Application of Biological Activated Carbon to Mitigate Algal Organic Matter Fouling of Ceramic Microfiltration Membranes

A thesis submitted in fulfillment of the requirements for the degree of Master of Engineering

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis/project is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed. I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Nusrat Rezwana Binte Razzak

March 2018
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Last but not the least; all praises to my almighty who has given me the enough strength to face all the difficulties and make this possible.
SUMMARY

Ceramic membranes are being used increasingly in water treatment because of their excellence in service such as high chemical and thermal stability, long operational life. However, membrane fouling affects their efficiency and remains as a major challenge for their widespread application for drinking water treatment. Algal blooms in water reservoirs lead to the release of algal organic matter (AOM) which causes severe fouling during microfiltration due to the presence of high molecular weight (HMW) organic matter. Feed water pre-treatment may minimize membrane fouling, however information regarding the potential of biological pre-treatment processes for mitigating the AOM fouling is very limited.

The core objective of this study was to determine the efficiency of biological activated carbon (BAC) process as a pre-treatment to mitigate the membrane fouling caused by AOM and also to acquire information on the fouling potential of AOM from the most common blooming algae species including *Chlorella vulgaris* and *Microcystis aeruginosa*. Fouling potential of soluble algal organic matter extracted from exponential phase (day 12) and stationary phase (day 25) of *C. vulgaris* (C-AOM) and *M. aeruginosa* (M-AOM) were examined in this study. For a better insight into the fouling effect of AOM present in surface water, the AOM was diluted either with pure water (Milli-Q) or natural surface water to prepare the feed solutions for the BAC and microfiltration (MF) tests. A constant DOC concentration of AOM was used in all feed preparation and significant flux decline was observed for both of the algal species at both of the growth phases.

The results obtained in the fouling study of single species AOM indicated that membrane fouling was influenced significantly by algal species, their growth phase, AOM characteristics and also on background water. Solutions containing AOM extracted from stationary phase exhibited the worse normalized flux (0.15) during MF and *C. vulgaris* posed highest fouling potential. BAC process removed more DOC (4.3 mgL\(^{-1}\)) than MF alone (3.1 mgL\(^{-1}\)). MF and BAC process was found to reduce the concentration of DOC and UVA indicated the removal of organic matter and humic substances in samples. Considerably better UVA removal than DOC removal was observed after MF (49% cf. 34%) and BAC process (46% cf. 62%) due to removal of UV-absorbing substances such as humic substances. After BAC followed by MF, M-AOM day 12 samples achieved higher DOC (74%) removal whereas day 25 samples achieved higher UVA
(76%) removal. In the case of *C. vulgaris* DOC (72%) removal was observed to be better than UVA (69%) removal after BAC followed by MF at both algal growth phases. C-AOM extracted from stationary phase lead to better organic removal after whole treatment process. According to the permeate analyses, AOM contained carbohydrate, protein and humic substances that deposited on/in membrane during MF and were considered as major foulants. More amounts of carbohydrate than protein as removed by MF whereas more protein than carbohydrate was removed by BAC pre-treatment.

Alum coagulation was investigated to examine its performance as a pre-treatment to improve membrane permeate flux. An optimum dose of 5 mg Al$^{3+}$ L$^{-1}$ was found efficient to mitigate the membrane fouling. AOM extracted from *C. vulgaris* led to greater fouling than that of *M. aeruginosa* similar to findings of previous study. Better flux improvement was obtained for alum compared with the BAC pre-treatment, however DOC and UVA removal was slightly higher after BAC than alum pre-treatment. This suggested that the fouling potential was not only depending on DOC concentration but also the other factors such as AOM characteristics. The alum treated M-AOM samples achieved better DOC reduction than the alum treated C-AOM samples. After alum and BAC pre-treatment, UVA removal was higher than the DOC removal which is due to the removal of UV absorbing substances. According to the characterization of the permeate, the better membrane flux obtained after pre-treatment was mainly due to the removal of the biopolymers such as protein and carbohydrate, and the humic substances.

The effect of mixed AOM derived from both algal species on the MF performance was then investigated and BAC was applied as a pre-treatment process for mitigating the fouling. A natural surface water was spiked with AOM extracted from the stationary phase of *C. vulgaris* and *M. aeruginosa* at the ratio of 1:1 in terms of DOC content. The flux for the untreated mixed AOM samples was comparable with the flux of stationary phase *M. aeruginosa*. The DOC and UVA removal by MF for the mixed species AOM was comparable with the DOC and UVA removal for single species AOM. Although having considerable removal in DOC and UVA, the poor flux for the BAC treated solution of the mixed AOM was attributed to the other characteristics of the organic matter rather than DOC level alone. BAC process provided a considerable reduction in carbohydrate and protein concentration from the solutions containing mixed species AOM. The EEM spectrum of the untreated water confirmed the presence of
fulvic-like acid (FA) and humic-like acid (HA) substances in the samples, which were removed by BAC process may reduced membrane fouling.

Two BAC columns packed with two different types of GAC were utilized to investigate the influence of carbon media on their pre-treatment performance. The performance of the two different BAC columns did not differ significantly in terms of flux profile and organic matter removal due to their similar GAC characteristics. Both of the BAC columns reduced fouling although less flux improvement was observed for mixed AOM species.

Overall, the integrated process of BAC pre-treatment for the MF system has the potential to mitigate the fouling of the ceramic MF membrane. Given the inherent advantages of the biological pre-treatment such as chemical-free process and low energy requirement, this study recommends further research to optimize the process to enhance its effectiveness for its possible applications in membrane based drinking water treatment.

**Recommendations for future work**

- The effectiveness of organic matter removal in BAC depends on EBCT. This study examined only one EBCT. Therefore, further study comparing the different EBCT can be done to observe its effect on the organic removal, with a view to optimizing the performance of the BAC.
- This work demonstrated the potential of BAC in terms of organics removal, but the cost-effectiveness of the system should be analysed and a comparison with the conventional methods conducted.
- This study demonstrated that the major foulants in membrane filtration are proteins, carbohydrates and humic substances, but further insight into the fractions responsible for fouling is needed. The exact role of the fractions and their interactions with the membranes should be investigated. This may be carried out by using model organic foulants.
- A larger scale study is required to assess the feasibility of this pre-treatment technology for its application at full scale.
## TABLE OF CONTENTS

DECLARATION  
ACKNOWLEDGEMENTS  
SUMMARY  
RECOMMENDATIONS FOR FUTURE WORK  
TABLE OF CONTENTS  
LIST OF FIGURES  
LIST OF TABLES  
NOMENCLATURE  

### CHAPTER 1: INTRODUCTION  
1.1 Background of the research 1  
1.2 Research objectives 2  
1.3 Thesis outline 3  

### CHAPTER 2: LITERATURE REVIEW  
2.1 Natural organic matter (NOM) 4  
2.1.1 Fouling characteristics by NOM 5  
2.2 Algal organic matter 5  
2.2.1 Algae and cyanobacteria 6  
2.2.2 *Microcystis aeruginosa* and *Chlorella vulgaris* 7  
2.2.3 Characteristics of AOM released from *M. aeruginosa* and *C. vulgaris* 8  
2.3 Application of membrane in water treatment 9  
2.3.1 Membrane materials 9  
2.3.2 Ceramic membranes 9  
2.3.3 Operation modes of membrane process 10  
2.3.4 Membrane fouling 12
2.3.4.1 Membrane fouling models 13
2.3.4.2 Reversible and Irreversible fouling 13
2.3.4.3 Membrane filtration resistance 13
2.3.5 Membrane cleaning 14
2.4 Feed pre-treatment to mitigate membrane fouling 15
  2.4.1 Application of BAC 16
    2.4.1.1 Mechanism of biological activated carbon 16
    2.4.1.2 Effectiveness of BAC process as pre-treatment 18
  2.4.3 Application of Coagulation 19
  2.4.4 Some integrated treatment process 21
2.5 Cost of different treatment options 22
2.6 Summary 24

CHAPTER 3: MATERIALS AND METHODS 25

3.1 Source water 25
3.2 Selection of Granular activated carbon (GAC) and significance of the properties 25
3.3 Biological Activated Column (BAC) Column Set up and operation 27
3.4 Ceramic Microfiltration test 27
3.5 Algae Culture and AOM extraction 28
3.6 Alum coagulation 29
3.7 Analytical methods 29
  3.7.1 pH and conductivity 29
  3.7.2 Color 29
  3.7.3 Turbidity and dissolved oxygen (DO) 30
  3.7.4 Dissolved organic carbon (DOC) 30
3.7.5 UV spectrophotometry 30
3.7.6 Specific ultraviolet absorbance (SUVA) 30
3.7.7 Carbohydrate 30
3.7.8 Protein 30
3.7.9 Determination of point of zero charge (pH_{pzc}) 31
3.7.10 Fluorescence EEM spectroscopy 31
3.7.11 Unified membrane fouling index (UMFI) 32

### CHAPTER 4: IMPACT OF BAC TREATMENT OF SOLUBLE AOM FROM CHLORELLA VULGARIS AND MICROCYSTIS AERUGINOSA ON THE FOULING OF A CERAMIC MICROFILTRATION MEMBRANE 33

4.1 Equilibration of BAC columns 33
4.2 Fouling study of single species AOM 36

4.2.1 Impact of AOM extracted from *C. vulgaris* on Ceramic MF membrane 36
4.2.2 Impact of BAC pre-treatment on the flux performance of MF of *C. vulgaris* solutions 40
4.2.3 Impact of AOM extracted from *M. aeruginosa* on Ceramic MF membrane 43
4.2.4 Impact of BAC pre-treatment on the flux performance of MF of *M. aeruginosa* solutions 46
4.2.5 DOC and UVA removal 49
4.2.6 Carbohydrate and protein content 50
4.2.7 Fluorescence EEMs of different solutions 53
4.2.8 Summary 55

4.3 Impact of alum coagulation pre-treatment on single species AOM 56

4.3.1 Determination of optimum coagulant dosages 56
4.3.2 Impact of alum coagulation pre-treatment on the flux performance of MF 57
4.3.3 DOC concentration and UVA removal 59
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Different operation modes of membrane</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Stages of DOC removal in BAC column</td>
<td>17</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic diagram of experimental setup (a) BAC process (b) Microfiltration</td>
<td>27</td>
</tr>
<tr>
<td>3.2</td>
<td>Cell density and DOC concentration with growth curve (a) <em>C. vulgaris</em> (b) <em>M. aeruginosa</em></td>
<td>28</td>
</tr>
<tr>
<td>4.1</td>
<td>Equilibration of GAC columns in terms of DOC concentration (BW=backwash)</td>
<td>34</td>
</tr>
<tr>
<td>4.2</td>
<td>(a) Determination of $pH_{pzc}$ for virgin GAC samples (b) Feed pH in early days of column operation.</td>
<td>35</td>
</tr>
<tr>
<td>4.3</td>
<td>Normalized flux vs specific volume for MF of solution containing C-AOM (day 12)</td>
<td>36</td>
</tr>
<tr>
<td>4.4</td>
<td>Normalized flux vs specific volume for MF of solution containing C-AOM (day 25)</td>
<td>37</td>
</tr>
<tr>
<td>4.5</td>
<td>(a) DOC concentration and (b) UVA of the samples before and after BAC and MF processes of samples containing AOM from <em>C. vulgaris</em> (note that Lorne water samples were collected on 24&lt;sup&gt;th&lt;/sup&gt; November 2016 and 19&lt;sup&gt;th&lt;/sup&gt; December 2016 for day 12 and day 25 samples, respectively)</td>
<td>38</td>
</tr>
<tr>
<td>4.6</td>
<td>Plot of flux vs specific volume for MF of C-AOM solution pre-treated by BAC pre-treatment (a) day 12 (b) day 25 (note that same Lorne water used for MF and BAC experiments)</td>
<td>41</td>
</tr>
<tr>
<td>4.7</td>
<td>Plot of flux vs specific volume for MF of C-AOM solution pre-treated by BAC pre-treatment (duplicate) (a) day 12 (b) day 25 (note that same Lorne water used for both experiments collected on 15&lt;sup&gt;th&lt;/sup&gt; June 2017)</td>
<td>42</td>
</tr>
<tr>
<td>4.8</td>
<td>Normalized flux vs specific volume for MF of solution containing M-AOM (a) day 12 (b) day 25</td>
<td>43</td>
</tr>
<tr>
<td>4.9</td>
<td>(a) DOC concentration and (b) UVA of the samples before and after BAC and MF processes of samples containing M-AOM (note that Lorne water samples were collected on 7&lt;sup&gt;th&lt;/sup&gt; March 2017)</td>
<td>45</td>
</tr>
</tbody>
</table>
Figure 4.10  Plot of flux vs specific permeate volume for MF of M-AOM solution pre-treated by BAC (GS 1300 or GA 1000N (note that same Lorne water used for MF and BAC experiments were collected on 7th March 2017)

Figure 4.11  UMFI values of the solutions containing AOM for untreated and BAC pretreated solutions

Figure 4.12  Plot of flux vs specific volume for MF of M-AOM solution pre-treated by BAC pre-treatment (duplicate) (a) day 12 (b) day 25 (note that same Lorne water used for MF and BAC experiments were collected on 15th June 2017)

Figure 4.13  Carbohydrate content in various samples containing AOM from (a) C. vulgaris (b) M. aeruginosa

Figure 4.14  Protein content in various samples containing AOM from (a) C. vulgaris (b) M. aeruginosa

Figure 4.15  Fluorescence EEM spectra of (a) Milli-Q water (b) Lorne water

Figure 4.16  Fluorescence EEM spectra of Lorne + M-AOM day 25 (a) before MF (b) after MF

Figure 4.17  EEM spectral volumes for the samples containing Lorne + M-AOM day 25 before and after MF process

Figure 4.18  Determination of optimum doses for alum coagulation of Lorne water and Lorne water plus 3 mgL⁻¹ M-AOM or C-AOM (day 25)

Figure 4.19  Normalized flux vs specific volume for MF of C-AOM solutions before and after alum coagulation

Figure 4.20  Normalized flux vs specific volume for MF before and after alum coagulation

Figure 4.21  DOC concentration for alum coagulation pre-treatment

Figure 4.22  UV absorbance at 254nm after various treatment process

Figure 4.23  UMFI for samples before and after alum pre-treatment

Figure 4.24  (a) Carbohydrate content (b) protein content of the solutions after various treatments

Figure 4.25  Fluorescence EEM spectra of Lorne + C-AOM (a) before alum (b)
after alum coagulation (c) alum coagulation + MF (d) FRI values

Figure 4.26 Fluorescence EEM spectra of Lorne + M-AOM (a) before alum (b) after alum coagulation (c) alum coagulation + MF (d) FRI values

Figure 4.27 Normalized flux vs specific volume for MF of solution containing mixture of M-AOM and C-AOM (1:1)

Figure 4.28 Plot of flux vs specific volume for MF of MC-AOM solution pre-treated by BAC

Figure 4.29 DOC concentration of the samples before and after BAC and MF processes

Figure 4.30 UV absorbance of the samples at 254nm before and after BAC and MF processes

Figure 4.31 UMFI for samples before and after BAC pre-treatment

Figure 4.32 (a) Carbohydrate content and (b) protein content in samples after various treatment

Figure 4.33 Fluorescence EEM spectra of MC-AOM mixed in Lorne water (a) untreated (b) after MF (c) BAC treated-GS 1300 followed by MF (d) FRI values

Figure C-1 Haemacytometer chamber
LIST OF TABLES

Table 3.1 Characteristics of the Lorne water samples 25
Table 3.2 Textural Properties of GAC samples 26
Table 4.1 Total fouling resistances before and after BAC pre-treatment for 48
  single species AOM
Table 4.2 Ratios of carbohydrate to protein after various treatment process 53
Table 4.3 Total fouling resistances before and after alum pre-treatment 59
Table 4.4 Total fouling resistances before and after BAC pre-treatment for 69
  mixed species AOM
Table B 1 Flux data for the determination of clean water flux 102
Table B 2 Flux data from the filtration test with AOM solution 102
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACH</td>
<td>Poly (aluminium) chlorohydrate</td>
</tr>
<tr>
<td>AOM</td>
<td>Algal organic matter</td>
</tr>
<tr>
<td>AP</td>
<td>Aromatic protein</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation process</td>
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<tr>
<td>BAC</td>
<td>Biological activated carbon</td>
</tr>
<tr>
<td>BCA</td>
<td>Bicinchoninic acid</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CEB</td>
<td>Chemically enhanced backwash</td>
</tr>
<tr>
<td>CIP</td>
<td>Cleaning in place</td>
</tr>
<tr>
<td>DAX-8</td>
<td>Acrylic ester resin</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon (mgL(^{-1}))</td>
</tr>
<tr>
<td>DBPs</td>
<td>Disinfection by-products</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty bed contact time (min)</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation-emission matrix</td>
</tr>
<tr>
<td>EOM</td>
<td>Extracellular organic matter</td>
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<tr>
<td>FA</td>
<td>Fulvic acid</td>
</tr>
<tr>
<td>FRI</td>
<td>Fluorescence regional integration</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>HA</td>
<td>Humic acid</td>
</tr>
<tr>
<td>HMW</td>
<td>High molecular weight</td>
</tr>
<tr>
<td>HPI</td>
<td>Hydrophilic fraction (= hydrophilic charged fraction + hydrophilic neutral fraction)</td>
</tr>
<tr>
<td>HPO</td>
<td>Hydrophobic acid fraction (= very hydrophobic acid fraction)</td>
</tr>
<tr>
<td>IOM</td>
<td>Intracellular organic matter</td>
</tr>
<tr>
<td>LMW</td>
<td>Low molecular weight</td>
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<tr>
<td>LPM</td>
<td>Low pressure membrane</td>
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<tr>
<td>MIEX</td>
<td>Magnetic ion exchange resin</td>
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<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>PACl</td>
<td>Polyaluminium chloride</td>
</tr>
<tr>
<td>PAS</td>
<td>Polyaluminium sulphate</td>
</tr>
<tr>
<td>pH(_{\text{pzc}})</td>
<td>Point of zero charge</td>
</tr>
<tr>
<td>PICI</td>
<td>Polymeric iron chloride</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PFC</td>
<td>Polyferric chloride</td>
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<tr>
<td>PFS</td>
<td>Polyferric sulphate</td>
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<tr>
<td>PS</td>
<td>polysulfone</td>
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<tr>
<td>PES</td>
<td>polyesethersulfone</td>
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<tr>
<td>RO</td>
<td>reverse osmosis</td>
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<tr>
<td>SMP</td>
<td>Soluble microbial products</td>
</tr>
<tr>
<td>SUVA</td>
<td>specific UV absorbance (UV absorbance per unit concentration of dissolved organic carbon) [L m(^{-1})mg(^{-1})]</td>
</tr>
<tr>
<td>SWRO</td>
<td>Sea water reverse osmosis</td>
</tr>
<tr>
<td>TPI</td>
<td>Transphilic fraction</td>
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<tr>
<td>UMFI</td>
<td>Unified membrane fouling index</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum ultraviolet irradiation</td>
</tr>
<tr>
<td>XAD-4</td>
<td>Polyaromatic resin</td>
</tr>
<tr>
<td>C-AOM</td>
<td>AOM extracted from C. vulgaris</td>
</tr>
<tr>
<td>J</td>
<td>Flux (Lm(^{-2}))</td>
</tr>
<tr>
<td>M-AOM</td>
<td>AOM extracted from M. aeruginosa</td>
</tr>
<tr>
<td>MC-AOM</td>
<td>Mixture of M-AOM and C-AOM</td>
</tr>
<tr>
<td>R</td>
<td>Hydraulic resistance (m(^{-1}))</td>
</tr>
<tr>
<td>µ</td>
<td>Dynamic viscosity (Pa.s)</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Background of the research

Microfiltration is a membrane technology which can provide high quality drinking water. Ceramic membranes have high mechanical and chemical stability, high operating fluxes and better separation characteristics compared to polymeric membranes (Heijman and Bakker, 2007, Hofs et al., 2011). Microcystis aeruginosa and Chlorella vulgaris, the main algal species of concern in this work, are liable for nuisance blooms (Vasconcelos et al., 1996), they can cause fouling (Babel and Takizawa, 2000) and limit widespread application of ceramic and polymeric microfiltration (MF) membranes (Zhang et al., 2013b). Membrane fouling reduces system productivity due to the interaction between the membrane, organic molecules and particulates present in water (Yuan and Zydney, 1999). Fouling reduces permeate flux, increases feed pressure and system downtime where frequent membrane maintenance leads to decrease in the lifespan of the membrane modules (Guo et al., 2012).

