INTEGRATED MEMBRANE SYSTEMS FOR THE REMOVAL OF CYANOBACTERIAL TOXINS AND TASTE AND ODOUR COMPOUNDS

Mike Dixon

BTech (Forensic and Analytical), BSc (Hons)
Flinders University, Adelaide, South Australia

This thesis is submitted for the degree of Doctor of Philosophy

in

School of Chemical Engineering

at

The University of Adelaide

December 2010
Adelaide Australia

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Abstract

Cyanobacteria are a major problem for the water industry as they can produce metabolites toxic to humans in addition to T&O compounds that make drinking water aesthetically displeasing. It is likely that this problem will be intensified by the effects of climate change through reservoir warming. Tropical cyanobacterial species are also becoming more prevalent in more temperate climates. The effective removal of cyanobacterial metabolites is therefore an increasingly important priority for the worldwide water industry.

Integrated membrane systems (IMSs) provide a potential water treatment method for the removal of cyanobacteria and their metabolites. The four types of membranes that have been applied for drinking water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The main parameter controlling the use of membranes for a particular application is normally the pore size. In general, important factors that affect membrane filtration are; pore size of the membrane compared with the size of the particles or molecules, surface chemistry of the membrane (charge, hydrophobicity), flux, recoveries and the degree of fouling.

Very few studies have investigated IMS for the removal of extracellular cyanobacterial metabolites and no studies are reported in the literature for these systems for the removal of cyanobacteria. In addition, no published literature is available on the removal of cylindrospermopsin or saxitoxin using membranes.

In general, high molecular weight cut-off membranes such as MF and UF may be used to remove cyanobacterial cells and intracellular cyanobacterial metabolites, while low molecular weight cut-off membranes such as NF and RO of the appropriate size range have the potential to remove a range of extracellular cyanobacterial metabolites. For a water supplier to be confident of removing both intracellular and extracellular metabolites, an integrated system with membrane technology paired with another treatment (possibly another membrane) is required.

This study assessed the application of IMS including UF and NF membranes, used in conjunction with coagulation and powdered activated carbon (PAC), for the removal cyanobacteria and their metabolites. The cyanobacteria *Microcystis aeruginosa*, *Anabaena circinalis* and *Cylindrospermopsis raciborskii* were studied, and the cyanobacterial metabolites cylindrospermopsin (CYN), microcystins, geosmin (GSM) and 2-methylisoborneol (MIB) were also investigated.

A rapid bench scale membrane test (RBSMT) unit was used to test NF membranes for removal of the cyanobacterial metabolites, microcystin, CYN, MIB and GSM. Results indicate that NF fouling can be caused by the cyanobacterial metabolites themselves. Each of the cyanobacterial metabolites were effectively removed to greater than 90% on average by NF membranes with molecular weight cut-off (MWCO) < 300Da (tight NF). A lower MWCO NF membrane (loose NF) provided improved removal of the neutral cyanobacterial metabolites (CYN, MIB and GSM) over the 220hr test period which may have been due to pore fouling. Removal of MCLR decreased over the 220hr test period in some tests.

The effect of fouling of the NF membranes and its impact on removal of cyanobacterial metabolites was studied in two treated waters of different NOM concentration,

Palmer water (average dissolved organic carbon concentration, DOC = 3.5 mg/L) and Myponga water (average DOC = 5.8 mg/L). The flux decline and the metabolite removal was the same in both waters throughout the trial, indicating that fouling was similar in the two waters. The results of our study showed that tight NF membranes removed MIB and GSM to above 75% and microcystin analogues and CYN to above 90%. MCRR, MCYR and MCLR removal was 50-80% by the loose NF membrane. MCRR appeared to be the least well removed of the variants while MCLA removal was >95%. This result is surprising as MCLA has the lowest molecular weight of the four variants and MCRR has the highest. However, the net charge of MCLA is two and zero for MCRR. Interestingly, this result is supportive of the observation that MCRR is the most readily removed by activated carbon, and MCLA is the least, suggesting a size exclusion effect, possibly due to a higher hydrodynamic diameter of MCLA, for both processes (permeation through membrane pores and diffusion through activated carbon pores). This finding warrants further investigation but this was not within the scope of this study.

While NOM concentration had no impact on the removal of most cyanobacterial metabolites, if a loose NF is selected to avoid NOM fouling then removal of cyanobacterial metabolites may be less effective.

This study has shown that NF can be an efficient treatment process for the removal of extracellular cyanobacterial metabolites and can be effective as the final step in an IMS. In general the removals are as expected with respect to the molecular weight of the compound and the MWCO of the membrane; however, molecular structure can also influence removals. In particular, nanofiltration is an effective process for the removal of MCLA, a compound that is recalcitrant to activated carbon removal and is less readily oxidised by chlorine than the other microcystin variants.

An IMS incorporating coagulation, PAC and UF was investigated for the removal of intracellular and extracellular cyanobacterial metabolites. Three species and their metabolites were studied: *A. circinalis, C. raciborskii* and *M. aeruginosa*. The impact of coagulation and PAC addition on the UF membrane flux was also studied. After testing the UF-IMS using Palmer WTP water, two natural blooms were used to further challenge the IMS. Similar cyanobacterial metabolite removals were observed for each feedwater.

