

CHAPTER 9

COMPARING PAC/UF AND CONVENTIONAL CLARIFICATION WITH PAC FOR REMOVING MICROCYSTINS FROM NATURAL WATERS

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ABSTRACT

PAC/UF was investigated for removing *M. aeruginosa* cells and microcystins from natural waters and its performance was compared with the conventional clarification with PAC addition (PAC+C/F/S). Ozonated and clarified waters from Tavira Water Treatment Plant were used. Both processes achieved an absolute removal of chlorophyll-a, but greater turbidity and microcystins (intra and extracellular) removals were reached by PAC/UF. With PAC/UF, 10 mg/L PAC resulted in a cycle-averaged concentration of microcystins in the permeate (0.72 µg/L MC-LR_{eq}) below the WHO guideline value, while the water quality obtained with 15 mg/L PAC+C/F/S was far beyond that guideline value. However, the occurrence of cell lysis during UF (with subsequent release of microcystins and UV_{254nm} absorbing substances) and the preferential removal of high molar mass compounds by coagulation yielded better UV_{254nm} removals by PAC+C/F/S. Natural organic matter showed a small impact onto microcystins removal, with greater effect of some algogenic compounds, but especially of high concentrations of humic and tannic-like compounds.

9.1 INTRODUCTION

Cyanotoxins are produced as secondary metabolites of cyanobacteria, under certain conditions of growth, and may occur both within cells (intracellular or cell-bound) or dissolved in water (extracellular). As they may cause a range of adverse health effects (gastroenteritis, liver damage, tumour promotion and, ultimately, death), their removal is a major goal in water treatment. Hepatotoxic microcystins are cyclic heptapeptides, consisting of five fixed and two variable amino acids, and are the most prevalent and significant cyanotoxins for water supply. Clear safe levels of maximum tolerable concentration are still under discussion, but 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 variant.

Conventional clarification by C/F/S (coagulation/flocculation/sedimentation) is able to remove algal cells and therefore the intracellular cyanotoxins. Nevertheless, due to their low specific density, morphological characteristics and negatively charged cell surfaces (Edzwald, 1993), algal cells are more difficult to remove than inorganic particles. In addition, while some authors reported no cell lysis by C/F/S (Kenefick *et al.*, 1993; Chow *et al.*, 1998, 1999; Drikas *et al.*, 2001; Ribau Teixeira and Rosa, 2007), others referred a negative effect (Himberg *et al.*, 1989; Lam *et al.*, 1995; Hruday *et al.*, 1999; Pietsch *et al.*, 2002). Coagulation is also particularly sensitive to the concentration and chemical composition of algogenic organic matter (AOM) (Widrig *et al.*, 1996; Chow *et al.*, 1999; Chen and Yeh, 2006; Pivokonsky *et al.*, 2006). High AOM concentration and protein-like compounds (whose concentration increases during cell lysis) inhibit coagulation (Bernhardt *et al.*, 1991; Takaara *et al.*, 2007). Coagulation has been shown to be most effective in removing larger compounds, like humic substances (Amy *et al.*, 1992), and it is considered ineffective for removing

dissolved cyanotoxins (Keijola *et al.*, 1988; Himberg *et al.*, 1989; Lawton and Robertson, 1999).

Compared to conventional clarification, ultrafiltration (UF) has demonstrated higher removal of particulate matter, higher disinfection efficiency (including virus, *Cryptosporidium* and *Giardia*) and higher ability to cope with variations on feed water quality. Moreover, as found by Chow *et al.* (1997) and Gijsbertsen-Abrahamse *et al.* (2006) and further confirmed in chapter 6, UF is able to completely remove cyanobacterial cells and therefore to effectively remove the intracellular cyanotoxins. Nevertheless, UF may lyse cyanobacterial cells with damaging increasing with cell ageing (chapter 6). Also, hydrophilic AOM (*e.g.*, polysaccharide-like compounds) may be responsible for high membrane fouling (Her *et al.*, 2004; Kimura *et al.*, 2006; Lee *et al.*, 2006; Park *et al.*, 2006; Yamamura *et al.*, 2007), especially when interacting with multivalent ions (chapters 6 and 7). Unless a significant adsorption occurs, UF membranes have a restricted removal of dissolved microcystins, since they are much smaller than the usual membrane pore size. Studies have shown a large range of results, between 0.8% and 78% of microcystins removal, essentially depending on the membrane material (Chow *et al.*, 1997; Gijsbertsen-Abrahamse *et al.*, 2006; Lee and Walker, 2006; chapter 6).

