereby photons given off were immediately transmitted to the solution due to the close contacts.

Photonic efficiencies of resorcinol oxidation were calculated using Equation 5.3, with the photon output of the lamp and the initial degradation rates of resorcinol, and the results are listed in Table 5.5.

Table 5.5 Initial photonic efficiency of resorcinol degradation in external and submerged light photoreactors.

Co	Photonic Efficiency, ζ^*		Increase in photonic efficiency (%) = (Submerged/External) x 100
	External Light	Submerged Light	
10	0.0150	0.0219	146
30	0.0220	0.0367	166
100	0.0295	0.0424	144
240	0.0297	0.0420	141
400	0.0291	0.0426	146

*Degradation of resorcinol was in batch reaction with 0.5 g/L TiO₂, pH = 5.6 and 2L/min air bubbling.

The photonic efficiency of resorcinol degradation ranged between $0.015 < \zeta < 0.0291$ for the external lamp reactor and $0.0219 < \zeta < 0.0426$ for the submerged light reactor. As noted in Section 5.2.2 it is not always possible to compare photonic efficiency directly between laboratories since photonic efficiency of photocatalysis was found to depend on wavelength, type of TiO₂, organic substrate, slurry or immobilized system [Stafford, 1994] and also on initial concentration of organics (Table 5.5). As a consequence, careful assessment of operating conditions becomes critical in reporting and comparing different systems.

As shown in Table 5.5, the initial photonic efficiency for the degradation of resorcinol increased with increasing initial concentration and a plateau was reached at about 100mg/L of resorcinol. A similar trend was observed for the calculated values of increase in efficiency (%) of the submerged light system and these trends can be used as a guide in getting a more appropriate comparison between reactors. If a comparison of reactor efficiency was done at a low concentration range of organics where most degradation kinetics were pseudo-first order and thus concentration dependent as shown in Section 4.4.1.4 (effect of initial concentration of BPA), the efficiency reported would be different for each concentration used. It

is thus recommended that the reported value of reactor efficiency should be done only at a range where the initial rate reached a constant value, i.e. the reaction approaches zero-order (Figure 5.9). The curve in Figure 5.9 is reminiscent of a Langmuir type isotherm, suggesting that r_o for photooxidation reached saturation at the higher organic concentrations. A new term, known as limiting photonic efficiency, ζ_{lim} , is thus proposed to be the photonic efficiency (free of concentration effects, i.e. values of the plateau in Table 5.5) for the comparison of reactor efficiency.

Figure 5.9 Dependence of initial degradation rate of resorcinol on the initial concentration.

Using the limiting photonic efficiency concept, the submerged light reactor with submerged UV lamps was approximately 43% more efficient than the external light reactor for the degradation of resorcinol. This was most probably due to a more effective design of light distribution in the system as discussed in Section 5.4.1.1. The average limiting photonic efficiencies (plateau average in Table 5.5) were 0.0424 and 0.0295 for the submerged and the external light systems, respectively. It should be recognized that the limiting photonic efficiencies presented in Table 5.5 are the lower limits of the actual quantum yield of the reactors. This is because TiO_2 particulates could never absorb all the incident photon flux from a given source owing to the different refractive indices of TiO_2 , the liquid medium and the glass material used to construct the photocatalytic system [Serpone et al., 1993].

The quantum yield of resorcinol, taking into account only the absorbed photons in the photoreaction, was found to be 0.06 [Okte et al., 2000]. Okte and co-workers [2000] obtained their value of actual quantum yield by determining the fraction of light absorbed by TiO_2 using normal spectroscopic methods. The fraction of light absorbed was found from the difference between the response of the instrument for solutions with and without the presence of colloidal TiO_2 particles. Their quantum yield of 0.06 was approximately 30% and 50% higher than the photonic efficiency calculated for the submerged and external light reactor, respectively. The higher yield reported is reasonable as it had been discussed previously that the limiting photonic efficiency was expected to be lower than the quantum yield due to TiO_2 particles inability to absorb all incident UV photons.

Using the proposed concept of limiting photonic efficiency, the photocatalytic efficiencies of the submerged and external light reactors in the degradation and mineralization of the two compounds, BPA and resorcinol, are compared in Figure 5.10. The increases in efficiencies of the submerged light reactor over the external light reactor are summarized in Table 5.6.

Figure 5.10 Limiting quantum yield of degradation and mineralization of resorcinol and BPA.

Table 5.6 Increase in efficiency of submerged light reactor over the external light reactor.

	<i>Increase in limiting photonic efficiency relative to the external light reactor (%)</i>
Resorcinol degradation	$146 \pm 3.6\%$
Resorcinol mineralization (TOC)	$145 \pm 4.1\%$
BPA degradation	$138 \pm 3.6\%$
<i>BPA mineralization (TOC)</i>	$132 \pm 6.2\%$

In both the external and submerged light reactors, the limiting photonic efficiencies of degradation and mineralization were higher for resorcinol than the BPA. The higher photonic efficiency observed for the resorcinol removal under similar conditions was most probably due to the difference in photodegradation susceptibility of the two compounds. As discussed in Section 5.4.2.2, photodegradation depends on the nature of the organics in terms of the adsorptive character and the sensitivity to oxidation due to different molecular structure [Serrano and Lasa, 1999]. Ksibi et al. [2003] studied the photocatalytic degradability of substituted phenols by comparing the initial degradation rates relative to the phenol degradation rate. They found that the reactivity followed the Hammett law with regard to the effect of the substituent nature group, such as hydroxyphenol or nitrophenol, on the electronic character of the phenolic functionality. Besides the effect of the substituent group, differences in degradability of the substrate with regard to initial degradation rate of phenol and Hammett constants were observed even within the same group of hydroxyphenol (OH substituent). In this study, BPA and resorcinol belong to the same group of hydroxyphenol and different photodegradability was thus expected according to the conclusion drawn by Ksibi et al. [2003]. In addition to this, Coleman et al. [2005] have also reported a higher mineralization rate of resorcinol than of BPA in their study.

The data presented in Table 5.6 further support those in Table 5.5 that the submerged light reactor utilized UV photons more efficiently than the external light reactor, increasing photon utilization efficiency by $132 \pm 6.2\%$ to $146 \pm 3.6\%$. A noteworthy point is that the reported photonic efficiencies were found to be dependent on the degradation or mineralization of the substrate. Most researchers have used a single reactant at the same initial concentration for the comparison between photoreactors [Ray, 1998; Lee et al., 2003; Disjstra et al., 2001]. For example, Ray [1998] compared the energy input efficiency ($\mu\text{mol}/(\text{m}^3 \cdot \text{s} \cdot \text{W})$) of a classical annular slurry reactor, an immobilized tube light reactor and a multiple-tube reactor for the degradation of 90% of dye at an initial concentration of $0.024 \text{ mol}/\text{m}^3$. The reaction kinetic at $0.024 \text{ mol}/\text{m}^3$ was reported to follow zero order kinetics. Although the work did not investigate and discuss in detail about the basis of comparison, it satisfies our previous suggestion that comparison of the reactor should be done in the region where the degradation rates are independent of concentration effects. In another work, Dijkstra et al. [2001] compared the quantum yield of a slurry reactor and an immobilized TiO_2 reactor of varying kinetics. They found that in the absence of oxygen, degradation of formic acid in the slurry reactor followed a pseudo-zero order kinetics whereas in the same concentration range, the immobilized system produced pseudo-first order kinetics. In spite of the direct comparison between the two reactors, they recognized that due to the difference in kinetics, the quantum yield in the immobilized system would decrease with initial concentration whereas it would remain constant in the suspended system. In any case, the comparison between reactors would be valid in the concentration range of interest as long as the initial concentrations of organic for the different reactors were kept similar.

In summary, the use of the limiting photonic efficiency parameter has eliminated concentration-dependent effects. The reporting of mineralization efficiency is as important as the reporting of the parent substrate degradation efficiency because the intermediates produced during the photocatalytic oxidation may be undesirable [Chiang et al., 2004]. In this study, the submerged light reactor was observed to be

145% ($\text{TOC}_{\text{resorcinol}}$) and 132% (TOC_{BPA}) more efficient than the external light reactor, confirming the benefit of the submerged UV light sources.

5.4.4 Performance of the Submerged light SMPR

The limiting photonic efficiency comparison of the two photoreactors in batch mode has demonstrated that the submerged light reactor was more efficient than the external light reactor in the utilization of incident photons. Figure 5.11 shows the start-up and steady state concentration for the continuous removal of 10mg/L of resorcinol in the submerged light SMPR.

Figure 5.11 Degradation and mineralization of resorcinol in the submerged light SMPR ($[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{mg/L}$, residence time = 1 hr).

With a residence time of 1 hr, the submerged light SMPR was able to degrade 92% of 10mg/L of resorcinol and achieve 83% of mineralization. As explained in Section 4.4.3, the difference between the initial concentrations of resorcinol and TOC as shown in Figure 5.11 was due to the fact that resorcinol contains 65% (weight %) of organic carbon according to Equation 4.7, i.e. 10mg/L of resorcinol contributed to a total of 6.5mg/L of measurable organic carbon. At steady-state

(approximately 120min), the TOC contributed by resorcinol was approximately 0.59mg/L ($0.91\text{mg/L} \times 0.65$) whereas the measured TOC was approximately 0.93mg/L. The difference of 0.34mg/L indicates the amount of TOC contributed by the intermediates that were generated during the photocatalytic process.

As observed previously in Figure 4.11 for the continuous removal of BPA, the discrepancy between the tank and permeate concentration was attributed to the adsorption/desorption of BPA on/from the membrane surface and pores which in turn caused the permeate concentration to be higher than the tank value before steady-state was reached. Since no difference between resorcinol and TOC in the permeate and the tank could be observed in this case, there was presumably negligible adsorption between the PVDF membrane and the resorcinol as well as its intermediates.

The different interactions between the two substrates with the PVDF membrane can be explained in terms of octanol–water partitioning coefficients ($\log K_{ow}$), a physical property found for organic analytes. The $\log K_{ow}$ is simply a measure of the hydrophobicity (water repulsing character) of an organic compound. Compounds with largely non-polar structures usually have high $\log K_{ow}$ values and for compounds with highly polar groups, it is usually very low.

The $\log K_{ow}$ of BPA and resorcinol are 3.40 [Table 4.1] and 0.8 [Table 5.1], respectively. BPA has a much higher octanol–water partitioning coefficient which means that it was less likely to be attracted to highly polar water molecules. Thus when it passed through the PVDF membrane, it tended to bind preferentially onto the membrane. Braeken et al [2005] have studied the extent of the adsorption of ten types of organics on three types of polymeric nanofiltration membrane material and found that compounds with the highest $\log K_{ow}$ showed the highest adsorption. Also, the more hydrophobic membrane was found to be the most susceptible to adsorption of organic compounds. They thus considered adsorption as being a hydrophobic-hydrophobic interaction between the membrane and the dissolved organic compound which was exactly similar in the case for hydrophobic PVDF

membrane and BPA. Another interesting finding was that Yoon et al. [2005] had actually taken advantage of this organic fouling phenomenon to remove traces of targeted organic substrates from the water by purely adsorption of these organics onto a suitable membrane surface. Once the surfaces were saturated, the membrane was regenerated and then re-used.

Similar to the study on the continuous removal of 10mg/L resorcinol, no differences in resorcinol concentration between the permeate and the tank concentration were observed in the experiments when the concentration of resorcinol was increased to 30mg/L and 50mg/L as shown in Figure 5.12 (a) and (b), respectively. By increasing the residence time from one hr to two hrs, 87% of 30mg/L resorcinol was able to be mineralized in the submerged light photoreactor when steady-state was reached at 120min. From the previous chapter, we have shown the importance of residence time in the controlling of the permeate quality with BPA feed. In this case, the residence time was increased whenever the concentration of resorcinol was increased. For a higher resorcinol concentration of 50mg/L, a residence time of 3.5 hr resulted in a high extent of mineralization at 94% being attained. This ad hoc increment of residence time could be improved with the introduction of a model simulating the process efficiency as will be discussed in the following Chapter 6.

Figure 5.12 Degradation and mineralization of resorcinol in the new SMPR. Conditions: (a) [TiO₂] = 0.5g/L, [Resorcinol]₀ = 30mg/L, residence time = 2hr. (b) [TiO₂] = 0.5g/L, [Resorcinol]₀ = 50mg/L, residence time = 3.5hr.

Since the submerged light reactor had been designed based on the conditions of being well-mixed (high mass transfer rate) and having well-distributed UV light, the UV utilization effectiveness of the reactor was thus expected to be good. Meng et al. [2005] reported and compared their UV utilization effectiveness with others reported in the literature using Equation 5.9.

$$E_{UV} = \frac{(C_o - C_{ss})V}{T \cdot U} = \frac{(C_o - C_{ss})V}{T \cdot I \cdot A_r} \quad (5.9)$$

where C_o is the influent TOC (mg/L), C_{ss} is the steady-state TOC, (mg/L), T is the residence time under continuous operation (hr), U is the UV power input (W), I is the radiation intensity (W/m^2), V is the volume of treated water and A_r is the radiation area (m^2).

For comparison, the test with 50mg/L resorcinol [Figure 5.12 (b)] was chosen for calculation because it was the highest concentration test carried out in the performance study and was expected to exhibit a higher UV utilization efficiency of the submerged light SMPR. The E_{uv} calculated was 1.27 $\mu g/L$ from $C_o = 31.5mg/L$, $C_{ss} = 1.5mg/L$, $V = 1.2L$, $A_r = 4 \times 0.0691$, $T = 3.5hr$, $I = 32.6W/m^2$. Table 5.7 shows that the UV utilization effectiveness of the SMPR was comparable to the design of Meng et al. [2005] and much higher than other continuous design. The comparisons in Table 5.7 also suggest that thin-film fixed bed immobilized systems are less effective than slurry reactors. However this conclusion is based on assumption of similar photodegradability of substrates, which may not be the case. Meng and co-workers' [2005] design was similar to that of Fu et al [2006], as shown in Figure 2.12, with reaction and filtration separated into two compartments within the same tank. In their case, the membrane was protected from the UV light in a different zone which was expected to need more space due to an extra zone for filtration compared to the current proposed design.

Table 5.7 Estimated values of UV utilization efficiency of photocatalytic reactors reported in the literature.

Reactor Type	Operation Mode	Treatment objective/ Removal description	E_{UV} ($\mu\text{g-TOC}/\text{J}$)	Ref
PTR ^a	One-pass	Groundwater with TCE, 582ppb/hr	1.2×10^{-3}	Mehos and Turchi [1993]
TFFBR ^b	One-pass	LF leachate, 70% of 300mgTOC/L in 5 hr	0.17	Bekbolet et al. [1996]
SRM ^c	One-pass	Polluted river water, 80% removal of COD and 50% removal of $\text{NH}_4^+ - \text{N}$ with HRT 3hr, $C_o = 70\text{mg/L}$	1.3	Meng et al. [2005]
Present work	One-pass	Resorcinol, $C_o = 31.5\text{mg/L}$, HRT = 3.5hr, 94% removal of TOC	1.27	

^aPTR, parabolic trough reactor^bTFFBR, thin-film fixed bed reactor^cSRM, Slurry reactor with membrane separation

5.4.4.1 Membrane Filtration Characteristics

The continuous operation of the submerged light reactor was also established to be less prone to fouling, as shown in Table 5.8. The membrane module with an area of 0.0041m^2 in test #1 was that used previously in the external light reactor and the second membrane module presented was that employed in the submerged light reactor. In test #1, the critical flux determined for the submerged light reactor, at similar TiO_2 amount (in terms of weight) and aeration, was $120\text{L}/(\text{m}^2.\text{hr})$. This is 1.5 times higher than the $80\text{L}/(\text{m}^2.\text{hr})$ presented previously in Figure 4.16. In the second test, aeration rate was kept constant at $2\text{L}/\text{min}$ for both the submerged light and external light reactor. Since the external light reactor diameter was 4 times

smaller than the submerged light reactor, a higher aeration intensity of $0.012\text{m}^3/(\text{m}^2.\text{s})$ equivalent to 0.012m/s superficial velocity resulted. In spite of this, the critical flux of the external light reactor was still lower than for the submerged light reactor.

Table 5.8 Critical flux determination of the external and submerged light reactors under respective conditions

Test	Membrane area (m^2)	Reactor	TiO ₂ concentration (g/L)	TiO ₂ absolute amount (g)	Aeration intensity $\text{m}^3/(\text{m}^2.\text{s})$	Aeration rate (L/min)	Critical flux $\text{L}/(\text{m}^2.\text{hr})$
#1	0.0041	New	0.33	0.4	0.0027	2	120
		Old	0.5			0.5	80
#2	0.0088	New	0.5	0.6	0.0027	2	120
		Old	0.7		0.012		80

Test #1 shows that the submerged light reactor was better in the utilization of the aeration intensity in controlling fouling. Due to the difference in the length to diameter ratio with respect to the external light ($L/D = 4.0$) and the submerged light ($L/D = 1.6$) reactor designs, the membrane module in the submerged light reactor was much nearer to the aeration device than in the external light reactor. The membrane in the submerged light reactor was placed 2.5cm from the bubble diffuser and in the external light reactor, the membrane was positioned 18.5cm away from the diffuser. Since the submerged light reactor membrane module was closer to the bubble diffuser, it was expected that most of the small bubbles ejected from the diffuser would contact the membrane immediately, creating higher shear forces. For bubbles rising in a swarm, some bubbles become unstable and coalesce to form larger bubbles as a result of collisions. Yeo et al. [2006] have shown that many small bubbles can be more effective than a few large bubbles at the same volumetric flow rate in preventing deposition of particles on a submerged membrane. A similar conclusion was drawn by Matis et al. [2004]. These observations point to the need for careful optimization of aeration and reactor configuration in the SMPR design.

5.4.5 Importance of Controlling Reaction Temperature

The design of a temperature cooling system as described in section 5.4.1.3 was based on the objective of keeping the temperature as a constant parameter when comparing results between different tests. As discussed previously, rising temperature was expected to increase the reaction rate. In a practical application of photocatalytic degradation, it was thought that since temperature increase was an intrinsic feature of the proposed submerged light reactor, it might be possible to make use of this feature for better degradation of resorcinol. Figure 5.13 shows the dependence of the degradation and mineralization profile of resorcinol on controlled and uncontrolled temperature situations.

