

# UNIVERSIDADE DO ALGARVE

FACULDADE DE CIÊNCIAS DO MAR E DO AMBIENTE

## REMOVAL OF CYANOBACTERIA AND CYANOTOXINS FROM DRINKING WATER BY POWDERED ACTIVATED CARBON ADSORPTION/ULTRAFILTRATION

(Tese para a obtenção do grau de doutor no ramo de Ciências e Tecnologias do Ambiente,  
especialidade de Tecnologias do Ambiente)

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“Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit”.

Marie Curie

Para o Nuno e os meus pais

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Margarida Campinas



# Removal of cyanobacteria and cyanotoxins from drinking water by powdered activated carbon adsorption/ultrafiltration

## ABSTRACT

PAC/UF was investigated to remove the cyanobacterium *Microcystis aeruginosa* and microcystins, focusing on toxins adsorption onto PAC and the combined effect of the water organic and inorganic matrices, the cells removal and lysis by UF, and PAC contribution to membrane fouling control and microcystins removal by PAC/UF.

The fine-grade mesoporous PAC presented high capacity and fast kinetics for microcystins adsorption from ultrapure-water. In model and natural waters, NOM size governed microcystins-NOM competition, and inorganics contribution was crucial. Main competitor was NOM of closer size, hindering microcystins adsorption through a pore-blocking mechanism. Ionic strength induced the competition of larger compounds and diminished the competition of similar-sized compounds. Kinetic models confirmed the competing mechanisms proposed based on kinetic and isotherm data.

UF ensured absolute removal of *M. aeruginosa* single-cells, although lysis was detected, particularly with cell ageing. However, AOM-driven microcystins rejection attenuated/avoided the permeate degradation. While not affecting the reversible fouling, PAC improved the permeate quality and membrane irreversible-fouling, minimising the chemical cleaning. The worst flux impairment was associated to polysaccharide-like AOM in background inorganics, for which PAC was apparently ineffective.

PAC/UF performed better than PAC+C/F/S. For the usual concentrations of dissolved microcystins in natural waters, 10-15 mgPAC/L achieved the WHO guideline-value.

**Key-Words:** PAC adsorption, ultrafiltration, cyanobacteria, microcystins, NOM, drinking water.



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### **TÍTULO DA TESE:**

**Processo integrado de adsorção em carvão activado em pó e ultrafiltração para remoção de cianobactérias e cianotoxinas em água para consumo humano.**

### **RESUMO**

Investigou-se a remoção de *Microcystis aeruginosa* e microcistinas por PAC/UF, principalmente a adsorção das toxinas pelo carvão e o efeito da composição da água, a remoção e lise celular por ultrafiltração, e a contribuição do PAC no controlo da colmatação da membrana e remoção de microcistinas por PAC/UF.

O PAC revelou elevada capacidade e rápida adsorção de microcistinas em água pura. Em águas modelo e naturais, o tamanho da NOM determinou a competição microcistinas-NOM, sendo fundamental o efeito dos iões. Verificou-se maior competição de compostos idênticos, retardando a adsorção por bloqueio de poros. Os iões induziram a competição de compostos maiores e diminuíram a de semelhantes. Os modelos cinéticos confirmaram os mecanismos de competição.

UF removeu totalmente as células de *M. aeruginosa*, mas ocorreu lise especialmente das mais velhas. O material algógeno promoveu a rejeição de microcistinas, atenuando/evitando a degradação do permeado. PAC melhorou a qualidade do permeado e a colmatação irreversível da membrana, minimizando a limpeza química. O fluxo foi especialmente afectado por AOM polissacarídico (com iões), para o qual o PAC foi aparentemente ineficaz.

PAC/UF apresentou melhor desempenho que PAC+C/F/S e com 10-15 mgPAC/L atingiu-se o valor-guia da OMS, partindo de concentrações típicas de microcistinas em águas naturais.

**Palavras-Chave:** PAC, ultrafiltração, cianobactérias, microcistinas, NOM, água para consumo humano



# TABLE OF CONTENTS

---

LIST OF FIGURES.....	xi
LIST OF TABLES.....	xix
ABBREVIATIONS AND SYMBOLS.....	xxi
1 INTRODUCTION.....	1
1.1 SCOPE OF THE THESIS.....	3
1.2 OBJECTIVES.....	6
1.3 RESEARCH STRATEGY.....	7
1.4 THESIS STRUCTURE.....	11
2 BACKGROUND.....	13
2.1 CYANOBACTERIA.....	15
2.2 CYANOTOXINS.....	16
2.2.1 General.....	16
2.2.2 Microcystins.....	19
2.3 LEGISLATION AND GUIDELINES.....	22
2.4 WATER TREATMENT FOR CYANOTOXINS REMOVAL.....	23
2.4.1 Removal of Cell-Bound Cyanotoxins.....	23
2.4.2 Removal of Dissolved Cyanotoxins.....	24
2.5 PAC ADSORPTION.....	28
2.5.1 General.....	28
2.5.2 Mechanisms of Adsorption.....	28
2.5.3 NOM Competition.....	30
2.5.4 Adsorption Isotherms.....	31
2.5.5 Adsorption Kinetic Models.....	33
2.6 ULTRAFILTRATION (UF).....	35
2.6.1 General.....	35
2.6.2 Mass Transport and Fouling.....	37
2.7 PAC/UF.....	40
2.7.1 General.....	40
2.7.2 Operating Conditions.....	42
2.7.3 Waste Disposal.....	44
2.8 REFERENCES.....	45

# TABLE OF CONTENTS

---

3 THE IONIC STRENGTH EFFECT ON MICROCYSTIN AND NATURAL ORGANIC MATTER SURROGATE ADSORPTION ONTO PAC.....	55
ABSTRACT.....	57
3.1 INTRODUCTION.....	59
3.2 MATERIALS AND METHODS.....	62
3.2.1 Adsorbates.....	62
3.2.2 Adsorbent.....	64
3.2.3 Model Solution Preparation.....	65
3.2.4 Analytical Methods.....	65
3.2.5 Adsorption Kinetics Experiments.....	67
3.2.6 Equilibrium Isotherms Experiments.....	68
3.3 RESULTS AND DISCUSSION.....	68
3.3.1 Effect of Monovalent Ion ( $K^+$ ).....	70
3.3.2 Effect of Divalent Ion ( $Ca^{2+}$ ).....	76
3.4 SUMMARY AND CONCLUSIONS.....	80
3.5 REFERENCES.....	82
4 RELATING THE COMPETITIVE ADSORPTION OF MICROCYSTINS WITH THE WATER BACKGROUND ORGANIC AND INORGANIC MATRICES:	
I. KINETIC STUDY.....	85
ABSTRACT.....	87
4.1 INTRODUCTION.....	89
4.2 MATERIALS AND METHODS.....	92
4.2.1 Adsorbates.....	92
4.2.2 Model Solutions.....	93
4.2.3 Natural Surface Water.....	94
4.2.4 Adsorbent.....	95
4.2.5 Analytical Methods.....	95
4.2.6 Adsorption Kinetics.....	96
4.3 RESULTS AND DISCUSSION.....	97
4.3.1 Kinetic Studies with Model Solutions and Fresh PAC.....	97
4.3.2 Kinetic Studies with Model Solutions and Preloaded PAC.....	101
4.3.3 Kinetic Studies with Natural Surface Water and Fresh PAC.....	104

# TABLE OF CONTENTS

---

4.3.4 Kinetic Models Analysis.....	105
4.4 SUMMARY AND CONCLUSIONS.....	112
4.5 REFERENCES.....	113
5 RELATING THE COMPETITIVE ADSORPTION OF MICROCYSTINS WITH THE WATER BACKGROUND ORGANIC AND INORGANIC MATRICES:	
II. EQUILIBRIUM STUDY.....	117
ABSTRACT.....	119
5.1 INTRODUCTION.....	121
5.2 MATERIALS AND METHODS.....	123
5.3 RESULTS AND DISCUSSION.....	124
5.3.1 Single-Solute Isotherms.....	124
5.3.2 Microcystins-NOM Competition: C <sub>0</sub> effect.....	127
5.3.3 Microcystins-NOM Competition: NOM surrogates.....	129
5.3.4 Microcystins-NOM Competition: NOM surrogates and ionic strength.....	133
5.3.5 Microcystins-NOM Competition: Natural surface water.....	137
5.4 CONCLUSIONS.....	139
5.5 REFERENCES.....	141
6 EVALUATION OF CYANOBACTERIAL CELLS REMOVAL AND LYSIS BY ULTRAFILTRATION.....	
ABSTRACT.....	145
6.1 INTRODUCTION.....	147
6.2 MATERIALS AND METHODS.....	150
6.2.1 Cyanobacterial Culture.....	150
6.2.2 UF Feed Waters.....	150
6.2.3 Membrane.....	151
6.2.4 Ultrafiltration Experiments.....	151
6.2.5 Analytical Methods.....	153
6.3 RESULTS AND DISCUSSION.....	155
6.3.1 Microcystins Rejection by UF.....	155
6.3.2 Characterisation of Cultures Growth Phases.....	156
6.3.3 Retention of Cyanobacterial Cells.....	158
6.3.4 Cell Lysis and Microcystins Release to Water.....	160

