CHAPTER 8

MICROCYSTINS REMOVAL BY PAC/UF SYSTEM

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ABSTRACT

Microcystins removal by PAC/UF was investigated, focusing on PAC dose and addition mode, microcystins concentration and the impact of background NOM, assessed through model compounds (humic acid (AHA) and tannic acid (TA)) and *Microcystis aeruginosa* culture. Constant flow experiments were performed with a hydrophilic UF hollow-fibre membrane and a mesoporous fine-powdered activated carbon. In the absence of background NOM, PAC/UF achieved 93-98% microcystins removal and a cycle-averaged permeate concentration below the WHO drinking water guideline-value for 10 mg/L PAC and up to 20 µg/L MC-LR_{eq} feed concentration. Single-pulse PAC dosing in the beginning of the UF-cycle allowed slightly lower microcystins concentration in the permeate compared to the multi-pulse PAC addition, while no differences were found in terms of transmembrane pressure. Hydraulic retention time of 34 and 55 minutes resulted in similar permeate quality. PAC dose required was mostly affected by NOM type and concentration, and by microcystins concentration. A PAC dose of 10 mg/L effectively controlled *ca.* 5 µgMC-LR_{eq}/L in a model water with 2.5 mg(AHA+TA)/L or with *M. aeruginosa* culture *(*cells and algogenic organic matter), whereas 15 mg PAC/L were unable to achieve the WHO quality with a water containing higher concentrations of NOM (5 mg/L) and microcystins (*ca.* 20 µgMC-LR_{eq}/L).

8.1 INTRODUCTION

Cyanotoxins are detrimental to drinking water due to their human and animal health hazard effects. They are produced as secondary metabolites of cyanobacteria, and among them, the hepatototoxic and tumour-promoters microcystins are the most commonly occurring cyanotoxins in surface water reservoir used for water supply. The World Health Organisation (WHO) adopted a provisional drinking water guideline value of 1.0 µg/L for microcystin-LR, one of the most frequent and toxic microcystin variant.

Dissolved microcystins are not effectively removed by water conventional clarification through coagulation/flocculation, sedimentation and filtration (Keijola *et al.*, 1988; Himberg *et al.*, 1989; Lawton and Robertson, 1999). Probably due to their cyclic nature, microcystins are extremely stable across a wide range of pH and temperature, although they have been shown to degrade with strong oxidants, like ozone or high doses of chlorine (Nicholson *et al.*, 1994; Tsuji *et al.*, 1997; Rositano *et al.*, 2001; Acero *et al.*, 2005, Ho *et al.*, 2006; Rodríguez *et al.*, 2007). However, at the usual doses for drinking water treatment, these oxidants do not completely oxidise the compounds, and may therefore originate potentially toxic by-products, whereas at high doses, restrictions may arise due to the formation of trihalomethanes or bromate (when ozone is applied to bromide-rich waters). In addition, the rate of intracellular cyanotoxins release to water by the oxidant-damaged cells may exceed its degradation, yielding a net increase in the dissolved toxin. The overall efficiency of the toxins oxidation depends on the oxidant dose, pH, alkalinity and natural organic matter (NOM) (Rositano *et al.*, 1998; Hoeger *et al.*, 2002; Pietsch *et al.*, 2002; Newcombe and Nicholson, 2004; Daly *et al.*, 2007).

Promising technologies for dissolved microcystins control are membrane pressure-driven processes, *e.g.* nanofiltration (NF) or the hybrid process of adsorption on powdered activated carbon/ultrafiltration (PAC/UF), since they act as physical barriers and do not form by-products. NF experiments have demonstrated high efficiency for cyanotoxins removal, with rejections above 97-99% for microcystins and higher than 94-96% for anatoxin-a, regardless of the variations in the feed water quality (Ribau Teixeira and Rosa, 2005, 2006; Gijsbertsen-Abrahamse *et al.*, 2006). However, permeate fluxes were significantly impacted by background organics (NOM and microcystins) and, especially, inorganics (pH and calcium) (Ribau Teixeira and Rosa, 2005, 2006).

PAC/UF joins the adsorption capacity of PAC with the UF membrane ability to retain microorganisms and particles (including PAC particles), therefore allowing the removal of low molar mass compounds which could not be removed by the UF membrane itself (large pore size). PAC/UF is a low-pressure (< 1 bar) process, and as so has a relatively low operating cost. It has a high disinfection capacity (for bacteria and also *Crypstosporidium* oocysts, *Giardia* cysts and viruses) and allows a simple and effective membrane cleaning by backwashing. Furthermore, in a previous work (chapter 7), PAC was found to have no effect on the membrane reversible fouling, and to improve the irreversible fouling, minimising the chemical cleaning, besides enhancing the NOM retention by UF (with subsequent advantages for the disinfection by-products control).

