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Performance of a stainless steel membrane in membrane bioreactor process

Rupak Aryal[a], M.A.H. Johir[a], Saravanamuthu Vigneswaran[a,*], Jaya Kandasamy[a], Robert Sleigh[b]

[a]*Faculty of Engineering and Information Technology, University of Technology, Sydney, Broadway, NSW 2007, Australia*
Email: Vigid.Vigneswaran@eng.uts.edu.au
[b]*Steriflow Filtration Systems, NSW, Australia*

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ABSTRACT

Stainless steel membrane has recently emerged as a durable membrane for microfiltration. An aerobic membrane bioreactor (MBR) equipped with a tubular stainless steel membrane of pore size 0.3 μm was submerged in a wastewater reactor to treat municipal wastewater of about 1,000 mg/L COD. The membrane operational performance was tested at three different permeate flux (7.5, 10 and 15 $L/m^2 h$ [LMH]) for 2 days each. In all cases, the rate of trans-membrane pressure (TMP) rise was very high at 30, 45 and 80 kPa for 7.5, 10 and 15 LMH, respectively. Different analytical techniques i.e. particle size distribution, UV spectrometry, fluorescent spectrometry and size exclusion chromatography were used to study the nature of mixed liquor and the fouling deposited on the membrane surface. Rapid rise of TMP and decrease in permeate flux was observed during the experiment. Analysis of the fouling indicated a negligible difference in nature of organics between it and the mixed liquor. Filtration flux test showed a high sludge cake and pore-blocking resistance of 4.4×10^{19} and $2.8 \times 10^{16}\,m^{-1}$, respectively, compared to a clean membrane resistance $5.4 \times 10^{12}\,m^{-1}$. The similar nature of organics in the mixed liquor and the foulant and recovery of flux after removal of the foulant after gentle washing in water, indicated a rapid sludge accumulation rather than the irreversible fouling.

Keywords: Stainless steel membrane; Membrane bioreactor; Municipal wastewater; Foulant

1. Introduction

In recent years, membrane bioreactor (MBR) employing microfiltration (MF) has become popular in water and wastewater treatment, due to their potential advantage of complete removal of suspended solids and colloidal materials from the effluent, good removal of nutrients and organics, high-loading rate capabilities, low sludge production and small footprint [1,2]. To achieve good separation, different types of membrane have been used. The surface morphology of the membrane is vital for its performance.

Most of the MF membranes are made of organic polymer, such as PVDF and polyamide. Due to frequent cleaning procedures and aging effects, these polymer membranes need to be replaced frequently. The life time of the organic membrane is 3–5 years. The development of more durable MF membrane made of porous stainless steel has the potential of expanding the application of MF in the application of water, wastewater and industrial treatment.

*Corresponding author.

One of the major hurdles of the membrane filtration system is the fouling of the membrane surfaces that decreases the efficiency of the membrane with time. The membrane fouling can be categorised as follows [3,4]:

(i) Sludging is referred to an accumulation of sludge on the membrane surface [5]. An intensive sludge accumulation on the membrane surface can be alleviated by smoothing the membrane surface and by providing sufficient external local shear stress.
(ii) Biofilm development due to an accumulation of cells and extracellular polymeric substances on the membrane surface [6,7]. A long-term operation is always marked by a sudden and inevitable jump in the transmembrane pressure (TMP), indicating severe membrane fouling. Several authors explain this phenomenon by pointing out the slow and inevitable accumulation of fouling compounds both on the outside and inside of the membrane material. [8–12]. This fouling rate can be minimised by providing shear stress on the membrane surface and ultimately cleaning it with chemicals.
(iii) Irreversible fouling is due to physico–chemical interactions (adsorption) of soluble compounds onto the membrane surface, which is usually cleaned with chemical(s) [11].

Membrane fouling causes a decline in membrane efficiency and a smaller permeate flux with time. According to Darcy's law, the relationship between permeate flux and TMP can be expressed as:

$$J = \frac{\Delta P}{\mu R_t} \quad (1)$$

$$R_t = R_m + R_f = R_m + R_{sc} + R_p \quad (2)$$

where J is the equilibrium permeate flux, ΔP is the equilibrium TMP, μ is the viscosity of the permeate; and R_t is the total membrane resistance, R_m is the intrinsic membrane resistance, R_c is the cake resistance, R_f is the fouling resistance and R_p is the resistance due to pore plugging and irreversible fouling. Flux and TMP data are used to calculate the total resistance (R_t) using Eq. (1); filtration of pure water with a new membrane before operation gives the values of R_m. $R_m + R_p$ is measured after removing the cake layer by washing the membrane with tap water and the operation is followed by filtering with pure water. Thus, R_p can be calculated from Eq. (2).

