Hybrid submerged membrane system with sorption media in suspension

Jia, Yue

2006

Jia, Y. (2006). Hybrid submerged membrane system with sorption media in suspension.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/12061>

<https://doi.org/10.32657/10356/12061>

Nanyang Technological University

Downloaded on 26 Apr 2023 20:01:09 SGT

HYBRID SUBMERGED MEMBRANE SYSTEM WITH SORPTION MEDIA IN SUSPENSION

JIA YUE

**SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2006

Hybrid Submerged Membrane System with Sorption Media in Suspension

Jia Yue

School of Civil & Environmental Engineering

**A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy**

2006

ACKNOWLEDGEMENTS

Here I would like to express my appreciation to my supervisor, Professor Tony Fane, pure-heartedly. It was my supervisor who led me in the field of membrane technology and helped me proceeding all the way in the past three years. His profound knowledge gave me a powerful guidance on this project.

I would attribute my progress sincerely to my co-supervisor, Dr. Rong Wang. Her abundant experiences in the chemical engineering processes & reactors modeling provided me a solid support. By her patient and selfless assistance, I was encouraged to overcome the difficulties any time I met.

In addition, I would thank Dr. Li Hongyu, who helped me on the start-up of my Ph.D. study as my co-supervisor as well as Dr. Wong Fook-Sin, who has been showing attention to this research all along. My appreciation also goes to all the members in Advanced Water & Membrane Center, Ms. Lee Liang Dan and other friends working in CEE and IESE for their help and advices.

Finally, I greatly acknowledge the support of Agency of Science, Technology and Research of Singapore (A*STAR) for funding the Temasek Professor Program in Membrane Technology for Sustainable Water.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

SUMMARY AND PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE OF CHAPTER 2

NOMENCLATURE OF CHAPTER 4

NOMENCLATURE OF CHAPTERS 5, 6, 7

1. INTRODUCTION

1.1. Background of submerged membrane filtration	1
1.2. Hybrid membrane system	2
1.3. Objectives of this research	4
1.4. Scope of this research	5
1.5. Organization of this thesis	5

2. MEMBRANE FILTRATION SYSTEMS WITH ACTIVATED CARBON ADSORPTION PRETREATMENT – LITERATURE REVIEW

2.1. Basic concepts of membrane filtration	8
2.1.1. Membrane and applications	8
2.1.2. Membrane configurations	11
2.1.3. Dead-end and cross-flow operations	12
2.1.4. Characteristics of membrane performance	13
2.1.5. Limitation of membrane filtration- flux decline/TMP increase	15
2.1.6. Critical flux	17
2.2. Gas-liquid two-phase flow in submerged membrane systems	18

2.2.1. Submerged membrane systems with bubbling	18
2.2.2. Two-phase flow	20
2.2.3. Factors affecting the performance of submerged hollow fibers	22
2.2.3.1. Effect of air flow rate	22
2.2.3.2. Effect of bubble size and frequency/intensity	23
2.2.3.3. Effect of fiber diameter, density and length	24
2.2.3.4. Effect of fiber orientation and spacing	25
2.3. Activated carbon adsorption process	26
2.3.1. General concepts	26
2.3.2. Physical properties of activated carbon	26
2.3.3. Adsorption theory	27
2.3.3.1. Adsorption equilibrium	28
2.3.3.2. Adsorption kinetics	29
2.3.3.3. Factors affecting carbon adsorption	31
2.3.4. Granular activated carbon (GAC) and powdered activated carbon (PAC)	32
2.4. Membrane filtration combined with PAC adsorption pretreatment	33
2.4.1. Factors influencing PAC adsorption performance in hybrid systems	34
2.4.2. Effect of PAC pretreatment on membrane performance	36
2.4.2.1. Beneficial effects	37
2.4.2.2. Negative effects	39
2.4.3. Hybrid system simulation	40
2.4.4. Submerged membrane system with PAC adsorption	43
2.5. Activated carbon regeneration	44
2.6. Summary	49
 3. EFFECT OF AIR BUBBLING ON PAC ADSORPTION – COMPETITIVE ADSORPTION OF IMPURITIES	
3.1. Introduction	50
3.2. Experimental	52

Nanyang Technological University

3.2.1. Materials	52
3.2.2. Methods of adsorption equilibrium tests	54
3.2.3. Methods of batch kinetic tests	56
3.2.4. Sampling method	57
3.2.5. Analysis of atrazine	57
3.3. Results and discussion	57
3.3.1. Adsorption isotherm test	57
3.3.2. Initial tests with magnetic stirring and air bubbling	59
3.3.3. Effect of pH increase during bubbling	61
3.3.4. N ₂ and O ₂ competitive adsorption with atrazine solutes	63
3.3.5. Mixing mechanism	65
3.3.6. Contaminants introduced with the air	66
3.3.7. Bubbling tests with stainless steel tubing	69
3.4. Conclusions	71
Acknowledgement	72
4. ATRAZINE ADSORPTION BY PAC	
– IMPROVED MASS TRANSFER BY AIR BUBBLING	
4.1. Introduction	73
4.2. Background	75
4.3. Experimental	77
4.3.1. Materials	77
4.3.2. Methods	78
4.4. Results and discussion	78
4.4.1. Continuous bubbling	78
4.4.2. Correlation between the bubbling rate and the magnetic stirring speed	81
4.4.3. Determination of mass transfer coefficient K _l	83
4.4.4. Intermittent bubbling	86
4.5. Conclusions	89

5. DETERMINATION OF THE ADSORPTION KINETIC COEFFICIENTS

5.1. Introduction	90
5.2. Theoretical model	92
5.2.1. Formulation of adsorption	92
5.2.2. Nondimensionalization of describing equations	94
5.2.3. Numerical scheme	97
5.3. Experimental	98
5.4. Results and discussion	99
5.5. Conclusions	106

6. SINGLE-STAGE HYBRID PAC-SUBMERGED MEMBRANE SYSTEM SIMULATION AND OPTIMIZATION

6.1. Introduction	108
6.2. Formulation of the hybrid PAC-submerged membrane model	110
6.2.1. Batch dosing of PAC	111
6.2.2. Continuous dosing of PAC	113
6.3. Experimental method for continuous flow hybrid PAC- submerged hollow fiber system	115
6.4. Results and discussion	117
6.4.1. Model verification and membrane performance	118
6.4.2. Model predictions	121
6.4.2.1. Different carbon dosages	122
6.4.2.2. Different air bubbling rates	124
6.4.2.3. Different filtration fluxes	126
6.4.2.4. Batch and continuous PAC dosing	129
6.4.3. Effect of high PAC concentration on membrane performance	129
6.5. Conclusions	132

7. SIMULATION OF COUNTERCURRENT OPERATION OF TWO-STAGE HYBRID PAC-SUBMERGED MEMBRANE SYSTEM

7.1. Introduction	134
7.2. Model development	137
7.2.1. Formulation of adsorption in tank #2	138
7.2.2. Formulation of adsorption in tank #1	140
7.2.3. Numerical approach	140
7.3. Model predictions and discussion	141
7.4. Conclusions	149

8. PAC REGENERATION WITH PHOTOCATALYTIC OXIDATION IN A SUBMERGED MEMBRANE SYSTEM

8.1. Introduction	151
8.2. Experimental	153
8.2.1. Materials	153
8.2.2. Methods	153
8.2.2.1. Adsorption kinetic tests	153
8.2.2.2. Hybrid photocatalytic-PAC submerged membrane reactor	154
8.2.2.3. BPA and TOC analysis	155
8.3. Results and discussion	155
8.4. Conclusions	159
Acknowledgement	160

9. CONCLUSIONS AND RECOMMENDATIONS

9.1. Overall conclusions	161
9.1.1. Investigation of the factors associated with air bubbling	161
9.1.2. Determination of Mass transfer coefficients	162
9.1.3. Modeling of a continuous flow single-stage hybrid PAC-submerged membrane system with air bubbling	163

Nanyang Technological University

9.1.4. Modeling of continuous countercurrent two-stage hybrid PAC-submerged membrane system with air bubbling	164
9.1.5. PAC regeneration by TiO ₂ photocatalytic oxidation (PCO)	165
9.2. Recommendations for future research	166
REFERENCES	167
APPENDIX A	187
APPENDIX B	201

SUMMARY AND PUBLICATIONS

The hybrid powdered activated carbon (PAC) adsorption-submerged membrane system combines the advantages of both processes for dissolved organics removal from water. The objective of this research was to investigate the performance of the hybrid PAC-submerged membrane system for trace organics treatment from water through both experimental studies and mathematical simulations.

Experimental study on PAC adsorption tests demonstrated that smaller carbon particles showed an obviously higher adsorption rate and slightly enhanced adsorption capacity for the target compound removal. The adsorption kinetics could be enhanced by increasing the bubbling rates to an upper limit. Some additional factors introduced by air bubbling were examined to identify their contributions to the change of adsorption rate. In addition, high-intensity intermittent bubbling with longer rest duration showed more benefit to the adsorption rate than low-intensity bubbling with shorter rest duration.

To quantify the benefit of bubbling on the adsorption kinetics that is characterized by k_f (liquid film diffusion) and D_s (surface diffusion), both a simple approach and a complex procedure were carried out based on the batch test data. In the simple approach, the difficulty of searching for D_s was avoided by assuming that the adsorption rate was only controlled by the film diffusion in the initial stages of the tests. k_f was thus obtained through a first order equation and the data for the first minute of each batch experiment. For comparison, the theoretical value of k_f was also calculated using the expressions developed for conventional mechanical stirred systems by correlating the bubbling rates to a group of equivalent magnetic stirring speeds. In the complex approach, the single solute homogeneous surface diffusion model (HSDM) was solved numerically using the orthogonal collocation method. The differences between the model solutions and corresponding experimental results were minimized by means of the Levenberg-Marquardt algorithm so that

two kinetic parameters k_f and D_s , which are involved in HSDM, were obtained simultaneously. The D_s was found to be $1.14 \times 10^{-16} \text{ m}^2 / \text{s}$ while the k_f altered with different mixing mechanisms as well as mixing intensities. The k_f value was improved by an increase in the bubbling rates (continuous bubbling) and bubbling intensity (intermittent bubbling) to a certain limit. Based on this analysis, k_f was correlated with both bubbling rate Q_b and carbon dosage C_c for further application in the hybrid system simulation.

Mathematical models have been developed to describe PAC adsorption processes in both single-stage continuous flow and two-stage countercurrent submerged hollow fiber membrane system, respectively, with air bubbling for trace organics removal from water. The single-stage hybrid system performances under two operation strategies of batch and continuous dosing of PAC were simulated based on the HSDM and corresponding mass balance equations. The results were verified with experiments using atrazine as the model trace organic compound. The developed models were used to predict the product water quality at different operation conditions such as different air bubbling rates, carbon dosages as well as water fluxes. Based on the model predictions on the two-stage countercurrent hybrid system, it was found that the PAC adsorption capacity can be utilized more efficiently than the single-stage reactors. Lower flux operation requires less frequent PAC replacement and achieves more carbon utilization than higher flux operation. ‘Pseudo-steady state’ reuse of PAC can be achieved by setting the PAC replacement rate to a very low value and thus a constant PAC replacement and a stable water product quality can be maintained.

Finally, a novel in-situ regeneration method for the saturated PACs in the hybrid submerged membrane system was studied in preliminary experiments by applying photocatalytic oxidation with the assistance of TiO_2 particles to the suspension of spent PAC. The recovered PAC adsorption capacity was confirmed by both the batch adsorption tests and continuous flow hybrid submerged membrane filtration tests.

PUBLICATIONS

In Journals

Jia, Y., Wang, R., Fane, A. G., and Krantz, W.B. (2005) “Effect of air bubbling on atrazine adsorption in water by powdered activated carbons– competitive adsorption of impurities”. Separation & Purification Technology, Vol. 46, pp. 79-87.

Jia, Y., Wang, R. and Fane, A. G. (2006) “Atrazine adsorption from aqueous solution using powdered activated carbon-Improved mass transfer by air bubbling agitation”, Chemical Engineering Journal, Vol. 116, pp. 53-59.

Jia, Y., Wang, R. and Fane, A. G. (2006) “Adsorption kinetics study for activated carbon adsorption in a bubbled solution”, Chemical Engineering Science, submitted.

Jia, Y., Wang, R. and Fane, A. G. (2006) “Modeling of single-stage hybrid PAC-submerged membrane system for trace organics treatment from water”, to be submitted.

Jia, Y., Wang, R. and Fane, A. G. (2006) “Modeling of countercurrent two-stage hybrid PAC-submerged membrane system for trace organics treatment from water”, to be submitted.

In International Conferences

Chin, S.S, Chiang, K., **Jia, Y.,** Wang, R. and Fane, A. G. (2005) “Trace organics removal from water by low pressure membranes”, Proceedings of IDA World Congress on Desalination and Water Reuse, Singapore, IBSN: 0-9745019-8-0.

Jia, Y., Wang, R. and Fane, A. G. (2005) “Adsorption kinetics study on trace organic removal by PAC from water”, Proceedings of 1st International Conference on Pollution Control and Resource Reuse for a Better Tomorrow and Sustainable Economy, Shanghai, China, pp. 100-108.

LIST OF TABLES

Table 2.1.	Summary of the main pressure-driven processes
Table 2.2.	Three important fluxes and their users (after Howell, 2004)
Table 3.1.	Norit SA-2 general characteristics
Table 3.2.	Atrazine characteristics
Table 3.3.	Freundlich adsorption isotherm parameters for atrazine and DEHP (from Snoeyink and Summers, 1999)
Table 4.1.	Conversion of the bubbling rates to equivalent stirring speeds
Table 4.2.	Comparison of K_l from different methods
Table 5.1.	Comparison between k_f values determined through different methods, $C_c = 5\text{mg} / L$
Table 5.2.	Comparison of the kinetic coefficients between continuous and intermittent bubbling at the same net bubbling rate
Table 6.1.	Characteristics of the MF hollow fiber membrane module
Table 6.2.	k_f at different bubbling rates and carbon dosages, ($d_p = 6.3\mu\text{m}$, $C_0 = 200\mu\text{g} / L$)

LIST OF FIGURES

- Figure 2.1. Schematic representation of a two-phase system separated by a membrane
- Figure 2.2. Membrane classification
- Figure 2.3. Application ranges of membrane separation processes
- Figure 2.4. Schematic representation of dead-end and cross-flow filtration
- Figure 2.5. Membrane fouling for two operation modes
- Figure 2.6. Schematics of external and submerged membrane configurations.
(a). External cross-flow system; (b). Submerged system
- Figure 2.7. Flow patterns for gas-liquid two-phase flow (Ghosh and Cui, 1999)
- Figure 2.8. The effect of gas velocity on final flux in filtration with submerged system (vertical axial bubbling), for two fiber diameters (Fane et al, 2002)
- Figure 2.9. Effect of bubble size on permeate flux at various frequencies.
- Figure 2.10. Pore sizes in an activated carbon particle
- Figure 2.11. Activated carbon adsorption process
- Figure 2.12. Schematics of hybrid submerged membrane system
- Figure 2.13. Overview of spent AC adsorbents regeneration techniques
(after Sheintuch et al, 1999)
- Figure 2.14. Schematic diagram for thermal regeneration of loaded AC
(after Moreno-Gastilla et al, 1995; Snoeyink and Summers, 1999)
-
- Figure 3.1. Particle size distributions of PAC pulverized for different times
- Figure 3.2. Freundlich adsorption isotherm, 48h vs. 72h, $d_{50} = 6.3\mu m$,
 $C_0 = 200\mu g / L$
- Figure 3.3. Schematic diagram of air bubbling system (Batch kinetic study)

Nanyang Technological University

- Figure 3.4. Freundlich adsorption isotherm for PACs of different sizes, $C_0 = 200 \mu\text{g} / \text{L}$, 48h
- Figure 3.5. Adsorption rate of atrazine on PAC of different particle sizes, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.6. Effect of air bubbling on atrazine adsorption by PAC, PVC tubing, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.7. Effect of air bubbling on atrazine adsorption by PAC of different concentrations, PVC tubing, Bubbling rate= $1.5 \text{L} / \text{min}$
- Figure 3.8. pH increase in the bubbling batch kinetic tests, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.9. Effect of pH on adsorption kinetics, pre-bubbled Milli-Q water, $C_c = 5 \text{mg} / \text{L}$, Bubbling rate= $2.7 \text{L} / \text{min}$
- Figure 3.10. Effect of air bubbling on adsorption after adsorption equilibrium, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.11. Effect of Helium gas bubbling on adsorption after adsorption equilibrium, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.12. Bubbling test followed by magnetic stirring, $C_c = 5 \text{mg} / \text{L}$, Bubbling rate= $2.7 \text{L} / \text{min}$
- Figure 3.13. Investigation of the tubing contaminants leakage using magnetic stirring tests, $C_c = 5 \text{mg} / \text{L}$
- Figure 3.14. Investigation of the tubing contaminants leakage using bubbling tests, $C_c = 5 \text{mg} / \text{L}$, Bubbling rate= $2.7 \text{L} / \text{min}$
- Figure 3.15. Analysis of DEHP with HPLC
- Figure 3.16. Effect of air bubbling on atrazine adsorption by PAC, stainless steel tubing, $C_c = 5 \text{mg} / \text{L}$
-
- Figure 4.1. Effect of air bubbling on atrazine adsorption by PAC, $C_c = 5 \text{mg} / \text{L}$
- Figure 4.2. Effect of air bubbling on atrazine adsorption by PAC, $C_c = 10 \text{mg} / \text{L}$

Nanyang Technological University

- Figure 4.3. Response of AOB dye concentration at the top of liquid, magnetic stirring
- Figure 4.4. Linear regression of the stirring speeds vs. time required to achieve 60% of complete mixing
- Figure 4.5. Response of AOB dye concentration at the top of liquid, air bubbling
- Figure 4.6. Effect of bubbling rate on mass transfer rate in the initial stage of adsorption, $C_c = 5\text{mg} / L$
- Figure 4.7. Effect of intermittent bubbling adsorption kinetics, $C_c = 5\text{mg} / L$
(a). 0.5L/min; (b). 1.5L/min; (c). 2.7L/min
- Figure 4.8. Comparison between intermittent and continuous bubbling with equivalent flow rate, $C_c = 5\text{mg} / L$
-
- Figure 5.1. Schematic diagram of activated carbon particle structure and mechanisms in the HSDM
- Figure 5.2. Flow chart of the adsorption kinetic coefficients searching program
- Figure 5.3. Verification of the adsorption kinetic coefficients searching methods, magnetic stirring=62 rpm, $C_0 = 200\mu\text{g} / L$
- Figure 5.4. HSDM fit to the bubbling batch kinetic tests data, $C_c = 5\text{mg} / L$,
- Figure 5.5. HSDM fit to the bubbling batch kinetic tests data, $C_c = 10\text{mg} / L$
- Figure 5.6. HSDM fit to the bubbling batch kinetic tests data, $C_c = 15\text{mg} / L$
- Figure 5.7. k_f and Q_b at different carbon concentrations
- Figure 5.8. HSDM fit to the intermittent bubbling batch kinetic tests data, $C_c = 5\text{mg} / L$
-
- Figure 6.1. Schematic diagram of a hybrid PAC adsorption-submerged membrane system
- Figure 6.2. Schematic diagram of dosing PAC at tiny time intervals (for continuous PAC dosing mode)

Nanyang Technological University

- Figure 6.3. Experiment set-up of PAC-submerged hollow fiber membrane reactor
- Figure 6.4. Model verification for continuous flow hybrid system with batch PAC dosing, Flux= $60 \text{ L} / \text{m}^2 \text{h}$, $Q_b = 0.4 \text{ L} / \text{min.L}$, $C_0 = 200 \mu\text{g} / \text{L}$, $D_s = 1.14 \times 10^{-16} \text{ m}^2 / \text{s}$)
- Figure 6.5. Model verification for continuous flow hybrid system with continuous PAC dosing, ($Q_b = 0.4 \text{ L} / \text{min.L}$, $C_0 = 200 \mu\text{g} / \text{L}$, $D_s = 1.14 \times 10^{-16} \text{ m}^2 / \text{s}$)
- Figure 6.6. Permeability of hybrid submerged PAC-MF test and Milli-Q water test, Flux= $60 \text{ L} / \text{m}^2 \text{h}$, $Q_b = 0.4 \text{ L} / \text{min.L}$; for hybrid test: $C_0 = 200 \mu\text{g} / \text{L}$, $C_c = 8 \text{ mg} / \text{L}$, batch PAC dosing
- Figure 6.7. SEM photos of new membrane and used membrane
- Figure 6.8. Model predictions for hybrid submerged PAC-MF at different carbon dosages (batch dose of PAC)
- Figure 6.9. Model predictions for hybrid submerged PAC-MF at different carbon dosages (continuous dose of PAC)
- Figure 6.10. Model predictions for hybrid submerged PAC-MF at different bubbling rates (batch dose of PAC)
- Figure 6.11. Model predictions for hybrid submerged PAC-MF at different bubbling rates (continuous dose of PAC)
- Figure 6.12. Concentration profile with the change of the volume of treated water 480min, batch dose of PAC, fixed PAC amount. (Scenario())
- Figure 6.13. Concentration profile with the change of the volume of treated water 480min, batch dose of PAC, fixed PAC amount. (Scenario())
- Figure 6.14. Model predictions for hybrid submerged PAC-MF at different filtration fluxes (continuous dose of PAC)
- Figure 6.15. TMP and flux at carbon concentration of $5.8 \text{ g} / \text{L}$
- Figure 6.16. TMP and flux at carbon concentration of $14.0 \text{ g} / \text{L}$
- Figure 6.17. Summary of TMP vs. flux at different carbon concentrations

Nanyang Technological University

- Figure 7.1. Freundlich adsorption isotherm curve
- Figure 7.2. Concept of countercurrent operation
- Figure 7.3. Schematic of countercurrent two-stage hybrid PAC-Submerged Membrane system
- Figure 7.4. Schematic of batch dosing of PAC and the PAC replacement point
- Figure 7.5. Countercurrent operation, $J = 60L/m^2h$
- Figure 7.6. Adsorbed phase concentration, $J = 60L/m^2h$
- Figure 7.7. Countercurrent operation, $J = 100L/m^2h$
- Figure 7.8. Adsorbed phase concentration, $J = 100L/m^2h$
- Figure 7.9. Countercurrent operation, $C_2^* = 0.1$
- Figure 7.10. Countercurrent operation, $RR=1\%$, $J = 60L/m^2h$
- Figure 7.11. Countercurrent operation, $RR=1\%$, $J = 60L/m^2h$
-
- Figure 8.1. Schematic diagram of a hybrid PPSM system
- Figure 8.2. Continuous flow PAC-SM test followed by PCO, $J = 100L/m^2h$, $M_c = 0.08g$, $V = 0.8L$, Bubbling= $1.0L/min$
- Figure 8.3. Adsorption kinetics for virgin PAC and 4-h PCO regenerated PAC, $BPA=5mg/L$, stirred at 180rpm, $PAC/TiO_2=1/5$ (by mass)
- Figure 8.4. Adsorption kinetics for virgin PAC and TiO_2 mixed particles at different mixing ratios.
- Figure 8.5. Comparison between 4-h and 12-h PCO regenerations of PAC
- Figure 8.6. Continuous flow test using hybrid submerged membrane system, started with Milli-Q water, $J = 100L/m^2h$, Bubbling= $1.0L/min$, Feed $BPA=5mg/L$
-
- Figure B.1. Check on the accuracy of the numerical solution developed in Chapter 5, Batch test, $C_0 = 200\mu g/L$, $M_c = 8mg$, $V = 1.0L$,

$$K = 70.06(L/mg), k_f = 1.37 \times 10^{-4} m/s, A = 0.0166(m^2)$$

Figure B.2. Check on the accuracy of the numerical solution developed in Chapter 6 , Continuous flow, Batch input of PAC, $C_0 = 200 \mu g/L$, $M_c = 1000 mg$, $V = 50L$, $K = 70.06(L/mg)$, $k_f = 1.37 \times 10^{-4} m/s$, $A = 2.07(m^2)$

Nomenclature for Chapter 2:

- A_m : the membrane area (m^2)
- C_c : the solute concentration near the cake later ($mg\ L^{-1}$)
- C_e : the solute equilibrium concentration in the liquid phase ($mg\ L^{-1}$)
- C_f : the solute concentration in the feed ($mg\ L^{-1}$)
- C_p : the solute concentration in the permeate ($mg\ L^{-1}$)
- ΔC : concentration (or activity) gradient
- d_s : the diameter of the solute particle (m)
- ΔE : electrical potential difference
- J : permeate flux ($L\ m^{-2}h^{-1}$)
- K : Freundlich isotherm capacity constant
- L_p : the hydraulic permeability ($L\ m^{-2}h^{-1}Pa^{-1}$)
- n : number of pores
- $1/n$: Freundlich isotherm constant
- P_m : the transmembrane pressure (KPa)
- ΔP : pressure gradient (KPa)
- q_e : the solute equilibrium concentration in the solid phase (mg / g)
- ΔT : temperature difference (K)
- r : pore radius (m)
- R : retention, the fraction of retained species by the membrane using the feed and permeate concentrations, dimensionless
- R_f : fouling resistance and concentration polarization (m^{-1})
- R_m : hydraulic resistance of the clean membrane (m^{-1})
- R_c : cake layer resistance(m^{-1})
- R_t : the total filtration resistance (m^{-1})
- V_c : the volume of the cake (m^3)

Nanyang Technological University

ΔX : the membrane thickness (m)

Greek letters

τ : pore tortuosity

ε_m : membrane surface porosity

ε_c : the cake layer porosity

μ : viscosity of solution (cp , or $10^{-3} Kg / ms$)

Nomenclature for Chapter 4:

a :	specific interfacial area based on the liquid volume (m^{-1})
C_0 :	initial adsorbate concentration in bulk solution ($\mu g / L$)
C :	adsorbate concentration in bulk solution at any time t ($\mu g / L$)
C_s :	liquid phase adsorbate concentration at solid-liquid interface ($\mu g / L$)
d_a :	stir bar diameter (m)
d_p :	carbon particle diameter (m)
D_v :	volumetric diffusivity for dilute liquid solutions (cm^2 / s)
K_l :	mass transfer coefficient in liquid film (m / s)
M_B :	molecular weight of solvent (g / mol)
n :	stirring speed (rpm)
Q_b :	bubbling rate (L / min)
Re:	Reynolds number
Sc:	Schmidt number
Sh:	Sherwood number
T :	absolute temperature (K)
t :	operation time (min)
$t_{0.2}$:	the required time to achieve 20% of the initial target concentration
u_0 :	velocity of approaching stream (m / s)
u_m :	the magnetic stirring speed (rpm)
V_A :	molar volume of solute as liquid at its normal boiling point, ($cm^3 / gmol$)

Greek letters

ρ :	density of solution (Kg / m^3)
μ :	viscosity of solution (cp , or $10^{-3} Kg / ms$)
ψ_B :	association parameter for solvent, for water $\psi_B = 2.6$

Nomenclature for Chapters 5,6,7:

- B_i : Biot number based on surface diffusion (non-dimensional)
- C : liquid phase adsorbate concentration in bulk solution at any time in single stage operation (M / L^3)
- C^* : dimensionless liquid phase adsorbate concentration in bulk solution at any time in single stage operation
- C_1, C_2 : liquid phase adsorbate concentration in and leaving tank #1 & #2 at any time in the counter current two-stage operation (M / L^3)
- C_1^*, C_2^* : dimensionless liquid phase adsorbate concentration in and leaving tank #1 & #2 at any time in the counter current two-stage operation (M / L^3)
- C_0 : initial liquid phase adsorbate concentration (M / L^3)
- C_e : liquid phase adsorbate concentration at adsorption equilibrium (M / L^3)
- C_c : carbon mass per unit volume of the treated water (M / L^3)
- C_s : liquid phase adsorbate concentration at solid-liquid interface (M / L^3)
- C_s^* : dimensionless liquid phase adsorbate concentration at solid-liquid interface
- D_s : surface diffusion coefficient (L^2 / T)
- $E_{mb}, E_{b1}, E_{b2}, E_{b3}, E_{mb11}, E_{mb12}, E_{mb22}, E_{mb3}, E_{mb4}$:
parameters in the mass balance (dimensionless)
- d_p : adsorbent particle diameter (L)
- K : Freundlich isotherm capacity constant
- k_f : liquid film mass transfer coefficient (L / T)
- M_c : total mass of carbon in the test (M)
- m : the number of data points in the nonlinear least squares problem
- $1/n$: Freundlich isotherm intensity constant (dimensionless)

Nanyang Technological University

- p : the number of ΔT contained by T
- $q(r,t)$: adsorbed adsorbate concentration (M / M)
- $q^*(R,T)$: dimensionless adsorbed adsorbate concentration
- q_0 : initial adsorbed phase adsorbate concentration (M / M)
- q_e : adsorbed phase adsorbate concentration at adsorption equilibrium
(M / M)
- q_s : adsorbed phase adsorbate concentration at solid-liquid interface (M / M)
- q_s^* : dimensionless adsorbed phase adsorbate concentration at solid-liquid
interface (M / M)
- q_{avg} : average adsorbed phase adsorbate concentration (M / M)
- q_{avg}^* : dimensionless average adsorbed phase adsorbate concentration
- $q_{avg,(t-\beta)}$: average adsorbed phase adsorbate concentration on the particles that
entered the reactor at time β , (M / M)
- $q_{avg,(t-\beta)}^*$: dimensionless average adsorbed phase adsorbate concentration on the
particles that entered the reactor at time β^*
- $q_{1avg,t}$: average adsorbed phase adsorbate concentration in tank #1 in counter
current operation(M / M)
- $q_{1avg,T}^*$: dimensionless average adsorbed phase adsorbate concentration in tank #1
in counter current operation(M / M)
- $q_{2avg,t}$: average adsorbed phase adsorbate concentration in tank #2 before PAC
replacing in counter current operation (M / M)
- $q_{2avg,T}^*$: dimensionless average adsorbed phase adsorbate concentration in tank #2
before PAC replacing in counter current operation (M / M)
- $q_{2p-avg,t}$: average adsorbed phase adsorbate concentration in tank #2 on previously
loaded PAC in counter current operation (M / M)

Nanyang Technological University

$q_{2p-avg,T}^*$	dimensionless average adsorbed phase adsorbate concentration in tank #2 on previously loaded PAC in counter current operation (M / M)
$q_{3avg,t}$	average adsorbed phase adsorbate concentration in tank #2 on renewed PAC (M / M)
$q_{3avg,T}^*$	dimensionless average adsorbed phase adsorbate concentration in tank #2 on renewed PAC (M / M)
Q	liquid flow rate (L^3 / T)
Q_b	air bubbling rate in the batch kinetic test ($L^3_{(air)} / TL^3_{(liquid)}$)
r	radial coordinate (L)
R	dimensionless radial coordinate
RR	replacement rate
t	time (T)
T	dimensionless time base on surface diffusion
ΔT	the time step
V	liquid volume (L^3)
β	the time at which the carbon particles are added into the reactor (T)
β^*	dimensionless time at which the carbon particles are added into the reactor
ρ_p	apparent particle density (M / L^3)

1.

INTRODUCTION

1.1. Background of submerged membrane filtration

There is a worldwide interest in using membrane filtration systems as an alternative to conventional water production and wastewater treatment systems. Low-pressure driven membrane technologies are especially attractive where space and water resources are limited. Improved membrane technology, and reduced membrane cost as well as stringent regulation of drinking water quality make membrane filtration process more competitive than the traditional processes.

The submerged membrane system, firstly applied in membrane bioreactors (MBRs) in the late 1980s (Yamamoto et al, 1989), is a comparatively new step in membrane applications. In the submerged membrane system, the membranes are mounted or immersed directly in the reactor and the permeate is withdrawn under suction through the membranes. Compared with reactors with the external membrane systems, the internal system involves substantially more membrane area per unit volume, operates at a much lower transmembrane pressure (TMP) and potentially, requires a much lower power cost for the membrane component (Enege et al, 2003). However, concentration polarization phenomenon and membrane fouling can compromise the performance of the membrane operation. One of the strategies to control these phenomena is to induce shear stress at the membrane surface. In the submerged membrane bioreactor (MBR) system, air bubbling is applied to fulfill this task in addition to its functions of oxygen supply and mixing provision.

1. Introduction

Although the submerged membrane concept was initially introduced for MBRs it is now widely applied in water treatment and other hybrid membrane processes.

1.2. Hybrid PAC-membrane system

A membrane process usually has good removal efficiency of particles or solutes larger than the membrane pore size. The smaller the size of the species, the tighter the membrane required and this results in more pressure/energy required. As a low pressure membrane process, microfiltration (MF) has been widely applied in separating suspended fine particles, large colloidal materials and macromolecules from liquid economically and efficiently. However, MF is not suitable to filter dissolved organics especially trace organic compounds, taste and odor-causing materials and synthetic organic chemicals from water because the membrane pore sizes are normally larger than the molecular sizes of those pollutants.

This situation can be changed if a hybrid membrane system is applied. One promising feature of hybrid membrane systems is that they integrate the membrane separation with another unit operation to surpass the limitation of the single membrane system. The optimal combination of the processes depends on the characteristics of the raw feed and the desired product quality. One attractive method is to combine powdered activated carbon (PAC) adsorption with low-pressure driven membrane processes.

The adsorption process has been applied for dissolved impurities removal in liquid-phase applications for many years. More recently, activated carbon has been widely used for purification of water in both industrial and municipal applications due to its large surface area per unit volume and its affinity for a wide range of dissolved organics. Powdered activated carbon has additional advantages of being a relatively cheap material, requiring minimal capital expenditure for feeding and contacting equipment as well as being applied only when needed (Najm et al, 1991).

1. Introduction

In the hybrid system which combines PAC adsorption process with a membrane filtration process, the small molecular species not usually rejected by the MF membrane alone are adsorbed onto the PAC particles. This pretreatment converts dissolved organic matter to a particulate phase that can be easily rejected by the membranes. The MF process then separates fine PAC particles, with adsorbed small molecules in the pores, from the treated water. One commercial example of this combination is the CRISTAL® (Combination of Reactors, Including membrane Separation Treatment and Adsorption in Liquid) process, which utilizes the PAC-membrane system in an external loop, and has been applied in drinking water production in France since 1993 (Laine et al, 2000).

Theoretically, an appropriate combination of a PAC adsorption process and membrane filtration process can incorporate the advantages of both processes and make the water treatment more efficient and economical. This hybrid system can offset the disadvantage of the large equipment size and space requirement when PAC adsorption is applied in a traditional way, as membranes provide more efficient separation of PAC from treated water than sedimentation or other traditional filtration processes. Moreover, the adsorption pretreatment ensures high pollutant removal while the low pressure MF process requires relatively low energy.

There have been many studies of the PAC-membrane hybrid system for the removal efficiency of the target compounds and to examine the membrane performance in the last two decades. However, most of the studies have been using external membrane systems, i.e., the ‘contained’ membrane modules and the adsorption reactors were arranged in a circulation loop. Due to the additional advantages of the submerged membrane process, further study with the combination of PAC adsorption and the submerged membrane system could be beneficial for industrial applications.

One of the main features of submerged system is the employment of air bubbling to provide mixing and to prevent membrane fouling. Therefore optimizing the operational strategies for both the adsorption process and the membrane filtration

1. Introduction

process are required. The strategies include PAC dosing methods, bubbling rate and bubble frequency for adequate mixing and fouling prevention, hydraulic retention time, the flow patterns, i.e. concurrent flow or countercurrent flow of PAC and raw water, etc.

1.3. Objectives of this thesis

The objective of this research is to investigate the performance of the hybrid PAC-submerged membrane system for trace organics removal through both experimental studies and mathematical simulations. The hybrid submerged membrane system is operated by immersing the membrane module (MF hollow fiber module) vertically inside an atmospheric reaction tank with PAC in suspension. By evaluating the performance of the system at different operating conditions, an optimal strategy should be attainable resulting in good trace organic compounds removal, decreased fouling, and a much longer PAC life span.

This research involves the following aspects:

- Experimental study on PAC adsorption isotherms and kinetics of selected target organic compound with PAC of different sizes.
- Study on mass transfer rate in the liquid film of PAC particles in a bubbled solution through a simple approach which utilizes the data from specially-designed experiments and the well-developed mechanical stirred system theories.
- Determination of the diffusion kinetic coefficients of the trace organic compound adsorption on PAC in bubbled liquid solution with the application of the widely used homogeneous surface diffusion model (HSDM).

1. Introduction

- Model development to simulate the trace organics removal at different operating conditions in a concurrent single-stage PAC-submerged membrane system.
- Model verification with experimental data using a vertically submerged hollow fiber system in which the PAC particles are suspended by the injected air bubbling.
- System optimization through the model predictions at different PAC dosing modes, bubbling rates and operating fluxes.
- Simulation of the countercurrent two-stage PAC-submerged membrane system for trace organics treatment at different working conditions such as fluxes, PAC replacement rates and desired residue target concentrations in the product water.
- Preliminary assessment of in-situ PAC regeneration in the hybrid submerged membrane system using photocatalytic oxidation with the assistance of TiO_2 particles and UV light.