During the blooms, algae may have different forms and concentrations of algal organic matter (AOM) which causes severe fouling during MF of the affected water. AOM is known to pose high fouling potential to ceramic membranes due to the presence of high molecular weight (HMW) organic matter (Zhang et al., 2013a). These HMW compounds include biopolymers such as polysaccharides and proteins where the MW is higher than 10 kDa (Her et al., 2004, Fogg, 1983). The AOM composition depends on the species, the algal growth phase, and on the culture conditions (Henderson et al., 2008b, Pivokonsky et al., 2006). During MF, proteins, polysaccharides and humic-like substances deposit onto the membrane surface to form a cake layer due to the Lifshitz–van der Waals forces and small molecules are adsorbed into the membrane pores (Huang et al., 2014).

The impact of AOM extracted from M. aeruginosa and C. vulgaris in different growth phases on fouling potential during ceramic membrane MF was investigated by Devanadera and Dalida (2015) and Zhang et al. (2016a). They diluted AOM either with Milli-Q water or tap water to study the AOM fouling characteristics and to replicate the presence of AOM in drinking water. They observed greater flux decline for AOM from stationary phase and this higher fouling
potential was attributed to the difference in biopolymer properties (Zhang et al., 2013a). However, it is also important to observe the AOM effect in a real water environment where interaction of AOM from different algae and natural water can take place, which may also affect the membrane fouling.

Feed water pre-treatment is generally applied to reduce the organic foulants which effectively cause membrane fouling and is usually easy to implement into an existing conventional treatment plant. Pre-treatment increases membrane flux, but efficacy prediction can be difficult due to the complexity of the fouling phenomenon. Bio-filtration using biological activated carbon (BAC) process is considered as a cost effective solution to remove organic matter from drinking water (Laurent et al., 1999, Walker and Weatherley, 1999). Granular activated carbon (GAC) acts as water filtration media which has biofilm on its surface and removes significant amount of dissolved organic carbon (DOC) by biodegradation is termed as biological activated carbon (BAC). BAC process involves the breakdown of HMW biopolymers through biodegradation by the biofilm and adsorption of humic substances on the carbon media which subsequently reduces membrane fouling (Pramanik et al., 2014). A previous study by Pramanik et al. (2014) demonstrated that BAC pre-treatment can enhance low pressure polymeric membrane performance by transforming HMW organics to lower MW substances in the MF of a secondary effluent.

The previous research has revealed the efficiency of BAC process as pre-treatment to reduce the AOM fouling potential in wastewater (Pramanik et al., 2015b). To date, there has been no report of the application of BAC as a pre-treatment to mitigate fouling of ceramic MF membranes in the filtration of fresh water containing AOM. Hence the aim of this research was to investigate the efficiency of BAC process as a pre-treatment to mitigate AOM fouling in the MF of surface water using a ceramic membrane. In this research the natural bloom condition was simulated by spiking the fresh water with algal organic matter to study the impact of the possible interaction between algal organic matter and surface water. The effect of algal growth phase on fouling potential has also been considered in the study.

1.2 Research objectives

The specific objectives of this research were to:
• Determine whether BAC pre-treatment of AOM in fresh water reduces fouling of the ceramic MF membrane caused by a mixture of the AOM from the two common algae species.
• Compare the performance of BAC columns containing two manufacturer recommended GACs with slightly different properties.
• Compare the effectiveness of BAC treatment and alum coagulation for reducing AOM fouling.

1.3 Thesis outline

This thesis comprises 5 chapters to address the research questions. Chapter 1 provides background information and objectives of the study. Chapter 2 contains relevant literature including characteristics of AOM, membrane configuration, membrane fouling, feedwater pretreatment options. Chapter 3 describes the experimental methods and materials. Experimental results of AOM fouling study are presented in chapter 4 which is divided into 4 subsections: Equilibration of BAC columns, Fouling study of single species AOM, Impact of alum coagulation pre-treatment, Impact of mixed species AOM on Ceramic MF membrane. Chapter 5 includes the conclusions of the study.
CHAPTER 2

LITERATURE REVIEW

Membrane filtration is the physical separation of compounds from the fluid phase using semi-permeable membrane (Anselme et al., 1994). Microfiltration (MF), ultrafiltration (UF), nano filtration (NF), and reverse osmosis (RO) are pressure-driven processes where trans membrane pressure (TMP) acts as driving force. Low pressure membrane (LPM) filtration can produce better quality water, have a smaller footprint, and relatively low cost compared to conventional treatment process (Freeman et al., 2006, Furukawa, 2008, Wiesner and Chellam, 1999). LPMs are operated at quite low TMP (less than 1 to 2 bar, typically), and include MF and UF membranes having pore size 0.1-10 µm and 0.01-0.1 µm, respectively.

2.1 Natural Organic Matter

Natural organic matter (NOM) exists in natural water environment and is derived from the degradation of vegetation and animal matter. NOM primarily contains carbon, oxygen, and hydrogen, however depending on the source it can also contain nitrogen and sulphur (Croue et al., 2000). The composition of NOM varies significantly depending on number of factors including its source, characteristics of the water body, and the chemical and biological degradation (Wilson, 1988; McDonald et al., 2004).

According to the origin, NOM is autochthonous and allochthonous (McKnight and Aiken, 1998). Allochthonous NOM is mainly aromatic and derived from the degradation of vegetation. Autochthonous NOM is mostly aliphatic with high concentrations of carboxylic acid functional groups and derived from water sources, such as algae (Lee et al., 2006, McKnight and Aiken, 1998, Pivokonsky et al., 2006).

NOM is mainly composed of humic substances that provide yellowish brown color to natural water (Fan et al., 2001). HA and FA present in NOM are anionic polyelectrolytes comprising negatively charged carboxylic acid (COOH\textsuperscript{-}), methoxyl carbonyls (C=O) and phenolic (OH\textsuperscript{-}) functional groups (Zularisam et al., 2006b).
2.1.1 Fouling Characteristics of NOM

NOM is a heterogeneous mixture with varied ranges of molecular weight and functional groups. NOM can be divided into three fractions based on their hydrophobicity: the hydrophobic (HPO) fraction, which is adsorbable by XAD-8 resin includes humic substances; the transphilic (TPI) fraction, which is adsorbable by XAD-4 resin; and the simple hydrophilic (HPI) fraction which is not adsorbed by either of the resins (Thurman, 1985). Humic substances consist of mainly humic acids, some fulvic acids and humin, and are hydrophobic due to their HMW and high aromaticity (Croue, 1999, Zularisam et al., 2006a).

Previous research has mentioned that non-biodegradable organic matter, including humic substances causes membrane fouling (Elimelech et al., 1997, Li and Elimelech, 2004, Manttari et al., 2000, Yuan and Zydney, 1999, Wong et al., 2002). Several research groups reported hydrophilic NOM (carbohydrate or protein) as a major membrane foulant (Elimelech et al., 1997, Kimura et al., 2004, Kimura et al., 2006, Manttari et al., 2000). Van der Waals attraction and hydrophobic interaction between membranes and hydrophobic domains in hydrophilic NOM can lead to binding between hydrophilic NOM and membranes (Elimelech et al., 1997, Manttari et al., 2000). According to the findings of Lee et al. (2008) medium to low MW components of NOM (300-1000 Da) are responsible for MF/UF membrane fouling. Aggregate formation through molecular interaction (Bowen and Cao, 1998, Myat et al., 2014, Xiao et al., 2013) between humic substances and biopolymer-like substances such as polysaccharides and proteins (Elimelech et al., 1997, Kimura et al., 2004, Manttari et al., 2000) cause fouling of low pressure polymeric membranes.

2.2 Algal Organic Matter

AOM can be referred to as algal-derived NOM and has different characteristics compared with NOM (Henderson et al., 2008, Pivokonsky et al., 2006). AOM is released into the surrounding water during algal growth and on the death and breakdown of the algal cells.

AOM is generally hydrophilic in nature and contains high molecular weight compounds including neutral and charged polysaccharides, proteins, oligosaccharides, nucleic and amino acids, peptides, lipids and traces of other organic acids (Fogg, 1983, Her et al., 2004). It is established that AOM can cause severe fouling of low-pressure polymeric and ceramic
membranes due to the presence of high MW organic matter (Goh et al., 2011, Qu et al., 2012, Zhang et al., 2013a). AOM contains greater proportions of low MW (<1 kDa) and HMW (>100 kDa) polysaccharides (Pivokonsky et al., 2014). Biopolymers such as proteins and carbohydrates contained in AOM are considered as major organic constituents that contribute to the fouling layer. Polysaccharides play a significant role in formation of solid phase gel due to non-covalent bonds (Fishman et al., 2006, Wang and Waite, 2009). According to Yamato et al. (2006) irreversible fouling of a PVDF membrane is dominated by the protein present in dissolved fraction. Humic matter in AOM can be different from that in NOM in several aspects such as hydrophobicity, specific UV absorbance (SUVA) value, and MW distribution (Chon et al., 2013, Henderson et al., 2008).

AOM can be classified into extracellular organic matter (EOM) and intracellular organic matter (IOM) (Li et al., 2012). EOM, generated from metabolic excretion, comprises polysaccharides and proteins, and IOM is the result of cell autolysis (Henderson et al., 2008). EOM is important from water treatment perspective (Babel et al., 2002, Qin et al., 2006).

Excretion of EOM depends on algal type, growth phase and growth conditions (Paralkar and Edzwald, 1996). Specially in high temperatures and light intensity Chlorella can release high amount of EOM. Babel et al. (2002) mentioned that Chlorella cells become coated with EOM under unfavorable conditions which causes higher filtration resistance.

2.2.1 Algae and Cyanobacteria

Abundance of algae in source water is challenging for the drinking water treatment systems. The main groups of algae found in Australian freshwater are green algae, diatoms, euglenoids and cyanobacteria (RCI, 2016). The presence of algae in water environment can have ecological, aesthetic, and human health impacts. When present in drinking water supply systems, they can produce taste and odour problems, disinfection by-products, obstruct coagulation, clog rapid sand filters (Ghernaout et al., 2010). Algae are photosynthetic aquatic plants that utilize inorganic nutrients such as nitrogen and phosphorus (Henderson et al., 2008, Manahan, 2000). They can be classified into different phyla: 1) Chlorophyta (green algae), 2) Phaeophyta (brown algae), 3) Cyanophyta (blue-green algae or cyanobacteria), 4) Pyrrhophyta (dinoflagellates), 5) Chrysophyta (Yellow-Green or golden-brown algae), 6) Euglenophyta, 7) Cryptophyta
(Cryptomonads) and 8) Rhodophyta. Algae are eukaryotes and have a nucleus, mitochondria, and a chloroplast within each cell (education, 2014).

Cyanobacteria are multi-cellular, photosynthetic and aquatic organisms and larger in size. Cyanobacteria are prokaryotic organisms and are sometimes considered as algae. Cyanobacteria have a distinctive pigment used in photosynthesis, called the phycobiliproteins (phycobilins), which can give some of them a blue-green color. Cyanobacteria or blue-green algae are some of the most notorious microscopic organisms that grow naturally in freshwater bodies water and can sometimes multiply to form harmful algal blooms (HAB) (Ou et al., 2011). According to the National Oceanic and Atmospheric Administration (USA), harmful algae bloom affects animals, people i.e. the local ecology (CDC, 2016). HABs can potentially produce toxins posing a threat to the conventional water treatment process (Ndong et al., 2014). WHO reports human illness associated with the consumption of contaminated drinking water with toxic algae in many countries like USA, Australia, South Africa and China (Foundation for Water Research, 2015). Toxins can be released from algae during the growth phase and also when the algae die and decay. Toxins produced by cyanobacteria are termed cyanotoxins. Cyanotoxins include cytotoxins and biotoxins; biotoxins are responsible for acute lethal, acute, chronic and sub-chronic poisonings of wild/domestic animals and humans (Carmichael, 2001). The presence of cyanobacteria cause increased coagulant demand, clogging of filtration units and increased chlorine demand resulting in the formation of disinfection by products (DBPs), such as Trihalomethanes, (Collingwood, 1979, Hutson et al., 1987, SAFARIKOVA et al., 2013). Use of activated carbon during the active blooms of algae has the potential to decrease the level of cyanotoxins in drinking water (Chorus and Bartram, 1999).

2.2.2 Microcystis aeruginosa and Chlorella vulgaris

*Microcystis aeruginosa* is one of the most common freshwater cyanobacterial species responsible for nuisance blooms (Vasconcelos et al., 1996). Diameter of the cells is in the range from 2.61 to 5.40 μm, and can be either ovoid or spherical in shape. Cyanobacterium growth rate is highest at laboratory temperature of 32°C (Microbewiki, 2017). Removing *M. aeruginosa* and its secreted AOM from water or wastewater is a prime concern for efficient water treatment.
*Chlorella*, a green alga, causes fouling of MF membranes (Babel and Takizawa, 2000, Babel et al., 2002, Hung and Liu, 2006, Aksu and Tezer, 2005). *C. vulgaris* is a small, spherical alga and is known as freshwater microalgae. The size of *C. vulgaris* is 5-10 µm (Microbewiki, 2017).

2.2.3 Characteristics of AOM released from *Microcystis aeruginosa* and *Chlorella* and membrane fouling

The composition and fouling potential of AOM strongly depends on the algal species, its growth phase, and on the culture conditions (Henderson et al., 2008, Pivokonsky et al., 2006). *C. vulgaris* in stationary phase released higher DOC per cell than *M. aeruginosa* (Henderson et al., 2008). Zhang et al. (2016a) found relatively lower DOC concentration for AOM of *M. aeruginosa* than for *C. vulgaris*. In a study with *M. aeruginosa* and *C. vulgaris*, Zhang et al. (2016a) observed that AOM obtained from log phase contains a lower proportion of protein and humic-like substances than from stationary phase. However the proportion of humic-like substances was found to be higher in *C. vulgaris* than *M. aeruginosa*, and was associated with higher irreversible fouling caused by *C. vulgaris*. DOC concentration per cell of algae also increase with culture age (Henderson et al., 2008). The amount of protein relative to carbohydrate increase significantly with growth phase for *M. aeruginosa* whereas the increment rate is not significant for *C. vulgaris* (Henderson et al., 2008).

AOM obtained from *C. vulgaris* than *M. aeruginosa* contains very HMW biopolymers (>20,000 Da), medium-MW components such as humics and building blocks (350-1000 Da), and low-MW substances (<350 Da) which cause membrane fouling (Qu et al., 2012, Huber et al., 2011). The biopolymers, i.e. proteins and carbohydrates, in the AOM of *M. aeruginosa* contained a higher proportion of HPO components than that from *C. vulgaris* and can cause severe irreversible fouling (Dramas and Croue, 2013, Zhang et al., 2016a). The content of MW >500 kDa in AOM is higher in *M. aeruginosa* than that in *C. vulgaris*. AOM extracted from *M. aeruginosa* can form three fouling layers (i.e., outer, middle and inner layer) on a ceramic MF membrane. The inner layer largely containing HMW and LMW hydrophilic compounds contributed to hydraulically irreversible fouling (Zhang et al., 2013b). Henderson et al. (2008) observed that proteins that have MW > 500 kDa govern hydrophobicity in the absence of humic/fulvic acids-like substances.
Zhang et al. (2016a) observed that MF of AOM obtained from \textit{C. vulgaris} can remove higher amount of large MW humic-like compounds than from \textit{M. aeruginosa} due to the higher content of the humic-like substances present in \textit{C. vulgaris}. They have also mentioned that the rejection of HMW compounds by MF was higher than that of medium and low MW compounds for individual species. MF of C-AOM can also reject the medium or low MW compounds possibly due to the formation of dense cake layer by the HMW biopolymer like substances (Villacorte et al., 2015).

2.3 Application of membrane in water treatment

2.3.1 Membrane materials

Membrane fouling can be affected by the types and properties of membrane materials. Membranes are made of various organic or inorganic materials. Polyvinylidene fluoride (PVDF) and isotactic polypropylene (PP) are most commonly used polymeric MF membranes which are hydrophobic in nature (Mulder, 2012, Lozier et al., 2008). Positively charged hydrophobic membranes with bigger molecular weight cut-off (MWCO) are generally fouled more readily than hydrophilic membranes (Howe and Clark, 2002).

The majority of MF and UF membranes are of a hollow fiber configuration, either symmetric (uniform composition) or asymmetric (Peng et al., 2012). Individual hollow fibers are potted and bundled together within a pressure vessel to create an element or module that can be operated in either a dead-end mode (dominant) or cross-flow mode with either outside-in flow (dominant) or inside-out flow.

2.3.2 Ceramic Membranes

Ceramic membranes are monolithic filter modules, made from inorganic materials like aluminium oxide, titanium oxide, and zirconium oxide which serve as filtration barrier (AMTA, 2014). Ceramic filter modules are housed in vessels and plumbed together to create a membrane filtration system. Ceramic microfiltration membranes commonly have a nominal pore size of 0.1 \( \mu \text{m} \). The surface of porous ceramic membrane is comprised of metallic oxide which is hydrophilic and the degree of hydrophilicity depending on the materials used (He et al., 2011).

Ceramic membranes are being used not only in the food, beverage and dairy industries but also in drinking water treatment plants (Daufin et al., 2001, Finley, 2005).
Ceramic membranes are a cost-competitive alternative having many advantages over conventional polymeric membranes (Pendergast and Hoek, 2011) in terms of higher permeate fluxes and better separation characteristics due to high porosity and narrow pore size, they also withstand higher pressures due to higher mechanical stability (Heijman and Bakker, 2007). Compared to polymeric membranes, ceramic membranes have a longer lifetime due to their high chemical stability (Buekenhoudt, 2008, Van Gestel et al., 2003). Ceramic membranes also have greater hydrophilicity resulting in high water fluxes at low pressures (Cornelissen et al., 2009, Hofs et al., 2009, Moulin et al., 1991). The decreasing order of chemical and hydrothermal stability for ceramic membrane is TiO$_2$, ZrO$_2$, Al$_2$O$_3$, SiO$_2$ and ZrO$_2$, Al$_2$O$_3$, TiO$_2$, SiO$_2$, respectively (Van Gestel et al., 2003, Buekenhoudt, 2008). Guerra and Pellegrino (2013) found that the cost of full-scale ceramic membranes system is 12% greater than the cost for a polymeric membrane system. But ceramic membranes experience less fouling and higher nominal Peclet (Pe) number which makes the ceramic membrane more competitive in terms of costs. (Peclet number is dimensionless which represents the effectiveness of mass transport by advection to the effectiveness of mass transport by either dispersion or diffusion (Fetter, 1999)).