Cyanobacterial cells were completely removed using a UF membrane alone and when UF was used in conjunction with coagulation. Alum was the least effective coagulant for this purpose. Extracellular metabolites were removed by PAC addition; however, coagulation hindered this removal in some instances due to entrapment of the PAC particles within flocs. UF membrane fouling by NOM was reduced by coagulation and PAC addition. A specialized blended coagulant combined with PAC was the superior coagulant for reducing fouling of the membrane.

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

Declaration

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Acknowledgments

I wish to thank the following people and organizations for their support throughout my PhD studies:

- Water Research Foundation, Water Quality Research Australia, United Water International, SA Water (Australian Water Quality Centre) and Veolia North America for their contributions to this project.
- The project advisory committee from Water Research Foundation members Zdravka Doquang, Samer Adham and Dawn Lei for their advice on the direction of this project.
- Djanette Khiari, the project manager from the Foundation for her consistent support of the project.
- Intern students Jennifer Dreyfus, Charlotte Falconet and Yann Richard from the School of Chemistry, Physics and Electronics in Lyon, France for their efforts in the laboratory at the Australian Water Quality Centre.
- Jules Leach from the Australian Water Quality Centre for her tireless efforts in the lab growing algae; one of the most frustrating aspects to this study.
- My supervisors Lionel Ho, Chris Chow and Gayle Newcombe from the Australian Water Quality Centre for their daily support, sound advice and expertise in water research.
- My principal supervisor Brian O’Neill for support from the School of Chemical Engineering at The University of Adelaide.

Preface

This thesis is submitted as a portfolio of publications according to the "PhD Rules & Specifications for Thesis" of the University of Adelaide. The journals in which the papers were published or submitted are closely related to the research field of this work.

The main body of the thesis is based on the following four papers:

1. Dixon M.B., Falconet C., Ho L., Chow C.W.K., O'Neill B.K. and Newcombe G. (2010) Nanofiltration for the removal of algal metabolites and the effects of fouling**,** *Water Science and Technology*, 61(5), 1189-1199.

2. Dixon M.B., Falconet C., Ho L., Chow C.W.K., O'Neill B.K. and Newcombe G. (2011) Removal of cyanobacterial metabolites by nanofiltration from two treated waters, *Journal of Hazardous Materials*, 188(1-3), 288-295.

3. Dixon M.B., Richard Y., Ho L., Chow C.W.K., O'Neill B.K. and Newcombe G. (2011) Integrated membrane systems incorporating coagulation, activated carbon and ultrafiltration for the removal of toxic cyanobacterial metabolites from Anabaena circinalis, *Water Science and Technology*, 63(7) 1405-1411.

4. Dixon M.B., Richard Y., Ho L., Chow C.W.K., O'Neill B.K. and Newcombe G. (2011) A coagulation - powdered activated carbon - ultrafiltration multiple barrier approach for removing toxins from two Australian cyanobacterial blooms, *Journal of Hazardous Materials*, 186(2-3), 1553-1559.

Each author had differing contributions to the above publications which is noted below and a percentage of total preparation time for each paper indicated. For all experiments Mike Dixon (51%) carried out the detailed experimental plan, undertook laboratory equipment design and construction, monitored the progress of the experiment, undertook trouble shooting, interpreted results and prepared the manuscript. Charlotte Falconet and Yann Richard (33% on respective papers) were intern students that executed the experiments in the laboratory and undertook toxin and taste and odour analyses. Supervisors Lionel Ho (5%), Gayle Newcombe (5%) and Chris Chow (5%) assisted with interpretation of the results and reviewed the manuscripts. Brian O'Neill offered support from Adelaide University and reviewed manuscripts (1%).

Relevant components of the work have been published as peer reviewed conference papers, peer-reviewed conference abstracts and as industry reports. These have been included in the thesis as appendices.

a) Ho L., Dixon M., Hoefel D., Falconet C., McDowall B., Chow C., Saint C. and Newcombe G. Tightening the net on blue-green algae: Application of novel filtration processes. *Proceedings of the AWA South Australian Regional Conference and Operators Forum*, August 2009, Adelaide, Australia.

b) Dixon M., Ho L., Chow C., Newcombe G., Croue, J-P., Treuger, R., Alloway, C. And Cigana, J. *Water Research Foundation Report #4016: Evaluation of integrated membranes for taste and odour and algal toxin control*, 2010, Published by Water Research Foundation, Denver, Colorado, USA.

c) Dixon M.B., Dreyfus J., Steele D., Ho L., Chow C.W.K. and Newcombe G. Enhancing nanofiltration processes for retention of algal metabolites using plasma polymerised nano-coatings, *Proceedings of the AWA Membranes and Desalination Specialty Conference*, February 2009, Sydney, Australia.

d) Dixon M., Dreyfus J., Steele D., Ho L., Chow C.W.K. and Newcombe G. Enhancing nanofiltration performance through plasma polymerisation. *Proceedings of the 11th Pacific Polymer Conference*, December 2009, Cairns, Australia.