The filtration resistance in MF is mainly determined by the amount and the composition of the filter cake deposited on the membrane surface. Build-up of the cake layer, depends on the surface structure of the membrane. Evaluation of the cake layer developed on a stainless steel membrane surface during municipal wastewater treatment is a pre-requisite for its application in wastewater treatment.

In this study, a tubular stainless steel membrane module was tested at filtration flux of 7.5–15 $L/m^2 h$ (LMH). This corresponds to a hydraulic retention time of 30–15 h. The performance of the metallic membrane was evaluated in terms of the TMP and the characteristics of the foulant deposited on the membrane surface using several optical techniques.

2. Experimental

2.1. Experimental set-up and operating conditions

2.1.1. Pilot set-up

A tubular stainless steel membrane with an average pore size 0.3 μm and an area of 0.03 m^2 was submerged in a 7 L bioreactor (Fig. 1). The mixed liquor was continuously agitated using air bubbles released from the bottom of the reactor. Larger bubbles (2–4 mm in diameter), at an aeration rate (1.0 $m^3/h/m^2$), were continuously injected onto the surface area of membrane from the bottom of the reactor to produce shear stresses on the membrane surface and minimise sludge accumulation. Membrane filtration was performed in a continuous mode from outside to inside, with no relaxation or backwash procedure. This permeate was extracted by a peristaltic pump at a constant flux. Pressure transducers with online data acquisition captured the TMP, every 5 min.

Prior to each run, the membrane was cleaned with NaOH solution (5%) for 3 h, followed by citric acid (0.5%) for 12 h and sodium hypochloride (200 ppm) for 3 h. In order to ensure proper cleaning, the clean membrane flux was measured before commencing

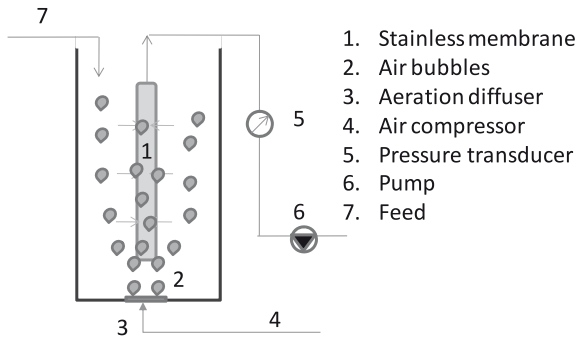


Fig. 1. Schematic diagram of MBR process.

each experiment and checked against a virgin membrane.

2.1.2. Feed and operating conditions

Activated sludge collected (the return sludge from the secondary sedimentation tank) from a local municipal wastewater treatment plant (Sydney, Australia), without any adjustment, was used as seed for the MBR. The MBR was continuously fed with a synthetic substrate (ethanol, ammonium chloride, potassium dihydrogen phosphate) to keep the ratio of COD:N:P equal to 150:5:1, with an organic load of 1.5 kg COD/m^3 d. During the acclimation period, the permeate flux was maintained at 10 LMH. Total suspended solid concentration was maintained between 4 and 6 g/L with dissolved oxygen concentrations kept above 2.5 mg/L. The MBR was acclimated over a period of 45 days prior to running the experiments. Three runs at different permeate flux of 7.5, 10 and 15 LMH were performed for 2 days. Each experiment was duplicated for consistency. After each run, the membrane was taken out and washed with water by submerging it in a water tank to remove the excess sludge accumulated on the membrane. The foulant attached on the membrane surface was then extracted with NaOH solution (5% w/v), using a horizontal shaker for 3 h, followed by backwash for 10 min.

For a comparative study, the extracted foulant was filtered through 1.2 μm filter and diluted to make the DOC equivalent to 5 mg/L. The extracted foulant was then analysed and the term foulant here refers to that extracted with NaOH solution.

The mixed liquor suspension was monitored by COD measurement and the soluble microbial products (SMP) were measured after filtering through 1.2 μm filter. In SMP, protein was quantified using the Lowry method using Bovine Serum Albumin (BSA) as the standard (Sigma) (550 nm in UV/Visible spectrometer) and polysaccharide was quantified by the Dubois method using glucose as the standard (550 nm in UV/Visible spectrometer).

