



## Temporal variation of foulant characteristics in membrane bioreactor

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### ABSTRACT

Many studies have been performed to analyse the influence of compounds present in different fractions of the membrane foulants. The aim of this study was to reveal the changing chemistry of compounds present in membrane foulant with the evolution of time. Membrane fouling in a side stream membrane bioreactor (MBR) reactor was investigated. Constant flux filtration was employed in an MBR operation. Air bubbles were injected at  $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$  for six different durations (2, 4, 6, 9, 15 and 20 days) of MBR operation. The foulant on the membrane surface was extracted using NaOH solution (5%) and analysed using fluorescent spectroscopy. The spectra showed the changing chemistry of foulant with the evolution of time. It showed low molecular weight substances such as amino acids and small aromatic proteins were dominant in the foulant at the beginning of the experiment but its concentration decreased with time. On the other hand BOD<sub>5</sub> type substances concentration increased with time from the beginning of the experiment up to 9 days and there after decreased. The concentration of larger molecular weight soluble microbial by-products increased with evolution of time. Air bubbles at two aeration rate of  $1 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$  and  $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$  were also injected from the bottom of the membrane tanks to produce shear stresses on the membrane surface during 5 days of MBR operation to compare the effect of aeration in fouling propensity.

**Keywords:** Membrane bioreactor; Fouling; Soluble microbial by-products

### 1. Introduction

Membrane bioreactor (MBR) is an innovative activated sludge process using membrane filtration instead of a secondary clarifier to achieve biomass separation [1,2]. A small footprint and high sludge concentration makes a MBR process an attractive option where space is limited and high water quality is required. The microfiltration and ultrafiltration membrane produces excellent effluent quality free of particulates and coliforms, which is suitable for many

reuse applications [3,4]. Rapidly decreasing membrane cost is another important driver for the wide spread application of MBRs [5].

The composition of activated sludge in MBRs is very complex, and includes a broad spectrum of natural organic matter, soluble microbial by-products (SMPs) ranging from a few hundred daltons to several million daltons which is produced by the biomass, bacteria, viruses and protozoas [6,7]. The SMPs mainly consist of proteins and polysaccharides. Two major drawbacks in MBR are membrane fouling and high energy consumption [8,9]. Three different types of membrane fouling occur in a MBR: (i) irreversible

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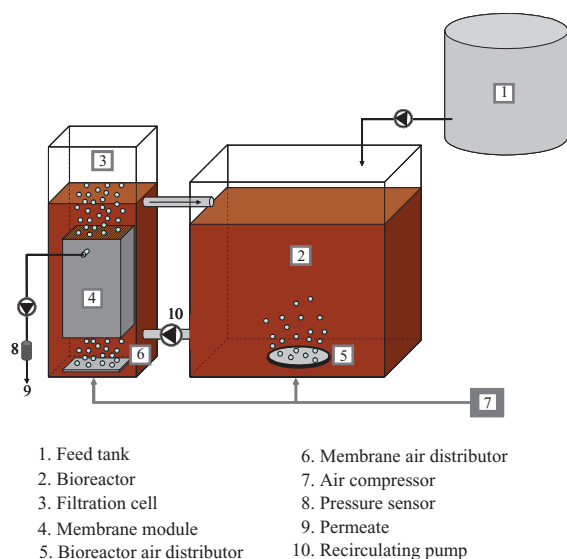


Fig. 1. MBR configuration.

fouling due to physico-chemical interactions (adsorption) of soluble compounds onto the membrane surface that can be cleaned only by chemical(s), (ii) biofilm development due to an accumulation of cells and SMPs on the membrane surface and (iii) sludging or the sludge accumulation on the membrane surface [10–12].

It is generally accepted that biology, membrane characteristics, configuration and operational conditions of the membrane modules all play important roles in the control of membrane fouling [13,14]. In MBRs, crossflow filtration is employed to control particle deposition onto the membrane surface. The hydrodynamics of the membrane system have been intensively studied. The results show that increasing crossflow velocity improved particle back transport and reduced membrane fouling [15–17]. Literatures report divergence in the fouling phenomenon interpretation: Bouhabila et al. [16] reported that the supernatant contributed almost 76% to the total fouling resistance whereas Lee et al. [18] reported that the relative contribution of the supernatant to membrane fouling was about 37%. Wisniewski and Grasmick [19] observed 50% of the total resistance was due to soluble compounds. Recent studies show that SMPs in the sludge water phase are closely related to MBR fouling. The difference in result is probably due to experimental conditions and/or the less attention paid to the changing nature of the fouling chemistry as it evolves over time.

