INTEGRATED MEMBRANE SYSTEMS FOR TOXIC CYANOBACTERIA REMOVAL

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ABSTRACT

As membrane technology improves and becomes more cost effective for water authorities, coupled with consumers and regulators demand for higher quality water, the application of membrane treatment will inevitably expand in the international water industry. While taste and odour (T&O) compounds and toxins produced by cyanobacteria (blue-green algae) may not be the key drivers for the application of membrane technology, they do warrant further research into the application of such treatment for their mitigation. This study assessed the application of an integrated membrane system (IMS) incorporating ultrafiltration (UF) in conjunction with coagulation and powdered activated carbon (PAC), for the removal of cyanobacteria and their metabolites. The cyanobacterial metabolite studied was saxitoxin from the cyanobacterial species *Anabaena circinalis*.

INTRODUCTION

Blue-green algae (cyanobacteria) are a major problem for the water industry as they can produce metabolites toxic to humans in addition to taste and odour (T&O) compounds that make drinking water aesthetically displeasing (Carmichael, 1992, 1994; Chorus and Bartram, 1999; Fleming *et al*., 2002). It is likely that this problem will be intensified by the effects of climate change through reservoir warming (Paerl and Huisman, 2008; Paul, 2008; Davis *et al.,* 2009). The effective removal of cyanobacterial metabolites is therefore an increasingly important research priority.

Ultrafiltration (UF) is a potential solution for dealing with blooms of toxic cyanobacteria. In the past, coagulation and sand filtration has been successfully used for removal of cyanobacteria (Drikas *et al*., 2001), however as membrane technology has become more economically viable, the demand for information on the application of membranes for cyanobacterial metabolite removal has increased. UF pore size is a key matter as cyanobacterial metabolites should permeate such membranes. However, if cyanobacterial metabolites remain within the cyanobacterial cells, (for example, microcystin can be up to 98% intracellular (Chow *et al.,* 1997)), UF might be effective through the removal of these intact cells. With regard to extracellular metabolites, powdered activated carbon (PAC) has been shown to be an effective method for removal of toxins and T&O compounds, including 2-methylisoborneol and geosmin (Newcombe, 2006). Our study aimed to investigate an integrated membrane system

(IMS) incorporating coagulation, PAC and UF for the removal of intracellular and extracellular cyanobacterial metabolites.

The aim of this study was to investigate the use of an IMS system incorporating coagulation, PAC and UF for the removal of intracellular and extracellular cyanobacterial metabolites and the impact of these treatments on the UF flux. This is the first IMS study to investigate the removal of cultured cyanobacterial blooms to establish removal of both intracellular and extracellular saxitoxin from *Anabaena circinalis*.

METHOD

Cell Culture

A laboratory strain of *A. circinalis* (ANA 188B), known to produce saxitoxins, was grown in artificial seawater medium (ASM-1) (Gorham *et al*., 1964) at 25^{o}C under continuous illumination. Cultures were harvested at the late exponential phase of growth, which corresponded to 14d after inoculation.

Analysis

Samples analysed for saxitoxin were undertaken via enzyme linked immunosorbent assay (ELISA) purchased from 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 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 detection and coefficient of variation for the Abraxis ELISA assays were 0.02ppb and <15%, respectively. Conversion factors (Oshima, 1995) were used to express the toxicity of the sum of the variants as STX-equivalents (STX_{eq}) owing to the differing toxicities and concentrations of the individual saxitoxin variants.

A. circinalis cells were enumerated on a compound microscope in a Sedgewick–Rafter counting chamber after preservation in Lugol's iodine. Cell counts were carried out to a minimum precision of 30%.

A Hach ratio turbidimeter (model 2100AN) was used to give a direct reading of the turbidity of a sample in NTU.

Samples for dissolved organic carbon (DOC) and UV absorbance (UVabs) were filtered through 0.45µm pre-rinsed membranes. UVabs was measured at 254nm through a 1cm quartz cell. DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA).