The fouling characteristics of ceramic membranes mostly depend on solution chemistry such as ionic strength, divalent ion concentration and pH (Gray et al., 2008, Jones and O’Melia, 2000), the intrinsic membrane properties such as surface charge (Benavente et al., 1993, Bowen and Mukhtar, 1993), hydrophobicity/hydrophilicity (Yuan and Zydney, 2000, Zhang et al., 2009) and the interactions between solutes and the membrane surface (De Lara and Benavente, 2009, Yuan and Zydney, 2000).

Ceramic membranes can be subjected to the cleaning regimes with more aggressive solutions which enable greater restoration of flux and thus more water production per membrane unit area. Their higher pressure tolerance means efficient backwashing, and use of more aggressive cleaning chemicals and higher pressure work together to yield more consistent permeability and more stable plant capacity over the long run (Freeman and Shorney-Darby, 2011).

2.3.3 Operation modes of membrane processes

Microfiltration operation is commonly classified in terms of direction of the flow of the feed that is being processed. Microfiltration may be done under two distinct modes of operation, shown in
Dead-end filtration is the basic form of filtration operation for most LPM systems. In the dead-end filtration mode, flow direction is perpendicular toward the medium surface. The water is pushed through the membrane by pressure. Essentially, all of the liquid passes through the medium as permeate, and all the suspended particles larger than the pore size of the medium are taken by the medium (Bai and Leow, 2002). Dead-end filtration systems are relatively simpler than cross flow systems and require lower capital and maintenance costs. The dead-end configuration is feasible when the particle loading in the feed is high.

Figure 2.1: Different operation modes of membrane

In cross-flow filtration, the feed water is forced to flow at fairly high velocity tangentially across the surface of the filter, rather than into the filter through the membrane surface (Koros et al., 1996). The solutes present in feed water deposit on the membrane to form a thin cake layer. High liquid velocity is applied to release the rejected materials from the cake layer and therefore to reduce fouling (Mulder, 1996). Cross-flow filtration can deliver higher permeate fluxes over a longer operation time than dead-end filtration. However, the cross-flow system consumes higher energy (Bai and Leow, 2002). Tarleton and Wakeman (1993) reported cross flow microfiltration systems are susceptible to reversible or irreversible fouling, like dead-end systems. Cross flow filtration is usually preferred for higher solids loading.

Membrane systems can be operated in either constant permeate flux (flow rate per unit membrane area, Lm⁻²h) with variable TMP or constant TMP with variable permeate flux.
Membrane fouling occurs during an increase in TMP to maintain a constant flux or during a decrease in flux when the system is operated at constant pressure as the cake build-up with the time causes fouling (Guo et al., 2012). Lee et al. (2008) reported constant flux operation as most beneficial which is being used in the industry.

2.3.4 Membrane Fouling

Filtration performance is usually expressed in terms of the filtrate flux, the volume of filtrate that passes through a unit membrane area per unit time. Flux decline takes place due to several factors. When membrane performance drops with filtration time, the phenomenon is called membrane fouling. Membrane fouling can be caused by particulates, organic molecules, inorganic compounds and microbes (Goosen et al., 2005). Of these, organic fouling is the most significant hindrance in the widespread use of MF membrane as it decreases the membrane flux, performance and increases TMP and operating cost. Organic fouling is due to the attachment of dissolved components and colloids (humic and fulvic acids, hydrophilic and hydrophobic materials and proteins) by adsorption (Guo et al., 2012). Key mechanisms for membrane fouling are the feed components undergoing adsorption, pore clogging, physical and chemical interaction between fouling constituents and membrane materials, gel formation, and bacterial growth. Pore blocking is the primary stage of particulate fouling and more severe than cake formation on the MF membrane surface (Soffer et al., 2004, Yang and Kim, 2009, Guo et al., 2012). Colloids close to the membrane pore size can block pores whereas particles larger than membrane pores cause cake formation (Huang et al., 2008).

Membrane fouling depends on many factors such as the characteristics of foulants, surface morphology, hydrophobicity, charge and molecular weight cut-off (Combe et al., 1999, Gray et al., 2008), process configuration (Tarabara et al., 2002), operating conditions (Meyn and Leiknes, 2010), water quality parameters (Howe and Clark, 2002), water chemistry (pH, ionic strength, and divalent cation concentration), temperature, mode of operation, hydrodynamic conditions (initial permeate flux and cross flow velocity) (Li and Elimelech, 2004) and cleaning strategies (Lee et al., 2001, Lim and Bai, 2003).
2.3.4.1 Membrane fouling models

Hermia (1982) developed four filtration mechanisms (complete blocking, intermediate blocking, standard blocking, cake filtration) to explain membrane fouling and flux decline for dead end filtration under constant pressure as described below (Ye et al., 2005):

i) Complete blocking is the closing of pores by particles with no particle superimposition,

ii) Intermediate blocking is the closing of pores by particles with particle superimposition,

iii) Standard blocking is the deposition of particles smaller than the pore size onto the pore surface reducing the pore size,

iv) Cake filtration is the deposition of particles larger than the pore size onto the membrane surface.

2.3.4.2 Reversible and Irreversible fouling

Membrane fouling is either reversible or irreversible depending on how strong is the attachment of foulant to the membrane surface. Reversible fouling can be separated by a strong shear force or backwashing and can be transformed into an irreversible fouling during continuous filtration process due to formation of a strong matrix of fouling layer with the solute (Chen et al., 1997). Chemical cleaning is done by removing foulants layer producing irreversible fouling; it reduces the foulant’s affinity through chemical reactions and consequently release the colloids from the membrane surface (Huang et al., 2008). Severe irreversible fouling reduces membrane effectiveness, leading to the need for frequent membrane replacement which increases operating cost. Kimura et al. (2004) observed irreversible fouling of hydrophobic UF membrane which is due to the presence of polysaccharide.

2.3.4.3 Membrane filtration resistance

The hydraulic resistance of a clean membrane is constant and independent of the feed composition and applied pressure. The total hydraulic resistance in membrane filtration comprises resistances exerted by the membrane, pore blocking, pore adsorption, the cake layer, and concentration polarisation (Van den Berg and Smolders, 1990). Initial phase of the particulate fouling is pore blocking which is more severe than cake formation on the MF
membrane surface (Soffer et al., 2004, Yang and Kim, 2009, Guo et al., 2012). Colloids close to the size of membrane pores can cause pore blocking whereas particles larger than membrane pores lead to cake formation (Huang et al., 2008). Rapid flux decline usually occurs by cake layer formation though other phenomena such as the pore plugging, infiltration of fines into the cake (Tanaka et al., 1994) or membrane fouling by macro solutes can also influence flux decline. Adsorption of solute molecules on the membrane surface or within membrane pores also contributes to the total resistance (Mulder, 2012). Thekkedath et al. (2007) stated that humic acid fouling in MF/UF membrane is mainly due to cake formation mechanism which increases the total hydraulic resistance and plays a important role in flux decline.

2.3.5 Membrane Cleaning

Membrane cleaning is vital to maintain membrane performance, cleaning must be done when performance falls below the desired permeate yield or feed pressure increase by about 10% and/or differential pressure increase by 15–50% (Al-Amoudi and Farooque, 2005).

During cleaning, energy can be applied to the foulant as kinetic energy, thermal energy or chemical energy (Romney, 1990). Cleaning methods depend on the foulant characteristics, membrane material, and membrane configuration. Physical cleaning can be categorized into hydraulic, mechanical, ultrasonic, and other cleaning (Wang et al., 2014). Physical methods include sponge ball cleaning, forward and reverse flushing, backwashing, air flushing and CO₂ back permeation (Al-Amoudi and Lovitt, 2007, Ebrahim, 1994).

Backwashing is applied to remove the layer of entrapped material thus reduce membrane fouling and can be done either by reducing operation pressure below the osmotic pressure of the feed solution or by increasing the permeate pressure (Sagiv and Semiat, 2005, Abadi et al., 2011). Backwash is beneficial for ceramic membranes as it has improve chemical and thermal resistance of materials (Guerra and Pellegrino, 2012). Normally backwashes ranging from 3–90 minutes are applied for ceramic and polymeric membranes (Sondhi and Bhave, 2001). In cross flow microfiltration similar technique back flushing (Redkar and Davis, 1995) is applied for 5-10s in every 3-15 minutes by reversing trans membrane pressure (Kroner et al., 1984, Matsumoto et al., 1988, Srijaroonrat et al., 1999). The major difference between back pulsing and backwashing is the speed and force applied to remove the deposited matter on the membrane surface (Sondhi and Bhave, 2001). Back pulsing is similar to back flushing. Compared to back
flushing, flow reversal in back pulsing happens every few seconds (Parnham and Davis, 1996). Back pulsing can restore membrane flux by effective removal of the particles from the membrane pores. Both are usually suitable in cross-flow filtration with tubular ceramic membranes (Sondhi and Bhave, 2001). Sondhi and Bhave (2001) mentioned that membranes with larger pore diameter provides greater effectiveness during back pulsing and found that 0.2 µm and 0.5 µm ceramic membranes with back pulsing enhances the membrane flux up to 2.5 times.

In case of continuous operation, membrane filtration resistance increases gradually and fouling cannot be entirely controlled by regular physical cleaning. Chemical cleaning is a vital part of the operation of MF and UF systems in the water industry (Liu et al., 2001). Chemical cleaning alleviates irreversible fouling by using a chemical reagent, such as bases (caustic soda), acids (hydrochloric, sulfuric, citric, oxalic, etc.), and oxidants (hypochlorite and hydrogen peroxide) (Liu et al., 2001). The selection of these cleaning reagents and conditions depends on the material deposited, and the chemical and thermal resistance of the membrane, the module and rest of the equipment (Tragardh, 1989). Changes in the foulant morphology or the alternation of fouling layer surface chemistry generates the chemical reaction between chemical agents and the foulants (Weisa et al., 2003). Chemical cleaning process depends on several factors like temperature, pH, concentration of cleaning chemicals, contact time between the chemical solution and membrane and operation conditions (Mohammadi et al., 2003).

Chemically enhanced backwash (CEB) prevents foulant build up and maintains the membrane permeability. CEB is carried out with low reagent concentration, relatively short soaking time and normal ambient temperature (Zhang et al., 2016b). Cleaning in place (CIP) is used to restore flux after dense fouling (Pearce, 2007). However, frequent chemical cleaning may reduce the lifespan of low pressure membranes, and disposal of the reagents poses another problem (Lozier et al., 2003).

**2.4 Feed pre-treatment to mitigate membrane fouling**

An appropriate pre-treatment can increase the performance of membrane filtration of water containing AOM. Feed water pre-treatment can affect LPM filtration in three ways: altering contaminant size distributions, changing mutual affinities of contaminants or their affinities to
membrane surfaces, and suppressing undesirable microbial growth or removing biodegradable contaminants (Huang et al., 2009). The pre-treatments may include coagulation, adsorption, oxidation, magnetic ion exchange resin (MIEX) and integration of several pre-treatments (Gao et al., 2011).

Coagulation is commonly applied as pre-treatment for MF/UF for drinking water (Huang et al., 2009, Laine et al., 2000). The MIEX process was developed in Australia for the removal of NOM in water treatment (Slunjski et al., 2000). MIEX can effectively remove the low and medium molecular weight DOC, and also decrease high and medium MW DOC during MF (Fabris et al., 2007, Kitis et al., 2007). Biological filtration processes are effective to reduce the biodegradable organic matter content of drinking water, and hence have the potential to be a pre-treatment for membrane filtration (Goldgrabe et al., 1993, Laurent et al., 1999, Miltner and Summers, 1992).

2.4.1 Application of BAC

2.4.1.1 Mechanism of Biological Activated Carbon

Biological activated carbon (BAC) is a cost effective process for wastewater treatment in terms of low energy consumption and is more environmentally friendly than traditional water treatment processes as it does not produce a chemical sludge (Walker and Weatherley, 1999). The BAC process uses GAC as water filtration media to physically remove micro-organisms and organic/inorganic matter (Simpson, 2008). The performance of activated carbon depends on its surface area where physical adsorption takes place, on the heteroatom content and the adsorbate properties (Rattier et al., 2012). GAC has an affinity for attachment of organics by van der Waals’ dispersion forces and electrostatic interactions even at low concentrations (Moreno-Castilla and Rivera-Utrilla, 2001). Moreover, the crevices and macropores of activated carbon provide an excellent surface for colonization by microorganisms and shear stress protection (Voice et al., 1992, Ghosh et al., 1999). It is these microorganisms which biodegrade the organics and thus remove them, this activity leading to the conversion of GAC to BAC (Rattier et al., 2012). Activated carbon pores comprise of micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). About 90% of the total surface area of activated carbons is located in the micropores and contributes in adsorption processes where mesopores and macropores act as
transport arteries through which the adsorbate molecules reach the micropores (Moreno-Castilla and Rivera-Utrilla, 2001).

![Figure 2.2: Stages of DOC removal in a BAC column](image)

The mechanism of BAC treatment can be described in three phases (Sirotkin et al., 2001) and is shown in Figure 2.2. In the initial phase organic matter is removed by adsorption on the GAC. In the second phase a biofilm grows over time, biodegradation begins and then the adsorption and biodegradation rates become comparable. Bacterial colonization leads to the growth of the biofilm layer on the rough porous GAC surface as media particles slowly become exhausted (Hattori, 1988, Scholz and Martin, 1997, Takeuchi et al., 1997). In the third phase the biodegradation rate exceeds the adsorption rate, and desorption from the pores might occur resulting in regeneration of carbon. The biological activity facilitates immediate adsorption and biodegradation and so prolongs the life span of activated carbon filters (Lowry and Burkhead, 1980, Walker and Weatherley, 1999, Yapsakli and Cecen, 2010).

The growth of a biofilm on activated carbon in water and wastewater treatment applications is a typical consequence of the favorable environment provided by this material. The effects of microbial growth have been variously reported as beneficial (Johnson and Baumann, 1971, Parkhurst et al., 1967, Weber Jr et al., 1970, Weber et al., 1972, Weber and Ying, 1977) and disadvantageous (Bishop et al., 1972, Bishop et al., 1967) to the primary adsorptive function of the carbon. However, excessive biofilm growth in BAC filters causes clogging, pressure drop
and the breakthrough of substrates and microorganisms including pathogens (Scholz and Martin, 1997, Schreiber et al., 2007). It is necessary to maintain an active biofilm inside a BAC filter and avoid filter clogging. To serve this purpose, backwashing is done frequently to remove excessive biomass.

### 2.4.1.2 Effectiveness of BAC process as pre-treatment

The performance of BAC is reported as effective as pre-treatment to mitigate fouling of polymeric MF membranes caused by secondary effluent containing AOM (Pramanik et al., 2015b). The BAC process reduced both reversible and irreversible foulants and offers better performance than GAC system (Pramanik et al., 2014).

Biopolymers and humic substances formed cake layer on the membrane during the MF of secondary effluent and building blocks can adsorb on to the membrane pores and cause fouling (Pramanik et al., 2014). According to their analysis carbohydrate molecules have greater contribution in fouling membranes than protein molecules. BAC process involved biodegradation of biopolymers such as carbohydrate, protein and adsorption of humic substances and thus reduced membrane fouling (Pramanik et al., 2014). BAC performed better in terms of organics reduction and flux improvement when comparing with coagulation pre-treatment (Pramanik et al., 2014). The organic removal rate depends on a number of factors such as empty bed contact time (EBCT) concentration and type of organic matter, and properties of activated carbon (De Waters and DiGiano, 1990, Huck et al., 1994). BAC treatment can also reduce the concentration of cyanotoxin (Pramanik et al., 2015b).

BAC filtration systems can run for a long time. In case of continuous operating system, BAC performed better for biopolymer removal whereas the removals of humic substances decrease with time (Pramanik et al., 2016). From the analysis of pore size distribution it was shown that the adsorption capacity of the activated carbon reduced with operation time. Simpson (2008) has reported that the BAC process decreased HMW biopolymers by biodegradation and also reduced LMW organics, but the removal efficiency of HMW humic substances was observed to be decreased eventually reduced the fouling potential.
2.4.3 Application of Coagulation

Coagulation is an essential physico-chemical process to treat water and wastewater. Coagulants have been used to remove impurities from water since early 20th century (Duan and Gregory, 2003). Coagulation process reduces the repulsive potential of electrical double layer of colloids to produce micro-particles. The commonly used inorganic coagulants are aluminum or iron salts which are effective to remove dissolved organics and colloidal matter (Duan and Gregory, 2003). Some aluminium based coagulant like alum (Al$_2$(SO$_4$)$_3$), aluminium chloride (AlCl$_3$), polyaluminium chloride (PACl) and polyaluminium sulphate (PAS) and ferric based coagulants like ferric chloride (FeCl$_3$) and ferric sulphate (Fe$_2$(SO$_4$)$_3$), polyferric sulphate (PFS), polymeric iron chloride (PICl) or polyferric chloride (PFC) are commonly used for treatment process (Tan et al., 2000). Aluminium-based and iron-based coagulants are known to remove hydrophobic, charged and larger-sized substances rather than hydrophilic substances, neutral and smaller-sized substance (Carroll et al., 2000).

The commonly used ferric salts in coagulation processes include ferric chloride (FeCl$_3$) and ferric sulphate (Fe$_2$(SO$_4$)$_3$). The relative solubility and pH range for FeCl$_3$ is different from those of alum. pH between 4.5 and 6 is considered as optimum for ferric-based coagulants to remove NOM (Matilainen et al., 2010). DOC removal efficiency can be increased in a ferric dose up to 100 mg L$^{-1}$ (Uyak et al., 2007).

Nowaday the use of prehydrolyzed aluminium coagulants, such as polyaluminium chloride (PACl) and polyaluminium sulphate (PAS) have been reported (Zouboulis et al., 2007). PACl is made by partially neutralizing AlCl$_3$ to different basicity ratios, and its use has been continuously increasing. Prehydrolyzing the AlCl$_3$ is considered as producing the most efficient Al species to remove contaminant from water. The uses of polymeric iron coagulants, including polyferric sulphate (PFS), polymeric iron chloride (PICl) or polyferric chloride (PFC) is also increasing. The advantages of these coagulants are wider working pH range, less susceptible to water temperature (Matilainen et al., 2010).

In alum coagulation pH of the water plays an important role as solubility of the aluminum species in water is pH dependent. The minimum solubility of the coagulants for ferric chloride and aluminum chloride is 5.8 and 6.3, respectively. So at pH higher than the minimum solubility
the hydrolysis products are HMW polymers or colloidal species whereas at a pH lower than the minimum solubility the hydrolysis products are primarily medium polymers or monomers (Yan et al., 2008). The optimum condition for the alum coagulation occurs in between pH 6 and 8 due to negatively charged alum. But for the pH of the water in between 4 and 5, alum forms of positively charged ions such as Al(OH)\(^{2+}\), Al\(_8\)(OH)\(^{4+}\), and Al\(^{3+}\). The possible reaction taken place after addition of coagulants which depends on pH are shown below for alum coagulants (Gebbie, 2006).

\[
\text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O} \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 18\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 6\text{H}^+ + 3\text{SO}_4^{2-} + 12\text{H}_2\text{O}
\]

The main coagulation mechanisms are charge neutralization of negatively charged colloids at high doses by positively charged hydrolysis and incorporation of impurities in sweep flocculation (Duan and Gregory, 2003). The efficiency of system depends on pH and coagulant dosage. The other mechanisms to remove NOM include entrapment, adsorption and complexation with coagulant ions into insoluble particulate aggregates and the removal mechanism particularly depends on NOM composition. (Jarvis et al., 2004).

