

A coagulation–powdered activated carbon–ultrafiltration – Multiple barrier approach for removing toxins from two Australian cyanobacterial blooms

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ABSTRACT

Cyanobacteria are a major problem for the world wide water industry as they can produce metabolites toxic to humans in addition to taste and odour compounds that make drinking water aesthetically displeasing. Removal of cyanobacterial toxins from drinking water is important to avoid serious illness in consumers. This objective can be confidently achieved through the application of the multiple barrier approach to drinking water quality and safety. In this study the use of a multiple barrier approach incorporating coagulation, powdered activated carbon (PAC) and ultrafiltration (UF) was investigated for the removal of intracellular and extracellular cyanobacterial toxins from two naturally occurring blooms in South Australia. Also investigated was the impact of these treatments on the UF flux. In this multi-barrier approach, coagulation was used to remove the cells and thus the intracellular toxin while PAC was used for extracellular toxin adsorption and finally the UF was used for floc, PAC and cell removal. Cyanobacterial cells were completely removed using the UF membrane alone and when used in conjunction with coagulation. Extracellular toxins were removed to varying degrees by PAC addition. UF flux deteriorated dramatically during a trial with a very high cell concentration; however, the flux was improved by coagulation and PAC addition.

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1. Introduction

Cyanobacteria are a major problem for the worldwide water industry as they can produce metabolites toxic to humans in addition to taste and odour compounds that make drinking water aesthetically displeasing [1–4]. It is likely that this problem will be intensified by the effects of climate change through reservoir warming [5–7]. Tropical cyanobacterial species are also becoming more prevalent in temperate climates [8]. Cyanobacteria are even being detected more frequently in colder climates, such as in Canada [9]. The effective removal of cyanobacterial metabolites is therefore an increasingly important priority for the worldwide water industry.

While it is not definitively known why cyanobacteria produce toxins, it has been suggested that toxins are evolutionary carry-overs and may function as protective secretions since researchers

have shown some cyanobacterial toxins to be potent inhibitors of aquatic invertebrate grazers [1]. Toxins are formed at all stages of cyanobacterial growth. They generally remain within the cell (intracellular toxin) until stress, damage or cell death and lysis causes their release into surrounding water (extracellular toxin) [10]. Intracellular toxin content is typically highest in the late growth phase and the toxin content has shown a positive correlation with cyanobacteria biomass [11].

Many options for treating water affected by cyanobacterial blooms exist including conventional coagulation and sand filtration, membrane filtration, powdered activated carbon (PAC) addition, granular activated carbon filtration and chemical oxidation by ozone or chlorine. In the absence of any damage to the cells, conventional treatment can be effective for the removal of the intact cells and therefore the majority of the metabolites, for example, microcystin can be up to 98% intracellular [12]. Extracellular metabolites can be effectively removed by PAC [13]. The safest option for water suppliers is to apply a multiple barrier treatment process that is capable of removing both cyanobacteria cells and dissolved metabolites. A multiple barrier process that has the potential to remove both intra- and extracellular metabolites is the combination of coagulation, PAC application and ultrafiltration (UF).

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Two studies have investigated PAC and UF for the removal of microcystin-LR (MCLR) [14,15]. Lee and Walker [14] showed that a PAC–UF system was efficient for MCLR removal using both polyethersulfone (PES) and cellulose acetate (CA) membranes. However, the removal profiles differed for the two membranes. The CA membrane, without PAC addition, did not remove MCLR while the addition of PAC resulted in 70% removal of the toxin. The removal of MCLR by PAC alone was similar to the PAC–UF system indicating that PAC adsorption was the dominant removal mechanism. In the case of the PES membrane, it was shown that this UF membrane alone had adsorptive properties for MCLR with removals similar to that of the combined PAC–UF system. Lee and Walker [14] also studied the effects of natural organic matter (NOM) on MCLR removal. While the CA membrane was not affected by NOM, flux measurements suggested the PES membranes were fouled by NOM. Campinas and Rosa [15] also investigated MCLR removal using a PAC–UF system. The impact of NOM was assessed using model compounds (a mixture of tannic and humic acids) and *Microcystis aeruginosa* culture. Constant flow experiments were performed with a hydrophilic UF hollow-fibre membrane and a mesoporous PAC. In contrast to the findings of [14], NOM had no effect on removal of toxins by their PAC–UF system at 5 mg/L of dissolved organic carbon (DOC) and 15 mg/L PAC.

Gijsbertsen-Abrahamse et al. [16] showed that UF could cause lysis of *Planktothrix agardhii*. They found that a small amount of cell-bound microcystin was released and was measured in the permeate at concentrations equal to or lower than the extracellular microcystin concentrations of the feedwater. Campinas and Rosa [17] observed that *M. aeruginosa* cell lysis occurred at all cell growth phases although greater damage was observed for older cultures. Cell lysis is an issue for a coagulation–PAC–UF system as extracellular toxin would require a higher dose of PAC, making the process more costly.

