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Towards stable operation of a dynamic membrane bioreactor (DMBR): Operational process, behavior and retention effect of dynamic membrane

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ABSTRACT

An experimental study was conducted for characterizing the whole operational cycle of a dynamic membrane bioreactor (DMBR). With a nylon mesh of 25 μm pore size as support material, the filtration flux was suddenly halved within 5 min, indicating a rapid cake layer formation. Then the flux declined gradually and became stable at $t=4$ h, indicating the maturation of the dynamic membrane (DM) for stable operation. By periodical bottom aeration, the flux kept stable until $t=24$ h before physical cleaning should be conducted for DM regeneration. In such an operational cycle, effluent turbidity about 3 NTU was only detected at the start, dropped to about 0.5 NTU after 5 min and kept lower afterwards. Effective and stable removal of chemical oxygen demand (COD), ammonia, phosphorus was achieved in the 2-month continuous operation period. Although air backwashing brought about effective recovery of the flux, additional surface brushing could further remove the "irremovable fouling". By morphological and physicochemical analysis, it was identified that the DM could retain 15.3% of COD and 10.6% of polysaccharides from the activated sludge, as well as certain amount of protein-like and humic-like substances. These membrane fouling substances should be removed by physical cleaning for DM regeneration.

1. Introduction

Membrane bioreactors (MBR) have been widely used for wastewater treatment. However, the main obstacles constraining its more widespread applications are the expensive membrane costs, high energy demand, and membrane fouling. Recently, the dynamic membrane (DM) technology was introduced as a substitute for MBR, which could effectively resolve the problems encountered in the MBR process due to the low cost of the membrane module, high flux and easy backwash [1]. The bioreactor by means of DM is called the dynamic membrane bioreactor (DMBR) either operated aerobically [2–4], or anaerobically [5–8]. However, more attention has been paid to the aerobic DMBR. When a DM module is immersed in a bioreactor, a cake layer can be formed on the support material, such as nylon mesh, filter cloth and stainless steel mesh, by retaining suspended solid particles (e.g. sludge flocs and microbial cells) on it. Once the cake layer grows too thick to result in a high filtration resistance, it can be removed easily and then replaced by a new deposited layer.

The stable operation of DMBR depends much on the initial sludge deposition to coarse-pore materials. Therefore, different from a MBR, the operational process of DMBR often consists of several important stages, including DM layer formation, stable filtration, and cleaning for DM regeneration. In the DM layer formation stage, the initial flux can be as high as 1000 L/m^{2}h, and it may take 0.3–24 h for the DM layer to be formed [9], depending on the characteristics of the support material and the operation conditions. When a support material with pore size as large as more than 100 μm is adopted, a high flux can be obtained but a considerably longer formation time is also needed. In this stage, high effluent quality may not easy to maintain while activated sludge flocs may be lost from the bioreactor. Therefore, return of initial effluent back to the bioreactor often becomes a common option for the DMBR. When a stable DM is formed, the operation enters the stable stage, in which high effluent quality can be obtained due to the good solid–liquid separation performance of the well formed DM. The flux can usually be stabilized at 20–150 L/m^{2}h and the filtration time can last for several hours to several days [10]. Because the behavior of the DM in this stage determines the performance and effectiveness of the DMBR,

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efforts should be made to optimize the operational condition to extend the stable filtration duration. As the continuous DMBR operation is accompanied by undesired deposition of sludge flocs and accumulation of fouling-causing substances to induce an increase of filtration resistance and deterioration of the permeability of the DM, cleaning for DM regeneration is required as the third stage.

The commonly used methods for DM cleaning are by physical means such as water backwashing, air backwashing, and/or brushing without application of any chemical reagents [10]. Air backwashing can efficiently improve the cleaning effect and less residual may exist in the DM layer when air pressure is increased [11–14]. In one study, bottom aeration has been found to be more effective to remove all clogs from the DM [15]. Chemical cleaning has also been tried in a large pilot scale DMBR by using 0.2% hypochlorite for 4 h and 0.2% hydrochloric acid for 4 h, which resulted in an almost complete restoration of flux in a 3-month operation period [9]. The flux of a fouled DM can be totally recovered by brushing, presumably the best option for DM cleaning [16,17].

The three stages discussed above are in fact interrelated with each other. From the viewpoint of practical operation of a DMBR, it would be ideal that the operational condition can be optimized to shorten the DM layer formation stage, to make the DM to work stably, to clean the DM effectively and more importantly to merge the three stages in a smooth manner so that a real continuous operation can be realized. However, many of the studies by far are targeting inconsistent issues but few attentions were paid simultaneously to the whole operation process.

