Desalination and Water Treatment
www.deswater.com
16 (2010) 120–128
April
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doi: 10.5004/dwt.2010.1092

Comparing PAC/UF and conventional clarification with PAC for removing microcystins from natural waters

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Received 18 April 2009; Accepted 16 December 2009

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's 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.

Keywords: PAC/UF; Clarification; Microcystins; AOM; NOM

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 coagulatison/flocculation/sedimentation (C/F/S) 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 [1], algal cells are more diffiscult to remove than inorganic particles. In addition, while some authors reported no cell lysis by C/F/S [2–4], others referred a negative effect [5–6]. Coagulation is also particularly sensitive to the concentration

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and chemical composition of algogenic organic matter (AOM) [2,7]. High AOM concentration and protein-like compounds (whose concentration increases during cell lysis) inhibit coagulation [8]. Coagulation has been shown to be most effective in removing larger compounds, like humic substances [9], and it is considered ineffective for removing dissolved cyanotoxins [10].

Compared to conventional clarification, ultrafiltration (UF) has demonstrated higher removal of particulate matter, higher disinfection efficiency (including virus, *Cryptosporidium oocysts* and *Giardia* cysts) and higher ability to cope with variations on feed water quality. Moreover, UF is able to completely remove cyanobacterial cells and therefore to effectively remove the intracellular cyanotoxins [11–13]. Nevertheless, UF may lyse cyanobacterial cells with damaging increasing with cell ageing [13]. Also, hydrophilic AOM (*e.g.* polysaccharide-like compounds) may be responsible for high membrane fouling [14–16], especially when interacting with multivalent ions [13]. Unless a significant adsorption occurs, UF membranes have a restricted removal of dissolved microcystins, since these are much smaller than the usual membrane pore size. Studies have shown a wide range of results, between 0.8% and 78% of microcystins removal, essentially depending on the membrane material [11–13,17].

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 variations, like those brought during cyanobacterial blooms. PAC is usually applied at the rapid mixing stage (coagulation), a procedure that enables its removal during sedimentation and/or filtration. More recently, PAC is integrated with UF, allowing the simultaneous removal of dissolved contaminants by PAC adsorption and particles by 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 much influenced by NOM size and character [18–19] and by NOM interaction with water background inorganics [13,20], a phenomenon that may significantly reduce the adsorption kinetics. Hence, competitive adsorption is site-specific, and studies must therefore be performed with the natural water to be treated.

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

Table 1
Characteristics of natural waters.

Parameters	TOW	TCW
pH	7.5	7.5
Conductivity (μS/cm)	150	198
Turbidity (NTU)	1.66	0.634
UV_{254nm} (cm^{-1})	0.015	0.006
TOC (mg C/L)	2.3	1.4
DOC (mg C/L)	2.1	1.3
SUVA (L/(m.mgC))	0.71	0.42
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

2. Materials and methods

2.1. Cyanobacterial cells and cyanotoxins

Microcystis aeruginosa culture (Pasteur Culture Collection, PCC 7820) was grown in laboratory, in BG11 medium (2 L erlenmeyers), at 23–24ºC, under a light regimen of 12 h fluorescent light, 12 h dark. This PCC 7820 culture produced four microcystins variants (MC-LR, -LY, -LW, -LF), with a dominance of MC-LR. 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 procedure of Meriluoto and Spoof with the adaptations described in [20]) 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 waters' pH (6–9).

2.2. Natural waters

Ozonated (TOW) and clarified (TCW) natural waters were studied (Table 1). These waters were collected at Tavira's water treatment plant (WTP), located in western Algarve, southern Portugal, and run by Águas do Algarve, SA. Tavira's WTP treatment train consists of pre-ozonation, coagulation by aluminium polychloride with PAC addition and pH adjustment, floc blanket clarification, rapid sand filtration and chlorination.

