CHAPTER 2

BACKGROUND

2.1 CYANOBACTERIA

Cyanobacteria belong to *Bacteria* Domain, presenting some characteristics of bacteria and some of algae. They are prokaryotic organisms, yet they are similar to algae in size and contain both chlorophyll-a and accessory pigments to perform oxygenic photosynthesis (Mur *et al.*, 1999; Kaebernick and Neilan, 2001). The accessory pigment phycocyanin, a bluish phycobilin, is unique to cyanobacteria and, as so, they are also referred to as blue-green algae (Zurawell *et al.*, 2005).

The basic morphology comprises unicellular, colonial and multicellular filamentous forms (Mur *et al.*, 1999), with cell sizes varying from less than 2 μm to 40 μm in diameter (Kaebernick and Neilan, 2001). Cyanobacteria may have special adaptations such as heterocysts (for nitrogen fixation), gas vacuoles (light triggered, confer buoyancy), and akinetes (cells with reserve materials, enabling survival under unfavourable conditions), allowing them an advantage over many competitors (Mur *et al.*, 1999; Kaebernick and Neilan, 2001; Svrecek and Smith, 2004).

Cyanobacteria are important primary producers and generate several metabolites that are pharmaceutically useful substances. However, under some conditions, cyanobacteria form undesirable blooms, associated with a number of water-related problems, including tastes and odours (*e.g.*, geosmin and methylisoborneol), turbidity, and oxygen depletion as the cyanobacteria decay (Metcalf and Codd, 2004). Furthermore, cyanobacteria blooms cause poor settling, filter clogging, disinfectant consumption and production of disinfection-by-products in water treatment plants (WTP) (Paralkar and Edzwald, 1996; Her *et al.*, 2004). Of particular concern is the ability of several cyanobacteria strains to produce, under certain conditions of growth, potent toxins as secondary metabolites – cyanotoxins, which function is

still unknown. Secondary metabolites are those compounds not used by an organism for its primary metabolism, *i.e.*, cell division or energy production (Svrecek and Smith, 2004).

The cyanobacteria class includes 150 genera, among which 40 genera are estimated to be potential toxin producers (Van Apeldoorn, 2007). Surveys of many fresh cyanobacterial blooms have shown that up to 50-70% of them are toxic (Sivonen and Jones, 1999) and that the most commonly occurring toxic genera is Microcystis, in particular, the species *M. aeruginosa* (WHO, 2003; MHNZ, 2005).

The reasons for cyanobacterial blooms occurrence are not straightforward and continue to be controversially debated. Blooms are not always associated with pollution and have been found in reservoirs with near-pristine catchments (Sivonen and Jones, 1999). It has been suggested that a stable water column, warm water, high nutrient concentrations (P, N), low N:P and high pH are advantageous conditions for the development of blooms, but no single factor has been directly related with it (Mur *et al.*, 1999; Zurawell *et al.*, 2005). Timing and duration of the cyanobacterial bloom season depend largely on the climatic conditions of the region. In temperate zones, cyanobacterial blooms are most prominent during the late summer and early autumn and may last for 2-4 months. In warmer climates, like the ones of Portugal and Spain, blooms may occur for up to 6 months or longer (Sivonen and Jones, 1999).

2.2 CYANOTOXINS

2.2.1 General

Cyanotoxins may occur both within cells (cell bound or intracellular) or dissolved (extracellular). Intracellular toxin content is typically highest in the late logarithmic growth

phase, and the toxin content apparently shows a positive correlation with cyanobacterial biomass (Carmichael, 2001). Toxin release into water may be natural (natural cell lysis caused by age or through active release) or induced (toxin release, resulting from cell destruction in treatment processes caused by mechanical and chemical stresses) (Sivonen and Jones, 1999; Pietsch *et al.*, 2002; Schmidt *et al.*, 2002). In natural environments, healthy blooms populations produce little extracellular toxin (with the exception of *Cylindrospermopsis* genera which produces similar fraction of intra and extracellular toxins throughout the cell life) (Sivonen and Jones, 1999). The range of measured concentration for dissolved cyanotoxins, in all cases except those where a major bloom is obviously breaking down, is 0.1-10 μg/L (Jones and Orr, 1994; Lahti *et al.*, 1997). Cell-bound concentrations are several orders of magnitude higher.

Environmental factors affect the toxin content but only within a range of less than an order of magnitude (Sivonen and Jones, 1999). For instance, for microcystins (toxins produced by *Microcystis*), while the toxin variants produced by a particular strain are rather constant, the ratios of individual microcystins may change with time, temperature and light. However, for microcystins, it has been shown that toxicity of a strain mainly depends on whether there is the gene for microcystin production (WHO, 2003).

According to their chemical structure cyanotoxins are classified in cyclic peptides, alkaloids and lipopolysaccharides (LPS) (Sivonen and Jones, 1999). In terms of their mode of action, cyanotoxins are hepatotoxins, neurotoxins, cytotoxins and irritant or inflammatory agents (WHO, 2006; Meriluoto and Spoff, 2007). General important characteristics of cyanotoxins were compiled and are presented in Table 2.1.

Table 2.1 - Properties of cyanotoxins (Carmichael, 1997; Sivonen and Jones, 1999; Hitzfeld *et al.*, 2000; Codd, 2000; Metcalf and Codd, 2004; Van Apeldoorn *et al.*, 2007; Meriluoto and Spoof, 2007).

	Chemical Structure	Toxicity	LD_{50} (μg/kg)[a]	Structural Variants	Molecular Weight (Da)	Net charge	Hydrophobicity	Main Producer Genera
Microcystins	Cyclic peptides	Hepatotoxic	25- 600	> 80	900-1100 [b]	-2; -1; 0	Relatively Hydrophobic[c]	Microcystis, Anabaena, Planktothrix, Nostoc, Anabaenopsis
Nodularin	Cyclic peptides	Hepatotoxic	50	*ca.* 6	824	Negative	Relatively Hydrophobic	Nodularia
Anatoxin-a	Alkaloid	Neurotoxic	375	5	166	+1	Hydrophilic	Anabaena, Planktothrix, Aphanizomenon
Anatoxina-a (S)	Alkaloid	Neurotoxic	20	1	252	0	Hydrophilic	Anabaena
Saxitoxins	Alkaloid	Neurotoxic	7.6 - 10.5	*ca.* 20	256 - 491	0 (C-Tox); +1 (GTX); +2 (STX)	Hydrophilic	Anabaena, Aphanizomenon, Cylindrospermopsis, Lyngbya
Cylindrospermopsin	Alkaloid	Hepatotoxic Cytotoxic	200 - 2000	2	415	0	Very Hydrophilic	Cylindrospermopsis, Aphanizomenon, Umezakia
LPS	Lipopolysacharides	Potential irritant	--	> 3	--	Negative	--	All

[a] Toxicity measured by mouse intraperitoneal; [b] Estimated MW are 500-4000 Da, with the most known between 900-1100 Da; [c] hydrophobicity depends on the variable amino acids; LPS: Lipopolysacharides; C-Tox: doubly sulphated saxitoxins; GTX: singly sulphated saxitoxins (gonyautoxins); STX: non sulphated saxitoxins.

Based on current knowledge, microcystins (MC) and cylindrospermopsin (CYN) are considered to present the greatest risk to human health, since they have both acute and chronic effects, and occur most frequently in fresh water systems whereas the cyanobacterial neurotoxins appear in high concentrations only occasionally. Nodularin and microcystins have comparable toxicity, but as *Nodularia spumigena* (an obligate brackish and saline tolerant cyanobacteria) is currently the only species known to produce nodularin, this toxin is unlikely to occur in drinking water (MHNZ, 2005; WHO, 2006). The genera producing CYN usually form toxic blooms in subtropical, tropical or arid zones water bodies (Sivonen and Jones, 1999). However, increasing occurrences of *C. raciborskii* in Europe are reported, namely in France, Germany, Hungary, Austria, Greece, Slovakia, Spain and Portugal (Quesada *et al.*, 2006; Van Apeldoorn *et al.*, 2007). Cylindrospermopsin may thus become relevant in temperate zones in the future (WHO, 2003).

2.2.2 Microcystins

Microcystins are cyclic heptapeptides, containing seven peptide-linked amino acids, with the two terminal amino acids joined to form a cyclic compound. All microcystins contain a specific amino acid (Adda) side chain which is largely responsible for their toxicity (Carmichael, 1994). There are currently more than 80 known variants of microcystins (WHO, 2006), based on five common amino acids and varying with respect to the methyl groups and the two amino acids in positions 2 and 4 within the ring (Carmichael, 1997). Each variant is named according to the variable amino acids present. MC-LR, with leucine and arginine occupying the 2 and 4 positions (Figure 2.1), is among the most frequent and most toxic microcystins congeners (Svrcek and Smith, 2004; MHNZ, 2005; WHO, 2006). Other common microcystins analogues are MC-LA, -RR and -YR (Ho *et al.*, 2006 a).

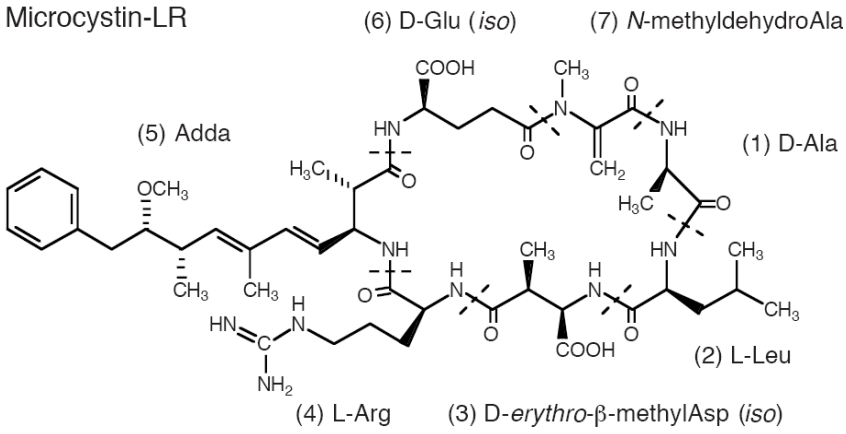

Figure 2.1 - Structure of microcystin-LR (Meriluoto and Spoof, 2007).