On the other hand, the removal of pollutants by DMBR depends much on the retention effect of the cake layer formed on the support mesh [1]. It is reported that a well-formed DM alone could reduce the influent COD, UV_{254}, TOC and NH_3–N by 9.9%, 10.2%, 9.7% and 6.5%, respectively [18]. However, many of the pollutants retained by the DM are membrane foulants, such as fine particles and extracellular polymeric substance (EPS), which may induce a rapid increase of filtration resistance or decline of membrane flux. The intrinsic resistance of the support material is usually as low as $1–2 \times 10^9\ m^{-1}$, but the resistance of a fouled DM could increase to $0.15–60 \times 10^{11}\ m^{-1}$ [15,19]. Nevertheless, few studies have so far been conducted to characterize the retention of fouling substances in the DMBR process.

With all these in mind, the present study was conducted to investigate the whole process of DMBR operation with attention paid firstly to the formation and regeneration of the DM layer, secondly to the behavior of the DMBR for pollutants removal in the stable operation stage, and thirdly to the characteristics of the DM layer, including its physicochemical components and retention effect.

2. Materials and methods

2.1. Experimental setup and operational parameters

The lab-scale DMBR with an effective volume of 34 L (Fig. 1) is located at a local wastewater treatment plant (WWTP) in Xi'an, China. One flat-sheet DM module was immersed vertically between two baffle plates. A nylon mesh with an equivalent aperture of 25 μm and an effective filtration area of 0.04 m^2 was used as support material for the DM formation. The aeration device at the lateral parts of the reactor was run continuously to induce circulation flow in the reactor (30 L/min). Another diffuser was installed below the DM module for air scouring (30 L/min), which worked periodically at an interval of 5 min every 8 h.

After sludge inoculation from the local WWTP, it took two

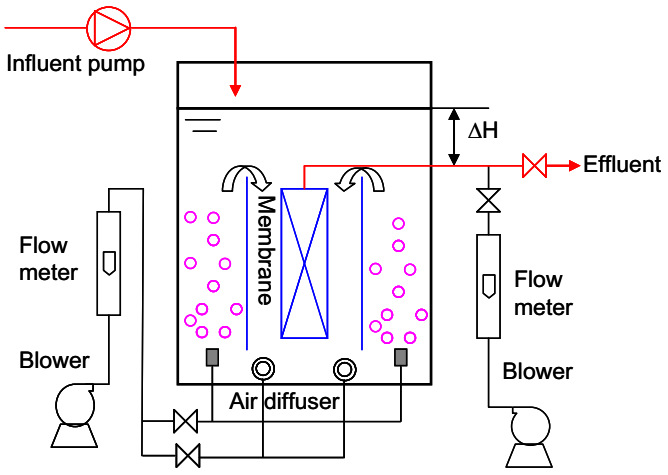

Fig. 1. Flow diagram of the DMBR.

weeks for sludge acclimation. Then the DMBR was operated continuously for about 2 months. The sludge retention time (SRT) of the DMBR was maintained at 30 d by discharging a predetermined amount of the mixed liquor daily. The MLSS concentration was kept at about 3000 ± 500 mg/L. The dissolved oxygen (DO) concentration in the reactor was in the range of 4–6 mg/L. Real domestic wastewater, the characteristics of which is presented in Table 1 was fed into the DMBR. The effluent was withdrawn continuously by 10 cm water level difference between the bioreactor and the effluent port. The flux decreased gradually with time under this constant pressure operation mode. When the flux dropped to 10% of the initial flux, two different cleaning methods (air backwashing, air backwashing plus surface brushing) were used for permeability recovery. Air backwashing was implemented at a flow rate of 72 L/min for 5 min, while for air backwashing plus surface brushing additional surface brushing was conducted. During the early stage of the DMBR operation, six-time consecutive operational cycles were conducted to compare the performance of the two different cleaning methods. For the following two-month operation, air backwashing plus surface brushing was adopted because it was found to be more effective in DM regeneration compared to air backwashing.

2.2. Analytical methods

2.2.1. Cake sludge collection

Cake sludge formed on the DM surface was scraped off by a plastic sheet as the DM module was taken out from the DMBR, which was operated according to the previous study [1,14,20]. In detail, firstly the collected cake sludge was diluted with deionized water to a similar MLSS concentration as that of the activated sludge in the bioreactor, and then the diluted sample was placed on a magnetic blender and gently mixed to form a uniform liquor, which was subjected to the following measurements.

Table 1
Characteristics of raw wastewater.

Parameters	Range
COD (mg/L)	111.4–270.7
NH_3–N (mg/L)	20.8–40.7
TP (mg/L)	2.7–4.6
Turbidity (NTU)	17.4–74.2
pH	7.4–8.0
Temperature (°C)	10–22

2.2.2. EPS extraction and analysis

EPS extraction of sludge samples was conducted according to the thermal treatment method as reported previously [21]. The analysis of the extracted EPS samples was carried out for proteins using the modified Lowry method [22] with bovine serum albumin (BSA) as the standard, and for polysaccharides using the phenol-sulfuric acid method [23] with glucose as the standard.