Optimisation of PAC dosing and selection of the correct UF material is important as various effects of PAC on UF flux have been reported in the literature. Some authors have reported a reduced flux, longer backwash intervals or a reduced frequency of chemical cleaning when using PAC pre-treatment [18–20]. Others have shown little effect [21–23] or increased flux when using PAC [24–26]. Some studies have shown that the membrane hydrophobicity is the key to reduced flux when pre-dosing PAC. Several studies [27–29] observed that PAC reduced flux of hydrophilic membranes and increased the flux of hydrophobic membranes. A multiple barrier approach incorporating coagulation and PAC may improve removal of cyanobacterial toxins and reduce membrane fouling by NOM, as both coagulation and PAC can remove NOM.

Previous studies detailed above have not demonstrated the removal of cyanobacterial cells from natural waters or naturally occurring blooms which may differ from laboratory cultures. No studies to date have used polyvinylidene fluoride (PVDF), a commonly used hollow fibre UF membrane, in a multiple barrier approach to investigate removal of cyanobacteria or to establish removal of both intracellular and extracellular cyanobacterial metabolites.

In this study the use of a multiple barrier approach incorporating coagulation, PAC and a PVDF UF membrane for the removal of intracellular toxin (via cell removal) and extracellular cyanobacterial toxins from naturally occurring blooms in South Australia was investigated. In order to determine the effectiveness of combining coagulation and coagulation–PAC with UF, the efficiency of each treatment barrier was assessed. Also investigated was the impact of these treatments on the UF flux.

2. Methods

2.1. Materials

The PAC used in the laboratory experiments was Acticarb PS1000 (Activated Carbon Technologies, Australia). It is a coal based, steam activated carbon. Aluminium chlorohydrate (ACH) was used as the coagulant for this study as Al_2O_3 (Omega Chemicals, Australia) and was dosed as a 23% solution. Coagulant dose was expressed in terms of Al^{3+} for direct comparison of coagulants with other studies. A commercially available membrane was used for the UF trials (Toray, Japan).

2.2. Feedwater

In November 2009 a bloom of *Anabaena circinalis* occurred in Myponga Reservoir in South Australia at a cell concentration of 460,000 cells/mL. A sample of the bloom material was collected, counted and tested for viability and used in the trial on the following day. Concentrations of cyanobacteria were quantified using gridded a Sedgewick–Rafter chamber. For dense algal populations, a gridded Sedgewick–Rafter chamber allowed for accurate cell identification and concentration without the layering of cells. To quantify *Anabaena*, the number of colonies per chamber, as well as the number of cells in 20 filaments, was determined. This method is accurate to 30%.

In March 2010 a bloom of *Microcystis flos-aquae* occurred in the Torrens Lake, Adelaide, South Australia. The samples taken from this bloom were used as the feedwater to challenge the system. *M. flos-aquae* cell numbers in the sample were 14,800,000 cells/mL which also contained a small number of *Planktothrix mougeotii*, *A. circinalis* and *M. aeruginosa* (<1%). Samples were counted and tested for viability on the same day as the trial.

2.3. Ultrafiltration – integrated membrane tests

A laboratory scale UF unit (Fig. 1) was used which consisted of hollow fibre PVDF membranes with a nominal pore size of 0.02 μm . Ten 10 cm UF fibres were potted using epoxy resin and compacted using ultrapure water (Millipore Pty Ltd, USA). Membranes were operated in an outside-in configuration at a pressure of 160 kPa. Membrane integrity was established using turbidity removal. Each experiment showed removal of turbidity down to 0.1 NTU from raw water values of 12–15 NTU. Each experiment consisted of four operation periods. The first was an ultrapure water flush, the second using only the feedwater, the third using coagulant dosing and the final using both coagulant and PAC at 20 mg/L. Coagulant and PAC were dosed into a flocculation tank agitated at 20 rpm with a detention time of 9 min. A membrane tank prior to the membrane housing ensured a total floc growth time of 11 min. Between each operation period a 2 min backwash involving air scouring and ultrapure water was performed. After each experiment the membrane was cleaned using two protocols: (1) citric acid at pH 2 and (2) NaOH at pH 10. The same membrane was used for each experiment.

2.4. Saxitoxin analysis

Samples analyzed for saxitoxin were undertaken via enzyme linked immunosorbent assay (ELISA) purchased from a commercial supplier (Abraxis LLC, USA). Samples for analyses were diluted in order to bring the samples within the working range of the assay (1:20). These analyses were carried out according to the manufacturer's protocol. The Abraxis ELISA is an antibody-based assay and cross-reactivities for the following saxitoxin analogues are: <0.2% GTX1&4, 1.3% for NEO, 23% for GTX2&3, 29% dcSTX and 100% for STX, as stated by the manufacturer. The lower limit of detec-