Both waters have neutral pH, low concentration in organic matter, low SUVA values and low alkalinity. TOW is soft water and TCW is in the boundary between soft and moderately hard water. Given the low value of the specific UV absorbance (SUVA), NOM is essentially hydrophilic and with low molar mass [21]. As expected, the two waters differ in turbidity and NOM (due to

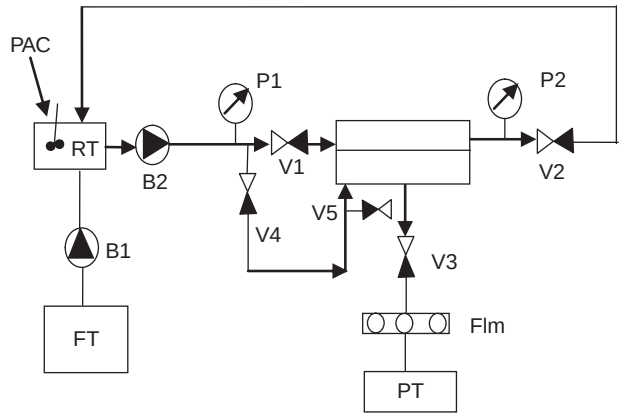

Fig.1. Flow diagram of UF apparatus (FT - Feed tank; RT - Stirred recirculating tank; PT - Permeate tank; Flm - Flowmeter; P - Manometers; B1 - Peristaltic pump; B2 - Positive displacement pump; V1, V4, V5 - Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).

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 of ca. 10 µg/L was achieved (Table 2), corresponding to guidance level 1 for recreational waters and ten times higher than WHO alert level 1 for drinking waters [22]. These waters were further supplemented with a specific volume of microcystins stock-solution to increase the concentration of dissolved cyanotoxins to ca. 5–8 µg/L MC-LR_{eq} (Table 2). Spiking with cells and dissolved microcystins resulted in slight increases in conductivity (150 to 169 µS/cm for TOW used in PAC/UF runs (Table 2) and 198–211 µS/cm for TCW) and hardness (from the divalent ions present in the growth medium), turbidity (1.7 to 3 NTU and 0.6 to 2.1 NTU) and UV absorbance (0.015 to 0.036 cm^{-1} and 0.006 to 0.016 cm^{-1}) but the nature of NOM was kept essentially hydrophilic.

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) [23] which was proven to be advantageous for the removal of microcystins [24,25]. PAC Norit SA-UF was not used in C/F/S experiments since it has an extremely fine grade (average particle diameter of 6 µm), especially designed for UF membranes 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's 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.

Table 2
Characteristics of the feed waters used in PAC/UF and PAC+C/F/S experiments (TCW or TOW spiked with *M. aeruginosa* culture and dissolved microcystins).

Parameters	UF and PAC/UF		PAC+C/F/S
	TCW	TOW	TOW
pH	7.5	7.4	7.3
Conductivity (µS/cm)	211	169	197
Turbidity (NTU)	2.10	2.97	2.94
UV_{254nm} (cm^{-1})	0.016	0.036	0.041
Chl-a (µg/L)	11	11	12
Extra MC-LR_{eq} (µg/L)	6.2	5.6	7.1
Intra MC-LR_{eq} (µg/L)	1.6	1.6	1.4

2.4. UF and PAC/UF runs

UF cellulose acetate hollow-fibre membrane from Aquasource was used. This hydrophilic membrane has a molar mass cut-off of 100 kDa and a hydraulic permeability of 250 L/(h.m^2.bar) (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 1.

The membranes were first compacted with deionised water until achieving a steady permeate flux at the pressure and cross-flow velocity to be used in the experiments. UF runs were performed at a 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 (Reynolds number of 463, laminar conditions at which the industrial UF plants are usually operated). A single-pulse PAC dosing of 10 mg/L was applied at the beginning of each run to the continuously stirred recirculation tank (Figure 1). 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 Cl_2) and flushed with deionised water for 3 min, a procedure that allowed the complete recovery of the membrane initial permeability to deionised water.