# TABLE OF CONTENTS

---

6.3.5 Membrane Fouling by AOM.....	165
6.4 CONCLUSIONS.....	168
6.5 REFERENCES.....	170
7 ASSESSING THE PAC CONTRIBUTION TO THE NOM FOULING CONTROL IN PAC/UF SYSTEMS.....	173
ABSTRACT.....	175
7.1 INTRODUCTION.....	177
7.2 MATERIALS AND METHODS.....	179
7.2.1 NOM Solutions.....	179
7.2.2 UF Membrane and PAC.....	181
7.2.3 UF Experiments.....	182
7.2.4 Analytical Methods.....	184
7.3 RESULTS AND DISCUSSION.....	185
7.3.1 UF Fouling Potential of NOM Surrogates.....	185
7.3.2 UF Fouling Potential of Algal Organic Matter.....	187
7.3.3 UF Fouling Potential of PAC.....	190
7.3.4 NOM Fouling Potential in PAC/UF System.....	192
7.3.5 Membrane Cleaning.....	194
7.4 CONCLUSIONS.....	197
7.5 REFERENCES.....	198
8 MICROCYSTINS REMOVAL BY PAC/UF SYSTEM.....	203
ABSTRACT.....	205
8.1 INTRODUCTION.....	207
8.2 MATERIALS AND METHODS.....	210
8.2.1 Microcystins Extraction.....	210
8.2.2 Solutions.....	210
8.2.3 PAC.....	211
8.2.4 UF Membrane.....	212
8.2.5 Ultrafiltration Runs.....	212
8.2.6 Adsorption Kinetics.....	214
8.2.7 Analytical Methods.....	214

# TABLE OF CONTENTS

---

8.3 RESULTS AND DISCUSSION.....	215
8.3.1 Microcystins Removal by PAC/UF.....	215
8.3.2 Effect of NOM on Microcystins Removal by PAC/UF.....	219
8.4 CONCLUSIONS.....	223
8.5 REFERENCES.....	225
9 COMPARING PAC/UF AND CONVENTIONAL CLARIFICATION WITH PAC FOR REMOVING MICROCYSTINS FROM NATURAL WATERS.....	229
ABSTRACT.....	231
9.1 INTRODUCTION.....	233
9.2 MATERIALS AND METHODS.....	235
9.2.1 Cyanobacterial Cells and Cyanotoxins.....	235
9.2.2 Natural Waters.....	236
9.2.3 PAC.....	237
9.2.4 UF Runs.....	238
9.2.5 C/F/S Experiments.....	239
9.2.6 Analytical Methods.....	239
9.3 RESULTS AND DISCUSSION.....	240
9.3.1 Microcystins Removal from Natural Waters by UF and PAC/UF.....	240
9.3.2 Comparing PAC/UF and PAC+C/F/S.....	244
9.4 CONCLUSIONS.....	248
9.5 REFERENCES.....	249
10 CONCLUSIONS AND FUTURE WORK.....	253
10.1 CONCLUSIONS.....	255
10.2 FUTURE WORK.....	263

# TABLE OF CONTENTS

---

## LIST OF FIGURES

---

Figure 1.1 - Bench-scale UF <i>apparatus</i> designed and assembled for PAC/UF experiments.....	8
Figure 1.2 - Hollow-fibre module used in PAC/UF experiments.....	8
Figure 1.3 - Laboratory cultures of <i>Microcystis aeruginosa</i> used in the experiments.....	9
Figure 1.4 - Research strategy followed in this thesis (MC = microcystins; IS = ionic strength).	10
Figure 2.1 - Structure of microcystin-LR (Meriluoto and Spoof, 2007).....	20
Figure 2.2 - Hydraulic mode of operation: dead-end (left) and cross-flow (right) (USEPA, 2005).....	36
Figure 2.3 - Typical UF operation in most applications (Kim <i>et al.</i> , 2001).....	37
Figure 2.4 - Mechanisms of membrane fouling: Cb, complete blocking; Sb, standard blocking (pore constriction); Ib, intermediate blocking; Ck, cake formation.....	39
Fig. 2.5 - Adsorbate concentration profiles ( $C/C_0$ ) in the permeate resulting from wasting PAC at the end of the filtration cycle and using two PAC dosing procedures (Snoeyink <i>et al.</i> , 2000).....	43
Figure 2.6 - Schematics of PAC/UF process configuration (Snoeyink <i>et al.</i> , 2000).....	43
Figure 3.1 - Surface charge <i>versus</i> pH of PAC Norit SA-UF.....	65
Figure 3.2 - Adsorption kinetics in Milli-Q water for microcystin variants (left) and NOM surrogates (right) (left: 26 $\mu\text{g}$ MC-LR/L, 2.4 $\mu\text{g}$ MC-LY/L, 1.8 $\mu\text{g}$ MC-LW/L, 3.9 $\mu\text{g}$ MC-LF/L, PAC dose of 5 mg/L; right: 2.9 mg AHA/L, 2.8 mg TA/L, 1.7 mg SA/L, PAC dose of 20 mg/L).....	69
Figure 3.3 - Adsorption kinetics of salicylic acid in Milli-Q water and in KCl electrolyte with an ionic strength of 2.5 mM (1.6 mg SA/L, 20 mg PAC/L).....	70
Figure 3.4 - Adsorption kinetics of microcystin variants in Milli-Q water and KCl electrolytes of increasing ionic strength: 2, 10 and 100 mM (22 $\mu\text{g}$ MC-LR/L, 2.0 $\mu\text{g}$ MC-LY/L, 1.8 $\mu\text{g}$ MC-LW/L, 2.9 $\mu\text{g}$ MC-LF/L, 5 mg PAC/L).....	71
Figure 3.5 - Adsorption kinetics of tannic acid (left) and Aldrich humic acid (right) in Milli-Q water and in KCl electrolyte with an ionic strength of 2.5 mM (2.8-2.9 mg TA/L, 2.8-2.9 mg AHA/L, 20 mg PAC/L).....	71
Figure 3.6 - Adsorption isotherms of MC-LR in Milli-Q water and in KCl electrolytes with ionic strengths of 2.5 mM and 10 mM.....	74
Figure 3.7 - Adsorption isotherms of tannic acid in Milli-Q water and in KCl electrolytes with ionic strengths of 2.5 mM and 10 mM.....	75

## LIST OF FIGURES

---

Figure 3.8 - Adsorption kinetics of SA in Milli-Q water, and in KCl and KCl+CaCl <sub>2</sub> electrolytes with an ionic strength of 2.5 mM and 10 mM.....	77
Figure 3.9 - Adsorption kinetics of microcystin variants Milli-Q water and in three KCl+CaCl <sub>2</sub> electrolytes of increasing ionic strength: 2, 10 and 100 mM (18 µg MC-LR/L, 2.3 µg MC-LY/L, 1.6 µg MC-LW/L, 2.4 µg MC-LF/L, 5 mg PAC/L).....	77
Figure 3.10 - Adsorption kinetics of TA (left) and AHA (right) in Milli-Q water, and in KCl, KCl+CaCl <sub>2</sub> and MgSO <sub>4</sub> electrolytes with an ionic strength of 2.5 mM (2.8-2.9 mg TA/L, 2.6-2.9 mg AHA/L, 20 mg PAC/L).....	78
Figure 3.11 - Adsorption isotherms of MC-LR in Milli-Q water and in KCl+CaCl <sub>2</sub> electrolytes with ionic strengths of 2.5 mM and 10 mM.....	79
Figure 4.1 - Adsorption kinetics in the absence (open symbols) of competition and under competition (full symbols) between microcystins and AHA+SA (left) or microcystins and TA (right) (5 mg/L PAC; left: 34 µg MC-LR <sub>eq</sub> /L, 1.6 mg SA/L, 2 mg AHA/L; right: 33-137 µg MC-LR <sub>eq</sub> /L, 2-3.2 mg TA/L).....	97
Figure 4.2 - Competitive adsorption kinetics of microcystins with AHA+SA (left) or TA (right) in the absence (open symbols) and in the presence (full symbols) of 2.5 mM background ionic strength (left: 32-46 µg MC-LR <sub>eq</sub> /L, 1.7-2 mg AHA/L, 1.6-1.9 mg SA/L; right: 33-137 µg MC-LR <sub>eq</sub> /L, 2-3.2 mg TA/L)..	99
Figure 4.3 - AHA (left) and TA adsorption kinetics in the absence (open symbols) and in the presence (full symbols) of microcystins (left: 32-46 µg MC-LR <sub>eq</sub> /L, 1.7 - 2.7 mg AHA/L; right: 31-137 µg MC-LR <sub>eq</sub> /L; 2-3.2 mg TA/L).....	101
Figure 4.4 - Competitive adsorption kinetics of microcystins onto fresh and NOM preloaded PAC (32-46 µg MC-LR <sub>eq</sub> /L in Milli-Q water (left and right) and in 2.5 mM IS solution (center)).....	102
Figure 4.5 - Displaced desorption of AHA (left) and TA (right) by microcystins addition (32-37 µg MC-LR <sub>eq</sub> /L; 5 mg PAC/L).....	103
Figure 4.6 - Adsorption kinetics of microcystins onto fresh PAC in the presence of natural surface water (TCW) (left) and comparison with NOM model compounds effect (right) (28-39 µg MC-LR <sub>eq</sub> /L).....	104
Figure 4.7 - Pseudo-first order plots for microcystins adsorption from organic free-water and NOM model solutions.....	107