Some researchers reported that coagulation has a very positive influence in membrane filtration process (Carroll et al., 2000, Lerch et al., 2005). It can remove NOM but small molecular weight, non-ionic and hydrophilic fraction of the NOM can not be effectively removed after coagulation and are responsible for the fouling after coagulation pre-treatment (Carroll et al., 2000). The effectiveness of removing NOM depends on the nature of the NOM, i.e. molecular weight, charge density, hydrophobicity and the characteristics of the water and the initial mixing conditions (Letterman et al., 1999). Whereas Pikkarainen et al. (2004) mentioned that the increase in coagulant dosage can decrease the specific cake resistance developed by NOM.

Coagulation is also considered as effective to improve the flux performance of surface water containing AOM and lowered the frequency of hydraulic or chemical cleaning (Babel and Takizawa, 2000, Zhang et al., 2016a, Matsushita et al., 2005). Coagulation can minimize the fouling by reducing the organic load to the membrane, by removing high fouling potential biopolymer compounds and by increasing the particle size of organics (Huang et al., 2009, Kim et al., 2005, Shon et al., 2004). However the performance to mitigate membrane fouling depends on experimental conditions (bench-scale or pilot-scale) and requires dose optimization (Howe et
al., 2006, Karimi et al., 1999, Maartens et al., 1999, Huang et al., 2009). Low coagulant (Fe$^{3+}$) doses can cause internal fouling of the membrane due to the incomplete aggregation of colloidal particles and precipitation of humic materials (Judd and Hillis, 2001).

Pikkarainen et al. (2004) studied aluminium and ferric based coagulants and reported high removal of UV absorbance at 254 nm ($\text{UV}_{254}$) and DOC by all coagulants. They have found ferric chloride to remove better DOC whereas ferric sulphate provided lower filter cake specific resistance. Ferric chloride coagulation leads to increased rejection of organics during MF/UF due to precipitation and adsorption of NOM on the precipitate surface (Schafer et al., 2001).

Alum coagulation is reported as effective pre-treatment before UF process to remove HMW organics, such as biopolymers and humic substances (Lai et al., 2015). Kabsch-Korbutowicz and Malgorzata (2005) have studied three aluminium based coagulants and mentioned that fouling reduction is significantly influenced by the type and coagulant dosage, feed organic characteristics, solution chemistry and hydrodynamic conditions. However, Tabatabai (2014) have reported coagulation as ineffective to remove small molecules in AOM. Zhang et al. (2014) was also used a variety of coagulants (aluminium and iron based) to reduce AOM fouling of a ceramic MF membrane. All four coagulants at their optimum dosages produced marked reductions in both reversible and irreversible fouling. They have mentioned ACH as a more cost-effective coagulant to mitigate fouling of AOM containing water.

### 2.4.4 Application of integrated treatment processes

Some of the literature shows the efficiency of BAC process when coupled with other treatment process. For example:

BAC process coupled with ozonation is an established approach to treat drinking water by removing NOM, DBPs, taste and odor compounds. Reungoat et al. (2012) used ozonation followed by BAC filtration to treat domestic waste water and suggested it was an effective system to achieve higher removals for DOC, trace organic compounds including non-specific toxicity, and estrogenicity. Ozonation followed by ceramic microfiltration can remove higher amount of biopolymers (Filloux et al., 2012, Ibn Abdul Hamid et al., 2017).

Buchanan et al. (2008) applied vaccum ultraviolet (VUV) irradiation followed by BAC treatment for the treatment of surface water. VUV irradiation breaks down the high MW hydrophobic
molecules into more hydrophilic biodegradable moieties and provided a considerable amount of reduction in DOC concentration after BAC process. BAC system removed hydrogen peroxide residual produced by VUV irradiation and the VUV BAC system reduced the DBP formation potential.

UV-H$_2$O$_2$ coupled with BAC treatment was used by Toor and Mohseni (2007) to reduce the concentration of DBPs in drinking water. They have reported a good amount of reduction in DBPs, total organic carbon, and UV$_{254}$ after combined advanced oxidation process (AOP)–BAC treatment. Similar comment was made by Fahmi and Okada (2003) who have observed the reductions in DOC concentration with H$_2$O$_2$-O$_3$ AOP followed by biological treatment. AOP pretreatment followed by biological process effectively minimizes chlorine dosage and reduces bacterial re-growth in the distribution system (Wu et al., 2003).

Ibn Abdul Hamid et al. (2017) investigated the impact of ozonation and BAC filtration pre-treatment for the ceramic membrane to treat secondary effluent. Ozonation was reported to provide better permeability of ceramic MF membrane than BAC by removing greater extent of biopolymers (100%) and humic substances (84%). Whereas ozonation+BAC+micrrofiltration was found to have lower removal rates (biopolymer 96%, humic substance 66%) and permeability when compared to ozonation followed by microfiltration only.

The performance of ceramic membranes coupled with coagulation, ozonation and UV/H$_2$O$_2$ and also their combinations were studied by Myat et al. (2018) for recycled water. Higher filtration flux was observed for coagulation followed by either ozone or UV/H$_2$O$_2$. Higher amount of biopolymer removal was also observed for pre-treatments such as coagulation, ozonation followed by coagulation, UV/H$_2$O$_2$ followed by coagulation.

2.5 Cost of different treatment options

Biological processes for water and wastewater treatment are much cheaper than chemical ones in terms of investment and operation costs. Investment and treatment costs for biological process are 5-20 and 3-10 times lower, respectively, than chemical processes such as ozone or peroxide (Marco et al., 1997). Capital cost for the construction of a BAC filter includes filter structure, filter media, backwash pumping, intermediate lift pumping, yard piping, site work and electrical
and control systems (McGivney and Kawamura, 2008). Plumlee et al. (2014) noted that capital costs is similar for BAC and GAC irrespective to treat water or wastewater.

A study mentioned MF-UF as the cheapest technology for smaller capacities (100 and 500 m\(^3\)/day) and the cost was found to have decreased slightly from 2002 to 2008 compared to the cost of conventional water treatment (Dore et al., 2013). There has been continuous cost decreases in MF and UF membranes in large systems (William et al., 2002), making this option attractive also for pre-treatment in large sea water reverse osmosis (SWRO) systems operating on surface feed water, originating from an open intake source. Ceramic membranes are becoming feasible because of the decreasing production costs. Heijman and Bakker (2007) reported that installation costs of ceramic membrane system are competitive with the installations of polymeric membrane system.

MIEX was developed and has been extensively trialed in Australia since early ‘90s (Bourke et al., 1999, Bursill et al., 1996, Morran et al., 1996, Nguyen et al., 1997) for water treatment. Using MIEX the Wanneroo Groundwater Treatment Plant (GWTP) removes approximately 40-50\% of DOC concentration. In terms of DOC removal the capital cost for ozone-BAC process is 93\% of MIEX resin process and the operating cost of MIEX resin process is 32\% of ozone/biological GAC process having carbon life not more than 2 months for BAC process (Cadee et al., 2000).

The overall cost of an ozonation system is dependent on capital and operation & maintenance expenses. Hybrid technology like Ozone- Biologically active filtration treatment is 40\% and 50\% less expensive compared to RO in terms of capital cost and operation cost respectively (Zhu et al., 2014)

Loi-Brugger et al. (2006) compared the operational performance and economic feasibility of ceramic and polymeric membranes. The specific treatment costs for both membrane systems are similar if wastewater discharge costs is not taken in to consideration. For example, both for ceramic and polymeric membranes, plants with capacities over 1000 m\(^3\)h\(^{-1}\) specific treatment cost are below 10 €/t. but the cost for polymeric membrane would be higher than the ceramic membrane when considering the cost of wastewater discharge.
2.6 Summary

This chapter has reviewed the related literature on membrane fouling for water treatment; reasons and mechanisms and application of pre-treatment process to minimize the fouling. Fouling during membrane filtration happens due to fouling by particulates, organic molecules, inorganic compounds and microbes. Protein, carbohydrate and humic substances present in AOM are considered as major foulants during membrane filtration. Feed water pre-treatment is considered as effective to reduce the foulant level thus to minimize fouling. BAC pre-treatment was reported to improve the flux performance for secondary effluent but the information regarding the filtration of natural surface water and the performance of BAC pre-treatment to improve the efficiency of the filtration system is required. The following research questions were evolved to address the gap in existing literature:

- Does BAC pre-treatment mitigate AOM fouling in ceramic microfiltration of surface water?
- Is BAC pre-treatment more effective for AOM from some species than others and also from their mixtures?
- Do the slightly different properties of carbon media influence the performance of BAC process?
- Is BAC or alum coagulation more applicable as pretreatment to reduce fouling?
Materials and methods used in this study are described in this chapter.

3.1 Source water

A surface water collected from the Allens Reservoir of Lorne, Victoria, was used for this study, which was termed as ‘Lorne water’in this thesis. Samples were collected on November 24 2016, December 19 2016, March 03 2017 and June 15 2017, respectively. Samples were stored at 4°C and warmed to room temperature prior to use. The characteristics of the raw samples collected from the reservoir are given in Table 3.1

Table 3.1: Characteristics of the Lorne water samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value (on date of collection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.9</td>
</tr>
<tr>
<td>DO (mg L⁻¹)</td>
<td>8.5</td>
</tr>
<tr>
<td>UV₂₅₄ₐ₅₈ (1/cm)</td>
<td>0.17</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.81</td>
</tr>
<tr>
<td>Conductivity (µS cm⁻¹)</td>
<td>183.8</td>
</tr>
<tr>
<td>DOC (ppm)</td>
<td>6.3</td>
</tr>
<tr>
<td>SUVA (L m⁻¹ mg⁻¹)</td>
<td>2.7</td>
</tr>
</tbody>
</table>

3.2 Selection of Granular activated carbon (GAC) and significance of the properties

Anthracite coal-based Acticarb GA 1000N and sub-bituminous coal-based Acticarb GS 1300 GACs were selected to investigate if there was any difference in their performance as GAC. According to the supplier (Activated Carbon Technologies Pty Ltd, Australia) both are suitable to use for the treatment of solutions containing high concentrations of organic micropollutants with short empty bed contact times (EBCT). GACs were ground and sieved in the laboratory to
achieve the particle size 0.5-0.7 mm (12x40 mesh) hence the ratio of column diameter to particle size was less than 30 which facilitates liquid phase adsorption where intraparticle diffusion controls the adsorption rate (Suzuki, 1990) and avoids wall effects. The properties of the ground GAC did not change significantly from the original GAC provided by the manufacturer, as summarized in Table 3.2. Each measurement was triplicated and values were averaged to give the standard deviation of the results.

Table 3.2: Textural Properties of GAC samples

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Acticarb GA1000N</th>
<th>Acticarb GS 1300</th>
<th>Acticarb GA1000N</th>
<th>Acticarb GS 1300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5-0.7 mm (Ground in the laboratory)</td>
<td>0.8-1.0 mm (Original provided by the manufacturer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface area (BET m² g⁻¹)</td>
<td>1123 ± 19.3</td>
<td>1173 ± 65.3</td>
<td>1083 ± 12</td>
<td>1188 ± 31.1</td>
</tr>
<tr>
<td>Total Pore volume (cm³ g⁻¹)</td>
<td>-</td>
<td>0.33</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>Micropore volume (cm³ g⁻¹)</td>
<td>0.17 ± 0.006</td>
<td>0.15 ± 0.006</td>
<td>0.19</td>
<td>0.15</td>
</tr>
<tr>
<td>Average micropore diameter (nm)</td>
<td>1.89 ± 0.03</td>
<td>1.89 ± 0.025</td>
<td>1.93 ± 0.014</td>
<td>1.9 ± 0.02</td>
</tr>
<tr>
<td>Average mesopore diameter (nm)</td>
<td>14.25 ± 1.1</td>
<td>14.42 ± 0.88</td>
<td>14.07 ± 0.24</td>
<td>15.18 ± 1.42</td>
</tr>
<tr>
<td>Average macropore diameter (nm)</td>
<td>110.02 ± 4.1</td>
<td>109.9 ± 3.1</td>
<td>112 ± 3.8</td>
<td>115.5 ± 3.7</td>
</tr>
<tr>
<td>Micropore content (%)</td>
<td>92 ± 1.2</td>
<td>91</td>
<td>91</td>
<td>92 ± 1.4</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>Water soluble ash content (%)</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Iodine Number</td>
<td>-</td>
<td>-</td>
<td>1000</td>
<td>&gt;1200</td>
</tr>
</tbody>
</table>

The quality of activated carbons is usually evaluated by the the BET surface area obtained from nitrogen adsorption at 77 K (Li et al., 2002). Samples were prepared by degassing at 250°C for 12 h under vacuum to remove moisture. The specific surface area, pore size and volume of granular activated carbon samples were measured by adsorption desorption isotherms of nitrogen.
at 77.15 K (Micromeritics). The specific surface area and pore size distribution of the activated carbons were determined by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) equations, respectively. Apparent density, ash content of the materials and iodine number was obtained from manufacturer’s data.

3.3 Biological Activated Carbon (BAC) Column Set Up and Operation

Glass columns with internal diameter of 1.5 cm were packed with GAC to an effective bed height of 12 cm. Prior to column packing, the GAC was washed with Milli-Q water to remove fine particles and degassed. Figure 3.1 (a) shows the schematic of the BAC column set up and process. Feed water collected from the treatment plant was then passed through the carbon media in down flow mode. To reduce the clogging of the carbon media the columns were backwashed for 10 minutes every 2 weeks with 25-30% bed expansion. Column effluents were collected periodically to monitor dissolved organic carbon (DOC), dissolved oxygen (DO) and UV absorbance at 254 nm (UVA$_{254}$). BAC columns were equilibrated with Lorne reservoir water for 95 days before experiments with algal organic matter (AOM).

![Figure 3.1: Schematic diagram of experimental setup (a) BAC process (b) Microfiltration](image)

3.4 Microfiltration Test

A lab scale membrane filtration rig (XLAB5 Pall) with a ceramic MF membrane (Pall) with nominal pore size of 0.1 μm, surface area of 0.005 m$^2$ and made of alumina was used. Prior to each MF run, Milli-Q water was passed through the membrane to remove membrane cleaning
agents for 10 minutes. The initial water flux was obtained by filtering Milli-Q water at TMP of 70 kPa. Dead-end mode multi cycle MF for 120 minutes (unless otherwise stated) was performed at a constant TMP of 70 ± 2 kPa at room temperature (20ºC-24ºC). After each filtration cycle backpulsing with compressed air for 2 sec was done to remove foulants. After MF tests the fouled membrane was soaked in NaOCl solution (approximately 1000 ppm available chlorine) for 3 hours for cleaning and restoring the pure water flux. Figure 3.1 (b) describes the whole microfiltration process.

3.5 Algae Culture and AOM extraction

Algae strains *Chlorella vulgaris* (CS-41) and *Microcystis aeruginosa* (CS-1036) were purchased from the Australian National Algae Culture Collection at CSIRO, Tasmania, in November 2016. It should be noted that strictly speaking cyanobacteria, e.g. *M. aeruginosa* used in this study, are not algae. However, they have been known as blue-green algae for decades and for convenience, *M. aeruginosa* will be referred to as algae in this work. Algae were cultured in MLA medium (Bolch and Blackburn, 1996) at 22ºC under humidified aeration in 5-L Schott bottles. Cleaned and autoclaved (121ºC for 60 minutes) glassware was used for culturing purposes. A 16/8 hour light/dark cycle for both algal cultures was provided in the incubator (Fisher and Paykel). Figure 3.2 shows the relationship between culture times and DOC concentration of *C. vulgaris* and *M. aeruginosa* with cell count.

![Figure 3.2](image_url)

Figure 3.2: Cell density and DOC concentration with growth curve (a) *C. vulgaris*  
(b) *M. aeruginosa*
AOM was extracted at the 12th and 25th day of culture i.e. from exponential and stationary growth phase by centrifugation (3270 × g for 30 mins) of the algal cell suspensions and then filtration (0.8 µm membrane) of the supernatant. For different experimental purposes AOM was diluted to 3 mg DOC L⁻¹ with Milli-Q water or the reservoir water.

3.6 Alum Coagulation

Coagulation was performed using alum, Al₂(SO₄)₃.18H₂O having molar mass of 666.4 g mol⁻¹ (Chem-Supply, Pty Ltd., Australia). Alum is widely used as coagulant to remove the high molecular weight organics from water and waste water. Stock solution having 1000 mg Al³⁺ L⁻¹ was prepared with Milli-Q water in the laboratory. Coagulation experiments were conducted at room temperature (20 ± 2 °C) in a laboratory jar tester unit (Phipps and Bird, PB-700). Samples were placed to rapid mixing for 1 min at 200 rpm, followed by slow mixing for 20 min at 30 rpm and then allowed to settle for 2 hours. After settling supernatant was taken for MF tests. pH of the samples was adjusted to 8 before and after coagulation using 1M H₂SO₄ or 1M NaOH.

A range of dosages (2.5-20 mg Al³⁺ L⁻¹) was tested to determine the optimum dosage with Lorne water. After determination of optimum dose for Lorne water alone a range of dosages (2.5-15 mg Al³⁺ L⁻¹) was tested to determine the optimum dosage for Lorne water containing AOM and the optimum dose was used for alum coagulation pre-treatment.

3.7 Analytical methods

3.7.1 pH and conductivity

pH meter (Mettler Toledo) was used to measure pH of the sample and calibrated before using. Conductivity was measured using a Hach Sension 5 conductivity meter. Calibration of conductivity meter was done with 500, 1413 and 2760 µS cm⁻¹ potassium chloride (KCl) standard solutions. Samples were measured in triplicate and the results were averaged.

3.7.2 Color

A Hach spectrophotometer (model DR 5000) was used for the determination of color at 455 nm. Samples were filtered through 0.45 µm membrane (prewashed with Milli-Q water) prior to the analyses. Samples were measured in triplicate and the results were averaged.
3.7.3 Turbidity and dissolved oxygen (DO)

A Hach 2100 AN 1S Turbidimeter and Hach – HQ d meter were used to determine turbidity and dissolved oxygen (DO) concentration, respectively, of the water samples. Samples were measured in triplicate and the results were averaged.

3.7.4 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) is defined as the measurable concentration of organic carbon that passes through a 0.45 µm filter (USEPA, 2009). DOC was measured using Sievers 5310 C TOC analyser. Each measurement was triplicated and the results were averaged.

3.7.5 UV spectrophotometry

UV absorbance was measured using spectrophotometer (UV2-2700) at 254 nm with quartz cuvette. Samples were measured in triplicate and the results were averaged.

3.7.6 Specific ultraviolet absorbance (SUVA)

SUVA is a good indicator of the humic fraction of the DOC which has been used as a surrogate measurement for DOC aromaticity (Traina et al., 1990). SUVA can be determined by the following equation

\[
SUVA = \frac{UVA_{254}}{DOC} \times 100
\]

Eq. 3.1

3.7.7 Carbohydrate

Carbohydrate content was determined by using phenol-sulfuric method and D-glucose was used as the standard carbohydrate substance for calibration and read at 490 nm (Dubois et al., 1956). Each measurement was triplicated and the results were averaged.