Despite its special aptitude, to my knowledge, there is only one recently published study on PAC/UF for cyanotoxins removal from drinking water. With a PAC (micro/mesoporous) dose of 5 mg/L, 4 hours contact time and a MC-LR feed concentration of 50 μg/L, Lee and Walker (2006) reached a 98-99% retention of MC-LR by PAC/UF in the absence of background

aqueous NOM and a 78-90% retention in the presence of 5 mg/L of fulvic acid. These authors used cellulose acetate (20 kDa membrane cut-off) and polyethersulphone (5 kDa and 20 kDa) flat-sheet membranes, operated in a batch recirculating mode (the UF permeate and concentrate both recirculated to the feed tank), operating conditions far distant from those used in full-scale applications. Much of the previous PAC/UF research has focused the optimisation of the operating parameters through the application of mathematical models (Adham *et al.*, 1991, 1993; Campos *et al.*, 1998, 2000 a, b, c, 2001; Snoeyink *et al.*, 2000; Matsui *et al.*, 2001 a, b). PAC/UF performance has shown to be dependent on operating conditions like backwashing frequency, reactor size and configuration, filtration mode and PAC dosing procedure. PAC and therefore PAC/UF performance is also dependent on NOM concentration and characteristics, as previously addressed in chapters 4 and 5.

Given the present state-of-the-art, the aim of this study is to investigate PAC/UF performance for microcystins removal from drinking water, including the assessment of the key-operating conditions and the impact of water background NOM. Two microcystins feed concentrations, different PAC doses, PAC dosing procedure and hydraulic retention time are studied, as well as the effect of NOM competition (of different nature and concentration). Experimental conditions close to full-scale applications are used, namely a hollow-fibre cellulose acetate membrane (100 kDa), and filtration cycles at constant permeate flow with membrane backwashing/cleaning in between.

8.2 MATERIALS AND METHODS

8.2.1 Microcystins Extraction

Microcystins are cyclic heptapeptides that share a general structure containing five fixed amino acids and two variable L-amino acids (for MC-LR, the most commonly occurring microcystin, the variable amino acids are leucine and arginine). They are relatively hydrophobic compounds, neutral or slightly negative at pH 6-9 and with a molecular weight varying between 900 Da and 1100 Da. Microcystins used in the present study were extracted from *Microcystis aeruginosa* laboratory grown cultures (Pasteur Culture Collection - PCC 7820) in BG11 medium, at 23-24ºC, with a light regimen of 12h fluorescent light/12 h dark). The extraction procedure was adapted from Meriluoto and Spoof (2005 a). Once harvested, the cultures were centrifuged (6000 x g, 10 min), the supernatant was discarded and the pellet was frozen-thawed twice. Microcystins were extracted in 75% aqueous methanol during an 18h minimum period at 4ºC, the methanolic extract was centrifuged twice and the pellet was discarded. The microcystins stock solution was filtered through 1.2 μm glass filters (Whatman, GF-C) and kept in the freezer until use. Prior to microcystin solutions preparation, the microcystins stock concentration was determined by high performance liquid chromatography with photodiode-array detection (HPLC-PDA), the necessary volume was rotary evaporated and the dry extract was dissolved in deionised water. The microcystins variants detected in HPLC were MC-LR, -LY, -LW and -LF (dominance of MC-LR) and the overall concentration was always quantified in μg/L MC-LR equivalent concentration.

8.2.2 Solutions

PAC/UF experiments were performed with two microcystins feed concentrations, *ca.* 5 and 20 μg/L $MC\text{-}LR_{eq}$. The set of trials performed to assess the NOM interference in the

microcystins retention used NOM model compounds and *M. aeruginosa* culture (cells and algogenic organic matter (AOM)). Purified (Hong and Elimelech procedure described in Campinas and Rosa, 2006) Aldrich humic acids (AHA) (hydrophobic, high molar mass) and Sigma tannic acid (TA) (relatively hydrophilic, 1700 Da) were used as NOM model compounds. A background electrolyte of 2.5 mM ionic strength (1 mM IS KCl and 1.5 mM IS $CaCl_2$, as described in chapters 6 and 7) and pH 7±0.3 (adjusted by KOH and H_2SO_4 addition) was used in all PAC/UF experiments except on those performed with *M. aeruginosa* culture, because salts were already present on the cyanobacterial growth medium. In such cases, deionised water was first amended with KCl to reach a final conductivity of 260-300 µS/cm, and it was afterwards spiked with the volume of *M. aeruginosa* culture necessary to obtain the final chlorophyll-a (chl-a) concentration of *ca.* 20 µg/L.

8.2.3 PAC

Commercially available PAC Norit SA-UF was used in PAC/UF experiments. PAC doses between 5 and 15 mg/L were tested. This PAC has a large pore size distribution (38 % of primary microporous volume; 22% of secondary microporous volume and 40 % of mesoporous volume) (Campos *et al.*, 2000 c; Li *et al.*, 2002; Li *et al.*, 2003), which is important to adsorb microcystins in the presence of NOM. Moreover, the low diameter of the PAC particles (6 µm mean diameter) is advantageous for fast adsorption kinetics and for ultrafiltration retention (low ratio of PAC particles diameter to UF fibres diameter). PAC Norit SA-UF displays a positive net charge for a pH below 9.6 (pH_{zc}, point of zero charge). Carbon was pre-wetted overnight before use.

8.2.4 UF Membrane

A hollow-fibre UF module (Aquasource) was used, with hydrophilic cellulose acetate membrane, of 100 kDa MWCO and 250 L/(h.m^2.bar) hydraulic permeability (manufacturer data). The module (16 fibres, 1.1 m length and 0.93 mm internal diameter; 0.05 m^2 total membrane area) was operated in a cross-flow filtration mode using the inside-out configuration during the filtration cycles and under outside-in flow during backwashing. The module was mounted in the lab system schematically illustrated in Figure 8.1.