1.4. Scope of this research

Atrazine was chosen as a model test compound to represent trace organic compound in natural water. Its removal efficiency using PAC adsorption and the performance of a submerged hollow fiber (MF) system were monitored based on a bench-scale experiment set-up. In the bench-scale saturated PAC regeneration tests, Bisphenol A(BPA) was used as a model compound and TiO_2 particles were applied to facilitate the photocatalytic oxidation process.

1.5. Organization of this thesis

1. Introduction

Chapter 1 includes an introduction to the background of hybrid submerged membrane systems as well as description of the research objectives and scope.

Chapter 2 gives a detailed literature review on membrane separation techniques, submerged membrane systems, adsorption processes, the hybrid PAC-membrane system and spent PAC regeneration methods.

Chapter 3 studies the change of the adsorption rate caused by the air bubbling through batch kinetic tests. The factors introduced by the use of air bubbling, such as pH increase, N_2 and O_2 competitive adsorption, mixing efficiency and contaminant release from PVC tubing have been investigated.

Chapter 4 introduces a study on the mass transfer in the liquid film surrounding the PAC particles. The experimental mass transfer coefficients in the bubbling system are compared favorably with values calculated using correlations developed for conventional magnetic stirring systems, with the help of a conversion of the bubbling rates to the equivalent stirring speeds based on specially-designed experiments.

Chapter 5 presents the determination of the adsorption kinetic coefficients in a bubbling mixed system by solving the HSDM numerically using the orthogonal collocation method and the Levenberg-Marquardt algorithm in combination with experimental data. The mass transfer coefficient in the liquid film surrounding PAC particles, k_f , is correlated with both Q_b (air bubbling rate per volume of water) and C_c (PAC concentration) for further application in the PAC-submerged membrane system modeling.

Chapter 6 focuses on the mathematical simulation and optimization of the concurrent single-stage PAC-submerged membrane system for trace organics removal from water. The verified models are used to predict the product water quality at different operating conditions such as different PAC dosing strategies, air bubbling rates, carbon dosages as well as water fluxes.

1. Introduction

Chapter 7 presents the development of the mathematical models to describe the trace organic removal using the countercurrent two-stage PAC-submerged membrane system. In addition, model predictions at different working conditions are presented for better understanding of the potential benefit of the countercurrent multi-stage hybrid membrane system.

Chapter 8 concerns the in-situ regeneration of the fully loaded PAC using a photocatalytic oxidation method by conducting batch adsorption and photocatalysis tests as well as continuous flow submerged membrane filtration tests in which PAC and TiO_2 particles are suspended simultaneously in the water polluted by trace organics.

Chapter 9 summarizes the overall research, presents general conclusions and recommendations for future work.

2.

MEMBRANE FILTRATION SYSTEMS WITH CARBON ADSORPTION PRETREATMENT -LITERATURE REVIEW

2.1. Basic concepts of membrane filtration

2.1.1. Membranes and applications

Among the broad range of membrane applications, the use of membranes in water and wastewater treatment has gained increasing attention. A membrane can be cons-

Figure 2.1 Schematic representation of a two-phase system separated by a membrane

idered as a thin permselective barrier existing between two homogeneous phases (Figure 2.1), which allows certain components in feed to permeate freely, while

2. Literature review

hindering the permeation of other components. Transport through the membrane takes place when a driving force is applied to the components in the feed. The driving force can be a pressure gradient, concentration (or activity) gradient, temperature or an electrical potential difference.

Classification of membranes can be made from the following aspects (Figure 2.2):

Figure 2.2. Membrane classification

Pressure-driven membrane processes are widely used in water or wastewater treatment. The characteristics of these processes are that the solvent (water) is the continuous phase and the concentration of the solute is relatively low. The particle or molecular size and chemical properties of the retained solute are often the selective criteria for the pore size and pore size distribution of the membrane employed.

2. Literature review

The main pressure-driven membrane processes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) according to the molecular size of the separated components. The characteristics of these processes can be seen in Table 2.1. The tighter the membrane, the more energy/driving force is required to be applied for its operation.

Table 2.1. Summary of the main pressure-driven processes

	MF	UF	NF	RO
Membranes	(a)symmetric porous	Asymmetric porous	Composite	Asymmetric or composite
Thickness	10-150 μm	150 μm	Sublayer=150 μm Toplayer=1 μm	Sublayer=150 μm Toplayer=1 μm
Pore sizes	0.05-10 μm	1-100 nm	<2nm	<2nm
Driving force	Pressure (<2bar)	Pressure (1-10bar)	Pressure (10-25bar)	Pressure: Brackish water (10-25bar) Sea water (40-80 bar)
Separation principle	Sieving mechanism	Sieving mechanism	Sieving and/or Solution-diffusion	Solution-diffusion
Membrane material	- Polymeric - Ceramic	- Polymeric, - Ceramic	- Polyamide	- Cellulose triacetate - Aromatic polyamide - Polyamide and poly (ether urea)

Figure 2.3 summarizes the pore size ranges of various membranes and their basic applications in water treatment. The *microfiltration* (MF) process is commonly applied to separate suspended fine particles and large colloidal materials from liquid. Generally, the pore sizes of microfiltration membranes range from 0.05 μm to 10 μm . MF is used mainly as a clarification technique; separating suspended particles from dissolved substances, provided the particles meet the size requirements for MF membranes. *Ultrafiltration* (UF) is commonly used to restrict the passage of macromolecules and colloids from a solution. The pore sizes of UF membranes range from 0.001 μm to 0.1 μm . UF can be used as a method for simultaneously purifying, concentrating, and fractionating macromolecules or fine colloidal suspensions (Mulder, 1997; Cheryan, 1999). *Nanofiltration* (NF) is used to soften fresh waters and remove disinfection by-product (DBP) precursors. *Reverse osmosis*

2. Literature review

(RO) is used to remove salts from brackish water or seawater, or in reclamation of the treated effluent.

Figure 2.3. Application ranges of membrane separation processes

Typically, the cost of membrane treatment increases as the size of the contaminant removed decreases. Therefore, MF and UF membranes have attracted considerable attention in recent years and have been widely used in water treatment because they require relatively lower pressure for operation than the tight NF and RO membranes. Hybrid processes, which couple MF or UF with another separation process (such as adsorption), allow the low pressure processes to remove low molecular weight contaminants.

2.1.2. Membrane configurations

Generally, flat and tubular geometries are the two main types of membrane configuration in membrane applications. Plate-and-frame and spiral-wound membrane modules involve flat membranes, whereas capillary and hollow fiber modules are based on tubular membrane configurations (Mulder, 1997).

2. Literature review

Hollow fibers normally have asymmetric structure in the radial direction: the dense skin membrane on the outside and the porous membrane on the inside. For water industry applications, hollow fiber membranes are often used in submerged systems because they can be designed to provide a high membrane surface area per unit volume. This operating feature, combined with chemical stability, ensures reliability and long life expectancy.

2.1.3. Dead-end and cross-flow operations

Two main membrane filtration modes, known as dead-end and cross-flow, are shown in Figure 2.4. In *dead-end* operation, the entire feed flow passes through the membrane perpendicularly, so that the retained particles accumulate and form a cake layer at the membrane surface. This is also known as ‘frontal filtration’. The thickness of the cake increases with filtration time and consequently the permeation flux decreases with cake layer thickness increase when the transmembrane pressure is maintained constant.

Figure 2.4. Schematic representation of dead-end and cross-flow filtration

In a *cross-flow* operation, the feed flow moves parallel to the membrane surface and only a portion of the flow passes through the membranes under the driving pressure while the remaining flow (retentate) is recycled on the feed side. A shear force is

2. Literature review

created by the tangential flow velocity gradient. The tangential shear causes back transport of particles and accordingly, minimizes the accumulation of the contaminants on the membrane surface. Thus in cross-flow mode, the permeate flux can be maintained at a higher level than in dead-end mode.

2.1.4. Characteristics of membrane performance

The performance of membrane processes can be characterized by the retention (in percentage) of the solute (or particles), the permeate flux, and the solute concentration in the permeate stream.

Retention (R), used to express the selectivity of a membrane towards a mixture, is defined as the fraction of retained species by the membrane using the feed and permeate concentrations:

$$R = 1 - \frac{C_p}{C_f} \quad (2.1)$$

where C_p is the solute concentration in the permeate, C_f is the solute concentration in the feed.

Permeate flux is defined as the volume flowrate per unit membrane area. Its commonly accepted unit is $Lm^{-2}h^{-1}$. The flux can also be described as:

$$J = L_p \cdot \Delta P \quad (2.2)$$

where L_p is the hydraulic permeability and ΔP is the pressure difference across a membrane.

In pressure driven membrane processes, the hydraulic resistance can be made up of concentration polarization, cake layer and pore blockage or pore restriction. The

2. Literature review

fouling resistances are reversible or irreversible. Then the volume flux is usually described by Darcy's Law:

$$J = \frac{P_m}{\mu \cdot R_t} = \frac{P_m}{\mu \cdot (R_m + R_f)} \quad (2.3)$$

where:

P_m - the transmembrane pressure,

i.e. the average pressure difference between the feed bulk pressure and the permeate pressure.

μ - viscosity of the permeate,

R_t - the total filtration resistance, $R_t = R_m + R_f$,

R_m - hydraulic resistance of the clean membrane,

R_f - fouling resistance (resistance from cake layer, pore blockage and pore restriction) and concentration polarization.

The simplest representation of membrane hydraulic resistance (R_m) can be estimated from the Hagen-Poiseuille equation assuming that all the membrane pores are parallel cylindrical pores and have the same radius:

$$R_m = \frac{8 \cdot \tau \cdot \Delta X}{\varepsilon_m \cdot r^2} = \frac{8 \cdot \tau \cdot \Delta X}{n_p \cdot \pi \cdot r^4} \quad (2.4)$$

in which:

τ - pore tortuosity,

ΔX - the membrane thickness,

ε_m - membrane surface porosity ($\varepsilon = n_p \pi r^2$),

n_p - number of pores,

r - pore radius,

2. Literature review

Fouling by pore blockage reduces ε_m and fouling by pore restriction reduces r (note that a 10% reduction in r produces about 50% increase in R_m). In practice, R_m of a clean membrane can be obtained by measuring the flux of pure water under a given pressure and using equation (2.3) with $R_f = 0$. The cake layer resistance (R_c) is often expressed by the Kozeny-Carman relationship and can be described as:

$$R_c = \frac{180 \cdot (1 - \varepsilon_c)^2 \cdot C_f \cdot V_c}{(d_s)^2 \cdot \varepsilon_c^3 \cdot C_c A_m} \quad (2.5)$$

where:

ε_c - the porosity of the cake,

C_f - the concentration in the feed,

V_c - the volume of the cake,

d_s - the diameter of the solute particle,

C_c - the concentration near the cake layer,

A_m - the membrane area.

2.1.5. Limitation of membrane filtration-flux decline/TMP increase

The deterioration of permeability with operating time is the main problem which undermines the economy of membrane technologies. The permeability decrease may be attributed to a number of factors such as membrane fouling, concentration polarization, changes in membrane properties and changes in characteristics of the feed water (Laine et al, 1989).

Membrane fouling is an important consideration in the design and operation of a membrane system. It is characterized as the adherence or deposition of solutes or particles inside the pores of the membrane or on the membrane surface. The adherence may be caused by electrostatic, Van der Waals or hydrophobic interactions. The forces causing deposition may be between particles or between

2. Literature review

particles and the membrane. Fouling can be biological, organic or inorganic. It must be considered in the selection of membranes to minimize membrane-solute or membrane-particle interactions that lead to fouling. The main strategies to minimize fouling include frequent cleaning, feed pretreatment, operating conditions optimization, membrane surface modification, and solution hydrodynamics alteration.

Concentration polarization is a concentration gradient between the membrane surface and the bulk flow of feed suspension due to the buildup of the retained species. It increases with increasing permeate flux, and reduces the driving force for permeation, which can result in a lower flux and a less selective separation (Bitter, 1991).

Figure 2.5. Membrane fouling at two operation modes

As illustrated in Figure 2.5 when membranes are fouled, the permeate flux may decline with operating time for constant pressure operation or, the TMP increases significantly for constant flux operation. During the microfiltration of particles or macromolecules, if the convection overcomes the back transport forces, the accumulation of particles or macromolecules occurs and eventually forms a cake layer on the membrane surface. The cake layer presents an additional resistance barrier for the filtration and may cause the adsorption of species in the cake layer to the membrane surface. In such a situation, a method is required to restrict the degree

2. Literature review

of concentration polarization and fouling. Therefore, the concept of ‘critical flux’ was proposed, as discussed in the next section.

2.1.6. Critical flux

The term ‘critical flux’ was initially defined by Howell (1995) and Field et al. (1995) as that flux below which there was no membrane fouling and the transmembrane pressure at a given permeate flux would be the same as with a pure solvent. Two forms of the critical flux hypothesis were then proposed, the strong and weak form. The strong form states that a flux exists which is equivalent to the corresponding clean water flux at the same TMP. The weak form states that on start-up a constant flux is rapidly established and maintained after some initial fouling due to adsorption or some large pore blocking (Wu et al, 1999). For both forms, a linearity between transmembrane pressure and permeate flux is observed before the flux reaches the critical value, and the break point of this linearity is used to identify critical flux. The difference between them is that for the strong form, the proportionality of the linearity is the same as the pure solvent; while for the weak form, the proportionality is different from pure solvent.

To measure the critical flux quantitatively, a number of researchers have developed several methods for their individual systems. One popular approach (Chen et al, 1997; Defrance et al, 1999; Chan and Chen, 2001; McAdam et al, 2005; Ye et al, 2005) known as ‘flux stepping’ is to operate the systems at a fixed flux for around 30 minutes and monitor the TMP simultaneously. With a step change in the flux from lower to higher values, a condition is reached where the TMP is no longer constant but rises with time. The corresponding flux is determined as the critical flux. Another approach (Espinasse et al, 2002) is also to vary the flux in steps but this is followed by returning back to a previous flux in alternative steps. If the TMP remains the same as before any fouling observed at the higher flux was considered to be reversible. The contrary condition was considered as irreversible and that flux was determined as the critical flux.

2. Literature review

In a review of ten years study on the critical flux concept, three important fluxes were summarized by Howell (2004) as being suitable for three groups of ‘users’ (Table 2.2). It was mentioned that both the advantages and limitations of this concept had to be considered and its application in the operations of real water and wastewater treatment plants needed to be evaluated further.

Table 2.2. Three important fluxes and their users (after Howell, 2004)

	User	System	Definition
<i>Critical Flux</i>	Theoretician	Ideal system	A flux at which for a defined particle in defined conditions there is no net force on the particle towards the membrane A flux at which particle/surface interactions just become irreversible
<i>Transition Flux</i>	Experimentalist	Defined system	A flux at which the linearity between TMP and flux breaks down under controlled flux operation A flux at which higher flux fouling cannot be reversed by reducing flux
<i>Sustainable Flux</i>	User	Real system	A flux pattern which is repeatable in a periodic cycle of operating and cleaning conditions such that there is no residual fouling A periodically repeatable flux pattern wherein the residual fouling remains below a target level for an economic time

2.2. Gas-liquid two-phase flow in submerged membrane systems

2.2.1. Submerged membrane systems with bubbling

The use of submerged hollow fibers in a membrane bioreactor (MBR) process is believed to be firstly reported by Yamamoto et al (1989). Unlike the cross-flow membrane filtration processes (Figure 2.6a) in which, transport of water through membranes is produced by providing transmembrane pressure with a recirculation pump, in the submerged membrane system (Figure 2.6b), the membranes are

2. Literature review

mounted or immersed either horizontally or vertically in the reactor and the permeate is withdrawn through the membrane by a pump or by gravity. Air bubbling is applied to the reaction tank to supply oxygen (MBRs), provide mixing

(a) External cross-flow filtration system

(b) Submerged membrane system

Figure 2.6. Schematics of external and submerged membrane configurations

(a). External cross-flow system; (b) Submerged system

in the tank, and to produce shear force at the membrane surface to control concentration polarization and fouling. The advantages of using submerged hollow

2. Literature review

fibers are that a high energy-consuming pump is not needed, the membranes are self-supported (no pressure vessel) and the modules are fabricated simply and economically.

Many studies have shown that the introduction of air bubbles into the membrane system, which results in a gas-liquid two-phase cross flow, is an effective technique to enhance the filtration with both UF (Cheng et al, 1998; Ghosh and Cui, 1999) and MF membranes (Ueda et al, 1997; Vera et al, 2000; Chang & Fane, 2000a, b; Judd et al, 2001; Chang and Judd, 2002). The influence of air injection on cross-flow membrane filtration (UF/MF) can be ascribed to the following aspects (after Chang & Fane, 2000a; Cui et al, 2003):

- 1) High gas flowrate injections into the feed stream results in increase in turbulence and superficial velocity, which can result in an improvement of permeate flux.
- 2) The augment of the airflow rate or the aeration intensity (as air flowrate per unit flow area) may reduce the suction pressure. The possible mechanism is that moving slugs cause pressure pulsing in the liquid around it, with a higher pressure at its nose and lower pressure at its tail.
- 3) Moving bubbles generate secondary flows and wakes which disrupt the mass transfer boundary layer and promote local mixing near the membrane surface.
- 4) Gas slugs can penetrate into the concentration polarization layer and displace the upper part of it, thus resulting in a less thick boundary layer.
- 5) The injection of air bubbles may prevent the deposition of suspended particles or membrane fouling to some degree by enhancing the movement of the fibers, which may stimulate the cake-removing efficiency. Furthermore, it can also alter the structure of the cake or fouling layer, thus reducing the specific cake resistance.

2. Literature review

2.2.2. Two-phase flow

Depending on the gas and liquid flowrates as well as the module geometry, a number of different two-phase flow patterns can be produced, which include bubble flow, slug flow, churn flow, annular flow and mist flow as shown in Figure 2.7.

Figure 2.7. Flow patterns for gas-liquid two-phase flow (Ghosh and Cui, 1999)

Among those patterns, slug flow was reported (Cabassud et al, 1997; Vera et al, 2000) to provide substantial flux enhancement in membrane filtration processes with tubular membranes. In the slug flow, most of the gas is located in large bullet shaped bubbles which have a diameter almost equal to the pipe diameter and are sometimes designated as ‘Taylor bubbles’ (Taitel et al, 1980; Chang, 2000b). The Taylor bubbles occupy most of the cross-sectional area of the tube, while a thin liquid falling film flows around it adjacent to the membrane surface and causes turbulence in the wake of the Taylor bubbles. Thus when the slug passes, high and transient shear stresses are produced as a result. Ghosh and Cui (1999) studied the beneficial effect of slug flow on the flux enhancement in the UF process through a mathematical approach by dividing one gas-liquid slug unit into three distinct zones, i.e., a falling film zone, a wake zone and a liquid slug zone. With this model the mass transfer coefficients can be estimated for each zone, and further used to predict the UF permeate flux. In addition, from the predicted results the authors

2. Literature review

suggested that gas sparging was more effective at higher TMP. The more potential concentration polarization the greater the effect of transient shear stresses.

Judd et al (2001) studied the impact of introducing slug flow into a tubular 'in-to-out' MBR and confirmed that it was the shear stress which enhanced the mass transfer and permeate flux. The effect of inter-fiber two-phase flow for controlling particle deposition or fouling of hollow fibers was studied by Chang and Fane (2000). By injecting the air into the space between the fibers rather than inside the fiber lumen it was shown that bubbling was effective in enhancing filtration performance. However the enhancement was not sensitive to changes in the two-phase flow mixture velocity when the operation was controlled by deposition in the falling film zone induced by slugs.

2.2.3. Factors affecting the performance of submerged hollow fibers

The performance of submerged hollow fibers can be influenced by various factors, such as air flow rate, bubble size, bubble efficiency, imposed flux, fiber diameter/density and length, fiber spacing and orientation, etc.

2.2.3.1. Effect of air flow rate

Ueda et al (1997) studied the effect of aeration on cake removal and suction pressure in a submerged membrane bioreactor (MBR) and concluded that an increase in the air flow rate could stimulate the cake-removal efficiency up to a critical value.

Fane et al (2002) performed experiments evaluating the effect of bubble flow rate on the hollow fiber filtration. Their results for the filtration of yeast suspension with two fiber diameters (shown in Figure 2.8) illustrate that airflow could significantly enhance flux as gas velocity increases from zero to a plateau, (0.3m/s), beyond which the increase in gas velocity did not improve the steady state flux of the pressure controlled filtration.

2. Literature review

Figure 2.8. The effect of gas velocity on final flux in filtration with submerged system (vertical axial bubbling), for two fiber diameters (Fane et al, 2002)

2.2.3.2. Effect of bubble size and frequency/intensity

Li et al (1997) performed experiments on lumen-feed fiber two-phase flow with dextran solutions to evaluate the effect of bubble size on the steady state flux under fixed transmembrane pressure. The results of flux vs. bubble size can be divided into two regions (Figure. 2.9). One was the increasing flux region with small bubbles and the other was a plateau region with larger slugs. Through increasing the air flowrate under a given bubbling frequency (air flow rate divided by bubble volume, i.e. time required for each cycle of bubbling) they obtained bubbles with increased sizes, and the increasing bubble size would result in a stronger wake, which could enhance the local mixing and mass transfer. As a result, an increase in permeate flux was observed in the first region. However in the plateau region, slugs occupied almost the whole cross-section area of the membrane tube and further increases in bubble volume could only increase the slug length for lumen-feed. Increasing the slug length has no effect on the wake size, which resulted in little

2. Literature review

effect on time-averaged shear stress inside the liquid film and no effect on permeate flux. The authors also indicated that permeate flux increased with a bubbling frequency increase from 0.1 to 0.2 Hz during examination for both dextran and human serum albumin (HSA) solutions. Increasing bubbling frequency means more bubble passages in unit time. Although these results were determined for lumen-side feed they may have parallels for air flow outside fibers (Yeo et al., 2006). Through investigation of a model submerged hollow fiber bundle of 9 fibers arranged in a 3 by 3 array, it was found that many small bubbles were more effective than a few large bubbles at the same volumetric flow rate. In addition, the authors used the standard deviations of the fluxes of the individual fibers as a representative indicator of uneven fouling inside the bundle to predict the imminent increase in the rise in TMP.

Figure 2.9. Effect of bubble size on permeate flux at various frequencies.

TMP=1.0(bar), feedstock dextran $C_F = 10.0(g\ L^{-1})$, liquid flow rate $1.0(L\ min^{-1})$, membrane length 1.18(m), frequency(s^{-1}).

*, 0.05; o, 0.1; Δ, 0.2; □, 0.5.

2.2.3.3. Effect of fiber diameter, flexibility and density

2. Literature review

The membrane filtration performance was sensitive to the change in fiber diameter as observed by Chang & Fane (2001a, b, 2002a, b). These authors found that smaller fibers had better performance than larger fibers in the two phase cross-flow. In the submerged system the benefit of small fibers was significantly enhanced by air injection because of the homogeneous slug flow formed in the small 'channel' between the fibers. In contrast, larger fibers were more sensitive to flux increments and reached the critical flux condition more quickly. Flexibility is another benefit of smaller fibers. By holding the fibers loosely rather than tightly, the suction pressure could be maintained constant, while a steady rise of the pressure was observed using a tight bundle (Chang & Fane, 2002c). However, an increased pressure drop on the lumen side and reduced length are the main drawbacks of smaller fibers which should be considered in fiber selection.

Fiber density also affects the membrane performance in the submerged system. Exploring the effect of fiber arrangement and density with different numbers of fibers, Chang & Fane (2001b) showed that for the 8mm fiber channel, the difference in flux decline with 4 and 8 fiber bundles was 12%, while for 24mm fiber channel, only 6% was observed. Therefore fiber density can be optimized in a submerged membrane system.

2.2.3.4. Effect of fiber orientation and spacing

Chang and Fane (2000b, 2002b) also observed that fluxes obtained with axial vertical fibers were significantly higher than those with the transversal fibers because of the trapped bubbles in the transverse orientation during a 2h filtration of 5g/L yeast suspension. The hollow fibers could benefit from the axial orientation due to mechanisms introduced in section 2.2.1, especially the surface shear transients which occurred as the bubbles moved upwards along the fibers and the lateral movement of the relatively loose fibers caused by the moving bubbles.

2.3. Activated carbon adsorption process

2. Literature review

2.3.1. General concepts

Activated carbon adsorption is a widely used separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the adsorbent surface than others or because the adsorption pores are too small to admit the larger molecules. In water treatment, activated carbon adsorption plays an important role in the improvement of water quality. It can be used to remove specific organic molecules that cause taste and odor, mutagenicity, and toxicity, as well as natural organic matter (NOM) that causes color and can react with chlorine to form disinfection by-products (DBPs) (Snoeyink and Summers, 1999).

Figure 2.10 shows the classification of pores in an activated carbon particle and their contribution to the adsorption process. Most adsorption on activated carbon takes place in the ‘micropores’ with mesopores and macropores providing accesses to the interior. This simplified view of activated carbon’s structure provides an insight into the special adsorptive properties of activated carbon and was used as a basis in describing carbon behavior under varying conditions (Perrish J. R., 1981).

Figure 2.10. Pore sizes in an activated carbon particle

2.3.2. Physical properties of activated carbon

2. Literature review

The performance of adsorption is determined by various characteristics of activated carbon including the raw material of manufacture, particle size distribution, apparent density, iodine number, and BET surface area, etc.

The predominately used *raw materials* to produce activated carbon for drinking water treatment are wood, peat, lignite, sub-bituminous coal, and bituminous coal. The manufacturing process involves two steps, which are carbonization and activation. In the former step, the raw materials are converted to char; followed by the latter step, in which the char is oxidized to develop the internal pore structure.

Particle size distribution refers to the relative quantity of different-size carbon particles in a given sample. It is important for the filtration properties of granular activated carbon (GAC) columns because the carbon particles play a dual role as filter and adsorber. GAC is typically in the range 400 μ m to 2.4mm (Snoeyink and Summers, 1999). Powdered activated carbon (PAC) is typically <50 μ m size.

BET surface area measures the adsorption isotherm for nitrogen gas and analyzes the data with the Brunauer-Emmett-Teller (BET) isotherm expression to determine the amount of nitrogen required to form a complete monolayer of nitrogen molecules on the carbon surface. The results normally indicate larger surface area than that is available for water treatment because the nitrogen molecule is relatively small compared to the adsorbates in water. Typical surface areas are of the order 1000 m^2 / gm , which signifies significant internal pore area.

Apparent density is the mass of nonstratified dry activated carbon per unit volume of carbon, including the volume of voids between grains. *Iodine number* measures the amount of iodine (mg / gm) that will adsorb under a specified set of conditions, and generally correlates well with the surface area available for small molecules.

2.3.3. Adsorption theory

2. Literature review

2.3.3.1. Adsorption equilibrium

Adsorbates are held on the activated carbon surface by various types of chemical forces such as hydrogen bonds, dipole-dipole interactions, and van der Waals forces. As for many compounds adsorbed on activated carbon, this process is reversible and referred to as desorption. The molecules accumulate on the surface continuously until the rate of the adsorption equals to the rate of desorption. Thus the equilibrium, which is termed as 'adsorption equilibrium', is reached and no further net accumulation will occur. Usually, adsorbed quantities at equilibrium increase with an increase in the solute concentration (see below).

The 'adsorption isotherm' is the relationship between the quantity of solute adsorbed per unit mass of adsorbent and the equilibrium concentration in bulk solution, at constant temperature. For single-solute adsorption, the Freundlich adsorption equation is the most widely used empirical equation to describe the relationship between adsorbent phase concentration and liquid phase concentration at equilibrium. The equation has the form:

$$q_e = KC_e^{1/n} \quad (2.6)$$

where q_e and C_e are the solute equilibrium concentration in the solid phase and liquid phase respectively, K and $1/n$ are Freundlich isotherm constants for a given system. K is related primarily to the capacity of the adsorbent for the adsorbate and its unit is determined by the units of q_e and C_e ; $1/n$ is dimensionless and represents a function of the adsorption bond. A large $1/n$ value indicates a strong adsorption bond and q_e is essentially a constant representing an irreversible isotherm. Conversely, a small $1/n$ indicates a weak adsorption bond and thus, q_e is sensitive to the change of the C_e value.

Equation 2.6 can also be written in logarithmic form:

2. Literature review

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (2.7)$$

The linear correlation of the Freundlich isotherm on a log-log scale based on equation 2.7 can be used to determine the K and $1/n$ values and further, to estimate the minimum amount of activated carbon required to reduce any initial solute concentration to a predetermined final concentration.

2.3.3.2. Adsorption kinetics

The activated carbon adsorption process generally occurs in the following steps as shown in Figure 2.11:

Figure 2.11. Activated carbon adsorption process

(1) External diffusion:

Adsorbates transport from the bulk solution to the liquid film layer surrounding the activated carbon particle by convection diffusion.

(2) Film diffusion:

Adsorbates migrate by molecular diffusion through the surface film to reach the exterior surface of the carbon. The higher the bulk fluid flow rate past the carbon particles, the thinner the layer thickness.

(3) Internal diffusion:

2. Literature review

Adsorbates transport from the particle surface into interior sites by diffusion into the pores (macropore, mesopore, micropore) of the activated carbon. This transport may occur by molecular diffusion through the solution in the pores (pore diffusion), or by diffusion along the carbon inner surface (surface diffusion).

(4) Adsorption:

Adsorbates are adsorbed on the active sites in the pores under the adsorption bond between the adsorbates and the carbon.

The effective rate of adsorption is controlled mostly by the step that exerts the greatest resistance to mass transfer - that is, the slowest step. In turbulent flow reactors, either the film diffusion or the internal diffusion could be the slowest step, and thus controls the overall rate of carbon adsorption. However, it is common that the adsorption rate is film diffusion controlled in the initial stage of the adsorption process in batch reactors. As the carbon becomes loaded with the adsorbents, surface diffusion becomes the controlling factor (Faust et al, 1987).

The dynamics of the adsorption process can be described using the well-developed homogeneous surface diffusion model (HSDM) (Crittenden et al, 1978a, b). This model has been applied by a number of researchers for adsorption of various organic compounds onto granular activated carbon (GAC) and powdered activated carbon (PAC) from water (Cook et al, 1998; Gillogly et al, 1998; Slaney et al, 1998; Campos et al, 1998, 2000a, b, c; Li et al, 2002). The kinetic parameters incorporated in the HSDM are the liquid film mass transfer coefficient, k_f (the rate of diffusion of the organic compound through the stagnant liquid film layer around the carbon particle), and the surface diffusion coefficient, D_s (the diffusion rate of the compound on the carbon surface within the carbon pores). There have been several reports on the solution of the HSDM (Hand et al, 1983; Traegner et al, 1989; Roy et al, 1993). Traegner et al (1989) developed an effective solution using the Levenberg-Marquardt numerical algorithm, which minimized the differences between actual batch data and the HSDM numerical solution. A simplified solution

2. Literature review

developed by Roy et al (1993) applied Laplace transforms to the partial differential equations. Solving the transformed equations and applying the inverse Laplace transform to the solution resulted in a set of non-linear algebraic equations as a function of time. An excellent match with other more complicated methods was also shown.

2.3.3.3. *Factors affecting carbon adsorption*

The adsorptive properties, including specific surface area, pore size distribution, the chemical nature of the surface, and water chemistry properties have strong effects on both the adsorption capacity and the adsorption rate (Perrish, 1981; Faust and Aly, 1987; Najm et al, 1991; Snoeyink and Summers, 1999).

1) *Adsorbate characteristics*

Branched-chain compounds are more adsorbable than straight-chain compounds, while depending on the type and location of the functional group. Adsorbates with low polarity and solubility tend to be adsorbed preferentially. Larger molecules diffuse slower than smaller ones and thus have lower adsorption rates.

Ionization is generally adverse to carbon adsorption as strongly ionized materials are poorly adsorbed.

2) *Activated carbon properties*

The maximal adsorption capacity is proportional to the amount of surface area within carbon pores that is accessible to the adsorbates.

For a given weight of carbon, decreasing the particle size can increase the surface area and shorten the time for achieving the equilibrium.

Pore size distribution within the carbon determines the favored adsorbate accordingly. Micropores correspond to adsorption capacity for small molecules, whereas mesopores and macropores correlate capacity for large molecules.

2. Literature review

Oxygenation (by aqueous chlorine) of the carbon surface leads to a decrease of adsorption capacity for simple aromatic compounds.

3) *Liquid and operating conditions*

High temperature usually slows or retards the adsorption process because the adsorption reaction is generally exothermic. Low temperature tends to favor adsorption, although rates and efficiency are affected in different ways.

Liquid pH suitable for molecule ionization may lead to a decrease in adsorption capacity.

Inorganic compositions of the liquid play different roles in the adsorption equilibrium depending on the adsorbate character and the variety of inorganic substances.

Increasing the initial concentration of the solute improves the adsorption capacity.

Good mixing and sufficient contact time are required for a better adsorption.

4) *Competitive adsorption by mixed molecules*

The extent of competition of multiple solutes on activated carbon depends on the relative molecular size and configuration, the relative adsorptive affinities, the relative concentration of the solutes, as well as the characteristics of the activated carbon.

2.3.4. Granular activated carbon (GAC) and powdered activated carbon (PAC)

Commonly available GAC particle sizes are 12×40 and 8×30 US Standard mesh, which range in apparent diameter from 1.68 to 0.42mm and from 2.38 to 0.59mm, respectively (Snoeyink and Summers, 1999). GAC is generally used in beds or columns that permit high adsorption capacities and easy process control. It can also be easily removed from the columns or beds for regeneration/reactivation when necessary.

2. Literature review

PAC differs from GAC primarily in particle size. Commercially available PACs typically show 65 to 90 percent passing a number 325 mesh (44 μ m) sieve, which is around ten times smaller than GACs. The primary advantages of the application of PAC in water treatment are the faster adsorption rate, low capital investment cost, flexibility of the addition point (intake, rapid mix, filter inlet, or slurry contactor preceding rapid mixing), and the ability to change dosage as water quality varies. On the other hand, the disadvantages lie in the inability to regenerate, the difficulty of completely removing PAC particles from water, and the increased difficulty of sludge disposal.

However, with the help of the membrane filtration technique, the drawbacks of the PAC can be partially overcome by removing PAC with high efficiency from the product water. In addition, the fast adsorption rate of the PAC can be utilized by adding the PAC at appropriate points to provide good mixing and sufficient contact times. PAC adsorption ensures a good pollutant removal and can work as a pretreatment for membrane fouling control. Therefore, in the following section the literature regarding the hybrid system, which combines the PAC adsorption with membrane filtration, is further reviewed.

2.4. Membrane filtration combined with PAC adsorption pretreatment

Combined PAC adsorption with membrane filtration (UF and MF) is a promising option for efficient removal of dissolved organic materials (DOC), such as trace organic compounds, natural organic matters (NOM), synthetic organic chemicals (SOCs), color, compounds responsible for taste and odor (T & O), and precursors of disinfection by-products (DBPs), etc. One commercial example is the CRISTAL® (Combination of Reactors, Including membrane Separation Treatment and Adsorption in Liquid) process which combines the advantages of membrane filtration and PAC adsorption. In this process, PAC can be dosed continuously at a constant rate to the membrane loop or dosed at the beginning of the membrane

2. Literature review

filtration cycle in the external membrane system. The membrane provides a physical barrier to prevent the passage of the PAC particles, therefore retaining the organic compounds adsorbed on the PAC, which otherwise would not be retained by the membrane. The main advantages of CRISTAL® process compared to conventional treatment systems were summarized by Laine et al (2000) as follows:

- It limits the competition effect between organic matter and trace organic compounds, since the adsorption kinetics of the trace organic compounds is faster than that of organic matters in a GAC filter or a sludge bed clarifier.
- It is flexible in that the dosage and type of PAC can be adapted to variations in influent water quality and spikes of particular pollutants.
- The filtration recirculation loop provides mixing energy, which helps to transfer the organic molecules and diffuse them towards the PAC (for the external membrane systems used); i.e. it improves the film mass transfer coefficient, k_f .
- There is no breakthrough or leakage of the kind observed at the outlet of GAC filters, since the PAC is added to the influent water on a continuous basis.

2.4.1. Factors influencing PAC adsorption performance in hybrid systems

Powdered activated carbon has an enhanced effectiveness of adsorption for removal of organic compounds, especially small molecular compounds, from water because of its large surface area. Based on gel permeation chromatogram (GPC) analysis results of lake water and pretreated water, Laine et al (1989,1990) reported that PAC was more effective in removing low-MW (molecular weight) compounds (MW<1,000) than the coagulation-flocculation process.

Many factors may affect the adsorption performance of PAC/ MF (UF) systems in drinking water treatment. Particle size distribution, pore size distribution, dosing procedure, and some other design and operational parameters such as temperature,

2. Literature review

pH, and the presence of different organic compounds or inorganic chemicals may affect the carbon performance (Randtke and Snoeyink, 1983).

The benefit of the addition of PAC includes (Najm et al, 1991a):

1. the provision of good mixing or good contact between the PAC and all the water being treated,
2. sufficient time of contact with adsorption of the contaminant,
3. minimal interference by treatment chemicals with adsorption on PAC,
4. no degradation of finished water quality.