UF-IMS laboratory testing

A laboratory scale UF unit (Fig. 1) was used which consisted of hollow fibre PVDF membranes with a 0.02µm pore size. Ten 10cm UF fibres were potted using epoxy resin and compacted using ultrapure water. Membranes were operated in an outside-in configuration at a pressure of 160kPa. Water quality parameters of the raw water used were (DOC) 4.0-6.2mg/L, UVabs 0.060 to 0.065cm^{-1} and turbidity 12-15NTU. Cultured *A. circinalis* cells were dosed at 100,000cells/mL into the feedwater. Membrane integrity was established using turbidity removal with each experiment showing

removal of turbidity to 0.1NTU. Each experiment consisted of four operation periods. The first was an ultrapure water flush, the second using only the feedwater (Raw water from Palmer water treatment plant dosed with *A. circinalis* cells), the third using coagulant dosing and the final using both coagulant and PAC (Acticarb PS1000) at 20mg/L. Three coagulants were trialed at 2.2mg/L of Al^{3+}: aluminium chlorohydrate (ACH), aluminium sulphate (alum) as $Al_2(SO_4)_3.18H_2O$ and high performance aluminium chlorohydrate (HPAC), which was developed by the Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences. The coagulant is a tailored formulation with high Al_{13} polymer speciation, designed for improved organics removal. Coagulant and PAC were dosed into a flocculation tank agitated at 20rpm with a detention time of 9mins. A membrane tank ensured a total floc growth time of 11mins. Between each operation period a 2min 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.

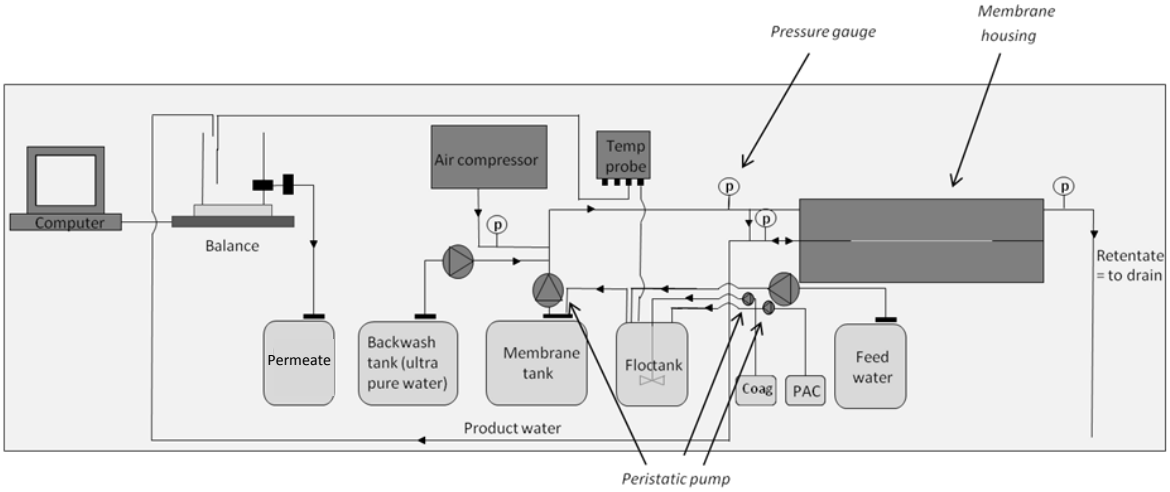

Fig.1: Process diagram of the UF-IMS

RESULTS AND DISCUSSION

Flux Decline

The decline in specific flux of the UF membrane alone fed with Palmer water dosed with *A. circinalis* cells is shown in Fig. 2 (T = 0-120min). The addition of coagulants improved flux with little difference between the coagulants (T = 120-190min). The addition of PAC further improved flux for HPAC but had little impact on the flux for the other two coagulants (T = 190-270min).

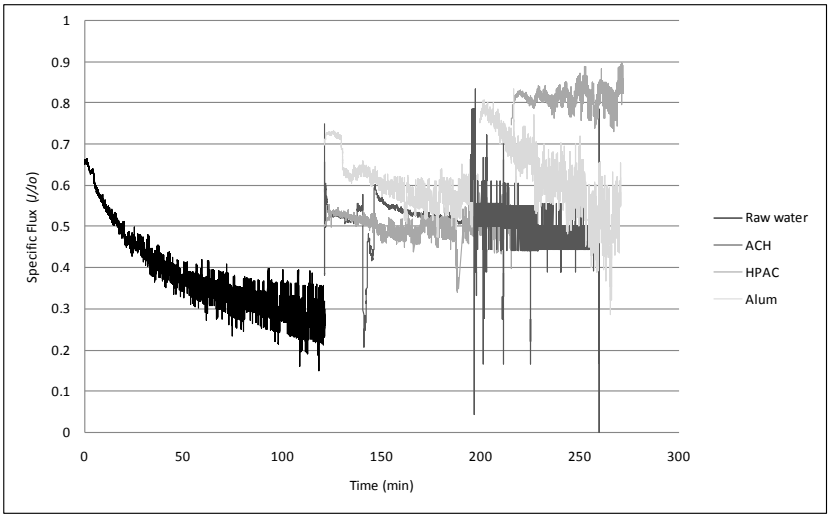

Fig.2: Specific Flux (J/Jo) of the UF membrane over three periods of dosing *A. circinalis* cells. Time 0 to 120mins using feedwater only, time 120 to 190min using feedwater dosed with coagulants (ACH, HPAC and alum) and time 190 to 270min dosed with coagulants and PAC (20mg/L).