2.2.3. Particle size distribution (PSD) analysis

PSD of the cake sludge and sludge in the bioreactor was analyzed and compared using a laser granularity distribution analyzer (LS 230/SVM+, Beckman Coulter Corporation, USA) with a detection range of 0.4–2000 μm. It was noted that the repeated measurements of the PSD of cake sludge samples showed quite similar results and good reproducibility, indicating the effectiveness of the adopted method in the pretreatment for cake sludge described in Section 2.2.1.

2.2.4. Scanning electron microscopy (SEM) and energy-diffusive X-ray (EDX) analysis

To observe and compare the morphology of membrane samples, the fouled module was taken out from the DMBR, and then a piece of membrane was cut from the middle of the fouled membrane. The samples were fixed with 2.0% glutaraldehyde for 8 h, followed by dehydrated with ethanol and coated with aurum-platinum alloy. Lastly, samples were observed using the SEM (VEGA 3LMH, Tescan Corporation, Czech). The EDX analyzer (Oxford INCA Energy 350, UK) was used to determine the inorganic components of the DM layer.

2.2.5. Fourier transform infrared (FTIR) spectroscopy analysis

After being collected using the method described in Section 2.2.1, the DM was oven-dried at 60 °C for 24 h. The organic composition of the DM was analyzed using a FTIR spectrometer (IR Prestige-21, Shimadzu Corporation, Japan). The powders of the sample were mixed with KBr powders at a mass ratio of 1:100 and pressurized into a pellet. The spectrum was then determined over the wave number ranging from 4000 to 400 cm^{-1}.

2.2.6. Three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy

The 3D-EEM fluorescence spectra of the dissolved organic matter (DOM) were measured using an FP-6500 spectroflurometer (Jasco Corporation, Japan). To obtain fluorescence EEM spectra, excitation wavelengths were incremented from 220 nm to 450 nm at 5 nm steps. For each excitation wavelength, the emission was detected from 220 nm to 550 nm in 5 nm steps. The scan speed was set at 2000 nm/min, generating an EEM spectrum in 15 min. The software Origin Pro 8.0 (Origin Lab Corporation, USA) were used to handle the EEM data and EEM spectra as the elliptical shape of contours was plotted and presented.

2.2.7. Gel filtration chromatography (GFC) analysis

The molecular weight distributions of DOM in different water samples were determined using a GFC analyzer (LC-2010A, Shimadzu Corporation, Japan). A Zenix SEC-100 type gel column (Sepax Technologies Corporation, USA) was used in this work with 150 mM sodium phosphate buffer (including Na_2HPO_4 and NaH_2PO_4) as eluent at a flow rate of 1.0 mL/min. The dissolved organic matter in samples was obtained by filtering a 0.22 μm prior to the injection (50 μL) and analyzed using a UV detector (SPD-10, Shimadzu Corporation, Japan).

2.2.8. Other analysis

Microscopy observation of sludge samples was captured by a digital camera (N90i, Nikon Corporation, Japan) attached to a microscope. The photography of the DM modules was taken by an SLR camera (EPM2, Olympus Corporation, Japan). Measurements of chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), ammonia (NH_3–N), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in the reactor were performed according to the Chinese National Environmental Protection Agency (NEPA) Standard Methods [24]. Due to the quick formation of DM (< 5 min), the effluent sampling time was set at 0.5–1 h after DM cleaning as an operational cycle finished, which had no obvious effect on the effluent quality. The supernatant of the cake sludge and activated sludge was characterized by evaluating soluble COD (CODs) and colloidal COD (CODc) according to the reported method [25]. Turbidity was measured with a turbidity meter (ET266020, Lovibond Corporation, Germany), pH with a pH meter (PHS-3C, China), dissolved oxygen (DO) concentration with a DO meter (Model HQ30d, Hatch Corporation, USA), and the filtration flux of the DM with the volumetric method.

3. Results and discussion

3.1. Three-stage operational cycle of the DMBR

Fig. 2 illustrates one typical profile demonstrating the variation in membrane flux and turbidity with operating time during one operational cycle of the DMBR, which corresponds to the start of filtration to the time when flux declines to 10% of the initial flux needing physical cleaning for DM regeneration. Based on the evolution of the flux, i.e., rapid drop, pseudo-steady-state and nearly complete restoration, the whole operational cycle of the DMBR was divided into three stages, including the formation and maturation of DM, stable operation period and physical cleaning for DM regeneration.

In Stage one, the flux suddenly halved from 465 L/m^2h to 222 L/m^2h within 5 min, and also the total filtration resistance of 1.6×10^{11} m^{-1} was higher than that of the intrinsic resistance (7.6×10^{10} m^{-1}). More importantly, it was found that effluent turbidity about 3.0 NTU was only detected at the start, which decreased rapidly below 0.5 NTU within 5 min. So it indicated that a rapid DM formation within 5 min was achieved, according to the