The fluorescent fingerprint technique has been widely used to identify the nature of organic substances in water and wastewater [20]. The outstanding advantage of fluorescence spectroscopy is that information regarding the fluorescence characteristics can

be entirely acquired by changing excitation wavelength and emission wavelength simultaneously without destroying the samples. Fouling contains a wide range of soluble microbial substances and humic substances. Results from the fluorescent spectra would be valuable for studying the chemical properties of foulants of various origins [21].

This research study aims to discover the change in the foulant chemistry in the MBR as it evolves over time. A similar hydrodynamic condition was maintained and the fouling characteristics were investigated with evolution of time. The foulants were analysed using fluorescent spectroscopy.

## 2. Experimental

Two bioreactors with a total volume 36 L was set up in the laboratory (Fig. 1). One was a side stream tank equipped with flat sheet module (10 L in volume) and another was for biological COD removal (26 L in volume). The flat sheet membrane module (PVDF with pore size  $0.14 \mu\text{m}$  with filtration area  $0.2 \text{ m}^2$ ) was submerged in the membrane tank. The selection of PVDF membrane is due to its strong tolerability to acidic and alkaline environment when membrane cleaning. The reactor was initialized with 2 L of treated sludge, obtained from secondary clarifier in domestic wastewater treatment plant in Sydney, and 34 L of tap water for seeding. The MBR was continuously fed with a synthetic substrate (ethanol, ammonium chloride and potassium dihydrogen phosphate) in ratio of COD:N:P equal to 150:5:1 at an organic load of  $3.0 \text{ kg COD m}^{-3} \text{ d}^{-1}$  (ethanol 2.7 ml/L, ammonium chloride 0.573 g/L and potassium dihydrogen phosphate 0.132 g/L) for more than 60 days to stabilize the reactor. After 60 days of operation the organic load was reduced to  $1.5 \text{ kg COD m}^{-3} \text{ d}^{-1}$  (ethanol 1.34 ml/L, ammonium chloride 0.28 g/L and potassium dihydrogen phosphate 0.066 g/L) prior to start experiments to resemble the organic load in domestic wastewater treatment plant. The mixed liquor of two tanks was continuously re-circulated with a peristaltic pump as shown in Fig. 1 at the rate of  $0.011 \text{ m}^3/\text{h}$ .

Bubbles of larger size (2–4 cm in diameter) were continuously injected from the bottom of the membrane tank at an aeration rate of  $2 \text{ m}^3/\text{h}/\text{m}^2$  to produce shear stresses to minimise sludge accumulation on the membrane surface. Air bubbles injected in the biological aeration tank contained fine bubbles (1 mm) to maximise oxygen mixing. Membrane filtration was performed from outside to inside in a continuous mode, with no relaxation or back-wash procedure. The permeate was extracted by a peristaltic pump at a

constant flux. During the experimental period the transmembrane pressure (TMP) was measured at intervals of 20 min with online data acquisition.

The organic load of  $1.5 \text{ kg COD m}^{-3} \text{ d}^{-1}$  was maintained during the experiment that resembles the domestic wastewater. A low filtration flux with  $10 \text{ L m}^{-2} \text{ h}^{-1}$  was applied to minimise the fouling propensity. Total suspended solids (TSS) concentration in mixed liquor was maintained between 4 and 5 g/L and dissolved oxygen greater than 2 mg/L after stabilizing MBR for almost 2 months. The hydraulic retention time (HRT) and total sludge retention time (SRT) were controlled at 0.75 day and 45 days, respectively. Proteins and polysaccharides commonly known as SMP in mixed liquor were monitored after filtering the mixed liquor through  $1.2 \mu\text{m}$  filter. The proteins in SMP were quantified using the Lowry method using Bovine Serum Albumin (BSA) as the standard (Sigma) and polysaccharides was quantified by Dubois method using sucrose as standard (UV/Visible spectrometer). The particle size distribution (PSD) of the biological suspension floc was measured using particle size analyser (MALVERN SB.0B UK).

Six experimental runs of different duration (2, 4, 6, 9, 15 and 20 days) were performed in time series at an aeration rate of  $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ . The membrane module after each experimental run was taken out from the reactor and immersed in water to remove the excess sludge accumulated in between the membrane sheets. The foulant attached on the membrane surface was then extracted with NaOH solution (0.5% w/v) using a horizontal shaker for 3 h. The extracted foulant was filtered through  $1.2 \mu\text{m}$  filter and diluted to make the DOC equivalent to 10 mg/L for comparative study. The extracted foulant was analysed by fluorescent spectroscopy (Hitachi F4500, Japan) at different excitation emission (Ex:Em) wavelength. In the result and discussion part the foulant refers to the foulant extracted with NaOH.