3.7.8 Protein

The bicinchoninic acid (BCA) method was employed for protein analysis in which the QPBCA QuantiPro™ BCA Assay Kit (Sigma Aldrich) was used. Bovine serum albumin (Sigma Aldrich) was used as standard protein substance (Zheng et al., 2009) to prepare calibration curve and the
absorbance was read at 562 nm. Each measurement was triplicated and the results were averaged.

3.7.9 Determination of Point of Zero Charge (pH_{pzc})

Determination of pH_{pzc} of the GACs was carried out by pH titration procedures (Rivera-Utrilla et al., 2001) to know the surface charge of activated carbon. Eight Erlenmeyer flasks were used and 50 mL of 0.01M NaCl solution was poured in each of them. The pH of the solution was adjusted to a value from 2.5 to 9 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then 0.15 g of activated carbon was added to each flask, shaken for 30 minutes and the final pH was measured after 48 h and plotted against initial pH. The pH_{pzc} is the point where the curve crosses the line pH_{final} = pH_{initial}.

3.7.10 Fluorescence EEM spectroscopy

Fluorescence excitation emission matrix (EEM) spectra were obtained using a fluorescence spectrophotometer (PerkinElmer, LS 55) for characterization of fluorescent organic components. EEM spectra are contour plots in which fluorescence intensities are plotted as a function of excitation and emission wavelengths. Excitation wavelengths represent the wavelength delivered to the aqueous sample, thus inducing fluorescence, while emission wavelengths represent the wavelength of the resulting fluorescence (Butturini and Ejarque, 2013). Excitation and emission wavelength range used was 200-550 nm at increments of 5 nm. Samples were filtered (0.45 μm) prior to analysis to remove interference by suspended matter.

Fluorescence regional integration (FRI) method (Chen et al., 2003) was used in characterizing DOC into the five excitation-emission regions. Regions I (Ex/Em: 220-270 nm/ 280-330 nm) and II (Ex/Em: 220-270 nm/330-380 nm) are associated with protein-like (AP) organic matter which comprise aromatic amino acids. Region III (Ex/Em: 220-270 nm/380-550 nm) is associated with fulvic acid-like (FA) compounds. Region IV (Ex/Em: 270-440 nm/ 280-380 nm) is associated with soluble microbial by-product-like (SMP) compounds, mainly proteins and polysaccharides. Region V (Ex/Em: 270-440 nm/380-550 nm) is associated with humic acid-like (HA) compounds.
3.7.11 Unified membrane fouling index (UMFI)

Slopes of the straight lines represent the UMFI values of the MF flux data for either constant pressure or constant flux conditions and was developed by Huang et al. (2007). The model for UMFI is shown by Eq. 3.2.

\[ \frac{J_0}{J} = 1 + (UMFI) \times V \]  \hspace{1cm} \text{Eq. 3.2}

UMFI can be determined using linear regression when the reciprocal of the normalized flux \((J_0/J)\) increases linearly with the specific permeate volume \((V)\).
CHAPTER 4

IMPACT OF BAC TREATMENT OF SOLUBLE AOM FROM CHLORELLA VULGARIS AND MICROCYSTIS AERUGINOSA ON THE FOULING OF A CERAMIC MICROFILTRATION MEMBRANE

The objective of this study was to evaluate the efficiency of biological activated carbon as a pre-treatment to mitigate membrane fouling during microfiltration of freshwater containing AOM. As cyanobacteria and green algae are prevalent in Australian fresh waters and Microcystis aeruginosa and Chlorella vulgaris are dominant species, they were used in this study. To examine the fouling potential of the AOM at different algal growth phases, AOM extracted from day 12 (exponential phase) and day 25 (stationary phase) was investigated. For a better insight into the fouling effect of AOM present in surface water, the AOM was diluted either with Milli-Q water or the reservoir water to prepare the feed solutions for the BAC and microfiltration tests. Two different BAC columns packed with two different GACs were utilized to investigate the influence of carbon media on pre-treatment performance.

4.1 Equilibration of BAC columns

The raw water collected from Lorne having DOC 6.6 mg L\(^{-1}\) was passed through the columns to establish biofilm within the carbon media. Figure 4.1 shows the DOC reduction in columns during the transition from GAC to BAC. At the beginning (day 4) GAC columns demonstrated high adsorption capacity and removal rates were comparable for the columns, 52% and 47% for GA 1000N and GS 1300, respectively.

According to the manufacturer, GA 1000N is acid washed and pH stabilized which prevents initial pH increment of effluent, removes soluble silica from the matrix of the activated carbon and reduces the commissioning time to a few hours instead of many days for large scale operation. The physical properties analysis (Table 3.1) showed both of the GACs had micropore content more than 90%, surface area and iodine number was over 1000 which facilitates initial adsorption (Karanfil, 2006) and high removal of DOC. Surface of the activated carbon can bind the organic matter to the pores by van der Waals’ dispersion forces and electrostatic interactions (Moreno-Castilla and Rivera-Utrilla, 2001) which significantly reduce effluent DOC levels.
Adsorption capacity is determined by the extent of the adsorbate-carbon surface interactions which is usually attributed to a carbon’s internal pore volume (Considine et al., 2001).

Equilibration of the columns was confirmed by the constant amount of reduction of DOC in effluent. The overall DOC removal rate by GA 1000N and GS 1300 after equilibration was 24% and 53%, respectively by day 95, the removal by GA 1000N is consistent to the DOC removal reported by Buchanan et al. (2008) and Kim et al. (1997) as 29% and 25%, respectively by BAC process. The higher DOC removal rate for GS 1300 compared to GA 1000N correlates well with the BET surface area and iodine number of the GACs, which showed that Activated GS 1300 exhibits higher iodine number (>1200) and slightly higher BET surface area (1,173 m² g⁻¹) compared to Activated 1000N (Iodine number and BET surface area is 1000 and 1123 m² g⁻¹). Iodine number indicates pore volume capacity and the ability to adsorb low molecular weight substances (Malik et al., 2007). Due to higher Iodine number, GS 1300 adsorbed higher amount of molecules which contributes to biodegradation and thus performed better.

![Equilibration of GAC columns in terms of DOC concentration (BW=backwash)](image)

Figure 4.1: Equilibration of GAC columns in terms of DOC concentration (BW=backwash)

The adsorption capacity of activated carbon not only relies upon its pore structure but surface chemistry is also an essential factor (Wong, 1998), therefore it is also important to know the
surface charges of the activated carbon. So the pH\textsubscript{pzc} was determined to know the surface charges of the virgin activated carbons.

The point of zero charge of activated carbon (pH\textsubscript{pzc}) is the pH where activated carbon has zero potential charge on its surface. pH\textsubscript{pzc} values of virgin GA 1000N and GS 1300 were measured to be 7.7 and 7.0 respectively are shown in Figure 4.2(a). pH of the feed during early days of BAC column equilibration as shown in Figure 4.2(b). pH of the influent was around 6.5-6.2 for GS 1300 and 7.4 for GA 1000N. The pH measured for the effluent were approximately 7.2-7.4 for both GACs. Surface charge of virgin GA 1000N and GS 1300 was positive as pH of the feed was below its pH\textsubscript{pzc} and favors the adsorption of anions. The suspended particles present in natural water have a negative surface charge (Beckett and Le, 1990). When feed was provided to the GAC columns through the peristaltic pump, activated carbon came into contact with water hence an electric charge difference is supposed to be developed depending on the pH of the feed and the surface characteristics of the carbon. pH of GS 1300 feed was observed to rise above its initial pH\textsubscript{pzc} after 12 days. This change in pH may alter the carbon surface charge (Moreno-Castilla and Rivera-Utrilla, 2001) because the negative surface charge increases with the increase in feed water pH (Bellona and Drewes, 2005) which may be attributed to the better performance by GS 1300 than GA 1000N during equilibration. Beckett and Le (1990) have noted that the surface charge density of surface water particles strongly depends on the adsorbed layer of NOM particularly the humic substance component.

![Figure 4.2](image-url)  
Figure 4.2: (a) Determination of pH\textsubscript{pzc} for virgin GAC (b) Feed pH in early days of operation.
4.2 Fouling study of single species AOM

AOM extracted from the two growth phases (exponential and stationary) of *C. vulgaris* (C-AOM) and *M. aeruginosa* (M-AOM) was used to evaluate the fouling effect during the multi-cycle MF tests. MF of AOM from both species at a concentration of 3 mg DOC L\(^{-1}\) mixed with either Milli-Q water or the reservoir water gave considerable flux reduction during whole filtration period. To observe the effect of longer time filtration, total 120 minutes of filtration were carried out for all solutions containing AOM except day 25 C-AOM where duration of each cycle was 30 minutes with back pulsing of 2 sec and the total filtration period was 30 minutes where duration of each cycle was 10 minutes. Yellow symbols on the data series represent the data immediately after the back-pulsing. Each MF run was duplicated and only single data were presented. The trend of flux decline was similar for duplicate runs but the extent of fouling varies with different batches of cultures used for different experiments.

4.2.1 Impact of AOM extracted from *C. vulgaris* on ceramic MF membrane

For day 12 C-AOM solutions, most of the flux decline occurred in the 1\(^{st}\) filtration cycle with a sharp drop before reaching the specific permeate volume of 50 Lm\(^{-2}\) and then was steady in the following cycles. This trend was valid both for C-AOM mixed with Milli-Q (C-AOM/Milli-Q) and Lorne water (C-AOM/Lorne water) as shown in Figure 4.3.

![Figure 4.3: Normalized flux vs specific volume for MF of solution containing C-AOM (day 12)](image-url)
Flux declined gradually for Lorne water with a sudden change in the last filtration cycle (>150 Lm\(^{-2}\)) after back pulsing. Back pulsing seemed to have no significant benefit suggesting that most of the fouling was due to irreversible foulants. At a chosen specific volume of 100 Lm\(^{-2}\), the trend of flux decline for day 12 C-AOM was C-AOM/Milli-Q (0.45) < Lorne water (0.43) < C-AOM/Lorne water (0.33).

Flux decreased gradually for day 25 in all filtration cycles after back-pulsing. The normalized flux \((J/Jo)\) values for day 25 solutions at 100 Lm\(^{-2}\) were Lorne water alone (0.41), C-AOM/Milli-Q (0.22) and C-AOM/Lorne water (0.15) as shown in Figure 4.4. Therefore the trend of flux decline was slightly different compared with day 12 solutions as explained below.

Figure 4.4: Normalized flux vs specific volume for MF of solution containing C-AOM (day 25)

A significant flux decline is observed for the Lorne water having DOC concentration of 7.68 mgL\(^{-1}\) and 6.3 mgL\(^{-1}\) as shown in Figure 4.3 and 4.4, respectively which indicates the presence of organic compounds such as humic substances in the natural surface water (Drikas, 2003). Surface water contains humic and nonhumic organic substances, and inorganic particulates which also have significant effect during MF as shown by the flux difference between Milli-Q and Lorne water. The concentration of DOC and UVA was measured before and after the various treatment processes for the solutions with and without AOM to observe their impact on fouling and are shown in Figure 4.5. It should be noted Figure 4.5 also contains the results for the BAC treatment, which will be discussed in Section 4.2.2.
The DOC concentration of the feed containing day 12 and day 25 C-AOM was 11.29 mgL$^{-1}$ and 9.18 mgL$^{-1}$, respectively. The concentration of AOM in feed water was 3 mg DOC L$^{-1}$ whereas rest was the contribution by the organic matter present in Lorne water. So, it is notable that the Lorne water used for day 12 experiments collected on the 24th November 2016 had higher DOC concentration than the Lorne water used for day 25 experiments, which was collected on the 19th December 2016. The characteristics of the samples can vary seasonally and may have various amounts and types of molecules which acted differently during the filtration process.
When C-AOM was mixed with Lorne water, solution led to much greater flux decline than Lorne water alone as shown in Figure 4.3 and Figure 4.4. This increased fouling was attributed to the presence of C-AOM in the solution. The characteristics of AOM and NOM are different because the AOM is much more hydrophilic than NOM, which are composed of hydrophobic compounds (Henderson et al., 2008). So when C-AOM was mixed with Lorne water that may have impact on the NOM characteristics of the Lorne water. Flux differences between Milli-Q and C-AOM (day 12 and day 25) mixed with Milli-Q water; Lorne water and C-AOM (day 12 and day 25) mixed with Lorne water verifies that the presence of C-AOM leads to greater impact on the performance of MF membranes. Total flux declination rate were 50% and 65% of their initial flux for C-AOM day 12/Milli-Q and C-AOM day 12/Lorne, respectively. During MF, algal biopolymer can bind on the surface of the ceramic MF membranes and cause the fouling (Villacorte et al., 2015). It is also mentionable that day 25 C-AOM (stationary phase) solutions exhibit lower filtration flux than C-AOM day 12 solutions similar to the result obtained by Zhang et al. (2016a) that stationary phase poses greater fouling potential during MF. The amount and type of DOC released from algae depends on their growth phases. DOC concentrations per cell is higher for the stationary growth phase than the exponential phase (Henderson et al., 2008). During exponential phase, the DOC was primarily produced by cell metabolism as hydrophilic fraction as cell death was low. Whereas during stationary phase, the biological productivity produced DOC as hydrophilic fraction but the cell decay resulted in intracellular compounds release as transphilic fraction, hydrophobic fraction and hydrophilic fraction with an increase of the hydrophobic fraction and the transphilic fraction contribution to AOM. So, the increase of AOM hydrophobicity during the stationary phase seemed to result from the release of intracellular organic material of high hydrophobic character and also due to the decreased charge density.

The overall DOC removal by the membrane for Lorne water alone was higher than C-AOM/Lorne water for exponential growth phase. The DOC removal for Lorne water was almost 40% whereas for C-AOM/Lorne it was 21% for day 12 (sample 1 collected on 24\textsuperscript{th} November 2016) and 34% for day 25 solutions (sample 2 collected on 19\textsuperscript{th} December 2016), respectively. When AOM was added to the Lorne water containing humic substances interaction between the compounds can take place which increase the average molecular radius and the amount of HMW compounds (Zhang et al., 2018). So, this higher amount of HMW substances are more UV-
absorbing and are removed by MF. UVA removal by MF was comparable for Lorne water and C-AOM/Lorne. For exponential and stationary growth phase removal was 0.1 and 0.09, respectively. UVA removal was considerably higher than the DOC removal, which might be related to the higher removal of humic substances by the membrane. Kim et al. (2010) and Yuan and Zydney (1999) suggested that the humic substances are more responsible for fouling in MF in a secondary effluent due to the higher retention of these substances.

4.2.2 Impact of BAC pre-treatment on the flux performance of MF of C. vulgaris solutions

It is clear that the existence of C-AOM and organic matter in feed water led to significant flux decline during ceramic membrane MF. As a means of reducing this, BAC treatment of the feed solutions prior to MF was undertaken. AOM extracted from C. vulgaris was mixed with Lorne water at a concentration of 3 mg DOC L⁻¹ and run through the two different BAC columns to study the pre-treatment efficiency to mitigate AOM fouling in the MF. An improvement in the flux was observed after the BAC treatment of the feed containing C-AOM is shown in Figure 4.6. For both cases, although the flux decline was rapid a higher flux was observed in 1st filtration cycle before reaching the specific volume of 50 Lm⁻². The flux profile was almost leveled off in the successive cycles. For example, at a specific permeate volume of 100 Lm⁻² the flux value for untreated day 12 solution was 0.33 whereas it was 0.36 and 0.39 after pretreated by GS 1300 and GA 1000N, respectively. For day 25 solutions, the BAC pre-treatment performance was comparable for GS 1300 and GA 1000N as it produced approximately same amount of permeate after each cycle for each. At a specific permeate volume of 100 Lm⁻² the flux value for untreated solution was 0.15 whereas it increased to 0.17 and 0.19 after pre-treatment by GS 1300 and GA 1000N, respectively. According to the flux, the pre-treatment performance of GA 1000N was slightly better compared to GS 1300. The day 25 C-AOM samples delivered better flux recovery than day 12 samples (21% cf. 15%).
After the BAC process, DOC removal was observed to be higher for day 25 than day 12 samples. DOC removal was slightly better for GS 1300 samples (3.5 mgL⁻¹ and 4.3 mgL⁻¹ for day 12 and day 25 C-AOM/Lorne, respectively) whereas the removal by GA 1000N was 2.8 mgL⁻¹ and 4.1 mgL⁻¹ for day 12 and day 25 C-AOM/Lorne solutions. Performance of both column in terms of UVA removal did not vary significantly. Removal efficiency for day 25 solutions was similar to the day 12 solutions. For example, the removal for day 12 and day 25 C-AOM/Lorne was 0.10 and 0.11, respectively for GS 1300 column. So, the reduced value of DOC and UVA suggested the removal of organic matter including humic substances from the samples by BAC process i.e. due to the simultaneous adsorption of bio-refractory compounds and bio-oxidation of biodegradable organic matter by BAC (Ibn Abdul Hamid et al., 2017).
BAC followed by MF provided a considerable increment in removal efficiency as shown by the overall lower DOC concentration and UVA. DOC removal by columns was comparable for day 25 solutions whereas a little difference was observed (7.6 mgL\(^{-1}\) by GS 1300 cf. 8.2 mgL\(^{-1}\) by GA 1000N) for day 12 solutions. Greater removal of UV absorbing substances was achieved for day 25 than day 12 and was 0.15 and 0.12, respectively. The higher removal by GA 1000N than GS 1300 was consistent with their flux trend.

![Figure 4.7 Plot of flux vs specific volume for MF of C-AOM solution pre-treated by BAC pre-treatment (duplicate run) (a) day 12 (b) day 25 (note that same Lorne water used for both experiments collected on 15\(^{th}\) June 2017)](image)

Figure 4.7 represents the plot of a second trial for MF and BAC runs for \textit{C. vulgaris} day 12 and 25. The initial DOC concentration for untreated samples containing C-AOM/Lorne was 11.5 mgL\(^{-1}\). The flux values at 100 Lm\(^{-2}\) for untreated samples were 0.27 and 0.32 for day 12 and day 25 solutions, respectively whereas for the first run the flux values at 100 Lm\(^{-2}\) for untreated samples were 0.33 and 0.15 for day 12 and day 25 solution, respectively. Gradual flux drop was
observed in the first 2 filtration cycles. At a specific volume of 100 Lm$^{-2}$, 1300 BAC pretreated samples achieved higher flux (0.36) for day 12 C-AOM/Lorne whereas 1000 BAC pretreated samples achieved higher flux for day 25 (0.39). Most of the flux recovery was obtained in the first filtration cycle which was observed to be similar for previous run as well. The different flux values for the two runs were attributed to the AOM coming from different *C. vulgaris* cultures.

### 4.2.3 Impact of AOM extracted from *M. aeruginosa* on ceramic MF membrane

At a chosen specific volume of 100 Lm$^{-2}$, the flux values for day 12 solutions were 0.28, 0.49, 0.56 and 1 for M-AOM/Lorne, M-AOM/Milli-Q, Lorne water alone and Milli-Q. At that same specific volume, the flux values for day 25 solutions were 0.18, 0.38, 0.56 and 1 for M-AOM/Lorne water, M-AOM/Milli-Q, Lorne water alone and Milli-Q, as shown in Figure 4.8.