Microcystins cause both acute and chronic effects. They are hepatotoxic, causing a breakdown in the liver structure by interfering with enzyme pathways (inhibit the activities of protein phosphatase 1 and 2A), and death may occur as little as 30 minutes from severe liver haemorrhage (Codd, 2000). Chronic exposure promotes tumour growth (MHNZ, 2005).

Concerning their chemical structure, microcystins are large compounds (900-1100 Da) in comparison with usual micropollutants and other cyanotoxins (Sivonen and Jones, 1999). Using molecular models, the diameter of microcystin-LR has been estimated to be between 1.2 and 2.6 nm (Donati *et al.*, 1994). The variable amino acids are responsible for different properties, like hydrophobicity and net charge, toxicities and molecular weight (Table 2.2). All microcystins have two carboxyl groups that are negatively charged at neutral pH (on D-glutamate and D-erythro-β-methylaspartic acid), but microcystin variants have different net charges, depending on the variable amino acid groups – *e.g.*, the arginine group has a positive charge, whereas the alanine and tyrosine groups have zero charge (Cook and Newcombe, 2002; Newcombe *et al.*, 2003; Meriluoto and Spoof, 2007).

Table 2.2 - Properties of the most frequent microcystins (Sivonen and Jones, 1999; De Maagd *et al.*, 1999; Cook and Newcombe, 2002; Newcombe *et al.*, 2003).

Analogue	Variable amino acids		LD_{50} [a]	Molecular Weight (g/mol)	Net charge (at neutral pH)
	X	Z			
MC-LR	Leucine	Arginine	50	994	-1
MC-YR	Tyrosine	Arginine	70	1044	-1
MC-LY	Leucine	Tyrosine	90	1001	-2
MC-LW	Leucine	Tryptophane	NR	1024	-2
MC-LF	Leucine	Phenylalanine	NR	985	-2
MC-LA	Leucine	Alanine	50	909	-2
MC-RR	Arginine	Arginine	600	1037	0

[a] Toxicity measured by mouse intraperitoneal (μg/kg); NR: not reported

Microcystins are relatively polar molecules and are soluble in water (Sivonen and Jones, 1999). Although the Adda residue gives them a partially hydrophobic character, microcystin-LR and most of its congeners are hydrophilic and generally not able to penetrate vertebrate cell membranes (Sivonen and Jones, 1999; Höeger, 2003; Van Apeldoorn *et al.*, 2007). Microcystin-LR becomes more hydrophobic in water with decreasing pH, but the pKa is very low (De Maagd *et al.*, 1999). Several microcystin variants have been identified as having greater hydrophobicity than microcystin-LR, such as microcystin-LL, -LF, -LW, -LY, -LA, -LV, and -LM (Svrecek and Smith, 2004; Cook and Newcombe, 2002). These cyclic peptides are extremely stable and resistant to chemical hydrolysis or oxidation at near neutral pH. In natural waters and in the dark, microcystins may persist for months or years. Microcystin-LR is not degraded by sun-light alone but in the presence of photosensitizers (*e.g.*, pigments, humic acids), although the degradation will be of significance only in very shallow water bodies (Sivonen and Jones, 1999).

2.3 LEGISLATION AND GUIDELINES

Cyanotoxins may cause waterborne disease mainly when ingested and through direct contact during recreational exposure. The World Health Organization (WHO) therefore established three guidance levels to recreational waters and two alert levels to raw drinking water (Table 2.3). Furthermore, in 1998 WHO established a provisional drinking water guideline value of 1.0 μg/L for MC-LR (cell-bound and extracellular). The WHO guideline value is stated as being provisional since it covers only microcystin-LR, given that the toxicology is limited and new data for toxicity of other cyanotoxins are being generated (WHO, 2006).

Table 2.3 - WHO guidelines for managing recreational waters and drinking waters which may contain cyanobacteria (Falconer, 1999; WHO, 2003).

	Risk level (guidance/alert level)	Density of algal cells	
		Cyanobacterial (cells/mL)	Chlorophyll-a (μg/L)
Bathing waters	Low (Guidance 1 level)	20 000	10
	Moderate (Guidance 2 level)	100 000	50
	High (Guidance 3 level)	Cyanobacterial scum formation[a]	
Drinking waters (raw waters)	Low (Vigilance)	< 2000	< 1
	Medium (Alert 1 level)	2 000	1
	High (Alert 2 level)	100 000	50

[a] Scum in recreational areas, where whole body contact and/or ingestion/aspiration risk occur.

A number of countries have developed regulations or guidelines for microcystins in drinking water (Table 2.4). Many are based on or directly incorporated the WHO guideline value, including Czech Republic, France, Great Britain, China, Italy, Japan, Korea, Norway, Poland (Burch, 2007), Canada, Australia, New Zealand, Brasil, Spain and, very recently, Portugal through the DL 306/2007 (dating from 27 August). USA have no guideline values nor standards, but cyanobacteria and their toxins have been listed on the USEPA contaminant candidate list (CCL) for further research (Chorus, 2005). Some variability in the expression of the concentration of microcystins has been observed, which in practice makes the values not

comparable. Sometimes the reference value is expressed in μg/L of microcystin-LR (*e.g.*, WHO, Canada, Portugal), others in microcystin-LR equivalents (*e.g.*, New Zealand), microcystin-LR toxicity equivalents (*e.g.*, Australia; it requires the use of toxicity equivalence factors) and there is also some cases where there is a lack of information, being only referred μg/L of microcystins (*e.g.*, Brasil and Spain), with no variants specified. Internationally, the main focus has been upon microcystins for they are widely regarded as the most significant potential source of human injury from cyanobacteria on a world-wide scale. However, there is a pronounced demand for a WHO guideline value for cylindrospermopsin (Chorus, 2005).

Table 2.4 - Guidelines/regulations of several countries for microcystins in drinking water

Country	Guidelines/ Regulation[a]	Units	Reference
WHO	1.0	μg/L MC-LR	WHO, 2006
Australia	1.3	μg/L MC-LR (toxicity equivalent)	Chorus, 2005; Burch, 2007
Brasil	1.0	μg/L Microcystins	Chorus, 2005
Canada	1.5	μg/L MC-LR	FPTCDW, 2002
New Zealand	1.0	μg/L MC-LReq	MHNZ, 2005
Spain	1.0	μg/L Microcystins	Chorus, 2005; Burch, 2007
Portugal	1.0	μg/L MC-LR	DL 306/2007

[a] Sum of cell-bound and extracellular toxin.

2.4 WATER TREATMENT FOR CYANOTOXINS REMOVAL

2.4.1 Removal of Cell-Bound Cyanotoxins

The technologies preferentially referred in scientific literature for the removal of cyanobacteria and cell-bound cyanotoxins are coagulation/flocculation (C/F) with sedimentation (S) or dissolved air flotation (DAF), and lately, membrane processes, like ultrafiltration (UF) and nanofiltration (NF). All the referred technologies are reported to be efficient for cells removal although with different removal efficiencies

(C/F/S < C/F/DAF < UF < NF). The main controversy is the effect of these technologies on cell integrity, with some studies indicating no effect (Kenefick *et al.*, 1993; Velzeboer *et al.*, 1995; Chow *et al.*, 1998; 1999; Drikas *et al.*, 2001a; Ribau Teixeira and Rosa, 2006 a, b, 2007), while others refer the occurrence of cell lysis (Lam *et al.*, 1995; Hrudey *et al.*, 1999; Chow *et al.*, 1999; Pietsch *et al.*, 2002; Gijsbertsen-Abrahamse *et al.*, 2006) mostly due to physical (*e.g.* shear stresses induced by mixing, pressuring) and/or chemical (*e.g.*, acid pH, coagulant overdosing) stresses. Several works have demonstrated that oxidation induces severe algae cell damage, with consequent toxin release (Tsuji *et al.*, 1997; Hoeger *et al.*, 2002; Pietsch *et al.*, 2002; Svrcek and Smith, 2004; Daly *et al.*, 2007) and should therefore be avoided in waters containing cyanobacterial cells. Further studies are still necessary to test cell lysis occurrence, especially for membrane processes like UF, given that Chow *et al.* (1997) and Gijsbertsen-Abrahamse *et al.* (2006) found a slight cell damaging (4-10% of *Microcystis* cells damaging or 14-34% of *Plantothrix* filaments damaging), although the quality permeate was not degraded.

2.4.2 Removal of Dissolved Cyanotoxins

Regarding dissolved cyanotoxins, the most studied processes are activated carbon adsorption and oxidation, and more recently biodegradation and membrane filtration (NF and hybrid adsorption/membrane processes).

PAC has demonstrated an efficient removal of microcystins, provided that the appropriate carbon and the correct dose is applied (Falconer *et al.*, 1989; Hart *et al.*, 1998; Pendleton *et al.*, 2001; Cook and Newcombe, 2002; Schmidt *et al.*, 2002; Newcombe and Nicholson, 2004). The exception is microcystin-LA, which is not readily removed by activated carbon, probably due to electrostatic interactions (Cook and Newcombe 2002; Newcombe *et al.*,

2003; Ho, 2004). However, PAC performance depends on NOM competitive adsorption (Donati *et al.*, 1994). There is general agreement that to achieve high toxin removal efficiency (> 85%), high doses of PAC are required (> 20 mg/L) and that the contact time is very important (Keijola *et al.*, 1988; Donati *et al.*, 1994; Hart *et al.*, 1998; Mouchet and Bonnélye 1998; Hrudey *et al.*, 1999). Although very easy to apply to conventional water treatment plants, PAC addition is responsible for a significant increase of treatment costs and sludge production and is therefore only recommended for short periods of time.

GAC filtration has demonstrated efficiency for toxin removal (Falconer *et al*., 1989; Donati *et al*., 1994; Lambert *et al.*, 1996; Hart *et al.*, 1998; Cook and Newcombe, 2002; Wang *et al.*, 2007), using both adsorption and biodegradation removal mechanisms and is recommended for a continuous application. However, GAC filtration still has some problems, such as the limited lifetime of adsorption due to quick GAC exhaustion by NOM, which may result in toxin breakthrough after a very short period of time (Lambert *et al*., 1996). The lifetime of GAC was referred to vary between one month to more than one year depending on the type of toxin and the water quality (Hart and Stott, 1993; Hart *et al.*, 1998; Newcombe, 2002; Newcombe and Nicholson, 2004). Another problem is the desorption of toxin after discontinuing the toxin input, as observed by Mesquita *et al.* (2006) for MC-LR, which brings concerns about cyanotoxin release after cyanobacterial blooms. Besides, it is difficult to understand the lifetime of a GAC filter and its overall removal efficiency as a function of operation time (Wang *et al.*, 2006).