PAC/UF experiments were performed with TCW and TOW spiked with *M. aeruginosa* culture and dissolved microcystins (cells + AOM + microcystins) (Table 2). For comparison purposes, UF experiments with no PAC addition were also conducted with TCW (Table 2). Given the difficult accurate control of the permeate flow (since no automatic control was available),

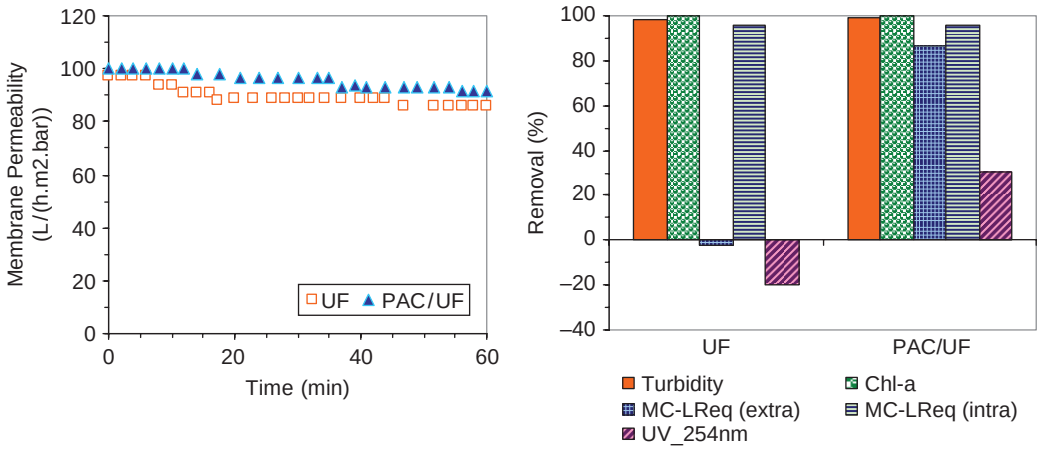

Fig. 2. Membrane permeability (left) and rejections (right) obtained during UF and PAC/UF (10 mg/L PAC) of Tavira's WTP clarified water (TCW) supplemented with *M. aeruginosa* culture and dissolved microcystins (7.8 µg/L total MC-LReq).

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

2.5. PAC+C/F/S experiments

The PAC+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 and (c) 1 h settling period. The aluminium polychloride coagulant PAX XL-14 (Quicom) was used at 50 mg/L. This dose is 2 to 2.5 times higher than the value used during Tavira's WTP regular operation (i.e. in the absence of cyanobacterial events), and was determined from earlier C/F/S lab tests designed to control the water turbidity during a cyanobacterial bloom with a chl-a concentration ten times higher than the WHO alert level 1 for drinking water. This scenario was simulated in the lab by supplementing *M. aeruginosa* culture to Tavira's ozonated water (water characteristics identical to those of TOW in Table 2 for PAC+C/F/S but with no microcystins).

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's WTP. PAC+C/F/S trials were performed in duplicate with TOW spiked with *M. aeruginosa* culture and dissolved microcystins (cells + AOM + microcystins) (Table 2). PAC doses of 5, 10 and 15 mg/L were tested.

2.6. Analytical methods

Samples were analysed for pH (at 20ºC, WTW 340 pH meter), conductivity (at 25ºC, 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, on pre-filtered samples through 0.45 µm filters) using standard methods of water analysis. For chl-a analysis, samples were filtered through GF/F filter paper and the chlorophylls were extracted using 10 mL acetone (90%). The optical densities of the extracts were measured at 665 nm and 750 nm using a Beckman DU 640B UV/VIS spectrophotometer and chl-a concentration was computed from Lorenzen equations [26]. 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's procedures [27–29] with the adaptations detailed by Ribau Teixeira and Rosa [4].