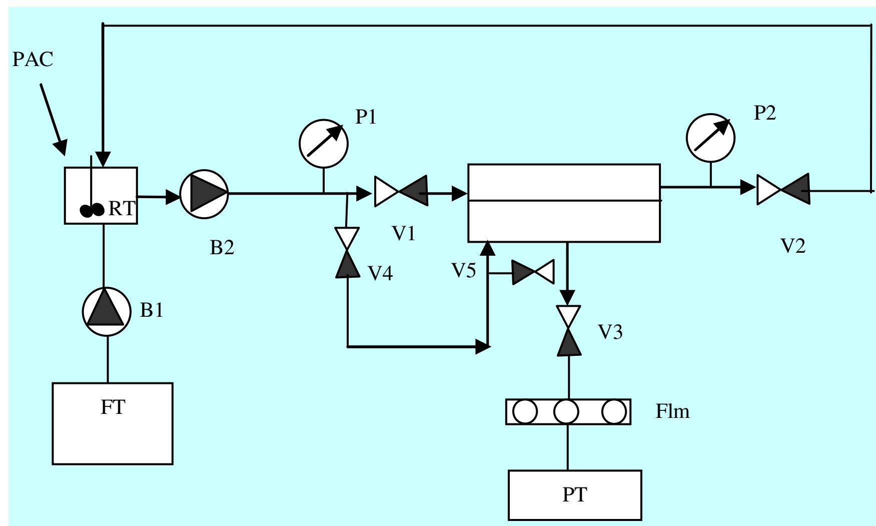

Figure 8.1 - Flow diagram of UF *apparatus* (FT - Feed tank; RT - Stirred recirculating tank; PT - Permeate tank; Flm - Flowmeter; P - Manometers; B1 - Peristaltic pump; B2 - Positive displacement pump; V1,V4,V5 - Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).

8.2.5 Ultrafiltration Runs

The membranes were first compacted with DI until achieving a steady permeate flux, at the pressure and cross-flow velocity to be used in the experiments. All the UF runs (1h-cycles) were performed at a constant permeate flow of 3.5 L/h and at an initial transmembrane pressure (TMP) of 0.65 bar. The permeate output was balanced by a constant input of 3.5 L/h

of fresh raw water which was fed from the feed to the recirculating tank (RT) by a peristaltic pump (Figure 8.1). The concentrate was circulated back to the RT and blended with the continuous make-up of fresh raw water, and permeate was continuously collected in 1L vessels. During a 1h filtration cycle four samples of permeate (the last one with ca. 0.5 L) were therefore collected. The permeate quality presented in the results section is the average of the four samples collected during each 1h filtration cycle.

Different volumes of water in the RT were tested to study different hydraulic retention times. The water in the RT was continuously stirred at 150 rpm. The positive displacement pump provided the necessary pressure and recirculation at a cross-flow velocity of 0.5 m/s (a variable frequency drive allowed the concentrate velocity in the hollow-fibres to be adjusted).

Permeate flow rate, temperature and TMP were periodically measured, and whenever necessary the permeate flow was adjusted by manual control of the concentrate valve. PAC was added directly into the RT and was only wasted at the end of the filtration cycle. Different dosing procedures were tested, *i.e.*, the addition of the total PAC mass at the beginning of the filtration cycle (single-pulse dosing) or the step addition of small portions of PAC throughout the filtration cycle (multi-pulse dosing). At the end of each filtration cycle, the membrane was backwashed (permeate line, outside-in flow) and flushed (inside-out flow). Backwashing was performed during 1 minute with a 5 mg/L (as Cl_2) sodium hypochlorite solution to inhibit the biological growth within the membrane module and the UF *apparatus*, and the flushing with deionised water lasted 3 minutes.

8.2.6 Adsorption Kinetics

For comparison purposes, an adsorption kinetic experiment was also performed with microcystins single-solute electrolyte with 2.5 mM background ionic strength, the same model solution used in PAC/UF runs. Experimental procedure and *apparatus* are detailed in chapter 4.

8.2.7 Analytical Methods

Samples were analysed for pH (at 20ºC, using a WTW 340 pH meter), electrical conductivity (at 25ºC, with a Crison GLP 32 conductimeter), turbidity (HACH 2100N turbidimeter of high resolution, 0.001 NTU) and dissolved microcystins concentration. Samples from experiments with microcystins and NOM (AHA, TA and *M. aeruginosa* culture) were further analysed for UV absorbance at 215 nm and 254 nm (UV/VIS spectrophotometer Beckman DU 640B). In a mixture of AHA and TA, UV_{215nm} best represents TA concentration, whereas UV_{254nm} is mostly related with AHA concentration. During *M. aeruginosa* runs, samples were also analysed for chlorophyll-a (measuring the optical densities at 665 nm and 750 nm on a UV-VIS spectrophotometer Beckman DU 640B) and intracellular microcystins concentration.