![Figure 4.8](image)
Considering the flux as an indicator of membrane fouling, the order of fouling potential as M-AOM day 25/Lorne water > M-AOM day 12/Lorne water > M-AOM Day 25/ Milli-Q > M-AOM Day 12 Milli-Q > Lorne water. Total flux declined approximately 36% and 64% from their initial flux for M-AOM day 12/Milli-Q and M-AOM day 12/Lorne, respectively. It is mentionable that most flux decline for all types of solutions mainly occurred until filtration volume < 20 Lm⁻² during the first filtration cycle. In this initial period, flux declined rapidly due to the pore blockage by larger molecules then became more gradual in the consecutive cycles.

The difference in flux of Milli-Q, Milli-Q mixed with day 12 and Milli-Q mixed with day 25 shows that presence of M-AOM in feed water led to significant flux decline. It is also mentionable that Day 25 M-AOM causes greater flux decline during MF than Day 12 M-AOM as was found for the first C. vulgaris experiment. This observation was consistent with the previous studies (Devanadera and Dalida, 2015, Zhang et al., 2013b) which mentioned that fouling potential of M-AOM increased with culture growth phase. This phenomenon is due to the difference in chemical properties of M-AOM which varies during growth phase and poses different fouling potential (Huang et al., 2012) and as noted for C. vulgaris. As cells age in stationary phase they break down so release internal organic matter which is more humic (hydrophobic) with higher UVA and fouling potential. Flux of M-AOM/ Lorne water was markedly lower compared to Lorne water alone (DOC 4.8 mgL⁻¹) and M-AOM/Milli-Q water as well. This observation was also similar for C-AOM experiments presented in section 4.2.1. When M-AOM was mixed with Lorne water the solution had higher DOC concentration (7.99 mg L⁻¹) and so resulted in lower filtration flux. Lorne water and M-AOM both contained organic substances and when mixed with each other, the organic load increased, causing the additional flux decline. The UVA for M-AOM mixed with Milli-Q water and Lorne water was 0.018 and 0.118 for day 12 and 0.049 and 0.15 for day 25, respectively as shown in Figure 4.9 (b). So the content of UV-absorbing substances increased for the M-AOM/Lorne mixtures which was observed to be similar for C-AOM/Lorne when compared with Lorne water alone. After back pulses of 2 sec, flux recovery was observed to be slightly better for M-AOM day 25/Lorne water and M-AOM day 25/Milli-Q compared to Lorne water alone.

Significant reduction of DOC and UVA was observed after MF process which indicates the reduction in organic matter and humic substances presence in feed as shown in Figure 4.9.
Figure 4.5 also demonstrated the similar situation obtained by C-AOM solutions. Huang et al., (2012) reported that MF of M-AOM removes molecules having MW > 10 kDa which mainly consisted of polysaccharides, proteins or humic substances. This statement probably applied for the C-AOM solutions as well according to the reduction in organic matter concentration. During MF these organics are deposited on the ceramic membrane surface and due to their physical characteristics form a thick layer and reduce permeate flux (Zhang et al., 2013b). It should be noted Figure 4.9 also contains the results for the BAC treatment, which will be discussed in Section 4.2.4.

Figure 4.9: (a) DOC concentration and (b) UVA of the samples before and after BAC and MF processes of samples containing M-AOM (note that Lorne water samples were collected on 7th March 2017)
4.2.4 Impact of BAC pre-treatment on the flux performance of MF of *M. aeruginosa* solutions

AOM extracted from *M. aeruginosa* was mixed with Lorne water at a concentration of 3 mg DOC L⁻¹ and run through either the GS 1300 or GA 1000N BAC column and effluents were taken for MF tests to investigate whether BAC pre-treatment would enhance the MF performance.

The flux declination for the day 12 pre-treated solutions was quite rapid in the initial cycle of filtration but then reached a nearly constant value in the last cycles with a transition in the middle cycles. At a specific volume of 100 Lm⁻², the flux value was 0.28 for untreated solution whereas flux improved at 0.33 and 0.35 for GS 1300 and GA 1000N treated samples, respectively, as shown in Figure 4.10 (a). Similarly for M-AOM day 25 solutions, at that same specific volume of 100 Lm⁻², the flux value for untreated solution was 0.18 whereas flux improved to 0.39 and 0.26 after GS 1300 and GA 1000N treatment, respectively as shown in Figure 4.10 (b). Normalized flux was observed to be improved in the last filtration cycles (>100 Lm⁻²) after 2 sec back pulsing.

![Figure 4.10: Plot of flux vs specific permeate volume for MF of M-AOM solution pre-treated by BAC (GS 1300 or GA 1000N) (a) day 12 (b) day 25 (note that same Lorne water was used for MF and BAC experiments and collected on 7th March 2017)](image)

The pretreated day 25 M-AOM samples gave slightly better flux profiles compared with the pretreated day 12 M-AOM solutions and greater flux recovery was observed for GS 1300
BAC pre-treatment provided considerable amount of reduction in DOC concentration and UVA both for day 12 and day 25 solutions and thus delivered better flux. Better DOC removal was observed for day 12 solutions whereas better UVA removal was observed for day 25 samples (Figure 4.9). The performance of both BAC columns was similar and was consistent with their respective MF performance. But for day 12 solutions, better DOC removal (3.4 mgL⁻¹ cf. 2.5 mgL⁻¹) was achieved by GS 1300 column and the observation was not consistent with their filtration flux profile. So it is understood that the concentration of DOC in solutions is not the only parameter which provided information about the fouling potential of the feed also mentioned by Huang et al. (2014) and Pramanik et al. (2014). but the other characteristics such as types of compounds, their molecular size and shape, surface charge and concentration also had a significant influence on treatment performance.

Feed water with a higher fouling potential is indicated by a higher value of UMFI. UMFI values for untreated and BAC pretreated samples are shown in Figure 4.11 and were calculated by the two-data point method (Zhang et al., 2015). Data points considered were first data of first cycle and last data of last cycle.

![Figure 4.11: UMFI values of the solutions containing AOM for untreated and BAC pretreated solutions](image)

Figure 4.11: UMFI values of the solutions containing AOM for untreated and BAC pretreated solutions

MF of feed containing day 25 M-AOM and C-AOM led to severe flux decline at the end of filtration period, where UMFI values for day 25 (0.024 m²L⁻¹ and 0.0536 m²L⁻¹) were markedly higher than for day 12 (0.0147 m²L⁻¹ and 0.0141 m²L⁻¹). This observation is consistent with the higher fouling potential by AOM from stationary growth phase. GS 1300 and GA 1000N pretreated samples showed lower UMFI values further indicating that BAC pre-treatment has
potential to reduce membrane fouling particularly for AOM from *C. vulgaris* and *M. aeruginosa* in stationary phase. Overall, GA 1000N BAC treatment seemed to lead greater flux improvement for both algal species.

The day 25 C-AOM solutions provided higher fouling resistance than others. Total fouling by C-AOM day 25 and M-AOM day 25 was $3.8 \times 10^{12} \text{ m}^{-1}$ and $3.1 \times 10^{12} \text{ m}^{-1}$, respectively, whereas total fouling resistance for C-AOM day 12 and M-AOM day 12 was $2.3 \times 10^{12} \text{ m}^{-1}$ and $2.6 \times 10^{12} \text{ m}^{-1}$, respectively as shown in Figure 4.1. The total fouling resistance obtained by the solutions was also consistent with their UMFI values. The reduced fouling resistance after day 25 BAC pre-treated solutions was $1.9 \times 10^{12} \text{ m}^{-1}$ (GA 1000N) and $1.7 \times 10^{12} \text{ m}^{-1}$ (GS 1300) for C-AOM and M-AOM, respectively. Similarly, the reduced fouling resistance for the pretreated day 12 solutions was $1.4 \times 10^{12} \text{ m}^{-1}$ (GA 1000N) and $2.0 \times 10^{12} \text{ m}^{-1}$ (GA 1000N) for C-AOM and M-AOM, respectively.

Table 4.1: Total fouling resistances before and after BAC pre-treatment for single species AOM

<table>
<thead>
<tr>
<th>Total fouling resistance, m$^{-1}$</th>
<th>With out BAC</th>
<th>After BAC</th>
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<tbody>
<tr>
<td></td>
<td>GS 1300</td>
<td>GA 1000N</td>
</tr>
<tr>
<td>C-AOM+Lorne water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 12</td>
<td>2.3$\times10^{12}$</td>
<td>1.6$\times10^{12}$</td>
</tr>
<tr>
<td>Day 25</td>
<td>3.8$\times10^{12}$</td>
<td>2.2$\times10^{12}$</td>
</tr>
<tr>
<td>M-AOM+Lorne water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 12</td>
<td>2.6$\times10^{12}$</td>
<td>1.8$\times10^{12}$</td>
</tr>
<tr>
<td>Day 25</td>
<td>3.1$\times10^{12}$</td>
<td>1.7$\times10^{12}$</td>
</tr>
</tbody>
</table>

Figure 4.12 shows the plot of duplicate MF and BAC runs for *M. aeruginosa* day 12 and day 25. The initial DOC concentration for untreated samples containing C-AOM/Lorne was 11.3 mgL$^{-1}$. The flux values at 100 Lm$^{-2}$ for untreated samples were 0.24 and 0.22 for day 12 and day 25 solution, respectively, whereas for the first run the flux values at 100 Lm$^{-2}$ for untreated samples were 0.28 and 0.18 for day 12 and day 25 solution, respectively. Flux decline was rapid in the first filtration cycle before reaching 50 Lm$^{-2}$. Similar trend was observed in the previous run.
presented in section 4.2.3. At a specific volume of 100 Lm\(^{-2}\), for both growth phases, 1300 BAC pretreated samples achieved slightly higher flux 0.34 and 0.29 for day 12 and day 25 M-AOM/Lorne solutions, respectively. Most of the flux recovery was obtained in the first filtration cycles which was observed to be similar for previous run.

![Figure 4.12](image_url)

Figure 4.12: Plot of flux vs specific volume for MF of M-AOM solution pre-treated by BAC pre-treatment (duplicate) (a) day 12 (b) day 25 (note that same Lorne water was used for both experiments were collected on 15\(^{th}\) June 2017)

4.2.5 DOC and UVA removal

C-AOM solutions had better UVA removal irrespective to growth phases than M-AOM solutions after the MF and BAC process. When comparing the DOC removal for the exponential phase AOM, better removal was attained by *M. aeruginosa* than *C. vulgaris* after MF and BAC process. In case of stationary phase AOM, better removal occurred for *C. vulgaris* after the MF and BAC process. After BAC followed by MF, day 12 samples had higher DOC removal whereas day 25 samples had higher UVA removal. DOC removal was almost comparable for
both growth phases of *M. aeruginosa*. Comparing the performance of two BAC columns, no particular trend was observed and performance was comparable for individual experiments. Overall, Better DOC and UVA removal was observed after BAC followed by MF for *C. vulgaris*.

### 4.2.6 Carbohydrate and protein content

To see which types of organic molecules were removed by BAC and MF and so impacted fouling the content of carbohydrates and proteins was determined for untreated and treated samples. As expected the carbohydrate concentrations of C-AOM/Lorne and M-AOM/Lorne was considerably higher as shown in Figure 4.13 (a) indicating that it varied from 1.7 to 2.2 mgL$^{-1}$ for Lorne water. The concentration was observed to be increased with growth phase for *C. vulgaris* which also had higher fouling potential during filtration process. On the other hand, the carbohydrate concentration of day 12 and day 25 M-AOM samples was comparable (5.4 mgL$^{-1}$ and 5.6 mgL$^{-1}$, respectively) as shown in Figure 4.13 (b) yet the fouling for day 25 was much greater.
The protein concentration in C-AOM day 12/Milli-Q was 1.4 mgL⁻¹ and increased to 1.85 for day 25/Milli-Q as shown in Figure 4.14 (a). The protein concentration in M-AOM day 12/Milli-Q increased from 1.62 mgL⁻¹ to 3.39 mgL⁻¹ for day 25 M-AOM /Milli-Q as shown in Figure 4.14 (b). Therefore significant increase with growth phase in protein concentration relative to carbohydrate for M-AOM than C-AOM was observed. This observation was consistent with the findings of Zhang et al. (2016a). The concentrations of carbohydrate and protein being higher both for C-AOM and M-AOM when mixed with Lorne water than the mixtures with Milli-Q water confirm the presence of carbohydrate and protein in Lorne water. The significant amount of carbohydrate (1.7-2.9 mgL⁻¹) and protein (1.2-1.5 mgL⁻¹) in Lorne water also supports the considerable flux decline caused by Lorne water.
After MF of C-AOM/Lorne water and M-AOM/Lorne water, the ratios of carbohydrate to protein were observed to decrease as shown in Table 4.2 indicating that more carbohydrate than protein was removed by the membrane which is consistent with the literature (Zhang et al., 2013a). For example, ratios before MF for M-AOM day 12 and M-AOM day 25 were 4 and 2.07 and decreased to 2.47 and 1.74 after MF for day 12 M-AOM and day 25 M-AOM, respectively. Neemann, et al. (2013) suggested that the carbohydrates are relatively larger than the proteins and thus are deposited on the membrane surface more easily than protein (Pramanik et al., 2014). Comparatively higher ratios of carbohydrate to protein were observed after BAC treatment compared to MF alone. For example, the ratios after BAC for M-AOM day 12 were 2.51 and 2.55 for GS 1300 and GA 1000N, respectively and for day 25 M-AOM ratios were 1.82 and 1.78 for GS 1300 and GA 1000N, respectively.

Figure 4.14: Protein content in various samples containing AOM from

(a) *C. vulgaris* (b) *M. aeruginosa*
Table 4.2: Ratios of carbohydrate to protein after various treatment processes

<table>
<thead>
<tr>
<th></th>
<th>Ratio of carbohydrate to protein</th>
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<tbody>
<tr>
<td></td>
<td>Before MF</td>
</tr>
<tr>
<td>Lorne+C-AOM Day 12</td>
<td>2.16</td>
</tr>
<tr>
<td>Lorne+C-AOM Day 25</td>
<td>2.45</td>
</tr>
<tr>
<td>Lorne+M-AOM Day 12</td>
<td>4</td>
</tr>
<tr>
<td>Lorne+M-AOM Day 25</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Micro-organisms within BAC columns biodegrade the proteins to amino acids and consume some of them and thus reduce nitrogen of effluent which was also observed by Zheng et al. (2010). In BAC treatment the micro-organisms also effectively removed carbohydrates which eventually reduced the fouling layer on the membrane surface and similar to that was noted by Pramanik et al. (2014). BAC process followed by MF provides a further removal in carbohydrate and protein concentration. Therefore BAC pre-treatment process involves biodegradation which reduces carbohydrate and protein concentration and enhances permeate flux.

4.2.7 Fluorescence EEMs of different solutions

Milli-Q water does not contain any fluorescent organic matter thus used as a reference for the experimental purposes as shown in Figure 4.15 (a). EEM spectral features are significantly different for Lorne water which showed presence of fluorescent organic matter such as HA-like and FA-like substances as shown in Figure 4.15 (b). Organic matter presence in Lorne water provided significantly different EEM spectral features such as presence of fluorescent matter in HA-like and FA-like regions.
The concentration of the fluorescent matter showed a marked increment in all regions after addition of AOM to Lorne water. This observation is similar to the findings in the literature for marine algae (Markager, 2005), surface water (Chen et al., 2003), EOM (Henderson et al., 2008). For example, Figure 4.16 (a) shows the EEM spectrum of Lorne water mixed with day 25 M-AOM. The fluorescence in aromatic proteins (AP) regions was introduced after the addition of AOM in the solution as observed by Zhang et al. (2013a). FA- and HA-like substances are generally smaller (MW is 350 -1000 Da), than biopolymers (MW >20,000 Da), and deposited on the membrane pore during filtration and thus can cause severe fouling (Zhang et al., 2016a).
Microfiltration of the solutions containing AOM provided reduction in all regions presented in Figure 4.17 suggested that all types of the organic matter could be retained by the membrane and cause the fouling of the MF membrane.

### 4.2.8 Summary

Membrane filtration was carried out to examine the effect of the AOM derived from the different algal species, their growth phases, background water on the fouling potential of the AOM. BAC pre-treatment of the AOM solutions was applied to determine its effect on the reduction of fouling potential of AOM. MF of surface water and all AOM solutions showed significant flux decline. The lower flux value for the mixture of AOM/Lorne water than AOM/Milli-Q water was due to the presence of higher concentration of organic matter and proportion of HMW substances.

At the filtration rate at 100 Lm$^{-2}$ specific volume, lowest flux occurred for day 25 C-AOM/Lorne and M-AOM/Lorne solutions which thus cause higher fouling. Comparing the fouling potential of AOMs from different species, *C. vulgaris* exhibited highest fouling. Considering the impact of growth phase of these algae on fouling potential, stationary phase poses higher fouling potential than the exponential phase. For the exponential phase AOM fouling potential was higher for M-AOM day 12 than C-AOM day 12. Different fouling potential by the cultures used for different experiments such as for duplicate runs indicated that extent of fouling may vary with AOM
characteristics in different batch of cultures. The performance of both BAC column having fairly similar GAC properties was comparable in terms of flux improvement and organics removal.

Protein concentration increased for M-AOM from exponential growth phase to stationary growth phase whereas C-AOM did not show any significant increase in protein concentration with growth phase. Concentration of carbohydrate in M-AOM did not increase significantly with growth phase. It was found more carbohydrate than protein were removed after MF. According to the characterisation of the AOM samples with fluorescence EEMs, protein and carbohydrate; protein, carbohydrate and humic substances played major role in membrane fouling. BAC reduced the concentrations of these foulants and consequently improved membrane flux. Therefore, BAC treatment has the potential to apply as a pre-treatment to reduce membrane fouling from single species AOM.

4.3 Impact of alum coagulation pre-treatment

Alum coagulation was carried out to investigate its the efficiency to minimize the membrane fouling and to compare with BAC pre-treatment efficiency. AOM extracted from stationary growth phase (day 25) of C. vulgaris and M. aeruginosa was mixed with Lorne water at a concentration of 3 mg DOC L⁻¹ and taken for alum coagulation and MF tests.

4.3.1 Determination of optimum coagulant dosages

In order to perform the alum coagulation pre-treatment, experiments were performed to investigate the optimum dose of coagulant. Figure 4.18 shows the determination of optimum doses of Al³⁺ in terms of DOC removal efficiency.

In case of Lorne water, the DOC removal percentage decreased from 45% to 18% with the increasing Al³⁺ dosage from 2.5 to 20 mg L⁻¹. So the optimum coagulant dose for Lorne water was determined as 2.5 mg Al³⁺ L⁻¹. For Lorne water mixed with AOM the DOC removal showed different trend than Lorne water. For M-AOM/Lorne, removal rate increased with the increment of dose from 2.5 to 5 mg L⁻¹ then decreased for the dose from 5 to 10 mg L⁻¹. For C-AOM/Lorne removal rate increased with the increment of dose from 2.5 to 5 mg L⁻¹ but then decreased for the dose from 5 to 15 mg L⁻¹ without any further increment. For both cases maximum DOC removal rate was obtained at 5 mg Al³⁺ L⁻¹ and therefore considered as optimum dose for coagulation pre-treatment.
Figure 4.18: Determination of optimum doses for alum coagulation of Lorne water and Lorne water plus 3 mgL$^{-1}$ M-AOM or C-AOM (day 25)

4.3.2 Impact of alum coagulation pre-treatment on the flux performance of MF

For C-AOM/Lorne solutions treated with alum, flux declined sharply before reaching 50 Lm$^{-2}$ and then continued steadily in the following cycles. A significant improvement in flux profile was observed after coagulation. Flux declined very slightly at end of each cycle and then recovered little bit after back pulsing. At the specific volume of 100 Lm$^{-2}$, the flux value for untreated sample was 0.21 and after coagulation pre-treatment it increased to 0.79 as shown in Figure 4.19.