Biodegradation is an efficient removal mechanism and may substantially increase the GAC lifetime for it allows a continuous regeneration. However, it may only occur after a lag period of several days or even months, due to microorganisms acclimatization to toxins (Drikas *et*

al., 2001 b; Newcombe *et al.*, 2002; MHNZ, 2005; Ho *et al.*, 2006 b). NOM was demonstrated to be important for MC-LR biodegradation, because the process is probably co-metabolic and depends on the available assimilable organic carbon (AOC), and MC-LR desorption is intensified by the presence of other soluble organic compounds in water (Mesquita *et al.*, 2006). The biodegradation shows great potential as a low cost, low technology process, particularly if the optimum conditions may be identified and, perhaps, imposed on the filter (Newcombe *et al.*, 2003; Newcombe and Nicholson, 2004). However, factors affecting the biological removal, such as biofilm mass and composition, acclimation periods, temperature and water quality, may not be easily controlled (Ho *et al.*, 2006 b; Wang *et al.*, 2007) and further research is required.

Dissolved cyanotoxins have been found to be efficiently degraded by oxidants, such as chlorine, permanganate and especially, ozone (Keijola *et al.*, 1988; Nicholson *et al.*, 1994; Tsuji *et al.*, 1997; Rositano *et al.*, 1998, 2001; Acero *et al.*, 2005; Ho *et al.*, 2006 a; Daly *et al.*, 2007; Rodríguez *et al.*, 2007 a, b). However, chlorine is relatively ineffective for anatoxin-a and MC-LA oxidation (Newcombe and Nicholson, 2004; Ho *et al.*, 2006 a; Rodríguez *et al.*, 2007 a, b). Oxidation depends on several conditions, difficult of simultaneously control, *e.g.*, residual dose, contact time and water quality, particularly the NOM content, pH, alkalinity and temperature (Hart and Stott, 1993; Nicholson *et al.*, 1994; Tsuji *et al.*, 1997; Rositano *et al.*, 1998, 2001; Senogles *et al.*, 2000; Hoeger *et al.*, 2002; Acero *et al.*, 2005; Ho *et al.*, 2006 a; Daly *et al.*, 2007; Rodríguez *et al.*, 2007 a, b). The formation of disinfection by-products, such as trihalomethanes (THM) and bromate, may be a restriction to the application of sufficiently high oxidant doses (Rodríguez *et al.*, 2007 a, b). The incomplete oxidation of toxins, producing compounds of unknown toxicity is also a concern, although the characterization of the decomposition products and their potential

health implications has yet not been adequately addressed (Hoeger *et al.*, 2002; Newcombe *et al.*, 2002; Svrcek and Smith, 2004; MHNZ, 2005).

Most of the research on dissolved cyanotoxins removal by membrane processes studied nanofiltration. NF was proven to be efficient for cyanotoxins removal (Hart and Stott, 1993; Muntisov and Trimboli, 1996; Smith *et al.*, 2002; Ribau Teixeira and Rosa, 2005 a, 2006 b; Gijsbertsen-Abrahamse *et al.*, 2006). Ribau Teixeira and Rosa (2005 a, 2006 b, c) and Gijsbertsen-Abrahamse *et al*. (2006) achieved a microcystins removal efficiency above 97% and a anatoxin-a rejection ≥ 96%, regardless of the variations in feed water quality (NOM and competitive toxin), the water recovery rate (up to 84%) and the pH values (Ribau Teixeira and Rosa, 2005 a, 2006 b, c). The major NF drawbacks were the permeate fluxes, which may be significantly impacted by background organics (NOM and microcystins) (Ribau Teixeira and Rosa, 2005 a, 2006 c, d) and, especially, inorganics (pH and calcium) (Ribau Teixeira and Rosa, 2005 b, 2006 c), although it was possible to operate at very high water recovery rates. Membrane hybrid processes, like PAC/UF, have been referred to be promising for cyanotoxins removal (Mouchet and Bonnélye, 1998; Zhou and Smith, 2002), but published data on this application are still rather scarce. Lee and Walker (2006) used cellulose acetate (20 kDa) and polyethersulphone (5 and 20 kDa) flat sheet membranes to study MC-LR rejection by PAC/UF. The authors obtained 97.7-98.8% MC-LR rejection in the absence of NOM and 77.7- 89.6% with 5 mg/L of fulvic acid addition (50 µg/L MC-LR; 5 mg/L PAC; 4 h contact time). Further research is recommended addressing conditions (module type, operating conditions) closer to full-scale applications.

2.5 PAC ADSORPTION

2.5.1 General

A typical activated carbon particle has a porous structure consisting of a network of interconnected macropores (> 50 nm in diameter), mesopores (2-50 nm), secondary micropores (0.8-2 nm) and primary micropores (< 0.8 nm) that provides a good capacity for the adsorption of organic molecules due to its high surface area (Aksu and Kabasal, 2005). Although the great majority of the structures are composed of carbon, all activated carbon contain some heteroatoms, mainly oxygen and hydrogen. PAC has a charge in aqueous solution, which is often attributed to oxygen surface groups (Newcombe and Cook, 2004). Both the raw material and the activation conditions affect activated carbon pore structure and surface chemistry (Quinlivan, 2001). The primary difference between PAC (powdered) and GAC (granular) is the smaller particle size of PAC, typically 65-90% of it passing a 44 μm sieve.

2.5.2 Mechanisms of Adsorption

For adsorption to take place, several transport steps must occur. The molecular size of the adsorbate and the adsorbent particle size have both important effects on the rate of adsorption. As the molecular size increases, the diffusion coefficients decrease, and thus longer time is required to remove the large-molecular-weight substances. The adsorbent particle size determines the time required for transport within the pore to available adsorption sites (Snoeyink and Summers, 1999). The transport steps are (Snoeyink and Summers, 1999, Newcombe and Cook, 2004):

1) Bulk diffusion to the boundary layer surrounding the PAC particle;

2) Diffusion through the boundary layer (stationary layer of water) to the external carbon surface (external mass transfer or film diffusion);
3) Diffusion through the pore structure to the most favourable adsorption site (intraparticle diffusion);
4) Adsorption.

These steps are influenced by a range of factors. Step 1 is affected by the molecular dimensions and shape of the adsorbate, but proper mixing may minimise these effects. In step 2, diffusion depends on flow rate (the higher the flow, the shorter the distance), and on adsorbate dimensions and shape, although it is generally considered to be fast under proper mixing. Step 3 is affected by pore structure (both external and internal), and molecular dimensions and shape of the adsorbate. In practical situations, step 3 is most likely to be rate-limiting (Newcombe and Cook, 2004). Step 4 is very rapid for physical adsorption and, in that case, one of the preceding diffusion steps controls the adsorption rate. When chemical adsorption occurs, step 4 may be slower than the diffusion steps and may therefore control the rate of compound uptake (Snoeyink and Summers, 1999). Physisorption is a readily reversible reaction and includes both mono and multilayer coverage. Chemisorption may be reversible (high adsorption energies), involves only monolayer coverage and is a site specific reaction, occurring at specific functional group locations (Alley, 2006).

The mechanism and extension of adsorption have been shown to depend on: i) adsorbate structure (size, shape, charge, polarity, functional groups); ii) PAC characteristics (pore volume distribution, surface charge, and hydrophobicity); iii) solution conditions (pH, ionic strength, temperature, adsorbate concentration and presence of competing compounds (Newcombe *et al.*, 1997; Newcombe and Cook, 2004; Aksu and Kabasal, 2005). Both surface chemistry and pore volume distribution of PAC will play a role in the adsorption, however, its

relative importance will vary depending on the adsorbates and carbons. For NOM, at pH 7, there is strong evidence that electrostatic effects are determinant for adsorption (Newcombe *et al.*, 1997; Bjelopavlic *et al.*, 1999; Quinlivan, 2001; Newcombe and Cook, 2004). On the other hand, for microcystins, Pendleton *et al.* (2001) and Newcombe and Cook (2002) concluded about the major influence of the pore volume distribution (with a positive correlation with the volume of secondary micropores and mesopores) whereas Donati *et al.* (1994) and Pendleton *et al.* (2001) showed no significant effect of the carbon surface chemistry.

The relationship between the size of the adsorbate and the PAC pore size distribution is very important, since it determines the fraction of the total pore volume that can be accessed. Compounds are preferentially adsorbed in a pore of approximately its size, where there will be greater number of contact points and more favourable adsorption energy (Newcombe *et al.*, 1997, Pelekani and Snoeyink, 1999) and they are size excluded if pores are too small compared to their size and shape. A correct pore size distribution provides not only the adsorption sites, but also the appropriate channels to transport, as a high volume of large transport pores (macro and mesopores), favours rapid diffusion to adsorption sites (Newcombe *et al.*, 2002).

2.5.3 NOM Competition

PAC performance for microcontaminant removal is greatly affected by NOM competitive adsorption, with pore blockage and direct site competition being considered the most likely competing mechanisms. Direct competition is responsible for a reduction in the adsorption capacity for the target compound (Snoeyink and Summers, 1999) and occurs when the competing compounds are able to access the same sites (*i.e.*, when the target and the

competing compounds have similar size), or when the target compound adsorbs in a larger pore (with lower adsorption energy) and the larger competing compound (with higher adsorption energy) is able to displace it (Newcombe *et al.*, 2002). Sometimes, competing molecules may not adsorb on the same sites as the target compound, because pores are too small, but are capable of constricting or blocking pores and disturb the target compound transport to final adsorption sites, reducing its rate of adsorption (Snoeyink and Summers, 1999). Several authors concluded that a broadening of PAC pore size distribution could reduce, and even avoid, pore blockage by NOM (Donati *et al.*, 1994; Newcombe *et al.*, 1997; Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Li *et al.*, 2003 a, b; Quinlivan *et al.*, 2005).

Several studies showed that the low molecular weight NOM compounds exerted higher competitive effect on micropollutants, which was directly associated with a direct site competition mechanism. However, recent studies have showed that the smaller NOM compounds may also participate in pore constriction/blockage (Pelekani and Snoeyink, 1999, 2001; Ebie *et al.*, 2001; Newcombe *et al.*, 2002; Li *et al.*, 2003 a, b). As suggested by Kilduff *et al.* (1998), these two mechanisms become indistinguishable as the competing and target compounds become closer in size.