Microcystins analysis followed the standard operation procedures developed by Meriluoto and Spoof (2005 a, b, c) with some adaptations. Extracellular microcystins were first isolated from cell-bound microcystins by sample filtration through a Whatman GF/C glass microfibre filter. To analyse dissolved microcystins, the samples were concentrated by solid phase extraction (isolute C18 cartridges) and eluted with 5 mL methanol (90%) containing 0.1% (v/v) trifluoracetic acid (further details in Ribau Teixeira and Rosa (2006)). For intracellular microcystins analysis, the filters were frozen-thawed twice and kept in methanol 75% (v/v) during 18-24h at 4ºC. The methanolic extracts (extra and intracellular) were rotary

evaporated (50ºC), resuspended in 500 µL methanol (75%), centrifuged (10000 x g, 10 min) and 150 µL of the supernatant were transferred to HPLC vials for analysis. Microcystins were analysed by HPLC-PDA, using a Dionex Summit System.

8.3 RESULTS AND DISCUSSION

8.3.1 Microcystins Removal by PAC/UF

Several PAC/UF experiments were performed to verify microcystins removal efficiency and to assess the influence of microcystins concentration and PAC dose, as well as PAC dosing procedure and hydraulic retention time on the recirculating tank. Figure 8.2 presents the microcystins feed and permeate concentrations (averaged cycle) obtained with two microcystins feed concentration ranges (*ca.* 5 and 20 µg MC-LR_{eq}/L) and two PAC dosages (5 and 10 mg/L, single-pulse dosing). For comparison purposes, data from analogous run with no PAC addition are also shown (*ca.* 12 µg MC-LR_{eq}/L).

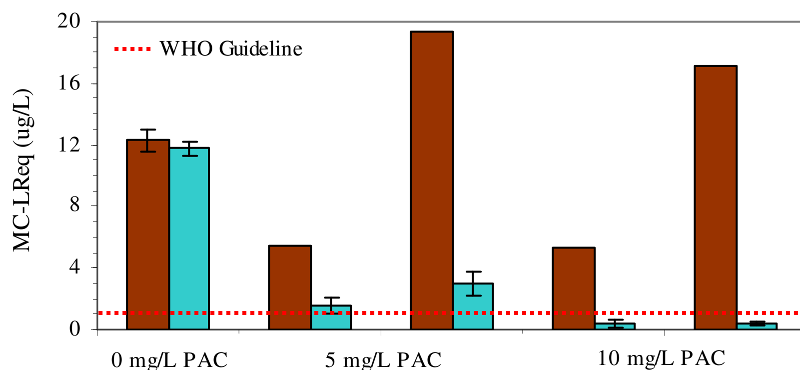

Figure 8.2 - Microcystins UF feed and cycle-averaged permeate concentrations obtained with different feed concentrations and PAC doses (feed: brown bars; permeate: blue bars). Error bars represents standard deviations.

As discussed in chapter 6, with no PAC addition, microcystins concentration in feed and permeate were similar, coherent with a low average adsorption (about 4%) by the cellulose acetate membrane. While the same trend was found in the literature for the same hydrophilic membrane material (Lee and Walker, 2006), when polyethersulphone (Gijsbertsen-Abrahamse *et al.*, 2006; Lee and Walker, 2006) or polysulphone (Chow *et al.*, 1997) membranes are used stronger adsorption was reported.

Figure 8.2 shows the remarkable benefit of PAC on the microcystins removal. Regardless of the microcystins feed concentration range tested (*ca.* 5 μg LR_{eq}/L or 17-20 μg LR_{eq}/L), high microcystins rejections were always reached, and increased with the feed concentration. Removal efficiencies were between 70-84% with 5 mg PAC/L and 93-98% with 10 mg PAC/L, which are consistent with the values of Lee and Walker (2006). They obtained *ca.* 88% of MC-LR removal for 50 μg/L MC-LR feed concentration, 5 mg/L of a wood-based PAC, a cellulose acetate membrane (flat-sheet, 20 kDa) and a contact time of 1 hour. Despite the high rejections obtained, PAC doses of 10 mg/L or higher were necessary to ensure a permeate concentration below the WHO guideline value (1 μg LR_{eq}/L).

Comparing PAC/UF (1h-cycle) with the 1 h adsorption kinetics performed with the same model solution and PAC doses (Figure 8.3), it can be concluded that the former had a lower microcystins adsorption. As recently found by Ivancev-Tumbas *et al.* (2008), this feature is probably associated with a poor distribution of PAC in the UF module and/or with a less favourable hydrodynamic regimen for microcystins adsorption onto PAC and is therefore an aspect to improve in PAC/UF systems. The hydrodynamic limitations of the commonly used PAC/UF systems operated under cross-flow mode were identified and discussed in chapter 7.

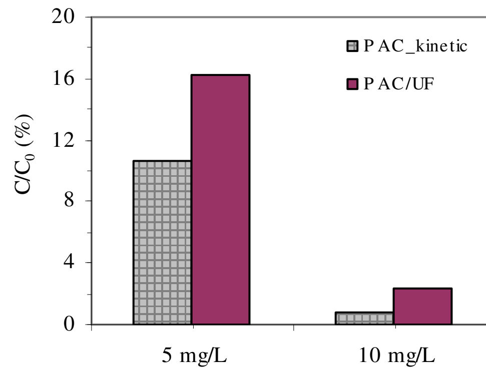

Figure 8.3 - Normalised microcystins concentration after PAC/UF and PAC adsorption kinetics performed in the same operating conditions (17.1 µg/L MC-LR_{eq} feed concentration, two PAC doses and 1 h contact time).