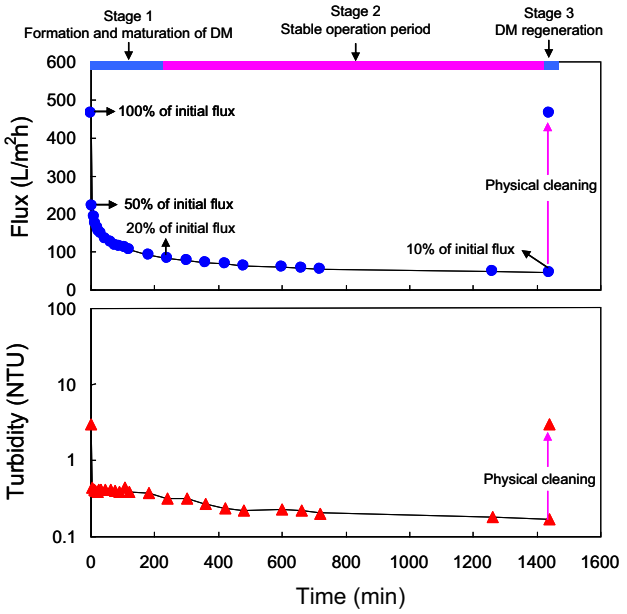

Fig. 2. Variations of flux and turbidity during one operational cycle of the DMBR.

previous studies which claimed that the effluent turbidity decreasing below 1.5–5 NTU (i.e. approximate zero SS concentration) was defined as the formation stage of DM [15,17,26]. Then the flux declined gradually and became stable for the following 4 h. In this period, the flux eventually decreased to 85 L/m^{2}h which accounted for about 20% of the initial flux, meanwhile the fouling resistance increased to 3.3×10^{11} m^{-1} and the effluent turbidity dropped continuously to a lower value. Liang et al. observed the similar phenomenon and attributed the subsequent flux decline to the subsequent "undesired" sludge deposition beyond the minimum deposited amount of sludge adequate for effective solid–liquid separation, accordingly, which caused the continuous increase in filtration resistance [26]. So the short initial period corresponded to the formation of the dynamic membrane, once the DM became maturation, the decline of the flux slowed [27]. However, it was also noted that large pore size of support material (50–100 μm) was commonly used resulting in the formation time of DM longer than 0.5 h in most cases [10,15]. It was because the coarse-pore support material itself could not effectively retain sludge particles smaller than the pore size of the nylon mesh. So, the larger the pore-size used, the longer the time needed for the DM formation and maturation. Moreover, long formation time of DM meant the decrease in the effluent quality and quantity and the loss of biomass in DMBR. So, it is important to bear in mind that Stage one is intimately related to the pore size of the support material for a given DMBR system.

The significant effect of mesh pore size during Stage one was further illustrated in Table 2. From Table 2, the nylon mesh with pore size of 25 μm showed the lowest DM formation time and effluent turbidity. Furthermore, compared to larger pore size, it was noted that mesh of 25 μm pore size presented the lowest stable flux as 85 L/m^{2}h, which, however, was much higher than that in a conventional MBR. Also Wu et al. compared the impact of mesh pore size in the range of 15–100 μm on DM filtration performance. In terms of turbidity best results were obtained with the smallest pore size (15 μm). But probably due to the retention of very fine particles, a gel layer formation was detected which led to significant flux decline [28]. Additionally, Walker et al. also conducted similar tests using a series of mesh pore sizes (10–140 μm) in an anaerobic DMBR, and it was also found that 10 μm mesh became clogged quickly while 30 μm mesh seemed to be the optimum option considering treatment performance and filtration property [6]. Due to the short formation time (<5 min), low initial (3.0 NTU) and stable effluent turbidity (<0.5 NTU) and acceptable flux (46–85 L/m^{2}h), no serious loss of biomass and impact on the effluent quality and flux could be expected when mesh of 25 μm pore size was used as support material for DMBR operation.

For Stage two, a stable operation period of 24 h was reached as evidenced by the stabilized turbidity and flux independent of the operating time. Eventually, the flux decreased to 10% of the initial flux (46 L/m^{2}h), and also the turbidity reached the minimum value (0.17 NTU). This stage was quite important, which determined the treatment performance and effectiveness of the DMBR process, so efforts should be made to extend the stable filtration time. In this study, a method using periodical bottom aeration (5 min aeration every 8 h) was proposed and verified. Under the preliminary attempt, it was evaluated that high frequent aeration (every 4 h or shorter) was not necessary due to little extra effect on extending the stable operation duration, while low frequent aeration (every 12 h or longer) would cause over accumulation and compactness of foulants in the DM, which was detrimental to prolonging the stable operation time. While the proposed periodical bottom aeration methods (5 min aeration every 8 h) enabled the whole operational cycle to be 24 h or longer, which seemed to be the optimum option in this study. Although some useful results were obtained, more efforts should be made in the future, including developing more efficient methods and their optimization and so on. Typically, the end of Stage two indicates that physical cleaning is needed for DM regeneration. Due to its important effects on the flux recovery and the stable operation of DMBR, Stage three will be discussed particularly.

3.2. Physical cleaning for DM regeneration

At the end of the above mentioned two stages, physical cleaning was essential for DM regeneration to obtain an acceptable flux towards long term operation, which was defined as Stage three of the whole operational cycle and was further investigated.