2.1.3. Particle size analysis

The particle size distribution of the mixed liquor was measured by a laser particle size analyser (Malvern SB.0B UK). The instrument was operated in the range between 1.8 and 180 μm.

2.1.4. Foulant analysis

UV analysis. The foulant was analysed using a UV spectrometer (Shimadzu, 1700). The UV spectrometer was operated at a bandwidth of 1 nm, with a quartz cell of 10 mm path length from 200 to 400 nm. The scanning speed was 190 nm/min (slow). The photometric accuracy was 0.004 Abs at 1.0 Abs.

Fluorescent analysis. Excitation emission matrices (EEMs) were obtained using a spectrofluorometer (Varian Eclipse) with a wavelength range of 280–500 nm by increasing the wavelength by 5 nm for excitation and emission. When the experiments were run at different aeration rates, the selected fluorescent intensities (excitation:emission) were picked up and compared for the abundance of fouling substances.

Molecular weight (MW) distribution analysis. The MWD of organics were measured using high pressure size exclusion chromatography (HPSEC, JASCO Corp., UK) with a size exclusion column (Protein-pak 125, Waters Milford, USA). MilliQ water with phosphate (pH 6.8) and NaCl (0.1 M) was used as eluent. The eluent flow rate was 1.0 mL/min. The UV wavelength of 254 nm and fluorescent wavelength (Ex:Em) of 250:340 were applied for the detection. Standards of MW of the various polystyrene sulfonates (PSS: 210, 1,800, 4,600, 8,000 and 18,000 Da) were used to calibrate the equipment.

3. Results and discussion

The detailed characterisation of particles in mixed liquor is important for a better understanding and treatment of wastewater. The particle size in the wastewater provides an indication of the floc size and stability of the reactor [13,14]. Fig. 2 shows the particle size distribution of the mixed liquor collected, during the experiment conducted at 10 LMH run. Bimodal distribution of particle sizes at 17 and 46 μm were observed during the experiments. This indicated that the mixed liquor contained two types of flocs. Such a

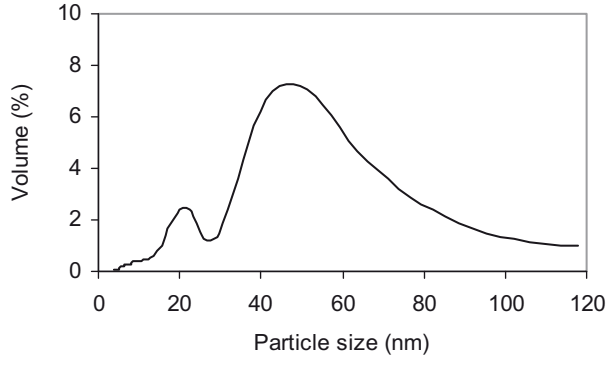


Fig. 2. Particle size distribution in mixed liquor.

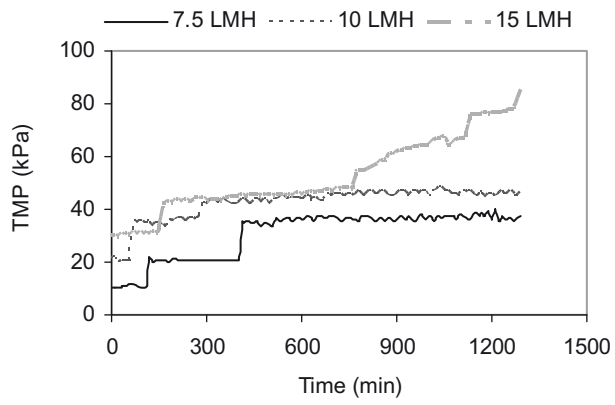


Fig. 3. TMP development at three different permeate flux values (7.5, 10 and 15 LMH) with acclimated mixed liquor.