As seen in Figure 5.13 (b), temperature increased rapidly in the initial stages of the experiment and slowed down to increase and finally remained at a constant value of approximately 40°C. The dependence of dissolved oxygen concentration on temperature was non-negligible and a difference of about 1mg/L was observed between a temperature of 25°C and 40°C (Figure 5.13 a). In spite of the fact that an increase in temperature led to a decrease in the dissolved oxygen level and would impart a potential detrimental effect on organic oxidation, the resorcinol removal rate (Figure 5.13 a) was not affected and the mineralization rate (Figure 5.13 b) actually increased for the uncontrolled temperature tests. This indicates that the dissolved oxygen available at higher temperature was not a limiting factor for actual resorcinol degradation; or the depletion in oxygen effect might have been compensated or enhanced by an increase in collisional frequency between the catalyst and substrate at higher temperature [Villasenor and Mansilla, 1996]. Photocatalytic reaction rate constant was also found to follow a linear dependence on temperature between 30°C to 60°C according to the Arrhenius equation [Reutergardh and Iangphasuk, 1997]. This means that the potentially temperature-dependent steps, such as adsorption, desorption, surface migration and rearrangements, appear to be rate determining.

Figure 5.13 Resorcinol (a) degradation and (b) mineralization profile with (■) and without (▲) control of temperature. Secondary axis in (a) shows dissolved oxygen of controlled temperature (□) and uncontrolled temperature (Δ) and in (b) temperature profile of controlled temperature (□) and uncontrolled temperature (Δ). Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 50\text{mg/L}$, residence time = 1.5hr.

For TiO_2 photocatalysis, irradiation is the primary source of electron-hole pair generation at ambient temperature as the band-gap energy is too high to be overcome by thermal excitation. Mozia et al [2005a] observed a linear dependence of the photocatalytic decomposition of Acid Red 18 at a temperature range of 20 – 60°C. However, when the temperature was increased to 70°C, the decomposition rate started to decrease. At temperatures near to the boiling point of water, the exothermic adsorption of the degraded compound was unfavourable and became the rate limiting step. In the report of Zhou et al [2003], they attributed the decrease in rate constant as a consequence of the reduction of the adsorptive capacity associated with the organics and dissolved oxygen. Since the temperature reached in our experiment was 40°C, the detrimental effect was thus not observed.

Another reason for the observed lower amount of TOC remaining after 5 hrs of experiment might be due to the possible removal of intermediates by air bubbling at the higher temperature. The intermediates produced during photocatalytic oxidation were smaller molecules and might have lower vapour pressures whereby an increase in temperature amplified the chance of evaporation of solution, eliminating the volatile organics from the solution. In a recent study by Mozia et al. [2005 b], photocatalysis was coupled with membrane distillation for the degradation of azo-dye Acid Red 18 in aqueous solution. Membrane distillation is a process of feed volatile components evaporation through a porous hydrophobic membrane and the process depends on the temperature and the solutions composition in the layers adjacent to the membrane. Mozia et al. [2005 b] found that even though the parent compound Acid Red 18 was non-volatile, the intermediates formed during the photocatalytic process were volatile and were collected with the evaporating water vapour as permeate at a temperature of 60°C. In practice, the loss of volatiles to the environment would be undesirable and this would lead to constrain reactor temperatures to be kept close to ambient.

Figure 5.14 Effect of temperature on the transmembrane pressure change.

During the five hr of non-controlled temperature, it was necessary to adjust the pump in order to maintain constant flux. It was then realized that the transmembrane pressure started to drop considerably when temperature increased to about 30°C (Figure 5.14). The final TMP at the constant flux operation dropped to about 87% of the initial TMP value. This was most probably due to decrease in viscosity of the water with the increase in temperature. In order to verify this, a pure water filtration experiment under uncontrolled temperature condition was done and a similar trend of TMP change was observed. According to Equation 3.1, TMP change is inversely proportionate to the viscosity of the solution with respect to membrane resistance. A decrease in viscosity would lead to a decrease in TMP as the membrane resistance remained constant. Babu et al [2001] observed a decrease in flux during their constant pressure operation from 27°C to 45°C. The decrease in viscosity assisted the flow of solutions near the membrane surfaces. They also reported a reduction in protein fouling due to a 20°C increase in temperature and attributed the observation to the increase in diffusivity of protein and/or the reduction in its adsorption tendency at higher temperature.

The effects of temperature on the operation of submerged membrane were not discussed in two recent studies dealing with photocatalysis with submerged lamps [Meng et al., 2005 and Fu et al., 2006a]. The absence of a cooling system might

indicate that their pilot plant systems were able to dissipate heat more effectively than a lab-scale experiment. In order to avoid issues with regards to non-controlled temperatures as discussed before, it is strongly recommended that temperature is kept constant when running long-term operations of the SMPR. The heat required to cool the reaction solution could be exchanged with other process operations which moderate warming.

5.4.6 Long-Term Operation

In order to evaluate the efficiency of the proposed submerged light SMPR design, long-term operation of the system was performed for a duration of 28 days [Figure 5.15 (a) and (b)]. Figure 5.15 (a) shows that the mean size of TiO_2 particles increased from an initial value of $0.34\ \mu\text{m}$ to $0.57\ \mu\text{m}$ after 3 days of continuous operation and thereafter, the particles stopped agglomerating and remained at around $0.55\ \mu\text{m}$. It is also shown that the steady-state resorcinol degradation remained substantially constant throughout the 28 days. However when the steady-state region in Figure 5.15 (a) is amplified in Figure 5.15 (b), an increasing trend can be observed for resorcinol and TOC concentration after 3 days of operation.

(a)

(b)

Figure 5.15 (a) Degradation and mineralization profile of long-term operation of SMPR (b) Amplification of steady-state concentration region of (a). Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 30\text{mg/L}$, residence time = 3.5hr, controlled temperature.

At day 3 (zone I), there was a gradual increase in TOC and resorcinol in the permeate which started to level out by day 4 or 5. This decrease in photoactivity was attributed to the formation of a TiO_2 layer on the lamp glass tubes at longer irradiation times. The formation of this layer limited the penetration of UV light through the tubes and consequently the photocatalytic degradation decreased gradually. Doll et al. [2005] encountered a decrease in TiO_2 photoactivity after 2 days of continuous degradation of pharmaceutical waste and the decrease was reported to be due to a TiO_2 covering layer being formed on the lamp envelope. In order to counteract this problem, their lamp envelope was mechanically cleaned every 24 hr. In the operation of Meng et al.'s [2005] membrane-photocatalytic setup, the quartz tubes were also wiped twice daily to maintain surface light intensity between $6 - 9 \text{ mW/cm}^2$. As shown in zone (I) the efficiency of the SMPR was recovered after cleaning of the glass tubes was performed. Mechanical cleaning of lamp glass tubes was not installed and for this long-term operation, the glass tubes were manually wiped every 48 hr for the rest of the experiment.

Steady-state permeate concentrations of about 1 mg/L for resorcinol and 1.9 mg/L for TOC were observed to be stable after first cleaning of the borosilicate glass tubes (Figure 5.15 b). The experiment was stopped after 28 days and the TiO_2 particles were recovered, washed with MQ water five times followed by UV irradiation for 15 minutes to degrade any surface adsorbed organics. The photocatalyst was then dried in an oven at 40°C and re-used for decomposition of resorcinol in batch mode. Compared to fresh TiO_2 degradation, negligible difference was found indicating the absence of irreversible deactivation of TiO_2 after 28 days of continuous usage. Also, the simple washing and irradiation of TiO_2 to recover its photoactivity showed that the intermediates produced were not persistent which supports the previous finding in Section 5.4.3 that the intermediates of resorcinol were able to be degraded quickly with regard to the parent compound.

Membrane stability was one of the other concerns during the long-term operation since the proposed submerged light reactor was built on the concept that the membrane was in direct contact with the reaction medium for a more compact

design. In Chapter 3, the stability of the membrane was explored under different filtration conditions. Having a very thin layer of TiO_2 cake formed on the membrane resulted in the fastest deterioration rate on the membrane, compared to thicker cake layers and the non-cake situation. With regard to this, a permeate flux of $36\text{L}/(\text{m}^2\cdot\text{hr})$ was used for the long-term test which was much below the critical flux of $120\text{L}/(\text{m}^2\cdot\text{hr})$ as determined in Table 5.8. Operating below critical flux would minimize the deposition of TiO_2 on the hollow fibre membrane module. As found in Section 4.4.5.3, intermittent permeation was the best approach in controlling fouling in a SMPR operating at high flux. As a safety measure for preventing fouling, the use of intermittent permeation was adopted in the long-term operation. The optimized IF of 0.03 as determined in Section 4.4.5.3 was used. Figure 5.16 shows the membrane TMP profile. Operating below critical flux and intermittent permeation enabled maintenance of a stable TMP for at least 18 days, where signs of an increase started to show after 18 days of continuous operation. The change in TMP after 18 days was estimated to be approximately $0.022\text{kPa}/\text{day}$ that is equivalent to an increase of only 3% during the experiment. Although the change in TMP was very small, Figure 5.16 provides indication that backwash may be required for long-term operation even if the operating flux is below the critical flux.

Figure 5.16 Long-term transmembrane pressure ratio change for the submerged light SMPR operating with a flux of $36\text{L}/(\text{m}^2\cdot\text{hr})$.

After 28 days of operation, the membrane was rinsed with MQ water and subjected to ultrasonication for 2 min to detach any loosely deposited TiO_2 . The water permeate flux (WPF) resistance test of the membrane was then taken and no change in the water flux could be detected before and after the experiment. This confirms that the slight TMP rise (Figure 5.16) was not due to irreversible fouling. The unchanged WPF also suggests that the membrane was not damaged by UV exposure. Although the chemical stability test using TOC analysis could not be employed in this case, other physical properties associated with polymer damage as discussed and encountered in Chapter 3 were used to evaluate the PVDF membrane. The integrity of the membrane was found to be satisfactory; i.e. no physical fragility of the membrane could be observed. Also, no change in membrane surface colour was seen which could be associated with polymer deterioration as observed previously with PES membrane. The inner layers of the washed membranes were screened several times using EDX for the presence of TiO_2 . An example of an EDX micrograph is shown in Figure 5.17. Peak (K) was the EDX background peak while the presence of the gold (AU) peak was due to the sputter gold coating prior to the EDX and SEM test. The fluorine (F) and carbon (C) peaks were contributed by the PVDF membrane materials. Most importantly, Figure 5.17 shows no evidence of TiO_2 particles. This result was consistent with the absence of TiO_2 particles in the permeate throughout 28 days of experiment. It also provides insight into the integrity of the membrane in terms of retention of TiO_2 particles in the photoreactor.

Figure 5.17 EDX micrograph of the inner surface of the washed PVDF membrane.

5.4.7 Practical Applicability of the Submerged Light SMPR

Endocrine disrupting chemicals and pharmaceuticals represent two classes of emerging contaminants that are ubiquitously present in municipal wastewater effluent. Some studies have shown that some of these trace organics include persistent organic pollutants which are especially difficult to be removed from water and usually present in trace concentrations, varying between nanogram and picogram [Zuelhlke et al., 2006; Liu et al., 2007]. Stackelberg et al. [2004] has also reported that 17 organic compounds out of a total of 106 studied, which include selected prescription and non-prescription drugs and their metabolites, fragrance compounds, cosmetic compounds and plasticizers, resisted removal through conventional drinking water treatment processes (usually in the range of a few hundreds m^3/day to thousands m^3/day [GE Corporate, 1997]) as shown in Figure 5.18.

Figure 5.18 Schematic diagram of a conventional drinking water treatment plant in United States of America [Stackelberg et al., 2004].

As discussed in Chapter 1, photocatalytic oxidation process has been considered as an innovative and “green” alternative for water treatment, especially for the treatment of trace organics [Glaze et al, 1993]. SMPR (highlighted in Figure 5.18) is thus recommended to be placed after the sand bed/activated carbon filtration so that trace levels (sub- $\mu\text{g/L}$) of persistent pharmaceutical residues and endocrine-disrupting compounds can be further removed.

Besides being able to integrate SMPR into a conventional drinking water system, it is also recommended that SMPR to be used in specialized treatment area such as treatment of specific pharmaceutical waste and also in the production of Ultrapure water in semiconductor and pharmaceutical industries. Although reverse osmosis (RO) in Ultrapure water production is designed to reject 99% of colloids, organic deposits, bacteria and viruses, there is still a chance that low concentration of organics, as low as parts per trillion (ppt), will be able to pass through the membranes [Chin, 1996]. For example, ultrapure water is found to contain trace amounts of impurities such as organics, colloids and microorganisms which needed to be treated further [Matsuda et al; 1996a]. Thus, the integration of SMPR in the system will further ensure the quality of the ultrapure water.

SMPR is always recommended to be used for the post-treatment of recalcitrant trace organics and due to the recommended use at the final polishing stage, it is thus important that the membrane employed in the SMPR is able to retain the photocatalysts in the suspension system totally. For easier recovery or removal of the suspended photocatalysts from the SMPR, modified types of TiO_2 which facilitate sedimentation is recommended to be used. A good example of modified TiO_2 is the magnetite photocatalysts [Beydoun et al., 2000] whereby recovery of TiO_2 can be done easily with introduction of external magnetic force.

5.5 Summary

A submerged light SMPR was proposed and designed. The UV light distribution in the submerged light reactor was optimized with the aid of direct measurement of the UV light source radiation field. A sodium chloride tracer test was performed and a 2L/min bubbling rate was chosen to be used in all tests to ensure complete mixing and to prevent possible attenuation of UV light by higher bubbling rates. Also, a cooling water jacket was incorporated into the design to maintain temperature at the desired level. The effect of catalyst concentration was apparent at higher resorcinol concentration due to greater chances of interaction between the available organic and the catalyst sites. The higher TiO_2 concentrations used were accompanied by higher mineralization rates and further increase beyond 1g/L resulted in a plateau being observed. Resorcinol was found to also follow the Langmuir-Hinshelwood kinetics with $K_{\text{LH}} = 3.9 \times 10^3$ and $k_{\text{LH}} = 1.7 \times 10^{-5}$. It was also noted that direct comparison of L-H constants between different compounds were inappropriate because L-H was specific for a particular substrate/catalyst combination. For the comparison of efficiency of the external light and submerged light reactor in batch mode, a new concept of limiting photonic efficiency was proposed. Limiting photonic efficiency is defined as the photonic efficiency calculated under substrate concentration-independent conditions. Also, ζ_{lim} was found to be compound dependent and it was strongly suggested that ζ_{lim} to be reported in terms of both degradation and mineralization efficiencies. The limiting photonic efficiencies of the submerged light reactor were found to be 146% ($\text{TOC}_{\text{resorcinol}}$) and 132%

(TOC_{BPA}) more effective than the external light reactor. In the continuous mode, no adsorption of resorcinol on the membrane surface was observed due to the low Log K_{ow} of resorcinol compared to BPA, whereby BPA with higher log K_{ow} would tend to bind onto the hydrophobic membrane more easily than resorcinol.

The submerged light SMPR design proposed was also shown to be competent compared to other reactors in the literature and less prone to fouling compared to the external light reactor. The critical flux for TiO₂ suspension obtained under identical conditions was found to be 120L/(m².hr) and 80L/(m².hr) for the submerged light and external light reactors, respectively. Although an increase in temperature was found to have no effect on the degradation of resorcinol, it was found to enhance the mineralization process. The enhancement was attributed to the increase in collisional frequency between the catalyst and substrate at higher temperature. It is also important to note that the possibility of air stripping in a SMPR at higher temperature should not be ruled out. Lastly, 28 days of long-term operation showed that substantially stable degradation of 50mg/L of resorcinol, with 3.5hr of residence time, could be achieved. Simple MQ water washing and a short UV irradiation time was able to regenerate the used TiO₂. In order to evaluate the effect of the membrane under the oxidative environment, WPF, SEM/EDX and direct observation were done and indicated that the membrane integrity was still intact. This successful demonstration with long-term operation has confirmed the favourability of the SMPR in the degradation of low concentrations of organics. Practical applicability of the SMPR has also been addressed taking into considerations the volume and contaminant concentration of the water to be treated as well as retention and recovery of the photocatalyst.

CHAPTER 6

KINETICS MODELING OF SUBMERGED MEMBRANE PHOTOCATALYTIC REACTOR (SMPR)

6.1 Introduction

The preceding Chapter 5 has demonstrated the development and performance of an improved SMPR and the design was found to be 46% more effective in degrading resorcinol than the external light reactor as presented in Chapter 4. In all previous studies, the residence time was arbitrarily increased whenever the feed concentration of resorcinol was increased so as to obtain a reasonable steady-state degradation in continuous operations. In these cases, the utilization of the SMPR in terms of degradation performance was not necessary optimized. Therefore, it would be useful to construct a versatile model which could be used to simulate the submerged light SMPR system response to changes in certain important reaction parameters and also to predict the steady-state degradation concentration of resorcinol.

Many modeling works have been developed using batch kinetic data and by modifying the original L-H kinetic equation to include more complicated conditions, for instance an equation that accounts for multicomponent systems and competition with intermediates formed during the reaction [Rideh et al., 1999; Chan

et al., 2001; Guettai and Amar, 2005]. Another equation that accounts for the rate of carbon dioxide formation during the photocatalytic oxidation of 4-chlorophenol makes use of a proportionality constant (γ) and a term relating to quantum yield (θ) [Mills et al., 1993]. Other modifications have also been made to account for changes in light intensity, the formations and the decays of holes and $\bullet\text{OH}$ radicals [Meng et al., 2002]. Besides modifying the original L-H equation, attempts have also been made to include experimental parameters when deriving the empirical kinetic models for batch reactions [Molinari et al., 2002; Fu et al., 2006b]. Molinari and co-workers [2002] have considered oxygen concentration, TiO_2 concentration, initial 4-nitrophenol concentration and light intensity in the global modeling of their batch reactor. In spite of the popularity of modeling reaction kinetics with data obtained from batch systems, the modeling of kinetics data for continuous suspended photocatalytic processes remains very limited.