Fig. 3 (A)–(D) shows the photographs of a new membrane, the fouled membrane, membrane after air backwashing, and membrane after both air backwashing and surface brushing. The picture of the fouled membrane showed that only several parts of the membrane surface obviously attached with a thick cake sludge, such as the latent part and bottom part. Other parts were covered with a thin cake layer, which was due to the uneven distribution of gas/liquid flow during the periodical bottom aeration conducted during Stage two. As shown in Fig. 3(C) and (D), after physical cleaning like air backwashing/surface brushing, no obvious foulants could be detected. Additionally, it was noted that after physical cleaning the used nylon mesh (Fig. 3 (B)–(D)) became flabby to some extent compared to the new one (Fig. 3 (A)), although no serious effect on the filterability of dynamic membrane was detected, more attention should be paid to this issue due to its potential impacts during long term DMBR operation. Above analysis showed that both cleaning methods seemed to be able to completely remove the fouled DM layer as that stated in previous studies [11–14,16]. But the accumulation of physically irremovable fouling might occur as that frequently detected in MBRs [29]. The phenomenon was also reported by one study, in which SEM analysis showed that the residual substances of support mesh were mainly on the intersection of the two stainless steel wires, which were further identified as biopolymers (polysaccharides and proteins) [1]. However, still little attention was paid to these residual substances which could cause certain extent of fouling problem.

Thus, further observation of the membrane was done by SEM. As presented in Fig. 3(a)–(d), the fouled membrane surface was covered by cake sludge, which consisted of small sludge particles, cells, biopolymers, etc. However, after air backwashing (Fig. 3(c)), the cake sludge could not be obviously detected on the support mesh material but some residues still existed mainly in the

Table 2
Properties of DM formation using nylon mesh with different pore size.

Membrane pore size (μm)	Time needed for turbidity $<$1NTU (min)	Initial flux (L/m^{2}h)	Flux after 4 h (L/m^{2}h)	Turbidity after 4 h (NTU)
25	<5	460 ± 20	85 ± 5	0.17 ± 0.03
38	10 ± 5	500 ± 20	100 ± 10	0.25 ± 0.05
48	30 ± 5	540 ± 25	120 ± 10	0.36 ± 0.04
75	90 ± 10	560 ± 25	130 ± 15	0.40 ± 0.05

Note: Values were obtained by batch tests and given as mean $\pm$ standard deviation, number of measurement: $n=3$. Operational conditions: MLSS$=2800\pm400$ mg/L, lateral aeration with a flow rate of 70 L/min was implemented while no bottom aeration was used.