Figure 4.19: Normalized flux vs specific volume for MF of C-AOM solutions before and after alum coagulation
This normalized flux (0.21) obtained at 100 Lm⁻² for untreated C-AOM/Lorne water was higher than the flux presented in section 4.2.1 for C-AOM day 25/Lorne water (0.15) probably due to the different batch of C-AOM used.

For M-AOM/Lorne solutions, flux profile showed continuous drop until reaching 20 Lm⁻² and then did not show any significant change (varied from 0.22-0.18). Rapid flux decline in early filtration period for both AOM preparations indicates the development of fouling layer on membrane. Back pulsing did not have any significant impact for the MF of untreated AOM solutions. Alum coagulation delivered a considerable improvement in flux profile. After alum coagulation, flux declined very slowly over the total filtration period. At the specific volume of 100 Lm⁻², the flux value for untreated sample was 0.20 and after coagulation pre-treatment it increased to 0.52 as shown in Figure 4.20. The normalized flux obtained at 100 Lm⁻² for untreated M-AOM/Lorne water was close to the flux presented in section 4.2.3 for M-AOM day 25/Lorne water (0.18).

![Normalized flux vs specific volume for MF before and after alum coagulation](image)

Figure 4.20: Normalized flux vs specific volume for MF before and after alum coagulation

Permeate flux decline for untreated C-AOM/Lorne sample was around 83% of the initial flux whereas the declination decreased to only 11% after alum coagulation. For M-AOM/Lorne untreated sample, permeate flux decline was around 63% of the initial flux whereas the declination decreased by 35% after alum coagulation. Significant flux improvement after alum coagulation using 5 mg L⁻¹ Al³⁺ was also observed by Fan et al. (2008) for secondary effluent containing EOM, M-AOM (Goh et al., 2011) and for M-AOM in drinking water (Zhang et al., 2014).
This flux declination trend was similar to the total fouling trend for samples. Total fouling resistance for C-AOM/Lorne and M-AOM/Lorne water was found to be $4.87 \times 10^{12}$ m$^{-1}$ and $4.25 \times 10^{12}$ m$^{-1}$, respectively, as shown in Table 4.3. After alum coagulation, total fouling was reduced to $1.47 \times 10^{12}$ m$^{-1}$ for C-AOM/Lorne where most of the contribution was by irreversible fouling ($1.34 \times 10^{12}$ m$^{-1}$). Similarly, for M-AOM/Lorne total fouling was reduced to $2.02 \times 10^{12}$ m$^{-1}$ and most of the contribution was by irreversible fouling ($1.89 \times 10^{12}$ m$^{-1}$). Reversible fouling for C-AOM decrease from $7.65 \times 10^{11}$ m$^{-1}$ to $1.27 \times 10^{11}$ m$^{-1}$ and for M-AOM from $2.47 \times 10^{11}$ m$^{-1}$ to $1.3 \times 10^{11}$ m$^{-1}$. From the total fouling data it was shown that both reversible and irreversible fouling was decreased after alum pre-treatment.

Table 4.3: Total fouling resistances before and after alum pre-treatment

<table>
<thead>
<tr>
<th>Total fouling resistance, m$^{-1}$</th>
<th>With out alum</th>
<th>After alum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-AOM+Lorne water</td>
<td>$4.87 \times 10^{12}$</td>
<td>$1.47 \times 10^{12}$</td>
</tr>
<tr>
<td>M-AOM+Lorne water</td>
<td>$4.25 \times 10^{12}$</td>
<td>$2.02 \times 10^{12}$</td>
</tr>
</tbody>
</table>

Alum coagulation at 5 mg AL$^{3+}$ L$^{-1}$ gave a considerable flux improvement (53% and 59% of flux recovery for M-AOM and C-AOM, respectively) at the end of the filtration. The amount of flux recovery followed the trend of total fouling data and the flux decline as well after alum coagulation. Literature suggested that coagulation removed a very high amount of biopolymers and humic substances (Haberkamp et al., 2007) which therefore prevents the formation of fouling layer on the membrane thus reduced fouling as observed by Zhang et al. (2014).

4.3.3 DOC concentration and UVA removal

The DOC concentration of the untreated samples was 11.5 mgL$^{-1}$, 10.9 mgL$^{-1}$ and 8.2 mgL$^{-1}$ for M-AOM, C-AOM and Lorne water alone, respectively. The UVA for both AOM solutions were similar, the values were 0.183 and 0.180 for M-AOM and C-AOM solutions, respectively. The DOC concentration and UVA for M-AOM/Lorne and C-AOM/Lorne solutions before and after treatment processes are presented in Figure 4.21 and Figure 4.22, respectively.
The overall DOC and UVA removal by the membrane for C-AOM/Lorne and M-AOM/Lorne was comparable. For example, the DOC removal was approximately 3.2 mgL\(^{-1}\) and UVA removal were 0.06 after MF. DOC and UVA levels for Lorne water were reduced from 8.2 mgL\(^{-1}\) to 5.3 mgL\(^{-1}\) and from 0.17 to 0.11, respectively which was higher than the removal from AOM solutions. MF removed higher amount of UVA than the DOC which was consistent to the findings of previous study presented in 4.2.1. This results suggests that MF can remove higher amount of UV-absorbing organic materials.

Coagulation provided a slightly greater reduction than MF in both DOC and UVA removal for M-AOM, but the DOC removals were lower for C-AOM/Lorne. The DOC concentration after alum pre-treatment was reduced almost 3.7 mgL\(^{-1}\) and 1.1 mgL\(^{-1}\) for M-AOM/Lorne and C-AOM/Lorne. After alum followed by MF, the DOC removal remained almost unchanged for M-AOM (3.7 mgL\(^{-1}\)), but not so for C-AOM (3.62 mgL\(^{-1}\)). DOC removal from Lorne water after alum followed by MF was 3.2 mgL\(^{-1}\). It is seen that coagulation performance of the M-AOM pre-treated samples in terms of DOC removal was better than of C-AOM pre-treated samples.

The UVA removal percentage was markedly higher (43%, 77% and 55% for M-AOM, C-AOM and Lorne water, respectively) than the DOC removal percentage after alum pre-treatment (32%, 22% and 29% for M-AOM, C-AOM and Lorne water, respectively) indicating the better removal of UV-absorbing substances. The UVA removal for AOM/Lorne after alum followed by MF were 0.14 and for Lorne water was 0.10.
Figure 4.22: UV absorbance at 254 nm after various treatment process

The UMFI values for untreated and alum pre-treated samples are presented in Figure 4.23. Coagulation delivered a significant reduction in fouling potential as shown by the lower UMFI obtained after alum pre-treatment.

Figure 4.23: UMFI for samples before and after alum pre-treatment

4.3.4 Carbohydrate and protein removal

The carbohydrate and protein content were higher for untreated M-AOM/Lorne than C-AOM/Lorne as shown in Figure 4.24 which was consistent to the previous experiments. The concentration for both samples was reduced after MF, similar observation was also presented in 4.2.5. Coagulation was found to be effective to remove carbohydrate and protein. Carbohydrate and protein removal was greater for M-AOM than C-AOM both after MF and alum pre-treatment. For example, after MF, carbohydrate concentration was decreased from 7.2 mgL⁻¹ to 4.46 mgL⁻¹ for C-AOM from 7.55 mgL⁻¹ to 4.38 mgL⁻¹ for M-AOM whereas protein
concentration was decreased from 2.88 mgL$^{-1}$ to 2.22 mgL$^{-1}$ for C-AOM and from 3.47 mgL$^{-1}$ to 2.57 mgL$^{-1}$ for M-AOM.

Figure 4.24: (a) Carbohydrate content (b) protein content of the solutions after various treatments

A comparatively higher removal in carbohydrates than proteins was observed, similar for M-AOM solution was reported by Zhang et al. (2014). For example, carbohydrate concentration was decreased from 7.2 mgL$^{-1}$ to 3.8 mgL$^{-1}$ and protein concentration was decreased from 2.88 mgL$^{-1}$ to 2.3 mgL$^{-1}$ for C-AOM. Similar comment was made by Zhang et al. (2014) who suggested carbohydrates were removed at a greater extent by coagulation treatment as the biopolymers contained more polysaccharides than proteins, measured as DOC content. Carbohydrate and proteins are very surface active due to the presence of surface functional groups so they have a very high potential to bind with trivalent Al$^{3+}$ to form complexes.

For the permeate, i.e., after alum followed by MF treatment, showed an additional reduction in carbohydrate and protein content. Carbohydrate removal remained higher (48%-52%) than the protein removal (22%-26%). This removal trend also supports the lower UMFI value for alum pre-treated M-AOM/Lorne compared with C-AOM/Lorne samples.

### 4.3.5 Fluorescence EEMs of AOM solutions

Both C-AOM/Lorne and M-AOM/Lorne contained a considerable amount of fluorescence in FA-like and HA-like regions as shown in Figures 4.25 (a) and Figure 4.26 (a). According to the FRI values presented in Figure 4.25 (d) and Figure 4.26 (d) both of the solutions contained approximately similar amount of FA-and HA-like substances.
Alum coagulation reduced the fluorescent intensity which was consistent to previous findings using secondary effluent (Pramanik et al., 2015a) and tap water as the background water (Zhang et al., 2014). A larger reduction in FA-like and HA-like substances and smaller reductions for SMPs and AP was observed after alum treatment. For M-AOM, the removal percentages were 54%, 56% and 19% for FA-like, HA-like substances, and SMPs respectively where AP essentially shows no reduction according to FRI. For C-AOM, the removal percentages were 50%, 53%, 16% and 6% for FA like, HA-like substances, SMPs and AP respectively.
Alum pre-treatment followed by MF provided additional reduction in FA-like and HA-like regions which is consistent to the filtration data and analyses of DOC and UVA. The fluorescence intensity of FA-like substances, HA-like substances, SMPs and AP was reduced by 57%, 66%, 25%, 1% for M-AOM/Lorne and 54%, 64%, 16%, 11% for C-AOM/Lorne. In this study, the higher reductions in fluorescent humic-like substances than others were consistent with the reduction in UVA and indicated that the HA-like substances played an important role in membrane fouling. The percentage of humic-like substances removal was comparable for both AOM solutions which were consistent with the UVA removal.

4.3.6 Summary

The performance of alum coagulation as a pre-treatment to mitigate fouling caused by the AOM obtained from the stationary phase of *M. aeruginosa* and *C. vulgaris* was examined and
compared with BAC. Fouling potential caused by both algal species were similar in terms of flux obtained at 100 Lm\(^{-2}\). Total fouling resistance was higher for C-AOM/Lorne where major contribution was made by irreversible fouling. Compared to the BAC pre-treatment C-AOM samples provided better flux after alum coagulation which was also consistent with the reduction in fouling resistance obtained for this sample. Reduction in humic-like substances after alum and alum followed by MF were close both for M-AOM than C-AOM. Higher UVA but lower DOC removal was achieved for C-AOM solutions after alum coagulation probably due to the removal in aromatic compounds, whereas the MF after alum provided comparable amount of removal in DOC and UVA concentration for M-AOM and C-AOM. So better flux but similar organic removal by C-AOM compared to M-AOM indicated the influence of AOM characteristics in fouling potential. According to the characterization of permeate, the better membrane flux obtained after alum followed by MF was mainly due to the removal of the biopolymers, such as proteins and carbohydrates, and humic substances. BAC pre-treatment was found to be better to remove organic matter but better flux improvement was observed by alum coagulation pre-treatment.

4.4 Fouling study of mixed species AOM

In the real water environment fouling by a single algal species may not be entirely representative of an algal bloom since it may involve the interaction of more than one algal species. Therefore, for a better understanding of the fouling potential, a mixture of the AOM extracted from stationary phase (Day 25) of C. vulgaris and M. aeruginosa was investigated. Feed solutions (3 mg DOC L\(^{-1}\)) were prepared by diluting the two AOMs at a ratio of 1:1 (in terms of DOC concentration) either with Milli-Q water or Lorne water. Constant AOM concentration of 3 mg DOC L\(^{-1}\) was used for the BAC and microfiltration tests.

4.4.1 Impact of mixed species AOM on Ceramic MF membrane

The trends of flux decline for the mixture of the M-AOM and C-AOM (MC-AOM) are shown in Figure 4.27. Severe flux decline was observed over 120 minutes of filtration period for all samples compared with the Milli-Q water control which indicates the presence of foulant that deposited on and in membrane and formed a fouling layer. At the specific volume of 100 Lm\(^{-2}\), the flux values were 0.32, 0.22 and 0.19 for Milli-Q mixed with MC-AOM (MC-AOM/Milli-Q), Lorne mixed with MC-AOM (MC-AOM/Lorne) and Lorne water alone. This trend of flux
decline for the untreated samples was found to be consistent with the findings of the single species AOM presented in section 4.2. Flux declination for the Lorne water was much more rapid than for the AOM-containing samples. It showed a continuous flux drop after first back pulsing before reaching a specific volume of 100 Lm⁻² and then gradually become constant in later cycles. It is mentionable that the flux for Lorne water having DOC concentration of 8.2 mgL⁻¹ fell from 0.42 to 0.19 within a specific volume of 76 Lm⁻² and 100 Lm⁻², respectively, this may have happened due to presence of larger molecules. The mixture of MC-AOM/Lorne water having DOC concentration of 11.6 mgL⁻¹ showed a steady flux decline trend in the first filtration cycle (<50 Lm⁻²) and then flux became almost constant (approximately 0.2-0.22) in later cycles. The filtration rate varied with the different mixtures and was approximately 8.67, 5.84 and 5.21 mLmin⁻¹ for MC-AOM/Milli-Q, MC-AOM/Lorne and Lorne water alone at a specific volume of 100 Lm⁻², respectively.

![Figure 4.27: Normalized flux vs specific volume for MF of solution containing mixture of M-AOM and C-AOM (1:1)](image)

The flux trend for the new sample of Lorne water used in this experiment (collected on 15th June 2017) differs from the trend presented in section 4.2 where it followed a gradual declination trend and fouling potential was less than the AOM/Lorne and AOM/Milli-Q.

Considering the flux as an indicator of fouling, the fouling potential of mixed AOM was greater than the fouling potential of single species AOM. However, the fouling potential of mixed AOM/Lorne water showed similar flux decline to the M-AOM day 25 shown in section 4.2.3.
The final flux was approximately 0.19 for MC-AOM/Lorne water whereas the final flux for M-AOM day 25/Lorne water was 0.17. This observation was consistent to the findings of previous study by Zhang et al. (2016a) who mentioned that this happened due to the similarities in some AOM characteristics such as molecular weight distribution, hydrophobicity and charge properties.

### 4.4.2 Impact of BAC pre-treatment

Feedwater containing mixture of M-AOM and C-AOM (1:1) at a concentration of 3 mg DOC L⁻¹ mixed with Lorne water was run through the two BAC columns and effluents were collected for MF tests to determine if the BAC pre-treatment improved the MF performance of the AOM mixture. Membrane flux for the BAC pre-treated samples is given in Figure 4.28.

![Figure 4.28: Plot of flux vs specific volume for MF of MC-AOM solution pre-treated by BAC](image)

At the specific volume of 100 Lm⁻², the flux values for GS 1300 and GA 1000N treated samples were 0.23 and 0.19, respectively. There was a slight increase in flux value (0.23 cf. 0.22) for GS 1300 pre-treated samples whereas the GA 1000 pre-treated samples did not show an improvement in flux. The filtration rate for the GS 1300 treated samples increased to 6.21 mLmin⁻¹ from 5.84 mLmin⁻¹ whereas for GA 1000N treated samples it decreased to 5.18 mLmin⁻¹ at 100 Lm⁻². Comparing the flux values achieved at 100 Lm⁻² for single species AOM, flux increased from 0.15 to 0.19 and from 0.28 to 0.35 for C-AOM day 12 and M-AOM day 12, respectively. For C-AOM day 25 and M-AOM day 25, flux increased from 0.33 to 0.39 and from
0.18 to 0.39, respectively. So, the flux increment after BAC pre-treatment was higher for single species AOM than mixed AOM species.

Difference among various AOM is associated to the characteristics like charge density, hydrophobicity, protein:carbohydrate ratios and MW fractions. For example, the charge density of C-AOM and M-AOM is 3.2 meqg\(^{-1}\) and 0.1 meqg\(^{-1}\), respectively and the hydrophobicity of C-AOM and M-AOM is 11% and 30%, respectively, and the hydrophobic and hydrophilic components of NOM is 8.8 and 1.0 meqg\(^{-1}\), respectively (Henderson et al., 2008). NOM characteristics also vary in terms of organic concentration and characteristics due to temporal and spatial variations (Sharp et al., 2006). So when the mixture of two different AOM with different NOM character from Lorne water was run through BAC columns probably due to the elevated organics levels and the complex character of the mixture, the BAC process could not remove expected amount of organics from the solution.

Permeate flux declined by around 38% and 73% of the initial flux for MC-AOM/Milli-Q water and for MC-AOM/Lorne water, respectively. Feed water pre-treatment with BAC process reduced flux decline rate from 73% to 34% and 31% for GS 1300 and GA 1000N, respectively. The flux declination trend followed their corresponding fouling resistances. Total fouling resistances for MC-AOM/Milli-Q and MC-AOM/Lorne water were found to be 1.43x10\(^{12}\) m\(^{-1}\) and 3.04x10\(^{12}\) m\(^{-1}\), respectively as shown in Table 4.4.

When MC-AOM is mixed in Lorne water it would probably have more irreversible foulants present compared to Milli-Q water mixed with MC-AOM. Overall fouling resistance was reduced after BAC pre-treatment which indicates reduction in membrane fouling. Total fouling resistance for GS 1300 was reduced to approximately 2.47x10\(^{12}\) m\(^{-1}\), of this the contribution by reversible fouling was lower (2.84x10\(^{10}\) m\(^{-1}\)) than by the irreversible fouling (2.44x10\(^{12}\) m\(^{-1}\)). At the end of each filtration cycle back pulsing was done to clean the membrane. After 2 sec of back pulsing at the end of entire filtration period, as expected the flux recovery was comparatively higher for MC-AOM mixed with Milli-Q water (47%) than MC-AOM mixed with Lorne water (19%). Flux recovery increased slightly after BAC process, and was 28% for GS 1300 pre-treated sample which was higher than GA 1000N pre-treated sample (20%).
Table 4.4: Total fouling resistances before and after BAC pre-treatment for mixed species AOM

<table>
<thead>
<tr>
<th>Total fouling resistance, m⁻¹</th>
<th>Without BAC</th>
<th>After BAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-AOM+Lorne water</td>
<td>3.04x10¹²</td>
<td>2.47x10¹²</td>
</tr>
<tr>
<td>GS 1300</td>
<td>GA 1000N</td>
<td></td>
</tr>
</tbody>
</table>

4.4.3 DOC concentration and UVA

Analyses of DOC concentration and UVA for MC-AOM mixtures are presented in Figure 4.29 and Figure 4.30, respectively. The DOC concentration and UVA for the mixture of MC-AOM in Milli-Q water were 3.4 mgL⁻¹ and 0.026 and for the mixture of MC-AOM with Lorne water were 11.6 mgL⁻¹ and 0.210, respectively.