## LIST OF FIGURES

---

Figure 4.8 - Pseudo-second order plots for microcystins adsorption from organic free-water and NOM model solutions.....	108
Figure 4.9 - Intraparticle diffusion kinetics for microcystins adsorption in organic free-water and NOM model solutions.....	109
Figure 4.10 - Boyd <i>et al.</i> plots for microcystins adsorption of in organic free-water and NOM model solutions.....	110
Figure 5.1 - Single-solute isotherms of microcystins and NOM surrogates in the presence and absence of background ionic strength.....	125
Figure 5.2 - Microcystins residuals ( $C/C_0$ ) from microcystins-NOM competitive isotherms performed at different $C_0$ , in the absence (top) and in the presence (bottom) of background 2.5 mM IS.....	128
Figure 5.3 - Microcystins-NOM competitive isotherms performed at different $C_0$ , in the absence and in the presence of background 2.5 mM IS.....	129
Figure 5.4 - Microcystins-NOM adsorption isotherms (left: 202 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg SA/L; center: 221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg AHA/L; right: 211 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 2 mg TA/L)...	130
Figure 5.5 - Microcystins residuals in the presence of NOM surrogates (top) and comparison between microcystins and AHA residuals or microcystins and TA residuals (bottom) (211-221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg AHA/L, 2 mg TA/L).....	130
Figure 5.6 - Competitive adsorption isotherms of microcystins with AHA (left) or TA (right) in the absence (open symbols) and in the presence (full symbols) of background ionic strength (left: 3 mg AHA/L, 198-221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ; right: 2 mg TA/L, 202-211 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ).....	134
Figure 5.7 - Microcystins and TA residuals obtained during kinetics with low carbon dose (5 mg/L) (left: TA and microcystins single solute kinetics; center: MC-LR <sub>eq</sub> -TA competitive kinetics; right: MC-LR <sub>eq</sub> -TA competitive kinetics in the presence of 2.5 mM IS).....	136
Figure 5.8 - Microcystins-NOM competitive isotherms from preozonated, clarified surface water (TCW) (219 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ).....	138
Figure 5.9 - Characterisation of Tavira's natural water NOM by size exclusion chromatography (Dionex Summit HPLC; PDA detection at 254nm; TSK-3000SW column; phosphate buffer 20 mM, pH = 6.8; 0.5 mL/min; calibration against PSS standards).....	139

## LIST OF FIGURES

---

Figure 6.1 - Schematic diagram of laboratory UF installation (FT: Feed tank; RT: Recirculating tank; PT: Permeate Tank; Flm: Flowmeter; P: Manometers; V1, V4, V5: Valves for backwashing; V2: Concentrate valve; V3: Permeate valve; B1: Peristaltic pump; B2: Positive displacement pump).....	152
Figure 6.2 - Normalised flux (left) and dissolved microcystins rejection (centre) during UF concentration runs, and cycle-averaged concentration of microcystins on the feed and permeate during constant flow runs (right) with single-solute model solution....	155
Figure 6.3 - Characterisation of <i>M. aeruginosa</i> cultures growth phases.....	158
Figure 6.4 - Turbidity and chlorophyll-a feed profiles (left) and cycle-averaged concentrations (right) on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells of 2 M and 4 M.....	159
Figure 6.5 - Cycle-averaged concentration of microcystins on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells (1M and 3M). The error bars represents standard deviations.....	161
Figure 6.6 - Net contribution of adsorption and cell lysis computed from mass-balance equation developed for dissolved microcystins during constant flow UF cycles with <i>M. aeruginosa</i> cells (1 M and 3 M).....	162
Figure 6.7 - Concentration factors for cell-bound microcystins (left) and chlorophyll-a (right) during constant flow runs with <i>M. aeruginosa</i> cells (2M and 4M): experimental (bars) and expected (symbols) values based on mass-balance equation.....	163
Figure 6.8 - Net contribution of adsorption and cell lysis computed from mass-balance equation developed for dissolved microcystins during constant flow UF cycles with <i>M. aeruginosa</i> cells (2 M and 4 M).....	164
Figure 6.9 - Cycle-averaged concentration of microcystins (extra and intracellular) on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells (2 M and 4 M). The error bars represents standard deviations.....	165
Figure 6.10 - Normalised flux during UF concentration runs with <i>M. aeruginosa</i> cells (1 M and 3 M).....	166
Figure 6.11 - Feed (closed symbols) and permeate quality (open symbols), and rejections (asterisks) during UF concentration runs with <i>M. aeruginosa</i> cells (1 M and 3 M).....	168

## LIST OF FIGURES

---

Figure 7.1 - Flow diagram of UF <i>apparatus</i> (FT - Stirred feed tank; B - Positive displacement pump; P - Manometers; Flm- Flowmeter; PT - Permeate tank; V1,V4,V5- Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).....	181
Figure 7.2 - Concentration-time-depending fouling runs with NOM model compounds: normalised flux (left), feed and permeate quality, and rejection of TA (centre) and AHA (right) ( <i>ca.</i> 2.5 mg/L each NOM surrogate, 2.5 mM IS background electrolyte).....	185
Figure 7.3 - Normalised flux (left) and average rejection of organic matter (right) during time-depending fouling runs with different NOM (error bars represents standard deviations).....	189
Figure 7.4 - Normalised flux (left) and normalised feed turbidity (right) during UF and PAC/UF concentration-time-depending fouling runs at two cross-flow velocities (UF: no PAC addition; PAC/UF: 5 mg/L PAC addition (2.1.-2.9 NTU), 2.5 mM IS of background electrolyte).....	191
Figure 7.5 - Normalised flux during PAC/UF (10 mg/L PAC) and UF time-depending fouling runs with NOM surrogates (left) and algogenic organic fractions (right).....	193
Figure 7.6 - TOC (left) and UV <sub>254nm</sub> (right) rejections of NOM surrogates and algogenic organic fractions during PAC/UF (10 mg/L PAC) and UF fouling runs (error bars represents standard deviations).....	193
Figure 7.7 - Recovery of membrane pure water permeability after time-depending fouling runs with different NOM and with/without PAC addition (J <sub>1</sub> - pure water flux after backwashing; J <sub>0</sub> - initial pure water flux).....	195
Figure 7.8 - Recovery of membrane pure water permeability, after the concentration-time-depending fouling runs with TA, using different cleaning procedures (J <sub>1</sub> - pure water flux after membrane cleaning; J <sub>0</sub> - initial pure water flux).....	196
Figure 8.1 - Flow diagram of UF <i>apparatus</i> (FT - Feed tank; RT - Stirred recirculating tank; PT - Permeate tank; Flm - Flowmeter; P - Manometers; B1 - Peristaltic pump; B2 - Positive displacement pump; V1,V4,V5 - Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).....	212
Figure 8.2 - Microcystins UF feed and cycle-averaged permeate concentrations obtained with different feed concentrations and PAC doses (feed: brown bars; permeate: blue bars). Error bars represents standard deviations.....	215