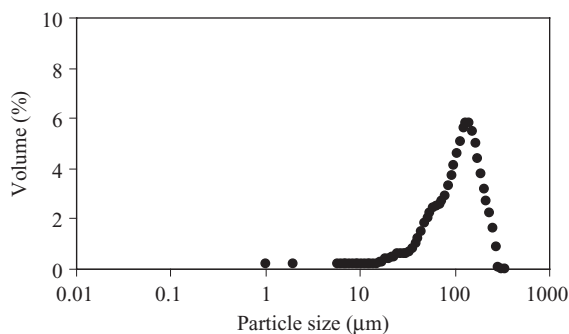


Fig. 2. Particle size distribution in biological suspension in MBR.

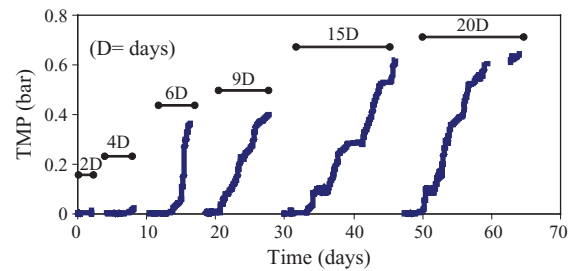


Fig. 3. TMP variation in experimental period.

Prior to each experiment the membrane was cleaned in three steps. In the first step, the membrane was immersed in NaOH solution (0.5% for 3 h) followed the second step of immersing in citric acid (0.5 % for 12 h) and finally it was dipped in sodium hypochlorite (200 ppm for 3 h). The cleaning solution was re-circulated at the rate of  $10 \text{ L m}^{-2} \text{ h}^{-1}$ . To ensure proper cleaning, membrane hydraulic resistance was measured before running each experiment.

### 3. Results and discussion

The COD, protein and polysaccharides in the stabilized MBR suspension was monitored for almost 2 months. The protein, polysaccharides and COD concentrations were  $18.1 \pm 2.3 \text{ mg/L}$ ,  $16.2 \pm 2.4 \text{ mg/L}$  and  $67.7 \pm 6.1 \text{ mg/L}$ , respectively [17]. The result indicated a stable operation of the MBR.

Fig. 2 shows the PSD obtained from particle size analyser (Malvern SB.0B UK) of a sample of biological suspension taken during the operation of the MBR. The MBR sludge showed a main peak at around  $140 \mu\text{m}$ . Two smaller peaks were observed at  $20 \mu\text{m}$  and  $60 \mu\text{m}$ . The colloidal fraction below  $1 \mu\text{m}$  was not detected as reported in literature [9,22].

Fig. 3 presents the time variation of TMP obtained from six different runs under the same flux of  $10 \text{ L m}^{-2} \text{ h}^{-1}$ . The number 2D, 4D and so on in the figure represents the number of days of each experiment. This figure shows that TMP does not become change at the early 3 days indicating stability of the MBR system. But after 3 days rapid rise in TMP was observed. But after 3 days rapid rise in TMP was observed. The break in the TMP in the 20 days run towards the later period was due to a power failure that stopped pump for several hours. Stopping of pump halted the TMP record during that period. Recommencement of electricity supply after several hours again continued the TMP development on membrane surface.

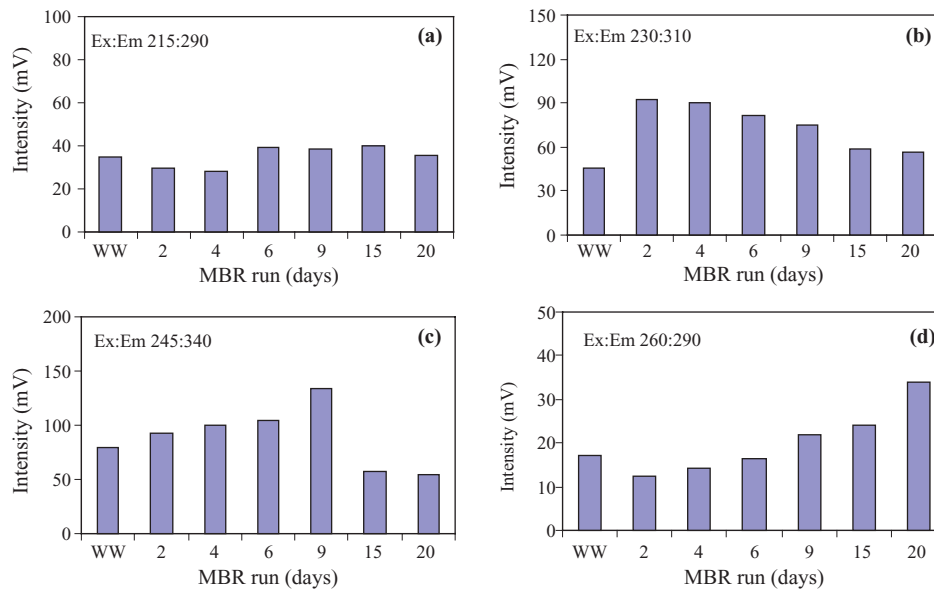


Fig. 4. Fluorescent intensity (mV) of foulant extract in different excitation emission region. Ex:Em 215:290 represents low molecular weight amino acid like substances (a); Ex:Em 230:310 represents low molecular weight amino acid and aromatic protein like substances (b); Ex:Em 245:340 represents BOD<sub>5</sub> type substances (c); and Ex:Em 260:290 represents soluble microbial by-products type substances (d).