The addition of powdered activated carbon (PAC) is an attractive option to overcome the limited removal of dissolved microcystins by both C/F/S and UF. PAC is widely used, as its porous nature and its large internal surface area confer it high adsorption capacity for a broad range of organic compounds. Besides, PAC requires minimal capital costs, is flexible, may be applied intermittently and at varying doses, being easily adapted to seasonal water quality changes, like those brought during cyanobacterial blooms. PAC is usually applied at the rapid

mixing stage (coagulation), which enables its removal during sedimentation and/or filtration. More recently, PAC is integrated with UF, simultaneously allowing particulate and dissolved contaminants removal by PAC adsorption and membrane filtration. However, comparative studies of PAC/membrane and PAC/conventional clarification for removing cyanobacterial cells and cyanotoxins are still missing.

PAC adsorption, either applied during C/F/S or UF, is most influenced by NOM size and character (Cook *et al.*, 2001; Pelekani and Snoeyink, 2001; Newcombe *et al.*, 2002, Li *et al.*, 2003) and NOM interaction with water background inorganics (chapter 3 and 4), which may significantly reduce the adsorption kinetics. As so, competitive adsorption is site-specific, and the studies must be therefore performed with the natural water to be treated.

This paper investigates PAC/UF removal of *M. aeruginosa* cells and microcystins from low-moderately hard natural waters with hydrophilic low molar mass organics, and compares PAC/UF and PAC+C/F/S performances.

9.2 MATERIALS AND METHODS

9.2.1 Cyanobacterial Cells and Cyanotoxins

Microcystis aeruginosa culture (Pasteur Culture Collection, PCC 7820) was grown in laboratory, in BG11 medium, at 23-24°C, under a light regimen of 12h fluorescent light, 12 h dark. This PCC 7820 culture produced four microcystins variants (MC-LR, -LY, -LW, -LF), with a dominance of MC-LR (chapter 3). Cultures were harvested after two months, corresponding to the late-exponential growth phase, and used to simulate cyanobacterial blooms in natural waters. Dissolved microcystins (extracted from *M. aeruginosa* cultures,

using the adapted procedure of Meriluoto and Spoof, as described in Campinas and Rosa, 2006) were used to supplement the assayed waters with the target contaminant. Microcystins are relatively hydrophobic hepatotoxins, with a molar mass between 900 and 1100 g/mol and are neutral or slightly negative at natural pH (6-9).

9.2.2 Natural Waters

Ozonated (TOW) and clarified (TCW) natural waters were studied (Table 9.1). These waters were collected at Tavira Water Treatment Plant (WTP), located in western Algarve, southern of Portugal, and run by Águas do Algarve, SA. Tavira's treatment train consists of pre-ozonation, coagulation with PAC addition and pH adjustment, floc blanket clarification, rapid sand filtration and chlorination.

Table 9.1 – Characteristics of natural waters.

Parameters	TOW	TCW
pH	7.5	7.5
Conductivity ($\mu\text{S}/\text{cm}$)	150	198
Turbidity (NTU)	1.66	0.634
UV _{254nm}	0.015	0.006
TOC (mg C/L)	2.3	1.4
DOC (mg C/L)	2.1	1.3
SUVA (L/(m.mg))	0.71	0.46
Alkalinity (mg CaCO ₃ /L)	40	60
Hardness (mg CaCO ₃ /L)	51	75
Ca (mg/L)	7.7	17
Mg (mg/L)	7.6	7.7

Both waters have neutral pH, low content in organic matter, low SUVA values and low alkalinity. TOW is soft water and TCW is moderately hard water. Given the low value of the specific UV absorbance (SUVA), NOM is essentially hydrophilic and with low molar mass

(Edzwald and Van Benschoten, 1990). As expected, the two waters differ in turbidity and NOM (due to PAC + clarification) and calcium hardness ions (due to pH adjustment).