## LIST OF FIGURES

---

Figure 8.3 - Normalised microcystins concentration after PAC/UF and PAC adsorption kinetics performed in the same operating conditions (17.1 $\mu\text{g/L}$ MC-LR <sub>eq</sub> feed concentration, two PAC doses and 1 h contact time).....	217
Figure 8.4 - Concentration profile (left) and cycle-averaged concentration (right) of microcystins in the permeate during PAC/UF cycles performed with two different PAC dosing procedures (16.8-19.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , 5 mg/L PAC).....	217
Figure 8.5 - Cycle-averaged concentration of microcystins in the permeate obtained in PAC/UF runs with two HRT in the recirculating tank (5.5-7.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , 5 mg/L PAC). Error bars represents standard deviations.....	219
Figure 8.6 - Cycle-averaged concentration of microcystins in the permeate of PAC/UF runs performed in the absence and in the presence of NOM surrogates for two microcystins feed concentration ranges: 5.3-7.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (left) and 17-23 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (right).....	220
Figure 8.7 - UV rejection (UV <sub>215nm</sub> , left; UV <sub>254nm</sub> , right) by PAC/UF of solutions containing microcystins and NOM model compounds (AHA+TA) (green bars: 19.5-23.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ; orange bars: 6.7-7.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ).....	221
Figure 8.8 - Cycle-averaged concentration of microcystins in the permeate of UF and PAC/UF runs with <i>M. aeruginosa</i> culture (2.1-2.3 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (total), 0.63-0.88 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (dissolved), ext./int. = 0.4-0.6).....	222
Figure 9.1 – Membrane permeability (left) and rejections (right) obtained during UF and PAC/UF (10 mg/L PAC) of Tavira’s WTP clarified water (TCW) supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.8 $\mu\text{g/L}$ total MC-LR <sub>eq</sub> ).....	240
Figure 9.2 - Cycle-averaged concentration of microcystins in the permeate during UF and PAC/UF (10 mg/L PAC) of TCW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.8 $\mu\text{g/L}$ total MC-LR <sub>eq</sub> ). Error bars represents standard deviations.....	242
Figure 9.3 – Membrane permeability (left) and cycle-averaged concentration of dissolved microcystins in the feed and permeate (right) obtained during PAC/UF (10 mg/L PAC) of ozonated (TOW) and clarified (TCW) natural waters and supplemented with <i>M. aeruginosa</i> culture (cells and AOM) and dissolved microcystins. Comparison is made with NOM surrogate runs from chapter 8 (right, C <sub>1</sub> : 1 mg AHA/L+1.5 mgTA/L; C <sub>2</sub> : 2.5 mg AHA/L+2.5 mg TA/L).....	243

## LIST OF FIGURES

---

Figure 9.4 - Percentage of microcystins remaining after PAC adsorption kinetics performed with TCW supplemented with dissolved microcystins (5.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> feed concentration, 1 h contact time).....	244
Figure 9.5 - PAC+C/F/S and PAC/UF performances with TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.2-8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , extra/intracellular = 4-5, 10 mg/L PAC).....	245
Figure 9.6 - Average microcystins concentration of treated waters produced by PAC+C/F/S and PAC/UF application to TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.2-8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , extra/intra = 4-5; 10 mg/L PAC)....	247
Figure 9.7 - Average microcystins concentration (intra+extra) of treated waters obtained by different PAC doses applied to PAC+C/F/S of TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ).....	248



## LIST OF TABLES

---

Table 2.1 - Properties of cyanotoxins (Carmichael, 1997; Sivonen and Jones, 1999; Hitzfeld <i>et al.</i> , 2000; Codd, 2000; Yunes <i>et al.</i> , 2003; Metcalf and Codd, 2004; Van Apeldoorn <i>et al.</i> , 2007; Meriluoto and Spoof, 2007).....	18
Table 2.2 - Properties of the most frequent microcystins (Sivonen and Jones, 1999; De Maagd <i>et al.</i> , 1999; Cook and Newcombe, 2002; Newcombe <i>et al.</i> , 2003).....	21
Table 2.3 - WHO guidelines for managing recreational waters and drinking waters which may contain cyanobacteria (Falconer, 1999; WHO, 2003).....	22
Table 2.4 - Guidelines/regulations of several countries for microcystins in drinking water.....	23
Table 3.1 - Properties of microcystin variants identified in this study (adapted from De Maagd, 1999; Sivonen and Jones, 1999; Newcombe <i>et al.</i> , 2003).....	63
Table 3.2 - Relevant PAC Norit SA-UF characteristics (adapted from Campos <i>et al.</i> , 2000; Li <i>et al.</i> , 2002, 2003).....	64
Table 3.3 - Conditions of kinetic and isotherm experiments.....	66
Table 3.4 - Isotherm (Langmuir or Freundlich) parameters for MC-LR and TA in Milli-Q water, KCl or KCl+CaCl <sub>2</sub> electrolyte solution with different ionic strengths (2.5mM and 10 mM).....	74
Table 4.1 - Characteristics of the natural surface water (TCW) used in adsorption kinetic experiments, after spiking with microcystins.....	94
Table 4.2 - Kinetic models investigated.....	106
Table 4.3 - Kinetic parameters calculated for pseudo-first order and pseudo-second order adsorption kinetic models.....	107
Table 4.4 - Kinetic parameters obtained from intraparticle diffusion model and Boyd <i>et al.</i> expression.....	111
Table 5.1 - Freundlich adsorption parameters of microcystins and NOM model compounds.....	125
Table 5.2 - Freundlich adsorption parameters for microcystins in single-solute isotherms and in competitive isotherms with NOM surrogates.....	131
Table 5.3 - Freundlich adsorption parameters for microcystins in competitive isotherms, in the absence and presence of ionic strength.....	134
Table 5.4 - Characteristics of the natural surface water used in isotherm experiments, after spiking with microcystins.....	137

## LIST OF TABLES

---

Table 6.1- Characteristics of <i>M. aeruginosa</i> suspensions used in the UF experiments.....	151
Table 7.1 - Cellulose acetate membrane specifications (manufacturer data).....	181
Table 7.2 - Characteristics of the NOM solutions.....	187
Table 9.1 - Characteristics of natural waters.....	236
Table 9.2 - Characteristics of the feed waters used in PAC+C/F/S and PAC/UF experiments (TOW spiked with <i>M. aeruginosa</i> culture and dissolved microcystins).....	245

# ABBREVIATIONS AND SYMBOLS

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## ABBREVIATIONS

AHA	Aldrich humic acid
AOC	Assimilable organic matter
AOM	Algogenic organic matter
CF	Cross-flow
C/F/S	Coagulation/flocculation/sedimentation
CFV	Cross flow velocity
CSTR	Continuous stirred tank reactor
$C_0$	Initial concentration
Chl-a	Chlorophyll-a
CP	Concentration polarization
CYN	Cylindrospermopsin
DAF	Dissolved air flotation
DE	Dead-end
DI	Deionised water
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electric conductivity
EOM	Extracellular organic matter
Extra MC-LReq	Extracellular microcystin-LR equivalents
FBR	Floc blanket reactor
FT	Feed Tank
GAC	Granular activated carbon
HF	Hollow-fibre
HPLC	High performance liquid chromatography
HPSEC	Size exclusion chromatography
HRT	Hydraulic retention time
Intra MC-LReq	Intracellular microcystin-LR equivalents
IOM	Intracellular organic matter
IS	Ionic strength
LD <sub>50</sub>	Lethal dose (50%)
M	Month
MC	Microcystin

## ABBREVIATIONS AND SYMBOLS

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MC-LA	Microcystin-LA
MC-LF	Microcystin-LF
MC-LR	Microcystin-LR
MC-LR <sub>eq</sub>	Microcystin-LR equivalents
MC-LW	Microcystin-LW
MC-LY	Microcystin-LY
MIB	Methylisoborneol
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PAC/UF	Powdered activated carbon adsorption/ultrafiltration
PDA	Photo diode array
PFR	Plug flow reactor
pH <sub>zc</sub>	pH of zero charge
PSS	Polystyrene sulphonate standards
RT	Recirculating tank
SA	Salicylic acid
SUVA	Specific ultraviolet absorbance
TA	Tannic acid
TCE	Trichloroethylene
TCW	Tavira's clarified water
THM	Trihalomethanes
TMP	Transmembrane pressure
TOC	Total organic carbon
TOW	Tavira's ozonated water
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WRR	Water recovery rate
WTP	Water treatment plant

# ABBREVIATIONS AND SYMBOLS

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## SYMBOLS

$b$	Langmuir energy of adsorption parameter
$Bt$	Boyd values
$C/C_0$	Normalised concentration
$C_e$	Equilibrium aqueous concentration
$h$	Initial adsorption rate
$J_1$	Pure water flux after backwashing
$J_0$	Initial pure water flux
$J/J_0$	Normalised flux
$K$	Freundlich unity-capacity parameter
$k_1$	Equilibrium rate constant
$k_i$	Intraparticle diffusion rate constant
$n$	Freundlich site-energy distribution parameter
$Q_{\max}$	Langmuir maximum capacity parameter
$q_t$	Surface concentration at a specific time
$q_e$	Surface concentration at equilibrium

## **ABBREVIATIONS AND SYMBOLS**

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# UNIVERSIDADE DO ALGARVE

FACULDADE DE CIÊNCIAS DO MAR E DO AMBIENTE

## REMOVAL OF CYANOBACTERIA AND CYANOTOXINS FROM DRINKING WATER BY POWDERED ACTIVATED CARBON ADSORPTION/ULTRAFILTRATION

(Tese para a obtenção do grau de doutor no ramo de Ciências e Tecnologias do Ambiente,  
especialidade de Tecnologias do Ambiente)

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“Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit”.