Two key-operating conditions of PAC/UF systems were investigated, namely the PAC dosing procedure and the hydraulic retention time. Experiments were performed with two different PAC dosing procedures: 1) single-pulse dosing (PAC_1x); 2) multi-pulse dosing (PAC_3x, *i.e.* three PAC portions, the first added at the beginning of the cycle and the others after 15 and 30 minutes). Figure 8.4 shows the concentration profile of microcystins permeating the membrane through the 1 h-cycle (left) and the averaged cycle permeate concentration (right) for both dosing procedures. Error bars represents standard deviations.

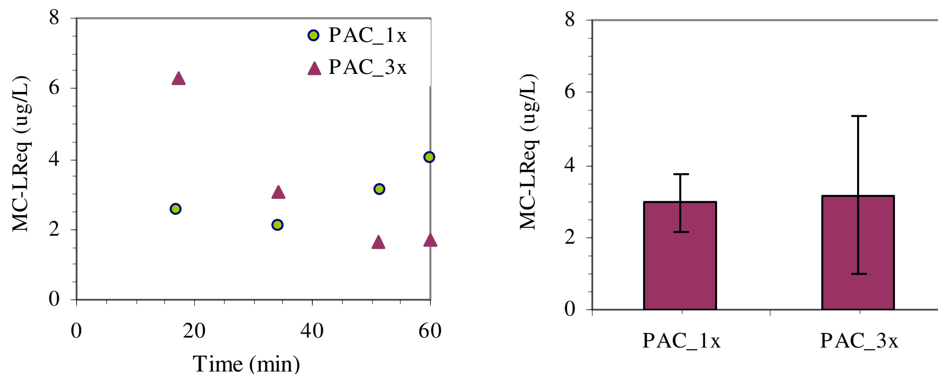

Figure 8.4 - Concentration profile (left) and cycle-averaged concentration (right) of microcystins in the permeate during PAC/UF cycles performed with two different PAC dosing procedures (16.8-19.4 µg/L MC-LR_{eq}, 5 mg/L PAC).

When the PAC was single-pulse dosed (PAC_1x), the microcystins concentration in the UF permeate decreased with running time and reached a minimum (after half hour of filtration), and then increased until the end of the cycle, doubling the minimum. However, for multi-pulse PAC addition (PAC_3x), maximum permeate concentration was observed at the beginning of the cycle and then decreased as the filtration progressed (Figure 8.4, left). These observations are consistent with the findings of Campos *et al.* (1998, 2000 b, c), Snoeyink *et al.* (2000) and Matsui *et al*. (2001 b). The PAC_1x and PAC_3x procedures resulted in an average microcystins concentration of 2.9 µg/L and 3.2 µg/L, respectively, and no differences were found between them in terms of transmembrane pressure necessary to maintain the constant flow. The single-pulse PAC dosing resulted in slightly lower cycle-averaged concentration of microcystins in the permeate, with lower standard deviations (Figure 8.4, right). Some authors have concluded that this dosing mode results in better permeate quality since all carbon particles have a retention time equal to the filtration time (Campos *et al.*, 1998, 2000 b, c; Snoeyink *et al.*, 2000), but others (Matsui *et al.*, 2001 b; Ivancev-Tumbas *et al.*, 2008) have not found benefits of such procedure when removing micropollutants from natural water, given the higher NOM competition. Analogous experiments in the presence of NOM competition are therefore recommended as future work.

The results of different hydraulic retention times (HRT of 34 and 55 minutes) in the recirculating tank are presented on Figure 8.5. The studied HRT had no effect on the cycle-averaged concentration of microcystins in the permeate. Different results were obtained by Campos *et al.* (2000 b) based on model predictions. They concluded that a HRT increase reduces the adsorption efficiency when feed water is considered as the initial solution in the reactor, as in the present study. However, when the model predicted the partial recycling of

the permeate to the reactor (therefore considering permeate as initial solution), HRT does not have a major impact on the adsorption efficiency.

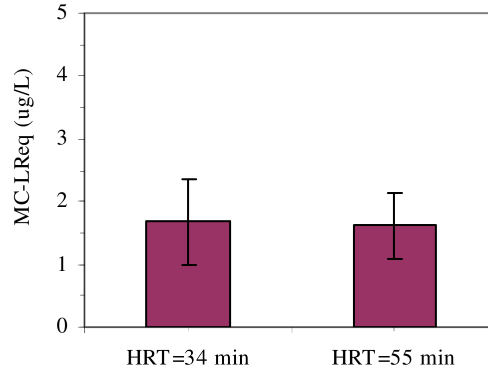

Figure 8.5 - Cycle-averaged concentration of microcystins in the permeate obtained in PAC/UF runs with two HRT in the recirculating tank (5.5-7.2 μg/L MC-LR_{eq}, 5 mg/L PAC). Error bars represents standard deviations.