Soparajee et al. [1999b], who worked with separate membrane and photocatalytic systems, tried to model their batch-recirculated photoreactor (comprising of a reservoir and a reaction vessel) as a combined continuous flow stirred tank (CFST) - plug flow reactor (PFR). The photoreactor was modeled as a simple PFR while the reservoir as a CFST whereby the CFST equation took into consideration the recycle flow from the photoreactor. Since photochemical reactions only occurred in the annular photoreactor, no kinetic component was included in the reservoir CFST equation. The most relevant publication for modeling the degradation of an organic compound in a continuous operation was the work done by Behnajady and Modirsahla [2006]. However, their model which could predict the concentration of Acid Orange dye (AO7) in different tubular photoreactor lengths for different volumetric flow rates and initial concentrations of H_2O_2 and AO7, was developed for homogeneous H_2O_2 oxidation. Thus, no membrane was required for the retention of solid catalyst particles during the continuous operation of the homogeneous photoreactor. Model evaluation showed that the constructed semi-empirical model was in good agreement with the experimental data.

In view of the potential applicability of the proposed SMPR configuration, the development of a model which can simulate its performance is expected to act as a key practical tool for process development and system optimization. In this Chapter, a classical model is developed to predict the rate of resorcinol degradation that occurs in the SMPR. The model is evaluated by comparing the calculated data with the experimental data. Due to the inadequacy of the original model, a correction factor known as the reaction surface coverage ratio (β) is introduced to account for the difference between the original model and the experimental data. The development of a universal equation for the determination of β with respect to the change in initial and bulk concentration of resorcinol is also demonstrated. With the use of the universal equation, the adequacy and versatility of the modified model in simulating the experimental data are evaluated.

6.2 Model Development

As presented in the preceding Section 5.4.1.2, the reactor bubbling system was designed to ensure a well-mixed condition in the photoreactor. Thus the exit stream from this reactor had the same composition as the fluid within the reactor (Figure 5.11). Furthermore, the reactor condition has been shown to be isothermal in Section 5.4.1.3 where the reaction was always kept at about 26°C. As a consequence of completely-mixed and isothermal conditions, modeling of the submerged light SMPR performance was derived based on the assumption that the SMPR behaves as an ideal continuous stirred tank reactor (CSTR). The general CSTR model can be derived by considering the material balance of resorcinol as shown in Equation 6.1 (Levenspiel, 1999).

Accumulation = Input – Output + generation - consumption

$$\frac{d[C_A]}{dt} V_R = Q_f C_{A,f} - Q C_A + r_A V_R - r_A V_R \quad (6.1)$$

where $d[C_A]/dt$ = change in concentration of A with respect to time

V_R = reactor volume (L)

Q_f = feed volumetric flow rate (L/min)

Q = output volumetric flow rate (L/min)

$C_{A,f}$ = feed concentration (mg/L)

C_A = output concentration (mg/L)

r_A = rate of reaction (mg/(L. min))

The general CSTR Equation 6.1 can be simplified to give Equation 6.3 using the following assumptions.

1. The system was assumed to be a completely mixed CSTR
2. Since the proposed reactor is a well-mixed reactor (Section 5.4.1.2), $Q = Q_f$ and the residence time, $\tau = V_R/Q$
3. The concentrations of dissolved oxygen and solvent contents were constant throughout the experiment.
4. The presence of the membrane did not play any role in the removal of substrate A from the reactor, i.e. the absence of organic adsorption on membrane.

Assumption #4 was made based on the previous finding that there was no adsorption of resorcinol on the membrane surface, which meant that the removal of resorcinol in the reactor was solely dependent on the efficiency of the photocatalytic oxidation process (this may not apply for other organics). Also, it was shown previously in Section 5.4.2.3 that the reaction of resorcinol in the photoreactor follows L-H kinetics (Equation 4.5)

$$r_0 = -\frac{dC}{dt} = \frac{k_{LH} K_{LH} C_o}{1 + K_{LH} C_o} \quad (4.5)$$

where r_0 is the initial rate of disappearance of organic compound, C_o is the initial concentration, K_{LH} is the L-H equilibrium adsorption constant and k_{LH} is the pseudo-first order initial reaction rate constant at maximum coverage for the experimental conditions.

Integrating Equation 4.5 yields Equation 6.2,

$$\ln\left(\frac{C_{Ao}}{C_A}\right) + K_{LH}(C_{Ao} - C_A) = k_{LH} K_{LH} t \quad (6.2)$$

where C_A is the concentration of A at time t , C_{Ao} is the initial concentration of A.

At the studied low concentrations of resorcinol, i.e. 0 to 50mg/L, where $K_{LH}C_{Ao} \ll 1$, the reaction can be expressed as Equation 6.3 which was similar to the first-order kinetic rate constant in Equation 4.4.

$$r_A = -\frac{dC}{dt} = k_{LH} K_{LH} C_A = k_{app} C_A \quad (6.3)$$

where k_{app} is the apparent first-order kinetic constant.

By substituting r_A from Equation 6.3 to Equation 6.1 gives

$$\frac{d[C_A]}{dt} = \frac{Q_f}{V_R} C_{A,f} - \frac{Q}{V_R} C_A - k_{app} C_A \quad (6.4)$$

$$\frac{d[C_A]}{dt} = \frac{1}{\tau} (C_{A,f} - C_A) - k_{app} C_A \quad (6.5)$$

where the initial concentration of resorcinol at time 0min, $C_A(0)$ equals to C_{Ao}

The above equation can be used to explore the effects of changing parameters (τ and C_{Ao}) or the influence of the change in kinetic rate constant with respect to time reaching steady-state conditions ($dC_A/dt = 0$).

Equation 6.4 is also separable and yields an analytical solution (Appendix B) as,

$$C_A(t) = C_{A,o} e^{-\left(\frac{1}{\tau} + k_{app}\right)t} + \frac{C_{A,f}}{1 + k_{app}\tau} \left[1 - e^{-\left(\frac{1}{\tau} + k_{app}\right)t} \right] \quad (6.6)$$

6.3 Results and Discussion

6.3.1 Determination of Kinetic Rate Constant

Equation 6.3 shows the simplified L-H equation during degradation of low concentrations of resorcinol. The k_{app} resulting from the product of k_{LH} and K_{LH} was reported to be similar to the pseudo first-order kinetic rate constant at low organic concentration [Bhatkhande et al., 2004; Valente et al., 2006]. The first-order kinetic rate constant, k_{app} , was calculated by using Equation 4.4 through a plot of $\ln(C_A/C_{AO})$ versus time (t) to yield a line with a slope representing the k_{app} value. Kinetic constants obtained from batch reaction data in Figure 5.8 under different initial concentrations of resorcinol are calculated and shown in Table 6.1.

Table 6.1 First-order kinetic rate constants of resorcinol, conditions: $[TiO_2] = 0.5\text{g/L}$, unadjusted pH = 5.6, air bubbling rate = 0.5L/min, Temperature = 26°C.

$\ln C_A/C_{AO}$ vs t		
C_{AO}	k_{app}	R^2
5	0.1366	0.978
10	0.0756	0.989
20	0.0418	0.986
25	0.0314	0.990
30	0.0263	0.993
50	0.0198	0.980

The regression coefficients (R^2) indicate the goodness of fit to Equation 4.4 for each batch data. The good regression indicated that degradation of resorcinol was indeed pseudo first-order kinetics as shown previously by the quasi-exponential curve in Figure 5.6. k_{app} was observed to decrease with initial concentration, which is quite common in photocatalytic studies for many organic compounds in dilute solutions [Hoffmann et al., 1995; Xu and Langford, 2000; Heredia et al., 2001]. On the basis of all previous considerations as discussed in Chapter 3 and 4, the rate determining steps of the photocatalyzed reaction are considered to be the reaction between the $OH^\bullet$ radicals and the organic molecules over the catalyst surface, i.e. the proximity of the organics and TiO_2 particles [Heredia et al., 2001]. The fact that k was higher

at low initial concentrations of resorcinol was attributed to the increase in the availability of reactive sites per organic molecule. With the same amount of TiO_2 surface and lower number of resorcinol molecules, lesser adsorption competition between resorcinol and the intermediates for TiO_2 sites was expected, leading to faster kinetics as observed.

A semi-empirical relationship (Equation 6.10) between the kinetic constants and the initial concentration of resorcinol was developed by using a modeling software (Sigma Plot version 8) and the fitting of data are shown in Figure 6.1.

$$k_{app} = a + b e^{-bC_{AO}} \quad (6.10)$$

where a, b and c are model parameters.

The model parameters with 95% confidence level were obtained using the software package Sigma-Plot (Version 8). The values of a, b and c are found to be 0.023, 0.244 and 0.136, respectively. This proposed model is useful in estimating the kinetic rate constant with respect to change in feed concentration.

Figure 6.1 Relationship between initial concentration of resorcinol and first-order kinetic rate constants.

6.3.2 CSTR Model Evaluation

For evaluation of the CSTR model (Equation 6.6), comparisons between the experimental data (results from Figure 5.11 and 5.12) and calculated values for the degradation of resorcinol in the continuous mode are shown in Figure 6.2 to Figure 6.4. The figures depict the initial start-up period and the approach to a steady-state exit concentration of resorcinol.

Figure 6.2 Experimental and calculated values of resorcinol concentration in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{mg/L}$, residence time = 1hr.

Figure 6.3 Experimental and calculated values of resorcinol concentration in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 30\text{mg/L}$, residence time = 2hr.

Figure 6.4 Experimental and calculated values of resorcinol concentration in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 50\text{mg/L}$, residence time = 3.5hr.

Figure 6.2 shows that the model agrees well with the experimental results when the initial concentration of resorcinol was 10mg/L. However, when the same model was fitted to the data obtained from experiments with higher initial concentrations of resorcinol, i.e. Figure 6.3 and Figure 6.4, the model fitted well only at the initial stage and began to deviate from the experimental results when the concentration of resorcinol in the continuous reactor decreased. The model was unable to describe satisfactorily the steady-state exit concentration of resorcinol.

6.3.3 Modification of Classic Model and Verification

6.3.3.1 Model Improvements

Due to the fact that the operating time of the CSTR was longer than the batch kinetic studies from which the kinetic constant k was obtained, it was then expected that during the continuous operation of the CSTR, the surface coverage effect may have been enhanced. Also, Figure 6.1 shows that the kinetic rate constants of resorcinol resemble an exponential decay with respect to increasing resorcinol concentration. The reason, as discussed before, was most probably attributed to the change in TiO_2 surface coverage at different initial concentrations of resorcinol. It was expected that changes in surface coverage would be magnified in the CSTR reaction, especially at low concentrations of targeted substrates. At low concentration of resorcinol, the available TiO_2 surface was higher and thus there would be less competition between the fresh resorcinol from the feed and that already present in the photoreactor for the active sites. In this case, a rapid change of TiO_2 surface coverage as a result of higher kinetics observed at low concentration was expected, i.e. fast adsorption or desorption of fresh or reacted resorcinol. This also explains why the model was not able to accurately fit the experimental data when higher concentrations of resorcinol were degraded to lower concentration as shown in Figure 6.3 and 6.4.

Given the inadequacies of the original model presented in section 6.3.2, a correction factor, known as the reaction surface coverage ratio (β) was introduced to the CSTR model. The introduction of β was based on the following rationale.

1. Degradation of resorcinol was shown to be mainly TiO₂ surface-oriented in Chapter 5, i.e. it followed L-H kinetics.
2. The bulk concentration of resorcinol changes during the course of the CSTR operation and therefore the adsorption of resorcinol on the TiO₂ surface, or reaction surface coverage ratio, is expected to change.

In addition to the rationale for introducing β , the following assumptions are made when developing the new improved model.

1. β is interconnected with the kinetics in the CSTR operation, i.e. β reflects the kinetics of the resorcinol reaction.
2. β is a function of bulk organic concentration and thus changes with time.
3. The residence time affects the contact time between TiO₂ and organics and thus the adsorption/desorption trend in the system.
4. The competition between the resorcinol and the intermediates, produced during photocatalytic oxidation, for the 0.5g/L TiO₂ active sites was minimal (while this applies for resorcinol as shown in Figure 5.1 (a) batch kinetics in which the degradation rate of resorcinol increased little with increased TiO₂, it may not apply for other organics).

The definition of the reaction surface coverage ratio was based on assumption #1 and #2. Since it was assumed that β was able to reflect the kinetic rate in a system, it is defined as the ratio change with respect to the kinetics change at respective resorcinol concentration, i.e. Equation 6.11.

$$\beta = \frac{k_i}{k_{ref}} \quad (6.11)$$

where k_i is the kinetic constant at the respective resorcinol concentration, C_A , and k_{ref} is the kinetic constant of the initial resorcinol concentration, C_{AO} .

Since C_A changes with time during the operation of the CSTR and β is a function of resorcinol bulk concentration (assumption #2), an empirical relationship relating β

to $C_A(t)$ was derived using the data from Table 6.1. The calculated values of changing β with respect to $C_A(t)$ at different initial resorcinol concentrations are shown in Table 6.2.

Table 6.2 Relationship between $C_A(t)$ and calculated reaction surface ratio, β .

$C_A(t)$	k	$\beta(t)$ (10mg/L)	$\beta(t)$ (20mg/L)	$\beta(t)$ (30mg/L)	$\beta(t)$ (50mg/L)
5	0.1366	1.79	3.10	5.97	6.90
10	0.0764	1.00	1.74	3.34	3.86
20	0.0440	0.58	1.00	1.92	2.22
30	0.0229	0.30	0.52	1.00	1.16
50	0.0198	0.26	0.45	0.86	1.00

By using the software Sigma Plot and the least square best fitting procedure, an empirical relationship in the form of $\beta(t)$ as a function of $C_A(t)$ was obtained (refer to Appendix C for the plots from Sigma Plot).

$$\beta(t) = a + b \exp^{-c C_A(t)} \quad (6.12)$$

where a , b and c are model parameters.

Using the data from Table 6.2, the model parameters for different initial concentrations of resorcinol were derived as shown in Equation 6.13 to 6.16.

$$C_{AO} = 10 \text{ ppm} : \beta(t) = 0.273 + 2.849 \exp^{-0.129 C_A(t)} \quad (6.13)$$

$$C_{AO} = 20 \text{ ppm} : \beta(t) = 0.470 + 4.938 \exp^{-0.129 C_A(t)} \quad (6.14)$$

$$C_{AO} = 30 \text{ ppm} : \beta(t) = 0.911 + 9.504 \exp^{-0.129 C_A(t)} \quad (6.15)$$

$$C_{AO} = 50 \text{ ppm} : \beta(t) = 1.038 + 10.828 \exp^{-0.129 C_A(t)} \quad (6.16)$$

In addition to Equations 6.13 to 6.16 which were to be used at respective C_{AO} , a universal empirical equation combining these four equations was further attempted. It can be seen that parameter (c) was 0.129 and was the same for all C_{AO} . Also, the

parameter (b) was approximately 10.5 times the parameter (a). Thus the general equation is

$$\beta(t) = a + (10.5a) \exp^{-0.129 C_A(t)} \quad (6.17)$$

where (a) is represented by Equation 6.18, obtained from the relationships between parameter (a) and respective C_{AO} as shown in Figure 6.5.

$$a = -0.0805 + [1.537(1 - \exp^{-0.0277 C_{AO}})] \quad (6.18)$$

Figure 6.5 Relationship between model parameter (a) and the initial concentration of resorcinol.

Table 6.3 shows the results obtained from the derived general Equation 6.17 and the individual C_{AO} Equation 6.13 and 6.15. The empirical $\beta(t)$ from the general equation compares well with the actual $\beta(t)$. The difference between the two correction factors is discussed further in the model verification section.

Table 6.3 Comparison of $\beta(t)$ values obtained from the general equation and the original equation.

$C_A(t)$	$\beta(t)$ (10mg/L)	$\beta(t)$ General Equation	$\beta(t)$ (30mg/L)	$\beta(t)$ General Equation
5	1.79	1.90	5.97	5.12
10	1.00	1.13	3.34	3.06
20	0.58	0.52	1.92	1.41
30	0.30	0.36	1.00	0.96
50	0.26	0.30	0.86	0.80

The correction factor β was then applied to the residence time, τ , in Equation 6.6 since it was assumed in #3 that residence time was the determining factor for controlling the adsorption/desorption equilibrium and thus the reaction kinetics during the photocatalytic process leading to the derivation of Equation 6.19.

$$C_A(t) = C_{A,o} e^{-\left(\frac{1}{\tau\beta(t)} + k_{app}\right)t} + \frac{C_{A,f}}{1 + k_{app}\tau\beta(t)} \left[1 - e^{-\left(\frac{1}{\tau\beta(t)} + k_{app}\right)t} \right] \quad (6.19)$$

Since $\beta(t)$ is dependent on $C_A(t)$ (Equation 6.17), a spreadsheet was created which took into account the interconnecting relationship between the two parameters. Appendix D shows an example of the Excel spreadsheet used for the calculation.

6.3.3.2 Verification of the Modified Model

The results obtained from the modified model are compared with the original model in simulation of the actual reaction conditions in Figures 6.6 and 6.7. It is clear from Figure 6.7 that the modified model ($R^2 = 0.996$) describes the experimental results more adequately than the original model ($R^2 = 0.784$). The calculated values were in good agreement with the experimental results even at the approach to steady state, i.e. at low concentrations of resorcinol. Furthermore, it is also shown that the

general Equation 6.17 can be used to determine the CSTR performance as satisfactorily as the individual Equations 6.13, 6.15 and 6.16 for 10mg/L, 30mg/L and 50mg/L, respectively.

Figure 6.6 Comparison of the original and modified model in predicting the degradation of resorcinol in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{mg/L}$, residence time = 1hr.

Figure 6.7 Comparison of the original and modified model in predicting the degradation of resorcinol in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 30\text{mg/L}$, residence time = 2hrs.

Figure 6.8 Comparison of the original and modified model in predicting the degradation of resorcinol in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 50\text{mg/L}$, residence time = 3.5hrs.

The effect of changing volumetric flow rate, which in turn affects the residence time of resorcinol in the system, is demonstrated in Figure 6.9. The resorcinol removal efficiency decreased as retention time decreased in the CSTR operation. This is anticipated for CSTR operation because decreasing the contact time reduces the chances for the TiO_2 photocatalysis to react with the targeted substrates. This behaviour was also observed and discussed previously during the continuous degradation of BPA in the preceding Section 4.4.4, Figure 4.14.