By separating the composite PAC into three particle size fractions using an air classifier before the adsorption isotherms tests and batch kinetic tests, Adham et al (1991) observed that adsorption kinetics for smaller PAC particle size fractions were much faster than for larger size fractions, and thus smaller particles would require shorter PAC retention time to achieve a specific removal of target compound. These would result in a smaller recycle loop volume and less pumping energy requirement. Similar conclusions were drawn by Randtke and Snoeyink (1983), who observed although pulverizing GAC before determining its adsorptive capacity did not affect the adsorption capacity significantly, the time required to reach equilibrium was reduced. Najm et al (1990) also indicated that particle size has no apparent effect on PAC adsorption capacity.

A study by Adham et al (1991) reported that different initial adsorbate concentrations would result in different equilibrium capacities of the activated carbon. In order to minimize the effect of the initial concentration of the target compound on the adsorption capacity, the author suggested using essentially identical initial concentrations in all conducted experiments. However the Freundlich isotherm constant $1/n$ was not expected to be a function of initial concentration, thus a new isotherm test would not be necessary but batch test capacity K_a was used instead of isotherm capacity K . Najm et al (1991b) also indicated that the effect of initial concentration of synthetic organic chemicals on

2. Literature review

PAC adsorption capacity was more significant in natural water than in distilled-deionized water because of the competition of the background organic matter on the surface of the carbon.

Compared with continuously dosing throughout the operation cycle, Campos et al (1998) observed that lower atrazine concentrations in the permeate could be obtained by operating the PAC/UF loop with one-time carbon addition at the beginning of the cycle. The author observed that 35% more mass of atrazine was adsorbed when PAC was dosed at one time, and which resulted in a lower average atrazine concentration in the permeate than continuously dosing.

Li et al (2002) examined the displacement effect of NOM on atrazine adsorption by different types of PAC. Their results showed that different pore size distributions of PAC lead to different displacing rates, which revealed the effect of pore size distribution on the performance of PAC in treating raw water with some competitive pollutants during adsorption. Campos et al (2000) observed similar phenomena and claimed that a significant reduction in PAC adsorption rate for atrazine was observed when the PAC was pre-exposed to NOM for 2 hours.

2.4.2. Effect of PAC pretreatment on membrane performance

The combination of PAC with low-pressure membrane systems (MF or UF) has been extensively studied in the last decade and many results of these studies confirmed the positive effect of PAC adsorption on the stable membrane performance. By using PAC adsorption as a pretreatment, membrane systems could further reduce DOC, DBPs, pesticides and taste- and odor-causing compounds without obvious membrane fouling phenomena or with improved membrane performance (Adham et al, 1991, 1993; Pirbazari et al, 1992; Seo et al, 1996, Suzuki et al, 1998; Pianta et al, 1998; Campos et al, 1998; Jack et al, 1998; Best et al, 2000; Laine et al, 1990, 2000; Tomaszewska et al, 2002). However, other researchers have observed that PAC had no considerable effect or had an adverse

2. Literature review

effect on the membrane performance (Lin et al, 1999, 2000; Farahbakhsh et al, 2002; Zhang et al, 2003, Mozia et al, 2005).

2.4.2.1. Beneficial effects

Adham et al (1991) studied the addition of PAC in continuous membrane filtration processes and indicated that PAC removed organics and reduced the irreversible fouling. Based on their further research, Adham et al (1993) speculated on the mechanism of reduced flux decline in the PAC-MF/UF system by suggesting that PAC might have a scouring effect or filtration aid effect, which resulted in a reduction in the thickness of the cake layer or a reduction in the hydrodynamic resistance of the cake layer. In addition, PAC might increase the performance of larger pore membrane processes by adsorbing the fouling causing organic compounds, because the adsorption of organic matters on the membrane was claimed to be the main cause of irreversible fouling of UF membranes by Laine et al (1989, 1990).

In their study on a PAC-MF system, Pirbazari et al (1992) observed that PAC not only effectively removed humic substances, but also contributed to fractional steady-state permeate flux enhancement. Even for the distilled deionized water, the steady-state permeate flux was also enhanced by PAC addition. The researchers attributed this to the reduction of the boundary layer thickness by PAC and consequently, the mass transfer coefficient was increased. However in the absence of solute there should be no film resistance, so their observation may have been due to removal of trace foulants. Mohammadi et al (2005) also presented similar improvements in permeate flux in the study of wastewater treatment using a hybrid UF/PAC system and ascribed the enhancement to the PAC induced shear stress at the membrane surface and thus a decreased cake layer thickness.

Braghetta et al (2000) also observed a slightly increased flux for the UF membranes in their pilot test for evaluating the impact of clarification and adsorption pretreatment of surface waters on membrane performance and organics removal

2. Literature review

efficiency. This beneficial effect on operational performance of the UF system was explained as the PAC contribution to the removal of small organics from feed waters and its surface scouring effect on the membrane.

The combination of UF and PAC can also stabilize membrane fluxes during periods of high turbidity with strong quality fluctuations in treating water. In their research, Pianta et al (1998) conducted tests on MF in dead-end mode (low turbidity) with PAC and affirmed that PAC/UF is a feasible process for the treatment of karstic spring water which containing micro pollutants such as trichlorethene (TRI), tetrachlorethene (PER) and atrazine. They observed a stable permeability and that PAC did not affect fouling at low feed turbidity.

Jack et al (1998) obtained data from their pilot study and claimed that substantial deposition of PAC did not appear to hinder pilot performance but slightly improved TOC and DOC removal over the course of a single test.

To check the effect of PAC cake layer on the membrane performance, Thiruvengkatachari et al (2005) purposely made a PAC pre-coated MF membrane with three types of PACs for a domestic wastewater treatment. The PAC pre-coated membrane effectively retained the organic material and successfully limited the rapid decline in the permeate flux. The more PAC coated, the less the flux declined, and the PAC particles were reported to have a negligible effect on the permeability of the wastewater. On the other hand, upon combination with the organic material, an effective PAC-organic/PAC-particle multilayer matrix was formed on the membrane surface which could alter the rejection of the organics and thus reduce the amount of fouling material clogging the membrane. In addition, it was also found that the organic removal could only be improved to a certain level by increasing the amount of coated PAC.

Therefore the possible mechanisms by which PAC facilitates the membrane filtration (reduces the flux or permeability decline) can be summarized as: . A scouring effect of PAC on the membrane surface results in an attenuation of the

2. Literature review

cake layer thickness; . The adsorption of the compounds which tend to cause fouling results in irreversible fouling reduction; . A filtration aided effect results in a reduction in the hydrodynamic resistance.

2.4.2.2. Negative effects

Experimental results of a PAC/UF system by Tomaszewska et al (2002) showed that PAC addition resulted in effective removal of organic substances of both low and high molecular weights. However, the authors also observed that a porous PAC cake layer with a thickness of 0.2-0.5mm was formed on the UF membrane surface by using Scanning Electron Microscope (SEM). The researchers claimed that although PAC particles were too large to block the membrane pores inside, they deposited on the membrane surface and partially plugged the surface area. The PAC cake resulted in an increase in the filtration resistance and, as a consequence, a lower permeate flux than distilled water without PAC. Suzuki et al (1998) also observed slowly decreasing membrane permeability in their hybrid system of MF and PAC for the removal of humic substances.

Zhang et al (2003) argued that PAC accumulation at the membrane surface would result in part of the fouling layer, which overwhelmed the PAC effect on reducing the NOM concentration reaching the membrane. They also claimed that the PAC particles' interaction with both the NOM and the membrane surface could affect the benefits of PAC-membrane system to some degree.

Based on their comparative experiments on membrane filtration performance with and without PAC, Mavrov et al (1998) reported that the addition of PAC to the feed before the membrane stage made no contribution to the removal rate of the contaminants. Farahbakhsh et al (2002) also found that under all dosing conditions, PAC seemed to increase the rate of membrane fouling when compared with the run with no PAC pretreatment and also, no significant reduction of disinfection byproduct (DBP) was observed.

2. Literature review

Using PAC for pretreatment of humic substances or in combination with different UF operating systems to reduce membrane fouling, Lin et al (1999, 2000) obtained a negative effect of PAC pretreatment on the membrane performance. Although PAC alone in deionized water did not affect flux at all, the flux decline for PAC-treated streams was worse than the original humic substances with the same TOC concentration. Similarly, the combined PAC-UF system exhibited a significant flux decline and a poor removal of DOC and trihalomethanes formation potential (THMFP). Mozia et al (2005) reported that the addition of PAC in the UF loop for humic acid (HA) treatment had negligible to negative effects on the permeate flux independent of the membrane properties. Although PAC added into distilled water did not affect the permeate flux for all tested membrane materials, with the presence of HA, the permeate flux declined for PSF and CA membrane. The effect was attributed to the HA coating on the negatively charged membrane surfaces. Li et al (2004) also observed an enhancement of organic removal and an increased membrane fouling at the same time.

In summary, the different results of PAC-membrane system performance can be attributed to the differences in water chemistry; interaction among NOM, PAC particles and the membrane surface when NOM exists in the raw water; the type of PAC; the type and concentration of the contaminant to be removed; the membrane characteristics and membrane filtration operation strategies. It is likely that the negative effects occur due to the presence of submicron fines in some PACs, and that operation at elevated flux may exacerbate the problem. In addition, where adsorbed species coat the PAC particles the filter cake could show a high resistance if the interstitial voids are filled with NOM.

2.4.3. Hybrid system simulation

Mathematical simulation is useful to gain a quantitative understanding of the water treatment efficiency using the hybrid PAC-membrane process, as well as to identify optimal operating parameters. Quantitative approaches have been presented by several groups of researchers since the early 1990s (Adham et al, 1991, 1993; Qi et

2. Literature review

al, 1994; Campos et al, 2000a,b; Matsui et al, 2001a,b; Li et al, 2004a,b; Guo et al, 2005, Chang et al, 2005).

Adham et al (1991) applied a model for adsorption in a continuously stirred tank reactor (CSTR) to the PAC-UF system with a good agreement between model predictions and experimental performance. In their modeling, an apparent equilibrium capacity constant K_a obtained from the plateau of the batch kinetic tests was applied rather than using the Freundlich isotherm capacity K to achieve an excellent agreement. In their following study (Adham et al, 1993) on the PAC-UF system consisting two reactors (a CSTR for PAC adsorption and a UF loop) in series, the modeling was divided into two steps which were individually applied to each reactor. For the first step, equilibrium and kinetic parameters for virgin PAC were used; whereas for the subsequent reactor, the parameters for loaded PAC were obtained from batch tests through an empirical approach and then applied to the modeling. In addition, the steady-state CSTR model and the pseudo-steady-state PAC-UF model were applied to each reactor, respectively. Later, Qi et al (1994) also modeled the PAC-UF side stream system for a trace organic removal as a steady state CSTR and verified their modeling with data from a pilot scale PAC-UF system.

Campos et al (2000a, b) developed a group of models to simulate the organic removal in continuous flow reactors containing membrane separation units which were operated without carbon wastage between backwash events. In their study, PAC adsorption in the continuous-flow reactor, which is either a CSTR or a plug flow reactor (PFR), was considered as a steady-state operation, whereas adsorption in the subsequent membrane reactor was modeled as a non steady-state process. By assuming the adsorption kinetics were only surface diffusion resistance controlled, the HSDM for description of the PAC adsorption dynamics was applied in combination with the mass balances for the three tested system configurations to predict the removal of low concentration ($<0.1\text{mg/L}$) organics from water. The developed model was verified successfully using a bench-scale membrane reactor containing a flat sheet membrane in dead-end operation mode, and further used to

2. Literature review

evaluate the effect of various operating parameters, such as backwashing frequency, PAC particle size and dosing methods. Similarly, Chang et al (2005) developed a simplified model for single solute trace organics removal by a PAC/membrane system by applying the HSDM and the process mass balance. The model was verified using a dead-end mode membrane stirred cell system.

For bi-solute systems, Matsui et al (2001a, b) developed a model to predict the synthetic organic chemical (SOC) removal from natural water using a PAC-UF system. The model was based on the residence time distribution of PAC in the UF system, bi-solute isotherm as well as a pore-surface diffusion model. Data from a PAC-UF pilot plant consisting of a PAC slurry contactor and a UF loop were used for model verification. More detailed modeling for competitive adsorption effects in a bi-solute (NOM and trace organic) system was presented by Li et al (2004a, b). NOM competition with the trace organics on the adsorption sites in the PACs made the surface diffusion coefficient of the trace organic compounds no longer a constant value. Based on this consideration, a kinetic model was developed for the hybrid PAC-membrane system to describe pore blockage effects on the trace organic compound adsorption and verified with the bench-scale PAC-MF system containing polystyrene sulfonate and atrazine.

It can be seen that most of the previous researches (experimental or mathematical) were focused on investigating the system performance using PAC-membrane external loop systems. In the external membrane system, the operating pressure can be an important factor for membrane performance which requires high energy input. Also, if the pressure is too high, PAC cake formation on the membrane surface would be fast which could result in inefficient adsorption and increased filtration resistance. Considering the advantages of the aerated submerged membrane system as discussed in previous sections, it is worth a more detailed investigation on whether the hybrid PAC-membrane system can also be benefited from applying the submerged membrane system instead of the external system. A more effective and efficient PAC-membrane system is required to meet the increasingly stringent

2. Literature review

drinking water criteria and wastewater disposal or reuse regulations, from both technological and economic points of view.

2.4.4. Submerged membrane system with PAC adsorption

The submerged membrane system is a comparatively new and developing process for drinking water and wastewater treatment. Figure 2.12 shows a hybrid submerged hollow fiber membrane system with PAC in the aeration tank.

Most combined PAC-membrane systems have been in the form of an external or detached stirred adsorption tank coupled with a membrane separation reactor, as a circulation loop. Until recently, only a few researchers have investigated the performance of the submerged membrane with PAC suspension in the membrane filtration reactor. Lebeau et al (1998) assembled hollow fibers in shell-less modules

Figure 2.12 Schematics of hybrid submerged membrane system

and immersed them in a reaction basin which contained 5 to 20mg/L PAC slurry. Based on operation at low fluxes and low transmembrane pressures, the PAC-MF process provided good performance. The results showed excellent water quality

2. Literature review

through significant removal of particulate matter as well as NOM and SOC, excellent response to the variations of the feed water quality and feasibility for plant upgrading by converting existing clarifiers or sand filters into membrane reactors. The authors claimed that the immersed PAC-MF configuration ensured optimal and cost-effective utilization of PAC by allowing PAC aging inside the completely mixed reaction zone. In addition, the configuration provided an optimal mixing and contact between water and PAC for maximum effectiveness.

Modeling of the aerated submerged membrane system has been rare except for the study by Guo et al (2005). They developed a model for synthetic wastewater treatment using a PAC-submerged membrane system. The Talu adsorption equilibrium model (Talu et al, 1996) and the HSDM kinetics model in combination with the mass balance including a membrane correlation coefficient, which described adsorption onto the PAC layer deposited on the membrane, were used in this work.

Evidently, further study of the hybrid PAC-submerged membrane system for both organics removal efficiency and membrane filtration performance, as well mathematical simulation are required for evaluating the feasibility of such a hybrid system in real applications.

2.5. Activated carbon regeneration

For economic and environmental considerations, the saturated activated carbon (AC) may be either regenerated for subsequent reuse or considered as a hazardous waste which requires a special treatment before disposal. Generally, the former approach is preferable and it is potentially feasible. In the regeneration process, the objective is to remove previously adsorbed materials from the porous structure of the carbon, thereby reinstituting its ability to adsorb impurities. Activated carbon regeneration technology, which is necessary for a wider application of the carbon adsorption process, has been studied for many years. The regeneration techniques are based

2. Literature review

either on desorption, induced by increasing temperature or extraction with a solvent, or on decomposition induced by thermal, chemical, electrochemical or microbial processes (Figure 2.13).

Figure 2.13. Overview of spent PAC adsorbents regeneration techniques
(after Sheintuch et al , 1999)

Thermal regeneration is the most commonly applied method to restore adsorptive capacity of AC with efficiency (Suzuki et al, 1978; Chihara et al, 1981a, b, 1982; Perrish, 1981; Cannon et al, 1994; Salvador et al, 1999, Dunn et al, 2001). It involves not only thermal desorption, but also several different processes and chemical reactions. The process consists of drying, thermal desorption, and high temperature heat treatment in the presence of limited quantities of oxidizing gases such as water vapor, carbon dioxide, and oxygen. As the temperature increases, the AC saturated with adsorbates normally undergoes a scenario from a pyrolytic stage to an oxidative stage as shown in Figure 2.14. In the subsequent stages, the gasification is the most critical step which affects the reactivation of the product

2. Literature review

quality and also, requires high energy consumption to keep the temperature above 800°C.

Figure 2.14. Schematic diagram for thermal regeneration of loaded AC
(after Moreno-Gastilla et al, 1995; Snoeyink and Summers, 1999)

However, the main drawback of the thermal regeneration technique is that the carbon adsorption capacity normally decreases to a certain level during successive adsorption-regeneration cycles because of the deterioration of the pore structure (Mollah et al, 1996), the carbon loss (5-15%) due to attrition, burn-off and washout (Miguel et al, 2001). In addition, the exhausted effluent (steam or heated inert gas) needs further treatment.

Another common technique is **extractive regeneration** in which the chemical reagents with solubilizing capacity are applied to the exhausted AC. The GAC can be regenerated repeatedly with little loss of adsorption capacity (Martin et al, 1987). This method can also be used in combination with the thermal method as a two-step regeneration process. Ferro-Garcia et al (1996) reported that the physisorbed

2. Literature review

fraction of the adsorbates was extracted with organic solvents and the resultant GAC was more efficiently regenerated with the subsequent thermal methods. However, the chemical extraction regeneration using either organic or inorganic chemicals will lead to the problem of treating the solvent-adsorbate solution as well as a certain loss of adsorption capacity after several cycles of operation. A comparatively newly developed method, supercritical CO₂ modified with high proportions of organic solvents, could be a rapid extraction method for the recovery of herbicides from GAC (Taylor et al, 1996). The herbicide recovery increases with increasing extraction temperature, decreasing extraction pressure and increasing the proportion of liquid solvent in the CO₂ stream. A total recovery of the adsorption capacity was achieved even after several cycles by using this relatively expensive method (Salvador et al, 1995).

Decomposition is a method to regenerate the exhausted AC by destroying the adsorbed organics to nonhazardous materials through *chemical, microbial, or electrochemical* processes.

The *chemical* process includes utilization of chemical agents with oxidizing capacity, such as oxidants (Huling et al, 2005) and catalysts (Matatov-Meytal et al, 1997, Sheintuch et al, 1999) to degrade the adsorbates. The cost of the reagents employed and the incomplete regeneration efficiency are the main concerns for wide application of the chemical regeneration methods.

In the *microbial* process or *biological regeneration*, the carbon saturated with the biodegradable substances is placed in contact with a dispersed culture of microorganisms, which perform a small local regeneration. This method applies the bacteria activity based on desorptive and migrational movements of the adsorbate from the adsorbent toward the biocenosis of bacteria located on the external surface of the AC grain (Klimenko et al, 2004) or further diffusion to bulk liquid where biodegradation may occur (Roy et al, 1999). Bio-regeneration is the most economical process, however it requires long reaction times (Nakano et al, 2000)

2. Literature review

and can only be applied when the adsorbate is biodegradable and no other inhibition of the degradation process is present (Kim et al, 1990).

Electrochemical desorption is electrochemically influenced sorption. The system contains at least two electrodes that are connected via an external electrical circuit. The electrodes are packed beds of carbon particles with liquid flowing through. The mechanism is due to the formation of AC microelectrodes in an electric field and the resultant AC particle microelectrodes in fluidization mode could improve the organic degradation adsorbed on the AC surface (Wu et al, 2005). In detail, the sorption behavior is affected by the applied electrical potential. When low potentials are applied the adsorption equilibrium can be changed and shifted to desorption. When the applied potentials are higher, electrochemical Faraday reactions occur in addition to equilibrium changes. By exchanging electrons with the electrode, adsorbed molecules can be oxidized or reduced, converting them to less absorbable components or even to carbon dioxide and water (Fischer, 2001). The electrochemical method can be operated in-situ and the efficiency can reach as high as 80-95%, depending on specific regeneration methods and operating conditions (Zhang, 2002a, b).

Ultrasonic regeneration shows potential as an alternative to the chemical and thermal regenerations of GAC. Using this method, the desorption is facilitated by ultrasound. The desorption rates of the adsorbed molecules from GAC were favored by increased ultrasound intensity especially as temperature increases (Hamdaoui et al, 2003). Synergetic enhancement of the desorption rate was also observed through coupling ultrasonic irradiation (21, 800 kHz) and chemical regeneration (Hamdaoui et al, 2005). The desorption rate enhancement was attributed to acoustic vortex micro-streaming according to Rege et al (1998).

Microwave irradiation is another alternative to the traditional carbon regeneration method. It has the advantages of rapid and precise temperature control, small space requirements, energy saving as well as higher efficiency in intermittent use (Van et al, 1998). The levels of adsorption rates and capacities of the regenerated GACs

2. Literature review

were measured to be as high as or even higher than that of the virgin GAC (Quan et al, 2004, Liu et al, 2004) because of the improved mesopore range after microwave heating.

In this study a preliminary assessment is made of in-situ PAC regeneration in a hybrid submerged membrane system using UV-photocatalysis. The practical advantage of this is that the PAC adsorption, the TiO_2 photocatalysis and the submerged membranes can be combined in a single process.

2.6. Summary

Submerged membrane systems not only take the advantage of membrane filtration process to remove the contaminants from water but also minimize the membrane fouling and concentration polarization phenomena by applying air bubbling to the submerged membrane surface. As an improvement of membrane application, submerged membrane systems have attracted worldwide interest in wastewater treatment in the MBRs. In addition, they have also shown potential in surface water treatment when combined with the PAC adsorption process for the dissolved or even trace organics removal from contaminated water. This combined process makes it possible to achieve effective trace organics removal with a low pressure driven membrane unit with the help of the high efficiency of PAC adsorption of the low molecular compounds separation. Air bubbles work as a mixing method for full contact of PAC with the contaminants.

Up to the present, the study of PAC adsorption combined with a submerged membrane system is still limited. A systematical investigation of this hybrid process is required for its application in the water industry. What is the aeration effect on the adsorption process? How to quantify the target compound removal efficiency mathematically? What are the optimal operating conditions for better carbon utilization and longer membrane lifespan? How to deal with the saturated carbon? All of these questions initiate this study and lead to the focus of this thesis.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

3.

EFFECT OF AIR BUBBLING ON PAC ADSORPTION – COMPETITIVE ADSORPTION OF IMPURITIES*

3.1. Introduction

Activated carbon has been widely used for water purification in both industrial and municipal applications due to its large surface area per unit volume, and strong affinity for a wide range of dissolved organics. Najm et al (1991) observed that PAC had further advantages of requiring low additional capital expenditure as well as having the flexibility to be applied when needed. Recently, with the development of membrane technology for water and wastewater treatment, PAC adsorption can be combined with membrane units for the removal of some specific organic compounds from water. In particular, microsolutes (<1000Da), which cannot be removed by low pressure microfiltration (MF) or ultrafiltration (UF), can be removed by the hybrid PAC-membrane process (Campos et al, 1998).

In this hybrid membrane system, PAC adsorption converts microsolutes or dissolved organic matter to a particulate phase. Microporous MF/UF membranes can then separate these fine PAC particles, with adsorbed microsolutes in their pores, from the treated water. There is a potential cost saving compared with low cutoff, high-pressure membrane processes, such as reverse osmosis or nanofiltration. In the low-pressure hybrid process, the membranes may be located externally to an adsorption tank or submerged in the tank directly. In the latter case, air bubbling

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

could be applied to the tank to provide mixing and introduce shear force at the membrane surface in order to enhance separation efficiency.

Previous studies have confirmed the competency of PAC-MF/UF hybrid external loop systems for dissolved organic compound removal (Campos et al, 1998; Adham et al, 1991, 1993; Pirbazari et al, 1992; Laine et al, 1990). The combination of PAC with submerged MF membranes was also reported (Lebeau et al, 1998) and was used as a polishing step following conventional clarification or a single step membrane process for natural organic matter (NOM) and synthetic organic chemicals (SOCs) elimination. A significant enhancement of NOM and SOCs removal and an excellent response to variations of the feed water quality were observed at relatively low flux and transmembrane pressure (TMP). It has also been reported by Ujang et al (2002) that microbes could be removed more efficiently by adding PAC directly into an immersed MF reactor. Further, the application of submerged UF membranes integrated with PAC alone or together with an enhanced coagulation process was shown to be a promising approach for organics removal at the pilot-scale (Best et al, 2000). This system operated well at high PAC concentrations and led to increased adsorption and higher efficiency of total organic carbon (TOC) removal. It was noted that the membrane performance might also be improved, as the organics were preferentially adsorbed onto the PAC rather than on the membrane and a dynamic PAC barrier on the membrane surface was formed that appeared to prevent the deposition of the organic compounds.

It is evident that the previous studies of PAC-MF/UF hybrid submerged membrane systems have mainly focused on evaluation of the overall contaminant removal efficiency. The effects of air bubbling on the PAC adsorption as well as on the whole system performance were rarely reported. However, air bubbling has been proven to be effective for a single membrane filtration process by creating gas-liquid two-phase flow which increases local mixing and mass transfer and introduces secondary flow at the membrane surface and thereby improves membrane filtration by controlling concentration polarization and membrane fouling (Cui et al, 1996, 2003).

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

The PAC-MF/UF hybrid submerged membrane system is different from a single membrane process, as the carbon particles are suspended in the adsorption/filtration tank by vertical movement of the injected air bubbles. Thus, the gas-liquid two-phase issue in a single membrane process has been converted to a complex gas-liquid-solid three-phase problem in the hybrid submerged membrane process. How the air bubbles interact with PAC and affect PAC adsorption, which ultimately associates with the overall removal efficiency, is a critical concern in order to gain a deeper insight on the performance of such a system.

Therefore, this chapter aims to evaluate the impact of air bubbling on the adsorption efficiency of trace organic compounds by PAC in water. The adsorption kinetics at different air bubbling rates were compared with each other along with the results of traditional mechanical stirring as a reference. In particular, factors introduced by air bubbling which are likely to influence the adsorption process such as pH, O₂/N₂ competitive adsorptions, contaminant release from the system as well as the mixing mechanism were investigated.

3.2. Experimental

3.2.1. Materials

Powdered activated carbon (Norit SA-2) with original mass median diameter (d_{50}) of 20.0 μ m was provided by Behn Meyer Chemical(s) Pte Ltd. The specification provided by the supplier is presented in Table 3.1. To obtain carbon particles of smaller sizes, the original PAC was pulverized using a milling machine for different times. The particle sizes of pulverized powders were measured using a particle size analyzer (Malvern Mastersizer), which measured particle sizes based on laser diffraction.

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Table 3.1. Norit SA-2 general characteristics

Property	Norit SA-2
Molasses number (EUR)	340
Methylene blue adsorption (g/100g)	15
Iodine number	850
Total surface area (BET) (m^2/g)	950
Apparent density (tamped) (kg/m^3)	460
Particle size d_{10} (μm)	3
Particle size d_{50} (μm)	20
Particle size d_{90} (μm)	140
Ash content (mass %)	9
Moisture (as packed) (mass %)	2

Figure 3.1. Particle size distributions of PAC pulverized for different times

action in the range of 0.05-550 μm . The particle size distributions of PACs pulverized for different times are shown in Figure 3.1. Following preliminary tests the smallest PAC, with 6.3 μm d_{50} , was chosen as a representative adsorbent in this study. The PACs were oven dried at 105 °C before weighing.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Atrazine, one of the most widely used herbicides, was chosen as the target compound to represent trace organics frequently found in natural waters. The U.S. Environmental Protection Agency (EPA) has set an enforceable level called the maximum contaminant level (MCL) of 3 µg/L for atrazine. Exposure to atrazine above the MCL may potentially cause low blood pressure, muscle spasms, cardiovascular damage and cancer. The physical and chemical characteristics of atrazine are shown in Table 3.2. Its molecular weight of 215.7Da makes it a candidate for the hybrid PAC adsorption-membrane process.

Table 3.2. Atrazine characteristics

Chemical Name	Atrazine
Molecular formula	C ₈ H ₁₄ ClN ₅
Molecular weight (g/mol)	215.7
Solubility at 22 °C water (mg/L)	34.7
Henry's law constant at 25 °C (atm-m ³ /mol)	2.96×10 ⁻⁹
Vapor pressure at 25 °C (µPa)	38
Melting point (°C)	173-175
Polarity	Non-polar
Density at 22 °C (g/cm ³)	1.23
Chemical structure

A stock solution was prepared by dissolving dry atrazine (Sigma-Aldrich Pte.Ltd.) in Milli-Q water (Millipore, distilled deionized water, TOC<7µg/L) at a concentration of 10mg/L. A magnetic stirring hotplate (Vision Scientific Co. Ltd.) was used to provide mixing at 35 °C until atrazine was completely dissolved. After cooling at room temperature, the stock solution was stored in amber bottles at 4 °C.

3.2.2. Methods of adsorption equilibrium tests

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

The Freundlich isotherm was applied to determine the adsorption capacity of activated carbon to a particular organic by the equation:

$$q_e = KC_e^{1/n} \quad (3.1)$$

Where q_e and C_e are the adsorbate concentration at equilibrium in solid and liquid phase, respectively. To determine the Freundlich equilibrium constants K and $1/n$, 48h isotherm experiments were conducted using the method introduced by Perrish (1981). 48 h is sufficient for the adsorption to achieve equilibrium as results compared to those of 72 h test (Figure 3.2). The isotherm curves were obtained by

Figure 3.2. Freundlich adsorption isotherm, 48h vs. 72h, $d_{50}=6.3\mu\text{m}$, $C_0=200\mu\text{g/L}$

treating fixed quantities of target solution (200mL, 200μg/L) in nine flasks with a series of increasing amounts of carbon (0.0-5.0mg/L) and stirring for 48 h at room temperature (25°C). Then samples were collected from each flask and filtered through 45μm filters (Orange Scientific Pte.Ltd.) to separate PAC from the solution, which was then ready for concentration analysis.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

3.2.3. Methods of batch kinetic tests

To evaluate the adsorption kinetics of atrazine on PAC at different mixing conditions, batch kinetic tests were conducted with two different mixing methods, magnetic stirring and air bubbling at room temperature, respectively. In the magnetic stirring operation, a predetermined amount of 5mg PAC was added into a 1L glass bottle containing Milli-Q water spiked with 200 μ g/L atrazine, and mixed by a magnetic stirrer (Fisher Scientific Pte.Ltd.).

Figure 3.3. Schematic diagram of air bubbling system (Batch kinetic study)

Figure 3.3 shows the apparatus for the air bubbling operation. Air bubbles with a median diameter of about 3.3mm were generated continuously by a supply from a purified air cylinder, which was connected to a ceramic diffuser with PVC soft tubing or stainless steel tubing. A membrane filter (PTFE, 0.2 μ m) and a 4L bottle of Milli-Q water were arranged in series between the air cylinder and the diffuser to further remove impurities from the air and humidify the air. The air diffuser was placed at the bottom of the 1L volumetric cylinder which contained 200 μ g/L atrazine solution. The bubbling rate was adjusted using an air flowmeter (65mm, Cole-Parmer) installed between the diffuser and the gas cylinder. The container was

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

covered to avoid concentration variation by evaporation. Mixing was continuously maintained during sampling in order to avoid carbon concentration changes. The pH value of the solutions and the temperature were monitored simultaneously during each operation.

3.2.4. Sampling method

Prior to the additions of PAC into the container, duplicate samples were collected from the container to determine the initial concentration of the target compound. Then the atrazine concentration over time was determined by collecting 5mL samples at specific time intervals. The first three samples were collected every 20 s from the beginning of the test, followed by longer interval sampling times. The samples were immediately filtered through 0.45 μ m membrane filters to separate PAC from the liquid solution, and refrigerated at 4°C for analysis.

3.2.5. Analysis of atrazine

Atrazine concentrations were analyzed using a high performance liquid chromatograph (HPLC) (WATERS 2695, Separations module, XTerra C₁₈ column) with photodiode array detector (PDA) (WATERS 2996). The mobile phase was acetonitrile (50%) and 10mM ammonium bicarbonate buffer (50%) at pH 10. The samples were analyzed at a mobile phase flowrate of 1mL/min at 30°C and UV absorbance at 223nm. Without sample pre-concentration, the detection limit was 3 μ g/L, which is the same as the MCL in drinking water system enforced by the U.S. EPA.

3.3. Results and discussion

3.3.1. Adsorption isotherm test

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

The Freundlich isotherm fits to the adsorption equilibrium test data are shown in Figure 3.4. The smaller particles had slightly higher adsorption capacity than the larger ones. This effect may be due to the release of some micropores, which contain active adsorption sites in the carbon particles. Therefore, the adsorption ca-

Figure 3.4. Freundlich adsorption isotherm for PACs of different sizes,
 $C_0 = 200 \mu\text{g/L}$, 48h

capacity for small atrazine molecules in the micropores of PAC was improved. The surface area of the smallest carbon particle ($d_{50} = 6.3 \mu\text{m}$) was measured to be $1019 \text{ m}^2/\text{g}$ using a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation). Compared with the total surface area of original PAC ($d_{50} = 20.0 \mu\text{m}$), $950 \text{ m}^2/\text{g}$ listed in Table 3.1, the smallest PAC contains slightly more available adsorption sites and has the Freundlich equation as:

$$q_e = 70.06 C_e^{0.151} \quad (3.2)$$

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Freundlich constants K and $1/n$ are determined to be $70.06(\mu\text{g}/\text{mg})(\text{L}/\mu\text{g})^{1/n}$ and 0.151, respectively. To attain a desirable atrazine residual concentration $3\mu\text{g}/\text{L}$ in a short time (a few hours), $5\text{mg}/\text{L}$ PAC which is double the required value ($2.42\text{mg}/\text{L}$) according to equation (3.2), was dosed in the subsequent batch kinetic tests.

3.3.2. Initial tests with magnetic stirring and air bubbling

Figure 3.5 shows the atrazine adsorption rate on PAC particles with different sizes under magnetic stirring. It was found that the adsorption rate could be improved by reducing the carbon particle size. The major benefit is from the initial PAC to the

Figure 3.5. Adsorption rate of atrazine on PAC of different particle sizes,
 $C_c = 5\text{mg}/\text{L}$

ground particles which suggests the grinding had opened up some internal pores for adsorption. The smallest PAC of $6.3\mu\text{m}$ was used in the subsequent air bubbling study. The effect of air flowrate on $6.3\mu\text{m}$ PAC adsorption rate is shown in Figure 3.6. The dosage of PAC was $5\text{mg}/\text{L}$. Comparing the curves of air bubbling with that of the blank (unstirred) test, it can be seen that air bubbling enhances the PAC

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

adsorption rate. The higher the air flowrate, the higher the adsorption rate observed. This is attributed to the improved mixing and to the improved liquid film mass transfer, which will be discussed in a later chapter (Chapter 4).

Figure 3.6. Effect of air bubbling on atrazine adsorption by PAC, PVC tubing, $C_c = 5 \text{ mg/L}$

However, the bubbling had two contradictory effects on adsorption compared to the magnetic stirring. Two stages could be observed in the bubble-assisted adsorption process, i.e., an enhanced uptake stage followed by a noticeable reversal stage. The residual concentrations of atrazine in the initial stage up to about 60 min were lower under bubble agitation than under magnetic stirring. This indicates that air bubbles have a beneficial effect on the adsorption rate and the effect can be enhanced by increasing air flowrate. However, in the second stage the residual atrazine concentrations started to rise and were then higher than that of magnetic stirring and the difference increased over time, suggesting that there was an ongoing trend of reduced adsorption efficiency. A similar reversal was observed for the case of doubled PAC dosage, as shown in Figure 3.7. During each operation, the solution temperature varied within only ± 1 .

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Figure 3.7. Effect of air bubbling on atrazine adsorption by PAC of different concentrations, PVC tubing, Bubbling rate=1.5L/min

The reversal of the trace organic adsorption is clearly undesirable. Several factors were postulated to account for the phenomena, as follows:

- (i) pH changes due to air stripping of absorbed CO₂;
- (ii) competitive adsorption of N₂ and O₂ from the air-saturated solution;
- (iii) mixing effects;
- (iv) contaminants introduction with the air supply, specifically plasticizers leaking from the PVC tubing.

The impact of each of these factors is examined below.

3.3.3. Effect of pH increase during bubbling

The pH of fresh Milli-Q water was consistently measured to be around 5.5. This is probably because distilled deionized water is an excellent solvent which can pick up

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

CO₂ from the atmosphere. After introducing CO₂-free air bubbles to pure Milli-Q water, its pH increased from 5.5 to 7.6 as a result of CO₂ removal from the water by air stripping, as shown in Figure 3.8. For the solutions containing atrazine and PAC, similar results were observed where the pH increased from 5.5 up to 8.0 during each bubbling test.