8.3.2 Effect of NOM on Microcystins Removal by PAC/UF

AHA and TA were used to investigate NOM interference on the removal of microcystins by PAC/UF. Figure 8.6 presents the 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 (5-7μg/L MC-LR_{eq} and 17-23 μg/L MC-LR_{eq}). Single-pulse dosing of 5, 10 and 15 mg PAC/L were studied.

For the lowest feed microcystins concentration (5.3-7.4 μg MC-LR_{eq}/L) and 10 mg/L PAC, the addition of 5 mg/L of NOM (AHA+TA) resulted in a significant increase in the cycle-averaged concentration of microcystins in the permeate (*ca.* 0.4 to 1.2 μg MC-LR_{eq}/L), corresponding to a 11% decrease in rejection (Figure 8.6, left). Only augmenting PAC dose to 15 mg/L made it possible to achieve 90% of microcystins removal and a permeate concentration below the WHO guideline value. When 2.5 mg/L of NOM was added (half the

previous value), there was only a 4.5% lost of microcystins removal and it was still possible to obtain a permeate concentration below 1 µg MC-LR$_{eq}$/L with 10 mg/L PAC. However, when 5 mg/L of NOM (AHA+TA) was added to the higher range of feed microcystins concentration (17.1-23.2 µg MC-LR$_{eq}$/L), there was a huge increase in the permeate concentration, from 0.4 to 6.4 µg MC-LR$_{eq}$/L, corresponding to a decrease of microcystins removal by 30% (Figure 8.6, right). Increasing PAC dosage from 10 to 15 mg/L raised microcystins removal from 67% to 81%, but this was not enough to achieve a permeate quality fulfilling the WHO guideline value. These results agree with the strong TA-microcystins competition investigated in chapters 4 and 5, and are not distant from those obtained by Lee and Walker (2006). In PAC/UF experiments with a flat-sheet cellulose acetate membrane, these authors obtained a MC-LR rejection decrease of 20% when 5 mg/L of fulvic acid was added to a solution containing 50 µg MC-LR/L, and associated it with direct competition between the two similar molecular size compounds.

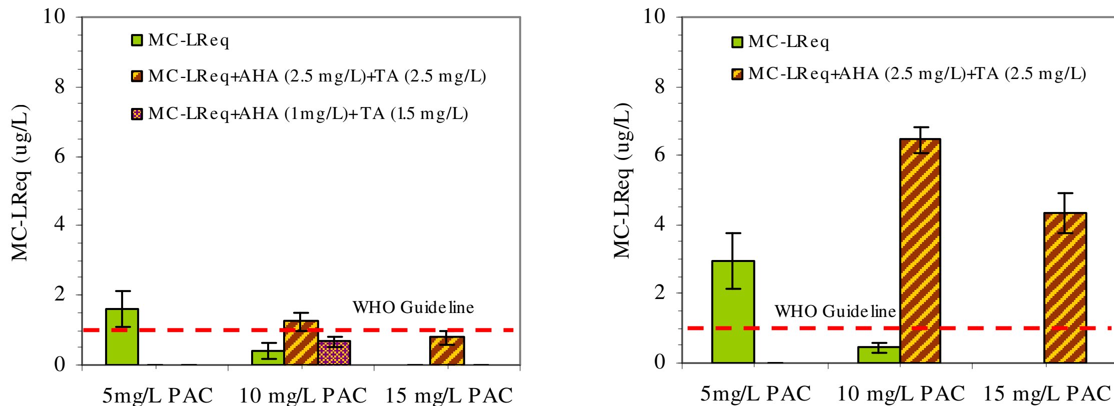

Figure 8.6 - Cycle-averaged concentration of microcystins in the permeate of PAC/UF runs performed in the absence and in the presence of NOM surrogates for two microcystins feed concentration ranges: 5.3-7.4 µg/L MC-LR$_{eq}$ (left) and 17-23 µg/L MC-LR$_{eq}$ (right).

Previous work on competitive adsorption kinetics and isotherms between microcystins and NOM surrogates (AHA, TA) (chapters 4 and 5) indicated that AHA with background ionic strength is responsible for pore blocking mechanism, slowing down the rate of adsorption and reducing PAC capacity for microcystins. The same studies pointed to a more severe effect of TA onto microcystins adsorption, with dominance of pore constriction mechanism and a contribution of direct competition for adsorption sites, especially at higher loadings.

Figure 8.7 presents the UF and the PAC/UF removals of the competing NOM from solutions containing microcystins, AHA and TA.