The experiments were performed with TOW and/or TCW, spiked with a predefined volume of *M. aeruginosa* culture until a chlorophyll-a (chl-a) concentration *ca.* 10 µg/L was achieved, corresponding to guidance level 1 for recreational waters and ten times higher than WHO alert level 1 for drinking waters (Bartram *et al.*, 1999). These waters were further supplemented with a specific volume of microcystins stock-solution to increase the concentration of dissolved cyanotoxins to *ca.* 5 µg/L MC-LR_{eq}. Spiking with cells and dissolved microcystins resulted in slight increases in conductivity (150 to 169 µS/cm for TOW and 198 to 211 µS/cm for TCW), turbidity (1.7 to 3 NTU and 0.6 to 2.1 NTU) and UV absorbance (0.015 to 0.036 and 0.006 to 0.016), but the nature of NOM was kept essentially hydrophilic.

9.2.3 PAC

PAC/UF experiments used the commercially available PAC Norit SA-UF, whereas C/F/S trials were performed with PAC Filtracarb WP7 (Quimitécnica). The former has a large pore size distribution (38% of primary micropore volume; 22% of secondary micropore volume and 40% of mesopore volume) (Campos *et al.*, 2000; Li *et al.*, 2002) which was proven to be advantageous for the removal of microcystins (Donati *et al.*, 1994; Pendleton *et al.*, 2001; Huang *et al.*, 2007). PAC Norit SA-UF was not used in C/F/S experiments since it has an extremely fine grade, especially designed for UF membranes (average particle diameter of 6 µm), and inadequate for efficient retention by a conventional separation process. C/F/S experiments were therefore performed with Filtracarb WP7, the PAC used in Tavira WTP.

Pore size distribution information was not available, but WP7 has an iodine number of 850 g/g and a methylene blue adsorption capacity of 180 mg/g.

9.2.4 UF Runs

UF cellulose acetate hollow-fibre membrane from Aquasource was used. This hydrophilic membrane has a molecular weight cut-off of 100 kDa and a hydraulic permeability of 250 L/(h.m².bar) (manufacturer data). The module has 16 fibres (1.1 m length and 0.93 mm internal diameter) with a total membrane area of 0.05 m² and was operated using the inside-out configuration. PAC/UF apparatus is already described in chapter 8.

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. UF runs were performed at constant permeate flow (3.5 L/h), an initial transmembrane pressure (TMP) of 0.65 bar and a cross-flow velocity of 0.5 m/s. A single-pulse PAC dosing of 10 mg/L was applied at the beginning of each run. Filtration cycles lasted 1 h, after which the PAC was wasted and the membrane was backwashed during 1 min with a sodium hypochlorite solution (5 mg/L as Cl₂) and flushed with deionised water for 3 min. Further details are presented in chapter 8.

PAC/UF experiments were performed with TCW and TOW spiked with *M. aeruginosa* culture and dissolved microcystins (cells + AOM + microcystins). For comparison purposes, UF experiments with no PAC addition were also conducted with TCW. Given the difficult accurate control of the permeate flow (since no automatic control was available), there were some minor oscillations of flow during the UF runs. Hence, membrane permeability rather than transmembrane pressure (TMP), was represented as a function of time. Membrane

permeability is given by $Q_p/(\Delta P \cdot A_m)$, where Q_p is the permeate flow (L/h), ΔP is TMP (bar) and A_m is the membrane area (m^2).

9.2.5 C/F/S Experiments

The C/F/S experiments were performed in a laboratory jar test *apparatus* with four flat paddles (Flocumatic, Selecta). Operating conditions were as follows: a) rapid mixing at 104 rpm (196 s^{-1} velocity gradient) for 3 min; b) slow mixing at 20 rpm (17 s^{-1}) during 20 min; c) 1 h settling period. An aluminium polychloride coagulant (PAX XL-14, Quicom) was used, at a dosage of 50 mg/L (optimised in earlier experiments). PAC Filtracarb WP7 was also added in the rapid mixing step, after 2 min of coagulation. An effective PAC contact time of 21 min was therefore ensured. Mixing conditions, coagulant type and conditions of PAC application were adjusted from Tavira WTP. C/F/S trials were performed in duplicate with TOW spiked with *M. aeruginosa* culture and dissolved microcystins (cells + AOM + microcystins). PAC doses of 5, 10 and 15 mg/L were tested.