Figure 3.8. pH increase in the bubbling batch kinetic tests, $C_c=5\text{mg/L}$

To examine the effect of pH on the adsorption kinetics, Milli-Q water was pre-bubbled for 100 min to maintain pH 7.9, and then spiked with atrazine followed by PAC dosing. Figure 3.9 shows the adsorption results for these solutions under bubbling and magnetic stirring, respectively, along with their counterparts prepared by fresh Milli-Q water. It can be seen that pH variance had little impact on the adsorption kinetics of atrazine. However, the reversal phenomena still appeared regardless of solution pH difference. To further confirm this, the atrazine solution was buffered at pH 6.9, 7.9 respectively before addition of PAC in another set of batch kinetic tests. The reversal still showed up in each test. Clearly, pH rise was not the main reason for the reversal phenomenon in the process of atrazine adsorption.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Figure 3.9. Effect of pH on adsorption kinetics, pre-bubbled Milli-Q water,

$C_c = 5\text{mg/L}$, Bubbling rate = 2.7L/min

3.3.4. N_2 and O_2 competitive adsorption with atrazine solutes

It is known that dissolved oxygen can be adsorbed by activated carbon at room temperature and 2-5% of the adsorbed oxygen can be displaced by nitrogen sparged water (Prober et al, 1975). It was postulated that the reversal could be caused by the competitive adsorption between N_2 , O_2 and atrazine solutes, as some adsorbed atrazine may give up active sites to N_2 and O_2 with bubbling time. To confirm this hypothesis, the solution, which had already reached adsorption equilibrium after 48-h of magnetic stirring, was aerated with air bubbles and the residual concentrations were analyzed every 30 min. The result is shown in Figure 3.10. The residual concentration was found to increase over bubbling time. The trend is more pronounced at higher bubbling rates. But surprisingly, the residual concentration continuously increased even after bubbling has been stopped for 12 hours.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Figure 3.10. Effect of air bubbling on adsorption after adsorption equilibrium, $C_c = 5\text{mg/L}$

Figure 3.11. Effect of He gas bubbling on adsorption after adsorption equilibrium, $C_c = 5\text{mg/L}$

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

To clear the confusion, similar experiments were performed using inert Helium gas instead of air as the bubbling source and the result is shown in Figure 3.11. The results were similar to those with air bubbling (Figure 3.10). Thus, the reversal observed in Figure 3.6 was not due to the competitive adsorption between N_2 , O_2 and atrazine.

3.3.5. Mixing mechanism

It was noticed that the gas bubbling provided vertical movement of the liquid in the cylinder and its mixing mechanism was qualitatively different from that of magnetic stirring. In order to check whether the different mixing mechanisms could contribute to the reversal phenomenon, a 6-h bubbling followed by a 74-h rest and

Figure 3.12. Bubbling test followed by magnetic stirring, $C_c=5\text{mg/L}$,
Bubbling rate= 2.7L/min

then a 44-h magnetic stirring was conducted. The result in Figure 3.12 shows that the lowest atrazine concentration ($C/C_0=0.07$) appeared after the first 120 min of

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

bubbling. From 2 h onwards, the atrazine concentration kept steadily increasing to about 0.33 at the end of the test whether it was mixed or not and irrespective of the type of mixing applied. This demonstrates clearly that once the reversal occurred after bubbling, even mechanical mixing could not restore the original adsorption efficiency. It appears that more and more atrazine solutes desorbed back into the liquid phase with time regardless of the mixing method. Therefore, the mixing mechanism was also excluded as the reason for the reversal phenomenon.

3.3.6. Contaminants introduced with the air

The reversal of the atrazine adsorption was characteristic of a competitive phenomenon. Therefore, the possibility of contaminant introduction was considered. In the original equipment set-up the air was introduced through a length of PVC tubing, the end of which (about 40cm) was immersed in the liquid (Figure 3.3). This raised the possibility of contaminant leakage from the tubing into the liquid. Furthermore, comparing the kinetic curves in Figure 3.6, the reversal is more obvious at the higher bubbling rate and this raises the possibility that contaminant could be extracted from the tubing by uptake into the transported air.

Therefore to examine the possibility of contaminant leakage, two magnetic stirring tests were conducted with one or two sections of 40cm long fresh PVC soft tubing submerged spirally in the bottle, respectively. From Figure 3.13 it can be seen that a similar reversal of atrazine concentration occurred as in the previous bubbling tests; recall that reversal was never observed in the magnetic stirring tests without PVC tubing in the solution. This strongly suggests that some contaminants released from the PVC tubing are the species competing for the activated carbon adsorption sites with the atrazine.

At the beginning of each test, the dominant solute in the solution would be atrazine while the contaminant concentration was comparatively low since the contact time of the tubing with the air and the solution was short. The adsorption of atrazine would be strongly driven by the concentration gradient between the bulk solution

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Figure 3.13. Investigation of the tubing contaminants leakage using magnetic stirring tests, $C_c=5\text{mg/L}$

and the carbon surface. Thus, the competition between atrazine solutes and contaminant molecules would be negligible and no reversal phenomenon would be observed in the initial stage. However, as adsorption proceeded, more and more contaminant would have leaked out and accumulated in the solution, while the atrazine residual concentration in the solution tended to approach equilibrium with that on the solid phase. Gradually the increasing contaminant concentration could not be ignored when compared with the decreasing atrazine concentration. These contaminant molecules appear to have displaced the adsorbed atrazine solutes from the active sites of the carbon and accordingly, the residual concentration of atrazine has been observed to increase at the later stages of the kinetic tests.

The results in Figure 3.14 further demonstrate the competitive adsorption between the contaminants and atrazine solutes. In an 8-h pre-bubbled solution, which had an initial contaminant concentration before PAC dosing, the atrazine adsorption efficiency was clearly much lower than that in the solution without contaminants at the beginning of the test. This implies that the affinity of the contaminant solutes for

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

PAC is very strong. The displacement resulted in the re-appearance of desorbed atrazine in the liquid and thus the increment of the residual concentration over time. Therefore, the contaminant released from the soaked PVC tubing was concluded to be the main reason of the reversal phenomenon.

Figure 3.14. Investigation of the tubing contaminants leakage using bubbling tests,
 $C_c=5\text{mg/L}$, Bubbling rate= 2.7L/min

The PVC tubing was made of virgin PVC and a plasticizer. The plasticizer consists of 2-Ethylhexyl Phthalate (DEHP), a commonly used material to impart flexibility to PVC. It has been reported that DEHP is not chemically bound to the PVC polymer and might vaporize or leak readily from PVC into the environment and present as a ubiquitous environmental contaminant (Inoue et al, 2003; Otake et al, 2001; Kambia et al, 2001). Thus in the bubbling tests, the contaminants released from the PVC tubing were probably DEHP or some other materials used in the plasticizer. Analysis of DEHP in atrazine solution was obtained by HPLC (SymmetryShield RP 8 column, 20% of Milli-Q water and 80% of acetonitrile). A section of PVC soft tubing was soaked in an atrazine solution ($200\mu\text{g/L}$) for 2 weeks and the solution was then analyzed. A small peak was detected at the same

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

detention time (Figure 3.15), around 9 min, as the standard DEHP (Fluka) and this indicates the occurrence of this compound in the atrazine solution and provides further evidence for our hypothesis.

Figure 3.15. Analysis of DEHP with HPLC

3.3.7. Bubbling tests with stainless steel tubing

To investigate the sole effect of air bubbles on the adsorption kinetics, batch tests were conducted using the previous system but substituting all PVC tubing with stainless steel hard tubing. As shown in Figure 3.16, the adsorption rate increased with an increase in bubbling rate. The higher the air bubbling rates, the faster the adsorption approached equilibrium. None of the tests exhibited the reversal of atrazine concentration that occurred in the previous experiments. This further confirms the detrimental effect of the contaminants released from the soft PVC tubing.

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

Figure 3.16. Effect of air bubbling on atrazine adsorption by PAC, stainless steel tubing, $C_c=5\text{mg/L}$

These observations have implications for the use of hybrid PAC-membrane processes for trace organics removal. It is already recognized that natural organics (humics etc.) can compete with the adsorption of low molecular weight trace organics (Ujang et al, 2002). However, the competition is likely to be greater in the situation examined in this study which involves relatively low molecular weight contaminants, such as DEHP. With a similar range of molecular weight, DEHP (MWt 390.6 Da) and atrazine (MWt 215.7 Da) may compete with each other for the active sites of the carbon particles. In addition, DEHP is believed to exhibit higher affinity for activated carbon than atrazine according to data tabulated by Snoeyink and Summers (1999). It is seen in Table 3.3 that the reported K value for DEHP ($K = 11,300$) is much higher than that for atrazine ($K = 289$). Although the data were determined for a different type of carbon from the PAC used in this study, they imply a significant difference in the relative adsorbability of the compounds. This evident difference in the Freundlich isotherm parameters supports the competitive adsorption effect between DEHP and atrazine, which resulted in a

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

portion of adsorbed atrazine (<10%) being displaced in the end of the 6-h batch tests. Therefore, the common practice of using certain types of plastic tubing for air delivery in submerged membrane systems may need to be reconsidered.

Table 3.3. Freundlich adsorption isotherm parameters for atrazine and DEHP
(from Snoeyink and Summers, 1999)

Compound	$K(\text{mg/g})(\text{L/mg})^{1/n}$	$1/n$
2-ethylhexyl phthalate (DEHP)	11300	1.5
Atrazine	289	0.291

3.4. Conclusions

The effects of air bubbling, and accompanying factors, on the trace organic adsorption kinetics by powdered activated carbon in water have been systematically investigated. The pH change during air bubbling was shown to have little influence on the adsorption efficiency. N_2 and O_2 were also found to have no competitive impact on the target atrazine adsorption in the bubbling condition though they might be adsorbed by carbon.

However, the contaminants released from PVC soft tubing had a negative effect on atrazine removal. Atrazine was observed to be displaced by the contaminants and desorbed from the carbon particles, which resulted in a reversal of adsorbed atrazine and reduced adsorption efficiency. This observation suggests that the use of PVC tubing for air or liquid transport should be avoided in PAC-UF/MF hybrid systems for water treatment, especially for water with trace pollutants at ppb levels. Our results from adsorption kinetic tests using stainless steel tubing for air transport confirmed this conclusion. However, this reversal effect can probably be ignored for treating wastewater with pollutants above the ppm level. The results also indicate that the adsorption process can benefit from higher air bubbling rates, this effect is discussed in more detail in Chapter 4. In addition, the bubble size can also

* The material in this Chapter has been published in:
“Separation and Purification Technology, 46 (2005) 79-87”

3. Effect of air bubbling on PAC adsorption-competitive adsorption of impurities

produce impact on the adsorption rate so that further investigation of this factor is needed in the future.

Acknowledgement

The author would like to acknowledge Professor William B. Krantz for his valuable advice in this part of the work.

4.

ATRAZINE ADSORPTION BY PAC - IMPROVED MASS TRANSFER BY AIR BUBBLING*

4.1. Introduction

In membrane filtration systems, moving bubbles generate shear and liquid movement that can disrupt the concentration polarization layer or cake formation, diminish the boundary layer resistance and accordingly, increase the permeability (Chang et al, 2001b) and prolong the operating lifespan (Ueda et al, 1997). Although the effect of bubbling on membrane processes has been actively studied and reviewed (Cui et al, 2003), the role of bubbling on the PAC adsorption process is not yet elucidated. Improved adsorption kinetics by bubbling were observed in Chapter 3 if no other impurity was introduced during the process of air bubbling. As introduced in Chapter 2, the adsorption process consists of four consecutive steps (Faust et al, 1987): (1) external diffusion in the bulk solution; (2) diffusion in the liquid film surrounding the carbon particle; (3) surface diffusion through the pores of the carbon and (4) the contaminant being adsorbed onto the active sites in the micropores. Of these, the bubbling may have effect on the first two steps.

Mass transfer in gas-liquid-solid systems has been intensively studied in chemical engineering for decades (Albal et al, 1983; Arters et al, 1986; Kluytmans et al, 2003; Ruthiya et al, 2004). However, different from a typical three-phase system, the bubbling applied to the PAC-submerged membrane system acts only to promote mixing and turbulence without involving mass transfer in the gas phase. The

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

situation is similar to a previous study (Sedahmed et al, 1989) on the rate of solid-liquid mass transfer with interfacial bubble generation, where mass transfer took place only at the solid-liquid interface and no mass was exchanged with the bubbles. Their study referred to: (a) the ascending bubble swarm causing an upward flow which reduces the diffusion layer thickness at the solid surface and (b) the detached bubbles inducing radial momentum transfer which brings a fresh supply of the liquid reactant to the solid surface. Although their discussions were based on a larger flat solid surface, it may still assist in understanding the effect of upward bubble motion on the mass transfer in the suspended PAC particle-liquid system. Other researchers (Sanger et al, 1981) have reported that the liquid-solid mass transfer coefficients increased with the gas velocity up to 0.06m/s, but were constant at higher gas throughputs. The particle Reynolds number (Re) was correlated to an energy dissipation rate to avoid the difficulty of estimating the relative velocity between the suspended particle and the fluid. This method is more suitable for relatively high Reynolds (>1500), which are not appropriate to our low air flows and small particle sizes; our Reynolds numbers are of the order 10^{-1} . However, we have observed improved adsorption kinetics by bubbling in our previous study (Jia et al, 2005), provided no other impurity was introduced during the process of air bubbling.

The enhancement of liquid-solid mass transfer by mechanical stirring has already been well studied (McCabe et al, 1993). Since the air bubbling in our system plays a similar role to mechanical stirring in enhancing mixing, we aim to link the superficial gas bubbling velocity to a mechanical stirring speed by a mixing experiment. Assuming a relationship between mixing and liquid flow patterns and mass transfer, we then use mass transfer correlations developed for conventional mechanically stirred systems to determine the effect of bubbling on mass transfer from liquid to PAC particles. In addition, as intermittent bubbling can be used to improve membrane performance instead of continuous bubbling to reduce energy consumption and cost, the effect of this approach on the PAC adsorption kinetics has also been examined. This chapter should provide insight into the preferred

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

bubbling conditions that could be applied in the hybrid membrane-adsorption process.

4.2. Background

The dynamics of the adsorption of organic compounds onto activated carbon in water can be described using the well-developed homogeneous surface diffusion model (HSDM) (Hand et al, 1983). The model incorporates the liquid film mass transfer coefficient and the surface diffusion coefficient to describe the overall carbon adsorption process. It is commonly recognized (Faust et al, 1987) that the adsorption rate is controlled by the boundary layer film diffusion in the initial stage of adsorption in batch reactors. Eventually as the carbon becomes loaded with the adsorbates, surface diffusion becomes the controlling factor. Therefore, to observe the bubbling effect on the mass transfer in the liquid film, an alternative to fitting data to the complex HSDM is to use a simple approach based on the general mass balance in a batch kinetic adsorption test to describe only the initial stage of an adsorption process. In a latter chapter (Chapter 5) the HSDM is applied to analyze the batch data. For the simplified approach we assume that the film diffusion is the rate-controlling step in the initial stage of atrazine adsorption (Aksu et al, 2004), and thus, the rate of concentration change is approximately equal to the film diffusion rate. The atrazine concentration change in the bulk liquid with adsorption time can then be described using the following equation:

$$\frac{dC}{dt} = -K_l a (C - C_s) \quad (4.1)$$

where C is the adsorbate concentration in the bulk solution at time t , C_s the liquid phase adsorbate concentration at the solid-liquid interface, K_l the mass transfer coefficient in the liquid film and a is the specific interfacial area based on the

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

liquid volume for a completely mixed batch reactor. At the beginning of the kinetic test, C_s is near zero and equation (4.1) can be simplified as:

$$\frac{dC}{dt} = -K_l a C \quad (4.2)$$

Solving the first order equation (4.2), the K_l can be written as:

$$K_l = -\frac{1}{a \cdot t} \ln \left(\frac{C}{C_0} \right) \quad (4.3)$$

where C_0 is the initial adsorbate concentration in the bulk solution at $t = 0$. Based on the experimental batch data, an estimate of the mass transfer coefficient at different bubbling rates in the initial stages can be obtained.

The experimental liquid film mass transfer coefficients surrounding a particle in the completely mixed batch reactor can be compared with available correlations (McCabe et al, 1993) via the Sherwood number:

$$K_l = \frac{Sh \cdot D_v}{d_p} \quad (4.4)$$

where Sh is the Sherwood number, D_v is the volumetric diffusivity for dilute liquid solutions, d_p is the carbon particle diameter. For mass transfer to an isolated sphere, the Sherwood number can be estimated from (McCabe et al, 1993):

$$Sh = 2.0 + 0.6 Re^{1/2} Sc^{1/3} \quad (4.5)$$

where Re is the Reynolds number and Sc is the Schmidt number. Equation (4.5) is claimed to be accurate for Reynolds number up to 1000. The Reynolds number for a particle in a fluid is defined as:

*The material in this Chapter has been published in:
 “Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

$$\text{Re} = \frac{u_0 \rho d_p}{\mu} \quad (4.6)$$

in which u_0 is the relative velocity of the particles to fluid. ρ the density of the solution and μ is the viscosity of the solution. For a mechanically stirred vessel the upper limit of u_0 would be the tip speed of the impeller, nd_a . In our situation d_p is of the order $10\mu\text{m}$ (10^{-5}m) which requires $u_0 > 100\text{m/s}$ to give $\text{Re} = 1000$. In the bubbled vessel, the used u_0 will be $< 1\text{ m/s}$. So equation (4.5) should apply.

The Schmidt number is defined as:

$$\text{Sc} = \frac{\mu}{\rho D_v} \quad (4.7)$$

The volumetric diffusivity for dilute liquid solutions can be calculated approximately from the following equation (McCabe et al, 1993) which is valid only at low solute concentrations:

$$D_v = 7.4 \times 10^{-8} \times \frac{(\psi_B M_B)^{1/2} T}{\mu V_A^{0.6}} \quad (4.8)$$

in which ψ_B is association parameter for the solvent (for water $\psi_B = 2.6$), M_B is molecular weight of solvent, T the absolute temperature and V_A is the molar volume of solute as liquid at its normal boiling point.

4.3. Experimental

4.3.1. Materials

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

PAC with a mass median diameter (d_{50}) of 6.3 μ m (milled) was used in the experiments. The preparation of the PAC particles and atrazine solution, as well as the atrazine concentration detection method were described in Chapter 3.

4.3.2. Methods

The bubbling mixed batch kinetic tests were conducted using the same set-up as in Chapter 3. Air was transported by stainless steel tubing in all the tests to avoid contaminant uptake. Intermittent bubbling was conducted using the same apparatus and a solenoid valve, which was installed between the gas cylinder and the reactor. Two intermittent regimes were compared with on/off periods of 0.5s-on-1.0s-off and 0.5s-on-2.0s-off, respectively.

To correlate air bubbling with magnetic stirring, a series of mixing tests were conducted. The vessel used for mixing was the same as that for batch adsorption, which was 0.06m in diameter, 0.44m in height and with an operating volume of 1L. Acridine Orange Base (AOB dye) was used as the target compound and a spectrophotometer (Jasco) was used to detect the target concentration at UV491nm. At the start of mixing, 5mL of the AOB dye at a concentration of 1g/L was injected quickly into the bottom of the vessel in which mixing was provided by either magnetic stirring or air bubbling. Immediately, a series of samples from the top of the liquid were taken by a peristaltic pump sipper (Jasco NPF-509) installed inside the spectrophotometer. Sample measurement was performed automatically after sample suction and the AOB concentrations were recorded after measurements by a connected computer.

4.4. Results and discussion

4.4.1. Continuous bubbling

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

The effect of air bubbling rate on the adsorption rate at a carbon dosage of 5 mg/L in the batch kinetic tests is compared with magnetic stirring results in Figure 4.1. Air bubbling was beneficial to adsorption provided air bubbles generated a little turbulence. For the 0.5L/min bubbling rate, atrazine adsorption was slightly slower than that of magnetic stirring. However, when compared with the unstirred test, the adsorption process performed much better if a few bubbles were sparged into the

Figure 4.1. Effect of air bubbling on atrazine adsorption by PAC ($C_c=5\text{mg/L}$)

system. The low bubble rate could still provide adequate mixing to facilitate PAC adsorption. For the 1.5, 2.7 and 5.0L/min bubbling tests, the initial slopes of the kinetic curves dropped more rapidly than that of magnetic stirring, indicating a faster adsorption rate. Therefore, bubbling is an effective mixing method for adsorption by suspended PAC and the bubbling rate is an important parameter to be considered for maximizing the adsorption rate economically.

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

Figure 4.2. Effect of air bubbling on atrazine adsorption by PAC, $C_c = 10 \text{ mg/L}$

Figure 4.2 shows the results of similar experiments as in Figure 4.1 but for double the PAC dosage. Comparing these two figures, the adsorption rate increased with the increase of PAC dosage at all conditions. In the 10 mg/L PAC tests, it was found that the adsorption rate could be improved significantly (compared with no stirring) by introducing only a low air flow rate (0.2 L/min). Almost complete atrazine removal could be rapidly achieved by introducing bubbles at the rate of 3.0 L/min . For the two carbon dosages, further increase in bubbling to 5.0 L/min (data not shown in Figure 4.2) did not noticeably enhance the removal rate indicating that there is a limit to bubble-induced mass transfer. From economic considerations, the optimum bubbling rate should be sought first through batch tests before being applied to the hybrid membrane system. However the scale-up of vessel size and sparging needs to be considered.

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

4.4.2. Correlation between the bubbling rate and the magnetic stirring speed

In order to compare the mass transfer coefficients in the bubble mixed batch kinetic tests with predictions for mechanical stirring, the air bubbling rate was correlated to the magnetic stirring speed through a set of mixing experiments. Figure 4.3 shows

Figure 4.3. Response of AOB dye concentration at the top of liquid, magnetic stirring

the results of the AOB dye tracer tests with concentration increase with time at different magnetic stirring speeds. It can be seen that the higher the stirring speed, the faster the concentration reaches a maximum value which represents a fully mixed solution. The times for achieving 60% of maximum concentration are 13.6, 11.8, 10.0s at magnetic stirring speeds of 26, 47, 85rpm, respectively. Sixty percent was chosen as the point of comparison because the curves of mixing extent over time were smooth in this medium region so that the sharp changes in the slopes of the curve around lower and higher percentages can be avoided for more reliable comparison. Plotting these time and stirring speed values gives a linear relationship (Figure 4.4):

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

$$u_m = -16.39t + 246.1 \quad (4.9)$$

where u_m is the magnetic stirring speed (rpm). Equation (4.9) provides a means for estimating what magnetic stirring speed has a similar mixing effect as a certain air bubbling rate.

Figure 4.4. Linear regression of the stirring speeds vs. time required to achieve 60% of complete mixing

As shown in Figure 4.5, the response to the air bubble mixing has a similar trend to the magnetic stirring. The higher the bubbling rate, the faster the liquid was fully mixed. The times to reach 60% of the maximum concentration are 12, 10.7, 4.6, 4.0s at 0.5, 1.5, 2.7, 5.0L/min bubbling rates, respectively. Using equation (4.9), the equivalent stirring speeds can be estimated, as listed in Table 4.1. It can be seen that 0.5, 1.5, 2.7, 5.0 L/min bubbling can be converted to 49, 71, 172, 181rpm of magnetic stirring, respectively, with an equivalent mixing ability using the same stirrer bar (16mm in diameter). This is consistent with the observation in Figure 4.1 that 1.5L/min bubbling results in an improved adsorption rate over that of the 62rpm magnetic stirred test, and that high bubbling rates do not continue to improve adsorption significantly.

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

Figure 4.5. Response of AOB dye concentration at the top of liquid, air bubbling

Table 4.1. Conversion of the bubbling rates to equivalent stirring speeds

Bubbling rate (L/min)	Time (s)	Converted to stirring speed (rpm)
0.5	12.0	49
1.5	10.7	71
2.7	4.6	172
5.0	4.0	181

4.4.3. Determination of mass transfer coefficient K_l

To estimate K_l , the averaged C/C_0 values in the first 1 min were used. These values were thought to be sufficiently early in the kinetic test (duration 6h) to be controlled by film diffusion but not be subject to ‘start-up’ errors. The correlation between the experimental K_l and the bubbling rates is plotted in Figure 4.6. It can be seen that the mass transfer rate K_l increased linearly with increase of the air bubbling rate

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

($R^2 = 0.9809$) over a certain range of the air bubbling rate, but further increase in the air bubbling rate (e.g. to 5.0 L/min) could not result in a more enhanced mass transfer. A similar trend was also seen in 10mg/L PAC dosage tests.

Figure 4.6. Effect of bubbling rate on mass transfer rate in the initial stage of adsorption, $C_c = 5\text{mg/L}$

Other researchers (Zarraq et al, 1991) have found that the solid-liquid mass transfer at a stationary single sphere placed in a bubbled shallow column was improved by increase of the superficial gas velocity to a limiting value. The mass transfer enhancement was attributed to the microscale high-intensity eddies induced by the rising bubbles. At very high gas velocity, the formed slug flow was not able to completely transfer energy into microscale eddies but only induce an overall circulation of liquid in the column. Similarly in this study, increasing the bubbling rate to a certain value may induce more microscale eddies which are associated with more generated shear. Accordingly, the thickness of the liquid film layer surrounding the particles is attenuated by the fluid shear. Therefore, the mass transfer through the liquid film surrounding carbon particles can be improved by increasing the bubbling. However, above the limiting bubbling, the thickness of the

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

film layer cannot be easily reduced and thus the mass transfer rate does not increase further. Therefore, optimization of the bubbling rate for the enhancement of adsorption efficiency is needed from the energy consumption point of view.

In our experiments, the PAC particles were well suspended in the liquid and moved with the eddies generated by the bubbles. However, direct contact of the particles and the bubbles was not obvious because of the low carbon dosage; there was no evidence of carbon segregation to the surface by flotation processes. Bubble coalescence during the upward motion in the vessel was also considered negligible because the operating conditions in this study were in the homogeneous regime of a multiphase system. According to Kluytmans et al (2001) the transition point from homogeneous to heterogeneous regimes for distilled water was at a superficial gas velocity of $0.03 \pm 0.005 \text{ m/s}$ and was delayed to $0.035 \pm 0.005 \text{ m/s}$ by addition of PAC particles ($d_p = 30 \mu\text{m}$) at 0.1-1.0g/L carbon concentrations. Compared to their tests, the carbon concentration in this study was much lower (5, 10mg/L) and the bubbling flowrates used were in the range 0.003-0.03m/s. Therefore, the liquid conditions in this study were closer to the homogeneous regime and the bubble coalescence should be insignificant.

The mass transfer coefficient K_l relevant to the bubbling condition can also be estimated from available mass transfer correlations using equations (4.4)-(4.8). The Reynolds number of a carbon particle in the bubbling system was estimated using the corresponding stirring speeds via the conversion data in Table 4.1 by assuming that the fluid velocity adjacent to the carbon particles is the same as the imposed fluid velocity in the vessel caused by the stirrer bar. The results are listed in Table 4.2 and compared with the experimental K_l obtained from the mass balance of equation (4.3). The differences between the two calculations are below 27%. This result shows us how the mass transfer in the bubbling system can be characterized quantitatively based on the correlations used for conventional mechanical stirred systems. Further analysis of batch kinetic data, using the HSDM method is given in Chapter 5.

*The material in this Chapter has been published in:
"Chemical Engineering Journal, 116 (2006) 53-59"

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

Table 4.2. Comparison of K_l from different methods

Bubbling rate (L/min.L)	K_l from data and equation (4.3) Average in 1 min ($\times 10^{-4}$ m/s)	Calculation from equations (4.4)-(4.8)			
		K_l ($\times 10^{-4}$ m/s)	u_o (m/s)	Re	Sh
0.5	3.27	4.43	0.01	0.09	3.97
1.5	4.02	4.88	0.02	0.13	4.37
2.7	5.83	6.35	0.05	0.32	5.69
5.0	6.20	6.47	0.05	0.34	5.79
Magnetic stirred 62rpm	3.43	4.70	0.02	0.12	4.22

Note: $D_v = 7.0 \times 10^{-6}$ (cm²/s), $Sc = 1274.54$

4.4.4. Intermittent bubbling

Figure 4.7 shows the trends of the adsorption rate at different bubbling rates which were introduced to the reactor intermittently at 0.5s-on-1.0s-off and 0.5s-on-2.0s-off, respectively. It is clear from Figures 4.7 (a-c) that a shorter non-bubbling pause (1.0s off) is more effective than a longer non-bubbling pause (2.0s off), but less efficient than the continuous bubbling. This indicates that more bubbles per unit

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

Figure 4.7. Effect of intermittent bubbling on adsorption kinetics, $C_c=5\text{mg/L}$

time injected facilitate the PAC adsorption. By comparing Figures 4.7 (a-c), it is also easily seen that the difference in the adsorption performance between the intermittent and continuous bubbling becomes less with an increase in net bubbling rates. This implies that the intermittent bubbling may be more suitable for higher air

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

flow rate operations in terms of both the energy consumption and adsorption performance.

Figure 4.8. Comparison between intermittent and continuous bubbling with equivalent flow rate, $C_c=5\text{mg/L}$

Figure 4.8 shows the required time for achieving 20% of the initial atrazine concentration for two intermittent operations which have approximately the same net air consumption of 0.5L/min but different intensities of air injection compared with 0.5L/min continuous bubbling. The intermittent conditions were 1.5L/min bubbling with 0.5s-on-1.0s-off intermittence and 2.7L/min bubbling with 0.5s-on-2.0s-off intermittence, respectively. It can be seen that 2.7L/min intermittent bubbling gave the most benefit ($t_{0.2} = 27 \text{ min}$) to the adsorption rate despite the 2.0s pause interval, followed by the 1.5L/min bubbling ($t_{0.2} = 36 \text{ min}$) with shorter pause interval of 1.0s. Continuous bubbling at 0.5L/min brought the least benefit ($t_{0.2} = 71 \text{ min}$) to the PAC adsorption. This example shows that for the same amount of air injection, intermittent higher intensity sparging is significantly more efficient than continuous lower intensity sparging in terms of PAC adsorption rate. The adsorption approaches the equilibrium faster in the former mode of bubbling. This result points to an important approach for improving the system performance

4. Atrazine adsorption by PAC - Improved mass transfer by air bubbling

economically. Obviously the intermittency and net bubbling rate can be optimized to minimize air and power usage.

4.5. Conclusions

Air bubbling was found to be a favorable approach to enhance PAC adsorption of a dilute organic solute as the mass transfer coefficient in the liquid film surrounding the PAC increased linearly with the increase of air bubbling rate over a certain range. Good mixing could be achieved by air bubbling at moderate flow rates. Even the slight turbulence generated by a few bubbles could provide a reasonable mixing to facilitate the PAC adsorption compared with the unstirred process.

The mass transfer coefficient through the liquid film in the bubbling system was estimated from the initial experimental data and the first order mass balance equations. These values were compared with mass transfer correlations, which were developed for conventional magnetic stirring systems, with the help of the conversion of the bubbling rates to the equivalent stirring speeds. The differences between experimental and predicted values were within 27%. In general, the results show that the mass transfer coefficient K_l is improved by the increase of air bubbling rate to a plateau value.

In addition, the use of intermittent air bubbling was found to have potential for higher air flow rate operations in terms of both the energy consumption and adsorption performance. For the same amount of net air injection applied to the process, intermittent higher intensity sparging is more efficient for the PAC adsorption than continuous lower intensity sparging. It is recommended to use intermittent bubbling with slightly higher air flow rates during injection, as this would not only assure the PAC adsorption efficiency but also potentially reduce the air/energy consumption. It should be mentioned that the bubbling intensity and frequency may also vary with PAC size and contaminant concentration in the water and thus more attention on this issue is required in real applications.

*The material in this Chapter has been published in:
“Chemical Engineering Journal, 116 (2006) 53-59”

5. Determination of the adsorption kinetic coefficients

5 .

DETERMINATION OF THE ADSORPTION KINETIC COEFFICIENTS

5.1. Introduction

In the hybrid PAC-submerged membrane system, the solute removal is mainly accomplished by carbon adsorption while the function of low-pressure driven membranes is to separate the powdered carbon particles from the treated water. Thus, to evaluate the efficiency of target solutes removal, the PAC adsorption performance has to be studied carefully.

PAC adsorption can be quantitatively analyzed by a mathematical approach. The adsorption isotherms, such as the Freundlich isotherm, are used to describe the maximal adsorption capacity of a certain mass of adsorbent. The homogeneous surface diffusion model (HSDM) has been extensively used to describe the kinetics of adsorption for organics in the liquid onto the activated carbon (Adham et al, 1991, 1993, Najm et al, 1993, 1996, Kim et al, 1996, Traegner et al, 1996, Slaney et al, 1998, Campos et al, 2000a, b, Chang et al, 2004). It has been used successfully to predict the adsorption dynamics for over 100 adsorbate-adsorbent systems which included a number of the organics found in both drinking water and wastewater treatment (Hand, et al, 1983). The HSDM contains two kinetic coefficients, i.e. the surface diffusion coefficient D_s and the liquid film mass transfer coefficient k_f ,

5. Determination of the adsorption kinetic coefficients

which are the crucial parameters to determine the accuracy of the model solutions and need to be known if a prediction based on the modeling is required.

For the systems without air bubbling, Hand et al (1983) have shown that the solution procedure of the HSDM can be simplified by eliminating the liquid film mass transfer coefficient k_f . However, certain experimental procedures are required to ensure a better D_s estimation. Traegner et al (1989) searched the two kinetic coefficients simultaneously by fitting the HSDM solutions to the experimental data, through a non-linear least squares fit. Roy et al (1993) introduced a simplified solution technique to solve the HSDM by using orthogonal collocation. The coefficients were determined by minimizing the difference between the model calculations and batch test data using the quasi-Newton method. In their study, 3 collocation points were chosen for simplicity.

For the PAC suspended submerged membrane system, the required operation procedure, which Hand et al (1983) presented, may not be applicable as the mixing mechanism is different. Therefore it has not yet been confirmed that the simple approach for non-bubbling systems can be applied to adsorption in the bubbled system.

The objectives of this chapter are to present a detailed HSDM solution procedure and to determine the two adsorption kinetic parameters for the carbon adsorption in an air bubbled system simultaneously. These can be later applied in a submerged membrane system model with similar air bubbling operations to simulate the process. The approach used is to solve the HSDM using the orthogonal collocation method (Finlayson, 1972) with 12 collocation points coupled with the Levenberg-Marquardt algorithm (Traegner et al, 1989) to minimize the difference between the experimental results and the model solutions. As such, D_s and k_f can be determined simultaneously. The experimental data used were collected from specifically designed kinetic tests using air bubbles to provide mixing instead of traditional mechanical stirring.

5. Determination of the adsorption kinetic coefficients

5.2. Theoretical model

5.2.1. Formulation of adsorption

Figure 5.1 shows schematically the four steps (external diffusion, film diffusion, surface diffusion, and adsorption) of activated carbon adsorption process:

Figure 5.1. Schematic diagram of activated carbon particle structure and mechanisms in the HSDM

The HSDM describes the kinetics of adsorbate or target compound uptake by activated carbon from liquid solution on the basis of the following assumptions:

5. Determination of the adsorption kinetic coefficients

- 1) adsorbate is assumed to adsorb first on the outer surface of the particle, and then enter the carbon particle by surface diffusion,
- 2) the adsorbate molecule diffuses in the adsorbed state along the surface of the carbon particle,
- 3) each particle is a spherical homogeneous solid, and the surface diffusive flux of the adsorbate can be described by Fick's First Law,
- 4) no reaction takes place between the adsorbate molecule and the adsorbent (carbon) surface.

For adsorption in a closed batch test, the overall mass balance is described as:

$$V \frac{dC}{dt} = -M_c \frac{dq_{avg}}{dt} \quad (5.1)$$

where C is the adsorbate concentration in the bulk solution, q_{avg} is the average mass of adsorbate adsorbed per unit mass of carbon particles, V is the liquid volume and M_c is the mass of carbon in the test. q_{avg} can be estimated from:

$$q_{avg} = \frac{3}{\left(\frac{d_p}{2}\right)^3} \int_0^{d_p/2} q(r,t) r^2 dr \quad (5.2)$$

where $q(r,t)$ denotes the adsorbate concentration within the particle, and d_p is the carbon particle diameter. The mass balance within an activated carbon particle is:

$$\frac{\partial q(r,t)}{\partial t} = D_s \left[\frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2\partial q(r,t)}{r\partial r} \right] \quad (5.3)$$

where D_s represents the surface diffusion coefficient within the carbon particles.

Equation (5.3) describes the changing rate of concentration $q(r,t)$ with time t at

5. Determination of the adsorption kinetic coefficients

any distance from the center of the carbon particle r during adsorption. The initial condition for equation (5.3) is

$$q(r,0) = 0, \quad t = 0, \quad 0 \leq r \leq d_p/2 \quad (5.4)$$

The boundary conditions are:

$$\frac{\partial q(0,t)}{\partial r} = 0, \quad t \geq 0, \quad r = 0 \quad (5.5)$$

$$\rho_p D_s \frac{\partial q(r,t)}{\partial r} = k_f (C - C_s), \quad t \geq 0, \quad r = d_p/2 \quad (5.6)$$

$$q_s = KC_s^{1/n}, \quad t \geq 0, \quad r = d_p/2 \quad (5.7)$$

where k_f denotes the mass transfer coefficient when adsorbates diffuse through the stagnant liquid film surrounding the carbon particles, and ρ_p represents the apparent particle density. C_s and q_s are the liquid phase and adsorbed phase adsorbate concentrations at the solid-liquid interface respectively, which are correlated based on the Freundlich isotherm expression of equation (5.7). K and $1/n$ are the Freundlich adsorption constants.