Figure 6.9 Effect of retention time in the degradation of resorcinol in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, $[\text{Resorcinol}]_0 = 10\text{mg/L}$.

Section 4.4.4 also provided evidence of the importance of understanding the dependence of removal efficiency with respect to the initial concentration of the organic substrate. From an application point of view, the concentration of feed might fluctuate or change over time and an effective model must be able to account for this change. It can be seen from Figure 6.10 that with the same residence time, a higher initial concentration of resorcinol resulted in a longer time before steady-state was reached. For the initial feed concentrations of 50mg/L and 30mg/L , steady-state concentrations of 1.5mg/L and 0.8mg/L (experimental) were achieved at 200min and 120min , respectively. With an increase in initial feed concentration from 30 to 50mg/L , the steady-state efficiency of the submerged light CSTR was reduced by about 50% . The model was able to predict this effectively.

Figure 6.10 Effect of initial feed concentration in the degradation of resorcinol in the submerged light SMPR. Conditions: $[\text{TiO}_2] = 0.5\text{g/L}$, residence time = 3.5hrs.

6.4 Summary

A classical CSTR model, with the use of a simple first-order kinetic rate constant, could not fit the experimental results adequately. When high initial concentrations of resorcinol were used, the model deviated from the experimental results when the resorcinol concentration was reduced below approximately 10mg/L and was not able to predict the steady-state concentration accurately. The inefficacy of the model in taking into account the changing adsorption/desorption phenomenon during photocatalytic reaction was postulated to be the reason for the observed divergence. Therefore, a modified model explicitly taking into account a correction factor, the reaction surface coverage ratio (β) was developed. It was assumed that β was a function of resorcinol concentration in the bulk solution and thus changed with time. A semi-empirical universal equation was derived successfully for the determination of β (t) with respect to different initial concentrations of resorcinol used. The new improved model was verified to be able to describe the CSTR performance more accurately than the original classic CSTR model. Furthermore, it has also been demonstrated that the new model is useful in predicting the steady-

state resorcinol concentrations for different feed concentrations and residence times. The new improved semi-empirical model is proposed to be useful for the optimization of the SMPR operation.

Nomenclature

V_R = reactor volume (L)

Q_f = feed volumetric flow rate (L/min)

Q = output volumetric flow rate (L/min)

$C_{A,f}$ = feed concentration of A (mg/L)

C_A = output concentration of A (mg/L)

r_A = rate of reaction of A (mg/L. min)

K_{LH} = Langmuir Hinshelwood equilibrium adsorption constant

k_{LH} = pseudo-first order initial reaction rate constant at maximum coverage

C_{AO} = the initial concentration of A

k_{app} = apparent first-order kinetic constant.

τ = residence time

a, b, c = model parameters

β = reaction surface coverage ratio

t = time (t)

CHAPTER 7

CONCLUSIONS & RECOMMENDATIONS

This chapter provides a summary of the experimental results obtained to date for the hybrid photocatalytic membrane system. Several suggestions are also given for potential future directions for this research. These suggestions are developed using the current proof-of-concept results as a technical springboard.

7.1 Conclusions

Based on the findings obtained in these studies, the following conclusions can be drawn:

7.1.1 Investigation of Stability of Polymeric Membranes

This study focused on the selection of polymeric membranes for the photocatalytic-membrane process and has provided a protocol for evaluating the stability of polymeric membranes in photocatalytic reactions. A detailed study was developed and ten membranes were evaluated under ultraviolet (UV) and TiO₂ photocatalysis conditions. Membrane stability was characterized by changes in pure water flux (PWF), release of total organic carbon (TOC) and scanning electron microscope (SEM) morphology analysis. The results revealed that polytetrafluoroethylene (PTFE), hydrophobic polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) membranes showed the greatest UV stability. However when exposed to a harsh oxidative environment, the PAN membrane was found to be unsuitable for the application. Tests with cross-flow filtration conditions to prevent titanium dioxide

(TiO₂) cake formation were carried out. It was shown that during non-cake situations, pH played a part in reducing the deterioration of the membrane by the activated TiO₂. Deposition of cakes with various thicknesses of TiO₂ affected the stability of the membranes to different extents. In general, the thicker the cake layer, the lesser was the damage of the photocatalytic reaction to the membrane. The results obtained using powdered activated carbon (PAC) as a separating layer showed that close proximity between the TiO₂ and the membranes was the main mechanism for the detrimental effect of TiO₂ on polymeric membrane.

7.1.2 Feasibility Study of a Low-Pressure Submerged Membrane-Photocatalytic System

The feasibility of a hybrid system combining photocatalysis and low-pressure membrane filtration in a single module for the treatment of low concentration of BPA was investigated. Adsorption of BPA on TiO₂ followed the Langmuir adsorption isotherm whereas the batch degradation of BPA could be satisfactorily expressed by the Langmuir-Hinshelwood (L-H) kinetic model. Acidic pHs were found to enhance the BPA degradation rate more significantly than the effects of TiO₂ concentration and aeration rate. An optimum aeration rate of 0.5L/min was used that balanced the competing effects of improved mass transfer and possible UV light attenuation by bubble clouds at high aeration rates. Membrane integrity tests confirmed that the 0.2µm PVDF hollow fibre membrane was able to retain the TiO₂ particles completely in the system, under different pH conditions. During continuous operation of the SMPR at 100L/m².hr, 97% photodegradation and more than 90% photomineralization of 10mg/L of BPA were achieved after 90 and 120 min of UV illumination, respectively. A difference in BPA concentration between the tank and permeate, which diminished at steady-state, was attributed to the strong adsorption of BPA on the membrane. It was revealed that intermittent permeation enhanced the sustainability of the submerged membranes and was preferred over bubbling to control fouling in the SMPR at high flux.

7.1.3 Development and Performance of an Improved Submerged Membrane Photocatalytic Reactor

A submerged light SMPR was designed and built to achieve better distribution of UV light and better utilization of reactor volume space. Direct measurement of light intensity extinction profile with respect to changing TiO_2 concentration was done which led to the proposed light arrangement in the reactor. Degradation of resorcinol, an additional model compound, was found to follow L-H kinetics and was found to have higher degradability compared to BPA. A submerged light concept of limiting photonic efficiency was introduced when comparing batch reactor efficiency. Limiting photonic efficiency, ζ_{lim} , is defined as the photonic efficiency of a reactor which is independent of concentration effect. The submerged light reactor was found to be 145% ($\text{TOC}_{\text{resorcinol}}$) and 132% (TOC_{BPA}) more efficient than the old reactor with external light source. No adsorption of resorcinol on the membrane surface was observed during the continuous operation of the submerged light SMPR. The difference in adsorption interactions between BPA and resorcinol was due to the difference in their $\log K_{\text{ow}}$ coefficients. The submerged light SMPR has also been shown to be reasonably competent, in terms of UV utilization effectiveness, compared to other existing reactors and was less prone to fouling compared to the old reactor. Increased temperature in the SMPR, up to 40°C , had no effect on the degradation rate of resorcinol but has shown enhancement in the mineralization rate. A long term evaluation of the SMPR process was done in which the importance of lamp envelope cleaning was demonstrated. Also, the activity of the TiO_2 particles and the PVDF membrane integrity remained satisfactorily for 28 consecutive days. Although not all issues concerning the long term operation of the SMPR have been addressed, the more critical findings such as membrane stability and TiO_2 activity have confirmed the favorability of the SMPR in the degradation of low concentrations of organics. Practical applicability of the SMPR has also been addressed taking into considerations the volume and contaminant concentration of the water to be treated as well as retention and recovery of the photocatalyst.

7.1.4 Submerged Membrane Photocatalytic Reactor Modeling

A modified CSTR model was developed and used in this study to predict the degradation of resorcinol in the submerged light SMPR. The modified model was constructed after the failure of the classical CSTR model, which employed simple first-order kinetic rate constants, in the simulation of the experimental results. The reaction surface coverage ratio, β , which was assumed to be a function of bulk resorcinol concentration, was introduced to the classical model. A semi-empirical universal equation was also derived successfully for the determination of β (t) with respect to different initial concentrations of resorcinol used. The submerged light improved model was verified to be able to describe the CSTR performance more accurately than the original CSTR model. Furthermore, the submerged light model was useful in predicting the steady-state resorcinol concentration for different feed concentrations and residence times. The semi-empirical model is proposed to be a key practical tool for system optimization.

7.2 Recommendations for Future Research

7.2.1 Investigation of Stability of Polymeric Membranes

In this study, the in-situ measurement of the deposited TiO_2 cake thickness was not possible. The membrane with the deposited cake was carefully taken out from the system and was subjected to drying followed by SEM imaging. This non in-situ measurement might lead to some unavoidable changes to the cake structures which would thus affect the actual thickness of the cake. It is thus suggested to employ the Field-Emission Environmental SEM which allows wet sample image to be taken rather than the current dry gold coated sample. Alternatively, a non-invasive method using ultrasonic time-domain reflectometry could be used for in-situ measurement of cake thickness. This method has been widely used to study the fouling of membranes using velocity and attenuation of sound wave to characterize the properties of the reflected cake layer [Li et al., 2002 (a) and 2002 (b)].

Due to the limitation of obtaining a wide variety of membranes, only ten types of polymeric membranes were tested. It would be recommended to continue searching using the proposed protocol for a polymeric membrane which is stable under photocatalytic reaction conditions and yet more economical than PVDF and PTFE membranes. Other membranes made of perfluoropolymer, with stable C-F bonds, are recommended. A life-cycle [Sadiq et al., 2005] and cost analysis comparison between ceramic membranes, which are well known for its robustness, and polymeric membranes could be done for a more concrete idea of the suitability of each type of material in the application of the photocatalysis process.

7.2.2 Feasibility Study of a Low-Pressure Submerged Membrane-Photocatalytic System

In addition to the parameters already studied in Chapter 4, a further feasibility study of the SMPR could also optimize other parameters such as intermittent light illumination, light sources, types of TiO_2 or types of membrane module configurations. The study of membrane configurations in reducing fouling is highly recommended. The types of configuration to be considered and compared to the current U-shaped hollow fibre module include flat sheets and curtain-type hollow fibres. The comparison might provide insights into the preferred membrane configuration for the filtration of small TiO_2 particles as well as the compactness of the reactor. In addition, the quantitative effect of the postulated attenuation of light by bubble clouds in TiO_2 slurry was not established. Separate works could be done in this field to understand further the light attenuation in the presence of aeration as well as other solid particles.

7.2.3 Development and Performance of an Improved Submerged Membrane Photocatalytic Reactor

During the design of a submerged light SMPR, the use of smaller diameter UV lamps might be employed so as to increase the compactness of the combined system. Thin and flexible optical fibres were initially considered in this thesis. Such light sources could be a good choice for this application but the difficulty of obtaining constant illumination along the length of the fibre would be a challenge. Therefore, assessments have to be done to improve the illumination pathway and also ensure UV/oxidative stability of the optical fibre before it can be applied in this system. It could be interesting to try to determine the relationship between different organic bondings and their adsorption ability on membrane. The characterization might be useful for future selection of membranes. Prolonged operation of the SMPR, greater than 28 days, should be carried out to monitor the TiO₂ photoactivity and membrane sustainability of the submerged light SMPR more thoroughly. It is also suggested to incorporate a TiO₂ self – regeneration procedure during the long term study. One suggestion could be to stop the feed into the photoreactor and allow the TiO₂ to self - clean with UV illumination for a certain period of time. The ability of the SMPR to remediate mixed waste streams would also be of great interest.

7.2.4 Submerged Membrane Photocatalytic Reactor Modeling

The current SMPR model applications could be widened by taking into account the issues regarding the organics adsorption on membranes as revealed in Chapter 4 during the continuous degradation of BPA. In this case, the simulation of SMPR performance for the removal of organic substrates which have high interactions with the membrane would then be possible. Also, it is strongly recommended to develop rate expressions applicable for determining the mineralization rate of the SMPR system. It is thus necessary to consider the presence of the intermediates and also to address the fundamental kinetics of the wastewater of interest when modeling the system. The submerged light mineralization model is expected to be

more useful and practical. Lastly, the submerged light or current model could be used to explore and compare efficiency of different reactor arrangements, for example, two CSTRs in series or one CSTR with a long retention time and many other options.

REFERENCES

Abdullah M., Low G.K.C. and Matthews R.W., (1990), Effects of Common Inorganic Anions on Rates of Photocatalytic Oxidation of Organic Carbon over Illuminated Titanium Dioxide, *Journal of Physical Chemistry*, v94, pp6820.

Allen N.S. and Edge M., (1992), *Fundamentals of Polymer Degradation and Stabilization*, Elsevier Applied Science, London.

Andrady A.L., Hamid S.H, Hu X. and Torikai A., (1998), Effects of Increased Solar Ultraviolet Radiation on Materials, *Journal of Photochemistry and Photobiology B: Biology*, v46(1-3), pp96.

Andreozzi R. and Marotta R., (2004), Removal of Benzoic Acid in Aqueous Solution by Fe (III) Homogeneous Photocatalysis, *Water Research*, v28, pp1225.

Augugliaro V., Garcia-L.E., Loddo V., Malato-R.S., Maldonado I., Marci G., Molinari R. and Palmisano L., (2005), Degradation of Lincomycin in Aqueous Medium: Coupling of Solar Photocatalysis and Membrane separation, *Solar Energy*, v79, pp402.

Babu P.R., Gaikar V.G., (2001), Membrane Characteristics as Determinant in Fouling of UF Membranes, *Separation and Purification Technology*, v24, pp23.

Balasubramanian G., Dionysiou D.D. and Suidan M.T., (2003), Titania Powder Modified Sol-Gel Process for Photocatalytic Applications, *Journal of Material Science*, v38, pp823.

Barbara B., Caviccioli A., Riva E., Zaroni L., Bignoli F. and Bellobono I.R., (1995), Laboratory-Scale Photodegradation of Phenol in Aqueous Solution by Photocatalytic Membranes Immobilizing Titanium Dioxides, *Chemosphere*, v30, pp1847.

Bauer R. and Fallmann H., (1997), The Photo-Fenton Oxidation – A Cheap and Efficient Wastewater Treatment Method, *Research Chemistry Intermediate*, v23, pp341.

Behnajady M.A. and Modirshahla N., (2006), Kinetic Modeling on Photooxidative Degradation of C.I. Acid Orange 7 in a Tubular Continuous-Flow Photoreactor, *Chemosphere*, v62, pp1543.

Bekbolet M., Suphandag S.S. and Uyguner C.S., (2004), An Investigation of the Photocatalytic Efficiencies of TiO₂ Powders on the Decolourisation of Humic Acids, *Journal of Photochemistry and Photobiology A: Chemistry*, v148, pp121.

Beydoun D., Amal R., Low G. and McEnvoy S., (2000), Novel Photocatalyst: Titanina Coated Magnetite – Activity and Photodissolution, *Journal of Physical Chemistry B*: v104 (18), pp4387.

Beydoun D., Amal R., Low G. and McEvoy S., (1999), Role of Nanoparticles in Photocatalysis, *Journal of Nanoparticle Research*, v1, pp439.

Bhatkhande D.S., Kamble S.P., Sawant S.B. and Pangarkar V.G., (2004), Photocatalytic and Photochemical Degradation of Nitrobenzene using Artificial Ultraviolet Light, *Chemical Engineering Journal*, v102, pp283.

Bhatkhande D.S., Pangarkar V.G. and Beenackers A.A.C.M., (2001), Photocatalytic Degradation for Environmental Applications – A Review, *Journal of Chemical Technology and Biotechnology*, v77, pp102.

Bischoff B.L., Fain D.E. and Stockdale J.A.D, Photocatalytic Reactor, United States Patent No: 5862449, Issued Jan 19, 1999.

Braeken L., Boussu K., der Bruggen B. V. and Vandecasteele C., (2005), Modeling of the Adsorption of Organic Compounds on Polymeric Nanofiltration Membranes in Solutions Containing Two Compounds, *ChemPhysChem*, v6, pp1606.

Brites A.M. and Pinho M.N., (1993), A New Approach to the Evaluation of the Effects of Protein Adsorption onto a Polysulfone Membrane, *Journal of Membrane Science*, v78 (3), pp265.

Butterfield M., Christensen P.A., Curtis T.P. and Gunlazaurd J., (1997), Water Disinfection using an Immobilised Titanium Dioxide Film in a Photochemical Reactor with Electric Field Enhancement, *Water Research*, v31, pp675.

Cai R., Hashimoto K., Itoh K., Buboto Y. and Fujishima A., (1991), Photokilling of Malignant Cells with Ultrafine TiO₂ Powder, *The Chemical Society of Japan*, v64 (4), pp1268.

Calvert J.G. and Pitts J.N., (1966), *Photochemistry*, John Wiley and Sons, Inc., New York.

Cao Y., Chen J., Huang L., Wang Y., Hou Y. and Lu Y., (2005), Photocatalytic Degradation of Chlorfenapyr in Aqueous Suspension of TiO₂, *Journal of Molecular Catalytic A: Chemical*, v233, pp61.

Cassano E.A. and Alfano O.M., (2000), Reaction Engineering of Suspended Solid Heterogeneous Photocatalytic Reactors, *Catalysis Today*, v58, pp167.

Chan Y.C., Chen J.N. and Lu M.C., (2001), Intermediate Inhibition in the Heterogeneous UV-Catalysis using a TiO₂ Suspension System, *Chemosphere*, v45, pp29.

Chen D. and Ray A.J., (1999), Photocatalytic Kinetics of Phenol and its Derivatives over UV Irradiated TiO₂, *Applied Catalysis B: Environmental*, v23 (2–3), pp143.

Chen D. and Ray A.K., (1998), Photodegradation Kinetics of 4-Nitrophenol in TiO_2 Suspension, *Water Research*, v32, pp3223.

Cheryan M., (1998), *Ultrafiltration and Microfiltration Handbook*, Technomic Publication, U.S.A.

Chiang K., Lim T.M., Tsen L. and Lee C.C., (2004), Photocatalytic Degradation and Mineralization of Bisphenol A by TiO_2 and Platinized TiO_2 , *Applied Catalysis A: General*, v261, pp225.