9.2.6 Analytical Methods

Samples were analysed for pH (at 20°C, WTW 340 pH meter), conductivity (at 25°C, Crison GLP 32 conductimeter), turbidity (HACH 2100N turbidimeter of high resolution, 0.001 NTU), chl-a and UV_{254nm} (UV/VIS spectrophotometer-Beckman DU 640B) using standard methods of water analysis. Dissolved and intracellular microcystins were analysed by high performance liquid chromatography with photo-diode array detection (HPLC-PDA Dionex Summit System), following Meriluoto and Spoof (2005 a, b, c) procedures with the adaptations detailed in chapters 6, 7 and 8.

9.3 RESULTS AND DISCUSSION

9.3.1 Microcystins Removal from Natural Waters by UF and PAC/UF

Figure 9.1 compares the membrane permeability and rejections during UF and PAC/UF experiments performed with TCW supplemented with *M. aeruginosa* culture and dissolved microcystins. The feed microcystins concentration was 7.8 µg/L total MC-LR_{eq} with an extracellular/intracellular ratio of 4.

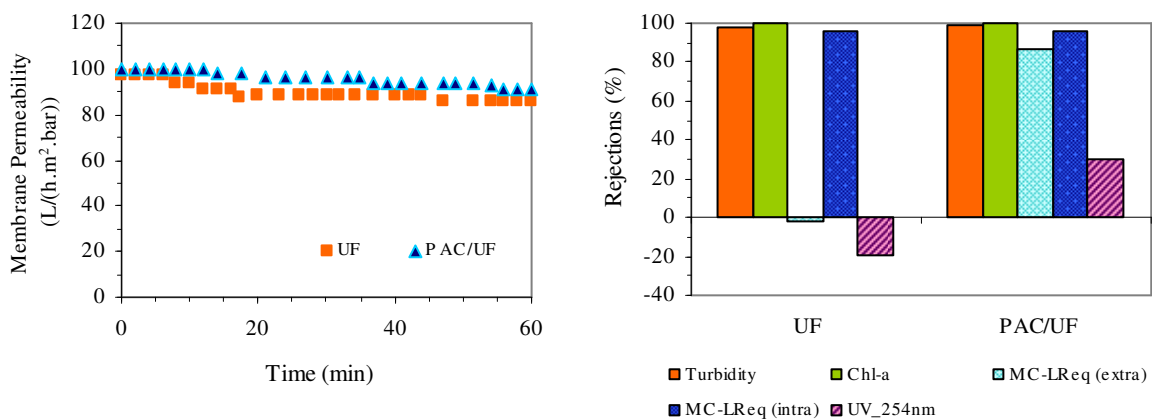


Figure 9.1 – Membrane permeability (left) and rejections (right) obtained during UF and PAC/UF (10 mg/L PAC) of Tavira’s WTP clarified water (TCW) supplemented with *M. aeruginosa* culture and dissolved microcystins (7.8 µg/L total MC-LR_{eq}).

In the UF run, a membrane permeability decline of 11% was observed and therefore the NOM present in TCW together with the AOM contribution and the *M. aeruginosa* cells did not show a great membrane fouling potential. In chapters 6 and 7, AOM was found to have greater detrimental impact on membrane fouling, especially for high content of polysaccharide-like compounds and multivalent ions. The fact that the experiments in this study were performed at lower fluxes (less than half the membrane capacity) and with lower multivalent ions concentration may explain this behaviour. PAC addition resulted in similar low membrane permeability decline, *ca.* 9% during 1 h-cycle. These results are in agreement

with those obtained in chapter 7, given that NOM nature did not change the PAC impact on flux decline.

Both UF and PAC/UF ensured an absolute removal of *M. aeruginosa* cells and an excellent overall control of particles. Chl-a was never detected in the permeate, intracellular microcystins content was always below the quantification limit (0.06-0.10 µg/L MC-LR_{eq}), corresponding to a rejection above 96%, and turbidity was below 0.1 NTU (> 98% rejection) (Figure 9.1, right).