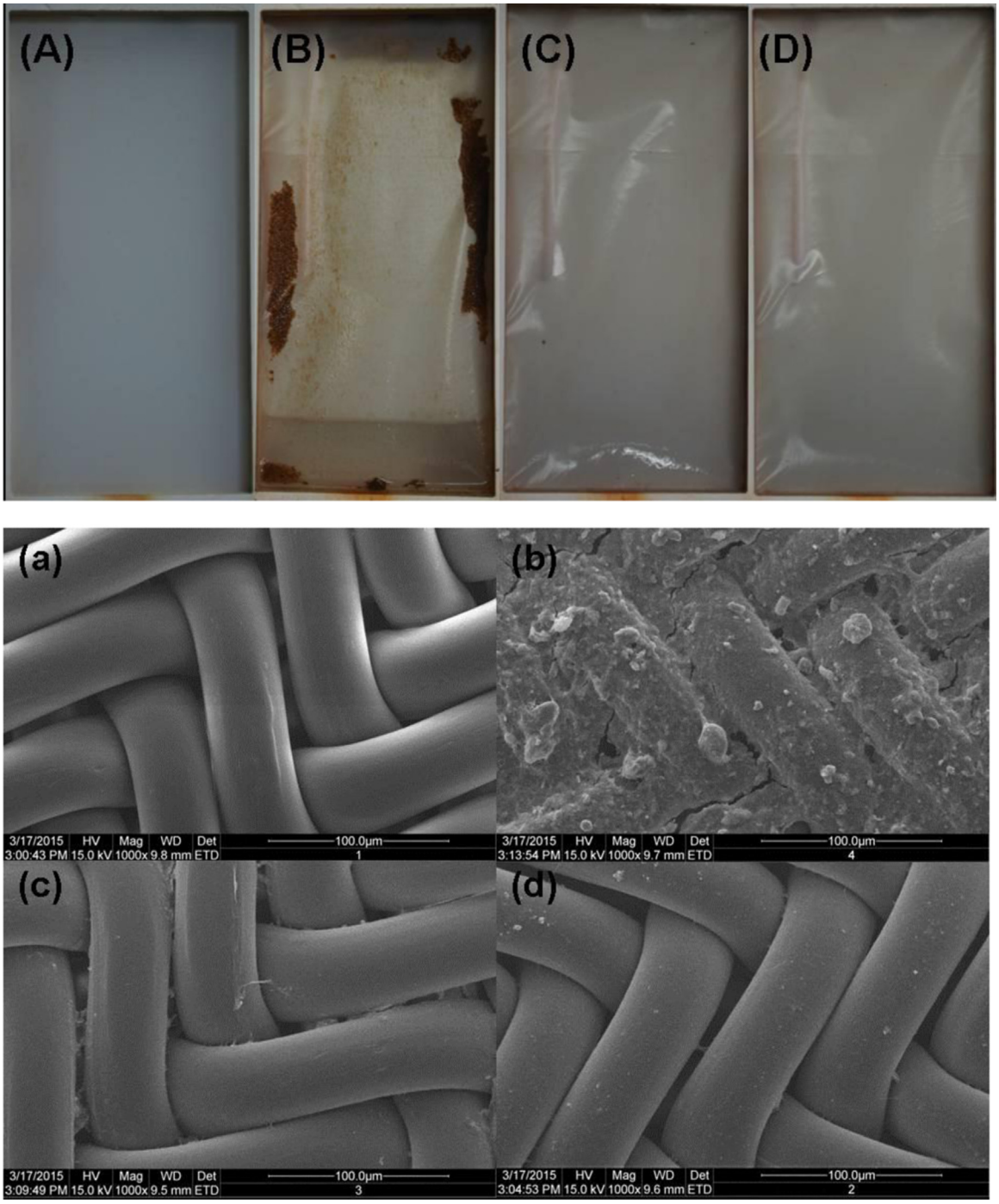

Fig. 3. Pictures of dynamic membrane module: (A) new membrane; (B) fouled membrane; (C) membrane after air backwashing; (D) membrane after both air backwashing and surface brushing; (a) SEM of new membrane; (b) SEM of fouled membrane; (c) SEM of membrane after air backwashing and (d) SEM of membrane after both air backwashing and surface brushing.

intersections of the mesh fibers and little in the mesh pores, which was the cause of physically irremovable fouling. Moreover, from Fig. 3(d) it was noted that after adopting the combination of air backwashing and surface brushing, less residues could be found on the cleaned mesh surface. Above analysis showed that two cleaning methods resulted in different morphology of meshes after cleaning, which would eventually affect the flux recovery efficiency as discussed below.

Also experiments were conducted to verify the impact of the two cleaning methods on flux restoration during six-time consecutive operational cycles as demonstrated in Fig. 4. It was found that the initial flux and stabilized flux differed to some extent depending on the cleaning method used. When air backwashing worked individually, the initial flux decreased quickly and eventually dropped to about 50% from the starting value after six-time cleaning tests, and also a certain decline of the stable flux could be observed although it was not so notable as that of the initial flux, which was attributed to the accumulation of physically irremovable fouling caused by residual substances as revealed before (Fig. 3(c)). Additionally, as shown in Fig. 4 no significant drop of the initial flux and stable flux with cleaning cycle was detected as adopting the combination cleaning method of air backwashing and surface brushing for DM regeneration, which was due to the fact that almost no remain of irremovable fouling caused by the

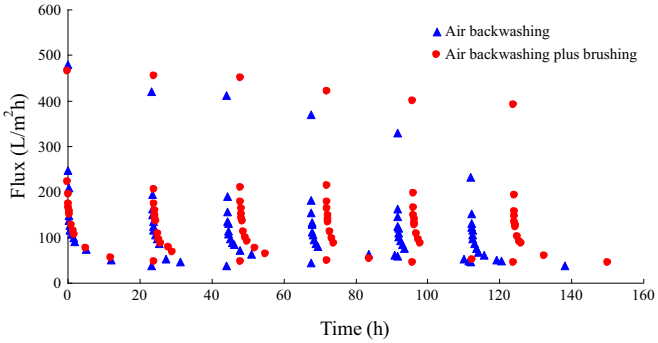

Fig. 4. Variations of flux with time adopting two cleaning methods for DM regeneration: air backwashing and air backwashing plus surface brushing.

residues existed (Fig. 3(d)). The results indicated that although air backwashing brought about effective recovery of the flux, additional surface brushing could further remove the irremovable fouling. From the point of practical application, air backwashing seemed to be still useful because of its easy operation. Air backwashing plus surface brushing could be a high-efficient way for DM regeneration, as one recent study by Walker et al. showed that a novel design of a DM module with a brushing device made continuous brushing of mesh surface and stable operation of the DMBR become possible [6]. Moreover, as for laboratory experiments, brushing has been applied in a number of studies as well as this study for DM cleaning [6,16,17]. However, it will be definitely difficult for adopting mechanical brushing in full scale DMBR operation. Therefore, further study is still needed to develop more practical methods for engineering application. In all, above results highlighted the existence of physically irremovable fouling as commonly noted in MBRs and also the effectiveness of physical cleaning methods for DM regeneration.