3. Results and discussion

3.1. Microcystins removal from natural waters by UF and PAC/UF

Figure 2 compares the membrane permeability and the cycle-averaged percent removal (i.e. based on the initial feed concentration and on the cycle-averaged concentration in the permeate) 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 $MC\text{-}LR_{eq}$ with an extracellular/intracellular ratio of 4.

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*

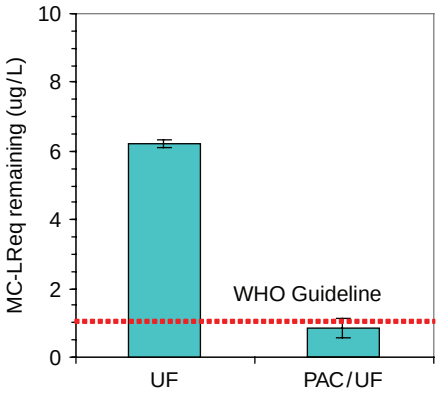

Fig. 3. Cycle-averaged concentration of microcystins in the permeate during UF and PAC/UF (10 mg/L PAC) of TCW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.8 µg/L total MC-LR$_{eq}$). Error bars represent standard deviations.

cells did not show a great membrane fouling potential. In previous trials, AOM was found to have greater detrimental impact on membrane fouling, especially for high content of polysaccharide-like compounds and multivalent ions [13]. The fact that the runs 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 corroborate the earlier finding that the PAC itself does not impose significant membrane fouling, not even in the presence of NOM [30]. Other studies reported that NOM acts as a glue that binds the PAC particles to one another and to the membrane surface, enhancing fouling [31,32].

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 2, 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$_{254nm}$, a simple experiment was performed. Cell lysis was induced to a *M. aeruginosa* culture two months old (freeze-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 3 depicts the cycle-averaged concentration of microcystins in the UF and PAC/UF permeate. 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.

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 4 presents the membrane permeability and the cycle-averaged concentrations of microcystins in the feed and 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 (humic acids-AHA and tannic acid-TA) in two different concentrations.

TOW and TCW presented similar permeability decline and removal of dissolved microcystins by PAC/UF,

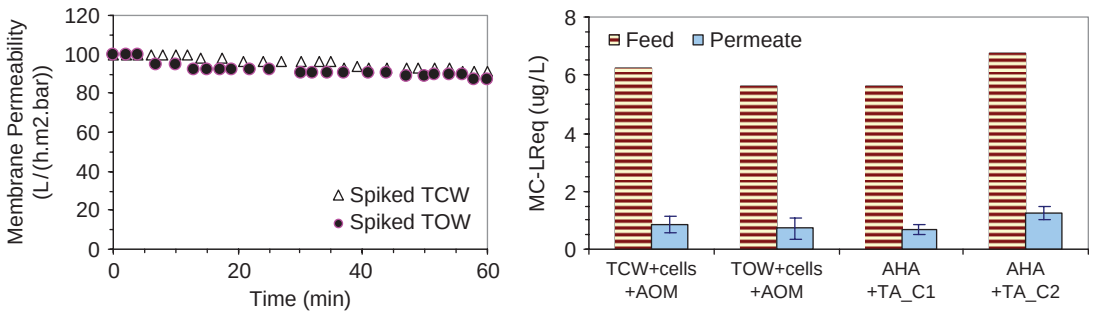

Fig. 4. Membrane permeability (left) and cycle-averaged concentration of dissolved microcystins in the feed and permeate (right) obtained during PAC/UF (10 mg/L PAC) of ozonated (TOW) and clarified (TCW) natural waters supplemented with *M. aeruginosa* culture (cells and AOM) and dissolved microcystins. Comparison is made with NOM surrogate runs (right, C1: 1 mg AHA/L+1.5 mg TA/L; C$_2$: 2.5 mg AHA/L+2.5 mg TA/L).

