2.1 Complete blocking model (n = 2)

Complete blocking model assumes that every molecule that reaches the membrane surface completely blocks the entrance of the membrane pores such that the molecules are never superimposed upon the other. This creates a single layer of particles blocking all pores on the membrane surface but not within the pores. Considering these two hypothesis, Hermia (1982) concluded that *n* was equal to 2 in this case.

For *n* = 2, Eq. (1) linearized and expressed in terms of the permeate flux versus time results in Eq. (2) (Lim and Bai, 2003).

$$ln\, J_p = ln\, J_o - K_c t \tag{2}$$

where J_p is the permeate flux (m/s), J_o is the initial permeate flux (m/s), and K_c is the constant corresponded to the complete blocking model (/m). The parameter K_c can be expressed as a function of the membrane surface blocked per unit of the total volume that permeates through the membrane, K_A, and as a function of J_o, according to Eq. (3) (Bowen et al., 1995). Therefore, the active membrane surface decreases as a consequence of their pores being completely blocked (de Barros et al., 2003).

$$K_c = K_A\, J_o \tag{3}$$

2.2 Standard blocking model (n = 1.5)

In standard blocking model, the molecules diameter is much smaller than the pore diameter, thus, the molecules can enter most pores, deposited over the pore walls. As a result, the volume of membrane pores decreases proportionally to the filtered permeate volume.

For the standard blocking model, permeate flux as a function of time is given by the linearized Eq. (4) (Bowen et al., 1995).

$$\frac{1}{\sqrt{J_p}} = \frac{1}{\sqrt{J_o}} + K_s t \tag{4}$$

where K_S is the constant corresponded to the standard blocking model (/√m•s). The parameter, K_s, is defined in Eq. (5), which depends upon the volume of molecules retained per unit permeate unit.

$$K_s = 2\frac{K_B}{A_o} A \sqrt{J_o} \tag{5}$$

where K_B is the parameter in the standard blocking model that represents the decrease in the cross-sectional area of membrane pores per unit of the total volume permeated through the membrane (/m), A is the membrane area (m^2), and A_o is the membrane

porous surface (m^2).

2.3 Intermediate blocking model (n = 1)

Almost similar to the complete blocking model, this model considers that, when a molecule approaches an open membrane pore, the molecule blocks the pore. However, intermediate blocking model is less restrictive in such a way that not every molecule that arrives to the membrane surface blocks a membrane pore. It considers that some molecules may deposited on other molecules that previously settled. This model examines the probability of a molecule to block a membrane pore. Considering these hypotheses, Hermia (1982) concluded that *n* was equal to 1 in this case.

Mohammadi et al. (2003) linearized Eq. (1) for *n* equal to 1 and expressed it in terms of permeate flux as a function of time.

$$\frac{1}{J_p} = \frac{1}{J_o} + K_i t \tag{6}$$

where K_i is the constant that corresponded to the intermediate blocking model (/m). The parameter K_i can be expressed as a function of blocked membrane surface per unit of the total volume that permeates through the membrane, K_A (Eq. (7)) (Bowen et al., 1995). The membrane surface that is not blocked is diminishes with time (Koltuniewicz and Field, 1996). Consequently, the probability of a molecule blocking a membrane pore continuously decreases with time.

$$K_i = K_A \tag{7}$$

2.4 Cake layer formation model (n = 0)

The cake layer filtration model is used to explain for the case of large solute molecules which built up multiple layers, causing resistance to the flow of fluid through the membrane. The linearized equation for permeate flux with time is the following (Lim and Bai, 2003):

$$\frac{1}{J_p{}^2} = \frac{1}{J_o{}^2} + K_{gl} t \tag{8}$$

where K_{gl} is the constant corresponded to the cake layer formation model (s/m^2). The parameter K_{gl} is given by Eq. (9) (Bowen et al., 1995), which depends on both cake resistance and concentration.

$$K_{gl} = \frac{2R_g K_D}{J_o R_m} \tag{9}$$

where R_m is the membrane resistance (/m).

2.5 Resistance-in-series model

While Hermia's model is good in identifying the predominant mechanism during fouling, resistance-in-series model which also apply Darcy's law able to find out the dominant resistance components that caused the flux decline. Resistance-in-series model has four factors in explaining the membrane fouling: membrane hydraulic resistance (R_m), concentration polarization resistance (R_c), cake layer resistance (R_g), and adsorption resistance (R_a).

$$J = \frac{\Delta P}{\mu(R_m + R_g + R_c + R_a)} = \frac{\Delta P}{\mu R_t} \quad (10)$$

The three resistances in the equation are operationally defined and can be identified as follow: R_m was measured by filtering pure water through new membrane at constant pressure assuming R_g, R_c, and R_a were zero. With the known ΔP and μ, R_m can be calculated using Eq. (11).

$$J_{membrane} = \frac{\Delta P}{\mu R_m} \quad (11)$$

R_t was measured from the operational data that was obtained from actual feed solution filtration.

$$J_{total} = \frac{\Delta P}{\mu R_t} \quad (12)$$

After that, the actual feed solution was removed and pure water was added back for filtration again. In this case, $R_m + R_g + R_a$ was calculated by eliminating the R_c from $R_m + R_g + R_c + R_a$. Due to no solute molecules in pure water during filtration, no concentration gradient occurred which leads to back-transport of the fluids.

$$J_{without\ R_c} = \frac{\Delta P}{\mu(R_m + R_g + R_a)} \quad (13)$$

After cleaning the membrane by peeling off the cake layer, filtration can be performed to obtained $R_m + R_a$. It is assumed that after the cake layer was removed, only the irreversible R_a and R_m are actually causing the fouling.