Marie Curie

Para o Nuno e os meus pais

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Margarida Campinas



# Removal of cyanobacteria and cyanotoxins from drinking water by powdered activated carbon adsorption/ultrafiltration

## ABSTRACT

PAC/UF was investigated to remove the cyanobacterium *Microcystis aeruginosa* and microcystins, focusing on toxins adsorption onto PAC and the combined effect of the water organic and inorganic matrices, the cells removal and lysis by UF, and PAC contribution to membrane fouling control and microcystins removal by PAC/UF.

The fine-grade mesoporous PAC presented high capacity and fast kinetics for microcystins adsorption from ultrapure-water. In model and natural waters, NOM size governed microcystins-NOM competition, and inorganics contribution was crucial. Main competitor was NOM of closer size, hindering microcystins adsorption through a pore-blocking mechanism. Ionic strength induced the competition of larger compounds and diminished the competition of similar-sized compounds. Kinetic models confirmed the competing mechanisms proposed based on kinetic and isotherm data.

UF ensured absolute removal of *M. aeruginosa* single-cells, although lysis was detected, particularly with cell ageing. However, AOM-driven microcystins rejection attenuated/avoided the permeate degradation. While not affecting the reversible fouling, PAC improved the permeate quality and membrane irreversible-fouling, minimising the chemical cleaning. The worst flux impairment was associated to polysaccharide-like AOM in background inorganics, for which PAC was apparently ineffective.

PAC/UF performed better than PAC+C/F/S. For the usual concentrations of dissolved microcystins in natural waters, 10-15 mgPAC/L achieved the WHO guideline-value.

**Key-Words:** PAC adsorption, ultrafiltration, cyanobacteria, microcystins, NOM, drinking water.



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**DATA:** 27 de Novembro de 2008

### **TÍTULO DA TESE:**

**Processo integrado de adsorção em carvão activado em pó e ultrafiltração para remoção de cianobactérias e cianotoxinas em água para consumo humano.**

### **RESUMO**

Investigou-se a remoção de *Microcystis aeruginosa* e microcistinas por PAC/UF, principalmente a adsorção das toxinas pelo carvão e o efeito da composição da água, a remoção e lise celular por ultrafiltração, e a contribuição do PAC no controlo da colmatação da membrana e remoção de microcistinas por PAC/UF.

O PAC revelou elevada capacidade e rápida adsorção de microcistinas em água pura. Em águas modelo e naturais, o tamanho da NOM determinou a competição microcistinas-NOM, sendo fundamental o efeito dos iões. Verificou-se maior competição de compostos idênticos, retardando a adsorção por bloqueio de poros. Os iões induziram a competição de compostos maiores e diminuíram a de semelhantes. Os modelos cinéticos confirmaram os mecanismos de competição.

UF removeu totalmente as células de *M. aeruginosa*, mas ocorreu lise especialmente das mais velhas. O material algógeno promoveu a rejeição de microcistinas, atenuando/evitando a degradação do permeado. PAC melhorou a qualidade do permeado e a colmatação irreversível da membrana, minimizando a limpeza química. O fluxo foi especialmente afectado por AOM polissacarídico (com iões), para o qual o PAC foi aparentemente ineficaz.

PAC/UF apresentou melhor desempenho que PAC+C/F/S e com 10-15 mgPAC/L atingiu-se o valor-guia da OMS, partindo de concentrações típicas de microcistinas em águas naturais.

**Palavras-Chave:** PAC, ultrafiltração, cianobactérias, microcistinas, NOM, água para consumo humano



# TABLE OF CONTENTS

---

LIST OF FIGURES.....	xi
LIST OF TABLES.....	xix
ABBREVIATIONS AND SYMBOLS.....	xxi
1 INTRODUCTION.....	1
1.1 SCOPE OF THE THESIS.....	3
1.2 OBJECTIVES.....	6
1.3 RESEARCH STRATEGY.....	7
1.4 THESIS STRUCTURE.....	11
2 BACKGROUND.....	13
2.1 CYANOBACTERIA.....	15
2.2 CYANOTOXINS.....	16
2.2.1 General.....	16
2.2.2 Microcystins.....	19
2.3 LEGISLATION AND GUIDELINES.....	22
2.4 WATER TREATMENT FOR CYANOTOXINS REMOVAL.....	23
2.4.1 Removal of Cell-Bound Cyanotoxins.....	23
2.4.2 Removal of Dissolved Cyanotoxins.....	24
2.5 PAC ADSORPTION.....	28
2.5.1 General.....	28
2.5.2 Mechanisms of Adsorption.....	28
2.5.3 NOM Competition.....	30
2.5.4 Adsorption Isotherms.....	31
2.5.5 Adsorption Kinetic Models.....	33
2.6 ULTRAFILTRATION (UF).....	35
2.6.1 General.....	35
2.6.2 Mass Transport and Fouling.....	37
2.7 PAC/UF.....	40
2.7.1 General.....	40
2.7.2 Operating Conditions.....	42
2.7.3 Waste Disposal.....	44
2.8 REFERENCES.....	45

# TABLE OF CONTENTS

---

3 THE IONIC STRENGTH EFFECT ON MICROCYSTIN AND NATURAL ORGANIC MATTER SURROGATE ADSORPTION ONTO PAC.....	55
ABSTRACT.....	57
3.1 INTRODUCTION.....	59
3.2 MATERIALS AND METHODS.....	62
3.2.1 Adsorbates.....	62
3.2.2 Adsorbent.....	64
3.2.3 Model Solution Preparation.....	65
3.2.4 Analytical Methods.....	65
3.2.5 Adsorption Kinetics Experiments.....	67
3.2.6 Equilibrium Isotherms Experiments.....	68
3.3 RESULTS AND DISCUSSION.....	68
3.3.1 Effect of Monovalent Ion ( $K^+$ ).....	70
3.3.2 Effect of Divalent Ion ( $Ca^{2+}$ ).....	76
3.4 SUMMARY AND CONCLUSIONS.....	80
3.5 REFERENCES.....	82
4 RELATING THE COMPETITIVE ADSORPTION OF MICROCYSTINS WITH THE WATER BACKGROUND ORGANIC AND INORGANIC MATRICES:	
I. KINETIC STUDY.....	85
ABSTRACT.....	87
4.1 INTRODUCTION.....	89
4.2 MATERIALS AND METHODS.....	92
4.2.1 Adsorbates.....	92
4.2.2 Model Solutions.....	93
4.2.3 Natural Surface Water.....	94
4.2.4 Adsorbent.....	95
4.2.5 Analytical Methods.....	95
4.2.6 Adsorption Kinetics.....	96
4.3 RESULTS AND DISCUSSION.....	97
4.3.1 Kinetic Studies with Model Solutions and Fresh PAC.....	97
4.3.2 Kinetic Studies with Model Solutions and Preloaded PAC.....	101
4.3.3 Kinetic Studies with Natural Surface Water and Fresh PAC.....	104

# TABLE OF CONTENTS

---

4.3.4 Kinetic Models Analysis.....	105
4.4 SUMMARY AND CONCLUSIONS.....	112
4.5 REFERENCES.....	113
5 RELATING THE COMPETITIVE ADSORPTION OF MICROCYSTINS WITH THE WATER BACKGROUND ORGANIC AND INORGANIC MATRICES:	
II. EQUILIBRIUM STUDY.....	117
ABSTRACT.....	119
5.1 INTRODUCTION.....	121
5.2 MATERIALS AND METHODS.....	123
5.3 RESULTS AND DISCUSSION.....	124
5.3.1 Single-Solute Isotherms.....	124
5.3.2 Microcystins-NOM Competition: C <sub>0</sub> effect.....	127
5.3.3 Microcystins-NOM Competition: NOM surrogates.....	129
5.3.4 Microcystins-NOM Competition: NOM surrogates and ionic strength.....	133
5.3.5 Microcystins-NOM Competition: Natural surface water.....	137
5.4 CONCLUSIONS.....	139
5.5 REFERENCES.....	141
6 EVALUATION OF CYANOBACTERIAL CELLS REMOVAL AND LYSIS BY ULTRAFILTRATION.....	
ABSTRACT.....	145
6.1 INTRODUCTION.....	147
6.2 MATERIALS AND METHODS.....	150
6.2.1 Cyanobacterial Culture.....	150
6.2.2 UF Feed Waters.....	150
6.2.3 Membrane.....	151
6.2.4 Ultrafiltration Experiments.....	151
6.2.5 Analytical Methods.....	153
6.3 RESULTS AND DISCUSSION.....	155
6.3.1 Microcystins Rejection by UF.....	155
6.3.2 Characterisation of Cultures Growth Phases.....	156
6.3.3 Retention of Cyanobacterial Cells.....	158
6.3.4 Cell Lysis and Microcystins Release to Water.....	160

