FOULING OF CERAMIC MICROFILTRATION MEMBRANE BY SOLUBLE ALGAL ORGANIC MATTER (SAOM) FROM *CHLORELLA* SP. AND *M. AERUGINOSA* AND ITS MITIGATION USING FEED-PRETREATMENT

DEVANADERA M.[1,2] and DALIDA M.[2]

[1] Department of Community and Environmental Resource Planning, College of Human Ecology, University of the Philippines, Los Banos, Laguna, 4031 Philippines,
[2] Environmental Engineering Graduate Program, College of Engineering, University of the Philippines, Diliman, Quezon City, 1101 Philippines
E-mail: medevanadera@up.edu.ph

ABSTRACT

Algal blooms can be a pressing environmental issue in surface water impoundments due to soluble algal organic matter (sAOM) released by the algae during growth and decay, causing problems in water quality and treatment efficiency of membrane processes. The fouling of a 0.1 µm tubular alumina ceramic membrane by sAOM extracted from *Chlorella* sp. and *Microcystis aeruginosa* cultures during exponential and stationary growth phase was investigated at laboratory scale. Organic matter in feed and permeate was analyzed in terms of DOC, UVA, carbohydrate and protein content, and fluorescent excitation emission matrices EEMs to characterize the membrane fouling. At the same DOC concentration, compared with *M.aeruginosa*, the sAOM from the exponential phase for *Chlorella* sp. led to less steep but slightly greater flux decline, and markedly greater flux decline for the stationary phase. Interestingly, mixtures of the sAOM preparations led to more rapid but overall similar flux decline as for the sAOM from *Chlorella* sp., suggesting some initial interaction between components as the fouling built up on the membrane surface. Flux recoveries and irreversible fouling were improved after feed pre-treatment by coagulation with alum for all the microfiltration runs.

Keywords: Ceramic microfiltration, fouling impact of mixed algae; coagulation as feed pre-treatment

1. Introduction

Cyanobacterial blooms present in surface water have been threatening the world for the longest time. In a tropical country such as Philippines, more cyanobacterial blooms may thrive in waterbodies and eutrophication can happen due to the continuous light source which supports the growth of blue-green algae. As domestic and agricultural wastewater effluent are directed to surface water without prior treatment, these leads to water contamination and high algal bloom. Some waterbodies in Mindanao and Laguna de Bay are confirmed with the occurrence of algal bloom. Most commonly found organisms in reservoirs and surface water are *M. aeruginosa*, a toxin producing cyanobacteria; and *Chlorella* sp., chosen as a representative green alga. Both have almost similar size and shape but different extrapolymeric substances (EPS). Their cells, extracellular organic matter (EOM) and intracellular organic matter (IOM) released during growth and decline phase, termed algal organic matter (AOM), contribute to membrane fouling during membrane treatment processes.

The study used *Chlorella* sp. (also used as feed for biofuel production) and *M. aeruginosa*, which since it releases toxins, is problematic in potable water supplies and also waste stabilization ponds. To understand the fouling potential during the life cycle of a bloom, the growth phases of *Chlorella* sp. and *M. aeruginosa* at exponential (Day 12) and stationary phases (Day 35) were investigated. As different species coexist in the natural surface water, possible fouling impact of mixed sAOM from representative organisms at ratios of *Chlorella* sp. to *M. aeruginosa* (C:M) 1:1 and 1:3 were considered in the study.

To understand the fouling caused by sAOM in membrane filtration process, an MF ceramic membrane will be used in the study. As reported by Spinnette, (2008) on Microfiltration of *M. aeruginosa*, the cells may have caused significant reversible fouling to the PVDF membrane but the release of AOM caused significant irreversible fouling. Babel, *et al*., (2002) also found that at unfavourable conditions, *Chlorella* cells become coated with extracellular organic matter (EOM) which causes higher filtration resistance. It was also found that specific cake resistance were caused by either an increase in quantity of EOM or by changes in EOM characteristics. The study will also factor in the growth phases of *Chlorella* sp., and *M. aeruginosa* and their specific fouling impact into microfiltration (MF) ceramic membrane. As *Chlorella* sp. are being tapped as a potential for biofuel stock, microalgae harvesting was done through membrane filtration. In a study on the effect of *M. aeruginosa* on membrane fouling, it showed that mid and late phase caused more fouling than the early growth phase leading to poorer flux profiles, lower permeate volumes and higher coagulant demand (Goh *et al*., 2011).