2.5.4 Adsorption Isotherms

An adsorption isotherm relates the equilibrium surface concentration (q_e, *i.e.*, the amount of adsorbate adsorbed per unit mass of adsorbent, expressed in μg/mg) with the equilibrium aqueous concentration (C_e, expressed in μg/L). Several models have been developed, including the well-known models proposed by Freundlich and Langmuir. The Freundlich isotherm is represented by (2.1):

$$q_e = KC_e^{\frac{1}{n}} \quad (2.1),$$

where K is a unit-capacity parameter (amount adsorbed at a value of C_e equal to unity) $(\mu g/mg)(L/\mu g)^{1/n}$ and n is a dimensionless parameter related to the site-energy distribution. This model applies if the data fit a straight line when plotted on a log-log basis (K is obtained from the y-axis intercept and 1/n from the slope). For favourably adsorbed chemicals, 1/n is between 0 and 1 (Alley, 2006), and the smaller the value of 1/n, the stronger the adsorption energy. Freundlich equation cannot be applied when saturation is achieved (q_e is constant and independent of C_e increase) (Snoeyink and Summers, 1999).

Langmuir equation handles the interaction between the adsorbent and the adsorbate as a linear, reversible, monolayer chemical reaction. The Langmuir equation is based on four assumptions: i) the surface of the adsorbent is uniform (all adsorption sites are equal); ii) adsorbed molecules do not interact; iii) all adsorption occurs through the same mechanism and iv) at the maximum adsorption, only a monolayer is formed, meaning that molecules of adsorbate do not deposit on other already adsorbed (Alley, 2006). The Langmuir equation is expressed by (2.2), and in its linear form by (2.3):

$$q_e = \frac{Q_{\max} b C_e}{1 + bC_e} \quad (2.2),$$

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \quad (2.3),$$

where Q_{max} (μg/mg) and b (L/μg) are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e *vs.* C_e is an obligatory condition for the application of Lagmuir model (Ong *et al.*, 2007).

2.5.5 Adsorption Kinetic Models

Kinetic models are used to investigate adsorption mechanisms and to identify the potential rate-controlling step(s). Some of the most commonly used models are the pseudo-first-order adsorption model, the pseudo-second order adsorption model and the intraparticle diffusion model.

The pseudo-first order adsorption model generally takes the form:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (2.4),$$

where q_e and q_t are the surface concentration (μg/mg) at equilibrium and at time t, respectively, and K_1 is the equilibrium rate constant (min^{-1}). A straight line of ln (q_e-q_t) *vs.* t (min) suggests the applicability of this kinetic model and the adsorption rate constant, K_1, is obtained from the slope of the linear plot. In order to use this model, the equilibrium sorption capacity must be known (q_e), by extrapolating the experimental data to t = ∝ or by using a trial-and error-method (Aksu and Kabasal, 2005).

The pseudo-second order adsorption model has the linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2.5),$$

where h is the initial adsorption rate (μg/(mg.min)) given by $K_2 q_e^2$ and K_2 (mg/(μg.min)) is the rate constant. If the pseudo-second order model is applicable, the plot of t/q_t against t should give a linear relationship from which the constants q_e, h and K_2 are determined. The pseudo-second-order equation is in agreement with chemisorption being the rate controlling step (Ho *et al.*, 2000; Badmus *et al.*, 2007).

The intraparticle diffusion equation, introduced by Weber and Morris, is given by (2.6):

$$q_t = K_i t^{0.5} + C \quad (2.6),$$

where K_i is the intraparticle diffusion rate constant (μg/(mg.min$^{0.5}$)) and C (μg/mg) is a constant proportional to the boundary layer thickness (Yalçin *et al.*, 2004). If intraparticle diffusion occurs, then the experimental q_t data against $t^{0.5}$ will be linear and K_i values may be obtained from the slopes of the straight-line portions and C from the y-axis intercept. Such plots may present a number of linear portions implying that two or more steps occur. The first, sharper portion is the external surface adsorption stage, the second is the intraparticle diffusion adsorption stage and the third portion is the final equilibrium stage (Yalçin *et al.*, 2004, Aksu and Kabasal, 2005). If the intra-particle diffusion is the rate limiting step of adsorption, the line will pass through the origin, otherwise, external mass transfer resistance may not be neglected (Abdelwahab, 2007). The kinetic data could be further analysed using the kinetics expressions derived by Boyd, Adamson and Myers (Reichenberg, 1953):

$$B_t = -2.30258 \log_{10}(1 - F) - 0.49770 \quad (2.7),$$

$$Bt = 6.28318 - 3.2899F - 6.28318(1 - 1.0470)^{1/2} \quad (2.8),$$

where B_t is a mathematical function of F ($F = q_t/q_e$) and is computed from (2.7) for F values above 0.85 and from (2.8) for F values between 0 and 0.85 (Reichenberg, 1953). The linearity of the plot of B_t values against time provides useful information to distinguish between external-transport (non linear) and intraparticle-transport-controlled rates of adsorption (linear and passing through origin) (Wang and Li, 2007).

2.6 ULTRAFILTRATION (UF)

2.6.1 General

Ultrafiltration is a low-pressure driven membrane process, usually applied for the removal of particulate and microbial contaminants. UF may be operated under positive (typically 0.2-2.8 bar) or negative pressure (between -0.2 to -0.8 bar) (USEPA, 2001). Most UF membranes used for water treatment have a molecular weight cut-off (MWCO) of 100 kDa (*i.e.*, they reject more than 90% of the compounds above 100 kDa) and nominal pore size of 0.01 μm (USEPA, 2005). UF membranes are either symmetric or asymmetric and are made from a wide variety of materials, including polyvinyl difluoride, polysulfone, polyethersulfone and cellulose acetate. Each material confers specific properties, including resistance to pH and oxidant, surface charge and hydrophobicity, which affect the exclusion characteristics (selectivity) of a membrane as well as the operating constraints, such as the potential use of pre-chlorination to control biological fouling (USEPA, 2001).

The most commonly available UF modules for water treatment are hollow-fibre (HF) modules, designed to facilitate backwash and yield a high surface area to volume ratio (Zhou and Smith, 2002; USEPA, 2005). Although specific dimensions vary by manufacturer, approximate ranges for internal fiber diameter is 0.3-1.0 mm and for fibre length is 1-2 meters (USEPA, 2005). HF membranes may be operated in either an inside-out or outside-in mode. Systems may operate in dead-end mode of operation and are periodically backwashed to remove the accumulated solids (USEPA, 2005) (Figure 2.2). Some systems use cross-flow (feed flow tangential to the membrane surface) (Figure 2.2), sometimes with the possibility to work on dead-end by simply closing the discharge valve (Pilutti and Nemeth, 2003). Cross-flow mode maintains a high scour velocity across the membrane surface, limiting the extent

of particle deposition and cake layer formation, but requires additional pumping for concentrate recirculation and may substantially increase the operating costs (USEPA, 2001, 2005). In this operation mode, the concentration of suspended material on the feed side of the membrane is higher than in the feed stream, given that the concentrate stream is recirculated and mixed with the incoming feed stream (USEPA, 2005).

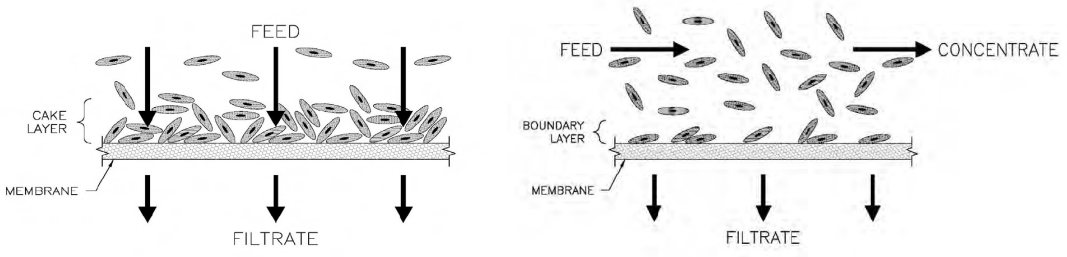

Figure 2.2 - Hydraulic mode of operation: dead-end (left) and cross-flow (right) (USEPA, 2005).

The operating flux (permeate flow per unit of membrane area; L/(h.m^2)) is one of the critical parameters of UF, affected by water quality and membrane fouling. Membrane systems running under critical flux result in maximum flux without significant fouling (Choi, 2003). Another important parameter is water recovery (the ratio of feed water that is converted to permeate), which is typically 85-97 % for UF systems. Typical UF systems incorporate a backwash cycle (Figure 2.3) with air, water (sometimes with chlorine) or a combination of both. Backwashing frequency depends on the feed water quality and usually increases with flux and recovery rates, due to higher operating pressure and higher solids concentration in the feed water. Typical backwash frequency for UF is 15-60 minutes, with backwash duration from 30 s to 3 minutes. Ideally the backwash restores the transmembrane pressure (TMP), but most systems experience a gradual increase of TMP that must be addressed by chemical cleaning (acid, caustic, chlorine and/or surfactants). Most systems are chemically cleaned every one to six months, depending on the system design and operation (USEPA, 2001).

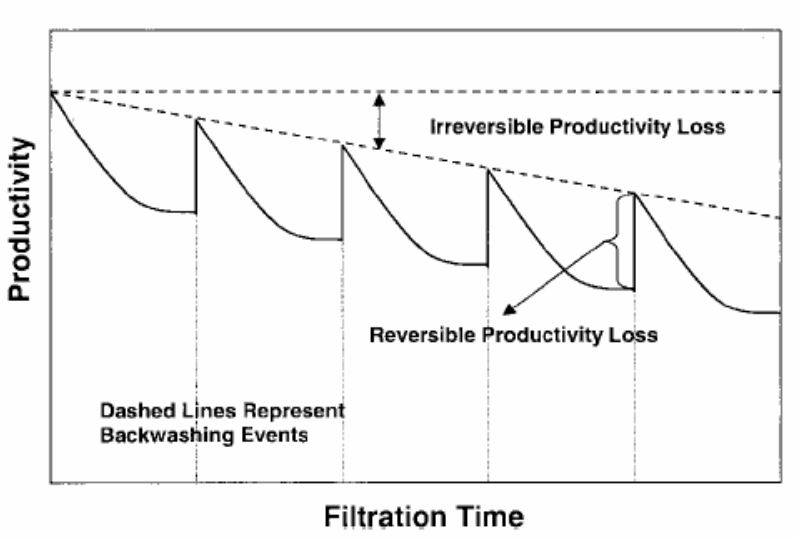

Figure 2.3 - Typical UF operation in most applications (Kim *et al.*, 2001).