# TABLE OF CONTENTS

---

6.3.5 Membrane Fouling by AOM.....	165
6.4 CONCLUSIONS.....	168
6.5 REFERENCES.....	170
7 ASSESSING THE PAC CONTRIBUTION TO THE NOM FOULING CONTROL IN PAC/UF SYSTEMS.....	173
ABSTRACT.....	175
7.1 INTRODUCTION.....	177
7.2 MATERIALS AND METHODS.....	179
7.2.1 NOM Solutions.....	179
7.2.2 UF Membrane and PAC.....	181
7.2.3 UF Experiments.....	182
7.2.4 Analytical Methods.....	184
7.3 RESULTS AND DISCUSSION.....	185
7.3.1 UF Fouling Potential of NOM Surrogates.....	185
7.3.2 UF Fouling Potential of Algal Organic Matter.....	187
7.3.3 UF Fouling Potential of PAC.....	190
7.3.4 NOM Fouling Potential in PAC/UF System.....	192
7.3.5 Membrane Cleaning.....	194
7.4 CONCLUSIONS.....	197
7.5 REFERENCES.....	198
8 MICROCYSTINS REMOVAL BY PAC/UF SYSTEM.....	203
ABSTRACT.....	205
8.1 INTRODUCTION.....	207
8.2 MATERIALS AND METHODS.....	210
8.2.1 Microcystins Extraction.....	210
8.2.2 Solutions.....	210
8.2.3 PAC.....	211
8.2.4 UF Membrane.....	212
8.2.5 Ultrafiltration Runs.....	212
8.2.6 Adsorption Kinetics.....	214
8.2.7 Analytical Methods.....	214

# TABLE OF CONTENTS

---

8.3 RESULTS AND DISCUSSION.....	215
8.3.1 Microcystins Removal by PAC/UF.....	215
8.3.2 Effect of NOM on Microcystins Removal by PAC/UF.....	219
8.4 CONCLUSIONS.....	223
8.5 REFERENCES.....	225
9 COMPARING PAC/UF AND CONVENTIONAL CLARIFICATION WITH PAC FOR REMOVING MICROCYSTINS FROM NATURAL WATERS.....	229
ABSTRACT.....	231
9.1 INTRODUCTION.....	233
9.2 MATERIALS AND METHODS.....	235
9.2.1 Cyanobacterial Cells and Cyanotoxins.....	235
9.2.2 Natural Waters.....	236
9.2.3 PAC.....	237
9.2.4 UF Runs.....	238
9.2.5 C/F/S Experiments.....	239
9.2.6 Analytical Methods.....	239
9.3 RESULTS AND DISCUSSION.....	240
9.3.1 Microcystins Removal from Natural Waters by UF and PAC/UF.....	240
9.3.2 Comparing PAC/UF and PAC+C/F/S.....	244
9.4 CONCLUSIONS.....	248
9.5 REFERENCES.....	249
10 CONCLUSIONS AND FUTURE WORK.....	253
10.1 CONCLUSIONS.....	255
10.2 FUTURE WORK.....	263

# TABLE OF CONTENTS

---

## LIST OF FIGURES

---

Figure 1.1 - Bench-scale UF <i>apparatus</i> designed and assembled for PAC/UF experiments.....	8
Figure 1.2 - Hollow-fibre module used in PAC/UF experiments.....	8
Figure 1.3 - Laboratory cultures of <i>Microcystis aeruginosa</i> used in the experiments.....	9
Figure 1.4 - Research strategy followed in this thesis (MC = microcystins; IS = ionic strength).	10
Figure 2.1 - Structure of microcystin-LR (Meriluoto and Spoof, 2007).....	20
Figure 2.2 - Hydraulic mode of operation: dead-end (left) and cross-flow (right) (USEPA, 2005).....	36
Figure 2.3 - Typical UF operation in most applications (Kim <i>et al.</i> , 2001).....	37
Figure 2.4 - Mechanisms of membrane fouling: Cb, complete blocking; Sb, standard blocking (pore constriction); Ib, intermediate blocking; Ck, cake formation.....	39
Fig. 2.5 - Adsorbate concentration profiles ( $C/C_0$ ) in the permeate resulting from wasting PAC at the end of the filtration cycle and using two PAC dosing procedures (Snoeyink <i>et al.</i> , 2000).....	43
Figure 2.6 - Schematics of PAC/UF process configuration (Snoeyink <i>et al.</i> , 2000).....	43
Figure 3.1 - Surface charge <i>versus</i> pH of PAC Norit SA-UF.....	65
Figure 3.2 - Adsorption kinetics in Milli-Q water for microcystin variants (left) and NOM surrogates (right) (left: 26 $\mu\text{g}$ MC-LR/L, 2.4 $\mu\text{g}$ MC-LY/L, 1.8 $\mu\text{g}$ MC-LW/L, 3.9 $\mu\text{g}$ MC-LF/L, PAC dose of 5 mg/L; right: 2.9 mg AHA/L, 2.8 mg TA/L, 1.7 mg SA/L, PAC dose of 20 mg/L).....	69
Figure 3.3 - Adsorption kinetics of salicylic acid in Milli-Q water and in KCl electrolyte with an ionic strength of 2.5 mM (1.6 mg SA/L, 20 mg PAC/L).....	70
Figure 3.4 - Adsorption kinetics of microcystin variants in Milli-Q water and KCl electrolytes of increasing ionic strength: 2, 10 and 100 mM (22 $\mu\text{g}$ MC-LR/L, 2.0 $\mu\text{g}$ MC-LY/L, 1.8 $\mu\text{g}$ MC-LW/L, 2.9 $\mu\text{g}$ MC-LF/L, 5 mg PAC/L).....	71
Figure 3.5 - Adsorption kinetics of tannic acid (left) and Aldrich humic acid (right) in Milli-Q water and in KCl electrolyte with an ionic strength of 2.5 mM (2.8-2.9 mg TA/L, 2.8-2.9 mg AHA/L, 20 mg PAC/L).....	71
Figure 3.6 - Adsorption isotherms of MC-LR in Milli-Q water and in KCl electrolytes with ionic strengths of 2.5 mM and 10 mM.....	74
Figure 3.7 - Adsorption isotherms of tannic acid in Milli-Q water and in KCl electrolytes with ionic strengths of 2.5 mM and 10 mM.....	75

## LIST OF FIGURES

---

Figure 3.8 - Adsorption kinetics of SA in Milli-Q water, and in KCl and KCl+CaCl <sub>2</sub> electrolytes with an ionic strength of 2.5 mM and 10 mM.....	77
Figure 3.9 - Adsorption kinetics of microcystin variants Milli-Q water and in three KCl+CaCl <sub>2</sub> electrolytes of increasing ionic strength: 2, 10 and 100 mM (18 µg MC-LR/L, 2.3 µg MC-LY/L, 1.6 µg MC-LW/L, 2.4 µg MC-LF/L, 5 mg PAC/L).....	77
Figure 3.10 - Adsorption kinetics of TA (left) and AHA (right) in Milli-Q water, and in KCl, KCl+CaCl <sub>2</sub> and MgSO <sub>4</sub> electrolytes with an ionic strength of 2.5 mM (2.8-2.9 mg TA/L, 2.6-2.9 mg AHA/L, 20 mg PAC/L).....	78
Figure 3.11 - Adsorption isotherms of MC-LR in Milli-Q water and in KCl+CaCl <sub>2</sub> electrolytes with ionic strengths of 2.5 mM and 10 mM.....	79
Figure 4.1 - Adsorption kinetics in the absence (open symbols) of competition and under competition (full symbols) between microcystins and AHA+SA (left) or microcystins and TA (right) (5 mg/L PAC; left: 34 µg MC-LR <sub>eq</sub> /L, 1.6 mg SA/L, 2 mg AHA/L; right: 33-137 µg MC-LR <sub>eq</sub> /L, 2-3.2 mg TA/L).....	97
Figure 4.2 - Competitive adsorption kinetics of microcystins with AHA+SA (left) or TA (right) in the absence (open symbols) and in the presence (full symbols) of 2.5 mM background ionic strength (left: 32-46 µg MC-LR <sub>eq</sub> /L, 1.7-2 mg AHA/L, 1.6-1.9 mg SA/L; right: 33-137 µg MC-LR <sub>eq</sub> /L, 2-3.2 mg TA/L)..	99
Figure 4.3 - AHA (left) and TA adsorption kinetics in the absence (open symbols) and in the presence (full symbols) of microcystins (left: 32-46 µg MC-LR <sub>eq</sub> /L, 1.7 - 2.7 mg AHA/L; right: 31-137 µg MC-LR <sub>eq</sub> /L; 2-3.2 mg TA/L).....	101
Figure 4.4 - Competitive adsorption kinetics of microcystins onto fresh and NOM preloaded PAC (32-46 µg MC-LR <sub>eq</sub> /L in Milli-Q water (left and right) and in 2.5 mM IS solution (center)).....	102
Figure 4.5 - Displaced desorption of AHA (left) and TA (right) by microcystins addition (32-37 µg MC-LR <sub>eq</sub> /L; 5 mg PAC/L).....	103
Figure 4.6 - Adsorption kinetics of microcystins onto fresh PAC in the presence of natural surface water (TCW) (left) and comparison with NOM model compounds effect (right) (28-39 µg MC-LR <sub>eq</sub> /L).....	104
Figure 4.7 - Pseudo-first order plots for microcystins adsorption from organic free-water and NOM model solutions.....	107