2. Materials and method

2.1. Water sample

Organisms used were *Chlorella* sp. and *M. aeruginosa*. *Chlorella sp.* was purchased from Victoria, Australia while *M. aeruginosa* from Tasmania, Australia. Both were cultured using MLA medium (Bolch and Blackburn, 1996) at 22ºC under humidified aeration. *Chlorella* sp. was cultured in 1-L Schott bottles with a 24 hour light source while *M. aeruginosa* in 5-L Schott bottles at a 16/8 dark/light cycle. *Chlorella* sp. and *M. aeruginosa* used 684 nm to obtain the optical density (OD_{684}) and correlated with cell count. Linear relationships were established for *Chlorella* sp. (R^2>0.96) and *M. aeruginosa (*R^2>0.99).

2.2. Experiments involving algal matter

AOM Extraction Procedure

*S*oluble AOM were characterized using the process: centrifuged at 4,000g; 4ºC for 15 min and filtered the supernatant through a 0.45 µm. This is similar with the method used in the extraction of EPS and EOM from activated sludge and algae solution by Dominguez, *et al* (2010).

2.3. Microfiltration Test

Ceramic membrane (Membralox system) was used in the study. It is made of alumina with a 0.1 µm pore size and a membrane surface area of 50 cm^2. Dead end filtration was used in the filtration. Feed tank held a volume of 3.5 L while the capacity of the air pump was 500 ml by volume. A minimum TMP value of 50 kPa was used. All experiments were conducted at room temperature (20 ± 2°C). Clean water flux (CWF) was determined using MQ water for 10 minutes (flux of 480 ± 5% at 50 kPa). Permeate flux was determined using a top-loading electronic balance (OHAUS Explorer) with data logging function of 1-min interval. Hot sodium hypochlorite solution (70ºC; 45 minutes; 1000 ppm available chlorine) was used to restore the initial clean water flux (CWF) after each run. After fouling (observed after 80-90 mins), CWF (J_{TF} – total fouling) was taken by filtering MQ water for 5 minutes, then back pulsing (BP) was applied for 5 seconds. After BP, CWF (J_{BP}) was again measured for 5 minutes using MQ water. Flux recovery, and resistances due to total fouling, irreversible fouling and reversible fouling were calculated using Equations 1-5.

$$\text{Flux recovery, \%} = (J_{BP}/J_o)*100 \quad (1)$$

$$\text{Resistance Membrane, } R_M = \Delta P / \mu J_o \quad (2)$$

$$\text{Resistance (Total Fouling), } R_{TF} = \Delta P / \mu J_{TF} - R_M \quad (3)$$

$$\text{Resistance (Irreversible fouling), } R_{IF} = \Delta P / \mu J_{BP} - R_M \quad (4)$$

$$\text{Resistance (Reversible fouling), } R_{RF} = R_{TF} - R_{IF} \quad (5)$$

where: change in transmembrane pressure, $\Delta P = P_2 - P_1 = 50{,}000$ Pa

$\mu = 0.000958$ Pa.s; J_{BP}; J_o; $J_{TF} = m^3/(m^2.s)$

2.4. Analytical methods

DOC was measured using a Sievers 820 TOC analyser. UVA_{254} and OD_{684} were measured using UV/vis spectrophotometer (Shimadzu UV2700). The pH was measured using a Hach Sension 156 pH meter. Fluorescent Excitation-Emission Matrices (EEMs) were measured using Perkin Elmer Luminescence Spectrometer LS50B. Excitation and emission ranged from 200-600 nm and 200-540 nm, respectively. For carbohydrate and protein analyse, phenol-sulphuric method and Quantipro™ BCA assay kit were used, respectively.