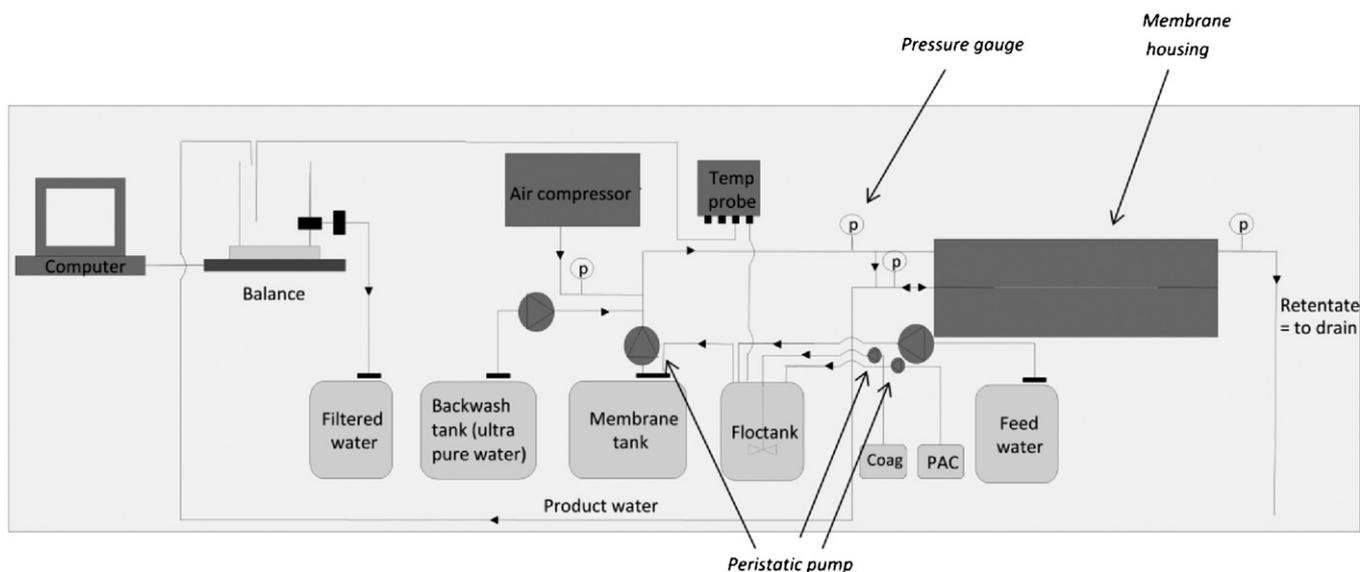


Fig. 1. Process diagram of the UF-IMS.

tion and coefficient of variation for the assay were $0.02 \mu\text{g/L}$ and $<15\%$, respectively. Samples for extracellular toxin were prepared by filtering the through a Whatman GF/C filter paper by gravity. Some cell lysis may have occurred during this process. Intracellular toxin concentration was calculated by subtracting the extracellular concentration from the total concentration.

2.5. Microcystin analysis

Prior to high performance liquid chromatography (HPLC) analysis, microcystin analogues (MCRR, MCLR, MCYR and MCLA) were concentrated from sample waters by solid phase extraction similar to the methods described in [30]. An Agilent 1100 series HPLC system consisting of a quaternary pump (G1311A), degasser (G1379A), autosampler (G1313A), column compartment (G1316A) and photodiode array detector (G1315B) driven by ChemStation software (Agilent Technologies, USA) was used for microcystin analysis. A $150 \text{ mm} \times 4.6 \text{ mm}$ Luna C18 column (Phenomenex, Australia) with a pore size of $5 \mu\text{m}$ was used. The HPLC method has a detection limit of $0.05 \mu\text{g/L}$. Full details of this analysis can be found in [31].

2.6. Dissolved organic carbon and UV_{254} absorbance analyses

Samples for DOC and UV absorbance (UV_{254}) were filtered through $0.45 \mu\text{m}$ pre-rinsed membranes. UV_{254} was measured at 254 nm through a 1 cm quartz cell using an Evolution 60 spectrophotometer (Thermo Scientific, USA). DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA).

2.7. Molecular weight distribution analyses

High performance size exclusion chromatography (HPSEC) was used for molecular weight (MW) distribution determination of NOM. The analysis was undertaken using an Alliance 2690 separations module and 996 photodiode array detector at 260 nm (Waters Corporation, USA). Phosphate buffer (0.1 M) with 1.0 M NaCl was passed through a Shodex KW802.5 packed silica column (Showa Denko, Japan) at a flow rate of 1.0 mL/min . This column provides an effective separation range from approximately 50 Da to an exclusion limit of $50,000 \text{ Da}$. Apparent MW was derived by calibration

with poly-styrene sulfonate (PSS) MW standards of 35, 18, 8 and 4.6 kDa .

2.8. Cell enumeration and viability determinations

Concentrations of cyanobacteria were quantified using gridded a Sedgewick–Rafter chamber. For dense algal populations, a gridded Sedgewick–Rafter chamber allowed for accurate cell identification and concentration without the layering of cells. To quantify *Anabaena*, the number of colonies per chamber, as well as the number of cells in 20 filaments, was determined. This method is accurate to 30% .