3.3. Pollutants removal by DMBR

The removal efficiency of turbidity, COD, NH_3–H, and TP by the DMBR was measured during a two-month stable operation period. Although the influent turbidity fluctuated highly from less than 20 NTU to 80 NTU and averaged at 44.3 NTU, the DM exhibited a good particle rejection capacity with the average effluent turbidity as 0.5 NTU, which was lower than those achieved in other studies [1,4] and similar to the value reported in a biologically enhanced powder activated carbon-diatomite DMBR [13]. Although coarse-pore nylon mesh themselves can not effectively reject suspended particles, the well formed DM enables the DMBR to exhibit excellent performance for solid–liquid separation.

Moreover, the DMBR also showed good removal efficiency for COD, NH_3–H and TP, especially for COD and NH_3–H. During the experiment, the concentrations of COD, NH_3–H, and TP in the influent were in the ranges of 110–210 mg/l, 20–43 mg/l and 2.7–4.6 mg/l, while their concentrations in the effluent were about 15.0, 0.4 and 2.1 mg/L, respectively, showing the removal efficiencies of 91%, 99% and 40%, respectively. In the DMBR, continuous aeration was supplied for the growth of microorganisms (mainly heterotrophic bacteria and nitrifying bacteria) while no anoxic or anaerobic environment existed for denitrifying bacteria and polyphosphate accumulating bacteria. So, under this aerobic environment the removals of COD and NH_3–H were quite efficient, and less removal of TN (10%–30%) and TP (32%–55%) was found, which was in accordance with previously reported result that the removals of COD, NH_3–H, TN and TP were in the range of 86%–89%, 92–99%, 34–38%, 18–33% by using an aerobic MBR coupled with a non-woven fabric filter [30]. The mechanisms contributing to pollutants removal in DMBR included microbial degradation and DM retention, commonly the former was considered to be more important while the later just enhanced the rejection of suspended particles and related pollutants [11]. By considering its efficient removals of various pollutants, high flux and easy regeneration, the DMBR could be regarded as a promising wastewater treatment process.

3.4. Morphology and physicochemical components of the DM

The activated sludge possessed dual effects on the operational cycle of the DMBR. One effect was that during Stage one, the activated sludge was the formation material of the DM, and the attachment of sludge particles determined the formation and filtration characteristics of the DM. The other one was that after the maturation of the DM, fine particles and related foulants could cause fouling problems because the pore size of the formed DM would diminish with operation time. So the behavior of the DM such as morphology, organic and inorganic components will be discussed and compared with that of activated sludge.

The morphology of the activated sludge and the cake sludge in the DM layer was found to be different by the microscope observation, in detail, the flocs of the activated sludge seemed to be porous and scattered while in cake sludge the flocs were much denser and larger. The results were further confirmed by the PSD analysis shown in Fig. 5. The mean particle sizes (d_m) of the activated sludge and cake sludge were 43 μm and 57 μm, respectively. The difference could be due to the following two aspects. Firstly, as coarse-pore mesh was used in the DMBR, small particles would not be retained but just permeate as effluent in the early stage, during which the selection effect of sludge flocs by mesh material is important. Secondly, with the gradual diminishment of the pore size of the DM, small particles, biopolymers (EPS) and inorganic matter would be intercepted by the DM, which would interact with each other and further enhance the PSD of retained particles. Also similar results related to the morphology of DM were reported by other researchers. It was illustrated that during the DM formation stage the deposition of large particles would be more prominent compared with the case in MF/UF processes due to the convection velocity of large particles towards support mesh greatly enhanced by the high initial filtration flux, then for the following stable operation stage DM fouling appeared to be controlled by the adhesion/cohesion strength among the involved particles largely related to the content of biopolymers in activated sludge, particularly carbohydrates [1,26]. So this analysis stressed the difference in morphology between the activated sludge and cake sludge, and also confirmed the potential effects of large particles and related foulants on the formation and morphology of

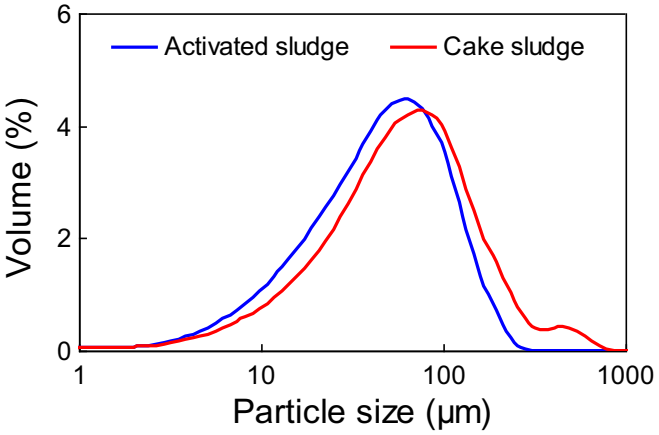

Fig. 5. PSD of activated sludge and cake sludge.

Table 3
Analysis results of the components of the cake sludge and activated sludge.