2.5. Pre-Treatment Method

Coagulation was conducted as pre-treatment for the sAOM feed solutions. Aluminum chloride was used as coagulant with concentrations 0, 2.5, 5, 7.5, 10, and 15 mg/l using the laboratory jar tester with six 2-L square jars (PB-700, Phipps and Bird). Rapid mixing was employed for 1 min at 200 rpm followed by slow mixing for 20 min at 30 rpm. Solutions were allowed to settle and then analyzed based on DOC. Coagulant dose with the highest DOC removal was used for pre-treatment.

3. Results and discussion

3.1. Membrane fouling and reversibility

To compare the fouling potential of each feed solution, the DOC value was adjusted to 2.5 mg/L for all microfiltration runs. Flux abruptly declined for Day 35 *Chlorella* sp. sAOM compared with Day 12. In 90 minutes, serious flux decline was observed with around 68 and 75% reduction of the initial CWF for Day 12 and Day 35 sAOM feed solutions, respectively. After the BP, membrane recovery was slightly higher for Day 12 than Day 35 with values of 42 and 40%, irreversible foulants maybe deposited during filtration.

For *M. aeruginosa*, final permeate flux declined to around 61 and 67% of the CWF for exponential and stationary phases, respectively. Zhang *et al*., (2013) also found that *M. aeruginosa* caused more fouling of the ceramic membrane at stationary phase compared with the late exponential phase. After the 5-second back pulsing, sAOM Day 12 and 35 resulted to a flux recovery of 80 and 44%, respectively. This indicated that sAOM extracted during exponential phase has reversible foulants while irreversible foulants were present in the stationary phase. Thus, sAOMs from cultures at stationary phase lead to a more critical problem in ceramic membrane fouling.
Mixed sAOM at Day 35 *Chlorella* sp.:*M.aeruginosa* (1:1) had the highest fouling potential (Fig. 1). After 90 minutes, all samples led to serious flux decline at around 60-76% from the initial CWF. Mixed sAOM samples caused greater fouling compared with single species runs for both organisms at exponential and stationary phase. The interaction between the characteristics of the organic molecules possessed by the different species, the green alga and cyanobacterium, appeared to have led to higher membrane fouling.

Reversible and irreversible fouling were observed in all filtration runs (see Fig. 2). High irreversible fouling was observed for almost all samples except for Day 12 *M. aeruginosa*, which exhibited more reversibility. With high irreversible fouling, pores could have been blocked or adsorbed into the surface of the ceramic membrane and thus resulted to serious flux decline. Similar with the study done by Spinette *et al*., (2008), membrane fouling due to algal organic matter was capable of significant and mostly irreversible fouling. It was found that AOM produced by different algae varied significantly in concentration and fouling potential varied as well.

3.2. sAOM rejection by ceramic MF membrane

Looking at the mixed sAOM with ratio of 1:3 and 1:1, fairly high rejection of DOC and UV_{254} were observed with around 34-36% and 63-69%, respectively compared with other MF runs except for Day 12 *M. aeruginosa*. Carbohydrates and protein rejected ranged from around 30-50% for the mixed sAOMs. As found by Laure and Croue, 2012, severe and irreversible fouling of algal exudates is mainly due to the biopolymer content such as polysaccharides and proteins in ceramic membrane fouling caused by marine organic matter such as *Chlorella* sp. which was found consistent in the study. However, it was not purely the high molecular weight fractions, adsorption of low molecular weight molecules also play a role in membrane fouling.