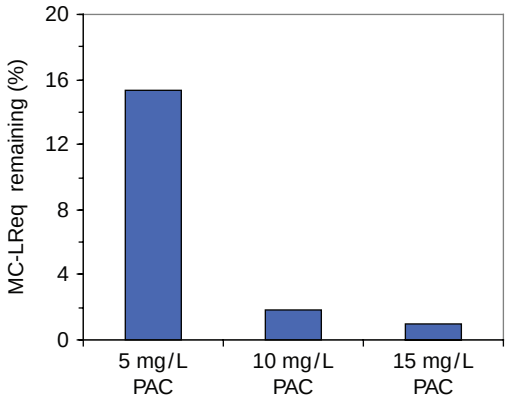

Fig. 5. Percentage of microcystins remaining after PAC adsorption kinetics performed with TCW supplemented with dissolved microcystins (5.2 µg/L MC-LR$_{eq}$ feed concentration, 1 h contact time)

which based on previous results with synthetic waters containing NOM surrogates [30,33] is not surprising since both waters have low NOM concentration of hydrophilic nature and low molar mass (Tables 1 and 2, as discussed in section 2.2) and identical low turbidity (Table 2).

In addition, the observed permeability loss is quite similar to that found in earlier experiments performed in the same conditions but with an electrolyte solution (deionised water amended with KCl to reach a final conductivity of 300 µS/cm) spiked with *M. aeruginosa* culture (which includes mono and divalent salts from the growth medium) [33]. This similar behaviour indicates no significant effect of the studied waters' background matrix on the membrane permeability loss.

Regarding the microcystins removal efficiencies, the combined effect of surface water NOM, AOM and cyanobacterial cells was not distant from that 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 µg/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 µg/L MC-LR$_{eq}$. A previous work showed that the effect of the model compounds is mostly associated with TA, since it has highs affinity for PAC Norit SA-UF and strong impairment on microcystins kinetics [34].

As for the natural waters with cells and AOM, based on preceding experiments [34], 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 µg/L MC-LR$_{eq}$). The results found for 1 h contact time and three PAC dosages are displayed in Figure 5.

Without cells and AOM, a very high removal of microcystins was achieved, respectively, 85% (15% microcystins remaining) and 98% (2% microcystins remaining) for 5 mg/L PAC and 10 mg/L PAC, which confirms the minor interference of TCW compounds onto microcystins rate of adsorption. Earlier results [34] 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 with pore blockage by some AOM compounds (segregated or from cell lysis).

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 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 6 compares the two treatment options in terms of several water quality parameters.

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

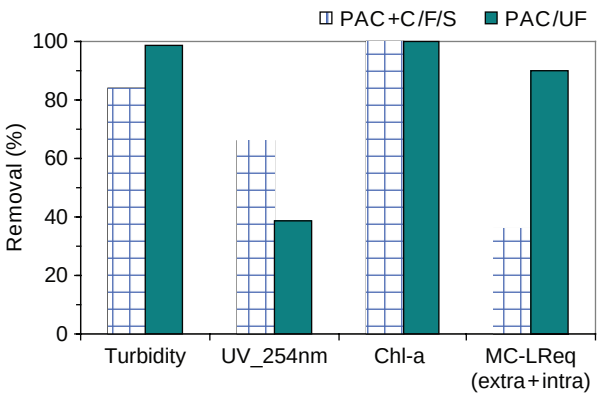

Fig. 6. PAC+C/F/S and PAC/UF performances with TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.2–8.5 µg/L MC-LR$_{eq}$, 4–5 extra/intracellular ratio, 10 mg/L PAC).