Chin K.K., (1996), Pretreatment to Produce Ultrapure Water from Reclaimed Sewage, *Desalination*, v106 (1-3) pp269.

Chin S.S., Chiang K. and Fane A.G., (2006), The Stability of Polymeric Membranes in a TiO_2 Photocatalysis Process, *Journal of Membrane Science*, v275, pp201.

Choe T.B.P., Masse A., Verdier A. and Clifton M.J., (1986), Membrane Fouling in Ultrafiltration of Polyelectrolyte Solutions: Polyacrylic Acid and Bovine Serum Albumin, *Journal of Membrane Science*, v26, pp17.

Choi W., Ko J.Y., Park H. and Chung J.S., (2001), Investigation on TiO_2 -Coated Optical Fibers for Gas-Phase Photocatalytic Oxidation of Acetone, *Applied Catalysis B: Environmental*, v31, pp209.

Choi Y-S. and Kim B-W., (2000), Photocatalytic Disinfection of E. coli in a UV / TiO_2 – Immobilised Optical-Fibre Reactor, *Journal of Chemical Technology Biotechnology*, v75, pp1145.

Coleman H.M., Chiang K. and Amal R., (2005), Effects of Ag and Pt on Photocatalytic Degradation of Endocrine Disrupting Chemicals in Water, *Chemical Engineering Journal*, v113, pp65.

Crittenden J.C., Liu J., Hand D.W. and Perram D.L., (1997), Photocatalytic Oxidation of Chlorinated Hydrocarbons in Water, *Water Research*, v31, pp429.

Cunningham J. and Sedlak P., (1993), In Ollis D.F. and Al-Ekabi H. (Editor), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam.

Cunningham J., Al-Sayyed G. and Srijaranai S., (1994), Adsorption of Model Pollutants onto TiO₂ Particles in Relation to Photoremediation of Contaminated Water, In *Aquatic and Surface Photochemistry*, Edited by Helz G., Zepp R. and Crosby D., Lewis Publication, CRC Press, pp317.

D'Oliviera J-C, Guillard C., Maillard C. and Pichat P., (1993), Photocatalytic Destruction of Hazardous Chlorine or Nitrogen-Containing Aromatics in Water, *Journal of Environmental Science and Health*, vA28 (4), pp941.

Dal-Cin M.M., Mclellan F., Striez C.N., Tam C.M., Tweddle T.A. and Kumar A., (1996), Membrane Performance with a Pulp Mill Effluent: Relative Contributions of Fouling Mechanisms, *Journal of Membrane Science*, v120, pp273.

Dal-Cin M.M., Striez C.N., Tweffke T.A., Capes C.E., Mclellan F and Buisson H., (1995), Effect of Adsorptive Fouling on Membrane Performance: Case Study with a Pulp Mill Effluent, *Desalination*, v101, pp155.

Danion A., Disdier J., Guillard C., Abdelmalek F. and Jaffrezic-Renault N., (2004), Characterization and Study of a Single-TiO₂-Coated Optical Fiber Reactor, *Applied Catalysis B: Environmental*, v52, pp213.

Davis R.H., (2001), Microfiltration in *Membrane Handbook*, Edited by Ho W.S.W. and Sirkar K.K., Kluwer Academic Publishers, U.S.A, pp457.

Degussa, (1989), Hochdisperse Metalloxide nach dem AEROSIL® -Verfahren (High-Dispersed Metallic Oxides Produced by the AEROSIL® - Process), Schriftenreihe Pigmente, v56, Degussa AG, Frankfurt, Germany.

Demeestere K., Visscher A.D., Dewulf J., Leeuwen M.V. and Langenhove H.V., (2004), A New Kinetic Model for Titanium Dioxide Mediated Heterogeneous Photocatalytic Degradation of Trichloroethylene in Gas-Phase, Applied Catalysis B: Environmental, v54, pp261.

Dijkstra M.F.J., Buwalda H., de Jong A.W.F., Michorius A., Winkelman J.G.M. and Beenackers A.A.C.M., (2001), Experimental Comparison of Three Reactor Designs for Photocatalytic Water Purification, Chemical Engineering Science, v56, pp547.

Dijkstra M.F.J., Michorius A., Buwalda H., Panneman H.J., Winkelman J.G.M. and Beenackers A.A.C.M., (2001), Comparison of the Efficiency of Immobilized and Suspended Systems in Photocatalytic Degradation, Catalysis Today, v66, pp487.

Dijkstra M.F.J., Buwalda H., Jong A.W.F., Michorius A., Winkelman J.G.M. and Beenackers A.A.C.M., (2001), Experimental Comparison of Three Reactor Designs for Photocatalytic Water Purification, Chemical Engineering Science, v56, pp547.

Dionysiou D. Dionysiou, Makram T.S., Evangelia B., Isabelle B. and Jean-Michel L., (2000), Effect of Ionic Strength and Hydrogen Peroxide on the Photocatalytic Degradation of 4-Chlorobenzoic Acid in Water, Applied Catalysis B: Environmental, v26, pp153.

Doll T.E. and Frimmel F.H., (2005), Cross-Flow Microfiltration with Periodical Back-Washing for Photocatalytic Degradation of Pharmaceutical and Diagnostic Residues-Evaluation of the Long-Term Stability of the Photocatalytic Activity of TiO₂, Water Research, v39, pp847.

El-Dein A.M., Libra J.A. and Weissmann U., (2003), Mechanism and Kinetic Model for the Decolourization of the Azo Dye Reactive Black 5 by Hydrogen Peroxide and UV Radiation, *Chemosphere*, v52, pp1069.

Emets E.P., Kolomeytsev G.Y., Polluektov P.P. and Timonin V.V., (1996), Control of Disactivation Processes by using a New Laser Bubble Sizer, *Journal of Aerosol Science*, v27, pp559.

Fane A.G, Chang S. and Chardon E., (2002), Submerged Hollow Fibre Membrane Module – Design Options and Operational Considerations, *Desalination*, v146, pp231.

Fane A.G., (1986), Ultrafiltration: Factors Influencing Flux and Rejection in Filtration and Separation, Edited by Wakeman R.J., Volume 4, Elsevier Scientific Publishing CO., Amsterdam.

Fechine G.J.M., Rabello M.S., Souto-Maior R.M., (2002), The Effect of Ultraviolet Stabiizers on the Photodegradation of Poly(Ethylene Terephthalate), *Polymer Degradation and Stability*, v75, pp153.

Fernandez-Ibanez P., Blanco J., Malato S. and Nieves F.J., (2003), Application of the Colloidal Stability of TiO₂ Particles for Recovery and Reuse in Solar Photocatalysis, *Water Research*, v37, pp3180.

Finklea H.O., (1998), In Finklea H.O. (Ed), *Semiconductor Electrodes*, Elsevier, Amsterdam, 1998, Chapter 2.

Fox M.A. and Dulay M.T., (1993), Heterogeneous Phaotocatalysis, *Chemistry Review*, v93, pp341.

Fu J., Ji M., Wang Z., Jin L and An D., (2006a), A New Submerged Membrane Photocatalysis Reactor (SMPR) for Fulvic Acid Removal using a Nano-Structured Photocatalyst, *Journal of Hazardous Materials*, v131, pp238.

Fu J., Ji M., Zhao Y., Wang L., (2006b) Kinetics of Aqueous Photocatalytic Oxidation of Fulvic Acids in a Photocatalysis–Ultrafiltration Reactor (PUR), *Separation and Purification Technology*, v50 (1), pp 107.

Fujishima A., Rao T.N. and Tryk D.A., (2000), Titanium Dioxide Photocatalysis, *Journal of Photochemistry and Photobiology: Photochemistry Revision*, v1, pp1.

Fukahori S., Ichiura H., Kitaoka T. and Tanaka H., (2003), Photocatalytic Decomposition of Bisphenol A in Water using Composite TiO₂-Zeolite Sheets Prepared by a Papermaking Technique, *Environmental Science Technology*, v37, pp1048.

Gabriels J.E., (1999), A Fast-Flow, Low Protein Binding Membrane for Sterile Filtration, <http://www.iscpubs.com/articles/abl/b9904gab.pdf>, Accessed on 5th April 2004.

GE Corporate, (1997), E Water and Process Technologies as Zenon Membrane Solutions, http://www.zenon.com/markets/drinking_water/, Accessed on 10th May 2007.

Geissen S-U, Xi W., Weidemeyer A., Vogelpohl A., Bousselmi L., Ghrabi A. and Ennabli A., (2001), Comparison of Suspended and Fixed Photocatalytic Reactor Systems, v44 (5), pp245.

Gesehues U., (2000), Influence of Titanium Dioxide Pigments on the Photodegradation of Poly (Vinyl Chloride), *Polymer Degradation and Stability*, v68, pp185.

Gillot S., Clercq B.D., Defour D., Simoens, Germaey K. and Vanrolleghem, (1999), Optimization of Wastewater Treatment Plant Design and Operation using Simulation and Cost Analysis, 72nd Annual Conference, WEFTEC, New Orleans.

Glaze W.H., Kenneke J.F. and Ferry J. L., (1993), Chlorinated Byproducts from the TiO₂-Mediated Photodegradation of Trichloroethylene and Tetrachloroethylene in Water, Environmental Science Technology, v27, pp177.

Gogate P.R. and Pandit A.B., (2004), A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions, Advanced in Environmental Research, v8, pp501.

Gorges R., Meyer S. and Kreisel G., (2004), Photocatalysis in Microreactors, Journal of Photochemistry and Photobiology A: Chemistry, v167, pp95.

Guettaï N. and Amar H. A., (2005), Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part II: Kinetics Study, Desalination, v185, pp439.

Hamid S.H., Maadhah A.G. and Amin M.B., (1992), Weathering Degradation of Polyethylene, In Handbook of Polymer Degradation, Edited by Hamid S.H., Maadhah A.G. and Amin M.B., Marcel Dekker Inc, New York.

Heredia J.B.D., Torregrosa J., Dominguez J.R. and Peres J. A., (2001), Oxidation of p-Hydroxybenzoic Acid by UV Radiation and by TiO₂ / UV Radiation: Comparison and Modelling of Reaction Kinetic, Journal of Hazardous Materials, vB83, pp255.

Hermann J-M, (1999), Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants, Catalysis Today, v53, p115.

Hertz R. K., (2004), Intrinsic Kinetics of First-Order Reactions in Photocatalytic Membranes and Layers, Chemical Engineering Journal, v99, pp237.

Higgins R.J., Bishop B.A. and Goldsmith R.L., (2000), A Photocatalytic Membrane Reactor for Enhanced Destruction of Chloro-Organics in Aqueous Media, Proc. NETL 2000 Conference, section 7.4.

Hisao H., Suzuki Y., Nohara K., Horikoshi S., Hisamatsu Y., Pelizzetti E. and Serpone N., (1996), Photocatalyzed Degradation of Polymers in Aqueous Semiconductor Suspensions. 1. Photooxidation of Solid Particles of Polyvinylchloride, Journal of Polymer Science Part A: Polymer Chemistry, v34, pp1311.

Hoffmann M.R., Martin S.T., Choi W. and Bahnemann D.W., (1995), Environmental Applications of Semiconductor Photocatalysis, Chemistry Review, v95, pp69.

Hofstadler K., Bauer R., Novalic S. and Heisler G., (1994), New Reactor Design for Photocatalytic Wastewater Treatment with TiO₂ Immobilized on Fused Silica Glass Fibers: Photomineralization of 4-Chlorophenol, Environmental Science Technology, v28, pp670.

Hong S.P., Bae T.H., Tak T.M., Hong S., and Randall A., (2002), Fouling Control in Activated Sludge Submerged Hollow Fiber Membrane Bioreactors, Desalination, v143, pp219.

Horie Y., Taya M. and Tone S., (1998), Evaluation of Photocatalytic Sterilization Rates of Escherichia Coli Cells in Titanium Dioxide Slurry Irradiated with Various Light Sources, Journal of Chemical Engineering of Japan, v31 (4), pp577.

Horikoshi S., Hidaka H. and Serpone N., (2001), Photocatalyzed Degradation of Polymers in Aqueous Semiconductor Suspensions. V. Photomineralization of Lactum Ring-Pendant Polyvinylpyrrolidone at Titania / Water Interfaces, *Journal of Photochemistry and Photobiology A: Chemistry*, v138, pp69.

Horikoshi S., Serpone N., Hisamatsu Y. and Hidaka H., (1998), Photocatalyzed Degradation of Polymers in Aqueous Semiconductor Suspensions. 3. Photooxidation of Solid Polymer: TiO₂-Blended Poly (Vinyl Chloride) Film, *Environmental Science Technology*, v32, pp4010.

Howell J.A., Chua H.C. and Arnot T.C., (2004), In Situ Manipulation of Critical Flux in a Submerged Membrane Bioreactor using Variable Aeration Rates, and Effects of Membrane History, *Journal Membrane Science*, v242, pp131.

Howell J.A. and Velicangil O., (1987), Theoretical Considerations of Membrane Fouling and its Treatment for Protein Ultrafiltration, *Journal of Applied Polymer Science*, v27, pp21.

Howell J.A., (1995), Sub-Critical Flux Operation, *Journal of Membrane Science*, v107, pp165.

Hu X., (1997), Wavelength Sensitivity of Photo-Oxidation of Polyethylene, *Polymer Degradation and Stability*, v55, pp131.

Ireland J.C., Klostermann P., Rice E.W. and Clark R.M., (1993), Inactivation of Escherichia Coli by Titanium Dioxide Photocatalytic Oxidation, *Applied and Environmental Microbiology*, v59, pp1668.

Jia Y., Wang R. and Fane A.G., (2006), Atrazine Adsorption in Water by Powdered Activated Carbon-Improved Mass Transfer by Bubbling, *Chemical Engineering Journal*, v116, pp53.

Kacmarek H., (1996), Changes to Polymer Morphology caused by U.V. Irradiation: 1. Surface Damage, *Polymer Papers*, v37 (2), pp189.

Kaneco S., Rahman M.A., Suzuki T., Katsumata H. and Ohta K., (2004), Optimization of Solar Photocatalytic Degradation Conditions of Bisphenol A in Water using Titanium Dioxide, *Journal of Photochemistry and Photobiology A: Chemistry*, v163, pp419.

Kaniou S., Pitarakis K., Barlagianni I. and Poulis I., (2006), Photocatalytic Oxidation of Sulfamethazine, *Chemosphere*, v60 (3), pp 37.

Karakulski K., Morawski W.A. and Grzechulska J., (1998), Purification of Bilge Water by Hybrid Ultrafiltration and Photocatalytic Processes, *Separation Purification Technology*, v14, pp163.

Kesting R. E., (1985), *Synthetic Polymeric Membranes: A Structural Perspective*, John Wiley & Sons, 2nd edition, New York.

Kim J-S, Lee S-L, Yoon S-H and Lee C-H, (1996), Competitive Adsorption of Trace Organics on Membranes and Powdered Activated Carbon in Powdered Activated Carbon-Ultrafiltration System, *Water Science Technology*, v34, pp223.

Kim K-J, Fane A.G., Nystrom M., Pihlajamaki A., Bowen W.R. and Mukhtar H., (1996), Evaluation of Electroosmosis and Streaming Potential for Measurement of Electric Charges of Polymeric Membranes, *Journal of Membrane Science*, v116 (2), pp149.

Kim M., Kojima J., Saito K., Furusaki S. and Sugo T., (1994), Reduction of Nonselective Adsorption of Proteins by Hydrophilization of Microfiltration Membranes by Radiation-Induced Grafting, *Biotechnology Progress*, v10, pp114.

Kiriakidou F., Kondarides D. I. and Verykios E., (1999), The Effect of Operational Parameters and TiO₂-Doping on the Photocatalytic Degradation of Azo Dyes, *Catalysis Today*, v54, pp119.

Korrmann C., Bahnemann D.W., Hoffmann M.R., (1991), Photolysis of Chloroform and other Organic Molecules in Aqueous Suspensions, *Environmental Science and Technology*, v25, pp494.

Kroschwitz J.I. and Mary Howe-Grant, (1996), *Encyclopedia of Chemical Technology* (4th Edition), Volume 18, John Wiley & Sons, Inc., New York.

Kroschwitz J.I. and Mary Howe-Grant, (1996), *Encyclopedia of Chemical Technology* (4th Edition), Volume 18, John Wiley & Sons, Inc., New York.

Ksibi M., Zemzemi A. and Boukchina R., (2003), Photocatalytic Degradability of Substituted Phenols over UV Irradiated TiO₂, *Journal of Photochemistry and Photobiology A: Chemistry*, v159, pp61.

Kulkarni S.S., Funk E.W. and Li N.N., (2001), *Ultrafiltration in Membrane Handbook*, Edited by Ho W.S.W. and Sirkar K.K., Kluwer Academic Publishers, U.S.A.

Kuo W.S., (2000), Preparation and Photocatalytic Activity of Metal-Supported Resin-Bonded Titania, *Journal of Environmental Science and Health, Part A: Toxic / Hazardous Substances and Environmental Engineering*, v35 (3), pp419.

Kuroda S., Mita I., Obata K., Tanaka S., (1990), Degradation of Aromatic Polymers: Part IV- Effect of Temperature and Light Intensity on the Photodegradation of Polyethersulfone, *Polymer Degradation Stability*, v27, pp257.

Kusvuran E., Samil A., Atanur O.M. and Erbatur O., (2005), Photocatalytic Degradation Kinetics of Di- and Tri-substituted Phenolic Compounds in Aqueous Solution by TiO_2 / UV, *Applied Catalysis B: Environmental*, v58, pp211.

Lasa H.D., Serrano-Rosales B. and Salaices-Arredondo M., (2004), *Photocatalytic Reaction Engineering*, Springer, New York, pp21.

Le-Clech P., Lee E-K., Chen V., (2006), Hybrid Photocatalysis / Membrane Treatment for Surface Waters Containing Low Concentrations of Natural Organic Matters, *Water Research*, v40, pp323.

Lee J.H., Nam W., Kang M., Han G.Y., Yoon K.J., Kim M-S, Ogino K., Miyata S. and Choung S-J, (2003), Design of Two Types of Fluidized Photoreactors and their Photo-Catalytic Performances for Degradation of Methyl Orange, *Applied Catalysis A: General*, v244, pp49.