Size exclusion by the membrane is the primary mechanism of UF separation. However, electrostatic repulsion and adsorption may significantly affect rejection, especially for compounds with dimensions similar to the size of UF membrane pores (Wiesner and Buckley, 1996; Scott, 1998). Low molecular-weight solutes, which may pass through UF pores, have been showed to cause drastic flux reductions due to adsorption (Jönsson *et al.*, 1997). In addition, these solutes may interact with larger molecules and be retained within the cake layer, especially when the layer is compressible (Choi, 2003).

2.6.2. Mass Transport and Fouling

Membrane separation involves various mass transport steps and many models have been developed to characterise it, not only through the membrane, but also in the membrane boundary layer. Mass transport may lead to the attachment, accumulation, or adsorption of materials onto membrane surfaces and (or) within membrane pores, causing membrane fouling.

Concentration polarization (CP) is a very important mass transport phenomenon on the membrane boundary layer. CP is the result of transport and rejection of solutes by membrane leading to an accumulation of these solutes on membrane wall and creating a solute concentration gradient for back-diffusion on the boundary layer. This concentration gradient is responsible for a maximum permeate flux (mass transport-limited flux), and depends on equilibrium between convective flux and diffusive flux (Wiesner and Aptel, 1996; Scott, 1998; Taylor and Wiesner, 1999). Concentration polarization effects have been shown to be small in comparison with pore blockage and surface deposition (Taylor and Wiesner, 1999). However, CP is often a precursor to cake or gel formation and the high concentrations near the membrane tend to exacerbate precipitative or adsorptive membrane fouling. CP is more pronounced at higher TMP, lower cross-flow velocity (CFV), and any other conditions which bring solute to the membrane surface very rapidly (*e.g.*, a very porous membrane). Increased back transport can be achieved by adoption of turbulence promoters/inserts/baffles to the membrane system, frequent backflushing of membrane, permeate backpressure, intermittent jets, pulsating flow, ultrasonic vibration, and establishing an electric field near the membrane (Choi, 2003).

Membrane fouling is characterised by a reduction in the permeate flux as a result of increased flow resistance due to concentration polarization, pore blocking (complete, standard or intermediate) and/or cake formation (compressible or incompressible) (Figure 2.4). Of particular importance is the size distribution of feed solution components relative to the membrane pore size (Zhou and Elimelech, 1997; Costa *et al.*, 2006). In the standard blocking (or pore constriction), the molecules are much smaller than the pores and fouling occurs because they deposit inside the pores, decreasing their size. In complete blocking (pore plugging), the molecules are of the same size as pores and block the entire pore entrance,

decreasing the total pore area. The intermediate blocking considers particles directly blocking the pores and also settling on other particles previously deposited, reducing the total pore area. In cake filtration, particles are much larger than pores and deposit on the membrane surface, forming a cake and adding a second resistance layer to the membrane surface (Neal, 2006). The cake can be classified as compressible or incompressible depending on the nature of the particles, such as shape, particle size distribution and rigidity. Fouling inside the membrane pores (adsorption) is often considered as an irreversible process. Concentration polarization and surface cake are considered reversible by decreasing the applied pressure or the permeate flux or by backwash, respectively (Zhou and Smith, 2002).

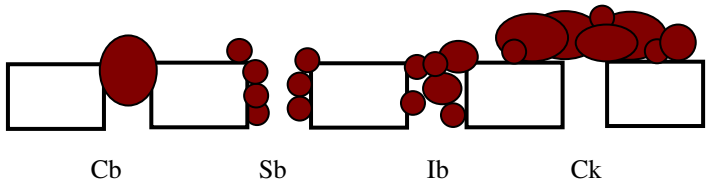

Figure 2.4 - Mechanisms of membrane fouling: Cb, complete blocking; Sb, standard blocking (pore constriction); Ib, intermediate blocking; Ck, cake formation.

Pore plugging is an important fouling mechanism for UF, in addition to particle cake formation on the membrane surface (Zhou and Elimelech, 1997). Several studies point out a transition of the fouling mechanism with the filtration time, specifically from pore blocking to cake formation above the blocked regions (Bowen *et al.*, 1995; Ho and Zydney, 2000; Costa *et al.*, 2006).

Membrane fouling depends on such parameters as membrane properties, characteristics of the feed water and hydrodynamic conditions (Anselme and Jacobs, 1996; Choi, 2003). Important membrane characteristics are pore size, charge, and roughness, with more permeable membranes showing faster flux decline (Cho and Amy, 1999; Yuan and Zydney, 2000; Costa

and Pinho, 2005; Costa *et al.*, 2006), probably associated with higher fluxes and higher convective transport (Costa *et al.*, 2006). Other important aspect is the feed water characteristics, *i.e.*, pH, ionic strength, calcium concentration, NOM content and character (Hong and Elimelech, 1997; Cho and Amy, 1999; Costa *et al.*, 2006). Several recent studies have shown that the hydrophilic neutral NOM is determinant for UF fouling (Her *et al.*, 2004; Lee *et al.*, 2004, 2006; Kwon *et al.*, 2005; Kimura *et al.*, 2006; Yamamura *et al.*, 2007). Hydrodynamic conditions are also determinant for membrane fouling, like CFV and TMP that governs the permeate flux and the convective transport of foulants towards the membrane (Hong and Elimelech, 1997). Costa *et al.* (2006) concluded that at high pressures the structure of the fouling layer is changed (the compactness and the specific resistance substantially increase), and significantly affect the extent of flux decline. CFV influences NOM fouling and its increment improves back-transport into the bulk solution, reducing the rate of cake deposition and the resultant cake thickness (Zularisam *et al.*, 2006).

2.7 PAC/UF

2.7.1 General

PAC/UF is an emergent hybrid membrane-adsorption system that incorporates the adsorption capabilities of activated carbon and the microorganism and particle removal ability of the UF membranes (Snoeyink *et al.*, 2000). In PAC/UF, PAC particles are applied to the influent of a UF membrane reactor and are retained by it, making possible the removal of the adsorbed dissolved organic compounds (Clark *et al.*, 1996). There are already several PAC/UF full-scale installations and the biggest ones are in Lausanne (Switzerland), Vigneux (France), Kopper (Slovenia) and San Antonio (Texas) (Amy, 2007), where the main applications are pesticides, taste and odours, and disinfection-by-products control (Clark *et al.*, 1996).

PAC/UF integrates the advantages of both UF and PAC adsorption and minimises some of their disadvantages. Some of the advantages of PAC/UF compared to higher-pressure membrane processes are (Clark *et al.*, 1996; Pilutti and Nemeth, 2003): a) the use of a low-pressure membrane, and therefore with lower operating cost, to remove dissolved organic compounds; b) the process flexibility since the PAC type and doses may be quickly changed according with the water quality; also, UF may work without PAC addition, at dead-end mode of operation, minimising the operating costs, and being changed to cross-flow only when necessary (semi dead-end operation); c) unlike the spiral-wound modules commonly used in nanofiltration and reverse osmosis, UF hollow fibre modules can be backflushed, minimising the frequency of chemical cleaning, and some of them have high tolerance to chlorine. Relatively to PAC conventional applications, the use of an UF membrane to retain PAC particles allows: a) higher disinfection capacity; b) the use of smaller PAC particles, with faster adsorption kinetics, but still with very efficient separation; c) the potential regeneration of PAC, given that it may be isolated from other reagents; d) the recirculation of PAC during the filtration cycles, which enhances the carbon residence time and adsorption efficiency while minimising the sludge production.

The effect of PAC on membrane fouling is controversial and requires further research. In recent studies, some authors referred a positive impact (Konieczny and Klomfas, 2002; Lee *et al.*, 2007), others a neutral effect (Mozia and Tomaszewaska, 2004; Matsui *et al.*, 2006) or a negative impact (Zhao *et al.*, 2005; Zularisam *et al.*, 2007). The effect of PAC seems to depend on the membrane hydrophobicity and the feed water characteristics, but studies on this subject are rather scarce and inconclusive.

To my knowledge, only one study has been published on microcystins removal by PAC/UF (Lee and Walker, 2006). These authors found high removal efficiencies (78-99%), although the type of module (flat-sheet) and the operating conditions were not the ones currently used in PAC/UF full-scale applications.

2.7.2 Operating Conditions

The adsorption performance of PAC/UF depends on the operating conditions, such as backwashing frequency, reactor size and configuration, filtration mode (dead-end *versus* cross flow) and PAC dosing procedure (Campos *et al.*, 2001). One important parameter is the PAC residence time on the membrane reactor, which is determined by PAC dosing and wasting procedures. PAC may be dosed at a constant rate (*i.e.*, step input) or at the beginning of the filtration cycle (*i.e.*, pulse input) and be wasted either continuously or at one time during backwash. One approach is to maintain constant the concentration of PAC in the membrane reactor, by continuously adding and wasting PAC, which will also maintain constant the adsorbate concentration in the permeate (Campos *et al.*, 2000 a). However, in PAC/UF full-scale applications, PAC is continuously dosed but is wasted only at the end of the filtration cycle (Campos *et al.*, 2000a), making the permeate adsorbate concentration not constant throughout the filtration cycle (Figure 2.5). When PAC is added at the beginning of the cycle and wasted during backwashing, the carbon retention time is the duration of the filtration cycle, which is typically between 30 and 90 minutes (Baudin *et al.*, 1997). In order to achieve longer contact times in the latter application, PAC may be dosed in a continuous-flow reactor (such as a stirred tank reactor (CSTR) or a plug flow reactor (PFR)) placed ahead of the membrane reactor (Figure 2.6).