However, there were some clear differences between UF and PAC/UF performance. A negative rejection of dissolved microcystins and UV_{254nm} (-2% and -20%, respectively) was observed with UF, which was most probably due to cell lysis. To confirm that cell lysis may increase UV_{254nm}, it was performed a simple experiment. Cell lysis was induced to a *M. aeruginosa* culture two months old (frozen-thawed twice and ultrasonicated), and after a 0.45 µm filtration, both natural and lysed cultures were analysed for UV absorbance. The results revealed an increase of 39% in UV_{254nm}, which supported the cell lysis occurrence during UF. PAC/UF resulted in a major improvement of dissolved microcystins and UV_{254nm} rejections, 87% and 30%, respectively. Given the cell lysis occurrence, these rejections must be underestimated.

Figure 9.2 depicts the cycle-averaged concentration of microcystins in the permeate during UF and PAC/UF runs. As expected, UF alone was not effective for microcystins removal, attaining a permeate concentration of 6.2±0.1 µg/L MC-LR_{eq}, by opposition to PAC/UF that allowed a concentration of 0.84±0.3 µg/L MC-LR_{eq} with a PAC dose of 10 mg/L.

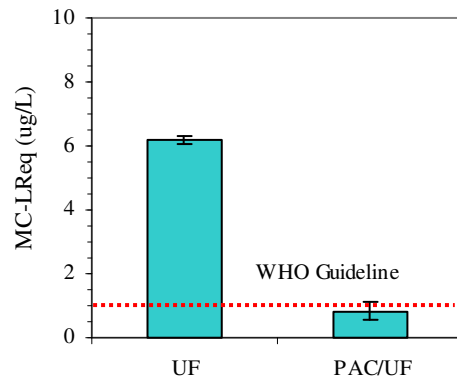


Figure 9.2 - Cycle-averaged concentration of microcystins in the permeate during UF and PAC/UF (10 mg/L PAC) of TCW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.8 $\mu\text{g/L}$ total MC-LR_{eq}). Error bars represents standard deviations.

One of the purposes of this study was to evaluate the combined effect of organic and inorganic matrices of surface natural waters, as well as AOM, on the removal of microcystins by PAC/UF, simulating a real scenario of a cyanobacterial bloom. Figure 9.3 presents the membrane permeability and cycle-averaged concentrations of microcystins in the feed and in the permeate of PAC/UF performed with TCW and TOW supplemented with *M. aeruginosa* culture and dissolved microcystins. Dissolved microcystins results were further compared with those obtained in the presence of NOM surrogates (AHA and TA) in two different concentrations (section 8.3.2).

TOW and TCW presented similar permeability decline and removal of dissolved microcystins by PAC/UF, which is not surprising given their identical organic composition. The combined effect of surface water NOM, AOM and cyanobacterial cells was not distant from the one obtained with the lower concentration of AHA and TA, with microcystins rejections of 87-88% and a cycle-averaged concentration of microcystins in the permeate of 0.66-0.84 $\mu\text{g/L}$ MC-LR_{eq}. A stronger impact was observed for the higher concentration of AHA and TA, diminishing microcystins rejection to 81% and increasing the concentration to

1.2 $\mu\text{g/L}$ MC-LR_{eq}. As already shown in chapter 4, the effect of the model compounds is mostly associated with TA, since it has high affinity for PAC Norit SA-UF and strong impairment on microcystins kinetics.