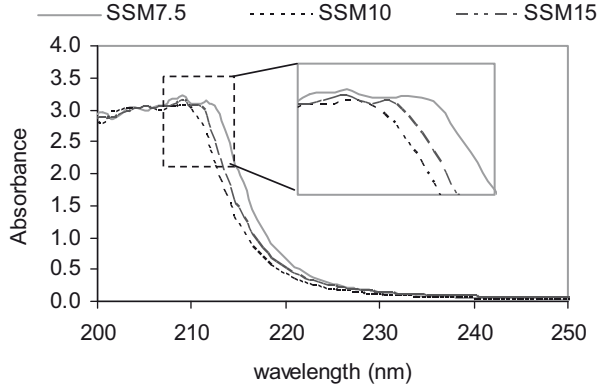
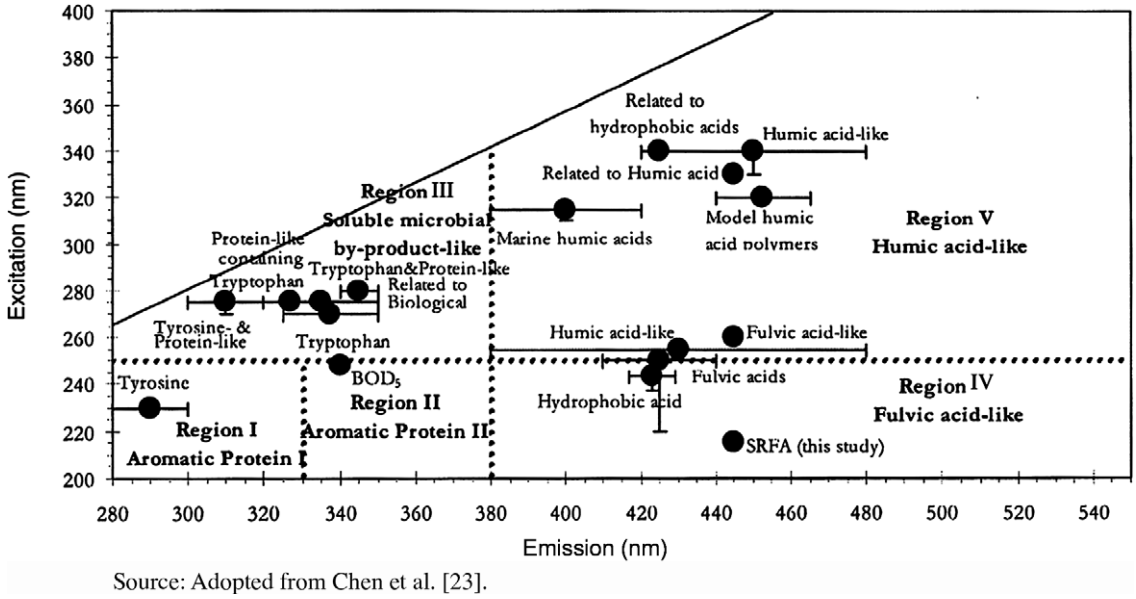


Fig. 4. UV spectra of foulant run at 7.5, 10 and 15 LMH.

bimodal/trimodal distribution has been observed previously [15–17]. Since the floc size is much higher than the membrane pore size, internal pore blocking in short run experiments was considered negligible.

The measurements of biological parameters, such as soluble mixed liquor proteins, polysaccharides and COD were 16 ± 3 mg BSA/L, 13 ± 2.6 mg Glucose/L and 53 ± 9 mg/L, respectively. These values indicated that the mixed liquor was stable during the operation period.

Fig. 3 shows three different TMP profiles over a period of 2 days. The rate of rise of TMP was high in all three cases and was highest at the largest flux of 15 LMH. The rate of rise of TMP and visual observation of the membrane surface showed that the TMP development was possibly due to a rapid accumulation of sludge on the membrane surface. Fig. 4 shows the UV spectra (200–250 nm) of three foulants collected from experiments run at three different fluxes. Three peaks were observed in the range of 209–214 nm. The observed peaks of flux 7.5, 10 and 15 LMH were at 210, 211 and 212 nm, respectively. UV of the foulant at the lower flux showed a peak at 212 nm (λ_{max}) and the UV shifted to a lower wavelengths of 211 and 210 nm with an increase of flux to 10 and 15 LMH. The shifting of peaks shows that the organic composition of foulant attached on the membrane surface has some difference in composition. The flux rate appears to influence the composition of membrane foulant, apart from the rate of deposition. According



Source: Adopted from Chen et al. [23].

Fig. 5. Location of EEM peaks of organic compounds based on literature reports.