$$J_{without\ R_g} = \frac{\Delta P}{\mu(R_m + R_a)} \quad (14)$$

3. EXPERIMENTAL METHODS

3.1 Materials

Three different types of flat sheet commercial membranes were purchased from Amfor Inc., Beijing, China. As reported by the manufacturer, ultrafiltration (UF) membrane, PES10 was made by polyethersulphone (PES) with the nominal molecular weight cut-off (WMCO) of 10 kDa and pH resistance ranging from 1 to 13. While for hydrophilic nanofiltration (NF) membrane, NF2 and reverse osmosis (RO) membrane, LE were made by polyamide (PA) thin film composite with 95% $MgSO_4$ and 99.4% NaCl rejection, respectively.

The feed solution used for membrane filtration was AnPOME collected after microalgae treatment in our previous study. Both centrifuged and non-centrifuged samples were taken from the medium with 3 days RT intervals, from day 0 to day 12 with the centrifugation speed of 8000 rpm for 5 minutes. The typical characteristics of these samples are summarized in Table 1.

Table 1 Typical characteristics of AnPOME after microalgae treatment at different retention time

Retention Time (Day)	Centrifugation	pH	COD (mg/L)	NH_3-N (mg/L)	PO_4^{3-} (mg/L)	TSS (mg/L)	Turbidity (NTU)
Day 0	Yes	7.78	2764.00	265.25	378.13	243.3	112.0
	No	7.80	3390.00	294.00	580.00	1186.0	366.0
Day 3	Yes	8.44	1936.27	190.00	300.00	198.3	34.1
	No	8.49	2238.30	215.30	390.00	401.7	98.1
Day 6	Yes	8.88	1608.10	190.30	307.50	189.7	36.1
	No	8.92	1933.30	195.70	414.20	471.7	124.0
Day 9	Yes	9.04	1522.77	167.70	304.20	170.0	36.7
	No	9.08	1867.92	179.70	416.70	508.7	154.0
Day 12	Yes	9.18	1403.30	144.00	285.00	156.0	38.1
	No	9.22	1812.92	160.30	469.20	561.0	219.7

3.2 Membrane filtration system

A laboratory bench-scale dead end test unit was used to study the performance of each membrane (UF, NF, RO) on both centrifuged and non-centrifuged effluent under different RT from microalgae treatment. The set-up of the dead-end membrane filtration test unit is depicted in Fig. 2. The unit mainly consisted of a membrane dead-end filtration cell, HP4750 (Sterlitech Corporation, WA, USA) with processing volume up to 300 mL, nitrogen gas to exert pressure on the permeation cell was controlled and monitored by a pressure gauge meter, stirrer to form a homogeneous feed inside the permeation cell throughout the membrane filtration process, and balance with data acquisition system for

measuring filtrate flow.

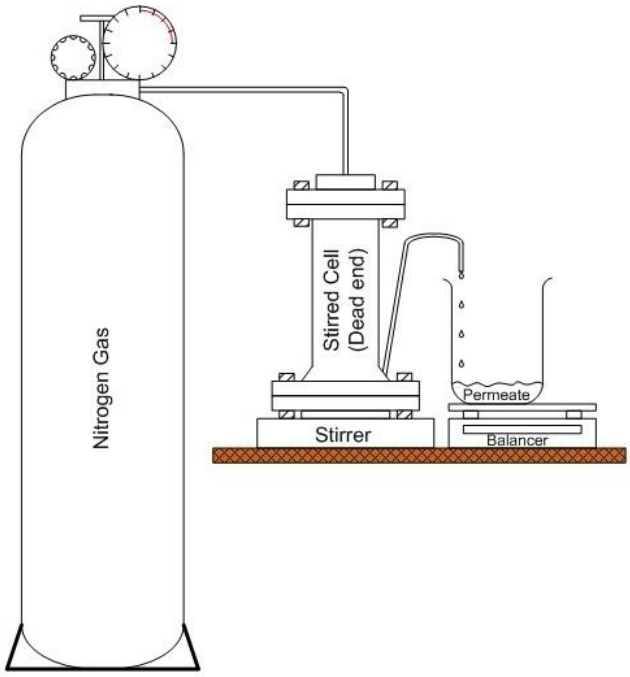

Fig. 2 Experimental set-up of dead-end membrane filtration.

All UF, NF, and RO flat sheet membranes were cut into the shape of disc with a diameter of 4.9 cm and the effective membrane filtration area was 14.6 cm^2 (excluding the area covered by the O-ring). The newly cut membrane was soaked in pure water and was left for a day to ensure complete removal from residual solvent/chemical. The membrane filtration test was performed by laying the front smooth surface of membrane facing the top of the membrane holder in the membrane test cell and then was tightened by a rubber O-ring. Different transmembrane pressures (TMP) was applied for each membrane, which is 5 bars, 7 bars, and 10 bars for UF, NF, and RO membrane, respectively. In order to alleviate the impact of compaction, pre-filtration study with pure water was first conducted at each respective TMP for 30 minutes until a steady-state flux was achieved. During the experiment, the AnPOME from microalgae treatment was poured into the dead-end filtration cell unit. The permeate flux was measured for every 30 mL of permeate collected. The permeate flux, *J* was calculated by the following equation:

$$J = \frac{V}{A\Delta t} \tag{15}$$

where V (m^3) is the volume of permeate water, A (m^2) is the membrane area, and Δt (h) is the operating time.