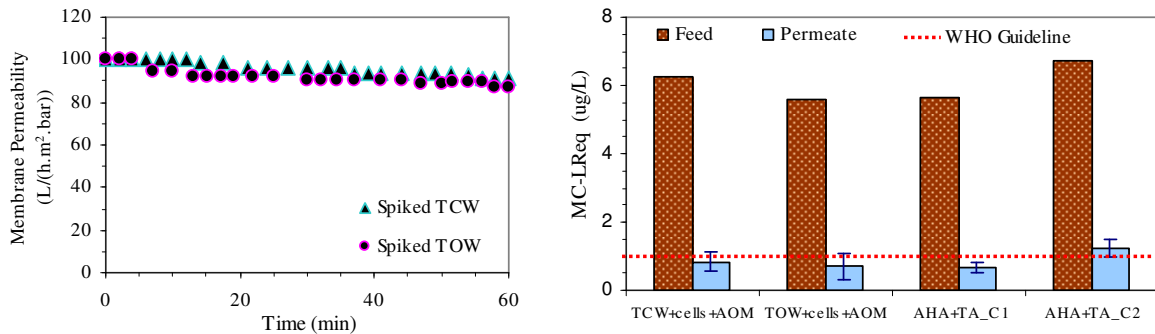


Figure 9.3 – Membrane permeability (left) and cycle-averaged concentration of dissolved microcystins in the feed and permeate (right) obtained during PAC/UF (10 mg/L PAC) of ozonated (TOW) and clarified (TCW) natural waters supplemented with *M. aeruginosa* culture (cells and AOM) and dissolved microcystins. Comparison is made with NOM surrogate runs from chapter 8 (right, C₁: 1 mg AHA/L+1.5 mg TA/L; C₂: 2.5 mg AHA/L+2.5 mg TA/L).

As for the natural waters with cells and AOM, according to the results of chapters 4 and 5, it was expected that the higher impact on microcystins adsorption would arise from AOM compounds and not from the surface water NOM. To confirm this hypothesis, adsorption kinetics were conducted with TCW spiked with dissolved microcystins (*ca.* 5 $\mu\text{g/L}$ MC-LR_{eq}). The results found for 1 h contact time and three PAC dosages are displayed in Figure 9.4. Without cells and AOM, it was achieved a very high removal of microcystins, respectively, 85% (15% microcystins remaining) and 98% (2% microcystins remaining) for 5 and 10 mg/L PAC, which confirms the minor interference of TCW compounds onto microcystins rate of adsorption. Results from chapters 4 and 5 showed that TCW would affect microcystins adsorption mostly through a direct site competition, not affecting microcystins

kinetics due to the small size of TCW compounds. The decrease of 10% observed for microcystins removal in the presence of TCW with cells and AOM is thus mostly associated to pore blockage by some AOM compounds (segregated or from cell lysis).

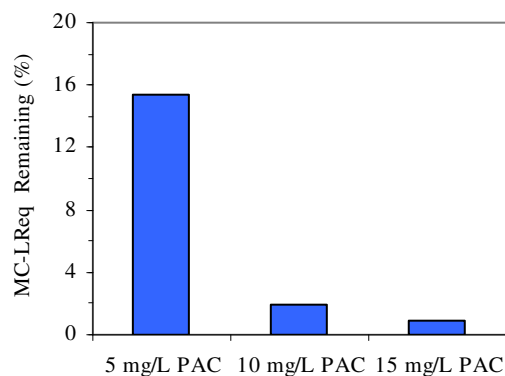


Figure 9.4 - Percentage of microcystins remaining after PAC adsorption kinetics performed with TCW supplemented with dissolved microcystins (5.2 $\mu\text{g/L}$ MC-LR_{eq} feed concentration, 1 h contact time).

9.3.2 Comparing PAC/UF and PAC + C/F/S

PAC/UF and PAC+C/F/S processes were compared through experiments conducted with identical TOW spiked with *M. aeruginosa* culture and further supplemented with dissolved microcystins (Table 9.2). PAC/UF and PAC+C/F/S used the same PAC dose (10 mg/L), but different PAC type (Norit SA-UF and Filtracarb WP7, respectively) and effective PAC contact time (1 h and 21 min, respectively), conditions that better represent the real full-scale scenario. Figure 9.5 compares the two treatment options in terms of several water quality parameters.

Table 9.2 – Characteristics of the feed waters used in PAC+C/F/S and PAC/UF experiments (TOW spiked with *M. aeruginosa* culture and dissolved microcystins).

Parameters	PAC+C/F/S	PAC/UF
pH	7.3	7.4
Conductivity ($\mu\text{S}/\text{cm}$)	197	169
Turbidity (NTU)	2.94	2.97
UV _{254nm}	0.041	0.036
Chl-a ($\mu\text{g}/\text{L}$)	12	11
Extra MC-LR _{eq} ($\mu\text{g}/\text{L}$)	7.1	5.6
Intra MC-LR _{eq} ($\mu\text{g}/\text{L}$)	1.4	1.6