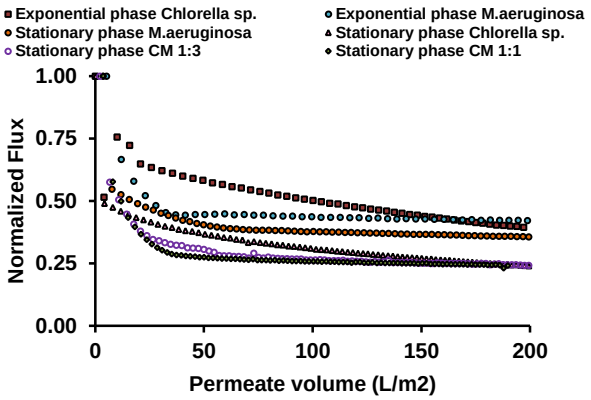

Figure 1: *Chlorella* sp. (exponential and stationary phase), *M. aeruginosa* (exponential and stationary phase), Mixed Stationary phase *Chlorella* sp.:*M.aeruginosa* (1:3) and (1:1)

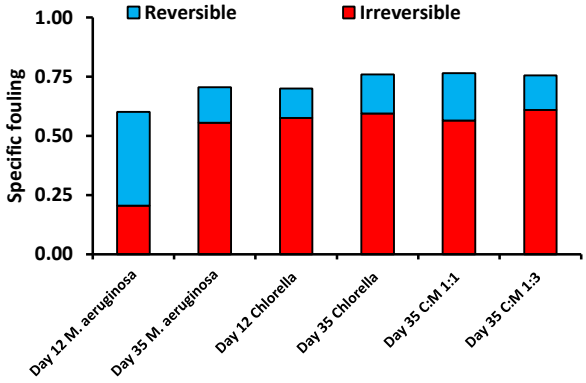

Figure 2: Reversible and irreversible fouling for respective microfiltration runs

3.3. Characterization of sAOM by fluorescence EEMs

Aromatic proteins and SMPs were greatly rejected for *Chlorella* sp. while fulvic acid-like and humic acid-like substances were rejected more for *M. aeruginosa*. For the mixed sAOM microfiltration runs, EEMS showed that aromatic proteins in the sAOM have caused the fouling of the microfiltration membrane. Removal of aromatic proteins I & II ranged from 30% - 50%, for both C:M 1:3 and C:M 1:1. While C:M 1:1 resulted to higher removal of fulvic acid-like substances compared to C:M 1:3. SMPs and humic acid-like substances were at the same range of rejection for both mixed sAOM feed solutions.

3.4. Feed Pre-Treatment

3.4.1. Membrane fouling and reversibility

Flux decline for the filtration runs treated with coagulation is given in **Figure 3**. All feed pre-treated samples (alum + MF runs) at stationary phase achieved lower flux decline. The fouling potential was minimized as the flux declined to around 25-50% as compared with 60-76% without feed pre-treatment.

Flux recoveries for feed pre-treated sAOMs from stationary phase (*M. aeruginosa*, *Chlorella* sp., CM 1:3 and CM 1:1) increased to 55-96% compared to non pre-treated runs with only around 40% recovery. This showed that single and mixed species fouling potential can be minimized by feed pre-treatment. However, mixed sAOMs were more complicated with only 55% and 70% flux recoveries for CM 1:3 and CM 1:1, respectively.

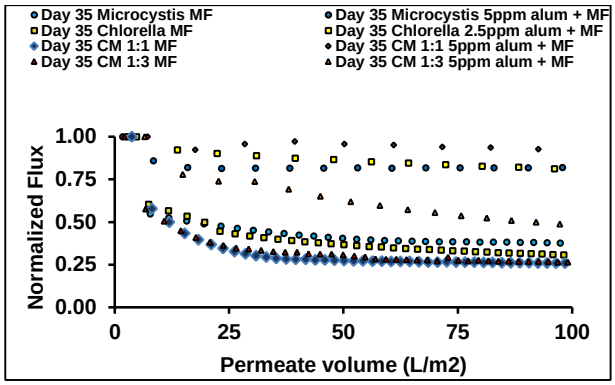

Figure 3: Comparison of flux decline of sAOMs at stationary phase *Chlorella* sp., *M. aeruginosa*, CM 1:1 and CM 1:3 (MF & alum coagulation + MF)

3.4.2. sAOM rejection by ceramic MF membrane

In terms of the characteristics of membrane foulants, with the employment of feed pre-treatment and microfiltration, high rejection of organic molecules were observed ranging from 58-64% (*Chlorella* sp., *M. aeruginosa*, CM 1:1) except CM 1:3, which is only 12%. Protein also played a role for the mixed runs (alum + MF) since this resulted to higher removal compared to microfiltration alone.