## LIST OF FIGURES

---

Figure 4.8 - Pseudo-second order plots for microcystins adsorption from organic free-water and NOM model solutions.....	108
Figure 4.9 - Intraparticle diffusion kinetics for microcystins adsorption in organic free-water and NOM model solutions.....	109
Figure 4.10 - Boyd <i>et al.</i> plots for microcystins adsorption of in organic free-water and NOM model solutions.....	110
Figure 5.1 - Single-solute isotherms of microcystins and NOM surrogates in the presence and absence of background ionic strength.....	125
Figure 5.2 - Microcystins residuals ( $C/C_0$ ) from microcystins-NOM competitive isotherms performed at different $C_0$ , in the absence (top) and in the presence (bottom) of background 2.5 mM IS.....	128
Figure 5.3 - Microcystins-NOM competitive isotherms performed at different $C_0$ , in the absence and in the presence of background 2.5 mM IS.....	129
Figure 5.4 - Microcystins-NOM adsorption isotherms (left: 202 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg SA/L; center: 221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg AHA/L; right: 211 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 2 mg TA/L)...	130
Figure 5.5 - Microcystins residuals in the presence of NOM surrogates (top) and comparison between microcystins and AHA residuals or microcystins and TA residuals (bottom) (211-221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ , 3 mg AHA/L, 2 mg TA/L).....	130
Figure 5.6 - Competitive adsorption isotherms of microcystins with AHA (left) or TA (right) in the absence (open symbols) and in the presence (full symbols) of background ionic strength (left: 3 mg AHA/L, 198-221 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ; right: 2 mg TA/L, 202-211 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ).....	134
Figure 5.7 - Microcystins and TA residuals obtained during kinetics with low carbon dose (5 mg/L) (left: TA and microcystins single solute kinetics; center: MC-LR <sub>eq</sub> -TA competitive kinetics; right: MC-LR <sub>eq</sub> -TA competitive kinetics in the presence of 2.5 mM IS).....	136
Figure 5.8 - Microcystins-NOM competitive isotherms from preozonated, clarified surface water (TCW) (219 $\mu\text{g MC-LR}_{\text{eq}}/\text{L}$ ).....	138
Figure 5.9 - Characterisation of Tavira's natural water NOM by size exclusion chromatography (Dionex Summit HPLC; PDA detection at 254nm; TSK-3000SW column; phosphate buffer 20 mM, pH = 6.8; 0.5 mL/min; calibration against PSS standards).....	139

## LIST OF FIGURES

---

Figure 6.1 - Schematic diagram of laboratory UF installation (FT: Feed tank; RT: Recirculating tank; PT: Permeate Tank; Flm: Flowmeter; P: Manometers; V1, V4, V5: Valves for backwashing; V2: Concentrate valve; V3: Permeate valve; B1: Peristaltic pump; B2: Positive displacement pump).....	152
Figure 6.2 - Normalised flux (left) and dissolved microcystins rejection (centre) during UF concentration runs, and cycle-averaged concentration of microcystins on the feed and permeate during constant flow runs (right) with single-solute model solution....	155
Figure 6.3 - Characterisation of <i>M. aeruginosa</i> cultures growth phases.....	158
Figure 6.4 - Turbidity and chlorophyll-a feed profiles (left) and cycle-averaged concentrations (right) on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells of 2 M and 4 M.....	159
Figure 6.5 - Cycle-averaged concentration of microcystins on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells (1M and 3M). The error bars represents standard deviations.....	161
Figure 6.6 - Net contribution of adsorption and cell lysis computed from mass-balance equation developed for dissolved microcystins during constant flow UF cycles with <i>M. aeruginosa</i> cells (1 M and 3 M).....	162
Figure 6.7 - Concentration factors for cell-bound microcystins (left) and chlorophyll-a (right) during constant flow runs with <i>M. aeruginosa</i> cells (2M and 4M): experimental (bars) and expected (symbols) values based on mass-balance equation.....	163
Figure 6.8 - Net contribution of adsorption and cell lysis computed from mass-balance equation developed for dissolved microcystins during constant flow UF cycles with <i>M. aeruginosa</i> cells (2 M and 4 M).....	164
Figure 6.9 - Cycle-averaged concentration of microcystins (extra and intracellular) on the feed and permeate during constant flow runs with <i>M. aeruginosa</i> cells (2 M and 4 M). The error bars represents standard deviations.....	165
Figure 6.10 - Normalised flux during UF concentration runs with <i>M. aeruginosa</i> cells (1 M and 3 M).....	166
Figure 6.11 - Feed (closed symbols) and permeate quality (open symbols), and rejections (asterisks) during UF concentration runs with <i>M. aeruginosa</i> cells (1 M and 3 M).....	168

## LIST OF FIGURES

---

Figure 7.1 - Flow diagram of UF <i>apparatus</i> (FT - Stirred feed tank; B - Positive displacement pump; P - Manometers; Flm- Flowmeter; PT - Permeate tank; V1,V4,V5- Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).....	181
Figure 7.2 - Concentration-time-depending fouling runs with NOM model compounds: normalised flux (left), feed and permeate quality, and rejection of TA (centre) and AHA (right) ( <i>ca.</i> 2.5 mg/L each NOM surrogate, 2.5 mM IS background electrolyte).....	185
Figure 7.3 - Normalised flux (left) and average rejection of organic matter (right) during time-depending fouling runs with different NOM (error bars represents standard deviations).....	189
Figure 7.4 - Normalised flux (left) and normalised feed turbidity (right) during UF and PAC/UF concentration-time-depending fouling runs at two cross-flow velocities (UF: no PAC addition; PAC/UF: 5 mg/L PAC addition (2.1.-2.9 NTU), 2.5 mM IS of background electrolyte).....	191
Figure 7.5 - Normalised flux during PAC/UF (10 mg/L PAC) and UF time-depending fouling runs with NOM surrogates (left) and algogenic organic fractions (right).....	193
Figure 7.6 - TOC (left) and UV <sub>254nm</sub> (right) rejections of NOM surrogates and algogenic organic fractions during PAC/UF (10 mg/L PAC) and UF fouling runs (error bars represents standard deviations).....	193
Figure 7.7 - Recovery of membrane pure water permeability after time-depending fouling runs with different NOM and with/without PAC addition (J <sub>1</sub> - pure water flux after backwashing; J <sub>0</sub> - initial pure water flux).....	195
Figure 7.8 - Recovery of membrane pure water permeability, after the concentration-time-depending fouling runs with TA, using different cleaning procedures (J <sub>1</sub> - pure water flux after membrane cleaning; J <sub>0</sub> - initial pure water flux).....	196
Figure 8.1 - Flow diagram of UF <i>apparatus</i> (FT - Feed tank; RT - Stirred recirculating tank; PT - Permeate tank; Flm - Flowmeter; P - Manometers; B1 - Peristaltic pump; B2 - Positive displacement pump; V1,V4,V5 - Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).....	212
Figure 8.2 - Microcystins UF feed and cycle-averaged permeate concentrations obtained with different feed concentrations and PAC doses (feed: brown bars; permeate: blue bars). Error bars represents standard deviations.....	215