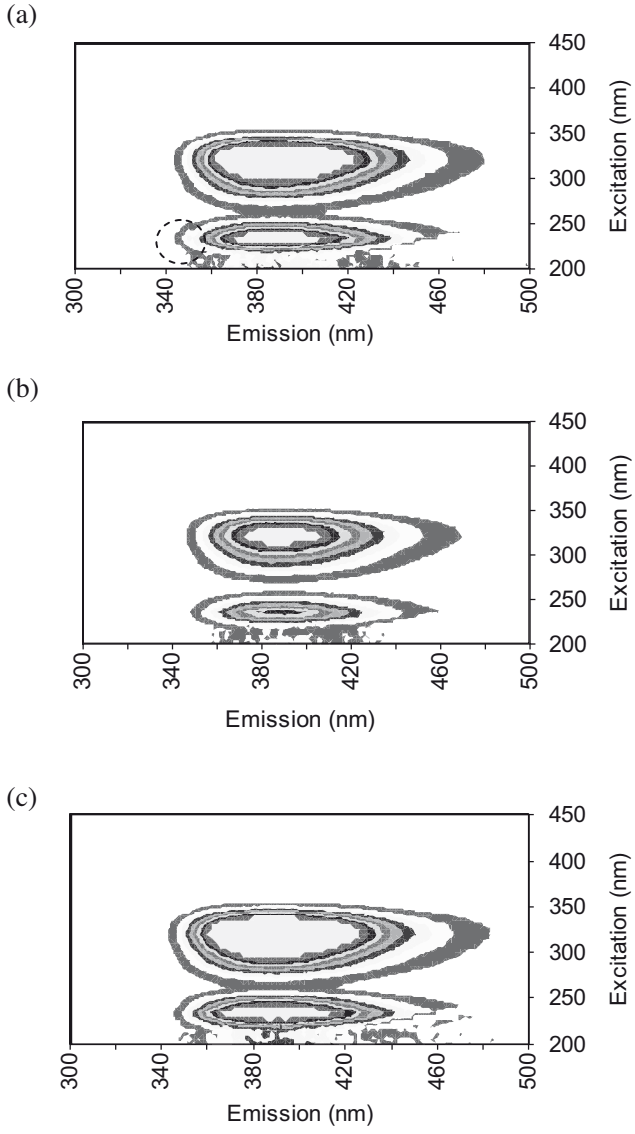


Fig. 6. EEM spectra of foulants at (a) 7.5 LMH, (b) 10 LMH and (c) 15 LMH.

to literature, the λ_{max} of 210 nm represents amino acid type substances and 212–214 nm represents polyaminoacids [18,19]. One of the possible reasons for a change in UV is the conversion of aminoacids to polyaminoacids by conjugation. This result is supported by Aryal et al. [20] in which the conversion of amino acid type substances to protein type substances were observed with the evolution of time (measured by excitation emission matrix analysis).

Fluorescence spectroscopy (excitation emission matrix) has been recently used in wastewater and membrane foulant analysis, as the spectra illustrates a wide range of organics. Excitation emission spectra are useful when studying the chemical properties of a foulant of various origins [20–22]. Based on nature of organics and its origin, the spectra are generally divided into five groups [23]. Regions I and II correspond to aromatic proteins and amino acid substances. Region III corresponds to the peptides and proteins (microbial by-products). Regions IV and V are for fulvic and humic acids type substances, respectively (Fig. 5).

Fig. 6 shows the excitation emission spectra (fluorescent spectra) of foulant at the three different operating conditions. As the foulant is mainly composed of aminoacids, proteins and polymeric substances, we focused on Region I (Ex:Em 200–250:280–330), II (Ex: Em 200–250:330–380) and III (Ex:Em 250–340:280–380). Region III is the best indicator of biopolymer development on the membrane surface.

At all the three flux rates, there was a negligible change in Region I, II and III. Close examination showed slightly more intense spectra in the Region II at lower permeate flux of 7.5 LMH (indicated by dotted circle in Fig. 6a). This indicates a possible difference in foulant organics at lower permeate flux compared to the others (which is also supported by UV spectra). Further, this indicated a sludge accumulation on the membrane surface and a negligible irreversible foulant development on the membrane surface. Previous studies have shown a change in the spectral behaviour of the foulant with the evolution of time [20,24].

Since proteins, peptides and amino acids have a large difference in MW, application of size exclusion chromatography can be a good tool to investigate the nature of the fouling in terms of MW. The nature of chemicals (in terms of MW) that appear in chromatogram is given in Table 1 [9].