Cell viability was determined for each experiment by flow cytometry using a method similar to [32]. The flow cytometric analysis was performed using a FACSCalibur™ flow cytometer (Becton-Dickinson, USA). A cyanobacteria suspension was stained with SYTOX™ bacterial viability stain (Invitrogen, UK) in order to obtain a live/dead ratio. In a microfuge tube, $980 \mu\text{L}$ of cyanobacteria suspension was mixed with $20 \mu\text{L}$ of SYTOX™ stain and incubated for 7 min at room temperature. The fluorescence of the sample was detected through 510 nm (type FL1, green) and 610 nm (type FL3, red) band pass filters.

3. Results and discussion

3.1. Myponga reservoir bloom

ACH was selected as the best coagulant for the trial, based on jar tests (data not shown) comparing ACH, aluminium sulfate and a blended polyaluminium chloride coagulant similar to our previous study [38]. An ACH dose was used (4.4 mg/L Al^{3+}) to ensure that the flux decline was minimized. A flux decline using the UF membrane alone was observed (Fig. 2). The addition of ACH improved flux with no further improvement observed in the presence of PAC. Similar DOC removals were obtained when using coagulant with and without PAC addition and these removals were greater than observed using the UF membrane alone (Table 1). Removal of NOM prior to the UF membrane may enhance its longevity [33].

Fig. 3 shows the MW profiles for the Myponga feedwater during the *A. circinalis* bloom. MW profiles after treatment by the UF membrane only, coagulation and coagulation with PAC addition are also displayed. The MW profile shows that coagulation and PAC

Table 1
The removal of *A. circinalis*, UV₂₅₄ and DOC during the IMS experiment using the Myponga reservoir bloom material.

	Cells (mL)	%Removal	UV ₂₅₄ (/cm)	%Removal	DOC (mg/L)	%Removal
UF only						
Feedwater	497,000		0.47		15.2	
Memb tank	444,000	11	0.36	23	11.9	21
Permeate	0	100	0.272	42	9.9	35
ACH (4.4 mg/L Al ³⁺)						
Feedwater	384,000		0.464		15.2	
Memb tank	101,000	74	0.108	77	6.6	57
Permeate	95	100	0.081	83	4.8	69
ACH (4.4 mg/L Al ³⁺) and PAC (20 mg/L)						
Feedwater	360,000		0.469		15.4	
Memb tank	48,100	87	0.079	83	5.6	63
Permeate	0	100	0.065	86	4.4	71

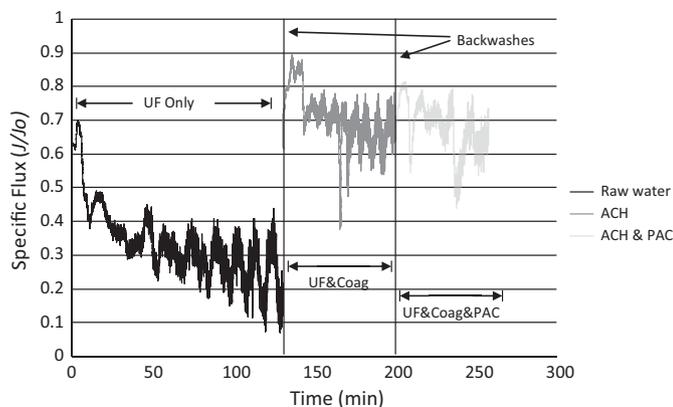


Fig. 2. Specific flux (l/jo) of the UF membrane over three periods using Myponga water with *A. circinalis* cells. Time 0–120 min using feedwater only, time 120–190 min using feedwater dosed with coagulant (ACH) and time 190–270 min dosed with coagulant and PAC (20 mg/L).

adsorption removes a greater amount of compounds in the region between 1500 and 3000 Da than the UF membrane alone. As flux was improved by coagulation and PAC addition, this suggests that removal of NOM in this MW range reduces fouling of the UF membrane. NOM of this MW range can cause pore restrictions rather than cake layer formation and removal of this MW range of compounds has been shown to improve the efficiency of microfiltration membranes [34].

Table 1 shows that the cells were completely removed by the UF membrane alone, which is consistent with the work of [12]. Cell removal was 74% by coagulation and 87% when PAC was added. Removal of DOC and UV₂₅₄ was >60% for the coagulation–UF and

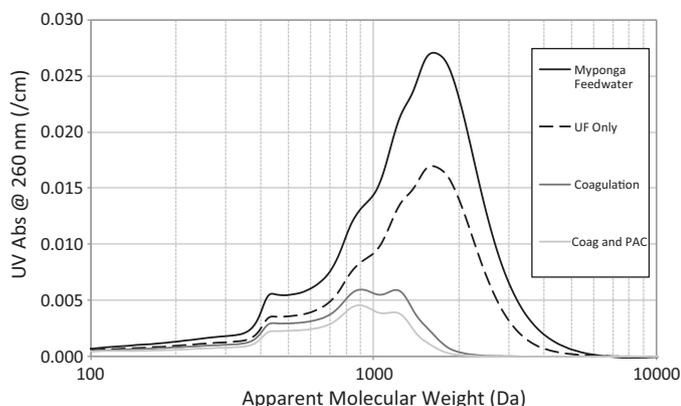


Fig. 3. Molecular weight (MW) profile of Myponga water with *A. circinalis* cells after treatment with the UF membrane only, coagulation and coagulation with PAC addition.