5.2.2. Nondimensionalization of describing equations

It is convenient to convert equations (5.1)-(5.7) into a non-dimensional form by substituting the following defined dimensionless parameters for the corresponding ones:

$$C^* = \frac{C}{C_0}, \quad q^* = \frac{q}{q_0}, \quad T = \frac{4D_s}{d_p^2} t, \quad R = \frac{2r}{d_p} \quad (5.8)$$

5. Determination of the adsorption kinetic coefficients

where C_0 represents the initial liquid phase adsorbate concentration, q_0 the adsorbed phase adsorbate concentration which is in equilibrium with the liquid phase concentration C_0 . Thus, the integrated form of equation (5.1) at time T with appropriate initial conditions as well as equations (5.2)-(5.7) can be rewritten non-dimensionally as follows:

$$C^* + E_{mb} q_{avg}^* = 1 \quad (5.9)$$

with E_{mb} representing the non-dimensional solute distribution parameter:

$$E_{mb} = \frac{M_c q_0}{V C_0} \quad (5.10)$$

and

$$q_{avg}^* = 3 \int_0^1 q^*(R, T) R^2 dR \quad (5.11)$$

$$\frac{\partial q^*(R, T)}{\partial T} = \frac{\partial^2 q^*(R, T)}{\partial R^2} + \frac{2 \partial q^*(R, T)}{R \partial R} \quad (5.12)$$

The initial and boundary conditions are:

$$q^*(R, 0) = 0, \quad T = 0, \quad 0 \leq R \leq 1 \quad (5.13)$$

$$\frac{\partial q^*(0, T)}{\partial R} = 0, \quad T \geq 0, \quad R = 0 \quad (5.14)$$

5. Determination of the adsorption kinetic coefficients

$$\frac{\partial q^*(1, T)}{\partial R} = B_i(C^* - C_s^*) , T \geq 0, R = 1 \quad (5.15)$$

$$q_s^* = C_s^{*1/n} \quad (5.16)$$

Equation (5.15) contains the non-dimensional Biot number defined as:

$$B_i = \frac{k_f d_p C_0}{2D_s \rho_p q_0} \quad (5.17)$$

The Biot number represents the ratio of the transport rate across the liquid film layer (numerator) to the diffusion rate within the particle (denominator).

The parameters required to solve the equations include geometrical and volumetrical quantities (ρ_p, M_c, V, d_p) , Freundlich equilibrium adsorption constants $(K, 1/n)$ and kinetic coefficients (D_s, k_f) . The geometrical and volumetrical quantities are directly measurable. The Freundlich adsorption constants can be determined by fitting the adsorption isotherm experimental data to the Freundlich isotherm equation (Randtke and Snoeyink, 1983). However, the kinetic diffusion coefficients cannot be measured directly and a numerical optimization technique is required to search the D_s and k_f . By input initial estimates of the parameters, the HSDM is calculated and then compared with corresponding experimental data of closed batch tests. The optimum D_s and k_f are finally identified by minimizing the difference between the model calculations and batch test data. This search procedure is known as a nonlinear least-squares fit as introduced by Dennis and Schnabel (1983) and Traegner et al (1989).

$$S^2 = \text{Minimize} [f(D_s, k_f)] = \sum_{i=1}^m [C^* - C_{\text{experiment}}]^2 \quad (5.18)$$

where m represents the number of data points.

5. Determination of the adsorption kinetic coefficients

5.2.3. Numerical scheme

The partial differential equation (5.12) can be solved numerically with associated initial and boundary conditions, the overall mass balance equation and the adsorption isotherm using the method of orthogonal collocation. The approach assumed 12 collocation points along the radial direction of a particle. This equation was written in a form suitable for its solution by the orthogonal collocation method, thus reducing the partial differential equation (PDE) to a set of ordinary differential equations (ODEs). The resulting ordinary differential equations were integrated in the time domain using the Gear's method (Kahaner et al, 1988). From this scheme, the concentration profile of the adsorbate in the carbon particle q_i^* at any time was obtained, which could lead to the adsorbate concentration in the bulk solution C^* via the mass balance equation.

The technique applied to solve the minimization problem (equation (5.18)) is a modified Levenberg-Marquardt algorithm and a finite-difference Jacobian, which was provided by the International Mathematics and Statistical Library (IMSL, 1990). A FORTRAN program was written to couple the HSDM and the Levenberg-Marquardt algorithm for the optimum parameters (D_s and k_f) determination. Figure 5.2 depicts the adsorption kinetics searching procedure. The iteration proceeds until the minimum sum of squares of the differences between the experimental residual liquid phase concentrations and the models solutions at the corresponding time point is found. The numerical derivation is presented in Appendix A. The correctness of the developed numerical solution was checked carefully in Appendix B. Firstly, a simple analytical solution was obtained by assuming that the surface diffusion is fast enough so that only the mass transfer in the liquid film external to the carbon surface controls the adsorption. For the model developed in this chapter, a low Biot number ($B_i = \frac{k_f d_p C_0}{2D_s \rho_p q_0}$) used also refers to a similar adsorption process, i.e., the mass transfer in the liquid film is the controlling step of the whole process. Thus a low Biot number was applied to the FORTRAN program to obtain a

5. Determination of the adsorption kinetic coefficients

numerical solution. The good agreement between the numerical solution and the analytical solution confirms the numerical solution is correct.

Figure 5.2. Flow chart of the adsorption kinetic coefficients searching program

5.3. Experimental

The same materials and protocols as described in previous chapters were used. Three groups of batch kinetic tests were conducted with carbon dosage of 5, 10, 15mg/L respectively using the bubbling batch test set-up described in Chapter 4. To compare the kinetics for different mixing strategies, three magnetic stirred kinetic tests at carbon dosages of 3, 5, and 8mg/L were also carried out.

5. Determination of the adsorption kinetic coefficients

5.4. Results and discussion

The Freundlich isotherm fit to the adsorption equilibrium test data has been presented in Figure 3.4 in Chapter 3 with the correlation regressed as equation (3.2). Thus, the Freundlich constants $K = 70.06(\text{mg/g})(\text{L}/\mu\text{g})^{1/n}$ and $1/n = 0.151$ were found for 6.3 μm PAC. Figure 5.3 depicts the HSDM fit to the experimental results of the magnetically stirred batch kinetic test with a carbon dosage of 5 mg/L. In this case the optimum kinetic coefficients were determined to be $1.14 \times 10^{-16} \text{ m}^2/\text{s}$ (D_s) and $5.17 \times 10^{-5} \text{ m/s}$ (k_f), respectively. Qi et al (1994) reported that the D_s value was unique for a certain carbon and was not the function of carbon dosage and initial adsorbate concentration over a wide range. Based on this, the determined D_s

Figure 5.3. Verification of the adsorption kinetic coefficients searching methods, magnetic stirring = 62rpm, $C_0 = 200 \mu\text{g/L}$

was used to predict the residual target compound concentration profile at different carbon dosages (3mg/L and 8mg/L) whilst the k_f was determined for the individual

5. Determination of the adsorption kinetic coefficients

cases. The prediction results are also shown in Figure 5.3 along with the experimental data. The excellent agreement between the modeling results and the experimental data demonstrates that the above introduced method for kinetic parameter searching works well. Therefore, it can be applied to determine the kinetic coefficients of the bubbling mixed adsorption system.

The bubbling batch kinetic test differed from the magnetic stirring test in the method of mixing. Bubbling has an unsteady state characteristic which may induce a local shear with a temporary time effect on the mass transfer. So it is possible for the mass transfer coefficient k_f to be changed at different mixing methods or mixing intensities. However, the surface diffusion coefficient which describes the diffusion along the inner surface within the carbon particles should not be affected by the external mixing mechanism (Randtke and Snoeyink, 1983). Instead, it is determined by the carbon characteristics such as carbon size and pore structure as well as the size and configuration of the adsorbate molecule (Faust and Aly, 1987). Therefore in the following section, the value of D_s , which was $1.14 \times 10^{-16} \text{ m}^2 / \text{s}$ obtained previously, was fixed whilst the k_f for different bubbling rate tests was variable in the best fit of the HSDM solutions with the bubbling batch tests data.

The HSDM fits to the bubbling tests data with 5mg/L PAC at different bubbling rates are shown in Figure 5.4. The fits are reasonably good, especially at higher bubbling rates. At the lowest bubbling rate, the deviation of the model solution from the experimental data may be due to the insufficient mixing caused by the low rate of bubbling, especially at a relatively low carbon concentration. It can be seen that the main difference among the experimental data of different bubbling rates lies in the initial stages of the first 180 minutes. There are no significant differences between the residual concentrations at the end of the 6 h kinetic tests. This indicates that the bubbling rate can affect the adsorption kinetics by influencing the time for adsorption to reach the equilibrium (plateau of the curves) without changing the adsorption capacity. At the latter stages, the adsorption tended to be controlled by the surface diffusion inside the particle and seemed not to be sensitive to the mixing

5. Determination of the adsorption kinetic coefficients

Figure 5.4. HSDM fit to the bubbling batch kinetic tests data, $C_c = 5\text{mg/L}$

conditions in the reactor. The similar residual concentrations at the end of the experiments at different bubbling rates further confirm that the surface diffusion parameter D_s was not altered by the bubbling rates. The k_f values at different bubbling rates were obtained using the method introduced above. It is clear that the mass transfer through the liquid film was enhanced by the increase in the bubbling rates, but further increase of the bubbling rate to 5.0 L/min.L (data not shown) did not improve the adsorption rate significantly. This result indicates that the bubbling mixing can facilitate the adsorption to a certain level, which represents the limit of the film mass transfer resistance above which the k_f can not be further reduced by increasing the bubbling rate. In other words, at higher bubbling rates the adsorption process is prone to be controlled by the internal surface diffusion and thus, not influenced by further enhancement of external mixing. The ‘plateau’ effect, where bubbling reaches a limiting effect has also been observed in fouling control by bubbling for submerged fibers (Chang and Fane, 2001b, Wicaksana et al, 2005).

5. Determination of the adsorption kinetic coefficients

Figure 5.5. HSDM fit to the bubbling batch kinetic tests data, $C_c = 10 \text{ mg/L}$

Figure 5.6. HSDM fit to the bubbling batch kinetic tests data, $C_c = 15 \text{ mg/L}$

The results of the bubbling mixed batch kinetic tests at carbon dosages of 10 mg/L and 15 mg/L are presented in Figures 5.5 and 5.6, respectively. Similar trends of k_f

5. Determination of the adsorption kinetic coefficients

as in 5mg/L carbon dosage tests can be observed and the summary of the k_f values at different bubbling rates (Q_b) and carbon dosages (C_c) is shown in Figure 5.7.

Figure 5.7. k_f vs. Q_b at different carbon concentrations

The correlation of k_f (m/s) with Q_b (L/min.L) and C_c (mg/L) can be regressed as the following equation with $R^2 = 0.9935$:

$$k_f = 1.30 \times 10^{-4} \cdot C_c^{0.06} Q_b^{1.29} \quad (5.19)$$

This empirical equation is suitable for the bubbling mixed adsorption process with the averaged bubble size of 3.3 mm at any bubbling rates below 3.0 L/min.L. From this equation, it can be found that the k_f is not very sensitive to the variation in carbon dosage compared to the air bubbling rate. The reason for this is that k_f is determined by the local velocity gradients which are generated by the bubble passage; solids content (in the 5 to 15 mg/L range) would have minor impact on local momentum transfer. Equation (5.19) provides a quantitative relationship for

5. Determination of the adsorption kinetic coefficients

further evaluating PAC adsorption in the hybrid submerged membrane system and system modeling (see Chapter 6).

Comparing the k_f values determined through fitting the HSDM to those determined in Section 4.4.3 through the first order equation (Table 5.1), it is evident that at lower bubbling rates as well as for the 62rpm magnetic stirring conditions, the HSDM produced lower k_f values than the first order method. This difference may be because the first order estimation was obtained by analysis of the data from

Table 5.1. Comparison between k_f values determined through different methods
($C_c=5\text{mg/L}$)

Bubbling rates	1st Order (Section 4.4.3)	HSDM
(L/min.L)	($\times 10^{-4}$ m/s)	($\times 10^{-4}$ m/s)
0.5	3.27	0.45
1.5	4.02	2.27
3.0	5.83	5.98
Magnetic stirred (62rpm)	3.43	0.52

the initial stage (1min) of the kinetic tests and this places too much reliance on the precision of the concentration analysis. However, the film mass transfer is very fast at the beginning and decreases over time. When the liquid concentration drops, the mass transfer slows down accordingly. So the values determined in Section 4.4.3 represent the initial trend of mass transfer coefficients among the different bubbling rates. In contrast, the HSDM determined k_f values are based on overall 6 h test data and searched simultaneously with the surface diffusion coefficient D_s through a complicated searching procedure. A k_f value represents the averaged liquid mass transfer of the whole process including the faster transfer at the beginning and slower transfer thereafter. That the difference decreases with the increase of the bubbling rate is possibly due to the thinner film layer at higher bubbling and accordingly the adsorption approaches the equilibrium faster. When the HSDM model was applied to the initial stage data (up to 60min) it produced a similar k_f

5. Determination of the adsorption kinetic coefficients

value to that obtained from the full batch data. Therefore the k_f and D_s simultaneously determined in this chapter are considered more accurate for describing the adsorption kinetics and are further applied in the following sections.

Figure 5.8. HSDM fit to the intermittent bubbling batch kinetic tests data,
 $C_c = 5 \text{ mg/L}$

Figure 5.8 shows the comparison of 0.5 L/min.L continuous bubbling results with those of intermittent bubbling at two different bubbling intensities but the same net bubbling rate. For the 1.5 L/min.L bubbling with 0.5s-on-1.0s-off and 3.0 L/min.L bubbling with 0.5s-on-2.0s-off, the net bubbling rates are both 0.5 L/min.L. It is evident that with the same net bubbling rate, high intensity bubbling with a longer rest interval is better than low intensity bubbling with a shorter rest interval. The k_f values for these three cases of intermittent bubbling tests were determined through the best fits to the experimental data and are shown in Table 5.2.

The k_f was improved from 4.50×10^{-5} , 1.18×10^{-4} to 4.18×10^{-4} m/s as bubbling intensity increased from continuous 0.5 L/min.L to intermittent 1.5 L/min.L (0.5s-

5. Determination of the adsorption kinetic coefficients

Table 5.2. Comparison of the kinetic coefficients between continuous and intermittent bubbling at the same net bubbling rate

Mixing Conditions	D_s	k_f
	($\times 10^{-16} \text{ m}^2/\text{s}$)	$\times 10^{-4} (\text{m/s})$
Continuous bubbling (0.5 L/min)	1.14	0.45
Intermittent bubbling (1.5 L/min, 0.5s/1.0s)	1.14	1.18
Intermittent bubbling (3.0 L/min, 0.5s/1.0s)	1.14	4.18

on-1.0s-off), and to 3.0 L/min.L (0.5s-on-2.0s-off). Thus, the carbon adsorption process can benefit from a higher intensity bubbling with longer rest periods rather than a continuous lower intensity bubbling. This may be due to the more energetic turbulence introduced by the higher intensity bubbling. These observations provide another strategy for optimization of the submerged hybrid membrane system combined with PAC adsorption.

5.5. Conclusions

The kinetics for carbon adsorption in a bubbling mixed system were evaluated through both mathematical and experimental methods. The homogeneous surface diffusion model (HSDM) was solved numerically using the orthogonal collocation method with 12 collocation points. The differences between the model solutions and corresponding experimental results were minimized by means of the Levenberg-Marquardt algorithm so that two kinetic parameters D_s and k_f , which are involved in the HSDM, were obtained simultaneously.

From the HSDM fit to batch kinetic tests data, the D_s was found to be $1.14 \times 10^{-16} \text{ m}^2/\text{s}$ while the k_f altered with different mixing mechanisms as well as mixing intensities, which is in correspondence with the different adsorption rates in

5. Determination of the adsorption kinetic coefficients

the initial stages of batch tests. The k_f value was found to be improved by increase in the bubbling rates over a certain range at three tested carbon dosages. A correlation between k_f and the air bubbling rate Q_b as well as the carbon dosage C_c was obtained by non-linear regression, which will be useful for the modeling of adsorption process in the submerged membrane system with the similar bubbling conditions.

The k_f value was also observed to be enhanced from $1.18 \times 10^{-4} m/s$ to $4.18 \times 10^{-4} m/s$ when the instantaneous bubbling intensity increased in intermittent bubbling tests. This indicates that high intensity intermittent bubbling is more efficient in improving the liquid film mass transfer. This observation should be valuable in further optimization of PAC suspended submerged membrane systems.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

6 .

SINGLE-STAGE HYBRID PAC-SUBMERGED MEMBRANE SYSTEM SIMULATION AND OPTIMIZATION

6.1. Introduction

Over the past 20 years, experimental and mathematical studies of the external loop PAC-membrane process have been carried out. Modeling the mixing tank and the recycle loop portion of the PAC/UF process as a steady state continuous stirred tank reactor (CSTR) for the removal of TOC (Adham et al, 1991, 1993) and trace organics (Qi et al, 1994) was successful, and the modeling results were verified by both large and small scale pilot plant operations. A series of mathematical models were developed by Campos et al (2000a, b) to evaluate different process designs of continuous-flow PAC-membrane reactors which were operated without carbon wastage between backwash events. The organics removal efficiency was studied by modeling various membrane reactor configurations with either a CSTR or a plug flow reactor (PFR) in combination. In these simulations, the liquid film resistance was neglected and the process was assumed to be controlled by surface diffusion only. Matsui et al (2001a, b) modeled trace synthetic organic chemical (SOC) removal and found that a pulse PAC addition at the beginning of a filtration cycle resulted in a better SOC removal than the continuous addition mode, and that the internal mass transfer was the rate-determining step. All these mathematical models can be used to facilitate the design of PAC-membrane external loop systems in

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

which the membrane filtration rig is installed separately from the adsorption reactor, and to help determine the optimal operating strategies for the proposed organic pollutants treatment from water.

With the development of the membrane filtration technique, the submerged membrane system has attracted worldwide interest. Since the first application in the membrane bioreactor in the late 1980s (Yamamoto et al, 1989), submerged membrane systems have shown advantages in reducing energy consumption and cost, improving product quality and reducing land requirement. Applying submerged membrane systems in water treatment for removal of natural organic matter (NOM) and synthetic organic chemicals (SOCs) is a relatively new and promising process. In the hybrid PAC-submerged membrane system, the membrane module is immersed into an adsorption tank which contains suspended PAC particles (Lebeau et al, 1998). Guo et al (2005) recently developed a mathematical model to simulate the total organic carbon (TOC) removal from synthetic wastewater in a submerged membrane adsorption system. In their simulation, the Talu adsorption equilibrium was used to quantify the adsorption capacity. The author incorporated the TOC adsorptions onto the membrane surface in their modeling and the total amount of PAC was added into the submerged membrane reactor in the batch mode. The effects of a series of operating parameters were evaluated including the pre-adsorption duration, aeration rate, backwash frequency, PAC dose and filtration flux.

In the submerged membrane-adsorption system, air bubbling is applied to the tank to provide mixing and introduce shear at the membrane surface in order to enhance separation efficiency. However, it is evident that studies of the PAC-MF/UF hybrid submerged membrane system have mainly focused on the evaluation of the overall contaminant removal efficiency. The effects of air bubbling on the PAC adsorption as well as on the whole system performance for both batch and continuous PAC dosing operations need further study.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

The mixing brought about by air bubbling is different from that of conventional mechanical stirring by generating vertical movement of the PAC particles in the solution. Thus, the kinetic parameters of PAC adsorption would be influenced by the manner of air bubble-induced mixing. Further study on the adsorption-submerged membrane system with consideration of the air bubble effect on the adsorption kinetics is necessary. The objective of this chapter is to develop and verify a mathematical model to describe trace organics adsorption by suspended PAC in a continuous flow single-stage submerged membrane reactor with continuous air bubbling for trace organics removal from water. Operations with both batch and continuous PAC dosing modes were simulated based on the single solute homogeneous surface diffusion model (HSDM) and corresponding mass balance equations. In addition, experiments using atrazine as the model organic compound were conducted to verify the modeling results. This work should help to better understand the hybrid system and to evaluate various operating strategies.

6.2. Formulation of the hybrid PAC-submerged membrane model

The formulation of the adsorption process model (equations 5.2-5.8, 5.11-5.17) and the procedure for determination of the adsorption kinetic coefficients is presented in Chapter 5. Based on the resulting D_s and k_f (equation (5.19)), the required values of kinetic coefficients for the continuous flow hybrid PAC-submerged membrane system can be obtained and the hybrid system operation can be simulated.

Figure 6.1 shows the schematic diagram of a hybrid PAC adsorption-submerged membrane system where two PAC dosing strategies were adopted. One is where the total amount of PAC was dosed at the very beginning of each operation, i.e. batch dosing, while the other is where the PAC was dosed into the membrane reactor continuously during the whole process, i.e. continuous dosing. The suspensions are assumed to be fully mixed by the air bubbling and the reactor works as a CSTR. For each dosing strategy, the adsorbate concentration in the influent was kept unchanged during the whole operation. The liquid flow rate was maintained the

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

same from the inlet to the outlet and no PAC was wasted during the operation until backwash of the membrane and the whole system.

PAC-MF Submerged Membrane Reaction Tank

Figure 6.1. Schematic diagram of a hybrid PAC adsorption-submerged membrane system

6.2.1. Batch dosing of PAC

In this mode of operation, the membrane reactor was assumed to be fully mixed by air bubbling once the total mass of PAC was added into the reactor. The solute mass balance in the reactor can be written as:

$$Q(C_0 - C) = \frac{d(VC + M_c q_{avg})}{dt} \quad (6.1)$$

The right hand side of equation (6.1) represents the sum of mass change of the adsorbate that remains in the reactor in the liquid phase and that adsorbed onto the solid phase over time.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

The dimensionless form of equation (6.1) is as follows by substituting equation (5.8):

$$\frac{dC^*}{dT} = \frac{1}{E_{b1}} \left(1 - C^* - E_{b2} \frac{dq_{avg}^*}{dT} \right) \quad (6.2)$$

where

$$E_{b1} = \frac{V}{Q} \frac{4D_s}{d_p^2} \quad (6.3)$$

$$E_{b2} = \frac{M_c q_0}{QC_0} \frac{4D_s}{d_p^2} \quad (6.4)$$

By combining equation (5.11) with equation (6.2), the following equation can be obtained:

$$\frac{dC^*}{dT} = \frac{1}{E_{b1}} \left(1 - C^* - 3E_{b2} \int_0^1 \frac{\partial q^*}{\partial T} R^2 dR \right) \quad (6.5)$$

The HSDM set of equations (5.12-5.17) coupled with equation (6.5) describe the absorbate concentration profile within the absorbent particle (q^*) and the corresponding absorbate concentration in the bulk solution (C^*) under the mode of batch dosing of PAC. The partial differential equation (5.12) can be reduced to a set of ordinary differential equations by applying the orthogonal collocation method with 12 collocation points. Therefore there were in total 13 ordinary differential equations which contain 13 variables of q_i^* ($i=1,...,12$) and C^* . The resulting ordinary differential equations were integrated in the time domain using the Gear's method. From this scheme, the concentration profile of the adsorbate q_i^* in the carbon particle and the adsorbate concentration in the bulk solution C^* at any time

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

were obtained. The correctness of the developed numerical solutions of this process was also checked. When the liquid flow Q approaches zero, the situation is similar to a batch test in Chapter 5. Thus low Biot number and liquid flow Q were applied to the FORTRAN program of the numerical scheme. The calculated results were compared with the analytical solution (Eq. B.8) and a good agreement was also obtained as shown in Figure B.2 of Appendix B.

6.2.2. Continuous dosing of PAC

In the mode of continuous dosing of PAC, the PAC was dosed into the submerged membrane reactor throughout the whole operation duration at a constant carbon concentration of C_c . The submerged membrane reactor was assumed to be fully mixed at any time and the solute mass balance in this case can be expressed as:

$$Q(C_0 - C) = V \frac{dC}{dt} + \frac{d}{dt} \left[\int_0^t q_{avg,(t-\beta)} C_c Q d\beta \right] \quad (6.6)$$

Figure 6.2. Schematic diagram of dosing PAC at tiny time intervals
(for continuous PAC dosing mode)

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

where β is the time at which the particles enter the reactor. As shown in the diagram of Figure 6.2, the small batch of PAC particles entering the reactor at time β have a corresponding adsorption time of $t - \beta$, and an average adsorbate concentration of $q_{avg,(t-\beta)}$ in PAC. $q_{avg,(t-\beta)} C_c Q d\beta$ represents the adsorbed organics mass when the adsorbent with a mass of $C_c Q d\beta$ entered the reactor during the time interval of $d\beta$. The integration of $q_{avg,(t-\beta)} C_c Q d\beta$ from 0 to time t gives the total adsorbed mass on the carbon particles at a given time of t . Thus, the right hand side of equation (6.6) gives the sum of mass change of the adsorbate that remains in the reactor in the liquid phase and that adsorbed onto the solid phase over time.

Another two dimensionless parameters were defined as:

$$q_{avg,(T-\beta^*)}^* = \frac{q_{avg,(t-\beta)}}{q_0}, \quad \beta^* = \frac{4D_s}{d_p^2} \beta \quad (6.7)$$

By making use of the dimensionless parameters in equations (5.8) and (6.7), equation (6.6) can be rearranged as:

$$\frac{dC^*}{dT} = \frac{1}{E_{b1}} \left\{ 1 - C^* - E_{b3} \left[\int_0^T \frac{dq_{avg,(T-\beta^*)}^*}{dT} d\beta^* \right] \right\} \quad (6.8)$$

where

$$E_{b3} = \frac{C_c q_0}{C_0} \quad (6.9)$$

The term $\int_0^T \frac{dq_{avg,(T-\beta^*)}^*}{dT} d\beta^*$ in the above equation can be developed as follows:

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

$$\int_0^T \frac{dq_{avg,(T-\beta^*)}^*}{dT} d\beta^* = \sum_{i=1}^p \left(\frac{dq_{avg}^*}{dT} \right)_i (\Delta T) \quad (6.10)$$

where ΔT is the time interval when the dimensionless adsorption time T is divided evenly into p parts.

Combining equation (5.11) with equations (6.8) and (6.10) yields:

$$\frac{dC^*}{dT} = \frac{1}{E_{b1}} \left\{ 1 - C^* - E_{b3} \sum_{i=1}^p \left(3 \int_0^1 \frac{dq^*}{dT} R^* dR \right)_i (\Delta T) \right\} \quad (6.11)$$

The HSDM set of equations (5.12-5.17) coupled with equation (6.11) describe the absorbate concentration profile within the absorbent particle (q^*) and corresponding absorbate concentration in the bulk solution (C^*) under the operating mode of continuous dosing of PAC. The numerical scheme to obtain the solution is similar to that used in the batch dosing strategy. The correctness of the developed numerical solutions for this case can be checked similarly as the procedure for batch dosing strategy.

6.3. Experimental method for continuous flow hybrid

PAC- submerged hollow fiber system

The PAC-submerged membrane reactor was set up as shown in Figure 6.3. It consisted of a 50L (effective volume) transparent reaction tank with 5 rows of air diffusing pipes (diffuser 1) located at the bottom. 40 diffusing holes of 0.6mm diameter were arranged in 5mm intervals along each pipe. Two other pipes (air diffuser 2) with 40 holes of the same size, were fixed at the bottom of two transparent baffles, and placed in front of each side of a MF hollow fiber module to provide bubbles around 3.5mm in diameter for membrane fouling control. The membrane module (Blue Star, China, see Table 6.1) was installed at the middle of

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

the tank. A dual channel pump head was mounted on a feed/suction peristaltic pump (Masterflux, C/L, Cole-Parmer) so that the feed solution was pumped into the reactor at the same flowrate as the permeate. The permeate was drawn out from the upper of the module at a constant flux (60 and $100 \text{ L} / \text{m}^2 \text{h}$). A similar type of peris-

Figure 6.3. Experimental set-up of PAC-submerged hollow fiber membrane reactor

Table 6.1. Characteristics of the MF hollow fiber membrane module

Parameter	Value
Material	PVDF (polyvinylidene fluoride)
Membrane pore size (μm)	0.2
Fiber outer diameter (mm)	1.00
Fiber inner diameter (mm)	0.65
Surface area (m^2)	0.4
Fiber length (m)	0.5
Hydrophilicity	Partially hydrophilic

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

taltic pump was used to dose PAC into the reactor. The flowrates of the feed solution and PAC slurry dosing were monitored by two flowmeters (150mm , Cole-Parmer). The concentrated PAC slurry was stirred with a magnetic stirrer (Vision Scientific Co., Ltd.) to maintain an even PAC concentration during dosing. The flowrates of influent and effluent of the reactor were monitored to minimize the water level change in the reactor during the filtration experiments. The permeate flux was measured by a flow sensor (Cole-Parmer) and the transmembrane pressure was measured by a pressure transducer (Cole-Parmer). The data were collected automatically by a data logging system. All the connectors and pipes used in the system were stainless steel to prevent pipe-leaked contaminants. The solute adsorbed by the membrane was checked by operating the system at a fixed flux of $100\text{ L}/\text{m}^2\text{h}$ for 12 hours without PAC addition. The raw water was sucked out through the membrane and then recycled to the reactor. The final atrazine concentration difference was within 3% so that the membrane adsorption can be neglected in this case.

In the continuous flow tests with batch PAC dosing, the total amount of PAC required in the whole operating cycle was added into the reactor which initially contained $200\mu\text{g}/\text{L}$ atrazine solution and was mixed with air bubbles. Prior to the PAC addition, the feed/suction pump was started for 10mins to precondition the system. The samples were collected from the permeate side at predetermined time intervals after the addition of PAC.

For the continuous PAC dosing, after the system was preconditioned the PAC was added into the submerged reactor in slurry phase from the concentrated PAC slurry tank ($200\text{mg}/\text{L}$) at a predetermined constant PAC flowrate. The permeate samples were collected at regular time intervals.

6.4. Results and discussion

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

6.4.1. Model verification and membrane performance

According to equation 3.2, the Freundlich isotherm constants K and $1/n$ were determined to be $70.06(\text{mg} / \text{g})(\text{L} / \mu\text{g})^{1/n}$ and 0.151 respectively. The adsorption kinetic coefficient D_s ($1.14 \times 10^{-16} \text{ m}^2 / \text{s}$) found in Chapter 5 is also applicable in this study since the same PAC particles were used. The other kinetic coefficient k_f values at different bubbling rates and carbon concentrations are available by applying the empirical equation (equation (5.19)) and summarized in Table 6.2.

Table 6.2. k_f at different bubbling rates and carbon dosages
($d_p=6.3\mu\text{m}$, $C_0=200\mu\text{g} / \text{L}$)

Carbon dosage	Air bubbling rate	Liquid film mass transfer coefficient
C_c (mg/L)	Q_b (L/min.L)	k_f ($\times 10^{-4} \text{ m/s}$)
3	0.4	0.43
4	0.4	0.44
5	0.4	0.44
5	0.8	1.08
5	1.2	1.82
5	1.6	2.63
5	2.0	3.51
5	3.0	5.92
8	0.4	0.46
10	0.4	0.46
10	0.8	1.13
10	1.2	1.90
10	1.6	2.76
10	2.0	3.67
10	3.0	6.19
12	0.4	0.47

Figure 6.4 shows the results of the continuous flow tests with batch dosing of PAC at 4 and 8 mg/L carbon dosages together with the model simulation. The permeate flux was maintained constant at $60 \text{ L} / \text{m}^2 \text{ h}$ and the bubbling rate per volume of treated water was 0.4 L/min.L for each operation. Excellent agreements between the model predictions and experimental data are observed.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

Figure 6.4. Model verification for continuous flow hybrid system with batch PAC

dosing, Flux = $60 \text{ L} / \text{m}^2 \text{ h}$, $Q_b = 0.4 \text{ L} / \text{min} \cdot \text{L}$, $C_0 = 200 \mu\text{g} / \text{L}$,

$$D_s = 1.14 \times 10^{-16} \text{ m}^2 / \text{s}$$

Figure 6.5 shows the model simulation compared with experimental performance for the continuous dosing of PAC. To check the accuracy of the model simulation at different permeate fluxes which determine the hydraulic residence time (HRT), the tests were conducted at 60 and $100 \text{ L} / \text{m}^2 \text{ h}$ with carbon dosages of 12 and $8 \text{ mg} / \text{L}$, respectively. Good agreements were also obtained between theoretical and experimental results. The slight over-prediction in the later part after about 120 min may be attributed to gradual PAC sedimentation in small dead zones such as the corners of the rectangular reactor as well as on some parts of the membrane holder underwater. Therefore, the fully mixed assumption in the model development was not perfectly achieved as the tests continued. Nevertheless, the results shown in these two figures indicate that the models for the two PAC dosing strategies can be used to describe the hybrid PAC-submerged membrane system performance with considerable reliability.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

Figure 6.5. Model verification for continuous flow hybrid system with continuous PAC dosing, $Q_b = 0.4 \text{ L/min.L}$, $C_0 = 200 \mu\text{g/L}$, $D_s = 1.14 \times 10^{-16} \text{ m}^2/\text{s}$

The membrane performance in the hybrid PAC-submerged MF hollow fiber tests was monitored simultaneously by recording the transmembrane pressure (TMP) and the flux every 30 seconds during each operation. As shown in Figure 6.6, the permeability during the hybrid test was nearly the same as that of the Milli-Q water during the test with a flux of $60 \text{ L/m}^2\text{h}$. This indicates that the air bubbling has effectively prevented the formation of the PAC cake layer on the membrane surface and as a result, stable membrane performance was achieved. From the SEM (scanning electron microscope) pictures shown in Figure 6.7, it can be observed that almost no PAC deposited on the membrane surface because of air bubbling.

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

Figure 6.6. Permeability of hybrid submerged PAC-MF test and Milli-Q water test

Flux = $60 \text{ L} / \text{m}^2 \text{ h}$, $Q_b = 0.4 \text{ L} / \text{min} \cdot \text{L}$, for hybrid test: $C_0 = 200 \mu\text{g} / \text{L}$,
 $C_c = 8 \text{ mg} / \text{L}$, batch PAC dosing

Figure 6.7. SEM photos of new membrane and used membrane (Note the image (b) taken at a slight angle to show the cross-section and the surface)

6.4.2. Model predictions

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

The model developed in Section 6.2 was used to predict the target compound removal by the hybrid PAC-submerged membrane system with changes to three aspects of the operating conditions: different carbon dosages, different air bubbling rates as well as different filtration fluxes for both the batch and continuous PAC dosing methods.

6.4.2.1. Different carbon dosages

Figure 6.8 shows the model predictions for the atrazine removal by dosing different amounts of PAC during the batch mode. The contaminated water flowed continuously to the tank which containing a large amount of PAC. The adsorption was fast at the beginning and the atrazine concentration in permeate achieved the lowest value very quickly and then gradually increased with the steady input of mo-

Figure 6.8. Model predictions for hybrid submerged PAC-MF at different carbon dosages (batch dosing of PAC)

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

re feed water. It can be observed that the time required to achieve maximum removal decreased with an increase in the amount of PAC that was dosed. For a better comparison, 90% atrazine removal was assumed to be desired and thus the permeate water quality C/C_0 above 0.1 was considered to be the 'breakthrough'. Obviously, the breakthrough appears later at higher carbon dosages. Comparison between the curves of PAC dosage of 5mg/L and 10mg/L indicates that doubling the carbon dosage can delay the breakthrough time by more than twice. This implies that for batch PAC dosing operations, adding more PAC at the beginning is beneficial for longer time operations so that the time intervals to recruit fresh PAC can be prolonged.

Figure 6.9. Model predictions for hybrid submerged PAC-MF at different carbon dosages (continuous dosing of PAC)

For the continuous dosing of PAC as shown in Figure 6.9, the adsorption achieved equilibrium conditions at different times and levels with different dosing rates of small amounts of PAC. Noting that the time required to achieve the maximum removal is different for different carbon dosages, the minimum carbon dosage for

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

achieving a desired target removal can be determined. Under this dosing mode, the atrazine concentration ratio in the permeate decreased gradually from 1.0 at the beginning to a certain level; therefore, the product quality in the beginning of each operation may not meet the requirements so that ‘start-up’ should involve an initial batch (Figure 6.8). With the continuous dosing mode it will be necessary to eventually reach a steady state where the PAC inventory in the system is fixed by continuous PAC removal. An approach to this type of modeling is discussed in Chapter 7.

6.4.2.2. Different air bubbling rates

Figure 6.10 shows the model predictions of the hybrid PAC-submerged system performance at different air bubbling rates for the batch PAC dosing mode. The target removal is improved by increasing the bubbling rates. As shown in the batch kinetic study (Chapter 5) higher bubbling rates can facilitate the adsorption kinetics, because the air bubbling mixes the suspension and assists the contact of the raw wa-

Figure 6.10. Model predictions for hybrid submerged PAC-MF at different bubbling rates (batch dosing of PAC)

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

ter with the total inventory of PAC particles. The diffusion resistance of the liquid film surrounding the particle surface can be reduced as the film thickness is attenuated by increasing the bubbling rates. Higher bubbling rates provided faster and more uniform mixing which results in a better permeate quality, however the effect is relatively marginal unless the bubbling is dropped to 0.4L/minLwater in our system.