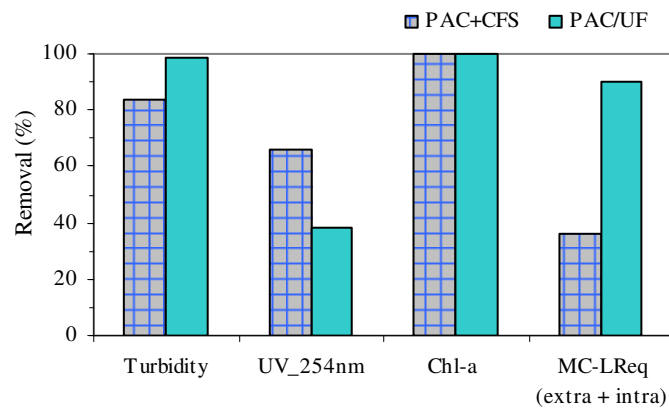


Figure 9.5 - PAC+C/F/S and PAC/UF performances with TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.2-8.5 $\mu\text{g}/\text{L}$ MC-LR_{eq}, extra/intracellular = 4-5, 10 mg/L PAC).

Chlorophyll-a was completely removed by both processes, but greater removals of turbidity (99% by PAC/UF vs. 84% by PAC+C/F/S) and particularly total microcystins (90% vs. 36%) were achieved by PAC/UF. Despite the much lower size of the PAC used, PAC/UF ensured a safer removal of particles. Improved microcystins removal is due to the fact that PAC/UF allows longer PAC retention time (much higher than the hydraulic retention time) and the use of smaller PAC particles and hence provides longer adsorption and faster kinetics. Disadvantages of PAC application to conventional clarification are the low contact time of the

carbon in suspension (given that during settling there is minimal or none adsorption), and the floc interference with PAC adsorption capacity. Cook *et al.* (2001) showed that during settling there was no removal of methylisoborneol and geosmin, and that PAC incorporation into the flocs reduced PAC adsorption capacity, especially in highly turbid waters (tight binding of the PAC in denser flocs). Similarly, Ho and Newcombe (2005) showed that high turbidity and high alum dose significantly decreased MIB adsorption due to the formation of larger flocs, which induced PAC incorporation, reducing the efficacy of mixing and diffusion kinetics.

The UV_{254nm} revealed better results for conventional clarification (66% vs. 39% removal), which is probably associated with the cell lysis occurrence during UF (disadvantage of UF) and the preferential coagulation of high molar mass compounds (advantage of C/F/S). PAC/UF improved the UF permeate quality in terms of UV_{254nm} but was unable to reach the PAC + C/F/S quality.

Figure 9.6 displays the average concentration of microcystins (intra and extracellular) in PAC + C/F/S and PAC/UF treated waters. The error bars depicted in the figure are standard deviations. PAC/UF achieved a high permeate quality, with a cycle-averaged concentration of dissolved microcystins of $0.72 \pm 0.4 \mu\text{g/L MC-LR}_{eq}$ and intra microcystins concentration below the quantification limit (0.06 - 0.1 $\mu\text{g/L}$). Higher removal of dissolved microcystins would be expected if cell lysis could be avoided or PAC adsorption improved, *e.g.*, using higher PAC dosages, smaller PAC particles or longer PAC retention time.

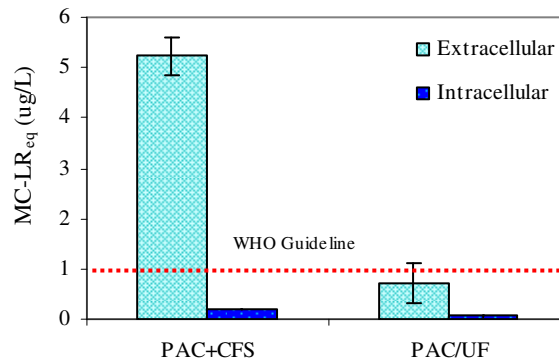


Figure 9.6 - Average microcystins concentration of treated waters produced by PAC+C/F/S and PAC/UF application to TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.2-8.5 $\mu\text{g/L}$ MC-LR_{eq}, extra/intra = 4-5; 10 mg/L PAC).