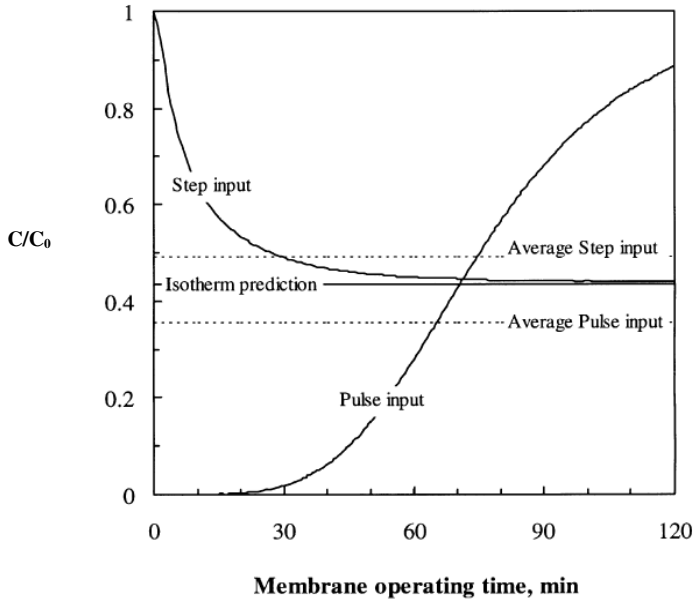

Fig. 2.5 - Adsorbate concentration profiles (C/C_0) in the permeate resulting from wasting PAC at the end of the filtration cycle and using two PAC dosing procedures (Snoeyink *et al.*, 2000).

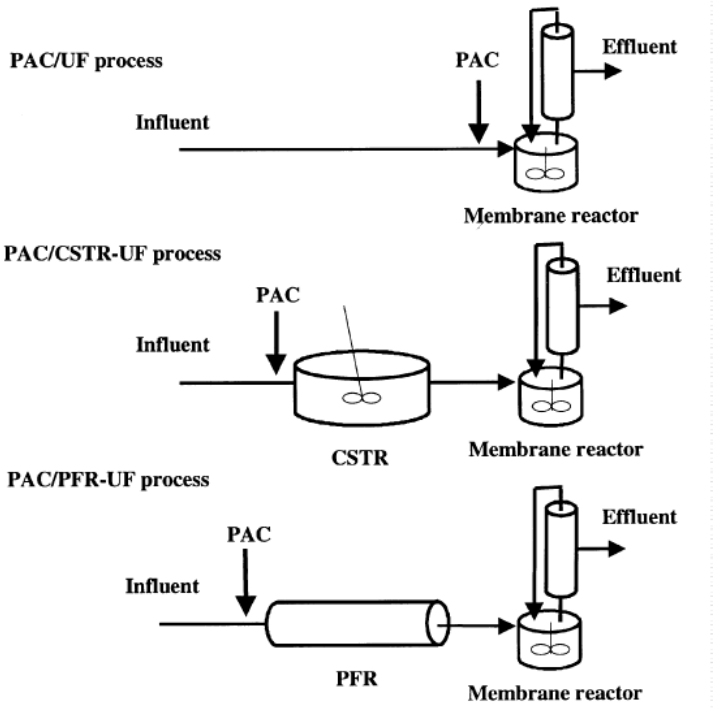

Figure 2.6 - Schematics of PAC/UF process configuration (Snoeyink *et al.*, 2000).

Another strategy to maximize the carbon surface loading is to recirculate the partially loaded PAC from the UF loop to an upflow floc blanket reactor (FBR), installed upstream of the PAC/CSTR-UF process and used for clarification (Baudin *et al.*, 1997; Campos *et al.*, 2000 a, b; Snoeyink *et al.*, 2000).

2.7.3 Waste Disposal

Membranes generate a concentrated waste that must be disposed according to applicable laws.

UF waste consists of backwash waters in the case of dead-end operation and of backwash waters and concentrate stream in cross-flow operation. In the hybrid process, the quantity and composition of PAC/UF waste depends on the rejection and water recovery, but it usually corresponds to a volume of 5-15% of the feed stream and consists of PAC (with adsorbed compounds) and other particulate matter and macromolecules retained (Clark *et al.*, 1996).

The waste requires a treatment due to the fairly high solids concentration (> 200 ppm) (Clark *et al.*, 1996) which sometimes contains high toxic compounds (as cyanotoxins and pesticides). The best option is the regeneration and recovery of PAC, but its application needs further research. Anselme and Jacobs (1996) have cited some works where good results where obtained with PAC regeneration (mass loss of 18-22% and more than 90% of adsorption capacity recovered). Shende and Mahajani (2002) recovered more than 98% of the adsorption capacity of PAC and GAC loaded with reactive dyes by wet oxidative regeneration (which requires no complicated dewatering and drying as all material remains in a slurry).

When PAC/UF is used after C/F/S, the PAC can be returned to the settler and processed with the normal sludge (Clark *et al.*, 1996). The treatment usually involves dewatering

(clarification and/or thickening, followed by conditioning and dewatering by centrifuges or press-filters) and after the waste goes to a wastewater treatment plant, is incinerated (Anselme and Jacobs, 1996) or deposited in a landfill.

2.8 REFERENCES

Abdelwahab O. (2007). Kinetic and isotherm studies of copper (II) removal from wastewater using various adsorbents. *Egyptian Journal of Aquatic Research*, 33(1), 125-143.

Acero J., Rodriguez E., Meriluoto J. (2005). Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins. *Water Research*, 39, 1628-1638.

Aksu Z., Kabasakal E. (2005). Adsorption characteristics of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution on powdered activated carbon. *Journal of Environmental Science and Health Part B*, 40, 545-570.

Alley R. (2006). Physical Treatment. *In Water Quality Control Handbook*. Second Edition, McGraw-Hill, Lisbon.

Amy G. (2007). Hybrid low pressure membranes. *In Membrane Technology in Drinking & Industrial Water Treatment*. Intensive short course, 1-5 October, UNESCO-IHE, Delft.

Anselme C., Jacobs E. (1996). Ultrafiltration. *In Water Treatment-Membrane Processes*, AWWARF, Lyonnaise des Eaux and WRCSA (Ed.), McGraw-Hill, Lisbon.

Badmus M., Audu T., Anyata B. (2007). Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells (*Typanotonus fuscatus*). *Turkish Journal Engineering Environmental Science*, 31, 251-263.

Baudin I., Chevalier M., Anselme C., Cornu S., Lainé J. (1997). L'Apié and Vigneux case studies: first months of operation. *Desalination*, 113, 273–275.

Bjelopavlic M., Newcombe G., Hayes R. (1999). Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume distribution. *Journal of Colloid and Interface Science*, 210(2), 271-280.

Bowen W., Calvo J., Hernandez A. (1995). Steps of membrane blocking in flux decline during protein microfiltration. *Journal of Membrane Science*, 101, 153–165.

Burch M. (2007). Effective doses, guidelines & regulations. *In Proceedings of the Interagency, International Symposium on Cyanobacterial Harmful Algal Blooms*. H. Kenneth Hudnell (Ed.). North Carolina, Sept. 2005.

Campos C., Mariñas B., Snoeyink V., Baudin I., Laîné J. (2000 a). PAC-Membrane filtration process. II. Model application. *Journal of Environmental Engineering*, 126(2), 104-111.

Campos C., Snoeyink V., Mariñas B., Baudin I., Laîné J. (2000 b). Atrazine removal by powdered activated carbon in floc blanket reactors. *Water Research*, 34(16), 4070-4080.

Campos C., Baudin I., Laîné J. (2001). Adsorption performance of powdered activated carbon-ultrafiltration systems. *Water Science and Technology: Water Supply*, 1 (5/6), 13-19.

Carmichael W. (1994). Toxins of cyanobacteria. *Scientific American*, 270(1), 78-86.

Carmichael W. (1997). The cyanotoxins. *Advances in Botanical Research*, 27, 211-256.

Carmichael W. (2001). Health effects of toxin-producing cyanobacteria. *Human and Ecological Risk Assessment*, 7, 1393-1407.

Cho J., Amy G. (1999). Interactions between natural organic matter and membranes: rejection and fouling. *Water Science and Technology*, 40(9) 131-139.

Choi Y. (2003). Critical Flux, Resistance and Removal of Contaminants in Ultrafiltration (UF) of Natural Organic Materials. PhD thesis. Pennsylvania State University, USA.

Chorus I. (2005). Current Approaches to Cyanotoxin Risk Assessment, Risk Management and Regulations in Different Countries. Ingrid Chorus (Ed.), Federal Environmental Agency.

Chow C., Panglisch S., House J., Drikas M., Burch M., Gimbel R. (1997). A study of membrane filtration for the removal of cyanobacterial cells. *Journal of Water Supply Research and Technology – Aqua*, 46(6), 324-334.

Chow C., House J., Velzeboer R., Drikas M., Burch M., Steffensen D. (1998). The effect of ferric chloride flocculation on cyanobacterial cells. *Water Research*, 32(3), 808-814.

Chow C., Drikas M., House J., Burch M., Velzeboer, R. (1999). The impact of conventional water treatment processes on cells of the cyanobacterium *Microcystis aeruginosa. Water Research,* 33(15), 3253-3262.

Clark M., Baudin I., Anselme C. (1996). Membrane-powdered activated carbon reactors. *In Water Treatment-Membrane Processes*. AWWARF, Lyonnaise des Eaux and WRCSA (Ed.), McGraw-Hill, Lisbon.

Codd, G. (2000). Cyanobacterial toxins, the perception of water quality, and the prioritisation of eutrophication control. *Ecological Engineering*, 16(1), 51–60.

Cook D., Newcombe G. (2002). Removal of microcystin variants with powdered activated carbon. *Water Science and Technology: Water Supply*, 2(5/6), 201-207.

Costa A., Pinho M.N. (2005). Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions. *Journal of Membrane Science*, 255(1–2), 49–56.

Costa A.R., Pinho M. N., Elimelech M. (2006). Mechanisms of colloidal natural organic matter fouling in ultrafiltration. *Journal of Membrane Science*, 281, 716-725.

Daly R., Ho L., Brookes J. (2007). Effect of chlorination on *Microcystis aeruginosa* cell integrity and subsequent microcystin release and degradation. *Environmental Science and Technology*, 41, 4447-4453.

De Maagd P., Hendriks A., Seinen W., Sijm D. (1999). pH-Dependent hydrophobicity of the cyanobacteria toxin microcystin-LR. *Water Research*, 33(3), 677-680.

Donati C., Drikas M., Hayes R., Newcombe G. (1994). Microcystin-LR adsorption by powdered activated carbon. *Water Research*, 28(8), 1735-1742.

Drikas M., Chow C., House J., Burch M. (2001a). Using coagulation, flocculation and settling to remove toxic cyanobacteria. *Journal of the American Water Works Association*, 93(2), 100-111.