Cell Removal

As expected, the UF membrane completely removed each cyanobacterial species under the conditions tested (results not shown), which has also been observed in a previous study by Chow *et al.* (1997) for *Microcystis aeruginosa* cells. Cell concentrations for the *A. circinalis* experiments ranged between 67,000-202,000cells/mL. Coagulation using HPAC and ACH removed 95% of the *A. circinalis* cells while alum coagulation only removed 65% (Fig. 3). The addition of PAC did not improve the removal of *A. circinalis* cells using HPAC and ACH. However, the use of PAC in conjunction with alum improved removal to 85%.

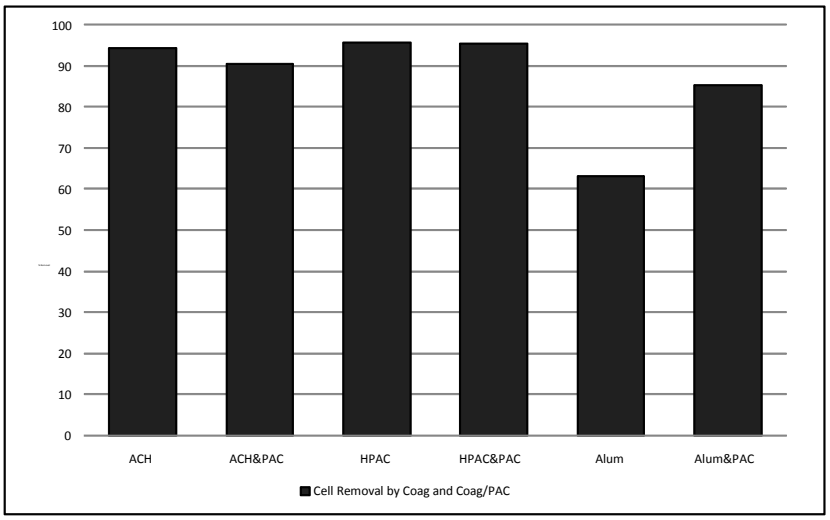

Fig.3: Percent removal of *A. circinalis* cells using coagulants, ACH, HPAC and alum (2.2mg/L of Al^{3+}) both with and without PAC (20mg/L).

Saxitoxin Removal

In the *A. circinalis* experiments, the total saxitoxin (intracellular and extracellular components) concentration was between 2.2-2.7μg/L STX_{eq} in the feedwater to the UF membrane, of which 31-38% was extracellular (0.7-0.8μg/L STX_{eq}). Fig. 4 shows that under all test conditions, greater than 95% removal of intracellular saxitoxin was achieved in the membrane tank. The addition of PAC removed up to 46% of the extracellular toxin and was most effective when used in conjunction with ACH. Coagulation may hinder the removal of cyanobacterial metabolites by PAC due to the floc encapsulating PAC particles and preventing metabolite adsorption (Cook *et al.*, 2001; Ho and Newcombe, 2005).

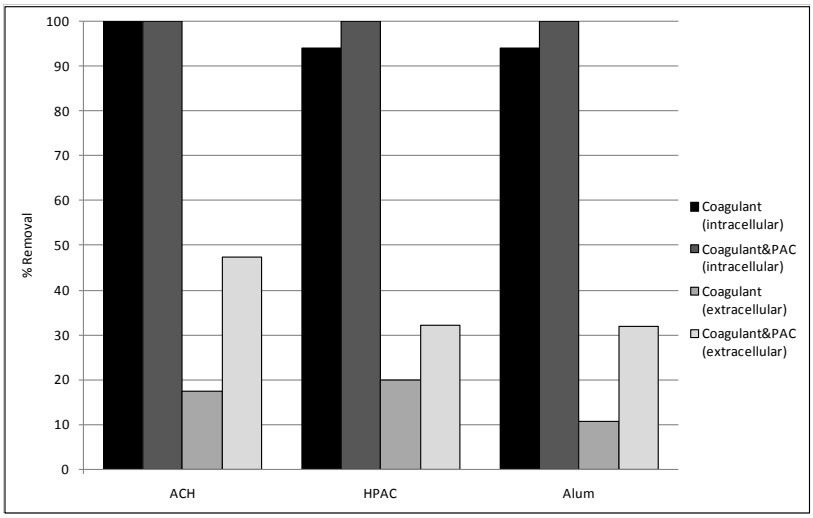

Fig.4: Percent removal of intracellular and extracellular saxitoxin using coagulants ACH, HPAC and alum (2.2mg/L of Al3+) with and without PAC (20mg/L).