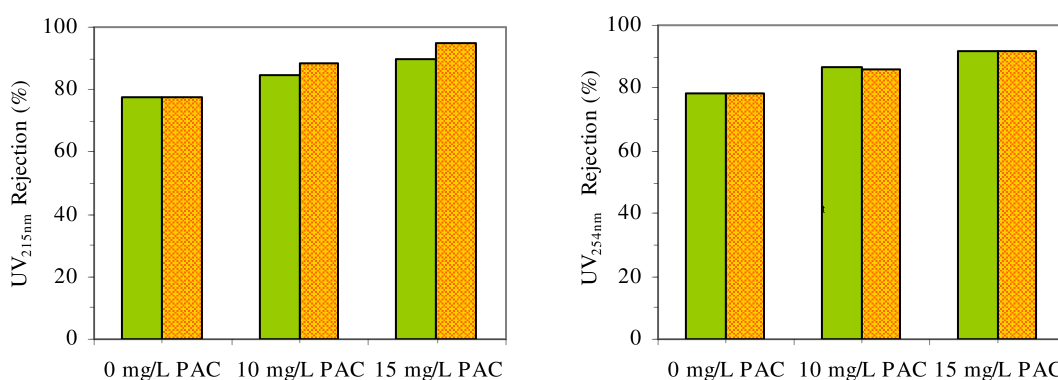

Figure 8.7 - UV rejections (UV_{215nm}, left; UV_{254nm}, right) by PAC/UF of solutions containing microcystins and NOM model compounds (AHA + TA) (green bars: 19.5-23.2 μg/L $MC\text{-}LR_{eq}$; orange bars: 6.7-7.4 μg/L $MC\text{-}LR_{eq}$).

With PAC addition, the UV_{215nm} rejection increased 8% (for the high feed concentration and 10 mg/L PAC) to 18% (for the low feed concentration and 15 mg/L PAC). The UV_{254nm} rejection increased 8% (for both feed concentrations and 10 mg/L PAC) to 14% (with 15 mg/L PAC), comparatively to UF alone. It was observed that lower feed microcystins concentration resulted in higher UV_{215nm} removals (best representing TA), but no differences were observed at 254nm (mostly related to AHA), which is probably an indicator of higher

TA removal. It was already observed in chapters 4 and 5 that microcystins and TA are mutually disturbed, indicating an identical adsorption path.

M. aeruginosa culture 2 months old (in the late-exponential growth phase) was also investigated. The *M. aeruginosa* culture contained cells (*ca.* 20 µg/L chl-a), extra and intracellular microcystins (2.3 µg/L total MC-LR_{eq} and extra/intra ratio of 0.4-0.6) and algal organic matter (AOM).

Both UF and PAC/UF achieved an absolute removal of *M. aeruginosa* single cells, yielding a permeate with no chlorophyll-a and with turbidity values below 0.1 NTU, which indicates that intracellular microcystins were also removed. Figure 8.8 compares the cycle-averaged concentration of (dissolved) microcystins in the permeate of UF (0 mg/L PAC) and PAC/UF (10 mg/L PAC) experiments.

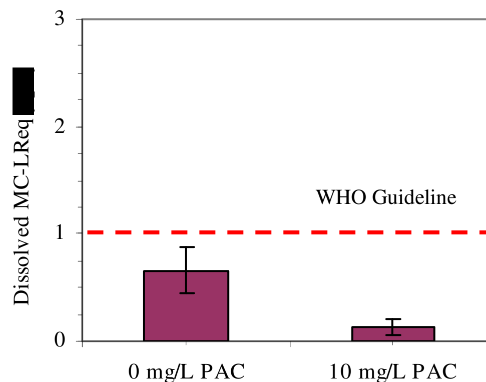

Figure 8.8 - Cycle-averaged concentration of microcystins in the permeate of UF and PAC/UF runs with *M. aeruginosa* culture (2.1-2.3 µg/L MC-LR_{eq} (total), 0.63-0.88 µg/L MC-LR_{eq} (dissolved), ext./int. = 0.4-0.6).

With UF only, the permeate and feed water had similar concentration of dissolved microcystins (0.66 and 0.63 µg MC-LR_{eq}/L, respectively). As already seen in chapter 6, UF

may cause cell damage and subsequent microcystins release to water, especially from older cells. However, in those experiments the quality of the permeate was never deteriorated as microcystins rejection also increased with cell ageing, probably associated with the greater content in segregated AOM (mucopolysaccharides) and protein lysed organic matter. The present data show that PAC/UF substantially improved the permeate quality, removing 86% of the dissolved microcystins (or higher in the case of cell lysis occurrence), and producing a permeate with a 1 h cycle-averaged concentration far below the WHO guideline (< 0.13 μg MC-LR_{eq}/L).

Concerning the NOM influence on microcystins removal by PAC/UF, important aspects are NOM molecular size, hydrophobicity and concentration. High concentrations of TA-like compounds may substantially decline the rate of microcystins adsorption. A good characterisation of the water to be treated by PAC/UF is therefore very important to minimise the membrane fouling and the NOM competition.

8.4 CONCLUSIONS

Microcystins removal by PAC/UF hybrid process was investigated, focusing on aspects like PAC dose, microcystins concentration, specific operating conditions (PAC dosing procedure and hydraulic retention time on the recirculating tank) and NOM interference (humic acids, tannic acid and *M. aeruginosa* culture (cells and AOM)).

In the absence of background NOM, PAC/UF achieved 93-98% of microcystins removal and a permeate concentration below the WHO drinking water guideline-value (1 μg/L MC-LR) with a PAC dose of 10 mg/L and for a microcystins feed concentration up to

ca. 20 µg/L MC-LR_{eq}. Hydrodynamic limitations were detected on PAC/UF operated under cross-flow mode, an aspect to improve in those systems.

The single-pulse PAC dosing at the beginning of the UF-cycle resulted in slightly lower cycle-averaged concentration of microcystins in the permeate, compared with the multi-pulse addition of the PAC throughout the filtration cycle. No differences were found between these two dosing procedures in terms of transmembrane pressure necessary to maintain the constant flow. HRT of 34 and 55 minutes resulted in similar cycle-averaged concentration of microcystins in the permeate.