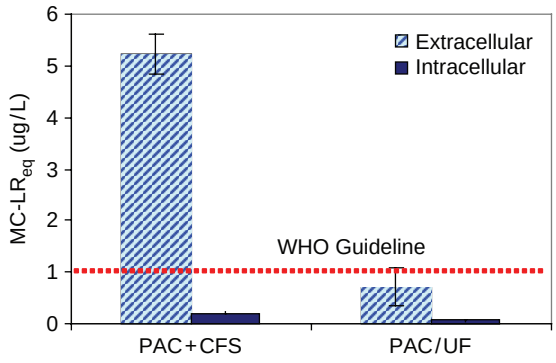

Fig. 7. Average microcystins concentration of treated waters produced by PAC+C/F/S and PAC/UF application to TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (7.2–8.5 µg/L MC-LR_{eq}, 4–5 extra/intracellular; 10 mg/L PAC)

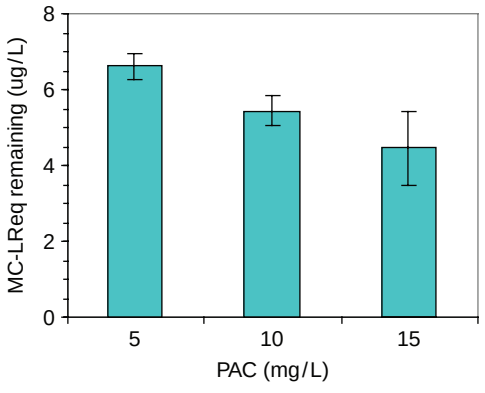

Fig. 8. Average microcystins concentration (intra+extracellular) of treated waters obtained by different PAC doses applied to PAC+C/F/S of TOW supplemented with *M. aeruginosa* culture and dissolved microcystins (8.5 µg/L MC-LR_{eq}).

ensured a safer removal of particles. Improved microcystins removal is due to the fact that PAC/UF allows longer PAC effective contact 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.* [18] concluded that during settling there was no removal of 2-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 [35] showed that high turbidity and high alum dose significantly decreased 2-methylisoborneol adsorption due to the formation of larger flocs, which induced PAC incorporation, reducing the mixing efficacy and the diffusion kinetics.

Conventional clarification exhibited better UV_{254nm} results than PAC/UF (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, although in the present study C/F/S was designed for conventional particle removal by adsorption/neutralisation rather than for enhanced coagulation of NOM). PAC/UF improved the UF permeate quality in terms of UV_{254nm} but was unable to reach the PAC + C/F/S quality.

Figure 7 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 ± 0.4 µg/L MC-LR_{eq} and intra microcystins concentration below the quantification limit (0.06 - 0.1 µg/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.

Conventional application of 10 mg/L PAC was unable to control the microcystins, resulting in an average concentration of 5.2 ± 0.4 µg/L extra MC-LR_{eq} and 0.21 ± 0.01 µg/L intra MC-LR_{eq} (the later very close to the quantification limit). PAC+C/F/S was also performed with 5 mg/L and 15 mg/L (Figure 8) and showed a slow water quality enhancement with PAC dose, from 6.6 ± 0.4 µg/L MC-LR_{eq} to 4.4 ± 1 µg/L MC-LR_{eq}. These results agree with the literature, which indicates a minimum of 20–30 mg PAC/L for effective control of MC-LR [5,24].

As a final note, and for both processes, it is important to avoid PAC addition to chlorinated waters. Gillogly *et al.* [36] found that free chlorine can oxidize adsorption sites containing 2-methylisoborneol, releasing it back to the aqueous phase. Huang *et al.* [25] found that residual chlorine reacts 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 [36].

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 the permeate quality in terms of dissolved microcystins and UV_{254nm} absorbing substances. PAC addition overcame this degradation and highly improved the permeate quality.

The investigated soft to 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% $MC\text{-}LR_{eq}$ removal 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-LReq 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.

Acknowledgments

The authors would like to thank the Portuguese Science and Technology Foundation, for providing a Ph.D. scholarship to Margarida Campinas (BD/10356/2002). Special thanks are also addressed to Águas do Algarve, SA (Portugal) for partially funding this project and for providing the natural waters, the coagulant and the PAC used in the conventional clarification experiments.

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