Lee J., Kim M. and Kim B., (2004), Photodegradation of Bisphenol-A with TiO_2 Immobilized on the Glass Tubes including the UV Light Lamps, *Water Research*, v38, pp3605.

Lee S-A, Choo K-H, Lee C-H, Lee H-I, Hyeon T., Choi W. and Kwon H-H, (2001), Use of Ultrafiltration Membranes for the Separation of TiO_2 Photocatalysts in Drinking Water Treatment, *Industrial Engineer Chemistry Research*, v40, pp1712.

Levenspiel O., (1999), *Chemical Reaction Engineering*, 3rd edition, John Wiley and Sons Inc., New York.

Li P.G. and Yue P.L., (2003), Modelling and Design of Thin-Film Slurry Photocatalytic Reactors for Water Purification, *Chemical Engineering Science*, v58, pp2269.

Li J., Hallbauer-Zadorozhnaya V.Y., Hallbauer D.K. and Sanderson R.D., (2002), Cake Layer Deposition, Growth and Compressibility during Microfiltration Measured and Modeled using a Noninvasive Ultrasonic Technique, *Ind. Eng. Chem. Res.*, v41, pp4106.

Li J., Sanderson R.D. and Jacobs E.P., (2002), Non-Invasive Visualization of the Fouling of Microfiltration Membranes by Ultrasonic Time-Domain Reflectometry, *Journal of Membrane Science*, v201, pp17.

Lin H.F., Ravikrishna R. and Valsaraj K.T., (2002), Reusable Adsorbents for Dilute Solution Separation. 6. Batch and Continuous Reactors for the Adsorption and Degradation of 1, 2-Dichlorobenzene from Dilute Wastewater Streams using Titania as a Photocatalysis, *Separation and Purification Technology*, v28, pp87.

Litter M.L., (1999), Heterogeneous Photocatalysis Transition Metal Ions in Photocatalytic System, *Applied Catalysis B: Environmental*, v23 (2–3), pp89.

Liu H., Qu J., Dai R., Ru J. And Wang Z., (2007), A Biometric Absorbent for Removal of Trace Level Persistent Organic Pollutants from Water, *Environmental Pollution*, v147, pp 337.

Liu R., Huang X., Wang C., Chen L. and Qian Y., (2000), Study on Hydraulic Characteristics in a Submerged Membrane Bioreactor Process, *Process Biochemistry*, v36, pp249.

Malato S., Blanco J., Caceres J., Fernandez-Alba A.R., Aguera A. and Rodriguez, (2002), Photocatalytic Treatment of Water-Soluble Pesticides by Photo-Fenton and TiO₂ using Solar Energy, *Catalysis Today*, v76, pp209.

Martin C.A., Baltanas M.A. and Cassano A.E., (1996), Photocatalytic Reactors II. Quantum Efficiencies Allowing for Scattering Effects. An Experimental Approximation, *Journal of Photochemistry and Photobiology A: Chemistry*, v94, pp173.

Martin J.W., Chin J.W. and Nguyen T., (2003), Reciprocity Law Experiments in Polymeric Photodegradation: A Critical Review, *Progress in Organic Coatings*, v47, pp292.

Matis K.A., Peleka E.N., Zamboulis D., Erwe T. and Mavrov V., (2004), Air Sparging during the Solid / Liquid Separation by Microfiltration: Application of Flotation, v40 (1), pp1.

Matsuda N., Agui W., Ogino K., Kawashima N., Watanabe T., Sakai H. and Abe M., (1996), Disinfection of Viable *Pseudomonas Stutzeri* in Ultrapure Water with Ion Exchange Resins, *Colloids and Surfaces B: Biointerfaces*, v7, pp91.

Matsunaga T., Tomoda R., Nakajima T., Nakamura N. and Komine T., (1988), Continuous – Sterilization System that uses Photoconductor Powders, *Applied and Environmental Microbiology*, v54, pp1330.

Matthews R., (1993), Photocatalysis in Water Purification: Possibilities, Problems and Prospects, In Ollis D.F. and Al-Elkabi H. editions, *Photocatalytic Purification and Treatment of Water and Air*, Elsevier Science Publishers, pp121.

Matthews R.W. and McEvoy S.R., (1992), Photocatalytic Degradation of Phenol in the Presence of Near-UV Illuminated Titanium Dioxide, *Journal of Photochemistry and Photobiology: Chemistry*, v64, pp231.

Meng Y., Huang X., Wu Y., Wang X. and Qian Y., (2002), Kinetic Study and Modeling on Photocatalytic Degradation of Para-Chlorobenzoate at Different Light Intensities, *Environmental Pollution*, v117, pp307.

Meng Y., Huang X., Yang Q., Qian Y., Kubota N. and Fukunaga S., (2005), Treatment of Polluted River Water with a Photocatalytic Slurry Reactor using Low-Pressure Mercury Lamps Coupled with a Membrane, *Desalination*, v181, pp121.

Michel Charman, (1997), *Homogenous Photocatalysis: Wiley Series in Photoscience & Photoengineering, Volume 2*, John Wiley & Sons Ltd., New York.

Mills A. and Hunte S.L., (1997), An Overview of Semiconductor Photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, v108, pp1.

Mills A. and Morris S., (1993), Photomineralization of 4-Chlorophenol Sensitized by Titanium Dioxide: A Study of the Initial Kinetics of Carbon Dioxide Photogeneration, *Journal of Photochemistry and Photobiology*, v71, pp75.

Miyamae T. and Nozoye H., (2001), Surface Characterization and Photochemical Behaviour of Poly (Ethylene Terephthalate) and TiO_2 / Polyethylene Terephthalate Interface by using Sum-Frequency Generation, *Journal of Photochemistry and Photobiology A: Chemistry*, v145, pp93

Molinari R., Grande C., Drioli E., Palmisano L. and Schiavello M., (2001), Photocatalytic Membrane Reactors for Degradation of Organic Pollutants in Water, *Catalysis Today*, v67, pp273.

Molinari R., Mungari M., Drioli E., Paola A.D., Loddo V., Palmisano L. and Schiavello, (2000), Study on a Photocatalytic Membrane Reactor for Water Purification, *Catalysis Today*, v55, pp71.

Molinari R., Palmisano L., Drioli E. and Schiavello M., (2002), Studies on Various Rector Configuration for Coupling Photocatalysis and Membrane Processes in Water Purification, *Journal of Membrane Science*, v206, pp399.

Molinari R., Pirillo F., Falco M., Loddo V and Palmisano L., (2004), Photocatalytic Degradation of Dyes by using a Membrane Reactor, *Chemical Engineering and Processing*, v43, pp1103.

Moritz T., Benfer S., Arki P. and Tomandl G., (2001), Influence of the Surface Charge on the Permeate Flux in the Dead-End Filtration with Ceramic membranes, *Separation and Purification Technology*, v25, pp501.

Mozia S., Tomaszewska M. and Morawski A.W., (2005a), Photocatalytic Degradation of Azo-Dye Acid Red 18, *Desalination*, v185, pp449.

Mozia S., Tomaszewska M. and Morawski A.W., (2005b), A New Photocatalytic Membrane Reactor (PMR) for Removal of Azo-Dye Acid Red 18 from Water, *Applied Catalytic B: Environmental*, v59, pp131.

Mulder M., (1989), *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, U.S.A

Mueller J. and Davis R.H., (1996), Protein Fouling of Surface-Modified Polymeric Microfiltration Membranes, *Journal of Membrane Science*, v116, pp47.

Muneer M. and Bahnemann D., (2002), Semiconductor-Mediated Photocatalyzed Degradation of Two Selected Pesticide Derivatives, Terbacil and 2, 4, 5-Tribromoimidazole, in Aqueous Suspension, *Applied Catalysis B: Environmental*, v36, pp95.

Muruganandham M. and Swaminathan M., (2006), Photocatalytic Decolourisation and Degradation of Reactive Orange 4 by TiO₂-UV Process, *Dyes and Pigments*, v68, pp133.

Nagoka H., Ueda S. and Miya A., (1996), Influence of Bacterial Extracellular Polymers on the Membrane Separation Activated Sludge Process, *Water Science and Technology*, v34, pp165.

Nakashima T., Ohka Y., Kubota Y. and Fujishima A., (2003), Photocatalytic Decomposition of Estrogens in Aquatic Environment by Reciprocating Immersion of TiO₂-Mediated Polytetrafluoroethylene Mesh Sheets, *Journal of Photochemistry and Photobiology A: Chemistry*, v160, pp115.

Negeshi N., Takeuchi K. and Ibusuki T., (1998), Surface Struture of the TiO₂ Thin Film Photocatalyst, *Journal of Material Science*, v33, pp5789.

O'Shea K.E. and Cardona C., (1995), The Reactivity of Phenol in Irradiated Aqueous Suspensions of TiO₂: Mechanistic Changes as a Function of Solution pH, *Journal of Photochemistry and Photobiology*, v91, pp67.

Ognier S., Wisnieswski C. and Grasmick A., (2001), Biofouling in Membrane Bioreactors: Phenomenon Analysis and Modeling in: *Proceedings of Third MBR Conference on Membrane Bioreactors for Wastewater Treatment*, Cranfield University, UK, pp29.

Ohko Y., Ando I., Niwa C., Tatsuma T., Yamamura T., Nakashima T., Kubota Y. and Fujishima A., (2001), Degradation of Bisphenol A in Water by TiO₂ Photocatalyst, *Environmental Science Technology*, v35, pp2365.

Okte A.N., Resat M.S. and Inel Y., (2000), Quantum Yields and Relative Photonic Efficiencies of Substituted 1, 3-Dihydroxybenzenes, *Journal of Photochemistry and Photobiology A: Chemistry*, v134, pp59.

Ollis D.F., (2000), Photocatalytic Purification and Remediation of Contaminated Air and Water, Surface Chemistry and Catalytics - Chemistry, v3, pp405.

Otaki M., Hirata T. and Ohgaki S., (1996), Aqueous Microorganisms Inactivation by Photocatalytic Reaction, Water Science and Technology, v42 (3-4), pp103.

Pace G., Berton A., Calligaro L., Mantovani A. and Uguagliati P., (1995), Elucidation of the Degradation Mechanism of 2-Chloroethanol by Hydrogen Peroxide under Ultraviolet Irradiation, Journal of Chromatography A, v706, pp345.

Pareek V., Brungs M.P. and Adesina A.A., (2003), A New Simplified Model for Light Scattering in Photocatalytic Reactors, Ind. Eng. Chem. Res., v42, pp26.

Parra S., Stanca S.E., Guasaquillo I. and Thampi K.R., (2004), Photocatalytic Degradation of Atrazine using Suspended and Supported TiO₂, Applied Catalysis B: Environmental, v51, pp107.

Peill N.J. and Hoffmann M.R., (1995), Development and Optimization of a TiO₂-Coated Fiber Optic Cable Reactor: Photocatalytic Degradation of 4-Chlorophenol, Environmental Science and Technology, v29, pp2974.

Perry R.H. and Green D.W., (1997), Perry's Chemical Engineers' Handbook, 7th Edition, McGraw-Hill Companies Inc., India.

Porter M.C., (1992), Ultrafiltration in Handbook of Industrial Membrane Technology, Edited by Porter M.C., Noyes Publications, California.

Poulios I., Avarans A.M., Refliti E. and Zouboulis A., (2000), Photocatalytic Oxidation of Auramine O in the Presence of Semiconducting Oxides, Journal Chemical Technology and Biotechnology, v75, pp205.

Pozzo R.L., Giombi J.L., Baltanas M.A. and Cassano A.E., (2002), Radiation Extinction of Slurried TiO_2 as a Function of Mechanical Action and Ionic Composition of the Suspending Media: A Key Factor in the Photocatalytic Efficiency, *Applied Catalysis B: Environmental*, v38, pp61.

Puma G.L. and Yue P.L., (2001), A Novel Fountain Photocatalytic Reactor: Model Development and Experimental Validation, *Chemical Engineering Science*, v56, pp2733.

Puma G.L. and Yue P.L., (2003), Modeling and Design of Thin-Film Slurry Photocatalytic Reactors for Water Purification, *Chemical Engineering Science*, v58, pp2269.

Ray A.K., (1998), A New Photocatalytic Reactor for Destruction of Toxic Water Pollutants by Advanced Oxidation Process, *Catalysis Today*, v44, pp357.

Ray A.K., (1999), Design, Modelling and Experimentation of a New Large-Scale Photocatalytic Reactor for Water Treatment, *Chemical Engineering Science*, v54, pp3113.

Reutergadh L.B. and Iangphasuk M., (1997), Photocatalytic Decolourization of Reactive Azo Dye: A Comparison between TiO_2 and US Photocatalysis, *Chemosphere*, v35, pp585.

Rideh L., Wehrer A., Ronze D. and Zoulalian A., (1999), Modeling of the Kinetic of 2-Chlorophenol Catalytic Photooxidation, *Catalysis Today*, v48, pp357.

Rivas L., Bellobono I.B. and Ascari F., (1998), Photomineralization of n-Alkanoic Acid in Aqueous Solution by Photocatalytic Membranes. Influence of Radiation Power, *Chemosphere*, v37, pp1033.

Rosenberg I., Brock J.R. and Heller A., (1992), Collection Optics of TiO₂ Photocatalyst on Hollow Glass Microbeads Floating on Oil Slicks, *Journal of Physical Chemistry*, v96, pp3423.

Sabate J. and Anderson M.A, (1992), Comparison of TiO₂ Powder Suspensions and TiO₂ Ceramic Membranes Supported on Glass as Photocatalytic Systems in the Reduction of Chromium (VI), *Journal of Molecular Catalysis*, v71 (1), pp57.

Sakthivel S., Shankar M.V., Palanichamy M., Arabindoo B., Bahnemann D.W. and Murugesan V., (2004), Enhancement of Photocatalytic Activity by Metal Deposition: Characterisation and Photonic Efficiency of Pt, Au and Pd Deposited on TiO₂ Catalyst, *Water Research*, v38 (13), pp3001.

Salaices M. Serrano B. and de Lasa H.I., (2002), Experimental Evaluation of Photon Absorption in an Aqueous TiO₂ Slurry Reactor, *Chemical Engineering Journal*, v90, pp219.

Sauer T., Neto G.C., Jose H.J. and Moreira R.F.P.M., (2002), Kinetics of Photocatalytic Degradation of Reactive Dyes in a TiO₂ Slurry Reactor, *Journal of Photochemistry and Photobiology A: Chemistry*, v149, pp147.

Schiavello M., Augugliaro V. and Palmisano L., (1991), An Experimental Method for the Determination of the Photon Flow Reflected and Absorbed by Aqueous Dispersions Containing Polycrystalline Solids in Heterogeneous Photocatalysis, *Journal of Catalysis*, v127 (1), pp332.

Sekulic J., Magraso A., Elshof J.E., Blank D.H.A, (2004), Influence of ZrO₂ Addition on Microstructure and Liquid Permeability of Mesoporous TiO₂ Membranes, *Microporous and Mesoporous Materials*, v72, pp49.

Sellami M.H., Hassen A. and Sifaoui, (2003), Modelling of UV Radiation Field inside a Photoreactor Designed for Wastewater Disinfection Experimental Validation, *Journal of Quantitative Spectroscopy & Radiative Transfer*, v78, pp269.

Serrano B. and Lasa H.D., (1999), Photocatalytic Degradation of Water Organic Pollutants: Pollutant Reactivity and Kinetic Modeling, *Chemical Engineering Science*, v54, pp3063

Serpone N., Sauve G., Koch R., Tahiri H., Pichat P., Piccinini P., Pelizzetti E., and Hidaka H., (1996), Standardization Protocol of Process Efficiencies and Activation Parameters in Heterogeneous Photocatalysis: Relative Photonic Efficiencies, *Journal of Photochemistry and Photobiology A: Chemistry*, v94 (2-3), pp191.

Serpone N., Terzian R., Lawless D., Kennepohl P. and Sauve G., (1993), On the Usage of Turnover Numbers and Quantum Yields in Heterogeneous Photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, v73 (1), pp11.

Singh N., Husson S.M., Zdyrko B. and Luzinov I., (2005), Surface Modification of Microporous PVDF Membranes by ATRP, *Journal of Membrane Science*, v262, pp81.

Socrates G., *Infrared Characteristic Group Frequencies: Tables and Charts*, John Wiley and Sons, England, 1994, Chapter 16.

Sofia A., Ng W.J. and Ong S.L., (2004), Engineering Design Approaches for Minimum Fouling in Submerged MBR, *Desalination*, v160, pp67.

Solvay Membranes: The filtration Spectrum, (2003), <http://www.solvaymembranes.com/infocus/whataremembranes/filtrationspectrum/0,6644,506-2-0,00.htm>, Accessed on 4th Dec 2003.

Soparajee K., Qasim S.A., Basak S. and Rajeshwar K., (1999a), An Integrated Flow Reactor-Membrane Filtration System for Heterogeneous Photocatalysis. Part II: Experiments on the Ultrafiltration Unit and Combined Operation, *Journal of Applied Electrochemistry*, v29, pp1111.

Soparajee K., Qasim S.A., Basak S. and Rajeshwar K., (1999b), An Integrated Flow Reactor-Membrane Filtration System for Heterogeneous Photocatalysis. Part I: Experiments and Modeling of a Batch-Recirculated Photoreactor, *Journal of Applied Electrochemistry*, v29, pp533.

Stackelberg P.E., Furlong E.T., Meyer M.T., Zaugg S.D., Henderson A.K. and Reissman D.B., (2004), Persistence of Pharmaceutical Compounds and Other Organic Wastewater Contaminants in a Conventional Drinking-Water-Treatment Plant, *Science of the Total Environment*, v329, pp 99.

Stafford U., (1994), Photocatalytic Oxidation of a Model Halogenated Aromatic Compound: A Mechanistic Study, Department of Chemical Engineering, University of Notre Dame.

Strathmann H., (1992), Synthetic Membranes and their Preparation, In *Handbook of Industrial Membrane Technology*, Edited by Porter M.C., Noyes Publications, California.

Sun D.D., Tay J.H. and Tan K.M., (2003), Photocatalytic Degradation of E. Coliform in Water, *Water Research*, v37 (14), pp3452.