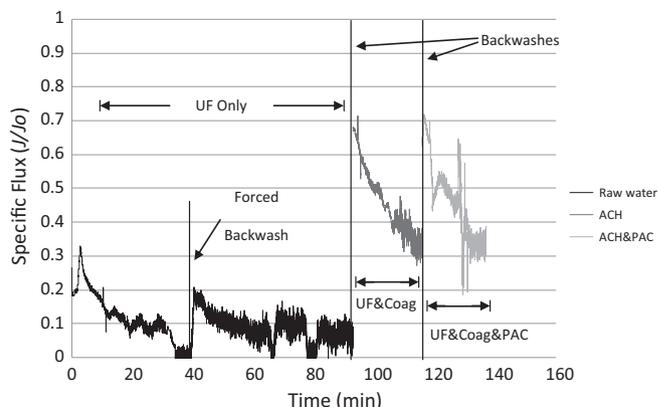


Fig. 4. Specific flux (l/jo) of the UF membrane over three periods. Time 0–90 min using Torrens water only, time 90–110 min dosed with ACH (4.4 mg/L Al³⁺) and time 110–140 min dosed with ACH (4.4 mg/L Al³⁺) with PAC (20 mg/L).

coagulation–PAC–UF. Removal of DOC and UV is higher than previously observed for reservoir water without cyanobacteria [35]. This improved efficiency in DOC and UV₂₅₄ removal is supported by the observations of [34] as discussed above.

The concentration of intracellular saxitoxin as STX equivalents (STX_{eq}) was 3.9 μg/L which was 77% of the total saxitoxins concentration (Table 2). The extracellular STX_{eq} concentration was 1.2 μg/L. Removal of intracellular saxitoxin was 87% with the UF membrane alone. Removal of intracellular saxitoxin was 46% with ACH and 74% with ACH and PAC. This is in agreement with the cell removal data which suggests that PAC addition assists coagulation. The enhancement of coagulation in the presence of PAC has been reported previously [36]. The concentration of extracellular saxitoxin was too low to calculate a meaningful removal percentage.

Table 2
Intracellular and extracellular saxitoxin concentrations and percent removal of intracellular toxin for the UF-IMS experiment using Myponga reservoir water during an *A. circinalis* bloom.

	Intra STX _{eq} (μg/L)	%Removal	Extra STX _{eq} (μg/L)
UF only			
Feedwater	3.9		1.2
Memb tank	3.7	5	0.8
Permeate	0.5	87	1.0
ACH (4.4 mg/L Al ³⁺)			
Feedwater	4.1		0.8
Memb tank	2.2	46	0.9
Permeate	0.4	90	0.7
ACH (4.4 mg/L Al ³⁺) and PAC (20 mg/L)			
Feedwater	3.9		1.0
Memb tank	1.0	74	0.5
Permeate	0.4	90	0.5

Table 3The removal of turbidity, *M. flos-aquae* cells, UV₂₅₄ and DOC during the UF-IMS experiment using Torrens water.

	Turbidity (NTU)	Cells (mL)	%Removal	UV ₂₅₄ (cm)	%Removal	DOC (mg/L)	%Removal
UF only							
Feedwater	429			0.244		13.7	
Memb tank	366			0.196	20	10.3	25
Permeate	0.22			0.099	59	4.8	65
ACH (4.4 mg/L Al ³⁺)							
Feedwater	340	13,200,000		0.232		9.6	
Memb tank	104	3,610,000	73	0.125	46	6.1	36
Permeate	0.16			0.066	72	3.4	64
ACH (4.4 mg/L Al ³⁺) and PAC (20 mg/L)							
Feedwater	549	1.48E + 08		0.227		9.6	
Memb tank	131	4,070,000	73	0.111	51	6.5	33
Permeate	0.119			0.057	75	3.2	66

3.2. Torrens lake bloom

The flux decline for the UF membrane alone was more rapid than the Myponga experiments ($T=0-90$ min) (Fig. 4). This may have been due to the higher turbidity and cell concentration in the Torrens water. The flux decline for the UF membrane alone was too high to continue filtration after 40 min and a backwash was needed to continue the experiment. A backwash was required before proceeding to the coagulation phase of the experiment. This suggests that coagulant dosing is essential for operation when a bloom of such high cell concentration occurs. The flux was similar for coagulation using 4.4 mg/L of Al³⁺ as ACH ($T=90-110$ min) and during PAC addition ($T=110-140$ min). Flux decline was approximately six times faster for Torrens feedwater than Myponga feedwater during coagulation and PAC addition. This suggests that despite coagulation or PAC addition, frequent backwashing is still required for high cell concentration feedwaters. While large differences in cell concentrations may have been the overriding factor, coagulation may also have been more efficient in the Torrens experiment due to the different cell morphologies of *M. flos-aquae* compared with *A. circinalis* in the Myponga experiment. [37] documented different coagulation performances when spherical cells (such as *Microcystis*) were compared with filamentous cells (such as *Anabaena*).