Fig. 4 illustrates examples of the fluorescence intensity peak obtained from the foulant extract in Ex:Em 215:290 (low molecular weight substances including amino acids) (a), Ex:Em 230:310 (low molecular weight amino acids and aromatic proteins like substances) (b), Ex:Em 245:340 (BOD<sub>5</sub> type substances), (c) and Ex:Em 260:290 (SMPs like substances) (d). The *x*-axis in the figure shows the MBR experiment run days and *y*-axis shows the fluorescent intensity. It is seen that some of the low molecular weight amino acids concentration (Ex:Em 215:290) remain unchanged in the foulant whereas other amino acids and aromatic protein like low molecular weight substances (Ex:Em 230:310) have relatively higher concentration during

the early days of the MRB operation and then decreased. The Ex:Em 245:340 intensity peaks show that the BOD<sub>5</sub> type substances increased at the beginning and then after 9 days of operation it decreased. Increase of bacterial activity in the beginning might have caused an increase of BOD<sub>5</sub> substances in the foulant. With time, production of microbial by-products and development of new layers hindered the microbial activity and caused a decline in BOD<sub>5</sub> type substances. This is supported by Ex:Em 260:290 peak intensities (SMPs). This region had low fluorescent intensity in the beginning which increased with the operation time. This result indicated that the foulant composition is more dominant with SMPs with time. Alteration of COD and protein concentration in filtration resistance has been described by Rojas et al. [23].

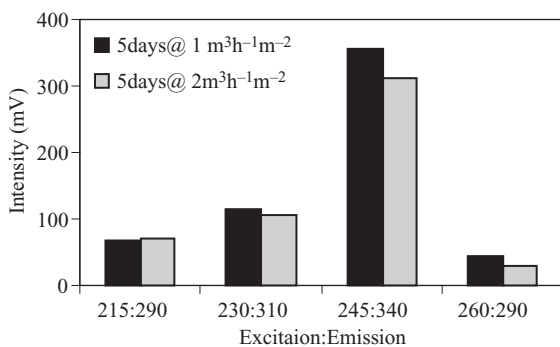


Fig. 5. Fluorescent intensity (mV) in foulant obtained at two different aeration rate.

Fig. 5 shows the fluorescence intensity peaks obtained from foulant extract when operated at two different aeration rate of 1 m<sup>3</sup> h<sup>-1</sup> m<sup>-2</sup> and 2 m<sup>3</sup> h<sup>-1</sup> m<sup>-2</sup> in Ex:Em 215:290 (low molecular weight substances including amino acids), Ex:Em 230:310 (low molecular weight amino acids and aromatic proteins like substances), Ex:Em 245:340 (BOD<sub>5</sub> type substances) and Ex:Em 260:290 (SMPs like substances). It can be seen that the low molecular weight substances had almost similar concentration at both aeration rates whereas the concentration of SMPs was lower at the higher aeration rate. This reduction of SMP will be more apparent at higher aeration rate for experiments

after 15 days of operation. The result showed increasing crossflow velocity improved particle back transport and reduced membrane fouling as reported by other researchers [15–17].

#### 4. Conclusion

The lab-scale side stream MBR with flat sheet membrane which was operated at similar hydrodynamic conditions and the chemical characteristics of the foulant was studied by running six experiments of different durations (2, 4, 6, 9, 15 and 20 days) in series. The foulant after each run was extracted using NaOH (0.5%) solution and investigated quantitatively using fluorescence spectrometer at different excitation emission wavelength.

Aeration of  $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$  showed lower fouling propensity compared to the aeration at  $1 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ . An increase of the aeration rate decreased the fouling propensity. At a similar aeration rate ( $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ ) low molecular weight substances such as amino acids showed virtually similar concentration in foulant for all runs whereas the concentration of other low molecular weight substances (aromatic protein type substances) decreased with the evolution of time.  $\text{BOD}_5$  type substances showed an increase in concentration from the beginning of the experiment up to 9 days and the concentration beyond that time decreased. This showed that the microbial activity was high in the beginning of the MBR operation and then slowly decreased. The SMPs concentration in foulant increased with time indicating the SMP as a major contributor to fouling. The higher aeration rate decreased the fouling propensity.

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