![Figure 4.29: DOC concentration of the samples before and after BAC and MF processes](chart)

As expected. The overall DOC removal by the membrane for MC-AOM/Lorne water was higher than the MC-AOM/Milli-Q water (3.0 mgL⁻¹ cf. 1.4 mg L⁻¹) and the UVA removal for MC-AOM/Lorne water was relatively higher (0.12) than that obtained for MC-AOM/Milli-Q water (0.01). Comparatively higher UVA removal than the DOC removal for MC-AOM/Lorne water by membrane was consistent to the result presented in section 4.2.1 and section 4.3.3. This indicated that the retained organic matter contained higher UV-absorbing organic materials and these UV absorbing substances in humics have small contribution in total DOC concentrations.
The DOC concentration after BAC pre-treatment was reduced to 9.16 mgL\(^{-1}\) and 9.74 mgL\(^{-1}\) for GS 1300 and GA 1000N, respectively, from 11.6 mgL\(^{-1}\). After BAC pretreatment followed by MF the DOC concentration was reduced from 11.6 mgL\(^{-1}\) to 7.19 mgL\(^{-1}\) (GS 1300) and 8.47 mgL\(^{-1}\) (1000N). It is seen that MF performance of the GS 1300 treated samples was a little better than of GA 1000N samples.

![Graph showing UV absorbance of the samples at 254 nm before and after BAC and MF processes](image)

Figure 4.30: UV absorbance of the samples at 254 nm before and after BAC and MF processes

The UVA removal for the samples pre-treated by GS 1300 and GA 1000N followed a similar trend to DOC removal. UVA after BAC pre-treatment was 0.133 and 0.146 for GS 1300 and GA1000N, respectively. The UVA removal percentage was higher (37% and 30% for GS 1300 and GA1000N, respectively) than the DOC removal percentage after BAC pre-treatment (21% and 16% for GS 1300 and GA1000N, respectively). Comparatively higher UVA removal than the DOC removal (40% cf. 25%) after BAC treatment by GS 1300 was also observed by Pramanik et al. (2015a) for secondary effluent. This indicated that the BAC process can reduce the concentration of the UV absorbing substances such as humic substances from the solution by adsorption.

The UVA after BAC and MF were 0.067 and 0.088 for GS 1300 and GA1000N, respectively. Significantly lower UVA was observed after BAC pre-treatment followed by MF than the BAC alone and GS 1300 performed better in both cases. The DOC and UV removal trend for GS 1300 and GA 1000N were consistent with their filtration fluxes.
The fouling potential of the untreated sample was higher as shown in Figure 4.31. This UMFI value obtained by the mixed AOM was close to the UMFI obtained by M-AOM day 25/Lorne solutions. UMFI of 1000N treated samples (0.0278 m²L⁻¹) showed that there was not much improvement after BAC treatment however GS 1300N pre-treated samples (0.0231 m²L⁻¹) gave a lower UMFI value. This observation was found to be consistent with flux trends, DOC and UVA removal trend.

![Figure 4.31: UMFI for samples before and after BAC pre-treatment](image)

### 4.4.4 Carbohydrate and protein content

The content of carbohydrates and proteins was determined for untreated and BAC treated samples and is shown in Figure 4.32. MC-AOM/Milli-Q water shows a considerable amount of carbohydrate and protein and so contributed to fouling and their concentration increased for MC-AOM/Lorne due to the combination from the Lorne water. The concentration was reduced after MF indicating that a considerable amount of protein and carbohydrate can be retained by the membrane as observed in section 4.2.6 and also by Zhang et al. (2013b). The carbohydrate and protein removal percentage by MF was almost similar for MC-AOM/Milli-Q water and MC-AOM/Lorne water.
After BAC pre-treatment the carbohydrate and protein removal was also comparable and the value was marginally greater than for the MF process alone. As noted earlier, Pramanik et al. (2014) suggested that the BAC processes can break down the carbohydrates and proteins by the microorganisms and thus reduce their concentrations. Analysis of permeate after BAC followed by MF showed slightly greater reduction in carbohydrate and protein concentration compared to MF and BAC alone. GS 1300 removed a higher amount of carbohydrate (43% cf. 36%) and protein (44% cf. 37%) than GA 1000N. This removal trend is consistent with the better flux profile and lower UMFI value obtained by GS 1300 pre-treated samples. It is notable that both of the BAC columns removed foulants from the samples and reduced the amount of carbohydrate and protein fouling on the membrane which was not consistent with the flux of GA 1000N.

4.4.5 Fluorescence EEMs of MC-AOM

Fluorescence excitation-emission matrix (EEM) spectra were obtained to compare the fluorescent organic components in samples before and after MF and BAC+MF processes. Presence of mixed AOM in Lorne water contained a considerable amount of FA-like and HA-like substances (Figure 4.33). This observation is similar to the observation shown in section 4.2.7.

Microfiltration reduced the fluorescent organics in all regions indicating that fluorescent organics were involved in membrane fouling, similar to the finding of Pramanik et al. (2015c). The removal of the fluorescent FA-like substances (33%) was markedly greater than of the AP
(20%), SMPs (22%) and HA-like substances (18%) according to FRI values as shown in Figure 4.33 (d).

There was further reduction in all fluorescent regions after BAC pre-treatment followed by MF which is also consistent with the better flux profile attained after BAC pre-treatment. The fluorescence intensity of FA-like substances, AP, SMPs and HA-like substances was reduced by 38%, 31%, 24%, 40% for GA 1000N and 37%, 42%, 30%, 41% for GS 1300.

![Fluorescence EEM spectra of MC-AOM mixed in Lorne water](image)

Figure 4.33: Fluorescence EEM spectra of MC-AOM mixed in Lorne water (a) untreated (b) after MF (c) BAC treated-GS1300 followed by MF (d) FRI values

The decrease in fluorescent content in all regions may be attributed to the loss of aromatic content of samples. Considerably greater reductions in EEM volumes in the HA-like and FA-like regions are consistent with the comparatively higher removal of UVA than DOC and contributed
in the reduction of membrane fouling. This observation shows that BAC process followed by MF can reduce humic substances which also contribute to reduced fouling.

4.4.6 Summary

This particular study investigated the influence of AOM on membrane fouling obtained from two algal species using different background water such as Milli-Q and surface water. Considering flux value, mixed species AOM posed similar fouling potential to M-AOM solutions. In terms of flux after BAC pre-treatment, mixed AOM solutions did not show any significant improvement.

After MF, the considerable reduction in UVA than the DOC concentration indicates the preferential removal of humic substances by MF process. The permeate analysis demonstrated the efficiency of the BAC process by reducing the organic foulants i.e. DOC concentration, UVA, protein and carbohydrate content. EEM spectrum of untreated water confirms the presence of FA-like and humic-like substances in samples which were reduced after BAC process and BAC followed by MF as well and thus reduced membrane fouling. The reduced concentration of these substances demonstrated the reduction in fouling by BAC pre-treatment which seemingly inconsistent to their flux.

Although having same DOC concentration and approximately similar GAC characteristics, the performance of the two different BAC columns varied slightly in terms of flux profile and foulants removal. GS 1300 pre-treated samples showed slightly better performance than GA 1000N in terms of organics removal. According to the literature, BAC treatment reduces organic substances from a solution by adsorption and microbial breakdown so the performance may differ with a relationship between the microbes present, molecular size of the organics and the pore size distribution of the GAC.

4.5 Discussion

This study investigated the performance of BAC as pre-treatment to reduce fouling by water containing AOM of ceramic MF membrane. Significant flux decline for the feed water occurred due to the deposition of particles and organic molecules during filtration process which caused severe membrane fouling. From the characterization done by fluorescence EEMs, protein and carbohydrate, both AOM samples contained humic substances, protein and carbohydrates which are known as major foulants during membrane filtration.
Different fouling potential was observed for the different AOM samples used for various experiments and suggested that the fouling potential of AOM depends on algal species and their growth phase and AOM characteristics. The extent of fouling was also depends on the background water and possibly on their interaction. Higher fouling resistance was found for the AOM released from the stationary phase of *C. vulgaris*, however the flux decline and total fouling resistance for the mixed species AOM was closer to that for the AOM extracted from *M. aeruginosa*.

After BAC pre-treatment better UVA removal was obtained for C-AOM solutions while after alum pre-treatment better UVA removal was obtained for M-AOM solutions. Alum coagulation and BAC pre-treatment provided better DOC removal for M-AOM and C-AOM solutions, respectively. According to the analyses of flux and permeate characteristics it is observed that the fouling potential of AOM does not entirely depend on the concentration represented by DOC but also on the characteristics of the AOM obtained from individual algal culture. Alum coagulation of stationary phase AOM delivered better flux than obtained after BAC pre-treatment. Moreover, it should be noted that only one EBCT was investigated for BAC treatment.

The analyses of the permeate illustrated the potential of BAC process and alum coagulation as pre-treatment by reducing the concentration of foulants. However further investigation and process optimization is required to observe their potentiality specially for mixed species AOM.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

With the increasing trend of population, the demand for fresh drinking water is also increasing. Due to the limited water resources, increased level of eutrophication, pollution etc. it is essential to think about alternatives such as reuse and recycle of water. So it is imperative to provide competitive treatment techniques for water and wastewater. This study provided information regrading the fouling potential of algae present in natural water environment and also investigated the potential of BAC process as a pre-treatment option. The outcome of this study may help to develop an alternative treatment solution to increase the productivity of the membrane filtration system when drinking water becomes contaminated by algal blooms.

5.1 Influence of algae species and growth phase on membrane fouling

The presence of soluble algal organic matter in feed water obtained from two different algal species resulted in a significant flux decline during MF. Normalized flux decline rates differed with different solutions, and were affected by the growth phase and also by the background water. Higher fouling potential was observed for AOM from stationary growth phase. AOM obtained from the stationary phase of C. vulgaris gave lower flux thus higher fouling potential than that from M. aeruginosa. AOM samples contain significant amount of humic substances, proteins and carbohydrates which played a major role in membrane fouling. Protein concentration was observed to be increased significantly with growth phase for M-AOM compared with carbohydrate.

5.2 Effect of BAC pre-treatment on membrane fouling

Current study showed that BAC treatment can minimize the membrane fouling caused by AOM from two common algae species. Flux improvement was not only related to the removal of DOC and UVA as some of the samples did not show significant flux improvement but better removal in DOC concentration and UVA. This study found BAC process removed biopolymer and humic substances which are known as primary foulant during MF thus may be applied as an pre-treatment process to reduce the fouling caused by AOM derived from C. vulgaris and M. aeruginosa.
5.3 Effect of the properties of activated carbon on BAC pre-treatment

The performance of two different GACs was compared to investigate the influence of carbon media on organic matter removal by the BAC. Both of the GACs have similar physical properties and performed effectively as water filtration media. The initial DOC adsorption during column equilibration was considerably higher for GS 1300 which was probably due to the difference in chemical properties. The performance of the both BAC columns did not differ significantly in terms of membrane flux improvement and organic foulant removal.

5.4 Effect of the alum coagulation as feed pre-treatment

Alum coagulation pre-treatment of AOM solutions obtained from *M. aeruginosa* and *C. vulgaris* offered a considerable amount of reduction in membrane fouling. The pretreated C-AOM solutions delivered comparatively better flux than M-AOM. Alum pre-treatment reduced the concentration of humic substances, protein and carbohydrate and thus reduced membrane fouling. Alum pre-treatment provided better flux improvement compared to BAC pre-treatment although the removal of organic matter was considerably higher for BAC pre-treatment than alum pre-treatment.

5.5 Effect of BAC pre-treatment on mixed species AOM

In natural water environment, the presence of AOM from more than one algae species is a common phenomenon. MF of the solutions containing mixed species AOM gave significant flux decline which was comparable to the fouling by single species M-AOM. The flux decline was primarily occurred due to the presence of humic substances, protein and carbohydrate. According to the permeate analysis BAC provided a considerable amount of reduction on their concentration and contributed on fouling reduction which was inconsistent to the flux.

Fouling effect of AOM extracted from two different growth phases of *M. aeruginosa* and *C. vulgaris* and their mixture was studied. This study found that BAC pre-treatment can improve the flux and reduce MF fouling. The findings of the current study will add knowledge to the pre-treatment options of AOM containing water to reduce the MF fouling more effectively.
5.6 Recommendations for future work

- The effectiveness of organic matter removal in BAC depends on EBCT. This study examined only one EBCT. Therefore, further study comparing the different EBCT can be done to observe its effect on the organic removal, with a view to optimizing the performance of the BAC.
- This work demonstrated the potential of BAC in terms of organics removal, but the cost-effectiveness of the system should be analysed and a comparison with the conventional methods conducted.
- This study demonstrated that the major foulants in membrane filtration are proteins, carbohydrates and humic substances, but further insight into the fractions responsible for fouling is needed. The exact role of the fractions and their interactions with the membranes should be investigated. This may be carried out by using model organic foulants.
- A larger scale study is required to assess the feasibility of this pre-treatment technology for its application at full scale.
References


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Appendix A

MLA nutrient medium preparation

The following solutions were made up in individual volumetric flasks

**Stock Solutions:**

1. MgSO$_4$·7H$_2$O  4.94 g / 200 mL
2. NaNO$_3$  17.0 g / 200 mL
3. K$_2$HPO$_4$  1.392 g / 400 mL
4. H$_3$BO$_3$  0.494 g / 200 mL

5. Vitamins

**Working Stock Solution**

To 100 mL of Milli-Q water, the following will be added:

- Biotin  0.05 mL primary stock
- Vitamin B$_{12}$  0.05 mL primary stock
- Thiamine HCl  0.01 g

Primary Stocks (per 100 mL Milli-Q H$_2$O)

- Biotin  0.01 g
- Vitamin B$_{12}$  0.01 g

6. Micronutrients

**Stock Solution [100 mL]**

To 80 mL of Milli-Q water, each of the following constituents will add separately, and mixed to dissolve after each addition:

- Na$_2$EDTA  0.436 g (added first & stirred on low heat to fully dissolve)
- Fe$_2$(SO$_4$)$_3$·6H$_2$O  0.1625 g or FeCl$_3$  0.095 g or FeCl$_3$·6H$_2$O  0.158 g
- NaHCO$_3$  0.060 g
- MnCl$_2$·4H$_2$O  0.036 g

then 1 mL of each of the following primary stocks will be added:

Primary Stocks (per 100 mL Milli-Q H$_2$O)

- CuCl$_2$·2H$_2$O  0.0683 g
- ZnCl$_2$  0.1043 g or ZnO$_4$·7H$_2$O  1 ml solution
- CoCl$_2$·6H$_2$O  0.10 g
- Na$_2$MoO$_4$·2H$_2$O  0.06 g
Finally, the micronutrient stock was made up to 100 mL with Milli-Q water.
If precipitate formed the pH was increased to 7.

7. NaHCO₃  1.69 g / 100 mL
8. CaCl₂.2H₂O  2.94 g / 100 mL

All solutions were stored at 4°C.

MLA nutrient stock preparation:

1. Preparation of Sterile MLA Medium (2000 mL)

To 560*2 mL Milli-Q (for 2L) water the following was added:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄.7H₂O</td>
<td>80 mL</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>160 mL</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>80 mL</td>
</tr>
<tr>
<td>Vitamin stock</td>
<td>80 mL</td>
</tr>
<tr>
<td>Micronutrient stock</td>
<td>80 mL</td>
</tr>
</tbody>
</table>

The solutions will then autoclaved (121°C for 60 min) to sterilize. After autoclaving and cooling, 400 mL of K₂HPO₄ will added by sterile filtration (0.22 μm).

2. Preparation of Sterile NaHCO₃ (100 mL)

To 100 mL of H₂O 1.69 g of NaHCO₃ will be added and the solution autoclaved (121°C for 20 min) to sterilize.

To 100 mL of H₂O 2.94 g of CaCl₂.2H₂O will be added and the solution autoclaved (121°C for 20 min) to sterilize.

MLA nutrient medium preparation for algal culturing:

To prepare an algal culture 1000 mL, add:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milli-Q water</td>
<td>972 mL</td>
</tr>
<tr>
<td>Sterile MLA Medium</td>
<td>25 mL</td>
</tr>
<tr>
<td>Sterile NaHCO₃</td>
<td>1 mL</td>
</tr>
<tr>
<td>Sterile CaCl₂.2H₂O</td>
<td>1 mL</td>
</tr>
<tr>
<td>Algal culture</td>
<td>1 mL</td>
</tr>
</tbody>
</table>
Appendix B

Example of data processing for a filtration experiment

Membrane type: MF ceramic filtration area = 0.005 m²

Filtration mode: multi-cycle cycle, dead end  Sample: Lorne+ MC-AOM 3 mg L⁻¹

Operating conditions: transmembrane pressure = 70 kPa, temperature = 20±2 °C

Table B 1: Flux data for the determination of clean water flux

<table>
<thead>
<tr>
<th>Time, t min</th>
<th>Permeate flow rate (ml min⁻¹)</th>
<th>Flux (LMH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>28.25</td>
<td>325.08</td>
</tr>
<tr>
<td>2</td>
<td>28.51</td>
<td>327.96</td>
</tr>
<tr>
<td>3</td>
<td>28.34</td>
<td>324.48</td>
</tr>
</tbody>
</table>

Jo = Average of the last 3 flux data = 325.84 Lm⁻²h⁻¹ = 9.05x10⁻⁵ m³ m⁻² s⁻¹

Hydraulic resistance of the clean membrane, Rm = ΔP/µJo

ΔP = 70,000 Pa  μ = 0.000958 Pa.s  Rₘ = 8.07x10¹¹ m⁻¹

Table B 2: Flux data from the filtration test with AOM solution

<table>
<thead>
<tr>
<th>Time, t (min)</th>
<th>Flow rate (mL min⁻¹)</th>
<th>Flux, J (mL min⁻¹)</th>
<th>Normalized flux J/Jo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.19</td>
<td>146.28</td>
<td>0.448932</td>
</tr>
<tr>
<td>1</td>
<td>9.74</td>
<td>116.88</td>
<td>0.358704</td>
</tr>
<tr>
<td>2</td>
<td>8.38</td>
<td>100.56</td>
<td>0.308618</td>
</tr>
<tr>
<td>3</td>
<td>8.19</td>
<td>98.28</td>
<td>0.30162</td>
</tr>
<tr>
<td>4</td>
<td>8.22</td>
<td>93.6</td>
<td>0.302725</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>5.33</td>
<td>144.762</td>
<td>0.196293</td>
</tr>
</tbody>
</table>

Clean water flux after the end of the filtration run = 147 L m⁻² h⁻¹ = 4.08x10⁻⁵ m³ m⁻² s⁻¹

Resistance by total fouling (Rₜₒₜₜ) = ΔP/(µxJₜ) - Rₘ = 9.84x10¹¹ m⁻¹
Appendix C

Cell counting using a Haemacytometer

- The grid is divided into 9 large squares, each 1 mm x 1 mm, by triple lines. Each large square is divided into 25 medium squares, each 0.23 mm on a side, and each medium square is further divided into 16 small squares, each 0.05 mm on a side.
- For all haemacytometers, the fundamental measurement is the average number of cells per 1mm square, so the centre large square is usually counted. To obtain the total number of cells in this large square, the number of cells in each of the 25 medium squares are counted, recorded then added.
- When counting cells bordering on triple rulings, the convention is to count only those cells touching the top and left-hand side rulings of each square.

Figure C-1: Haemacytometer chamber