Conventional application of 10 mg/L PAC was unable to control the microcystins, resulting in an average concentration of $5.2 \pm 0.4 \mu\text{g/L}$ extra MC-LR_{eq} and $0.21 \pm 0.01 \mu\text{g/L}$ intra MC-LR_{eq} (the later very close to the quantification limit). PAC+C/F/S was also performed with 5 and 15 mg/L (Figure 9.7) and showed a slow microcystins removal enhancement with PAC dose, e.g. from 5 to 15 mg/L PAC the water quality varied from $6.6 \pm 0.4 \mu\text{g/L}$ MC-LR_{eq} to $4.4 \pm 1 \mu\text{g/L}$ MC-LR_{eq}. These results agree with the literature, which indicates a minimum PAC dose of 20-30 mg/L for effective control of MC-LR (Donati *et al.*, 1994; Hrudey *et al.*, 1999).

As final note, and for both processes, it is important to avoid PAC addition to chlorinated waters. Gillogly *et al.* (1998) found that free chlorine can oxidize adsorption sites containing methylisoborneol, releasing it back to the aqueous phase. Huang *et al.* (2007) found that residual chlorine react with activated carbon causing a decrease in adsorption capacity of MC-LR. Accordingly, to maximize the efficiency of both the chlorine and PAC, their contact time should be eliminated or minimised (Gillogly *et al.*, 1998).

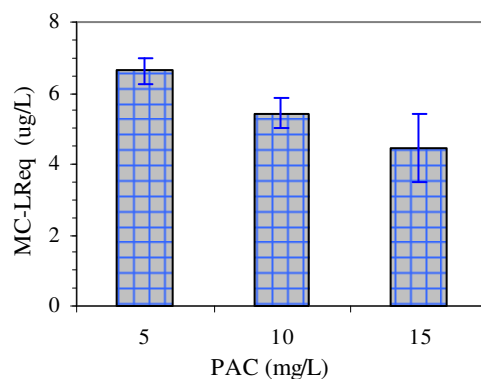


Figure 9.7 - Average microcystins concentration (intra+extra) of treated waters obtained by different PAC doses applied to PAC+C/F/S of TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (8.5 $\mu\text{g/L}$ MC-LR_{eq}).

9.4 CONCLUSIONS

UF and PAC/UF application to natural waters ensured an absolute removal of *M. aeruginosa* cells and an excellent overall control of particles. Chl-a was never detected in the permeate, intracellular microcystins content was always below the quantification limit (> 96% rejection), and turbidity below 0.1 NTU (> 98% rejection). Compared to UF, PAC/UF did not improve the membrane permeability, but notably increased the dissolved microcystins and UV_{254nm} rejections (from negative values to 87% and 30%, respectively). UF induced cell lysis with a subsequent negative effect on permeate quality in terms of dissolved microcystins and UV_{254nm} absorbing substances. The addition of PAC overcame this degradation and highly improved the permeate quality.

The organic and inorganic background matrices of the surface waters tested (low-moderately hard natural waters with hydrophilic low molar mass organics) had no significant impact on membrane fouling and microcystins removal by PAC/UF, achieving 87-88% removals with

10 mg/L PAC. Greater impact was attributed to AOM and especially to high concentrations of humic and tannic-like compounds.

PAC/UF was compared with PAC application to conventional clarification (PAC+C/F/S). Chlorophyll-a was completely removed by both processes, but PAC/UF ensured a remarkable improvement in turbidity (99% removal by PAC/UF vs. 84% by PAC+C/F/S) and particularly in total microcystins, *i.e.* 90% vs. 36% microcystins removal and 0.72 vs. 5.4 µg/L MC-LR_{eq} in the treated water. Even a PAC dosage of 15 mg/L to C/F/S was unable to control microcystins. Compared to conventional PAC application, PAC/UF favoured the adsorption kinetics since it allowed longer PAC effective contact time, smaller PAC particles and PAC was not incorporated into the flocs.

However, PAC+C/F/S presented higher removal of UV_{254nm} than PAC/UF (66% vs. 39%), explained by preferential coagulation of large compounds and UF cell damaging.

The fouling behaviour of AOM and the cell lysis occurrence during UF, with subsequent release of dissolved microcystins and AOM to water, indicate that UF with no PAC addition is inadequate to treat cyanobacterial-rich waters and emphasise the importance of a roughing clarification step prior to PAC/UF.

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