Figure 6.11. Model predictions for hybrid submerged PAC-MF at different bubbling rates (continuous dosing of PAC)

In contrast with the batch PAC dosing, operations with continuous PAC dosing shows no sensitivity to increase in the bubbling rates (Figure 6.11). There is no obvious difference in the permeate quality profile with different air bubbling rates. This is due to the small amounts of PAC which enter the submerged membrane tank at a constant dosing rate. The beneficial effect of high bubbling rates on the adsorption kinetics acts only on a small increment of PAC particles so that there is no considerable improvement in the overall final permeate quality when a higher bubbling rate is applied. Therefore, from an energy saving point of view, increasing

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

the bubbling rate is not an effective way to enhance the system effluent quality in this case. The bubbling rates for the continuous PAC dosing operation can be decided by aiming to provide proper mixing to keep the PAC in suspension and to maintain sustainable membrane performance. For these purposes, relatively low air bubbling rates can be applied or even the intermittent bubbling discussed in Section 4.4.4.

6.4.2.3. Different filtration fluxes

Figures 6.12 and 6.13 show the change in atrazine concentration in the permeate with time at batch dosing of PAC (from 40 to 200 L/m²h). Two scenarios are considered:

- () fixed PAC amount at different fluxes;
- () different PAC amounts at different fluxes, resulting in constant carbon concentration for different fluxes based on the volume of the treated water.

Figure 6.12. Concentration profile with the change of the volume of treated water, 480min, batch dose of PAC, fixed PAC amount. (Scenario ())

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

For scenario (), the same amount of PAC is dosed into each operation. The higher fluxes produce more water over a given time but with lower product quality because of the shorter HRT. Therefore in this case, the permeate of the higher flux operations reaches the ‘breakthrough’ earlier.

Figure 6.13. Concentration profile with the change of the volume of treated water, 480min, batch dose of PAC, fixed PAC concentration. (Scenario ())

For scenario (), the carbon dosage is based on the volume of the treated water (e.g. carbon concentration is 5mg/L for each flux, Figure 6.13), thus a higher filtration flux required more mass of PAC dosed. For instance, operating at a flux of $200 \text{ L/m}^2\text{h}$ actually required around 3.3 times the carbon mass of that used for a flux of $60 \text{ L/m}^2\text{h}$. It was noticed that after 480 min operation, a higher flux operation resulted in better permeate quality than a lower flux operation although from the lowest tested flux ($40 \text{ L/m}^2\text{h}$) to the highest one ($200 \text{ L/m}^2\text{h}$), the corresponding HRT is decreased from 187.5 min to 37.5 min. This is possible

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

because a higher volume of water is treated and the larger amount of PAC dosed can compensate for the time shortage for the adsorption. Therefore, higher flux operation is still reliable in terms of the permeate quality provided that the supply of PAC is based on the volume of the treated water.

Figure 6.14. Model predictions for hybrid submerged PAC-MF at different filtration fluxes (continuous dosing of PAC)

In contrast, for the continuous dose of PAC (Figure 6.14), the higher flux operation produced worse permeate quality with time due to the shorter HRT. For a certain carbon dosage, although the total carbon mass for the higher flux operation is also proportionately higher than that for lower flux ones, the carbon is dosed into and accumulates in the reactor steadily with operation time. Therefore in a small time interval, only a slightly higher carbon mass is added into the higher flux operation than the lower ones. This small amount of carbon cannot compensate for the shortage of retention time. Thus, in Figure 6.14 it can be observed that at the same carbon dosage based on the treated water volume, the permeate quality at a flux 40 of L/m^2h is better than for higher flux operations because its longer HRT ensures

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

more effective contact between the solution and the carbon particles. Obviously, the optimal working conditions for different operating strategies are different.

6.4.2.4. Batch and continuous PAC dosing

Although same total amount of carbon is added, the batch and continuous PAC dosing configurations may have different effects on the trace organic concentration in the product water. For the batch PAC dosing mode, the trace organic concentration in the product water reaches the lowest value very soon after the dosing of PAC. While for the continuous dosing mode, the lowest target organic concentration is approached gradually because of the less carbon mass in the beginning of a filtration cycle. Thus, another initial batch dose of PAC is required for a fast removal at the beginning. However in another aspect, for batch PAC dosing, a ‘breakthrough’ occurs at a certain time with the proceeding of the operation. A new batch of PAC is required to be added into the system to restore the water treatment capacity of the system. While at continuous PAC dosing mode, no ‘breakthrough’ happens and once product water quality meets the requirement, the operation can proceed on without changing any system parameter.

Based on the model predictions, the benefit of the batch PAC dosing is the sensitivity of the target organic concentration in the permeate to the different air bubbling rates and fluxes. Higher air bubbling rates and higher fluxes can facilitate the adsorption process and improve the product water quality. In contrast, the target concentration at the continuous PAC dosing operations shows no dependence on the bubbling rates. Therefore, a slight bubbling is sufficient for the mixing in this case and accordingly, reduces the energy consumption. Lower flux is preferable in the continuous PAC dosing operations to take advantage of longer HRT for a sufficient contact of PAC with the pollutants. Whereas for batch PAC dosing at the same carbon dosage (per volume of treated water), higher flux shows benefit.

6.4.3. Effect of high PAC concentration on membrane performance

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

It should be noted that the PAC inventory in the reactor is not at a steady state because the PAC is only wasted during the backwash of the membrane and the whole system. The reason for this is that the accumulation of PAC particles in the reactor does not cause rapid fouling of the MF membranes. Although a layer of PAC particles was observed on the fiber surface, the membrane performance was rarely influenced because of the particle size ranges and the porous structure of the PAC layer formed. In addition, the bubbling was able to reduce the deposition of the PAC on the membrane surface to some degree.

No obvious TMP increase can be observed in Figures 6.15 and 6.16 which show the TMP profiles at carbon concentrations of 5.8 and 14.0g/L in the reactor using the 'flux stepping' method (introduced in Section 2.1.6). Carbon concentrations of 5.8 and 14.0g/L actually equate to 290 and 700g of PAC in the 50L reactor which is equivalent to operating the submerged membrane system for 30d and 72d without carbon waste (at a flux of $100 \text{ L/m}^2\text{h}$, carbon dosage of 10mg/L of treated water).

Figure 6.15. TMP and flux at carbon concentration of 5.8g/L

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

Figure 6.16. TMP and flux at carbon concentration of 14.0g/L

Figure 6.17. Summary of TMP vs. flux at different carbon concentrations

The stability of the TMP can be observed in the Figures 6.15 and 6.16 and the TMP vs. flux is nearly the same as Milli-Q water line (Figure 6.17). The critical flux is

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

not observed in these two tests even though the flux was increased as high as $400\text{ L}/\text{m}^2\text{h}$. A similar observation was also reported by other researchers (Ye and Chen, 2005). Based on their experimental data on microfiltration of yeast only solution, the authors reported that the deposition of particles also did not show a discernable increase of TMP up to a permeate flux of $90\text{ L}/\text{m}^2\text{h}$ for $3.2\mu\text{m}$ latex particles and a permeate flux of $420\text{ L}/\text{m}^2\text{h}$ for $11.9\mu\text{m}$ latex particles, respectively. They stated that if the particles were relatively large compared to the pore size of the membrane, a high flux was required in order to cause sufficient resistance increase based on TMP measurements.

Therefore, the membrane performance may be maintained stable up to 1-2 months and the loaded PAC in the reactor can be removed during the backwash of the submerged system. It should also be noted that the observations on the effect of PAC on membrane performance in this study is based on treatment of trace organics (ppb level) from water. If the raw water contains NOM or domestic wastewater the situation may be different according to the studies in this area (Jack et al, 1998; Suzuki et al, 1998; Tomaszewska et al, 2002; Zhang et al, 2003; Thiruvengkatachari et al, 2005).

For a more practical operation in which the PAC inventory in the reactor is also at a steady state, a more complex modeling is required to monitor target solute concentration when the spent PAC particles are wasted from the reactor in a batch or a continuous mode. This work is shown as part of the modeling of a multi-stage system (Chapter 7) in which the PAC is dosed in an initial batch and afterward, continuously added and removed from the reactor.

6.5. Conclusions

Mathematical models were developed to describe the PAC adsorption-submerged membrane system with air bubbling for trace organics removal from water. The hybrid system performance using two PAC dosing strategies, batch dose and

6. Single-stage hybrid PAC-submerged membrane system simulation & optimization

continuous dose, were simulated using the developed model and the results were compared with experimental data. Very good agreement was observed.

The model is capable of predicting the trace organics removal by the hybrid PAC-submerged membrane system for different operating strategies. It was found that for the batch PAC dosing mode, the trace organic removal could be improved by increasing the bubbling rate or increasing the operation flux. In contrast, at the continuous PAC dosing mode, the target compound removal was independent of the bubbling rate which suggested the possibility of reducing energy consumption by inducing a low bubbling rate. Lower operation flux showed more benefit to the target compound removal because of the longer hydraulic retention time. Therefore, the model predictions can assist in evaluating the optimal working conditions for real applications in advanced water treatment.

In long-term submerged membrane applications, the PAC may be added into the reactor in step-mode (a few times per day). Thus, modeling of a more practical operation, in which the PAC inventory in the reactor is at a steady state by carbon addition, recycle and wastage, is going to be shown in the following chapter (Chapter 7). With a steady carbon inventory in the reactors for trace organic contaminants removal, the transmembrane pressure increase can be prevented and thus, the effect of pressure increase on the system performance can be avoided to a certain degree.

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

7.

SIMULATION OF COUNTERCURRENT OPERATION OF TWO-STAGE HYBRID PAC-SUBMERGED MEMBRANE SYSTEM

7.1. Introduction

In the previous chapter, trace organics removal by a continuous flow single-stage hybrid PAC-submerged membrane (SM) system has been studied experimentally and successfully simulated by the developed mathematical models. In the hybrid system, the target organic compound removal from water is due to the carbon adsorption process. The final target removal is controlled by the adsorption isotherm which describes the maximum adsorption capacity of the PAC particles when adsorption equilibrium is reached. As shown in Figure 7.1, at a lower equilibrium liquid concentration of C_{e1} , the adsorbed phase concentration of q_{e1} within the carbon particle is also lower. In contrast, if the final liquid concentration is higher, more carbon capacity can be utilized as observed as C_{e2} versus q_{e2} . Therefore, for trace organics removal using a single-stage reactor, in which a very low target (<10µg/L) concentration is expected at the end of the overall process, the utilization of carbon adsorption capacity is relatively low. In addition, the model simulation results on the continuous flow single-stage hybrid system indicate that using batch PAC dosing at the beginning of an operation leads to a very fast and effective target compound removal to meet the product water requirement. However, with the loading of the dosed PAC, a ‘breakthrough’ occurred gradually which

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

requires a periodic replacement of saturated PAC with fresh PAC particles. The organic loading on the PAC would be determined by the accepted 'breakthrough' concentration of target solute.

Figure 7.1. Freundlich adsorption isotherm curve

Continuous countercurrent adsorption systems have been extensively used in industry for several decades to improve the adsorbent utilization and thus reduce the adsorbent requirement. Liapis and Rippin (1979) reported that the carbon utilization in a single fixed bed was one third to one half of that in a continuous countercurrent adsorber of the same length. To avoid the difficulty in recirculation of the solid adsorbent in a real countercurrent system, simulated moving bed units were developed for a better fluid-solid contact. In the simulated moving bed process multiple fixed bed columns are operated with an appropriate sequence of column switching (Storti et al, 1988, Chu et al, 1995, Hassan et al, 1996). Apart from carbon adsorption, a five-stage countercurrent ion exchanger system was also found to be attractive because an increase in the number of stages in the countercurrent system not only caused decrease in the effluent concentration but also an increase in the ion loading on the resin particles (Kishore et al, 2005).

Based on the intrinsic advantages of the countercurrent system and considering the relatively easier recycling of the loaded adsorbent in a system of fully mixed

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

reactors compared with fixed bed reactors, a continuous countercurrent operation based on the hybrid submerged membrane reactors is likely to be promising. Thus, aiming to enhance the utilization of the PAC adsorption capacity, as well as to maintain a continuously stable product water quality, a few single hybrid PAC-SM reactors can be arranged in series as a multi-stage system and operated in a countercurrent manner. In the simplest multi-stage case (two-stages as shown in Figure 7.2), the liquid phase moves from one reactor to another while the solid phase transfers in the opposite direction between the reactors. As a result, in the first

Figure 7.2. Concept of countercurrent operation

stage more highly contaminated water contacts the loaded PAC coming from the second stage, whilst in the second stage the partially treated water containing fewer pollutants encounters fresh PAC. Thus, using such an operation, the final product water obtained from the second stage can be treated to achieve a very low concentration level and at the same time, the PAC capacity is more efficiently used in the first stage because the liquid has a relatively higher concentration compared to the second stage. Accordingly, the difference of adsorption capacity between the q_{e2} and q_{e1} (as shown in Figure 7.1) can be utilized in the countercurrent operation of a two-stage hybrid PAC-SM system.

In this chapter, a simplified mathematical model is developed to describe trace organic compound removal in the countercurrent two-stage hybrid PAC-SM system. In this operation, an initial batch of fresh PAC is added to the second stage and later the loaded PAC is separated by a predetermined percentage and transferred to the first stage for reuse. Simultaneously, the same amount of virgin PAC is

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

supplemented into the second reactor. The PAC replacement point is controlled by the final target concentration in the permeate from the second stage and accordingly, the product water quality can be maintained during the whole operating cycle to meet certain water quality criteria. The developed model has been used to predict the organics removal for different working strategies to provide an illustration of the performance of a real application for low concentration pollutant treatments.

7.2. Model development

Figure 7.3. Schematic of countercurrent two-stage hybrid PAC-submerged membrane system

In order to simplify the mathematical simulations of the countercurrent two-stage hybrid PAC-SM system as shown in Figure 7.3, some assumptions were made and these are described as follows:

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

- 1) The two submerged membrane tanks are completely mixed and behave as CSTRs by the air bubbling.
- 2) No PAC loss occurs in the separation unit 2 which is assumed to split the underflow perfectly into PAC and liquid.
- 3) Exactly the same amount of fresh PAC as removed is supplemented in tank #2 simultaneously.
- 4) In each PAC replacement point, the previously accumulated PAC in tank #1 is considered saturated in equilibrium with C_1 and wasted through the separation unit 1 before the addition of the loaded PACs from the tank #2.
- 5) Compared to the overall operation duration, the time for PAC replacement is short due to the highly efficient separation.

7.2.1. Formulation of adsorption in tank #2

It is known from Chapter 6 that the batch dosed PAC quickly produced water with a very low concentration of atrazine at the beginning, but this was followed by a concentration rebound because of the continuous loading of atrazine (Figure 7.4). The final effluent concentration of C_2 increases until it reaches a predetermined value (e.g. 0.05 of the feed concentration C_0), which is considered as ‘breakthrough’ and can be used as a control point for PAC replacement with a replacement rate of RR (e.g. 10% of inventory).

Figure 7.4 Schematic of batch dosing of PAC and the PAC replacement point

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

Before and after the first PAC replacement, the mass balances for the adsorption in tank #2 can be expressed as equations (7.1) and (7.2), respectively:

$$Q(C_1 - C_2) = \frac{d}{dt}(V_2 C_2 + M_c q_{2avg,t}) \quad (7.1)$$

$$Q(C_1 - C_2) = \frac{d}{dt}(V_2 C_2 + M_c (1 - RR) q_{2p-avg,t} + M_c \cdot RR \cdot q_{3avg,t}) \quad (7.2)$$

Transform equations (7.1) and (7.2) into dimensionless form by substituting:

$$C_1^* = \frac{C_1}{C_0}, \quad C_2^* = \frac{C_2}{C_0}, \quad q^* = \frac{q}{q_0}, \quad T = \frac{4D_s}{d_p^2} t, \quad R = \frac{2r}{d_p} \quad (7.3)$$

and rearrange the equations:

$$\frac{dC_2^*}{dT} = \frac{1}{E_{mb12}} (1 - C_2^* - E_{mb22} \frac{dq_{2avg,T}^*}{dT}) \quad (7.4)$$

$$\frac{dC_2^*}{dT} = \frac{1}{E_{mb12}} (C_1^* - C_2^* - E_{mb3} \frac{dq_{2p-avg,T}^*}{dT} - E_{mb4} \frac{dq_{3avg,T}^*}{dT}) \quad (7.5)$$

where

$$E_{mb12} = \frac{4 \cdot D_s \cdot V_2}{Q \cdot d_p^2} \quad (7.6)$$

$$E_{mb22} = \frac{4 \cdot D_s \cdot M_c \cdot q_0}{Q \cdot C_0 \cdot d_p^2} \quad (7.7)$$

$$E_{mb3} = \frac{4 \cdot D_s \cdot M_c \cdot (1 - RR) \cdot q_0}{Q \cdot C_0 \cdot d_p^2} \quad (7.8)$$

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

$$E_{mb4} = \frac{4 \cdot D_s \cdot M_c \cdot RR \cdot q_0}{Q \cdot C_0 \cdot d_p^2} \quad (7.9)$$

The averaged adsorbed phase concentration for the loaded PAC in tank #2, $q_{2p-avg,T}^*$, was calculated by taking the average of the adsorbed concentration in the previously loaded PAC and the supplemented fresh PAC in the last replacement step.

7.2.2. Formulation of adsorption in tank #1

The mass balance in tank #1 can be expressed as:

$$Q(C_0 - C_1) = \frac{d}{dt} (V_1 C_1 + M_c \cdot (1 - RR) \cdot q_{1avg,t}) \quad (7.10)$$

Transform into dimensionless form by substituting equation (7.3), thereby obtaining,

$$\frac{dC_1^*}{dT} = \frac{1}{E_{mb11}} (1 - C_1^* - E_{mb3} \frac{dq_{1avg,T}^*}{dT}) \quad (7.11)$$

where

$$E_{mb11} = \frac{4 \cdot D_s \cdot V_1}{Q \cdot d_p^2} \quad (7.12)$$

The loaded PAC used in tank#1 started from a loading rate of $q_{2p-avg,T}^*$ which is the averaged concentration in tank #2 in the previous step.

7.2.3. Numerical approach

The solution procedure is similar to that used for single-stage hybrid system modeling. The HSDM set of equations (5.12-5.17), coupled with equation (7.4)

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

describes the adsorbate concentration profile within the PAC (q_2^*) and corresponding liquid phase concentration in tank #2 (C_2^*) under the mode of batch dosing of PAC before any PAC replacement. The partial differential equation of equation 5.12 can be reduced to a set of ordinary differential equations by applying the orthogonal collocation method with 12 collocation points as introduced in previous chapters. Therefore, there were in total 13 ordinary differential equations which contain 13 variables of $q_2(i)^*$ ($i = 1, 2, \dots, 12$) and C_2^* . The resulting ordinary differential equations were integrated in the time domain using the Gear's method. The concentration profile of the adsorbate $q_2(i)^*$ in the carbon particle and the liquid concentration in tank #2 C_2^* at any time were obtained.

After the start of PAC replacement, tank #1 and tank #2 are related by the liquid phase concentration C_1^* and the averaged loading on the PAC, $q_{2p-avg,t}^*$. Therefore, equations (7.5) and (7.11) in combination with equations (5.12) to (5.17) describe the liquid and solid phase concentrations in the two-stage system. Similarly, the partial differential equation of (5.12) was reduced to a set of ordinary differential equations, resulting in a total of 14 ordinary differential equations which contain 14 variables of $q_2(i)^*$ ($i = 1, 2, \dots, 12$), C_1^* and C_2^* . The rest of the solving procedure is similar to the previous one. The 14 variables were determined simultaneously by running FORTRAN programs.

7.3. Model predictions and discussion

Figures 7.5 and 7.6 show the model predictions of the target compound in the liquid and within the PAC particles, respectively, for the countercurrent operation at a flux of $60L/m^2h$, in which 1000mg fresh PAC was dosed at the beginning, the following PAC addition is controlled by $C_2^* = 0.05$ and the PAC replacement rate is

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

10%. This process is effectively ‘batch-continuous’ mode (‘pseudo-steady state results are discussed later).

Figure 7.5. Countercurrent operation, $RR=10\%$, $C_2^*=0.05$, $J=60\text{L}/\text{m}^2\text{h}$,

$$M_c=1000\text{mg}, k_f=1.08 \times 10^{-4} \text{ m/s}, V_1=V_2=50\text{L}, \text{HRT}=125\text{min},$$

$$M_{c \text{ total}}=1800\text{mg}$$

It is clear that the final target concentration can be maintained below 0.05. Before the first replacement of PAC, the liquid concentration in tank #2 (C_2^*) decreases very fast at the beginning because of the adsorption by the first batch of fresh PAC. During this period C_1^* maintains at 1.0 since no PAC is dosed to tank #1. Progressively, more and more target compound is loaded onto the PAC in tank #2 (Figure 7.6) and the liquid phase concentration increases gradually (Figure 7.5). When C_2^* achieves 0.05 at around 408 min, 10% of the loaded PAC was replaced

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

by fresh PAC in tank #2 and reused in tank #1. Therefore, it is seen at time 408 min that C_2^* decreases again and simultaneously a decrease in C_1^* occurs (Figure 7.5).

Figure 7.6. Adsorbed phase concentration, $J=60\text{L}/\text{m}^2\text{h}$

The loaded PAC from tank #2 continues adsorbing the target solute at the higher concentration in tank #1 from an averaged solid phase concentration $q_{avg}^*(\text{tank \#1})$ of 0.52 as shown in Figure 7.6. Then $q_{avg}^*(\text{tank \#2})$ in tank #2 starts from a relatively lower value because the adsorption of both newly dosed fresh PAC and the further adsorption of the remaining proportion of the loaded PAC. In tank #1 the solid phase concentrations of $q_{avg}^*(\text{tank \#1})$, which is the final PAC loading at the breakthrough point, is 0.77. Compared to the single-stage hybrid system with the same total amount of PAC dosed at the beginning, the final carbon loading increases from 0.49 to 0.77 when $C_2^* > 0.05$ is considered as ‘breakthrough’. Thus

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

around 28% of the carbon capacity can be further utilized by the countercurrent operation compared with a single reactor.

Operating at same condition but at a higher flux of $100\text{L}/\text{m}^2\text{h}$, similar results can be observed in Figures 7.7 and 7.8. The final carbon loading at the ‘breakthrough’ point increased from 0.45 in single-stage system to 0.66 (tank #1) in the countercurrent system. Thus, around 21% of the carbon capacity can be further utilized by the countercurrent two-stage system when operated at a flux of $100\text{L}/\text{m}^2\text{h}$.

Figure 7.7. Countercurrent operation, $RR=10\%$, $C_2^*=0.05$, $J=100\text{L}/\text{m}^2\text{h}$,

$$M_c=1000\text{mg}, k_f=1.08 \times 10^{-4} \text{ m/s}, V_1=V_2=50\text{L}, \text{HRT}=125\text{min},$$

$$M_c \text{ total}=3000\text{mg}$$

Comparing Figures 7.6 and 7.8, it can be seen that 8 and 20 times of PAC replacement are needed for the fluxes of $60\text{L}/\text{m}^2\text{h}$ and $100\text{L}/\text{m}^2\text{h}$, respectively,

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

based on the simulation results. This difference is because a higher flux means more water is treated per unit of time and the PAC is loaded faster and more frequent renewal of PAC is required. In addition, relatively less PAC adsorption capacity is utilized at higher permeate flux operation.

Figure 7.8. Adsorbed phase concentration, $J=100\text{L}/\text{m}^2\text{h}$

A similar trend can be found when the PAC replacement is controlled by a higher final effluent concentration, $C_2^* = 0.1$ (Figure 7.9). By comparison (Figure 7.5 and 7.9), it can be seen that the lower the desired final target concentration, the more frequently the PAC needs to be refreshed. For the same RR , it requires 8 times of replacement at $C_2^* = 0.05$, while 6 times replacement at $C_2^* = 0.1$. In addition, if the allowed pollutant level in the final product water is higher, a slightly higher carbon capacity is achieved based on comparison between Figure 7.6 ($q_{avg(tank\#1)}^* = 0.77$) and Figure 7.9 ($q_{avg(tank\#1)}^* = 0.82$).

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

Figure 7.9. Countercurrent operation, $RR=10\%$, $C_2^* = 0.1$, $J=60\text{L}/\text{m}^2\text{h}$,

$$M_c=1000\text{mg}, k_f = 1.08 \times 10^{-4} \text{ m/s}, V_1=V_2=50\text{L}, \text{HRT}=125\text{min},$$

$$M_c \text{ total}=1600\text{mg}$$

Figure 7.10 shows the residual concentrations in the two reactors when the PAC replacement rate is as low as 1%. Under this scenario it requires more frequent PAC replacement (100 times) during 1080min compared to the case shown in Figure 7.5. The product quality is more stable at exactly 0.05 and the final carbon capacity usage is also increased from 0.50 for a single reactor to 0.74 in tank #1. According to this trend, the countercurrent two-stage hybrid system operated at very small PAC replacement rate is close to a process with continuous dosing of PAC and can be considered as ‘pseudo-steady state’. The low replacement rate reduces the volume of liquid loading on separation unit 2 each time and results in a faster and easier carbon separation from the liquid phase. Figure 7.11 shows the model predictions at this condition with a higher flux, which corresponds to a shorter HRT.

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

Loading on the PAC is now 0.46 for countercurrent and 0.39 for the single stage. It is worth noting that the ‘pseudo-steady state’ with a RR of 1% is slightly less efficient than the ‘batch-continuous’ operation with a RR of 10% (for a flux of $60L/m^2h$; $q_{avg}^*(\text{tan k\#1}) = 0.74$ vs. 0.77).

Figure 7.10. Countercurrent operation, $RR=1\%$, $C_2^*=0.05$, $J=60L/m^2h$,

$$M_c=1000\text{mg}, k_f = 1.08 \times 10^{-4} m/s, V_1=V_2=50L,$$

$$\text{HRT}=125\text{min}, M_c \text{ total}=2000\text{mg}$$

It should be pointed out that the model predictions of final product water quality are conservative as the loaded PAC particles accumulated in the tank #1 with time are not fully saturated as assumed (the maximum utilization predicted is 0.82 as shown in Figure 7.9). Hence, the concentration profile of C_1^* can be slightly lower than that presented, resulting in a slightly lower influent concentration for tank #2. Therefore, the actual replacement frequency may be slightly lower than predicted.

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

The saturated PAC in the submerged membrane tank #1 is periodically wasted through the separation unit 1 for carbon regeneration before the replacement of the partially loaded carbon in tank #2. With this operation, steady-state carbon concentrations in both reactors can be maintained.

Figure 7.11. Countercurrent operation, $RR=1\%$, $C_2^*=0.05$, $J=100\text{L/m}^2\text{h}$,

$$M_c=1000\text{mg}, k_f = 1.08 \times 10^{-4} \text{ m/s}, V_1=V_2=50\text{L},$$

$$\text{HRT}=125\text{min}, M_c \text{ total}=3850\text{mg}$$

It is worth noting that a single-stage PAC-SM reactor with a steady-state carbon inventory (mentioned in Section 6.4.3) works similarly to tank #2 in the countercurrent two-stage system (Figures 7.10 & 7.11) except that the target concentration in the influent of a single-reactor is as that in raw water. With the initial batch dosing of PAC, the product water concentration decreased faster than only continuous PAC dosing from the beginning as discussed in Section 6.4.2.1. The following continuous dosing of PAC maintains the product quality at a desired

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

level and avoids the ‘breakthrough’ phenomenon. Furthermore, with a continuous waste of the spent carbon (appropriate replacement rate, RR) the carbon concentration in the reactor can be maintained at a steady-state. Therefore, this “batch dosing - continuous dosing - continuous removal” strategy of PAC usage in a hybrid PAC-submerged membrane tank makes it a more practical process for long-term operations in the water industry. Countercurrent multi-stage hybrid systems, which combine several single-stage reactors working under this strategy (as discussed and simulated in this chapter), overcome the low carbon utilization of a single-stage system. This benefit needs to be weighed against the increased complexity of the system.

7.4. Conclusions

The countercurrent two-stage hybrid PAC-Submerged Membrane system has been simulated numerically in this chapter. The model predictions confirmed that the adsorption capacity of the PAC was further utilized and a stable product water quality was maintained in the countercurrent mode, which is in accordance with the principles of countercurrent operation. The system performance was successfully predicted at different working conditions such as permeate fluxes, replacement rates as well as the controlling effluent concentration. It was found that the adsorption capacity utilization is dependent on the permeate flux of the membrane filtration process. At the same working conditions, 28% of the PAC capacity can be further utilized by countercurrent two-stage operation compared with concurrent single-stage operation at a flux of $60L/m^2h$. In contrast, 21% of the adsorption capacity can be further used at a flux of $100L/m^2h$ by more frequent PAC replacement. If controlled at higher final effluent concentration (e.g. $C_2^* = 0.1$ instead of $C_2^* = 0.05$), a further 5% of the PAC adsorption capacity can be utilized. In addition, reducing the replacement rate will make the system similar to a system with continuous PAC replacing by presenting nearly constant product water quality. This reduces the loading on the separation unit 2 between the stages. However, this ‘pseudo-steady

7. Simulation of countercurrent operation of two-stage hybrid PAC-SM system

state' is slightly less efficient in terms of carbon usage compared with 'batch-continuous' operation.

Although the countercurrent multi-stage PAC-SM system has its complexity in real applications for water treatment, the results obtained from the two-staged system provide us with a better understanding of the countercurrent operations using hybrid membrane systems. This study gives us a quantitative idea of the performance of multi-stage hybrid systems for its further application and system optimization. Although there is a challenge in the separation of the loaded carbon from the second stage for its reuse in the first stage and for solids discharge from the first stage, it may still be a process worthy of further study. Topics for further research include combining another membrane module or other separation process to provide 'Separation Units' 1 and 2 and searching for an optimal PAC replacement rate.

8.

PAC REGENERATION WITH PHOTOCATALYTIC OXIDATION IN A SUBMERGED MEMBRANE SYSTEM*

8.1. Introduction

From an economic point of view, it would be desirable to regenerate spent activated carbon that is used in water and wastewater treatment. Among several regeneration processes, photocatalysis, which is a relatively new method, can decompose the organic compounds from the adsorbed phase with the assistance of titania (TiO_2) under UV-irradiation and thus, restore the carbon adsorption capacity. The combination of carbon adsorption with oxidative destruction may be a promising way which is not only economic (carbon reuse) but also environmentally friendly (harmless products degradation) to fulfill water treatment.

The synergistic effect of titania associated with activated carbon on organic compounds degradation has been studied for years in the photocatalysis area. A suspended mixture of PAC and titania under UV-irradiation was able to induce a substantial enhancement (by a factor of 2.5) in the photo-efficiency of the photocatalyst (Matos et al, 1998; Herrmann et al, 1999). This was ascribed to an extended carbon adsorption followed by mass transfer to photoactive TiO_2 through an AC- TiO_2 interface exchange but dependent of the properties of the activated carbon (Matos et al, 2001). A synergy factor (1.0-2.0) was described and compared

*The work reported in this Chapter was done in collaboration with others
(see Acknowledgement)

8. PAC regeneration with photocatalytic oxidation in a SM system

(Silva et al, 2003) to quantify the effect on the enhancement of the TiO_2 photoefficiency by nine different GACs.

In wastewater treatment, Qourzal et al (2004) added the TiO_2 (600 ° C) to the PAC and obtained a faster photocatalytical degradation of the organic pollutant than TiO_2 alone. Through studying urban wastewater treatment, Arana et al (2002) also showed that the TiO_2 and activated carbon(AC) mixed catalysts showed a high efficiency in obtaining a high level of disinfection, reducing organic materials and even eliminating some inorganic ions.

Improved degradation efficiency was also observed by using TiO_2 coated ACs in the photo-degradation of pollutants either from water (Tryba et al, 2003) or air (Ao et al, 2004). This positive effect was explained by Lee et al (2004) as that the high surface area of the AC provided sites for the organics adsorption, and the adsorbed organics continuously migrated onto the surface of TiO_2 particles which are located mainly at the exterior surface in the vicinity of the entrances of the macropores of the AC.

These previous studies confirmed the beneficial effect of the existence of activated carbon on the TiO_2 photocatalysis efficiency in the processes of water and wastewater treatment. In addition, they also shed light on the regeneration of the spent activated carbon, where the utilization of the photocatalyst under UV irradiation may further degrade the adsorbed organics and result in a recovered carbon capacity for reuse. This combined process could be operated in-situ to replace the complex procedure of separating the spent carbon, especially the AC in powdered phase (PAC) from the solution, thereby avoiding carbon loss.

This chapter reports on a preliminary study where PAC regeneration efficiency as well as the low concentration organic compound removal was studied by using a mixture of TiO_2 and PAC particles. The particle mixture was suspended in a submerged hollow fiber membrane reactor which was under UV irradiation. The PAC regeneration was examined with sequential batch tests of photocatalysis and

8. PAC regeneration with photocatalytic oxidation in a SM system

PAC adsorption. In addition, the effect of the mixed particles on the target compound removal using a continuous flow submerged membrane system was also investigated.

8.2. Experimental

8.2.1. Materials

High purity Bisphenol A (BPA, from Merck-Schuchardt) was used as the target compound in this study. Atrazine is not used as the target compound because it cannot be fully mineralized by UV photocatalytic oxidation. To have a more evident result of the investigation into the regeneration with photocatalysis process, BPA was used instead. TiO₂ (P25) used for the experiments was obtained from Degussa AG, Germany. The original PAC (Norit Hydrodarco C) was pulverized for 20 min to obtain small PAC particles with median particle size of 8.0 μm. All solutions were prepared using Milli-Q water with a resistivity of 18.2 MΩcm. A U-shaped hollow fiber membrane module consisting of 10 pieces of MF hollow fiber (pore size 0.22 μm, PVDF from Bluestar, China) with a total surface area of $8.2 \times 10^{-3} m^2$ was used in the submerged membrane reactor. The inner and outer diameters of the fibers are 0.65 mm and 1.0 mm, respectively.

8.2.2. Methods

8.2.2.1. Adsorption kinetic tests

Jar tests (2 h) were conducted to study the adsorption kinetics of BPA by the virgin PAC, mixed particles consisting of PAC and TiO₂, and the regenerated PAC respectively. Beakers containing BPA solution were spiked with particles and stirred mechanically at 180 rpm. Samples were taken at predefined times to be filtered through 0.22 μm filters for analysis.

8. PAC regeneration with photocatalytic oxidation in a SM system

8.2.2.2. Hybrid photocatalytic-PAC- submerged membrane reactor

A schematic diagram of the photocatalytic-PAC-submerged membrane (PPSM) system is shown in Figure 8.1 (after Chin et al, 2005). The reactor is made of borosilicate glass for the study on the photocatalytic degradation of BPA. A hollow fiber membrane module was placed in the center of the reactor. The UVA irradiation was provided by four 8W black light fluorescent lamps (NEC FL8 BL-B) located on the four sides of the reactor. During the experiment, a constant permeate flux of $100\text{L}/\text{m}^2\text{h}$ was maintained by suction provided by a peristaltic pump (Cole-Parmer). The permeate flux was measured using a balance (Mettler Toledo) which was connected to a computer for data recording. The transmembrane pressure (TMP) in all experiments was measured by a pressure gauge placed in the permeate line. A level sensor was installed and controlled an inlet pump which pumped the BPA solution into the system in order to keep the total volume of the reactor constant. An aeration rate at $1.0\text{L}/\text{min}$ was applied and samples were taken at predetermined time intervals from the permeate line for concentration analysis.

Figure 8.1. Schematic diagram of a hybrid PPSM system

8. PAC regeneration with photocatalytic oxidation in a SM system

8.2.2.3. BPA and TOC analysis

The concentration of BPA in samples was also measured using HPLC interfaced with a photodiode array detector. The separation was carried out using a Waters Xterra RP18 column (3.9mm x 150mm, 5 μ m) with a mobile phase consisting of water (50%)-acetonitrile (50%).

8.3. Results and discussion

Figure 8.2 shows the experimental results for a continuous flow hybrid PAC-submerged membrane (SM) test followed by photocatalytic oxidation (PCO) for carbon regeneration. The total PAC mass of 0.08g was dosed in batch mode at the beginning into the submerged reactor containing 800mL solution with 10mg/L of BPA. The PAC adsorption capacity was saturated after 5 h operation as the BPA

Figure 8.2. Continuous flow PAC-SM test followed by PCO, $J=100\text{L}/\text{m}^2\text{h}$,
 $M_c=0.08\text{g}$, $V=0.8\text{L}$, Bubbling rate= $1.0\text{L}/\text{min.L}$

8. PAC regeneration with photocatalytic oxidation in a SM system

concentration reached 0.96 of C_0 at the end of the 5 h test. Then the liquid flow was ceased and 0.4g of TiO_2 particles were added immediately to start oxidation under UV irradiation. It was detected that the liquid phase BPA was fully degraded after 2 h of PCO but the bubbling and UV light were further maintained for another 2 h to degrade the solid phase BPA loaded on the PAC particles.