As cells were shown to be completely removed by the UF membrane alone in previous experiments and in a previous study [38], UF permeate samples were not analyzed for cell number. Turbidity measurements were used as a surrogate for cell removal, and this showed a removal of 99.5% using the UF membrane alone. Cell removal by coagulation was 73% with and without PAC (Table 3). PAC addition did not enhance the cell removal due to the high turbidity of the Torrens water. The cell removal by ACH alone was similar to the Myponga experiment. Removal of DOC and UV₂₅₄ by coagulation and PAC addition was lower than in the Myponga experiment due to a higher UV₂₅₄ and DOC concentration in the

Torrens Lake. However, removal of DOC and UV₂₅₄ by the UF membrane alone was greater in the Torrens experiment. This may have been due to denser cake layer formation on the UF surface enhancing NOM removal as implied by [39]. In the Myponga experiment, there may have been a reduced cake density due to differing cell morphology. As *Microcystis* are spherical cells they may pack more tightly in the cake layer and as *Anabaena* are filamentous, the resultant cake layer may be less dense. Similar cake density observations have been made with differing floc sizes where larger floc produces a less dense cake layer [40].

The total concentration of microcystins in the Torrens feedwater was 5.9 µg/L which was comprised of 1.5 µg/L MCRR, 3.9 µg/L MCLR and 0.5 µg/L MCLA (Table 4). The extracellular component of the total microcystin concentration was 8.5% (0.5 µg/L MCRR only). Total microcystin removal was 70% by the UF membrane alone. Removal of total microcystins by coagulation was 66% and 35% with the addition of PAC. This result is contrary to the cell removal data and suggests that some cell lysis may have occurred as the extracellular microcystin concentration was as high as 3.9 µg/L. Cell lysis has been previously observed by Campinas and Rosa [17] and may be dependent on cell age. A percent removal for extracellular microcystins was difficult to obtain due to the cell lysis; however, concentrations are presented in Table 4. This cell lysis also complicated calculation of intracellular toxin, as extracellular toxin concentration was higher in the permeate for some cases. While a study of microcystin adsorption to PVDF membranes showed adsorption of up to 35% [41] removal by this mechanism could not to be determined due to cell lysis. In our previous study [38] it appeared that adsorption of saxitoxin to a PVDF membrane only occurred during the first experiment in a set of experiments and then the adsorption capacity of the membrane was exhausted. Lee and Walker [14] also showed microcystin adsorption by PES, but not for CA. Microcystin adsorption to PES appears to be greater than for PVDF [41]. Adsorption of saxitoxin to PVDF was observed in our

Table 4

Total and extracellular microcystin concentrations and percent removals for the UF-IMS experiment using Torrens water.

	Total microcystins (µg/L)				%Removal	Extracellular microcystins (µg/L)			
	RR	LR	LA	Total		RR	LR	LA	Total
UF only									
Feedwater	1.5	3.9	0.5	5.9		0.5	0	0	0.5
Memb tank	0.9	3.5	0.7	5.0	15	0.6	0.7	0	1.3
Permeate	1.8	0	0	1.8	70	3.9	0	0	3.9
ACH (4.4 mg/L Al ³⁺)									
Feedwater	1.8	1.0	0	2.8		0.6	0	0.3	0.9
Memb tank	0.4	0.6	0	1.0	66	1.4	0	0	1.4
Permeate	1.4	0	0	1.4	49	0.4	0	0	0.4
ACH (4.4 mg/L Al ³⁺) and PAC (20 mg/L)									
Feedwater	1.9	2.5	0	4.5		0.4		0.2	0.6
Memb tank	0.8	0.6	1.5	2.9	35	0.5	0.2	0	0.7
Permeate	0.4	0	0	0.4	92	0.7	0	0	0.7

previous study [38], but only for the first experiment in a series implying that PVDF becomes saturated for saxitoxin adsorption. This toxin saturation effect was also observed by Gijsbertsen-Abrahamse et al. [16]. Adsorption of toxin to the membrane may aid removal by providing another barrier, however removal by PAC appears to be a more reliable method as seen in our previous study [38].

As the removal of total microcystins was 35% during PAC addition, the adsorption properties of the PAC may have been hindered by the coagulation process due to the floc encapsulating PAC particles and preventing metabolite adsorption [36,42]. This was observed to a greater extent in Torrens Lake than in the Myponga experiment which may have been due to the higher turbidity and cell concentration of the Torrens water. While removal of total microcystins in the permeate was 70% by UF only, removal by coagulation–UF was lower at 49%. It appears that there was a higher concentration of MCRR in the permeate than in the membrane tank, which may have been due to cell lysis. This cell lysis was not seen in the coagulation–PAC–UF experiment and the removal of total microcystins was higher at 92%.

In comparison with our previous study [38], which involved the removal of saxitoxin from cultured cyanobacteria, removal of extracellular toxin was more difficult to quantify due to cell lysis. The naturally occurring blooms tested in this study afforded much higher cell concentrations than in our previous study and this greatly affected the flux of the UF, causing a faster flux decline and required a higher dose of coagulant to improve the flux of the UF.