## LIST OF FIGURES

---

Figure 8.3 - Normalised microcystins concentration after PAC/UF and PAC adsorption kinetics performed in the same operating conditions (17.1 $\mu\text{g/L}$ MC-LR <sub>eq</sub> feed concentration, two PAC doses and 1 h contact time).....	217
Figure 8.4 - Concentration profile (left) and cycle-averaged concentration (right) of microcystins in the permeate during PAC/UF cycles performed with two different PAC dosing procedures (16.8-19.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , 5 mg/L PAC).....	217
Figure 8.5 - Cycle-averaged concentration of microcystins in the permeate obtained in PAC/UF runs with two HRT in the recirculating tank (5.5-7.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , 5 mg/L PAC). Error bars represents standard deviations.....	219
Figure 8.6 - Cycle-averaged concentration of microcystins in the permeate of PAC/UF runs performed in the absence and in the presence of NOM surrogates for two microcystins feed concentration ranges: 5.3-7.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (left) and 17-23 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (right).....	220
Figure 8.7 - UV rejection (UV <sub>215nm</sub> , left; UV <sub>254nm</sub> , right) by PAC/UF of solutions containing microcystins and NOM model compounds (AHA+TA) (green bars: 19.5-23.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ; orange bars: 6.7-7.4 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ).....	221
Figure 8.8 - Cycle-averaged concentration of microcystins in the permeate of UF and PAC/UF runs with <i>M. aeruginosa</i> culture (2.1-2.3 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (total), 0.63-0.88 $\mu\text{g/L}$ MC-LR <sub>eq</sub> (dissolved), ext./int. = 0.4-0.6).....	222
Figure 9.1 – Membrane permeability (left) and rejections (right) obtained during UF and PAC/UF (10 mg/L PAC) of Tavira’s WTP clarified water (TCW) supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.8 $\mu\text{g/L}$ total MC-LR <sub>eq</sub> ).....	240
Figure 9.2 - Cycle-averaged concentration of microcystins in the permeate during UF and PAC/UF (10 mg/L PAC) of TCW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.8 $\mu\text{g/L}$ total MC-LR <sub>eq</sub> ). Error bars represents standard deviations.....	242
Figure 9.3 – Membrane permeability (left) and cycle-averaged concentration of dissolved microcystins in the feed and permeate (right) obtained during PAC/UF (10 mg/L PAC) of ozonated (TOW) and clarified (TCW) natural waters and supplemented with <i>M. aeruginosa</i> culture (cells and AOM) and dissolved microcystins. Comparison is made with NOM surrogate runs from chapter 8 (right, C <sub>1</sub> : 1 mg AHA/L+1.5 mgTA/L; C <sub>2</sub> : 2.5 mg AHA/L+2.5 mg TA/L).....	243

## LIST OF FIGURES

---

Figure 9.4 - Percentage of microcystins remaining after PAC adsorption kinetics performed with TCW supplemented with dissolved microcystins (5.2 $\mu\text{g/L}$ MC-LR <sub>eq</sub> feed concentration, 1 h contact time).....	244
Figure 9.5 - PAC+C/F/S and PAC/UF performances with TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.2-8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , extra/intracellular = 4-5, 10 mg/L PAC).....	245
Figure 9.6 - Average microcystins concentration of treated waters produced by PAC+C/F/S and PAC/UF application to TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (7.2-8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> , extra/intra = 4-5; 10 mg/L PAC)....	247
Figure 9.7 - Average microcystins concentration (intra+extra) of treated waters obtained by different PAC doses applied to PAC+C/F/S of TOW supplemented with <i>M. aeruginosa</i> culture and dissolved microcystins (8.5 $\mu\text{g/L}$ MC-LR <sub>eq</sub> ).....	248



## LIST OF TABLES

---

Table 2.1 - Properties of cyanotoxins (Carmichael, 1997; Sivonen and Jones, 1999; Hitzfeld <i>et al.</i> , 2000; Codd, 2000; Yunes <i>et al.</i> , 2003; Metcalf and Codd, 2004; Van Apeldoorn <i>et al.</i> , 2007; Meriluoto and Spoof, 2007).....	18
Table 2.2 - Properties of the most frequent microcystins (Sivonen and Jones, 1999; De Maagd <i>et al.</i> , 1999; Cook and Newcombe, 2002; Newcombe <i>et al.</i> , 2003).....	21
Table 2.3 - WHO guidelines for managing recreational waters and drinking waters which may contain cyanobacteria (Falconer, 1999; WHO, 2003).....	22
Table 2.4 - Guidelines/regulations of several countries for microcystins in drinking water.....	23
Table 3.1 - Properties of microcystin variants identified in this study (adapted from De Maagd, 1999; Sivonen and Jones, 1999; Newcombe <i>et al.</i> , 2003).....	63
Table 3.2 - Relevant PAC Norit SA-UF characteristics (adapted from Campos <i>et al.</i> , 2000; Li <i>et al.</i> , 2002, 2003).....	64
Table 3.3 - Conditions of kinetic and isotherm experiments.....	66
Table 3.4 - Isotherm (Langmuir or Freundlich) parameters for MC-LR and TA in Milli-Q water, KCl or KCl+CaCl <sub>2</sub> electrolyte solution with different ionic strengths (2.5mM and 10 mM).....	74
Table 4.1 - Characteristics of the natural surface water (TCW) used in adsorption kinetic experiments, after spiking with microcystins.....	94
Table 4.2 - Kinetic models investigated.....	106
Table 4.3 - Kinetic parameters calculated for pseudo-first order and pseudo-second order adsorption kinetic models.....	107
Table 4.4 - Kinetic parameters obtained from intraparticle diffusion model and Boyd <i>et al.</i> expression.....	111
Table 5.1 - Freundlich adsorption parameters of microcystins and NOM model compounds.....	125
Table 5.2 - Freundlich adsorption parameters for microcystins in single-solute isotherms and in competitive isotherms with NOM surrogates.....	131
Table 5.3 - Freundlich adsorption parameters for microcystins in competitive isotherms, in the absence and presence of ionic strength.....	134
Table 5.4 - Characteristics of the natural surface water used in isotherm experiments, after spiking with microcystins.....	137

## LIST OF TABLES

---

Table 6.1- Characteristics of <i>M. aeruginosa</i> suspensions used in the UF experiments.....	151
Table 7.1 - Cellulose acetate membrane specifications (manufacturer data).....	181
Table 7.2 - Characteristics of the NOM solutions.....	187
Table 9.1 - Characteristics of natural waters.....	236
Table 9.2 - Characteristics of the feed waters used in PAC+C/F/S and PAC/UF experiments (TOW spiked with <i>M. aeruginosa</i> culture and dissolved microcystins).....	245

# ABBREVIATIONS AND SYMBOLS

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## ABBREVIATIONS

AHA	Aldrich humic acid
AOC	Assimilable organic matter
AOM	Algogenic organic matter
CF	Cross-flow
C/F/S	Coagulation/flocculation/sedimentation
CFV	Cross flow velocity
CSTR	Continuous stirred tank reactor
C <sub>0</sub>	Initial concentration
Chl-a	Chlorophyll-a
CP	Concentration polarization
CYN	Cylindrospermopsin
DAF	Dissolved air flotation
DE	Dead-end
DI	Deionised water
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electric conductivity
EOM	Extracellular organic matter
Extra MC-LReq	Extracellular microcystin-LR equivalents
FBR	Floc blanket reactor
FT	Feed Tank
GAC	Granular activated carbon
HF	Hollow-fibre
HPLC	High performance liquid chromatography
HPSEC	Size exclusion chromatography
HRT	Hydraulic retention time
Intra MC-LReq	Intracellular microcystin-LR equivalents
IOM	Intracellular organic matter
IS	Ionic strength
LD <sub>50</sub>	Lethal dose (50%)
M	Month
MC	Microcystin

## ABBREVIATIONS AND SYMBOLS

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MC-LA	Microcystin-LA
MC-LF	Microcystin-LF
MC-LR	Microcystin-LR
MC-LR <sub>eq</sub>	Microcystin-LR equivalents
MC-LW	Microcystin-LW
MC-LY	Microcystin-LY
MIB	Methylisoborneol
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PAC/UF	Powdered activated carbon adsorption/ultrafiltration
PDA	Photo diode array
PFR	Plug flow reactor
pH <sub>zc</sub>	pH of zero charge
PSS	Polystyrene sulphonate standards
RT	Recirculating tank
SA	Salicylic acid
SUVA	Specific ultraviolet absorbance
TA	Tannic acid
TCE	Trichloroethylene
TCW	Tavira's clarified water
THM	Trihalomethanes
TMP	Transmembrane pressure
TOC	Total organic carbon
TOW	Tavira's ozonated water
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WRR	Water recovery rate
WTP	Water treatment plant

# ABBREVIATIONS AND SYMBOLS

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## SYMBOLS

$b$	Langmuir energy of adsorption parameter
$Bt$	Boyd values
$C/C_0$	Normalised concentration
$C_e$	Equilibrium aqueous concentration
$h$	Initial adsorption rate
$J_1$	Pure water flux after backwashing
$J_0$	Initial pure water flux
$J/J_0$	Normalised flux
$K$	Freundlich unity-capacity parameter
$k_1$	Equilibrium rate constant
$k_i$	Intraparticle diffusion rate constant
$n$	Freundlich site-energy distribution parameter
$Q_{\max}$	Langmuir maximum capacity parameter
$q_t$	Surface concentration at a specific time
$q_e$	Surface concentration at equilibrium

## **ABBREVIATIONS AND SYMBOLS**

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