PAC dose required was mostly affected by NOM type and concentration, and by microcystins concentration. For low microcystins concentration (*ca.* 5 µg/L MC-LR_{eq}), a PAC dose of 10 mg/L effectively controlled the microcystins in a model water with *M. aeruginosa* culture or with 2.5 mg/L of NOM surrogates (AHA+TA), but a PAC dose increase to 15 mg/L was necessary when NOM surrogate concentration doubled. For high concentrations of microcystins (*ca.* 20 µg/L MC-LR_{eq}) and NOM (5 mg/L), 15 mg/L of PAC were unable to achieve the WHO quality.

Depending on microcystins feed concentration, as well as on the type and concentration of the competing compounds, PAC doses may have to be adjusted to overcome the NOM presence. A good characterisation of the water to be treated (molecular size, hydrophobicity and functional groups) is therefore crucial to minimise the NOM competition and the membrane fouling. Controlling strategies include pre-treatment steps, increasing PAC doses (by 50%, 100%, or higher) and/or PAC contact time, adjusting PAC porous structure and/or particle size.

8.5 REFERENCES

Acero J., Rodriguez E., Meriluoto J. (2005). Kinetics reactions between chlorine and the cyanobacterial toxins microcystins. *Water Research*, 39(8), 1628-1638.

Adham S., Snoeyink V., Clark M., Bersillon J.-L. (1991). Predicting and verifying organics removal by PAC in an ultrafiltration system. *Journal of American Water Works Association*, 12, 81-91.

Adham S., Snoeyink V., Clark M., Bersillon J.-L. (1993). Predicting and verifying TOC removal by PAC in pilot-scale UF systems. *Journal of American Water Works Association*, 12, 58-68.

Campinas M., Rosa M.J. (2006). The ionic strength effect on microcystin and natural organic matter surrogate adsorption onto PAC. *Journal of Colloid and Interface Science*, 299, 520-529.

Campos C., Mariñas B., Snoeyink V., Baudin I., Laîné J. (1998). Adsorption of trace organic compounds in CRISTAL® processes. *Desalination*, 117, 265-271.

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

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

Campos C., Schimmoller L., Mariñas B., Snoeyink V., Baudin I., Laîné J. (2000 c). Adding PAC to remove DOC. *Journal of American Water Works Association*, 92(8), 69-83.

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

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

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.

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

Himberg K., Keijola A.-M., Hiisvirta L., Pyysalo H., Sivonen K. (1989). The effect of water treatment processes on the removal of hepatotoxins from *Microcystis* and *Oscillatoria* cyanobacteria: a laboratory study. *Water Research*, 23(8), 979-984.

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

Hoeger 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.

Ivancev-Tumbas I., Hobby R., Küchle B., Panglisch S., Gimbel R. (2008). Nitrophenol removal by combination of powdered activated carbon adsorption and ultrafiltration – comparison of different operational modes. *Water Research*, 42, 4117-4124.

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 Assessement: An International Journal*, 3, 643-656.

Lawton L., Robertson P. (1999). Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters. *Chemical Society Reviews*, 28, 217-224.

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.

Li F., Yuasa A., Ebie K., Azuma Y., Hagishita T., Matsui Y. (2002) Factors affecting the adsorption capacity of dissolved organic matter onto activated carbon: modified isotherm analysis. *Water Research*, 36, 4592

Li Q., Snoeyink V., Mariña B., Campos C. (2003). Elucidating competitive adsorption mechanism of atrazine and NOM using model compounds. *Water Research*, 37(20), 4863.

Matsui Y., Yuasa A., Ariga K. (2001 a). Removal of a synthetic organic chemical by PAC-UF systems-I: theory and modelling. *Water Research*, 35(2), 455-463.

Matsui Y., Yuasa A., Colas F. (2001 b). Effect of operational modes on the removal of a synthetic organic chemical by powdered activated carbon during ultrafiltration. *Water Science & Technology: Water Supply*, 1(5/6), 39-47.

Meriluoto J., Spoof L. (2005 a). SOP: Extraction of microcystins in biomass filtered on glass-fibre filters or in freeze-dried cyanobacterial biomass. *In Toxic Cyanobacterial Monitoring and Cyanotoxin Analysis*. J. Meriluoto and G. Codd (Ed.), Abo Akademi University Press, Finland.

Meriluoto J., Spoof L. (2005 b). SOP: Solid phase extraction of microcystin in water samples. *In Toxic Cyanobacterial Monitoring and Cyanotoxin Analysis*. J. Meriluoto and G. Codd (Ed.), Abo Akademi University Press, Finland.

Meriluoto J., Spoof L. (2005 c). SOP: Analysis of microcystins by high-performance liquid chromatography with photodiode-array detection. *In Toxic Cyanobacterial Monitoring and Cyanotoxin Analysis*. J. Meriluoto and G. Codd (Ed.), Abo Akademi University Press, Finland.

Newcombe G., Nicholson B. (2004). Water treatment options 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 chloramines. *Water Research*, 28(6), 1297-1303.

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.

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

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

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

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.

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

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*, 7, 1033-1041.