4. Conclusion

A multiple barrier approach incorporating coagulation, PAC and UF was investigated for the removal of intracellular and extracellular cyanobacterial toxins from two Australian blooms. Two dominant species occurred in these blooms: *A. circinalis* and *M. flos-aquae* which produced the toxins saxitoxin and microcystin, respectively. The impact of coagulation and PAC addition on the UF membrane flux was also studied.

Cyanobacterial cells were completely removed in the Myponga experiment using coagulation–PAC–UF. This system removed 90% of intracellular saxitoxin in the Myponga experiment and 92% intracellular microcystin from the Torrens experiment. It was difficult to quantify the removal of extracellular toxin by the system due to low concentrations and cell lysis. UF flux deteriorated dramatically during the Torrens Lake trial due to a very high cell concentration however, the flux was improved by coagulation and PAC addition. Coagulation and PAC addition removed cells and NOM prior to contact with the UF, improving the flux of the UF.

The application of a coagulation–PAC–UF is warranted as cyanobacteria can compromise water quality and treatment in many ways. This system can provide a multi-barrier treatment approach which is favoured in risk-based approaches including global water safety plans.

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References

- [1] W.W. Carmichael, Cyanobacterial secondary metabolites—the cyanotoxins, *J. Appl. Bacteriol.* 72 (1992) 445–459.
- [2] W.W. Carmichael, The toxins of cyanobacteria, *Sci. Am.* 270 (1994) 78–86.
- [3] I. Chorus, J. Bartram, *Toxic Cyanobacteria in Water: A Guide to Their Public Health Consequences Monitoring and Management*, World Health Organization/E&FN Spon/Routledge, London, 1999, ISBN: 0-419-23930-8.
- [4] L.E. Fleming, C. Rivero, J. Burns, C. Williams, J.A. Bean, K.A. Shea, J. Stinn, Blue green algal (cyanobacterial) toxins surface drinking water, and liver cancer in Florida, *Harmful Algae* 1 (2002) 157–168.
- [5] H.W. Paerl, J. Huisman, Climate. Blooms like it hot, *Science* 320 (2008) 57–58.
- [6] V.J. Paul, Global warming and cyanobacterial harmful algal blooms, in: K.H. Hudnell (Ed.), *Cyanobacterial Harmful Algal Blooms: State of the Science Research Needs Series: Advances in Experimental Medicine and Biology* 619 (2008) XXIV, 950.
- [7] T.W. Davis, D.L. Berry, G.L. Boyer, C.J. Gobler, The effects of temperature and nutrients on the growth and dynamics of toxic and non-toxic strains of Microcystis during cyanobacteria blooms, *Harmful Algae* 8 (5) (2009) 715–725.
- [8] I.R. Falconer, *Cyanobacterial Toxins in Drinking Water Supplies*. Cyndrospermopsins and Microcystins, CRC Press, Boca Raton, FL, 2005.
- [9] A. Giani, D.F. Bird, Y.T. Prairie, J.F. Lawrence, Empirical study of cyanobacterial toxicity along a trophic gradient of lakes, *Can. J. Fish. Aquat. Sci.* 62 (2005) 2100.
- [10] K. Sivonen, G. Jones, *Cyanobacterial Toxins*, in: I. Chorus, E. Bartram, F.N. Spon (Eds.), *Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring, and Management*, New York, 1999, pp. 41–111.
- [11] W.W. Carmichael, Health effects of toxin-producing cyanobacteria: the CyanoHABs, *Hum. Ecol. Risk Assess.* 7 (5) (2001) 1393–1407.
- [12] C.W.K. Chow, S. Panglish, J. House, M. Drikas, M.D. Burch, R. Gimbel, A study of membrane filtration for the removal of cyanobacterial cells, *J. Water SRT* 46 (6) (1997) 324–334.
- [13] G. Newcombe, Removal of natural organic material and algal metabolites using activated carbon, in: G. Newcombe, D. Dixon (Eds.), *Interface Science and Technology*, vol. 10, Interface Science in Drinking Water Treatment – Theory and Application, Elsevier, 2006, pp. 133–153 (Chapter 8).
- [14] J. Lee, H.W. Walker, Effect of process variables and natural organic matter on removal of microcystin-LR by PAC/UF, *Environ. Sci. Technol.* 40 (23) (2006) 7336–7342.
- [15] M. Campinas, M.J. Rosa, Removal of microcystins by PAC/UF, *Sep. Purif. Technol.* 71 (2010) 114–120.
- [16] A.J. Gijsbertsen-Abrahamse, W. Schmidt, I. Chorus, S.G.J. Heijman, Removal of cyanotoxins by ultrafiltration and nanofiltration, *J. Membr. Sci.* 276 (2006) 252–259.
- [17] M. Campinas, M.J. Rosa, Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, *Sep. Purif. Technol.* 70 (2010) 345–353.
- [18] S. Adham, V. Snoeyink, M. Clark, J.L. Bersillon, Predicting and verifying organics removal by PAC in an ultrafiltration system, *J. AWWA* 12 (1991) 81–91.
- [19] K. Konieczny, G. Klomfas, Using activated carbon to improve natural water treatment by porous membranes, *Desalination* 147 (2002) 109–116.
- [20] C. Lee, S. Bae, S. Han, L. Kang, Application of ultrafiltration hybrid membrane processes for reuse of secondary effluent, *Desalination* 202 (2007) 239–246.
- [21] S. Yantsios, A. Karabelas, An experimental study of humic acid and powdered activated carbon deposition on UF membranes and their removal by backwashing, *Desalination* 140 (2001) 195–209.
- [22] M. Tomaszewska, S. Mozia, Removal of organic matter from water by PAC/UF system, *Water Res.* 36 (2002) 4137–4143.
- [23] Y. Matsui, T. Sanogawa, N. Aoki, S. Mima, T. Matsushita, Evaluating submicron-sized activated carbon adsorption for microfiltration pretreatment, *Water Sci. Technol.* 6 (1) (2006) 149–155.
- [24] C.W. Li, Y.S. Chen, Fouling of UF membrane by humic substances: effects of molecular weight and powder-activated carbon (PAC) pre-treatment, *Desalination* 170 (2004) 59–67.
- [25] P. Zhao, S. Takizawa, H. Katayama, S. Ohgaki, Factors causing PAC cake fouling in PAC-MF (powdered activated carbon-microfiltration) water treatment systems, *Water Sci. Technol.* 51 (6–7) (2005) 231–240.
- [26] A. Zularisam, M.S. Ismail, M. Sakinah, H. Ozaki, The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes, *Desalination* 212 (2007) 191–208.
- [27] G. Crozes, C. Anselme, J. Mallevalle, Effect of adsorption of organic matter on fouling of ultrafiltration membranes, *J. Membr. Sci.* 84 (1993) 61–77.
- [28] C.F. Lin, S.H. Liu, O. Hao, Effect of functional groups of humic substances on UF performance, *Water Res.* 35 (10) (2001) 2395–2402.
- [29] S. Mozia, M. Tomaszewska, A. Morawski, Studies on the effect of humic acids and phenol on adsorption–ultrafiltration process performance, *Water Res.* 39 (2005) 501–509.
- [30] B.C. Nicholson, J. Rositano, M.D. Burch, Destruction of cyanobacterial peptide hepatotoxins by chlorine and chloramine, *Water Res.* 28 (6) (1994) 1297–1303.
- [31] L. Ho, G. Onstad, U. von Gunten, S. Rinck-Pfeiffer, K. Craig, G. Newcombe, Differences in the chlorine reactivity of four microcystin analogues, *Water Res.* 40 (6) (2006) 1200–1209.
- [32] R.H. Regel, J.M. Ferris, G.G. Ganf, J.D. Brookes, Algal esterase activity as a bio-measure of environmental degradation in a freshwater creek, *Aquat. Tox.* 59 (3–4) (2002) 209–223.
- [33] M.B. Dixon, M. Drikas, J.Y. Morran, Extending membrane longevity by using MIEEX as a pre-treatment, *J. Water SRT* 59 (2010) 2–3.
- [34] R. Fabris, E.K. Lee, C.W.K. Chow, V. Chen, M. Drikas, Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes, *J. Membr. Sci.* 289 (1–2) (2007) 231–240.
- [35] N. Lee, G. Amy, J.-P. Croue, H. Buisson, Morphological analyses of natural organic matter (NOM) fouling of low-pressure membranes (MF/UF), *J. Membr. Sci.* 261 (1–2) (2005) 7–16.