The residual liquid containing both PAC and TiO_2 was transferred to the jar test and topped up to 5mg/L BPA to test the adsorption kinetics after the 4 h PCO regeneration. The results are compared with the fresh PAC jar tests at the same conditions in Figure 8.3. Since there is no UV-irradiation provided, the photocatalytic oxidation cannot take place. The BPA removal only relies on the adsorption capacity of PAC in the jar. Compared to the BPA removal with virgin PAC (90%) in the mixed particles after 2 h, the regenerated PAC achieved 60% of target removal. This indicates that the saturated PAC (after 5 h adsorption shown in Figure 8.2) was partially regenerated during the 4 h PCO process.

Figure 8.3. Adsorption kinetics for virgin PAC and 4-h PCO regenerated PAC, BPA=5mg/L, stirred at 180rpm, PAC/ TiO_2 =1:5 (by mass)

8. PAC regeneration with photocatalytic oxidation in a SM system

It was noticed that the PAC and TiO_2 particles were suspended in the liquid simultaneously as a mixture; thus, the effect of the PAC- TiO_2 ratio on the PAC adsorption kinetics was tested and the results are shown in Figure 8.4. It is clear that when the PAC/ TiO_2 ratios were varied from 1/1 to 1/10, the adsorption kinetic curves were nearly identical. Compared to the sole PAC particle tests, it can be concluded that the presence of TiO_2 has no effect on the PAC adsorption. The TiO_2 particles at 1.0 g/L adsorbed only less than 5% of BPA as shown in the figure. Thus, compared to the strong adsorption by PAC, the BPA adsorbed by TiO_2 in the mixture at 0.5g/L was negligible. Therefore, the PAC/ TiO_2 at a ratio of 1/5 was used in the following regeneration tests.

Figure 8.4. Adsorption kinetics for virgin PAC and TiO_2 mixed particles at different mixing ratios

The effect of TiO_2 oxidation time on the PAC regeneration is shown in Figure 8.5. Compared to 4 h PCO (60% removal), 12 h PCO was able to further regenerate the loaded PAC to achieve 80% of BPA removal at the end of a 2 h jar test. The adsorption rate was improved mostly in the initial stages of the kinetic test followed by a very slow decrease of the residual BPA concentration in the liquid phase. It can also be observed that even 12 h UV oxidation could not fully recover the PAC

8. PAC regeneration with photocatalytic oxidation in a SM system

adsorption capacity. This may be due to adsorption of the intermediate products generated during the degradation of BPA, which are adsorbed strongly or deeply within the micropores and thus, difficult to be desorbed. In addition, the oxidative radicals produced by the TiO_2 have rather short lifetime (hundreds of ns to ms) which would not allow much penetration into the bulk of the PAC particles.

Figure 8.5. Comparison between 4-h and 12-h PCO regenerations of PAC

The performance of the regenerated PAC after 12 h PCO in the continuous flow hybrid submerged membrane system was compared to the virgin PAC and saturated PAC in Figure 8.6. At the beginning of each test, the initial concentration of BPA in the reactor was zero. With the suction of the permeate from the membrane, the feed solution containing 5mg/L of BPA was added at the same flowrate. The saturated PAC without regeneration presented nearly the same results as Milli-Q water, which indicates no adsorption happened in the process. Whereas the regenerated PAC causes a delayed breakthrough of BPA but still shows a weaker adsorption capacity compared to the virgin PAC. Therefore, more work is required to evaluate optimal working conditions for the PAC regeneration through PCO by considering various factors such as pH, stronger co-oxidants, temperature etc, and the electrical power consumption in the irradiation as well. There would also be benefit if smaller

8. PAC regeneration with photocatalytic oxidation in a SM system

PAC particles could be used as the regeneration process may only operate over a distance on the order of a micron.

Figure 8.6. Continuous flow test using hybrid submerged membrane system, started with Milli-Q water, $J=100L/m^2h$, Bubbling=1.0L/min, Feed BPA=5mg/L

Nevertheless, the results presented in this chapter confirmed the feasibility of regenerating the activated carbon in powdered phase by TiO_2 particles with the assistance of UV irradiation at natural pH and ambient temperature. In addition, the saturated PAC can be regenerated in-situ by turning on the UV light for a few hours in the hybrid submerged membrane reactor, which can avoid the trouble of separating spent PAC from the reactor and reduce supplemented amount of fresh PAC into the system.

8.4. Conclusions

8. PAC regeneration with photocatalytic oxidation in a SM system

The feasibility of spent PAC regeneration by photocatalytic oxidation of TiO_2 was examined in this chapter by conducting batch adsorption and UV oxidation tests. It was found that the PAC adsorption capacity can be partially recovered in natural conditions after 12 h oxidation. In addition, the application of the regenerated PAC in the continuous flow hybrid submerged membrane reactor further confirmed the enhanced adsorption capacity of regenerated PAC. The presence of TiO_2 was found to have no effect on the PAC adsorption process. This indicates that regenerating saturated PAC in-situ in the membrane reactor by TiO_2 photocatalytic oxidation is a promising process to reduce the costs of using traditional approaches to separate PAC and then regenerating PAC. It also potentially simplifies the whole system. However, other operating parameters need to be studied to evaluate the optimal working conditions to achieve full PAC regeneration in a short time. If this can be achieved, it would be possible to apply the hybrid PAC-PCO-submerged membrane system to practical applications to achieve a self-sustaining long term operation for the water treatment.

Acknowledgement

The author would like to acknowledge Dr. Park SeJin and Ms. Chin SzeSze for their selfless contributions to the experimental work in this section.

9.

CONCLUSIONS AND RECOMMENDATIONS

9.1. Overall conclusions

This thesis focuses on an experimental study and mathematical simulation as well as optimization of trace organics removal by hybrid PAC-submerged membrane systems with air bubbling. The mass transfer and factors associated with air bubbling that affect the adsorption kinetics were investigated. The air bubbling was found to have a beneficial effect on the PAC adsorption. Mathematical models were developed to simulate the adsorption of the organics by PAC in single-stage reactors with air bubbling for different operating strategies and verified by corresponding experiments. The modeling makes it possible to predict the performance of trace organics removal in the hybrid PAC-submerged membrane system with air bubbling and to identify optimal operation conditions. The trace organics removal in a two-stage hybrid system with air bubbling working in countercurrent flow was also simulated to gain a quantitative estimate of on the enhancement of the utilization of PAC adsorption capacity. The feasibility of the regeneration of spent PAC using TiO_2 photocatalytic oxidation was examined and confirmed. This provides a potential method to regenerate the spent PAC in-situ in the hybrid submerged membrane system consisting of a mixed suspension of PAC and TiO_2 particles.

9.1.1. Investigation of the factors associated with air bubbling

9. Conclusions and recommendations

The effects of accompanying factors brought about by air bubbling on the trace organic adsorption kinetics by PAC in water were systematically investigated.

- ✧ pH change during air bubbling was shown to have little influence on the adsorption efficiency.
- ✧ N_2 and O_2 were also found to have no competitive impact on the target atrazine adsorption in the bubbling condition.
- ✧ The contaminants released from PVC soft tubing competed with the trace organics on the adsorption sites and accordingly, resulted in a reversal of adsorbed atrazine and reduced adsorption efficiency in the removal of ppb level pollutants.
- ✧ Intermittent bubbling was found to be more beneficial to enhance PAC adsorption rates than continuous bubbling. At the same net bubbling rate, high intensity intermittent bubbling with a longer rest period is more efficient in improving the liquid film mass transfer than low intensity bubbling with shorter rest.

9.1.2. Determination of mass transfer coefficients

Air bubbling was found to be a favorable method to enhance PAC adsorption of a dilute organic solute. Good mixing could be achieved by air bubbling at moderate flow rates. The mass transfer coefficients to describe the adsorption kinetics were studied by both a simple approach and complex numerical simulation.

- ✧ In the simple approach, the surface diffusion within PAC particles was ignored as the initial stage was mostly controlled by liquid film mass transfer. Therefore, the mass transfer coefficients in the liquid film surrounding the PAC were estimated using the initial experimental data and the first-order mass balance equations. These values were compared with those derived from conventional mass transfer correlations, which were developed for magnetic stirring systems, with the help of the

9. Conclusions and recommendations

conversion of the bubbling rates to the equivalent stirring speeds. In general, the results showed that the mass transfer coefficient K_l was improved to a plateau value by increasing air bubbling rate.

- ✧ In the complex approach, the adsorption kinetic parameters were obtained by solving the homogeneous surface diffusion model (HSDM) model with the assistance of a series of independent closed batch adsorption tests with continuous air bubbling. The HSDM was solved numerically using the orthogonal collocation method with 12 collocation points. The differences between the model solutions and corresponding experimental results were minimized by means of Levenberg-Marquardt algorithm so that two kinetic parameters of D_s and k_f were obtained simultaneously. As a result, the D_s was found to be $1.14 \times 10^{-16} \text{ m}^2 / \text{s}$ while the k_f changed with several parameters. The k_f value was improved by an increase in the bubbling rates within a certain range. A formula to correlate k_f , the air bubbling rate Q_b , as well as the carbon dosage C_c was obtained by non-linear regression.

9.1.3. Modeling of a continuous flow single-stage hybrid PAC-submerged membrane system with air bubbling

Mathematical models were developed to describe trace organics removal by the single-stage PAC-submerged membrane system with air bubbling for two PAC dosing strategies, i.e. batch dosing and continuous dosing. The previously developed empirical correlation for k_f , Q_b and C_c was used to determine the kinetic coefficients needed at different conditions for the whole system modeling. Based on these parameters, the models were developed by applying the HSDM coupled with the mass balance of the continuous flow submerged membrane reactors and were verified by experimental data with very good agreement.

9. Conclusions and recommendations

The models are capable of predicting the trace organics removal by the hybrid PAC-submerged membrane system for different operating strategies.

- ✧ In the batch PAC dosing mode, the trace organic removal can be improved by increasing the bubbling rate or increasing the operating flux.
- ✧ In the continuous PAC dosing mode, the target compound removal is independent on the bubbling rate. Lower operating flux is favorable for the target compound removal because of the longer hydraulic retention time.

9.1.4. Modeling of continuous countercurrent two-stage hybrid PAC-submerged membrane system with air bubbling

For trace organics removal, the PAC adsorption capacity utilized in the single-stage hybrid PAC-submerged membrane (SM) system is limited because of the low target concentration in the product water at equilibrium. To enhance the usage of the PAC adsorption capacity, a countercurrent two-stage hybrid PAC-SM system was simulated numerically. In this system the loaded PAC in the second stage was reused to contact with feed water which containing higher target concentration in the first stage and as a result, further utilization of the remaining adsorption capacity of the carbon particles was achieved.

From the model prediction, it was found that the countercurrent operation can enhance the utilization of the PAC capacity to different extents based on different working conditions:

- ✧ If the PAC replacement was controlled at the time when the residual concentration in the liquid solution was 0.05 of the initial feed concentration, the final PAC adsorption capacity usage was enhanced by 28% of the total capacity at a flux of $60\text{ L}/\text{m}^2\text{h}$ and by 21% at a flux of $100\text{ L}/\text{m}^2\text{h}$ respectively. When the PAC replacement is controlled at higher target compound concentration in the product water, an improved utilization of the carbon capacity results.

9. Conclusions and recommendations

- ✧ Lower flux operation requires less frequent PAC replacement and has higher carbon utilization than higher flux operation.
- ✧ Reducing the PAC replacement rate makes the whole process more close to a pseudo-steady state, in which PAC is replaced with high frequency but very small amounts each time. The product water quality is maintained at a relatively constant value in this case.

9.1.5. PAC regeneration by TiO₂ photocatalytic oxidation (PCO)

The regeneration of the spent PAC which was saturated by the target compound BPA, using TiO₂ photocatalytic oxidation was confirmed through batch adsorption kinetic tests and batch PCO tests. A preliminary study was made of the feasibility of in-situ regeneration of the spent PAC suspended in the submerged membrane reactor through continuous flow hybrid system tests. Based on the experimental results, it was found that:

- ✧ The adsorption of the target compound by TiO₂ was negligible compared to the adsorption by PAC so that the TiO₂ and PAC mixed particles, even at a very high TiO₂ ratio, showed nearly the same adsorption kinetics as that of only the PAC particles.
- ✧ Longer PCO time could recover more PAC adsorption capacity than shorter time. However full regeneration was not achieved even after 12 h of batch PCO.
- ✧ The regenerated PAC was tested using both jar tests and continuous flow hybrid submerged membrane filtration tests. Both approaches confirmed the good, but partial recovery of PAC adsorption capacity.
- ✧ It should be possible to apply the hybrid PAC-PCO-SM system to trace organics removal from water by alternately running the PAC adsorption and PCO process without removing the saturated PAC out of the reactor for regeneration/disposal or adding fresh PAC.

9. Conclusions and recommendations

9.2. Recommendations for future research

For the countercurrent two-stage hybrid system, an effective and efficient separation unit between the two tanks has to be developed. It can be designed as another membrane filtration unit or a well-designed hydrocyclone or equivalent process. Experimental results from a lab scale countercurrent two-stage submerged membrane system with PAC in suspension are needed to verify the developed model. Based on this, the system optimization can be investigated in further detail. For its application in water industry, an economic analysis to access the commercial viability of this process is required

The optimal working conditions for more efficient and faster regeneration of spent PAC by PCO needs to be investigated by considering various parameters such as pH range, strong oxidants, temperature profile, intermediate product identification, etc. The use of ultra-fine PAC should be examined as this could increase the percent regeneration achieved. The feasibility of the in-situ regeneration of spent PAC in the submerged membrane tank with a mixed suspension of PAC and TiO_2 particles requires more study to develop a practical operating strategy. In addition, the effect of mixed particles and ultra-fine PAC on membrane filtration needs to be evaluated by methods such as critical flux analysis.

REFERENCES

Adham, S.S., Snoeyink, V.L., Clark, M.M. and Bersillon, J-L. (1991) “Predicting and verifying organics removal by PAC in an ultrafiltration system”, Journal of American Water Works Association, Vol.83, No. 12, pp. 81-91.

Adham, S.S., Snoeyink, V.L., Clark, M.M. and Anselme, C. (1993) “Predicting and verifying TOC removal by PAC in pilot-scale UF systems”, Journal of American Water Works Association, Vol. 85, No.12, pp. 58-68.

Adham, S. S., Jacangelo, J. G. and Laine, J. M, (1996) “Characteristics and costs of MF and UF plants”, Journal of American Water Works Association, Vol. 88, No. 5, pp. 22-32.

Aksu, Z. and Kabasakal, E. (2004) “Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon”, Separation and Purification Technology, Vol. 35, pp. 223-240.

Albal, R.S., Shah, Y.T., Schumpe, A. and Carr, N.L. (1983) “Mass transfer in multiphase agitated contactors”, The Chemical Engineering Journal, Vol.27, pp. 61-80.

Ao, C.H. and Lee, S.C. (2004) “Combination effect of activated carbon with TiO₂ for the photodegradation of binary pollutants at typical indoor air level”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 161, pp.131-140.

Arana, J. Herrera Melian, J.A., Dona Rodriguez, J.M. Gonzalez Diaz, O., Viera, A., Perez Pena, J., Marrero Sosa, P.M. and Espino Jimenez, V. (2002) “TiO₂–photocatalysis as a tertiary treatment of naturally treated wastewater”, Catalysis Today, Vol. 76, pp. 279-289.

Arters, D.C. and Fan, L.S. (1986) "Solid-liquid mass transfer in a gas-liquid-solid fluidized bed", Chemical Engineering Science, Vol.41, No.1, pp. 107-115.

Best, G., Singh, M., Mourato, D. and Chang, Y. J. (2000) "Application of immersed ultrafiltration membranes for organic removal and disinfection by-product reduction", Proceedings of the conference on membrane in drinking and industrial water production, Vol. 2, pp. 27-40.

Bitter, J. G. A., (1991) Transport mechanisms in membrane separation processes, Plenum Press, New York.

Braghetta, A., Price, M., Hentz, C., Stevenson, E. and Kolkhorst, C. (2000) "Impact of pretreatment on UF operation and removal of dissolved organics", Proceedings of the conference on membranes in drinking and industrial water production, Vol. 2, pp. 345-354.

Cabassud, C., Laborie, S., and Lain, J. M. (1997) "How slug flow can improve ultrafiltration flux in organic hollow fibers", Journal of Membrane Science, Vol. 128, pp. 93-101.

Campos, C., Marinas, B. J., Snoeyink, V. L. and Baudin, I. (1998) "Adsorption of trace organic compounds in CRISTAL processes", Desalination, Vol. 117, pp. 265-271.

Campos, C., Marinas, B. J., Snoeyink, V. L., Baudin, I. and Laine, J. M. (2000a) "PAC-membrane filtration process. I: model development", Journal of Environmental Engineering, Vol. 126, No. 2, pp. 97-103.

Campos, C., Marinas, B. J., Snoeyink, V. L., Baudin, I. and Laine, J. M. (2000b) "PAC-membrane filtration process. II: model application", Journal of Environmental Engineering, Vol. 126, No. 2, pp. 104-111.

Campos, C., Snoeyink, V. L., Marinas, B. J., Baudin, I. and Laine, J. M. (2000c) "Atrazine removal by powdered activated carbon in floc blanket reactors", Water Research, Vol. 34, No. 16, pp. 4070-4080.

Cannon, F.S., Snoeyink, V.L., Lee, R.G. and Dagois, G. (1994) "Reaction mechanism of calcium-catalyzed thermal regeneration of spent granular activated carbon", Carbon, Vol. 32, No. 7, pp. 1285-1301.

Chan, R. and Chen, V. (2001) "The effects of electrolyte concentration and pH on protein aggregation and deposition: critical flux and constant flux membrane filtration", Journal of Membrane Science, Vol. 185, pp. 177-192.

Chang, I. S. and Judd, S. J. (2002) "Air sparging for a submerged MBR for municipal wastewater treatment", Process Biochemistry, Vol. 37, pp. 915-920.

Chang, S. and Fane, A. G., (2000a) "Characteristics of microfiltration of suspensions with inter-fiber two-phase flow", Journal of Chemical Technology and Biotechnology, Vol. 75, pp. 533-540.

Chang, S. and Fane, A. G., (2000b) "Filtration of biomass with axial inter-fiber upward slug flow: performance and mechanisms", Journal of Membrane Science, Vol. 180, pp. 57-68.

Chang, S. (2001a) "Optimization of submerged hollow fiber membrane modules", PhD thesis, The University of New South Wales.

Chang, S. and Fane, A. G. (2001b) "The effect of fiber diameter on filtration and flux distribution-relevance to submerged hollow fiber modules", Journal of Membrane Science, Vol. 184, pp. 221-231.

Chang, S. and Fane, A. G. (2002a) "Modeling and optimizing submerged hollow fiber membrane modules", AIChE Journal, Vol. 48, No. 10, pp. 2203-2212.

Chang, S., Fane, A.G. and Vigneswaran, S. (2002b) "Experimental assessment of filtration of biomass with transverse and axial fibers", Chemical Engineering Journal, Vol. 87, pp. 121-127.

Chang, S. and Fane, A.G. (2002c) "Filtration of biomass with lab-scale submerged hollow fiber membrane module: effect of operational conditions and module configuration", Journal of Chemical Technology and Biotechnology, Vol. 77, pp. 1030-1038.

Chang, S., Waite, T.D., Ong, E.A, Schafer, A.I. and Fane, A.G. (2004) "Assessment of trace estrogenic contaminants removal by coagulant addition, powdered activated carbon adsorption and powdered activated carbon/microfiltration processes", Journal of Environmental Engineering, Vol. 130, No.7, pp. 736-742.

Chang, S., Waite, T.D. and Fane, A.G. (2005) "A simplified model for trace organics removal by continuous flow PAC adsorption/submerged membrane processes", Journal of Membrane Science, Vol. 253, pp. 81-87.

Chen, V., Fane, A.G., Madaeni, S. and Wenten, I.G. (1997) "Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation", Journal of Membrane Science, Vol. 125, pp. 109-122.

Cheng, T.W., Yeh, H.M. and Gau, C.T. (1998) "Enhancement of permeate flux by gas slugs for crossflow ultrafiltration in tubular membrane module, Separation Science and Technology, Vol. 33, pp. 2295-2309.

Cheryan, M., (1999), Ultrafiltration and microfiltration handbook, Technomic Pub. Co., Lancaster, Pa.

Chihara, K., Smith, J.M. and Suzuki, M. (1981a) "Regeneration of powdered activated carbon – I. Thermal decomposition kinetics", AIChE Journal, Vol. 27, No. 2, pp. 213-219.

Chihara, K., Smith, J.M. and Suzuki, M. (1981b) "Regeneration of powdered activated carbon – I. Steam-carbon reaction kinetics", AIChE Journal, Vol. 27, No. 2, pp. 220-225.

Chihara, K., Suzuki, M. and Smith, J.M. (1982) "Cyclic regeneration of activated carbon in fluidized beds", AIChE Journal, Vol. 28, No. 1, pp. 129-134.

Chin, S.S., Lim, T.M., Chiang, K. and Fane, A.G. (2005) "Hybrid low-pressure submerged membrane-photoreactor for the removal of Bisphenol A", 5th International Water Association (IWA) Specialty Conference on "Wastewater Reclamation and Reuse for Sustainability (WRRS2005)", Jeju, Korea, Nov. 7 – 11.

Chu, K.H. and Hashim, M.A. (1995) "Simulated countercurrent adsorption processes: a comparison of modeling strategies", The Chemical Engineering Journal, Vol. 56, pp. 59-65.

Crittenden, J.C. and Weber, W.J., Jr. (1978a) "Predictive model for design of fixed-bed adsorbers: Parameter estimation and model development", Journal of Environmental Engineering Division, ASCE, Vol. 104, No. EE2, pp.185-197.

Crittenden, J.C. and Weber, W.J., Jr. (1978b) "Predictive model for design of fixed-bed adsorbers: Single-component model verification", Journal of Environmental Engineering Division, ASCE, Vol. 104, No. EE3, pp.433-443.

Cook, D., Newcombe, G. and Sztajn bok, P. (1998) "Optimizing PAC dosing to remove MIB and geosmin four Adelaide metropolitan water treatment plants", 61st annual water industry engineers and operators' conference Civic Center-Shepparton, 2 and 3 September.

Cui, Z.F. and Wright, K.I.T. (1996) "Flux enhancements with gas sparging in downwards cross-flow ultrafiltration: performance and mechanism", Journal of Membrane Science, Vol. 117, pp. 109-116.

Cui, Z.F., Chang, S. and Fane, A.G. (2003) "The use of gas bubbling to enhance membrane processes", Journal of Membrane Science, Vol. 221, pp. 1-35.

Defrance, L. and Jaffrin, M.Y. (1999) "Comparison between filtrations at fixed transmembrane pressure and fixed permeate flux: application to a membrane bioreactor used for wastewater treatment", Journal of Membrane Science, Vol. 152, No.2, pp. 203-210.

Dennis J.E Jr. and Schnabel R.B. (1983) Numerical methods for unconstrained optimization and nonlinear equations, Prentice-Hall, Englewood Cliffs, New Jersey.

Dunn, J.G. and Fisher, N.G. (2001) "Thermal decomposition of frothing agents adsorbed onto activated carbon", Thermochimica Acta, Vol. 366, pp. 157-166.

Enegeess, D., Togna, P. and Sutton, P. M. (2003) "Membrane separation application to biosystems for wastewater treatment", Filtration and Separation, Feature article, 14 February.

Espinasse, B., Bacchin, P. and Aimar, P. (2002) "On an experimental method to measure critical flux in ultrafiltration", Desalination, Vol. 146, pp. 91-96.

Fane, A. G., Chang, S. and Chardon, E. (2002) "Submerged hollow fiber membrane module-design options and operational considerations", Desalination, Vol. 146, pp. 231-236.

Farahbakhsh, K. and Smith, D. W. (2002) "Performance comparison and pretreatment evaluation of three water treatment membrane pilot plants treating low

turbidity water”, Journal of Environmental Engineering and Science, Vol. 1, pp.113-122.

Faust, S. D. and Aly, O. M. (1987), Adsorption processes for water treatment, Butterworth, Boston.

Ferro-Garcia, M.A., Rivera-Utrailla, J., Bautista-Toledo, I. and Moreno-Gastilla, C. (1996) “Chemical and thermal regeneration of an activated carbon saturated with chlorophenols”, Journal of Chemical Technology and Biotechnology, Vol. 67, pp. 183-189.

Field, R. W., Wu, D., Howell, J. A. and Gupta, B. B. (1995) “Critical flux concept for microfiltration fouling”, Journal of Membrane Science, Vol. 100, pp. 259-272.

Finlayson B.A. (1972) The method of weighted residuals and variational principles (with application in fluid mechanics, heat and mass transfer), Academic Press, San Francisco, London, New York.

Fischer V. M. (2001) “In situ electrochemical regeneration of activated carbon”, PhD thesis, Koninklijke Wöhrmann, Zutphen, Netherlands, ISBN 90-367-1476-1

Gillogly, T. E. T., Snoeyink, V. L., Elarde, J. R., Wilson, C. M. and Royal, E. P. (1998) “C₁₄-MIB adsorption on PAC in natural water”, Journal of American Water Works Association, Vol. 90, No. 1, pp. 98-108.

Ghosh, R. and Cui, Z.F. (1999) “Mass transfer in gas-sparged ultrafiltration: upward slug flow in tubular membranes”, Journal of Membrane Science, Vol. 162, pp. 91-102.

Guo, W.S., Shim, W.G., Vigneswaran, S. and Nge, H.H. (2005) “Effect of operating parameters in a submerged membrane adsorption hybrid system: experiments and mathematical modeling”, Journal of Membrane Science, Vol. 247, pp. 65-74.

Hamdaoui, O., Naffrechoux, E., Tifouti, L. and Petrier, C. (2003) “ Effects of ultrasound on adsorption-desorption of *p*-chlorophenol on granular activated carbon”, Ultrasonics Sonochemistry, Vol. 10, pp. 109-114.

Hamdaoui, O., Naffrechoux, E., Suptil, J. and Fachinger, C. (2005) “Ultrasonic desorption of *p*-chlorophenol from granular activated carbon”, Chemical Engineering Journal, Vol. 106, pp. 153-161.

Hand, D. W., Crittenden, J. C., M. ASCE and Thacker, W. E. (1983) “User-oriented batch reactor solutions to the homogeneous surface diffusion model”, Journal of Environmental Engineering, Vol. 109, No. 1, pp. 82-101.

Hassan, M.M., Loughlin, K.F. and Biawas, M.E. (1996) “Optimization of continuous countercurrent adsorption systems”, Separation Technology, Vol. 6, pp. 19-27.

Herrmann, J.M., Matos, J., Disdier, J., Guillard, C., Laine, J., Malato, S. and Blanco, J. (1999) “Solar photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon in aqueous suspension”, Catalysis Today, Vol. 54, pp. 255-265.

Howell, J.A. (1995) “Sub-critical flux operation of microfiltration” Journal of Membrane Science, Vol. 107, pp. 165-171.

Howell, J.A. (2004) “A critique of critical flux, critical concentrations, critical Peclet numbers and critical pressure”, Proceedings of IWA Specialized Conference on Water Environment-Membrane Technology 2004 , Seoul, Korea.

Huling, S.G., Jones, P.K., Ela, W.P. and Arnold, R.G. (2005) “Fenton-driven chemical regeneration of MTBE-spent GAC”, Water Research, Vol. 39, pp. 2145-2153.

Inoue, K., Higuchi, T., Okada, F., Iguchi, H., Yoshimura, Y. Sato, A. and Nakazawa, H. (2003) "The validation of column-switching LC/MS as a high-throughput approach for direct analysis of di(2-ethylhexyl) phthalate released from PVC medical devices in intravenous solution", Journal of Pharmaceutical and Biomedical Analysis, Vol. 31, pp. 1145-1152.

International Mathematics and Statistical Library (IMSL), Fortran 90 MP library, (1990), IMSL, Visual Numerics, Houston, Texas.

Jack, A. M. and Clark, M. M. (1998) "Using PAC-UF to treat a low quality surface water", Journal of American Water Works Association, Vol. 90, No. 11, pp. 83-95.

Jia, Y., Wang, R., Fane, A.G. and Krantz, W.B. (2005) "Effect of air bubbling on atrazine adsorption in water by powdered activated carbons-competitive adsorption of impurities", Separation and Purification Technology, Vol. 46, pp. 79-87.

Judd, S. J., Le-Clech, P., Taha, T. and Cui, Z. F. (2001) "Theoretical and experimental representation of a submerged membrane bio-reactor system", Membrane Technology, Vol. 135, pp. 4-9.

Kambia, K., Dine, T., Gressier, B., Germe, A.F., Luyckx, M., Brunet, C., Michaud, L. and Gottrand, F. (2001) "High-performance liquid chromatographic method for the determination of di(2-ethylhexyl) phthalate in total parenteral nutrition and in plasma", Journal of Chromatography B, Vol. 755, pp. 297-303.

Kahaner, D., Moler, C. and Nash, S. (1988) "Numerical Methods and Software", Prentice Hall, Englewood Cliffs, N.J.

Kim, B.R. and Cognata, M.B. (1990) "PAC addition as a means of regenerating GAC in a GAC fluidized-bed reactor", Water Research, Vol. 24, No. 1, pp. 103-109.

Kim J.S., Lee S.J., 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 and Technology, Vol. 34, No. 9, pp. 223-229.

Kishore, K. and Verma, N. (2005) “Mass transfer study on counter current multi-stage fluidized bed ion exchanger”, Chemical Engineering and Processing, Vol. 45, pp. 31–45.

Klimenko, N., Smolin, S., Grechanyk, S., Kofanov, V., Nevynna, L. and Samoylenko, L. (2004) “Bioregeneration of activated carbons by bacterial degraders after adsorption of surfactants from aqueous solutions”, Colloids and Surface A: Physicochemical and Engineering Aspects, Vol. 230, pp. 141-158.

Kluytmans, J.H.J., van Wachenm, B.G.M., Kuster, B.F.M. and Schouten, J.C. (2001) “Gas holdup in a slurry bubble column: Influence of electrolyte and carbon particles”, Ind. Eng.Chem.Res., Vol. 40, pp. 5326-5333.

Kluytmans, J.H.J., van Wachem, B.G.M., Kuster, B.F.M. and Schouten, J.C. (2003) “Mass transfer in sparged and stirred reactors: influence of carbon particles and electrolyte”, Chemical Engineering Science, Vol. 58, pp. 4719-4729.

Laine J. M., Hagstrom, J. P., Clark, M. M. and Mallevalle, J. (1989) “Effects of ultrafiltration membrane composition”, Journal of American Water Works Association, Vol. 81, No. 11, pp. 61-67.

Laine J. M., Clark, M. M. and Mallevalle, J. (1990) “Ultrafiltration of lake water: Effect of pretreatment on the partitioning of organics, THMFP, and flux”, Journal of American Water Works Association, Vol. 83, No. 12, pp. 82-87.

Laine J. M., Vial D. and Pierre M. (2000) “Status after 10 years of operation--overview of UF technology today”, Desalination, Vol. 131, pp. 17-25.

Lebeau, T., Lelievre, C., Buisson, H., Cleret, D., Van de Venter, L. W. and Cote, P. (1998) "Immersed membrane filtration for the production of drinking water: combination with PAC for NOM and SOCs removal", Desalination, Vol. 117, pp. 219-231.

Lee, D-K., Kim, S-C., Cho, I-C, Kim, S-J and Kim, S-W (2004) "Photocatalytic oxidation of microcystin-LR in a fluidized bed reactor having TiO₂-coated activated carbon", Separation and Purification Technology, Vol. 34, pp. 59-66.

Li, C.W and Chen, Y.S. (2004) "Fouling of UF membrane by humic substance: Effects of molecular weight and powdered activated carbon (PAC) pre-treatment", Desalination, Vol. 170, pp. 59-67.

Li, Q. Y., Cui, Z. F. and Pepper, D. S. (1997) "Effect of bubble size and frequency on the permeate flux of gas sparged ultrafiltration with tubular membranes", Chemical Engineering Journal, Vol. 67, pp. 71-75.

Li, Q., Snoeyink, V. L., Compos, C. and Marinas, B. J. (2002) "Displacement effect of NOM on Atrazine adsorption by PACs with different pore size distributions", Environmental Science and Technology, Vol. 36, No. 7, pp. 1510-1515.

Li, Q., Marinas, B.J., Snoeyink, V.L. and Campos, C. (2004a) "Pore blockage effects on atrazine adsorption in a powdered activated carbon/membrane system. I: model development", Journal of Environmental Engineering, Vol. 130, No.11, pp. 1242-1252.

Li, Q., Marinas, B.J., Snoeyink, V.L. and Campos, C. (2004b) "Pore blockage effects on atrazine adsorption in a powdered activated carbon/membrane system. II: model verification and application", Journal of Environmental Engineering, Vol.130, No.11, pp. 1253-1262.

Liapis, A.I. and Rippin, D.W.T. (1979) "The simulation of binary adsorption in continuous countercurrent operation and a comparison with other operating modes", AIChE Journal, Vol. 25, No.3, pp. 455-460.

Lin, C. F., Huang, Y. J. and Hao, O. J. (1999) "Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment", Water Research , Vol. 33, pp. 1252-1264.

Lin, C. F., Lin, T. Y. and Hao, O. J. (2000) "Effects of humic substances characteristics on UF performance", Water Research , Vol. 34, pp. 1097-1106.

Liu, X., Quan, X., Bo, L., Chen, S. and Zhao, Y. (2004) "Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation", Carbon, Vol. 42, pp. 415-422.

McAdam, E. Judd, S.J., Gildemeister, R., Drews, A. and Kraume, M. (2005) "Critical analysis of submerged membrane sequencing batch reactor operating conditions", Water Research, Vol. 39, pp. 4011-4019.

Martin, R.J. and Ng, W.J. (1987) "The repeated exhaustion and chemical regeneration of activated carbon", Water Research, Vol. 21, No. 8, pp. 961-965.

Matatov-Meytal, Y.I., Sheintuch, M., Shter, G.E. and Grader, G.S. (1997) "Optimal temperatures for catalytic regeneration of activated carbon", Carbon, Vol. 35, No.10-11, pp. 1527-1531.

Matos, J., Laine, J. and Herrmann, J.M. (1998) "Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon", Applied Catalysis B: Environmental, Vol. 18, pp. 281-291.

Matos, J., Laine, J. and Herrmann, J.M. (2001) "Effect of the type of activated carbon on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania", Journal of Catalysis, Vol. 200, pp. 10-20.

Matsui, Y., Yuasa, A. and Ariga, K. (2001a) "Removal of synthetic organic chemical by PAC-UF systems - I: Theory and modeling", Water Research, Vol. 35, No. 2, pp. 455-463.

Matsui, Y., Colas, F. and Yuasa, A. (2001b) "Removal of synthetic organic chemical by PAC-UF systems - II: Model application", Water Research, Vol. 35, No. 2, pp. 464-470.

Mavrov, V., Chmiel, H., Kluth, J., Meier, J., Heinrich, F., Ames, P., Baches, K. and Usner, P. (1998) "Comparative study of different MF and UF membranes for drinking water production", Desalination, Vol. 117, pp. 189-196.

McCabe, W.L., Smith, J.C. and Harriott, P. (1993) Unit Operations of Chemical Engineering (5th edition), McGraw-Hill, Inc., New York.

Miguel, G.S., Lambert, S.D. and Graham, N.J.D. (2001) "The regeneration of field-spent granular activated carbons", Water Research, Vol. 35, No. 11, pp. 2740-2748.

Mohammadi, T. and Esmaeilifar, A. (2005) "Wastewater treatment of a vegetable oil factory by a hybrid ultrafiltration- activated carbon process", Journal of Membrane Science, Vol. 254, pp. 129-137.

Mollah, A.H. and Robinson, C.W. (1996) "Pentachlorophenol adsorption and desorption characteristics of granular activated carbon-I. Isotherms", Water Research, Vol. 30, No. 2, pp. 2901-2906.

Moreno-Gastilla, C., Rivera-Utrilla, J., Joly, J.P., Lope, Z., Ramon, M.V., Ferro-Carcia, M.A. and Carrasco-Marin, F. (1995) "Thermal regeneration of an activated

carbon exhausted with different substituted phenols”, Carbon, Vol. 33, No. 10, pp. 1417-1423.

Mozia, S., Tomaszewska, M. and Morawski, A.W. (2005) “Studies on the effect of humic acids and phenol on adsorption-ultrafiltration process performance”, Water Research, Vol. 39, pp. 501-509.

Mulder, M., (1997), Basic Principles of Membrane Technology, Kluwer Academic Publishers, Boston, London.

Najm, I. N., Snoeyink, V. L., Suidan M.T., Lee, C. H. and Rechar, Y. (1990) “Effect of particle size and background natural organics on the adsorption efficiency of PAC”, Journal of American Water Works Association, Vol. 82, No. 1, pp. 65-72.

Najm, I. N., Snoeyink, V. L., Lykins, B. W. Jr. and Adams, J. Q. (1991a) “Using powdered activated carbon: A critical review”, Journal of American Water Works Association, Vol. 83, No.1, pp. 65-76.

Najm, I. N., Snoeyink, V. L. and Richard, Y. (1991b) “Effect of initial concentration of a SOC in natural water on its adsorption by activated carbon”, Journal of American Water Works Association, Vol. 83, No. 8, pp. 57-63.