Sunada K., Watanabe T. and Hashimoto K., (2003), Studies on Photokilling of Bacteria on TiO₂ Thin Film, *Journal of Photochemistry and Photobiology A: Chemistry*, v156, pp227.

Szymanski W.W., (1996), Optical Behaviour of Fine Bubbles – Possibility of Real Time Size Characterization, *Journal of Aerosol Science*, v1, pp537.

Tabatabaie-Raissi A., Muradov N.Z. and Fairey P.W., Method of Photocatalytic Destruction of Harmful Volatile Compounds at Emitting Surfaces, United States Patent No: US 5604339, Issued Feb 18 1997.

Tang C. and Chen V., (2004), The Photocatalytic Degradation of Reactive Black 5 using TiO_2 / UV in an Annular Photoreactor, *Water Research*, v38, pp2775.

Teejateerawaej S., Nishino J. and Nosaka Y., (2006), Design and Evaluation of Photocatalytic Micro-channel Reactors using TiO_2 -coated Porous Ceramics, *Journal of Photochemistry and Photobiology A: Chemistry*, v179, pp263.

Theurich J., Lindner M. and Bahnemann D.W., (1996), Photocatalytic Degradation of 4-Chlorophenol in Aerated Aqueous Titanium Dioxide Suspensions: A Kinetic and Mechanistic Study, *Langmuir*, v12, pp6368

Torikai A. and Hasegawa H., (1998), Wavelength Effect on the Accelerated Photodegradation of Polymethylmethacrylate, *Polymer Degradation and Stability*, v61, pp361.

Turchi C.S. and Ollis D.F., (1990), Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack, *Journal of Catalysis*, v122, pp178.

UNEP (The U.S. Global Change research Information Office), (1998), Plastic Photodegradation, <http://gcric.org/UNEP1998/UNEP98p61.html>, Accessed on 14th Jan 2004.

Valente J.P.S., Padilha P.M. and Florentino A.O., (2006), Studies on the Adsorption and Kinetics of Photodegradation of a Model Compound for Heterogeneous Photocatalysis onto TiO_2 Chemosphere, v64 (7), pp 1128.

Vilker V.L., Colton C.K. and Smith K.A., (1981), Concentration Polarization in Protein Ultrafiltration: Part II. Theoretical and Experimental Study of Albumin Ultrafiltered in Unstirred Cell, *Journal of American Institute of Chemical Engineering*, v27 (4), pp637.

Villacres R., Ikeda S., Torimoto T. and Ohtani B., (2003), Development of a Novel Photocatalytic Reaction System for Oxidative Decomposition of Volatile Organic Compounds in Water with Enhanced Aeration, *Journal of Photochemistry and Photobiology A: Chemistry*, v160, pp121.

Villasenor J. and Mansilla H.D., (1996), Effect of Temperature on Kraft Black Liquor Degradation by ZnO-Photoassisted Catalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, v93, pp205.

Vulliet E., Chovelon J-M, Guillard C. and Hermann J-M, (2003), Factors Influencing the Photocatalytic Degradation of Sulfonylurea Herbicides by TiO₂ Aqueous Suspension, *Journal of Photochemistry and Photobiology A: Chemistry*, v159, pp71.

Wang K.H., Hsieh Y.H., Wu C.H. and Chang C.Y., (2000), The pH and Anions Effects on the Heterogeneous Photocatalytic Degradation of O-Methylbenzoic Acid in TiO₂ Aqueous Suspension, *Chemosphere*, v40, pp389.

Wang W. and Ku T., (2003), Photocatalytic Degradation of Gaseous Benzene in Air Streams by using an Optical Fiber Photoreactor, *Journal of Photochemistry & Photobiology A: Chemistry*, v159 (1), pp47.

Watanabe N., Horikoshi S., Kawabe H., Sugie Y., Zhao J. and Hidaka H., (2003), Photodegradation Mechanism for Bisphenol A at the TiO₂ / H₂O Interfaces, *Chemosphere*, v52, pp851.

Watts R.J., Kong S., Orr M.P, Miller G.C. and Henry B.E., (1995), Photocatalytic Inactivation of Coliform Bacteria and Viruses in Secondary Wastewater Effluent, *Water Research*, v29, pp95.

Wong C.C. and Chu W., (2003), The Direct Photolysis and Photocatalytic Degradation of Alachlor at Different TiO₂ and UV Sources, *Chemosphere*, v50, pp981.

Xi W. and Geissen S.U., (2001), Separation of Titanium Dioxide from Photocatalytically Treated Water by Cross-Flow Microfiltration, *Water Research*, v35, pp1256.

Xu L., Li W., Lu S., Wang Z., Zhu Q. and Ling Y., (2002), Treating Dyeing Waste Water by Ceramic Membrane in Crossflow Microfiltration, *Desalination*, v149 (1-3), pp199.

Xu Y. and Langford C.H., (2000), Variation of Langmuir Adsorption Constant Determined for TiO₂-Photocatalyzed Degradation of Acetophenone under Different Light Intensity, *Journal of Photochemistry and Photobiology A: Chemistry*, v133, pp67.

Yamazaki S., Matsunaga S. and Hori K., (2001b), Photocatalytic Degradation of Trichloroethylene in Water using TiO₂ Pellets, *Water Research*, v35 (4), pp1022.

Yamazaki S., Tsukamoto H., Araki K., Tanimura T., Tejedor-Tejedor I. and Anderson M.A., (2001a), Photocatalytic Degradation of Gaseous Tetrachloroethylene on Porous TiO₂ Pellets, *Applied Catalysis B: Environmental*, v33, pp109.

Yatmaz H.C., Wallis C. and Howarth C.R., (2001), The Spinning Disc Reactor – Studies on a Novel TiO₂ Photocatalytic Reactor, *Chemosphere*, v42, pp397

Yeo A.P.S, Law A.W.K. and Fane A.G., (2006), Factors Affecting the Performance of a Submerged Hollow Fiber Bundle, *Journal of Membrane Science*,. v280 (1-2), pp 969.

Yoon Y., Westerhoff P., Snyder S.A., Wert E. C. and Yoon J., (2005), Removal of Endocrine Disrupting Compounds and Pharmaceuticals by Nanofiltration and Ultrafiltration Membranes, *Proceedings of the 5th International Conference on Wastewater Reclamation and Reuse for Sustainability*, Jeju, Korea, 7-11 Nov., 2005

Zeman L.J. and Zydney A.L., (1996), *Microfiltration and Ultrafiltration: Principles and Application*, Marcel Dekker Inc., New York.

Zhang F., Zhao J., Shen T., Hidaka H., Pelizzetti E. and Serpone N., (1998), Photoassisted Degradation of Dye Pollutants II. Adsorption and Degradation Kinetics of Eosin in TiO₂ Dispersions under Visible Light Irradiation, *Applied Catalysis B: Environmental*, v15, pp147.

Zhang H., Quan X., Chen S., Zhao H. and Zhao Y., (2006), Fabrication of Photocatalytic Membrane and Evaluation its Efficiency in Removal of Organic Pollutants from Water, *Separation and Purification Technology*, v50 (2), pp 147.

Zhang Z., Hu X. and Luo Z., (1996), Wavelength Sensitivity of Photooxidation of Polypropylene, *Polymer Degradation and Stability*, v51, pp93.

Zhao Y., Zhong J., Li H., Xu N. and Shi J., (2002), Fouling and Regeneration of Ceramic Microfiltration Membranes in Processing Acid Wastewater Containing Fine TiO₂ Particles, *Journal of Membrane Science*, v208, pp331.

Zhou S. and Ray A.K., (2003), Kinetic Studies for Photocatalytic Degradation of Eosin B on a Thin Film of Titanium Dioxide, *Industrial Engineering Chemistry Research*, v42, pp6020.

Zuehlke S., Duennnbier S., Lesjean B., Gnirss R. and Buisson H., (2006), Long-Term Comparison of Trace Organics Removal Performances Between Conventional and Membrane Activated Sludge Processes, Water Environment Research, v78, pp 2480.

APPENDIX A

Oxidative Species Traveling Time Calculations

$$\text{Area of membrane} = 4.86 \times 10^{-3} \text{ m}^2$$

$$\text{Dead-end imposed flux} = \frac{30L}{\text{m}^2 \text{ hr}}$$

Volumetric flow rate of retentate through the TiO₂ cake layer

$$= \text{Imposed filtration flux} \times \text{area of membrane}$$

$$= \frac{0.03 \text{ m}^3}{\text{m}^2 \text{ hr}} \times 4.86 \times 10^{-3} \text{ m}^2$$

$$= 1.458 \times 10^{-4} \text{ m}^3 / \text{hr}$$

Velocity of retentate through the TiO₂ cake layer

$$= \frac{\text{volumetric flow rate through the membrane}}{\text{area of membrane}}$$

$$= \frac{1.458 \times 10^{-4} \text{ m}^3}{\text{hr}} \div 4.86 \times 10^{-3} \text{ m}^2$$

$$= 0.03 \text{ m/hr}$$

Thickness of TiO₂ cake layer = 5 μm

Thickness of TiO₂ cake layer, taking into account of the tortuous path through the layer ≈ 3 times the original cake thickness ≈ 15 μm

Therefore,

Time taken for the retentate to pass through the TiO₂ cake layer to reach the surface of membrane

$$\begin{aligned} &= \frac{\text{Thickness of TiO}_2 \text{ cake layer}}{\text{Velocity of retentate}} \\ &= \frac{15 \mu\text{m}}{0.03 \times 10^6 \mu\text{m} / \text{hr}} = 1.8 \text{ sec} \end{aligned}$$

APPENDIX B

Derivation of Equation 6.5 to Equation 6.6

$$\frac{d[C_A]}{dt} = \frac{1}{\tau} (C_{Af} - C_A) - k_{app} \quad \text{(Equation 6.5)}$$

$$\begin{aligned} & \int_{C_{Ao}}^{C_{At}} d[C_A] \\ &= \int_0^t \left[\frac{1}{\tau} (C_{Af} - C_A) - k_{app} C_A \right] dt \\ &= \int_0^t \left[\frac{1}{\tau} C_{Af} - \left(\frac{1}{\tau} + k_{app} \right) C_A \right] dt \end{aligned}$$

$$\int_{C_{Ao}}^{C_{At}} \frac{1}{\left(\frac{1}{\tau} + k_{app} \right) C_A} d[C_A] = \int_0^t dt$$

$$\text{Let } A = \frac{1}{\tau} C_{Af}, B = \frac{1}{\tau} + k_{app}, X = C_A$$

$$\int_{C_{Ao}}^{C_{At}} \frac{1}{A - BX} dx = t$$

$$\int_{C_{Xo}}^{C_{Xt}} \frac{1}{A - BX} dX = \left[-\frac{\ln(A - BX)}{B} \right]_{X_o}^{X_t} = t$$

$$\frac{\ln(A - BX_o)}{B} - \frac{\ln(A - X)}{B} = t$$

$$\ln(A - BX_o) - \ln(A - BX) = Bt$$

$$\ln(A - BX_o) - Bt = \ln(A - BX)$$

$$e^{\ln(A-BX_0)-Bt} = e^{\ln(A-BX)}$$

$$\frac{A-BX_0}{e^{Bt}} = (A-BX)$$

$$BX = A - \frac{A-BX_o}{e^{Bt}}$$

$$\begin{aligned} X &= \frac{1}{B} \left[A - \frac{A-BX_o}{e^{Bt}} \right] \\ &= \frac{1}{B} \left[A - \frac{A}{e^{Bt}} - \frac{B}{e^{Bt}} X_o \right] \\ &= \frac{X_o}{e^{Bt}} + \frac{A}{B} \left[1 - \frac{1}{e^{Bt}} \right] \end{aligned}$$

$$\begin{aligned} C_A(t) &= C_{Ao} e^{-(1/\tau + k_{app})t} + \frac{1/\tau C_{Af}}{1/\tau + k_{app}} \left[1 - e^{-(1/\tau + k_{app})t} \right] \end{aligned}$$

$$C_A(t) = C_{A,o} e^{-\left(\frac{1}{\tau} + k_{app}\right)t} + \frac{C_{A,f}}{1 + k_{app}\tau} \left[1 - e^{-\left(\frac{1}{\tau} + k_{app}\right)t} \right] \quad \text{(Equation 6.6)}$$

APPENDIX C

Simulation report from Sigma-Plot

$$C_{AO} = 10 \text{ ppm} : \beta(t) = 0.273 + 2.849 \exp^{-0.129 C_A(t)} \quad (6.13)$$

Nonlinear Regression

[Variables]

x = col(1)

y = col(2)

reciprocal_y = 1/abs(y)

reciprocal_ysquare = 1/y^2

'Automatic Initial Parameter Estimates

yhat(q) = q[size(q)]

[Parameters]

y0 = yhat(y) "Auto {{previous: 0.27318}}

a = max(y) - yhat(y) "Auto {{previous: 2.84872}}

b = if(x50(x, y - yhat(y)) = 0, 1, -ln(.5)/x50(x, y - yhat(y))) "Auto {{previous: 0.128897}}

[Equation]

f = y0 + a * exp(-b * x)

fit f to y

"fit f to y with weight reciprocal_y

"fit f to y with weight reciprocal_ysquare

[Constraints]

b > 0

[Options]

tolerance = 0.000100

stepsize = 100

iterations = 100

R = 0.99608443 Rsqr = 0.99218419 Adj Rsqr = 0.98436838

Standard Error of Estimate = 0.0792

	Coefficient	Std. Error	t	P
y0	0.2732	0.0657	4.1582	0.0533
a	2.8487	0.3455	8.2462	0.0144
b	0.1289	0.0227	5.6885	0.0295

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	1.5912	0.7956	126.9458	0.0078
Residual	2	0.0125	0.0063		
Total	4	1.6037	0.4009		

PRESS = 0.2818

Durbin-Watson Statistic = 3.3136

Normality Test: K-S Statistic = 0.2030 Significance Level = 0.9710

Constant Variance Test: Passed (P = 0.0500)

Power of performed test with alpha = 0.0500: 0.9928

Regression Diagnostics:

Row	Predicted	Residual	Std. Res.	Stud. Res.	Stud. Del. Res.
1	1.7686	0.0194	0.2449	1.2128	1.6673
2	1.0582	-0.0582	-0.7346	-1.2743	-2.0778
3	0.4895	0.0864	1.0918	1.4142	133.7405
4	0.3328	-0.0330	-0.4174	-0.5165	-0.3924
5	0.2777	-0.0146	-0.1846	-0.3004	-0.2174

Influence Diagnostics:

Row	Cook'sDist	Leverage	DFFITS
1	11.5325	0.9592	8.0863
2	1.0873	0.6676	-2.9448
3	0.4518	0.4040	110.1052
4	0.0473	0.3470	-0.2860
5	0.0495	0.6222	-0.2789

95% Confidence:

Row	Predicted	Regr. 5%	Regr. 95%	Pop. 5%	Pop. 95%
1	1.7686	1.4350	2.1022	1.2918	2.2453
2	1.0582	0.7798	1.3365	0.6183	1.4980
3	0.4895	0.2730	0.7060	0.0859	0.8931
4	0.3328	0.1321	0.5334	-0.0625	0.7281
5	0.2777	0.0090	0.5464	-0.1561	0.7115

Figure C-1 $\beta (t)$ versus $C_A (t)$ for 20ppm (Equation 6.13)

$$C_{AO} = 20 \text{ ppm} : \beta(t) = 0.470 + 4.938 \exp^{-0.129 C_A(t)} \quad (6.14)$$

Nonlinear Regression

```
[Variables]
x = col(1)
y = col(2)
reciprocal_y=1/abs(y)
reciprocal_ysquare=1/y^2
'Automatic Initial Parameter Estimates
yhat(q)=q[size(q)]
[Parameters]
y0 = yhat(y) "Auto {{previous: 0.469544}}
a = max(y)-yhat(y) "Auto {{previous: 4.93753}}
b = if(x50(x,y-yhat(y))=0, 1, -ln(.5)/x50(x,y-yhat(y))) "Auto {{previous: 0.12823}}
[Equation]
f=y0+a*exp(-b*x)
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
[Constraints]
b>0
[Options]
tolerance=0.000100
stepsize=100
iterations=100
```

R = 0.99605700 Rsqr = 0.99212955 Adj Rsqr = 0.98425909

Standard Error of Estimate = 0.1381

	Coefficient	Std. Error	t	P
y0	0.4695	0.1150	4.0833	0.0551
a	4.9375	0.5980	8.2565	0.0144
b	0.1282	0.0226	5.6661	0.0298

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	4.8094	2.4047	126.0575	0.0079
Residual	2	0.0382	0.0191		
Total	4	4.8476	1.2119		

PRESS = 0.8623

Durbin-Watson Statistic = 3.2970

Normality Test: K-S Statistic = 0.2115 Significance Level = 0.9581

Constant Variance Test: Passed (P = 0.0500)

Power of performed test with $\alpha = 0.0500$: 0.9927

Regression Diagnostics:

Row	Predicted	Residual	Std. Res.	Stud. Res.	Stud. Del. Res.
1	3.0701	0.0345	0.2496	1.2259	1.7388
2	1.8392	-0.1028	-0.7446	-1.2857	-2.1829
3	0.8495	0.1505	1.0897	1.4136	33.4983
4	0.5749	-0.0545	-0.3945	-0.4880	-0.3676
5	0.4777	-0.0277	-0.2002	-0.3268	-0.2375

Influence Diagnostics:

Row	Cook'sDist	Leverage	DFFITS
1	11.5860	0.9586	8.3619
2	1.0918	0.6646	-3.0727
3	0.4547	0.4057	27.6771
4	0.0421	0.3465	-0.2677
5	0.0592	0.6246	-0.3064

95% Confidence:

Row	Predicted	Regr. 5%	Regr. 95%	Pop. 5%	Pop. 95%
1	3.0701	2.4882	3.6519	2.2384	3.9017
2	1.8392	1.3547	2.3237	1.0725	2.6059
3	0.8495	0.4710	1.2280	0.1449	1.5541
4	0.5749	0.2251	0.9248	-0.1147	1.2645
5	0.4777	0.0080	0.9473	-0.2798	1.2351