- [36] D. Cook, G. Newcombe, P. Sztajn bok, The application of powdered activated carbon for MIB and geosmin removal: predicting PAC doses in four raw waters, *Water Res.* 35 (5) (2001) 1325–1333.
- [37] R. Henderson, S.A. Parsons, B. Jefferson, The impact of algal properties and pre-oxidation on solid–liquid separation of algae, *Water Res.* 42 (8–9) (2008) 1827–1845.
- [38] M.B. Dixon, Y. Richard, L. Ho, C.W.K. Chow, B.K. O'Neill, G. Newcombe, Integrated membrane systems incorporating coagulation, activated carbon and ultrafiltration for the removal of toxic cyanobacterial metabolites from *Anabaena circinalis*, *Water Sci. Technol.*, in press.
- [39] K.J. Kim, V. Chen, A.G. Fane, Ultrafiltration of colloidal silver particles: flux, rejection, and fouling, *J. Colloid Interface Sci.* 155 (1993) 347–359.
- [40] J. Wang, J. Guan, S.R. Santiwong, T.D. Waite, Characterization of floc size and structure under different monomer and polymer coagulants on microfiltration membrane fouling, *J. Membr. Sci.* 321 (2) (2008) 132–138.
- [41] J. Lee, H.W. Walker, Mechanisms and factors influencing the removal of microcystin-LR by ultrafiltration membranes, *J. Membr. Sci.* 320 (1–2) (2008) 240–247.
- [42] L. Ho, G. Newcombe, Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation, *Water Res.* 39 (15) (2005) 3668–3674.