Drikas M., Newcombe G., Nicholson B. (2001b). Water treatment options for cyanobacteria and their toxins. *Proceedings of the Water Quality Technology Conference*, American Water Works Association, Nashville (Denver, Colorado), 11–15 November.

Ebie K., Li F., Azuma Y., Yuasa A., Hagishita T. (2001). Pore distribution effect of activated carbon in adsorbing organic micropollutants from natural water. *Water Research*, 35(1), 167-179.

Falconer I., Runnegar M., Buckleley T., Huyin V., Bradshaw P. (1989). Using activated carbon to remove toxicity from drinking water containing cyanobacterial blooms. *Journal of American Water Works Association*, 2, 102-105.

Falconer I. (1999). An overview of problems caused by toxic blue-green algae (cyanobacteria) in drinking water. *Environmental Toxicology*, 14, 5-12.

FPTCDW (2002). Cyanobacterial Toxins − Microcystin-LR. *In Guidelines for Canadian Drinking Water Quality-Supporting Documentation*. Federal-Provincial-Territorial Committee on Drinking Water, Canada.

Gijsbertsen-Abrahamse A., Schmidt W., Chorus I, Heijman S. (2006). Removal of cyanotoxins by ultrafiltration and nanofiltration. *Journal of Membrane Science*, 276(1-2), 252-259.

Hart J., Stott P. (1993). Microcystin-LR removal from water. Foundation for Water Research, Report FR 0367, Marlow, UK.

Hart J., Fawell J., Croll B. (1998). The fate of both intra- and extracellular toxins during drinking water treatment. *Water Supply,* 16(1/2), 611-616.

Her N., Amy G., Park H., Song M. (2004). Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling. *Water Research*, 38, 1427-1438.

Hitzfeld B., Hoeger S., Dietrich D. (2000). Cyanobacterial toxins: removal during drinking water treatment, and human risk assessment. *Environmental Health Perspectives*, 108(1), 113–122.

Ho Y., McKay G., Wase D., Foster C. (2000). Study of the sorption of divalent metal ions on to peat. *Adsorption Science and Technology*, 18, 639-650.

Ho C., Zydney A. (2000). A combined pore blockage and cake filtration model for protein fouling during microfiltration. *Journal of Colloid and Interface Science*, 232(2), 389-399.

Ho L. (2004). The Removal of Cyanobacterial Metabolites from Drinking Water using Ozone and Granular Activated Carbon. PhD thesis, University of South Australia, Australia.

Ho L., Onstad G, Von Gunten U., Rinck-Pfeiffer S., Craig K., Newcombe G. (2006 a). Differences in the chlorine reactivity of four microcystin analogues. *Water Research*, 40(6), 1200-1209.

Ho L., Meyn T., Keegan A., Hoefel D., Brookes J., Saint C., Newcombe G. (2006 b). Bacterial degradation of microcystin toxins within a biologically active sand filter. *Water Research*, 40(4), 768-774.

Höeger S., Dietrich D., Hitzfeld B. (2002). Effect of ozonation on the removal of cyanobacterial toxins during drinking water treatment. *Environmental Health Perspectives*, 110(11), 1127-1132.

Höeger S. (2003). Problems During Drinking Water Treatment of Cyanobacterial-loaded Surface Waters: Consequences for Human Health. PhD thesis, Universität Konstanz , Germany

Hong S., Elimelech M. (1997). Chemical and physical aspects of NOM fouling of nanofiltration membranes. *Journal of Membrane Science*, 132, 159–181.

Hrudey S., Burch M., Drikas M., Gregory R. (1999). Remedial measures. *In Toxic Cyanobacteria in Water. A Guide to Their Public Health Consequences, Monitoring and Management.* 1st edition. I. Chorus and J. Bartram (Eds.), WHO, E& SPON, London.

Jones G., Orr P. (1994). Release and degradation of microcystin following algicide treatment of a *Microcystis aeruginosa* bloom in a recreational lake, as determined by HPLC and protein phosphatase inhibition assay. *Water Research*, 28(4), 871-876.

Jönsson A., Lindau J., Wimmerstedt R., Brinck J., Jönsson B. (1997). Influence of the concentration of a low-molecular weight organic solute on the flux reduction of a polyethersulphone ultrafiltration membrane. *Journal of Membrane Science*, 135, 117-128.

Kaebernick M., Neilan B. (2001). Ecological and molecular investigations of cyanotoxin production. *FEMS Microbiology Ecology*, 35, 1-9.

Kenefick S., Hrudey S., Peterson H., Prepas E. (1993). Toxin release from *Microcystis aeruginosa* after chemical treatment. *Water Science and Technology*, 27(3-4), 433-440.

Keijola A., Himberg K., Esala A., Sivonen K., Hiisvirta L. (1988). Removal of cyanobacterial toxins in water treatment processes: laboratory and pilot-scale experiments. *Toxicity Assessment: An International Journal*, 3, 643-656.

Kilduff J., Karanfil T., Weber Jr. W. (1998). Competitive effects of displaceable organic compounds on trichloroethylene uptake by activated carbon. II. Model verification and applicability to natural organic matter. *Journal of Colloid and Interface Science*, 205, 280-289.

Kim D., Hong S., Cho J. (2001). Effect of cake layer structure on the backwash efficiency of hollow fiber MF membranes. *Journal of Environmental Science and Engineering*, 3, 50-58.

Kimura K., Yamamura H., Watanabe Y. (2006). Irreversible fouling in MF/UF membranes caused by natural organic matters (NOMs) isolated from different origins. *Separation Science and Technology*, 41, 1331-1344.

Konieczny K., Klomfas G. (2002). Using activated carbon to improve natural water treatment by porous membranes. *Desalination*, 147, 109-116.

Kwon B., Lee S., Cho J., Ahn H., Lee D., Shin H. (2005). Biodegrability, DBP formation and membrane fouling potential of natural organic matter: characterization and controllability. *Environmental Science and Technology*, 39, 732-739.

Lahti K., Rapala J., Fardig M., Niemel M., Sivonen K. (1997). Persistence of cyanobacterial hepatotoxin, microcystin-LR in particulate material and dissolved in lake water. *Water Research*, 31(5), 1005-1012.

Lam A., Prepas E., Spink D., Hrudey S. (1995). Chemical control of hepatotoxic phytoplankton blooms: implications for human health. *Water Research*, 29(8), 1845-1854.

Lambert T., Holmes C., Hrudey S. (1996). Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment. *Water Research*, 30(6), 1411-1422.

Lee N., Amy G., Croué J.-P., Buisson H. (2004). Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research*, 38, 4511-4523.

Lee N., Amy G., Croué J.-P. (2006). Low-pressure membrane (MF/UF) fouling associated with allochthonous versus autochonus natural organic matter. *Water Research*, 40, 2357-2368.

Lee J., Walker H. (2006). Effect of processes variables and natural organic matter on removal of microcystin-LR by PAC-UF. *Environmental Science and Technology*, 40, 7336-7342.

Lee C., Bae S., Han S., Kang L. (2007). Application of ultrafiltration hybrid membrane processes for reuse of secondary effluent. *Desalination*, 202, 239-246.

Li Q., Snoeyink V., Mariñas B., Campos C. (2003 a). Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Research*, 37, 4863-4872.

Li Q., Snoeyink V., Mariñas B., Campos C. (2003 b). Elucidating competitive adsorption mechanism of atrazine and NOM using model compounds. *Water Research*, 37(20), 773-784.

Matsui Y., Sanogawa T., Aoki N., Mima S., Matsushita T. (2006). Evaluating submicron-sized activated carbon adsorption for microfiltration pretreatment. *Water Science and Technology*, 6(1), 149-155.

Meriluoto J., Spoof L. (2007). Cyanotoxins: sampling, sample processing and toxin uptake. *In Proceedings of the Interagency International Symposium on Cyanobacterial Harmful Algal Blooms*. Chapter 21. H. Kenneth Hudnell (Ed.). RTP North Carolina, Sept. 2005.

Mesquita E., Menaia J., Rosa M.J., Costa V. (2006). Microcystin-LR removal by bench scale biologically activated carbon filters. *In Recent Progress in Slow Sand Alternative Biofiltration Processes*. R. Gimbel, N. Graham and R. Collins (Ed.). IWA, London.

Metcalf J., Codd G. (2004). Cyanobacterial toxins in the water environment-a review of current knowledge. Foundation for Water Research, FR/R0009, United Kingdom.

MHNZ (2005). Guidelines for Drinking Water Quality Management for New Zealand. Vol. III-Datasheets, second edition, Ministry of Health of New Zealand.

Mouchet P., Bonnélye V. (1998). Solving algae problems: French expertise and world-wide application. *Journal of Water Science Research and Technology - Aqua*, 47(3), 125-141.

Mozia S., Tomaszewaska M. (2004). Treatment of surface water using hybrid processes-adsorption on PAC and ultrafiltration. *Desalination*, 162, 23-31.

Muntisov M., Trimboli P. (1996). Removal of algal toxins using membrane technology. *Water – Journal of the Australian Water Association*, 23(3), 34.

Mur L., Skulberg O., Utkilen H. (1999). Cyanobacteria in the environment. *In Toxic Cyanobacteria in Water: A guide to Their Public Health Consequences, Monitoring and Management*. 1st edition. I. Chorus and J. Bartram (Eds.), WHO, E& SPON, London.

Neal P. (2006). An Examination of the Nature of Critical Flux and Membrane Fouling by Direct Observation. PhD thesis, University of New South Wales, Australia.

Newcombe G., Drikas M., Hayes R. (1997). Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Research*, 31(5), 1065-1073.

Newcombe G. (2002). Removal of algal toxins from drinking water using ozone and GAC. AWWA Research Foundation Report, American Water Works Association, Denver.

Newcombe G., Morrison J., Hepplewhite C., Knappe D. (2002). Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitive effects. *Carbon*, 40, 2147-2156.

Newcombe G., Cook D., Brooke S., Ho L., Slyman N. (2003). Treatment options for microcystins toxins: similarities and differences between variants. *Environmental Technology*, 24(3), 299-308.

Newcombe G., Cook D. (2004). Removal of natural microcontaminants from drinking water using activated carbon. *In Encyclopedia of Surface and Colloid Science*. 1st Edition, P. Somasundaran (Ed.), Taylor & Francis, London.