During the IMS process incorporating coagulation, PAC and UF membrane, PAC adsorption was the major mechanism for the removal of extracellular saxitoxin as there was no further removal by the membranes. This was evident when using HPAC and alum as the coagulants. However, when using ACH as the coagulant during the IMS process an improvement in extracellular saxitoxin removal was observed (Fig. 5). The ACH experiment was the first in the series that was conducted and was carried out on the virgin UF membrane. It is likely that there was a larger component of extracellular saxitoxin adsorption to the membrane fibres before the fibres became saturated with saxitoxins resulting in lower extracellular removals for the subsequent trials using HPAC and alum as the coagulants. This is consistent with other previous studies (Chow *et al.*, 1997; Gijsbertsen-Abrahamse *et al.*, 2006; Lee and Walker, 2006; Campinas and Rosa, 2010).

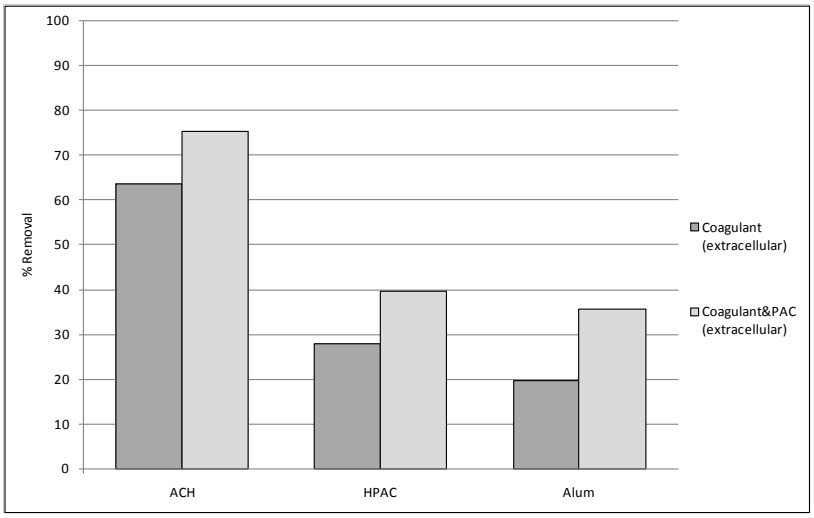

Fig.5: Percent removal of extracellular saxitoxin in the UF permeate after pretreatment using coagulants ACH, HPAC and alum both with and without PAC at 20mg/L.

CONCLUSIONS

An IMS (incorporating coagulation, PAC and UF) was investigated for the removal of intracellular and extracellular saxitoxin from *A. circinalis*. The impact of coagulation and PAC addition on the UF membrane flux was also studied.

A. circinalis cells were completely removed using the UF membrane alone as expected; however, when coagulation was used, cells were also removed prior to the UF membrane. Alum was the least effective coagulant for this purpose. Intracellular metabolites were removed by the UF membrane alone. Intracellular metabolites were removed prior to the UF membrane by coagulation. Extracellular metabolites were removed by PAC addition; however, coagulation may have hindered this removal. HPAC with PAC was the superior method for maximum UF specific flux.

ACKNOWLEDGEMENTS

This research was funded by grants from the American Water Works Research Foundation / Water Research Foundation (AwwaRF/WaterRF Project 4016; Project Manager Djanette Khiari), Water Quality Research Australia and United Water International.

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BRIEF BIOGRAPHY OF PRESENTER

Mike is currently the R&D Engineer for the Adelaide Desalination Project but has been working within SA Water at the Australian Water Quality Centre for 7 years in the field of water treatment research. Previously he has worked with MIEX, adsorbents and membrane technology with a focus on NOM removal as well as working with integrated membrane systems for the removal of blue green algal toxins and taste and odour compounds. He is completing his PhD in this field with The Adelaide University School of Chemical Engineering. Mike is also the Convenor of the AWA Young Water Professionals in South Australia and the 2009 YWP of the Year in SA.