Fig. 7 shows chromatograms of the foulant (obtained at three flux rates) and the mixed liquor. Among the three foulants, the one at the higher per-

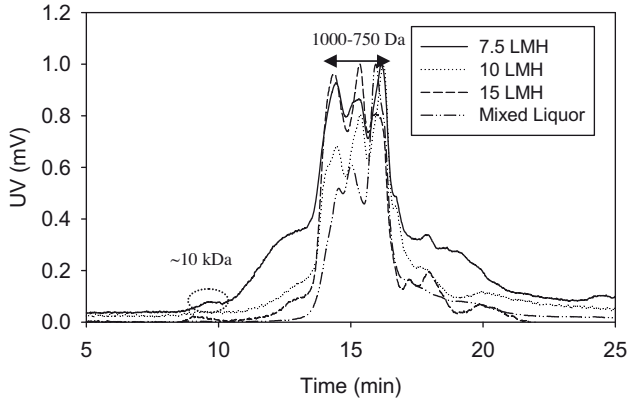


Fig. 7. UV response of foulants relating to MW distribution in three fluxes.

Table 1
MW for each substance and retention time in size exclusion chromatography

	Substance	MW (Da)	Retention time (in this work) (min)
BP	Biopolymers	35,000	9.54
HA	Humic acids	10,000	11.02
BB	Building block	750	14.38
AC	Low MW acids	250	16.50
AM	Amphiphilics	<200	17.7

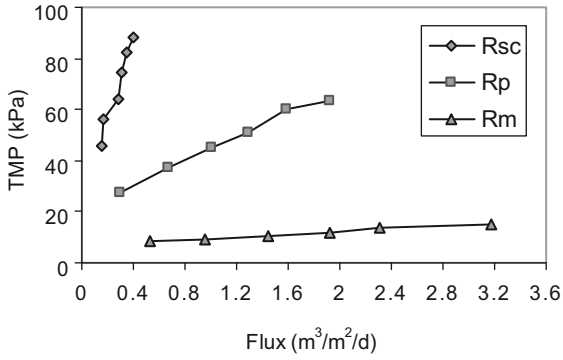


Fig. 8. Filtration flux test of the membrane.

meate flux (15 LMH), closely resembled mixed liquor. This shows that foulant at two flux rates (10 and 15 LMH) and mixed liquor have similar organics. The third foulant (7.5 LMH) displayed a small bulge in the region between 11 and 13 min (1,000–10,000 Da) and 17–20 min (lower MW acids at 250 Da) This observation also suggested that a lower flux rates favours a foulant of larger MW substances.

Fig. 8 shows the results of a filtration flux test for stainless steel membrane in clean deionised water; ($\mu_w = 0.96 \times 10^{-3}$) and the sludge suspension ($\mu_{sw} = 1.03 \times 10^{-3}$) to determine the individual resistance coefficients defined in Eqs. (1) and (2). A clean membrane had a filtration resistance (R_m) of $5.3 \times 10^{12}\,m^{-1}$. After the MBR operation for 2 days, the membrane had a sludge cake resistance (R_{sc}) of $4.4 \times 10^{19}\,m^{-1}$. After removing the cake sludge physically with distilled water, the filtration resistance (R_p) was $2.8 \times 10^{16}\,m^{-1}$. A high sludge cake resistance and pore blocking resistance indicated that the membrane fouling was mainly due to the sludge cake accumulation and pore blocking.

4. Conclusion

The performance of a stainless steel membrane for MF as part of a MBR treating municipal wastewater was assessed. The stainless steel membrane of pore size 0.3 μm was submerged in wastewater and run at three different permeate flux (7.5, 10 and 15 LMH) for 2 days each. The TMP development at three fluxes (7.5, 10 and 15 LMH) were 30, 45 and 80 kPa within 2 days of operation. The rate of rise at higher flux was almost 2.5 kPa/h indicating rapid flux decline. The foulant accumulated on the membrane surface after each run was analysed along with mixed liquor using three major analytical techniques: UV spectroscopy, fluorescence spectroscopy and HPSEC. All the instrumental analysis showed foulant and mixed liquor possessing a similar organic nature. This indicated possible sludge accumulation and pore blocking than the development of biopolymer fouling on the membrane surface. The sludge accumulation and pore blocking was tested by the filtration flux test which showed very high sludge cake and pore-blocking resistance of 4.4×10^{19} and 2.8×10^{16} m^{-1}, respectively, compared to clean membrane resistance ($5.4 \times 10^{12}\,m^{-1}$).

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