Figure C-2 $\beta(t)$ versus $C_A(t)$ for 20ppm (Equation 6.14)

$$C_{AO} = 30 \text{ ppm} : \beta(t) = 0.911 + 9.504 \exp^{-0.129 C_A(t)} \quad (6.15)$$

Nonlinear Regression

```
[Variables]
x = col(1)
y = col(2)
reciprocal_y=1/abs(y)
reciprocal_ysquare=1/y^2
'Automatic Initial Parameter Estimates
yhat(q)=q[size(q)]
[Parameters]
y0 = yhat(y) "Auto {{previous: 0.911394}}
a = max(y)-yhat(y) "Auto {{previous: 9.50404}}
b = if(x50(x,y-yhat(y))=0, 1, -ln(.5)/x50(x,y-yhat(y))) "Auto {{previous: 0.128897}}
[Equation]
f=y0+a*exp(-b*x)
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
[Constraints]
b>0
[Options]
tolerance=0.000100
stepsize=100
iterations=100
```

R = 0.99608443 Rsqr = 0.99218419 Adj Rsqr = 0.98436838

Standard Error of Estimate = 0.2641

	Coefficient	Std. Error	t	P
y0	0.9114	0.2192	4.1582	0.0533
a	9.5040	1.1525	8.2462	0.0144
b	0.1289	0.0227	5.6885	0.0295

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	17.7109	8.8555	126.9458	0.0078
Residual	2	0.1395	0.0698		
Total	4	17.8504	4.4626		

PRESS = 3.1361

Durbin-Watson Statistic = 3.3136

Normality Test: K-S Statistic = 0.2030 Significance Level = 0.9710

Constant Variance Test: Passed (P = 0.0500)

Power of performed test with $\alpha = 0.0500$: 0.9928

Regression Diagnostics:

Row	Predicted	Residual	Std. Res.	Stud. Res.	Stud. Del. Res.
1	5.9004	0.0647	0.2449	1.2128	1.6673
2	3.5303	-0.1940	-0.7346	-1.2743	-2.0778
3	1.6330	0.2884	1.0918	1.4142	133.7405
4	1.1102	-0.1102	-0.4174	-0.5165	-0.3924
5	0.9265	-0.0488	-0.1846	-0.3004	-0.2174

Influence Diagnostics:

Row	Cook'sDist	Leverage	DFFITS
1	11.5325	0.9592	8.0863
2	1.0873	0.6676	-2.9448
3	0.4518	0.4040	110.1052
4	0.0473	0.3470	-0.2860
5	0.0495	0.6222	-0.2789

95% Confidence:

Row	Predicted	Regr. 5%	Regr. 95%	Pop. 5%	Pop. 95%
1	5.9004	4.7874	7.0134	4.3097	7.4910
2	3.5303	2.6017	4.4588	2.0628	4.9978
3	1.6330	0.9108	2.3553	0.2865	2.9796
4	1.1102	0.4409	1.7796	-0.2087	2.4291
5	0.9265	0.0301	1.8229	-0.5209	2.373

Figure C-3 $\beta(t)$ versus $C_A(t)$ for 20ppm (Equation 6.15)

$$C_{AO} = 50 \text{ ppm} : \beta(t) = 1.038 + 10.828 \exp^{-0.129 C_A(t)} \quad (6.16)$$

Nonlinear Regression

```
[Variables]
x = col(1)
y = col(2)
reciprocal_y=1/abs(y)
reciprocal_ysquare=1/y^2
'Automatic Initial Parameter Estimates
yhat(q)=q[size(q)]
[Parameters]
y0 = yhat(y) "Auto {{previous: 1.03835}}
a = max(y)-yhat(y) "Auto {{previous: 10.828}}
b = if(x50(x,y-yhat(y))=0, 1, -ln(.5)/x50(x,y-yhat(y))) "Auto {{previous: 0.128897}}
[Equation]
f=y0+a*exp(-b*x)
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
[Constraints]
b>0
[Options]
tolerance=0.000100
stepsize=100
iterations=100
```

R = 0.99608443 Rsqr = 0.99218419 Adj Rsqr = 0.98436838

Standard Error of Estimate = 0.3009

	Coefficient	Std. Error	t	P
y0	1.0384	0.2497	4.1582	0.0533
a	10.8280	1.3131	8.2462	0.0144
b	0.1289	0.0227	5.6885	0.0295

Analysis of Variance:

	DF	SS	MS	F	P
Regression	2	22.9890	11.4945	126.9458	0.0078
Residual	2	0.1811	0.0905		
Total	4	23.1701	5.7925		

PRESS = 4.0707

Durbin-Watson Statistic = 3.3136

Normality Test: K-S Statistic = 0.2030 Significance Level = 0.9710

Constant Variance Test: Passed (P = 0.0500)

Power of performed test with $\alpha = 0.0500$: 0.9928

Regression Diagnostics:

Row	Predicted	Residual	Std. Res.	Stud. Res.	Stud. Del. Res.
1	6.7223	0.0737	0.2449	1.2128	1.6673
2	4.0221	-0.2211	-0.7346	-1.2743	-2.0778
3	1.8605	0.3285	1.0918	1.4142	133.7405
4	1.2649	-0.1256	-0.4174	-0.5165	-0.3924
5	1.0556	-0.0556	-0.1846	-0.3004	-0.2174

Influence Diagnostics:

Row	Cook'sDist	Leverage	DFFITS
1	11.5325	0.9592	8.0863
2	1.0873	0.6676	-2.9448
3	0.4518	0.4040	110.1052
4	0.0473	0.3470	-0.2860
5	0.0495	0.6222	-0.2789

95% Confidence:

Row	Predicted	Regr. 5%	Regr. 95%	Pop. 5%	Pop. 95%
1	6.7223	5.4543	7.9904	4.9101	8.5346
2	4.0221	2.9642	5.0800	2.3501	5.6940
3	1.8605	1.0376	2.6834	0.3264	3.3946
4	1.2649	0.5023	2.0275	-0.2377	2.7675
5	1.0556	0.0343	2.0768	-0.5935	2.7046

Figure C-4 $\beta(t)$ versus $C_A(t)$ for 20ppm (Equation 6.16).

APPENDIX D

Equation 6.19 Simulation (Spreadsheet)

$$C_A(t) = C_{A,o} e^{-\left(\frac{1}{\tau\beta(t)} + k_{app}\right)t} + \frac{C_{A,f}}{1 + k_{app}\tau\beta(t)} \left[1 - e^{-\left(\frac{1}{\tau\beta(t)} + k_{app}\right)t} \right] \quad (6.19)$$

$$\text{Let } B = \left(\frac{1}{\tau\beta(t)} + k_{app} \right) t$$

Therefore,

$$C_A(t) = C_{A,o} e^{-B} + \frac{C_{A,f}}{1 + k_{app}\tau\beta(t)} \left[1 - e^{-B} \right]$$

An example of the spreadsheet calculation for Figure 6.7 (modified model - original correction factor) data.

	A	B	C	D	E	F
1	C_{Ao}	30	ppm			
2	Residence Time	120	min			
3	$C_{A,f}$	30	ppm			
4	k_{app}	0.0263	min^{-1}			
5						
6						
7						
8						
9						
10	1	2	3	4	5	6
11	Time (min)	B term	Exp (- B)	C_{Ao}	$\beta(t)$	C(t) ppm
12	0	0.0000	1.0000	30.0000	1.1102	30.0000
13	2	0.0676	0.9346	30.0000	1.1102	28.4742
14	4	0.1341	0.8745	28.4742	1.1535	27.0465
15	6	0.1994	0.8192	27.0465	1.2024	25.7081
16	8	0.2634	0.7684	25.7081	1.2571	24.4509
17	10	0.3262	0.7216	24.4509	1.3180	23.2677
18	12	0.3878	0.6785	23.2677	1.3849	22.1519
19	14	0.4482	0.6388	22.1519	1.4582	21.0976
20	16	0.5075	0.6020	21.0976	1.5378	20.0998
21	18	0.5658	0.5679	20.0998	1.6238	19.1540
22	20	0.6231	0.5363	19.1540	1.7161	18.2564
23	22	0.6796	0.5068	18.2564	1.8149	17.4035
24	24	0.7354	0.4793	17.4035	1.9198	16.5926
25	26	0.7905	0.4536	16.5926	2.0310	15.8209
26	28	0.8450	0.4295	15.8209	2.1480	15.0863
27	30	0.8991	0.4069	15.0863	2.2709	14.3867
28	32	0.9528	0.3857	14.3867	2.3991	13.7204
29	34	1.0061	0.3657	13.7204	2.5326	13.0857
30	36	1.0591	0.3468	13.0857	2.6708	12.4812
31	38	1.1120	0.3289	12.4812	2.8134	11.9053
32	40	1.1646	0.3120	11.9053	2.9599	11.3570
33	42	1.2171	0.2961	11.3570	3.1099	10.8349
34	44	1.2696	0.2810	10.8349	3.2630	10.3379
35	46	1.3219	0.2666	10.3379	3.4186	9.8648
36	48	1.3743	0.2530	9.8648	3.5762	9.4148
37	50	1.4265	0.2401	9.4148	3.7354	8.9866
38	52	1.4788	0.2279	8.9866	3.8956	8.5794
39	54	1.5311	0.2163	8.5794	4.0565	8.1922
40	56	1.5835	0.2053	8.1922	4.2174	7.8240
41	58	1.6358	0.1948	7.8240	4.3781	7.4742
42	60	1.6882	0.1849	7.4742	4.5380	7.1417
43	62	1.7406	0.1754	7.1417	4.6968	6.8258
44	64	1.7931	0.1664	6.8258	4.8541	6.5257
45	66	1.8456	0.1579	6.5257	5.0096	6.2407
46	68	1.8982	0.1498	6.2407	5.1629	5.9701
47	70	1.9508	0.1422	5.9701	5.3139	5.7131
48	72	2.0034	0.1349	5.7131	5.4622	5.4691
49	74	2.0562	0.1279	5.4691	5.6076	5.2375
50	76	2.1089	0.1214	5.2375	5.7499	5.0177
51	78	2.1618	0.1151	5.0177	5.8889	4.8090
52	80	2.2147	0.1092	4.8090	6.0246	4.6110
53	82	2.2676	0.1036	4.6110	6.1568	4.4231
54	84	2.3206	0.0982	4.4231	6.2854	4.2449
55	86	2.3736	0.0931	4.2449	6.4103	4.0758
56	88	2.4267	0.0883	4.0758	6.5315	3.9153
57	90	2.4798	0.0838	3.9153	6.6489	3.7631
58	92	2.5330	0.0794	3.7631	6.7626	3.6188
59	94	2.5862	0.0753	3.6188	6.8725	3.4818

$$C_A(t) = (C_{Ao} * C12) + ((B3 / (1 + (E12 * B4 * B2))) * (1 - C12))$$

$$D13 = F12$$

$$\beta(t) = -0.9114 + 9.504 * \text{EXP}(0.1289 * D12)$$

	A	B	C	D	E	F
60	96	2.6394	0.0714	3.4818	6.9786	3.3520
61	98	2.6927	0.0677	3.3520	7.0811	3.2288
62	100	2.7461	0.0642	3.2288	7.1798	3.1120
63	102	2.7994	0.0608	3.1120	7.2749	3.0013
64	104	2.8529	0.0577	3.0013	7.3664	2.8962
65	106	2.9063	0.0547	2.8962	7.4544	2.7966
66	108	2.9598	0.0518	2.7966	7.5389	2.7022
67	110	3.0133	0.0491	2.7022	7.6200	2.6127
68	112	3.0668	0.0466	2.6127	7.6979	2.5278
69	114	3.1204	0.0441	2.5278	7.7726	2.4474
70	116	3.1740	0.0418	2.4474	7.8441	2.3711
71	118	3.2277	0.0396	2.3711	7.9126	2.2988
72	120	3.2813	0.0376	2.2988	7.9782	2.2302
73	122	3.3350	0.0356	2.2302	8.0409	2.1652
74	124	3.3888	0.0338	2.1652	8.1008	2.1037
75	126	3.4425	0.0320	2.1037	8.1581	2.0453
76	128	3.4963	0.0303	2.0453	8.2129	1.9899
77	130	3.5501	0.0287	1.9899	8.2651	1.9375
78	132	3.6039	0.0272	1.9375	8.3150	1.8878
79	134	3.6577	0.0258	1.8878	8.3626	1.8407
80	136	3.7116	0.0244	1.8407	8.4080	1.7960
81	138	3.7655	0.0232	1.7960	8.4513	1.7537
82	140	3.8194	0.0219	1.7537	8.4925	1.7136
83	142	3.8733	0.0208	1.7136	8.5318	1.6756
84	144	3.9272	0.0197	1.6756	8.5692	1.6396
85	146	3.9812	0.0187	1.6396	8.6048	1.6055
86	148	4.0352	0.0177	1.6055	8.6388	1.5731
87	150	4.0892	0.0168	1.5731	8.6710	1.5425
88	152	4.1432	0.0159	1.5425	8.7017	1.5135
89	154	4.1972	0.0150	1.5135	8.7310	1.4859
90	156	4.2512	0.0142	1.4859	8.7587	1.4599
91	158	4.3053	0.0135	1.4599	8.7852	1.4352
92	160	4.3593	0.0128	1.4352	8.8103	1.4118
93	162	4.4134	0.0121	1.4118	8.8341	1.3896
94	164	4.4675	0.0115	1.3896	8.8568	1.3686
95	166	4.5216	0.0109	1.3686	8.8784	1.3487
96	168	4.5757	0.0103	1.3487	8.8988	1.3298
97	170	4.6298	0.0098	1.3298	8.9183	1.3119
98	172	4.6840	0.0092	1.3119	8.9367	1.2950
99	174	4.7381	0.0088	1.2950	8.9543	1.2790
100	176	4.7923	0.0083	1.2790	8.9709	1.2638
101	178	4.8465	0.0079	1.2638	8.9867	1.2494
102	180	4.9006	0.0074	1.2494	9.0017	1.2357
103	182	4.9548	0.0070	1.2357	9.0159	1.2228
104	184	5.0090	0.0067	1.2228	9.0295	1.2106
105	186	5.0632	0.0063	1.2106	9.0423	1.1990
106	188	5.1174	0.0060	1.1990	9.0544	1.1880
107	190	5.1716	0.0057	1.1880	9.0660	1.1776
108	192	5.2259	0.0054	1.1776	9.0769	1.1677
109	194	5.2801	0.0051	1.1677	9.0873	1.1584
110	196	5.3343	0.0048	1.1584	9.0971	1.1496
111	198	5.3886	0.0046	1.1496	9.1065	1.1412
112	200	5.4428	0.0043	1.1412	9.1153	1.1332
113	202	5.4971	0.0041	1.1332	9.1237	1.1257
114	204	5.5514	0.0039	1.1257	9.1317	1.1186
115	206	5.6056	0.0037	1.1186	9.1392	1.1119
116	208	5.6599	0.0035	1.1119	9.1464	1.1055
117	210	5.7142	0.0033	1.1055	9.1532	1.0994
118	212	5.7685	0.0031	1.0994	9.1596	1.0937
119	214	5.8228	0.0030	1.0937	9.1657	1.0883

	A	B	C	D	E	F
120	216	5.8771	0.0028	1.0883	9.1715	1.0831
121	218	5.9314	0.0027	1.0831	9.1770	1.0782
122	220	5.9857	0.0025	1.0782	9.1822	1.0736
123	222	6.0400	0.0024	1.0736	9.1871	1.0693
124	224	6.0943	0.0023	1.0693	9.1918	1.0651
125	226	6.1486	0.0021	1.0651	9.1962	1.0612
126	228	6.2029	0.0020	1.0612	9.2004	1.0575
127	230	6.2572	0.0019	1.0575	9.2043	1.0540
128	232	6.3116	0.0018	1.0540	9.2081	1.0506
129	234	6.3659	0.0017	1.0506	9.2117	1.0475
130	236	6.4202	0.0016	1.0475	9.2150	1.0445
131	238	6.4746	0.0015	1.0445	9.2182	1.0416
132	240	6.5289	0.0015	1.0416	9.2213	1.0390
133	242	6.5832	0.0014	1.0390	9.2241	1.0364
134	244	6.6376	0.0013	1.0364	9.2269	1.0340
135	246	6.6919	0.0012	1.0340	9.2295	1.0317
136	248	6.7463	0.0012	1.0317	9.2319	1.0296
137	250	6.8006	0.0011	1.0296	9.2342	1.0275
138	252	6.8550	0.0011	1.0275	9.2364	1.0256
139	254	6.9093	0.0010	1.0256	9.2385	1.0238
140	256	6.9637	0.0009	1.0238	9.2404	1.0220
141	258	7.0180	0.0009	1.0220	9.2423	1.0204
142	260	7.0724	0.0008	1.0204	9.2441	1.0188
143	262	7.1267	0.0008	1.0188	9.2458	1.0174
144	264	7.1811	0.0008	1.0174	9.2473	1.0160
145	266	7.2355	0.0007	1.0160	9.2488	1.0146
146	268	7.2898	0.0007	1.0146	9.2503	1.0134
147	270	7.3442	0.0006	1.0134	9.2516	1.0122
148	272	7.3986	0.0006	1.0122	9.2529	1.0111
149	274	7.4529	0.0006	1.0111	9.2541	1.0100
150	276	7.5073	0.0005	1.0100	9.2552	1.0090
151	278	7.5617	0.0005	1.0090	9.2563	1.0080
152	280	7.6161	0.0005	1.0080	9.2574	1.0071
153	282	7.6704	0.0005	1.0071	9.2583	1.0063
154	284	7.7248	0.0004	1.0063	9.2593	1.0055
155	286	7.7792	0.0004	1.0055	9.2601	1.0047
156	288	7.8336	0.0004	1.0047	9.2610	1.0040
157	290	7.8879	0.0004	1.0040	9.2617	1.0033
158	292	7.9423	0.0004	1.0033	9.2625	1.0026
159	294	7.9967	0.0003	1.0026	9.2632	1.0020
160	296	8.0511	0.0003	1.0020	9.2638	1.0014
161	298	8.1054	0.0003	1.0014	9.2645	1.0009
162	300	8.1598	0.0003	1.0009	9.2651	1.0003