Newcombe G., Nicholson B. (2004). Water treatment option for dissolved cyanotoxins. *Journal of Water Supply: Research and Technology - AQUA*, 53 (4), 227-239.

Nicholson B., Rositano J., Burch M. (1994). Destruction of cyanobacterial peptide hepatotoxins by chlorine and chloramine. *Water Research*, 28(6), 1297-1303.

Ong S.-A., Seng C.-E., Lim P.-E. (2007). Kinetics of adsorption of Cu (II) and Cd (II) from aqueous solution on rice husk and modified rice husk. *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 6(2), 1764-1774.

Paralkar A., Edzwald J. (1996). Effect of ozone on EOM and coagulation. *Journal of American Water Works Association*, 4, 143-154.

Pelekani C., Snoeyink V. (1999). Competitive adsorption in natural water: role of activated carbon pore size. *Water Research*, 33(5), 1209-1219.

Pelekani C., Snoeyink V. (2001). A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: the importance of pore size distribution. *Carbon*, 39, 25-37.

Pendleton P., Schumann R., Wong S. (2001). Microcystin-LR adsorption by activated carbon. *Journal of Colloid and Interface Science*, 240(1), 1-8.

Pietsch J., Bornmann K., Schmidt W. (2002). Relevance of intra and extracellular cyanotoxins for drinking water treatment. *Acta hydrochimica et hydrobiologica*, 30(1), 7-15.

Pilutti M., Nemeth J. (2003). Technical and cost review of commercially available MF/UF membrane products. International Desalination Association, BAH03-029.

Quesada A., Carrasco D., Cirés S. (2006). Cianobacterias y cianotoxinas en aguas de consumo y de recreo: un problema para todos. *In Jornada sobre las Cianobacterias Tóxicas. Problemas Asociados. Seguimiento y Control*. CEDEX, Madrid.

Quinlivan P. (2001). Effects of Activated Carbon Surface Chemistry and Pore Structure on the Adsorption of Methyl Tertiary-butyl Ether and Trichloroethene from Natural Water. Master of Science Thesis, North Carolina State University, USA.

Quinlivan P., Li L., Knappe D. (2005). Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter. *Water Research*, 39, 1663-1673.

Reichenberg D. (1953). Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange. *Journal of American Chemical Society*, 75, 589-597.

Ribau Teixeira M., Rosa M.J. (2005 a). Microcystins removal by nanofiltration membranes. *Separation and Purification Technology*, 46, 192-201.

Ribau Teixeira M., Rosa M.J. (2005 b). The role of membrane charge on nanofiltration performance. *Journal of Membrane Science*, 265, 160-166.

Ribau Teixeira M., Rosa M.J. (2006 a). Comparing dissolved air flotation and conventional sedimentation to remove cyanobacterial cells of *Microcystis aeruginosa*. Part I: The key operating conditions. *Separation Purification Technology*, 52, 84-94.

Ribau Teixeira M., Rosa M.J. (2006 b). Integration of dissolved gas flotation and nanofiltration for *M. aeruginosa* and associated microcystins removal. *Water Research*, 40, 3612-3620.

Ribau Teixeira M., Rosa M.J. (2006 c). Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration. *Water Research*, 40, 2837-2846.

Ribau Teixeira M., Rosa M.J. (2006 d). The impact of the water background inorganic matrix on the natural organic matter removal by nanofiltration. *Journal of Membrane Science*, 279, 513-520.

Ribau Teixeira M., Rosa M.J. (2007). Comparing dissolved air flotation and conventional sedimentation to remove cyanobacterial cells of *Microcystis aeruginosa*. Part II: The effect of water background organics. *Separation Purification Technology*, 53, 126-134.

Rodríguez E., Onstad G., Kull T., Metcalf J., Acero J., Gunten U. (2007 a). Oxidative elimination of cyanotoxins: comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Research*, 41, 3381-3393.

Rodríguez E., Sordo A., Metcalf J., Acero J. (2007 b). Kinetics of oxidation of cylindrospermopsin and anatoxin-a with chlorine, monochlorine and permanganate. *Water Research*, 41, 2048-2056.

Rositano J., Nicholson B., Pieronne P. (1998). Destruction of cyanobacterial toxins by ozone. *Ozone: Science & Engineering*, 20, 223-238.

Rositano J., Newcombe G., Nicholson B., Sztajnbok P. (2001). Ozonation of NOM and algal toxins in four treated waters. *Water Research*, 35(1), 23-32.

Schmidt W., Willmitzer H., Bornmann K., Pietsch J. (2002). Production of drinking water from raw water containing cyanobacteria – pilot plant studies for assessing the risk of microcystin breakthrough. *Environmental Toxicology*, 17(4), 375-385.

Scott K. (1998). Handbook of Industrial Membranes. Second edition, Elsevier Advanced Technology, Oxford, United Kingdom.

Senogles P., Shaw G., Norris R., Chiswell R., Mueller J., Sadler R., Eaglesham G. (2000). Degradation of the cyanobacterial toxin cylindrospermopsin from *Cylindrospermopsis raciborskii* by chlorination. *Toxicon*, 38, 1203-1213.

Shende R., Mahajani V. (2002). Wet oxidative regeneration of activated carbon loaded with reactive dye. *Waste Management*, 22(1), 73-83.

Sivonen K., Jones G. (1999). Cyanobacterial toxins. *In Toxic Cyanobacteria in Water: A Guide to Their Public Health Consequences, Monitoring and Management*. 1st edition. I. Chorus and J. Bartram (Eds.), WHO, E & SPON, London.

Smith D., Falls V., Levine A., MacLeod B., Simpson M., Champlin T. (2002). Nanofiltration to augment conventional treatment for removal of algal toxins, taste and odour compounds, and natural organic matter. *In Proceedings of the Water Quality Technology Conference*, Seattle, Washington (USA), November 10-14.

Snoeyink V., Summers S. (1999). Adsorption of organic compounds. *In Water Quality & Treatment*. 5th Edition, AWWA, McGraw-Hill, Lisbon.

Snoeyink V., Campos C., Mariñas B. (2000). Design and performance of powdered activated carbon/ultrafiltration systems. *Water Science and Technology*, 42(12), 1-10.

Svreck C., Smith D. (2004). Cyanobacteria toxins and the current state of knowledge on water treatment options: a review. *Journal of Environmental Engineering Science*, 3, 155-185.

Taylor J., Wiesner M. (1999). Membranes. *In Water Quality & Treatment*. 5th Edition, American Water Works Association (AWWA), McGraw-Hill, Lisbon.

Tsuji K., Watanuki T., Kondo F., Watanabe M., Nakazawa H., Suzuki M., Uchida H., Harada K.-I. (1997). Stability of microcystins from cyanobacteria – IV. Effect of chlorination on decomposition. *Toxicon*, 35(7), 1033-1041.

USEPA (2001). Low-pressure Membrane Filtration for Pathogen Removal: Application, Implementation and Regulatory Issues. United States Environmental Protection Agency, Office of Water, EPA 815-C-01-001, April.

USEPA (2005). Membrane Filtration Guidance Manual. United States Environmental Protection Agency, Office of Water, EPA 815-R-06-009, November.

Van Apeldoorn M., Van Egmond H., Speijers G., Bakker G. (2007). Toxins of cyanobacteria – Review. *Molecular Nutrition& Food Research*, 51, 7-60.

Velzeboer R., Drikas M., Donati C., Burch M., Steffensen D. (1995). Release of geosmin by *Anabaena circinalis* following treatment with aluminium sulphate. *Water Science and Technology*, 31(11), 187-194.

Wang H., Newcombe G., Lewis D., Brookes J., Ho L. (2006). Adsorption and biological removal of microcystins in GAC filter. *Proceedings of Young Water Professionals*. IWA and Australia Water Association, New South Wales (Australia), 15-17 February.

Wang H., Ho L., Lewis D., Brookes J., Newcombe G. (2007). Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. *Water Research*, 41(18), 4262-4270.

Wang S., Li H. (2007). Kinetic modelling and mechanism of dye adsorption on unburbed carbon. *Dye and Pigments*, 72, 308-314.

WHO (2003). Guidelines for Safe Recreational Water Environments. Vol. 1 – Costal Water Environments. World Health Organization, Geneva.

WHO (2006). Guidelines for Drinking Water Quality. First addendum to third edition. Vol. 1 – Recommendations. World Health Organization, Geneva.

Wiesner M., Aptel P. (1996). Mass transport and permeate flux and fouling in pressure-driven processes. In Water Treatment Membrane Processes. J. Mallevialle, P. Odendaal, M. Wiesner (Ed.), McGraw-Hill, Lisbon.

Wiesner M., Buckley C. (1996). Principles of rejection in pressure-driven membrane processes *In Water Treatment Membrane Processes*. J. Mallevialle, P. Odendaal, M. Wiesner (Ed.), McGraw-Hill, Lisbon.

Yalçin M., G]urse A., Dogar C., Sözbilir M. (2004). The adsorption kinetics of *Cethyltrimethylammonium Bromide* (CTAB) onto powdered active carbon. Adsorption, 10, 339-348.

Yamamura H., Kimura K., Watanabe Y. (2007). Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment. *Environmental Science and Technology*, 41, 6789-9794.

Yuan W., Zydney A. (2000). Humic acid fouling during ultrafiltration. *Environmental Science Engineering*, 34, 5043–5050.

Zhao P., Takizawa S., Katayama H., Ohgaki S. (2005). Factors causing PAC cake fouling in PAC-MF (powdered activated carbon-microfiltration) water treatment systems. *Water Science and Technology*, 51(6-7), 231-240.

Zhou X., Elimelech M. (1997). Colloidal fouling of reverse osmosis membranes: measurements and fouling. *Environmental Science and Technology*, 31, 3654-3662.

Zhou H., Smith D. (2002). Advanced technologies in water and wastewater treatment. *Journal of Environmental Engineering and Science*, 1(4), 247-264.

Zularisam A., Ismail A., Salim R. (2006). Behaviours of natural organic matter in membrane filtration for surface water treatment - a review. *Desalination*, 194, 211-231.

Zularisam A., Ismail A., Salim M., Sakinah M., Ozaki H. (2007). The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes. *Desalination*, 212, 191-208.

Zurawell R., Chen H., Burke J., Prepas E. (2005). Hepatotoxic cyanobacteria: A review of the biological importance of microcystins in freshwater environments. *Journal of Toxicological and Environmental Health B*, 8, 1–37.