Najm I.N., Snoeyink V.L. and Richard Y. (1993) “Removal of 2,4,6-trichlorophenol and natural organic matter from water supplies using PAC in flocc-blanket reactors”, Water Research, Vol. 27, No. 4, pp. 551-560.

Najm I.N. (1996) “Mathematical modeling of PAC adsorption processes”, Journal of American Water Works Association, Vol. 88, No. 10, pp. 79-89.

Nakano, Y., Hua, L.Q., Nishijima, W., Shoto, E. and Okada, M. (2000) “Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon (GAC)”, Water Research, Vol. 34, No. 17, pp. 4139-4142.

Otake, T., Yoshinaga, J. and Yanagisawa, Y. (2001) "Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD", Environmental Science and Technology, Vol. 35, pp. 3099-3102.

Perrish, J.R., (1981), Activated carbon adsorption for wastewater treatment, CRC Press, Boca Raton, Fla.

Pianta, R., Boller, M., Janex, M. L., Chappaz, A., Birou, B., Ponce, R. and Walther, J. L.(1998) "Micro- and ultrafiltration of karstic spring water", Desalination, Vol. 117, pp. 61-71.

Pirbazari, M. and Badriyha, B. N. (1992) "MF-PAC for treating waters contaminated with natural and synthetic organics", Journal of American Water Works Association, Vol. 84, No. 12, pp. 95-103.

Prober, R., Pyeha, J.J. and Kidon, W. E. (1975) "Interaction of Activated carbon with dissolved oxygen", AIChE Journal, Vol.21, No.6, pp. 1200-1204.

Qi, S., Adham, S.S. Snoeyink, V.L. and Lykins, Jr. B.W. (1994) "Prediction and verification of atrazine adsorption by PAC", Journal of Environmental Engineering, ASCE , Vol.120, No.1, pp. 202-218.

Qourzal, S., Assabbane, A. and Ait-Ichou, Y. (2004) "Synthesis of TiO₂ via hydrolysis of titanium tetraisopropoxide and its photocatalytic activity on a suspended mixture with activated carbon in the degradation of 2-naphthol", Journal of Photochemistry and Photobiology A: Chemistry, Vol. 163, pp. 317-321.

Quan, X., Liu, X., Bo, L., Chen, S., Zhao, Y. and Cui, X. (2004) "Regeneration of acid orange 7- exhausted granular activated carbons with microwave irradiation", Water Research, Vol. 38, pp. 4484-4490.

Randtke, S.J. and Snoeyink, V.L. (1983) "Evaluating GAC adsorptive capacity", Journal of American Water Works Association, Vol. 75, No. 8, pp. 406-413.

Rege, S.U., Yang, R.T. and Cain, C.A. (1998) "Desorption by ultrasound: phenol on activated carbon and polymeric resin", AIChE Journal, Vol. 44, pp. 1519-1528.

Roy, D., Wang, G-T and Adrian, D. D. (1993) "A simplified solution technique for carbon adsorption model", Water Research, Vol. 27, No. 6, pp. 1033-1040.

Roy D., Maillacheruvu K. and Mouchon J. (1999) "Bioregeneration of granular activated carbon loaded with 2,4-D.", Journal of Environmental Science and Health, Part B, Vol. 34, No. 5, pp. 769-791.

Rushton, A., Ward, A.S., and Holdich, R.G. (1996) Chapter 10: Membrane technology, Solid-Liquid Filtration and Separation Technology, Weinheim, VCH, New York.

Ruthiya, K.C., van der Schaaf, J., Kuster, B.F.M. and Schouten, J.C. (2004) "Modeling the effect of particle-to-bubble adhesion on mass transfer and reaction rate in a stirred slurry reactor: influence of catalyst support", Chemical Engineering Science, Vol. 59, pp. 5551-5558.

Salvador, F. and Sanchez Jimenez, C. (1996) "A new method for regenerating activated carbon by thermal desorption with liquid water under subcritical conditions", Carbon, Vol. 34, No. 4, pp. 511-516.

Salvador, F. and Sanchez Jimenez, C. (1999) "Effect of regeneration treatment with liquid water at high pressure and temperature on the characteristics of three commercial activated carbons", Carbon, Vol. 37, pp. 577-583.

Sanger, P. and Deckwer, W.D. (1981) "Liquid-solid mass transfer in aerated suspensions", The Chemical Engineering Journal, Vol. 22, pp. 179-186.

Sedahmed, G.H. and Ahmed, A.M. (1989) "Effect of surface-active agents on the rate of solid-liquid mass transfer with gas generation at the interface", The Chemical Engineering Journal, Vol. 42, pp. 17-23.

Seo, G.T., Suzuki, Y. and Ohgaki, S. (1996) "Biological powdered activated carbon (BPAC) microfiltration for wastewater reclamation and reuse", Desalination, Vol. 106, pp. 39-45.

Sheintuch, M. and Matatov-Meytal, Y.I. (1999) "Comparison of catalytic processes with other regeneration methods of activated carbon", Catalysis Today, Vol. 53, pp. 73-80.

Silva, C.G. and Faria, J.L (2003) "Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation", Journal of Photochemistry and Photobiology A: Chemistry, Vol. 155, pp. 133-143.

Slaney, A. J. and Bhamidimarri, R.(1998) "Adsorption of pentachlorophenol (PCP) by activated carbon in fixed beds: application of homogeneous surface diffusion model", Water Science and Technology, Vol. 38, No. 7, pp. 227-235.

Snoeyink V.L. and Summers, R.S. (1999) "Chapter 13: Adsorption of Organic Compounds." in: Water Quality and Treatment, 5th ed., McGraw-Hill, New York.

Storti, G., Masi, M. and Carra, S. (1988) "Optimal design of multicomponent countercurrent adsorption separation processes involving nonlinear equilibria", Chemical Engineering Science, Vol. 44, No. 6, pp. 1329-1345.

Suzuki, M., Misic, D.M., Koyama, O. and Kawazoe, K. (1978) " Study of thermal regeneration of spent activated carbons thermogravimetric measurement of various single component organics loaded on activated carbons", Chemical Engineering Science, Vol. 33, No. 3, pp. 271-279.

Suzuki, T., Watanabe, Y., Ozawa, G. and Ikeda, S. (1998) "Removal of soluble organics and manganese by a hybrid MF hollow fiber membrane system", Desalination, Vol. 117, pp. 119-130.

Taitel, Y., Bonea, D. and Duker, A. E. (1980) "Modeling flow pattern transitions for steady upward gas-liquid flow in vertical tubes", AIChE Journal, Vol. 26, pp. 345-354.

Talu, O. and Meunier, F. (1996) "Adsorption of associating molecules in micropores and application to water on carbon", AIChE Journal, Vol. 42, No. 3, pp. 809-819.

Taylor, P.N. and Lester, J.N. (1996) "Rapid extraction of isoproturon and diuron from granular activated carbon", Chemosphere, Vol. 33, No. 7, pp. 1227-1240.

Thiruvengkatachari, R., Shim, W.G., Lee, J.W., Aim, R.B and Moon, H. (2005) "A novel method of powdered activated carbon (PAC) pre-coated microfiltration (MF) hollow fiber hybrid membrane for domestic wastewater treatment", Colloids and Surfaces A: Physicochemical and Engineering Aspects, in press.

Tomaszewska, M. and Mozia, S. (2002) "Removal of organic matter from water by PAC/UF system", Water Research, Vol. 36, pp. 4137-4343.

Traegner, U. K. and Sudan, M. T. (1989) "Evaluation of surface and film diffusion coefficients for carbon adsorption", Water Research, Vol. 23, No. 3, pp. 267-273.

Traegner U.K., Suidan M.T. and Kim B.R. (1996) "Considering age and size distributions of activated carbon particles in a completely mixed adsorber at steady state", Water Research, Vol. 30, No. 6, pp. 1495-1501.

Tryba, B., Morawski, A.W. and Inagaki, M. (2003) “Application of TiO₂-mounted activated carbon to the removal of phenol from water”, Applied Catalysis B: Environmental, Vol. 41, pp. 427-433.

Ueda, T., Hata, K., Kikuoka, Y. and Seino, O. (1997) “Effect of aeration on suction pressure in submerged membrane bioreactor”, Water Research, Vol. 31, pp. 489-494.

Ujang, Z., Au, Y.L. and Nagaoka, H. (2002) “Comparative study on microbial removal in immersed membrane filtration (IMF) with and without powdered activated carbon (PAC)”, Water Science and Technology, Vol. 46, No.9, pp. 109-115.

Van, W.E.J., Bradshaw, S.M. and Swardt, J.B.D. (1998) “The dependence of microwave regeneration of activated carbon on time and temperature”, Journal of Microwave Power and Electromagnetic Energy, Vol. 33, No. 3, pp. 151-157.

Vera, L. Villarroel, R., Delgado, S. and Elmaleh, S. (2000) “Enhancing microfiltration through an inorganic tubular membrane by gas sparging”, Journal of Membrane Science, Vol. 165, pp. 47-57.

Villadsen J.V. and Stewart W.E. (1967) “Solution of boundary-value problem by orthogonal collocation”, Chemical Engineering Science, Vol. 22, pp. 1483-1501.

Wicaksana, F., Fane, A.G. and Chen, V. (2006) “Fibre movement induced by bubbling using submerged hollow fibre membranes”, Journal of Membrane Science, Vol. 271, pp. 186-195.

Wu, D., Howell, J.A. and Field, R.W. (1999) “Critical flux measurement for model colloids”, Journal of Membrane Science, Vol. 152, pp. 89-98.

Wu, Z., Cong, Y., Zhou, M. and Tan, T. (2005) “*p*-Nitrophenol abatement by the combination of electrocatalysis and activated carbon”, Chemical Engineering Journal, Vol. 106, pp. 83-90.

Yamamoto, K., Hiaga, H., Mahmood, T. and Matsuo, T. (1989) “Direct solid-liquid separation using hollow fiber membrane in an activated sludge aeration tank”, Water Science and Technology, Vol. 21, Brighton, pp. 43-54.

Ye. Y. and Chen. V. (2005) “Reversibility of heterogeneous deposits formed from yeast and proteins during microfiltration”, Journal of Membrane Science, Vol. 265, pp. 20-28.

Yeo, A., Fane, A.G. and Law, A.W.K. (2006) “Performance of a submerged hollow fiber bundle”, Journal of Membrane Science, submitted.

Zarraa, M.A., El-Tawil, Y.A., Farag, H.A., El-Abd, M.Z. and Sedahmed, G.H. (1991) “Effect of gas sparging on the rate of mass transfer at a single sphere”, The Chemical Engineering Journal, Vol. 47, pp. 187-191.

Zhang, H. (2002a) “Regeneration of exhausted activated carbon by electrochemical method”, Chemical Engineering Journal, Vol. 85, pp. 81-85.

Zhang, H., Ye, L. and Zhong, H. (2002) “Regeneration of phenol-saturated activated carbon in an electrochemical reactor”, Journal of Chemical Technology and Biotechnology, Vol. 77, pp. 1246-1250.

Zhang, M. M., Li, C., Benjamin, M. M. and Chang, Y. (2003) “Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment”, Environmental Science and Technology, Vol. 37, pp. 1663-1669.

APPENDIX A

PROCEDURE FOR SOLVING THE PARTIAL DIFFERENTIAL EQUATION USING ORTHOGONAL COLLOCATION METHOD

This section presents a procedure for applying the orthogonal collocation method to solve the partial differential equation (5.12), which leads to the determination of the two kinetic coefficients, and the simulations of both the single-stage and the two-stage hybrid submerged membrane systems.

As an example, the method for solving the group of equations (5.9)-(5.17) is presented in this section in detail. The simulations in chapters 6 and 7 can be dealt with the same approach in combination with their specific conditions.

Orthogonal collocation method can be applied to solve the unsteady diffusion problems as introduced by Villadsen and Stewart (1967), Finlayson (1972). Briefly, orthogonal collocation method is to choose the trial functions to be sets of orthogonal polynomials which will result in forcing the residual function to be zero at M interior collocation points when substituting the trial functions into the differential equations. The M collocation points are actually the roots to the polynomials and are specifically determined. For unsteady state problems, normally only the space variables are discretized and thus the problem is reduced to a system of ordinary differential equations (ODEs) in time which are then integrated using integration technique. Following their theory, the partial differential equation (5.12) can be discretized into a set of ODEs:

$$\frac{\partial q_j^*}{\partial T} = \sum_{i=1}^{M+1} B_{ji} q_i^*, \quad (j=1,2,3,\dots,M) \quad (\text{A.1})$$

At boundary ($j=M+1$):

$$\sum_{i=1}^{M+1} A_{(M+1),i} q_i^* = B_i (C^* - C_s^*) \quad (\text{A.2})$$

where A_{ji} and B_{ji} are collocation matrices to replace the gradient and Laplacian operator, respectively. Substituting equation (5.16) into equation (A.2):

$$\sum_{i=1}^{M+1} A_{(M+1),i} q_i^* = B_i (C^* - q_{M+1}^{*n}) \quad (\text{A.3})$$

By transforming equation (5.9), we get:

$$C^* = 1 - E_{mb} q_{avg}^* \quad (\text{A.4})$$

Integrating equation (5.11) in space domain and substituting the resulting equation into (A.4):

$$C^* = 1 - E_{mb} \cdot 3 \cdot \left\{ \sum_{i=1}^M q_i^* \cdot X_{(i)}^2 \cdot [X_{(i)} - X_{(i-1)}] + q_{M+1}^* \cdot X_{(M+1)}^2 \cdot [X_{(M+1)} - X_{(M)}] \right\} \quad (\text{A.5})$$

where $X_{(i)}$ is the space variable. Substituting equation (A.5) into (A.3), the right hand side of equation (A.3) can be fully represented by $q_i^* (i=1,2,3,\dots,M+1)$.

Transforming the resultant equation leads to a nonlinear correlation:

$$\begin{aligned} \{A_{(M+1),(M+1)} + 3B_i E_{mb} \cdot X_{(M+1)}^2 \cdot [X_{(M+1)} - X_{(M)}]\} \cdot q_{M+1}^* + B_i \cdot (q_{M+1}^*)^n = \\ B_i \left\{ 1 - 3E_{mb} \cdot \sum_{i=1}^M q_i^* \cdot X_{(i)}^2 \cdot [X_{(i)} - X_{(i-1)}] \right\} - \sum_{i=1}^M A_{(M+1),i} q_i^* \end{aligned} \quad (\text{A.6})$$

Till now we have $(M+1)$ non-linear equations, i.e. equations (A.1), (A.6), which contain $(M+1)$ unknowns, i.e. $q_i^* (i=1,2,3,\dots,M+1)$. These ODEs can be

integrated in time domain using Gear's stiff variable step integration routine by FORTRAN programming. After q_i^* is calculated, equation (5.11) can easily be solved by substituting the calculated q_i^* at any time T to obtain the q_{avg}^* . Substituting q_{avg}^* into equation (A.5), the adsorbate concentration in the bulk solution, C^* , can be finally calculated. In this research, the number of collocation points, M , is set to be 12 for accuracy consideration.

For the simulations of both the single-stage and the two-stage hybrid submerged membrane systems, the solution procedure of the partial differential equation is the same as the approach presented above. The difference lies in the number of unknown parameters. For the case of single-stage hybrid system, 13 unknown parameters ($q_i^* (i = 1, 2, 3, \dots, M)$, C^*) can be determined by solving the 13 ODEs simultaneously. For the case of two-stage hybrid system, 14 unknown parameters ($q_i^* (i = 1, 2, 3, \dots, M)$, C_1^* , C_2^*) can be determined by solving 14 ODEs simultaneously. The specific expressions of dC^*/dT (single-stage) and dC_1^*/dT , dC_2^*/dT (two-stage) for the two cases have been presented respectively in the deduction sections of Chapters 6 and Chapter 7.

The collocation matrices A_{ji} and B_{ji} are given as follows for the case of 12 collocation points ($M=12$) in a spherical particle:

$$A(1, 1) = -0.1267573E+02$$

$$A(1, 2) = 0.2240150E+02$$

$$A(1, 3) = -0.1856304E+02$$

$$A(1, 4) = 0.1714794E+02$$

$$A(1, 5) = -0.1617115E+02$$

$$A(1, 6) = 0.1526265E+02$$

$$A(1, 7) = -0.1430187E+02$$

$$A(1, 8) = 0.1323029E+02$$

$$A(1, 9) = -0.1200370E+02$$

Nanyang Technological University

A(1,10)= 0.1056975E+02
A(1,11)=-0.8840296E+01
A(1,12)= 0.6609558E+01
A(1,13)=-0.2665904E+01
A(2, 1)=-0.2921653E+01
A(2, 2)=-0.6382667E+01
A(2, 3)= 0.1533585E+02
A(2, 4)=-0.1107106E+02
A(2, 5)= 0.9549302E+01
A(2, 6)=-0.8629919E+01
A(2, 7)= 0.7891424E+01
A(2, 8)=-0.7191713E+01
A(2, 9)= 0.6462572E+01
A(2,10)=-0.5654988E+01
A(2,11)= 0.4710798E+01
A(2,12)=-0.3513914E+01
A(2,13)= 0.1415974E+01
A(3, 1)= 0.7705882E+00
A(3, 2)=-0.4881232E+01
A(3, 3)=-0.4305550E+01
A(3, 4)= 0.1336271E+02
A(3, 5)=-0.8830490E+01
A(3, 6)= 0.7212420E+01
A(3, 7)=-0.6267076E+01
A(3, 8)= 0.5545729E+01
A(3, 9)=-0.4893458E+01
A(3,10)= 0.4232454E+01
A(3,11)=-0.3500071E+01
A(3,12)= 0.2599837E+01
A(3,13)=-0.1045863E+01
A(4, 1)=-0.3325815E+00
A(4, 2)= 0.1646356E+01

Nanyang Technological University

A(4, 3)=-0.6243201E+01
A(4, 4)=-0.3283188E+01
A(4, 5)= 0.1273568E+02
A(4, 6)=-0.7908895E+01
A(4, 7)= 0.6180047E+01
A(4, 8)=-0.5179698E+01
A(4, 9)= 0.4428952E+01
A(4,10)=-0.3757567E+01
A(4,11)= 0.3070812E+01
A(4,12)=-0.2265752E+01
A(4,13)= 0.9090308E+00
A(5, 1)= 0.1837223E+00
A(5, 2)=-0.8318426E+00
A(5, 3)= 0.2416755E+01
A(5, 4)=-0.7460318E+01
A(5, 5)=-0.2683627E+01
A(5, 6)= 0.1277357E+02
A(5, 7)=-0.7564306E+01
A(5, 8)= 0.5689792E+01
A(5, 9)=-0.4603172E+01
A(5,10)= 0.3783677E+01
A(5,11)=-0.3034992E+01
A(5,12)= 0.2216334E+01
A(5,13)=-0.8855895E+00
A(6, 1)=-0.1189752E+00
A(6, 2)= 0.5158004E+00
A(6, 3)=-0.1354360E+01
A(6, 4)= 0.3178749E+01
A(6, 5)=-0.8764307E+01
A(6, 6)=-0.2296490E+01
A(6, 7)= 0.1330995E+02
A(6, 8)=-0.7579312E+01

Nanyang Technological University

A(6, 9)= 0.5501954E+01
A(6,10)=-0.4281596E+01
A(6,11)= 0.3332394E+01
A(6,12)=-0.2394746E+01
A(6,13)= 0.9509417E+00
A(7, 1)= 0.8666140E-01
A(7, 2)=-0.3666373E+00
A(7, 3)= 0.9147967E+00
A(7, 4)=-0.1930806E+01
A(7, 5)= 0.4034418E+01
A(7, 6)=-0.1034625E+02
A(7, 7)=-0.2031895E+01
A(7, 8)= 0.1436088E+02
A(7, 9)=-0.7896999E+01
A(7,10)= 0.5522468E+01
A(7,11)=-0.4079844E+01
A(7,12)= 0.2856362E+01
A(7,13)=-0.1123159E+01
A(8, 1)=-0.6951339E-01
A(8, 2)= 0.2897210E+00
A(8, 3)=-0.7019149E+00
A(8, 4)= 0.1403193E+01
A(8, 5)=-0.2631324E+01
A(8, 6)= 0.5108605E+01
A(8, 7)=-0.1245223E+02
A(8, 8)=-0.1845198E+01
A(8, 9)= 0.1608069E+02
A(8,10)=-0.8540772E+01
A(8,11)= 0.5693091E+01
A(8,12)=-0.3806759E+01
A(8,13)= 0.1472412E+01
A(9, 1)= 0.6081897E-01

Nanyang Technological University

A(9, 2)=-0.2510603E+00
A(9, 3)= 0.5972646E+00
A(9, 4)=-0.1157016E+01
A(9, 5)= 0.2052866E+01
A(9, 6)=-0.3576144E+01
A(9, 7)= 0.6603188E+01
A(9, 8)=-0.1550709E+02
A(9, 9)=-0.1711936E+01
A(9,10)= 0.1883080E+02
A(9,11)=-0.9592190E+01
A(9,12)= 0.5842459E+01
A(9,13)=-0.2191960E+01
A(10, 1)=-0.5806078E-01
A(10, 2)= 0.2381761E+00
A(10, 3)=-0.5600630E+00
A(10, 4)= 0.1064237E+01
A(10, 5)=-0.1829408E+01
A(10, 6)= 0.3017148E+01
A(10, 7)=-0.5006307E+01
A(10, 8)= 0.8929258E+01
A(10, 9)=-0.2041555E+02
A(10,10)=-0.1617798E+01
A(10,11)= 0.2342226E+02
A(10,12)=-0.1106986E+02
A(10,13)= 0.3885965E+01
A(11, 1)= 0.6138806E-01
A(11, 2)=-0.2508188E+00
A(11, 3)= 0.5854919E+00
A(11, 4)=-0.1099473E+01
A(11, 5)= 0.1855044E+01
A(11, 6)=-0.2968575E+01
A(11, 7)= 0.4675508E+01

Nanyang Technological University

A(11, 8)=-0.7524329E+01
A(11, 9)= 0.1314654E+02
A(11,10)=-0.2960948E+02
A(11,11)=-0.1554172E+01
A(11,12)= 0.3181662E+02
A(11,13)=-0.9133756E+01
A(12, 1)=-0.7606602E-01
A(12, 2)= 0.3100686E+00
A(12, 3)=-0.7207602E+00
A(12, 4)= 0.1344448E+01
A(12, 5)=-0.2245079E+01
A(12, 6)= 0.3535496E+01
A(12, 7)=-0.5424969E+01
A(12, 8)= 0.8338223E+01
A(12, 9)=-0.1327051E+02
A(12,10)= 0.2319219E+02
A(12,11)=-0.5272925E+02
A(12,12)=-0.1515818E+01
A(12,13)= 0.3926202E+02
A(13, 1)= 0.1826342E+00
A(13, 2)=-0.7437746E+00
A(13, 3)= 0.1725993E+01
A(13, 4)=-0.3210926E+01
A(13, 5)= 0.5340098E+01
A(13, 6)=-0.8357288E+01
A(13, 7)= 0.1269832E+02
A(13, 8)=-0.1919855E+02
A(13, 9)= 0.2963779E+02
A(13,10)=-0.4846412E+02
A(13,11)= 0.9010910E+02
A(13,12)=-0.2337193E+03
A(13,13)= 0.1740000E+03

Nanyang Technological University

B(1, 1)=-0.2016180E+03
B(1, 2)= 0.2572020E+03
B(1, 3)=-0.8183565E+02
B(1, 4)= 0.4168294E+02
B(1, 5)=-0.2565055E+02
B(1, 6)= 0.1750850E+02
B(1, 7)=-0.1274959E+02
B(1, 8)= 0.9681732E+01
B(1, 9)=-0.7538401E+01
B(1,10)= 0.5916217E+01
B(1,11)=-0.4560737E+01
B(1,12)= 0.3241313E+01
B(1,13)=-0.1279815E+01
B(2, 1)= 0.6661881E+02
B(2, 2)=-0.2386264E+03
B(2, 3)= 0.2179564E+03
B(2, 4)=-0.6779890E+02
B(2, 5)= 0.3490342E+02
B(2, 6)=-0.2184299E+02
B(2, 7)= 0.1514715E+02
B(2, 8)=-0.1116320E+02
B(2, 9)= 0.8526480E+01
B(2,10)=-0.6608270E+01
B(2,11)= 0.5053592E+01
B(2,12)=-0.3574934E+01
B(2,13)= 0.1408894E+01
B(3, 1)=-0.1000139E+02
B(3, 2)= 0.1028407E+03
B(3, 3)=-0.2622054E+03
B(3, 4)= 0.2131617E+03
B(3, 5)=-0.6441251E+02

Nanyang Technological University

B(3, 6)= 0.3292582E+02
B(3, 7)=-0.2061703E+02
B(3, 8)= 0.1432575E+02
B(3, 9)=-0.1055034E+02
B(3,10)= 0.7988861E+01
B(3,11)=-0.6020613E+01
B(3,12)= 0.4223319E+01
B(3,13)=-0.1658797E+01
B(4, 1)= 0.3121202E+01
B(4, 2)=-0.1960034E+02
B(4, 3)= 0.1306035E+03
B(4, 4)=-0.2933328E+03
B(4, 5)= 0.2244685E+03
B(4, 6)=-0.6633097E+02
B(4, 7)= 0.3358844E+02
B(4, 8)=-0.2093722E+02
B(4, 9)= 0.1447928E+02
B(4,10)=-0.1054931E+02
B(4,11)= 0.7764323E+01
B(4,12)=-0.5373986E+01
B(4,13)= 0.2099477E+01
B(5, 1)=-0.1376476E+01
B(5, 2)= 0.7231320E+01
B(5, 3)=-0.2828294E+02
B(5, 4)= 0.1608659E+03
B(5, 5)=-0.3387234E+03
B(5, 6)= 0.2500508E+03
B(5, 7)=-0.7272164E+02
B(5, 8)= 0.3651088E+02
B(5, 9)=-0.2260365E+02
B(5,10)= 0.1545816E+02
B(5,11)=-0.1096053E+02

Nanyang Technological University

B(5,12)= 0.7431242E+01
B(5,13)=-0.2879639E+01
B(6, 1)= 0.7533276E+00
B(6, 2)=-0.3628479E+01
B(6, 3)= 0.1159188E+02
B(6, 4)=-0.3811429E+02
B(6, 5)= 0.2004893E+03
B(6, 6)=-0.4069428E+03
B(6, 7)= 0.2938355E+03
B(6, 8)=-0.8455028E+02
B(6, 9)= 0.4214287E+02
B(6,10)=-0.2583254E+02
B(6,11)= 0.1724468E+02
B(6,12)=-0.1132234E+02
B(6,13)= 0.4333182E+01
B(7, 1)=-0.4819490E+00
B(7, 2)= 0.2210616E+01
B(7, 3)=-0.6376953E+01
B(7, 4)= 0.1695630E+02
B(7, 5)=-0.5122671E+02
B(7, 6)= 0.2581512E+03
B(7, 7)=-0.5133449E+03
B(7, 8)= 0.3660126E+03
B(7, 9)=-0.1046870E+03
B(7,10)= 0.5182036E+02
B(7,11)=-0.3116793E+02
B(7,12)= 0.1942325E+02
B(7,13)=-0.7288869E+01
B(8, 1)= 0.3494468E+00
B(8, 2)=-0.1555587E+01
B(8, 3)= 0.4230852E+01
B(8, 4)=-0.1009216E+02

Nanyang Technological University

B(8, 5)= 0.2455720E+02
B(8, 6)=-0.7092655E+02
B(8, 7)= 0.3494782E+03
B(8, 8)=-0.6891826E+03
B(8, 9)= 0.4891861E+03
B(8,10)=-0.1396769E+03
B(8,11)= 0.6839325E+02
B(8,12)=-0.3887786E+02
B(8,13)= 0.1411667E+02
B(9, 1)=-0.2828081E+00
B(9, 2)= 0.1234979E+01
B(9, 3)=-0.3238627E+01
B(9, 4)= 0.7254297E+01
B(9, 5)=-0.1580222E+02
B(9, 6)= 0.3674518E+02
B(9, 7)=-0.1038960E+03
B(9, 8)= 0.5084593E+03
B(9, 9)=-0.1006797E+04
B(9,10)= 0.7178488E+03
B(9,11)=-0.2052663E+03
B(9,12)= 0.9681617E+02
B(9,13)=-0.3307531E+02
B(10, 1)= 0.2546269E+00
B(10, 2)=-0.1098060E+01
B(10, 3)= 0.2813380E+01
B(10, 4)=-0.6063488E+01
B(10, 5)= 0.1239791E+02
B(10, 6)=-0.2584018E+02
B(10, 7)= 0.5900102E+02
B(10, 8)=-0.1665559E+03
B(10, 9)= 0.8235434E+03
B(10,10)=-0.1666906E+04

Nanyang Technological University

$$B(10,11)=0.1209134E+04$$

$$B(10,12)=-0.3433804E+03$$

$$B(10,13)=0.1027003E+03$$

$$B(11,1)=-0.2583067E+00$$

$$B(11,2)=0.1105039E+01$$

$$B(11,3)=-0.2790115E+01$$

$$B(11,4)=0.5872706E+01$$

$$B(11,5)=-0.1156796E+02$$

$$B(11,6)=0.2269952E+02$$

$$B(11,7)=-0.4669805E+02$$

$$B(11,8)=0.1073198E+03$$

$$B(11,9)=-0.3098858E+03$$

$$B(11,10)=0.1591127E+04$$

$$B(11,11)=-0.3416092E+04$$

$$B(11,12)=0.2574024E+04$$

$$B(11,13)=-0.5148555E+03$$

$$B(12,1)=0.3119330E+00$$

$$B(12,2)=-0.1328268E+01$$

$$B(12,3)=0.3325647E+01$$

$$B(12,4)=-0.6906740E+01$$

$$B(12,5)=0.1332691E+02$$

$$B(12,6)=-0.2532453E+02$$

$$B(12,7)=0.4944899E+02$$

$$B(12,8)=-0.1036608E+03$$

$$B(12,9)=0.2483577E+03$$

$$B(12,10)=-0.7678069E+03$$

$$B(12,11)=0.4373796E+04$$

$$B(12,12)=-0.1126623E+05$$

$$B(12,13)=0.7482687E+04$$

$$B(13,1)=0.6336380E+02$$

$$B(13,2)=-0.2579163E+03$$

$$B(13,3)=0.5979668E+03$$

Nanyang Technological University

$B(13, 4) = -0.1110805E+04$

$B(13, 5) = 0.1843310E+04$

$B(13, 6) = -0.2875107E+04$

$B(13, 7) = 0.4345485E+04$

$B(13, 8) = -0.6512271E+04$

$B(13, 9) = 0.9892465E+04$

$B(13, 10) = -0.1562948E+05$

$B(13, 11) = 0.2636557E+05$

$B(13, 12) = -0.3702258E+05$

$B(13, 13) = 0.2030000E+05$

APPENDIX B

CHECK ON THE CORRECTNESS OF THE NUMERICAL SOLUTIONS

In this section, the correctness of the numerical solutions developed in Chapter 5 and 6 was checked carefully. Firstly, a simple analytical solution was derived by assuming that the surface diffusion is fast enough so that only the mass transfer in the liquid film external to the carbon surface controls the adsorption. For the model developed in these chapters, a small Biot number ($B_i = k_f d_p C_0 / 2D_s \rho_p q_0$) used also refers to a similar adsorption process, i.e., the mass transfer in the liquid film is the controlling step of the whole process. Thus a small Biot number was applied to the FORTRAN program of the numerical scheme to obtain a numerical solution. The comparison between the numerical and the analytical solutions will provide a judgment on whether the numerical solutions are correct.

The derivation of the analytical solution is as follows. For adsorption in a closed batch test, the overall mass balance is described as:

$$V \frac{dC}{dt} = -M_c \frac{dq_{avg}}{dt} \quad (5.1)$$

The mass transferred through the liquid film is written as :

$$A \cdot k_f (C - C_s) = -V \frac{dC}{dt} \quad (B.1)$$

The liquid phase and adsorbed phase adsorbate concentrations at the solid-liquid interface, C_s and q_s , are correlated based on the Freundlich isotherm expression:

$$q_s = KC_s^{1/n} \quad (5.7)$$

Since the surface diffusion is assumed to be fast enough to be ignored, the averaged adsorbed phased concentration in the carbon particle (q_{avg}) approximates to the one at the carbon surface q_s . Therefore, equation (5.1) is converted into:

$$V \frac{dC}{dt} = -M_c \frac{dq_s}{dt} \quad (B.2)$$

Integrating equation (B.2) and rearranging the resulting equation give the following expression:

$$q_s = -\frac{V}{M_c}(C - C_0) \quad (B.3)$$

To simplify the procedure, the Freundlich constant $1/n$ is assumed to be 1.0 to transform equation (5.7) into a linear relationship:

$$C_s = \frac{q_s}{K} \quad (B.4)$$

Substituting equation (B.3) into (B.4):

$$C_s = \frac{V}{KM_c}(C_0 - C) \quad (B.5)$$

Substituting equation (B.5) into (B.1):

$$\frac{dC}{dt} = -\frac{A \cdot k_f}{V} \left[C - \frac{V}{KM_c}(C_0 - C) \right] \quad (B.6)$$

Rearranging equation (B.6) and integrating the resulting equation give:

$$\int_{C_0}^C \frac{1}{\left[\left(1 + \frac{V}{KM_c}\right)C - \frac{VC_0}{KM_c} \right]} \cdot dC = \int_0^t -\frac{A \cdot k_f}{V} dt \quad (\text{B.7})$$

Thus the analytical solution of liquid concentration C is expressed as :

$$C = \frac{C_0}{\left(1 + \frac{V}{K \cdot M_c}\right)} \left[e^{-\left(\frac{A \cdot k_f}{V} + \frac{A \cdot k_f}{K \cdot M_c}\right)t} + \frac{V}{K \cdot M_c} \right] \quad (\text{B.8})$$

Given the known parameters C_0 , K , V , M_c , A , k_f , the solute concentration in the liquid phase C at any time t can be easily determined. Using the same group of known parameters and applying $1/n = 1.0$ and a low B_i to the FORTRAN program in Chapter 5, the numerical solution (HSDM prediction) can also be determined. The comparison between the two groups of solutions is presented in Figure B.1.

The two concentration profiles fit each other reasonably well so that the procedure of producing the numerical solutions in Chapter 5 can be confirmed to be correct. The little deviation at the later plateaus in the figure is probably due to the fact that the Biot number used is not small enough ($B_i = \frac{k_f d_p C_0}{2D_s \rho_p q_0} = 0.004$) to completely remove the effect of surface diffusion within the carbon particle. But if a too small Biot number was given, it is difficult to get a numerical solution as a result of converging problem. Nevertheless, solving the low Biot number case provides a check on the numerical solution and it confirms that the development of the numerical solutions in Chapter 5 is successful and correct.

Figure B.1. Check on the accuracy of the numerical solution developed in Chapter 5.

Batch test, $C_0 = 200 \mu\text{g} / L$, $M_c = 8 \text{mg}$, $V = 1.0 L$, $K = 70.06 (L / \text{mg})$,
 $k_f = 1.37 \times 10^{-4} \text{m} / \text{s}$, $A = 0.0166 (\text{m}^2)$

For the continuous flow system with batch dosing of PAC (Chapter 6), the original equations can be expressed similar to the above procedure:

$$V \frac{dC}{dt} = Q(C - C_0) - A \cdot k_f (C - C_s) \quad (\text{B.9})$$

In combination with equations (5.7) and (6.1)

$$Q(C_0 - C) = \frac{d(VC + M_c q_{\text{avg}})}{dt} \quad (\text{6.1})$$

When the liquid flow Q approaches zero, the situation is similar to a batch test and equations (B.9) and (6.1) are simplified to (B.1) and (5.1) respectively. Therefore, the analytical solution (B.8) is also applicable to this situation at $Q \approx 0$. Using the

same group of known parameters and applying $1/n = 1.0$, $Q = 1.0 \times 10^{-8} (L/min)$ and a low B_i to the FORTRAN program of continuous flow system (Section 6.2.1), the numerical solution (HSDM prediction) can also be determined for comparison (Figure B.2). The good agreement confirms of the correctness of the numerical solutions developed in Section 6.2.1.

Figure B.2. Check on the accuracy of the numerical solution developed in Chapter 6.

Continuous flow, Batch input of PAC; $C_0 = 200 \mu g / L$, $M_c = 1000 mg$,
 $V = 50 L$, $K = 70.06 (L / mg)$, $k_f = 1.37 \times 10^{-4} m / s$, $A = 2.07 (m^2)$

For the continuous flow system with continuous dosing of PAC (Chapter 6), equation (B.9) and (5.7) can be combined with equation (6.6).

$$Q(C_0 - C) = V \frac{dC}{dt} + \frac{d}{dt} \left[\int_0^t q_{avg,(t-\beta)} C_c Q d\beta \right] \quad (6.6)$$

Nanyang Technological University

The only difference between equations (6.1) and (6.6) lies in the second term of right hand side of each equation. The term in equation (6.6) contains an integration which is described in Section 6.2.2 in much detail so that it is can be easily checked. Therefore, the numerical solution developed for continuous PAC input system in Section 6.2.2 is also confirmed to be correct based on the previous discussion in this appendix.