3.4.3. Characterization of sAOM by fluorescence EEMs

No removal of humic and fulvic acid-like substances were found after alum coagulation + MF as observed in EEMs. This could have been the reason for lesser flux recovery and higher reversible fouling of mixed samples compared to the other single species runs (*Chlorella* sp. and *M. aeruginosa*). For the single species runs, high rejection of all EEM components was observed which could be attributed as reversible foulants and thus resulted to higher flux recovery. With the application of coagulation as a feed pre-treatment, high molecular weight substances in the sAOM could have been removed thus reducing the fouling potential of sAOM. Similar with the findings of Bernhardt *et al*, 1985, which resulted to removal of high molecular weight algal compounds due to ability of coagulation process in removing EOM polysaccharides of several algal species, C*hlorella* sp., *Cyanobacterium pseudonabaena*. In a study done by Zhang *et al*., 2013, removal of low MW AOM compounds was also possible with the application of coagulation as a feed pre-treatment. Spinette, 2008 also found that microfiltration membrane fouling caused by waters with low SUVA may be reduced to varying extents with coagulation/flocculation pretreatment. Coagulation also resulted to reduction of fouling potential and compressibility of AOM and enhanced removal as found by Alizadeh Tabatabai *et al* (2014). The overall analysis of sAOM characteristics indicated that the membrane fouling depended on the synergies that arose from specific combinations of the fluorescence excitation-emission matrix (EEM), molar weight sizes (Huang *et al*, 2014) and hydrophobicity of feed characteristics. Coagulation as a feed pre-treatment was found effective in reducing ceramic microfiltration fouling for sAOMs. Irreversible fouling was reduced from 50-60% to 10-20% in all micro filtration runs (Fig. 4).

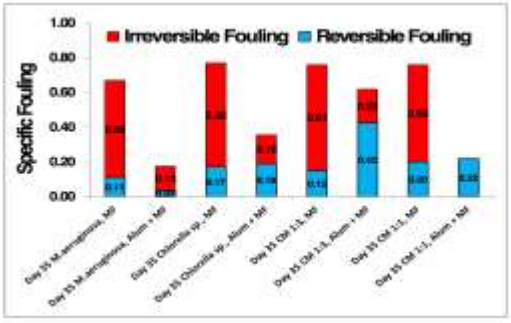

Figure 4. Reversible and irreversible fouling for respective micro filtration

4. Conclusion

Mixed soluble algal organic matter from both *Chlorella* sp. and *M. aeruginosa*, had the highest fouling impact to the ceramic microfilter. Flux declined the most due to greater aromaticity, and higher protein concentration. Qualitatively, based on the fluorescence regional integration, with high aromatic proteins together with the SMPs coming from *Chlorella* sp. and high fulvic acid-like and humic acid-like substances from *M. aeruginosa*, this could have led to higher fouling potential of the mixed sAOM as compared with the single species microfiltration. However, all sAOM filtration runs experienced high irreversible fouling except for Day 12 *M. aeruginosa*.

Alum coagulation as a pre-treatment was effective in decreasing the fouling potential due to the mixed sAOM. Irreversible fouling decreased from 50-60% to around 10-20%. This is very significant to membrane processes as fouling is the major drawback of membrane filtration systems. Coagulation pre-treatment is indeed effective in reducing the flux decline and improving the fouling reversibility in the ceramic microfiltration system.

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