Sample	VSS	CODc	CODs	Inorganic matter	Total
Cake sludge (g/m^2)	15.47 (73.0%)	0.3 (1.4%)	0.1 (0.5%)	5.33 (25.1%)	21.2 (100%)
Activated sludge (g/L)	2.90 (74.4%)	0.01 (0.3%)	0.02 (0.5%)	0.97 (24.9%)	3.90 (100%)

the DM.

Also, the main components of cake sludge were detected using chemical analysis, FTIR and EDX. The cake layer consists of biomass (VSS), colloidal particles, solutes, and inorganic matter [25]. From Table 3, it can be seen that the contributions of VSS, colloidal particles and solutes, and inorganic elements accounted for 73%, 2% and 25% of the total amount in cake sludge, respectively. This highlights the importance of biomass and inorganic substances during the formation of the DM. By comparison the difference in the components content between the cake sludge and the activated sludge, it was found that the relative content of VSS in cake sludge decreased (73.0% vs. 74.4%) while the relative content of CODc increased (1.5% vs. 0.5%), indicating that apart from biomass the colloids might preferentially accumulate in the DM.

FTIR was used to measure the main functional groups of biopolymers in the cake layer (Fig. 6(a)). The spectrum showed a broad region of adsorption at a peak of 3433 cm^{-1}, which was attributed to the stretching of the O–H bond in hydroxyl functional groups [31]. A sharp peak at 2924 was due to the stretching of the C–H bonds [31]. Moreover, the amide I (1700–1600 cm^{-1}), amide II (1600–1500 cm^{-1}), and amide III (1300–1200 cm^{-1}) ranges were all associated with proteins, whereas 1200–900 cm^{-1} was attributed to polysaccharides and nucleic acids [32]. So, the two peaks (1653 cm^{-1} and 1553 cm^{-1}) in the spectrum indicated that proteins were one of the components of the DM cake layer. Additionally, the broad peak around 1104 cm^{-1} exhibited the presence of polysaccharides or polysaccharide-like substances. The absorption peaks smaller than 1000 cm^{-1} belonged to the finger print region [1]. Based on FTIR spectrum, the major organic components of the cake layer were identified as proteins (PN) and polysaccharides (PS). The results were consistent with one previous study, in which the deposited biopolymers in DM were also indentified mainly as PN and PS [1]. In conventional MBR biopolymers such as EPS were commonly considered as the predominant cause of membrane fouling, while these organics would also played an important role in irremovable fouling of the DMBR as discussed in Section 3.2.

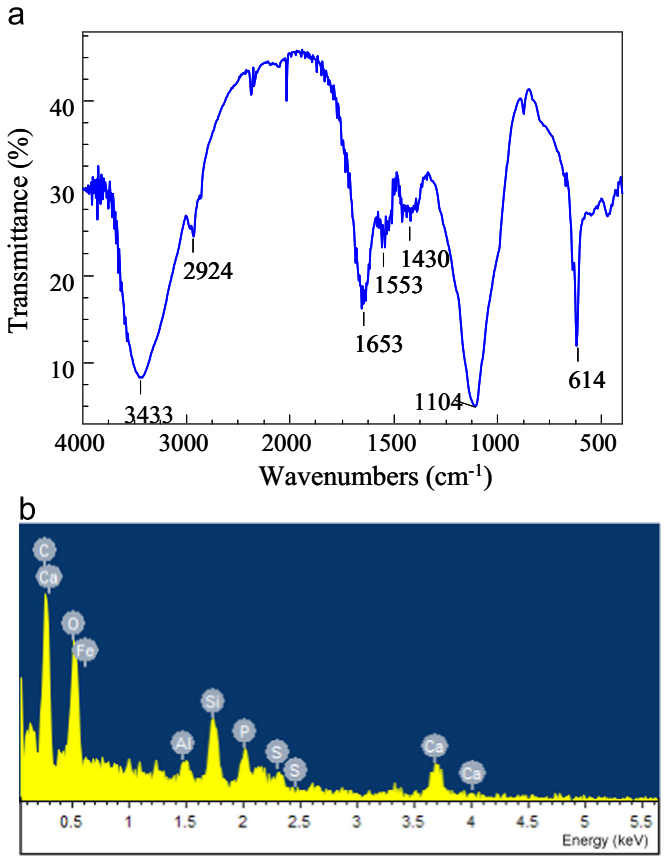

Fig. 6. Analysis of organic and inorganic components in a dynamic membrane by (a) FTIR and (b) EDX.

Further analysis by EDX showed the presence of C, O, P, S, Si, Fe, Al, and Ca (Fig. 6(b)). Although these inorganic matter constituents accounted for a small part of the cake sludge (Table 3), Al, Fe, and Ca had significant effects on the formation of the cake layer. This is because high valent cations bridged negatively charged functional groups within the EPS, which helped aggregate and stabilize the matrix of biopolymer and microbes, and further enhanced the compactness of the cake layer [1,33] Also, this cation bridging might play a major role in the rapid formation of the DM [1]. Through morphological and physicochemical analysis of the DM layer, it was demonstrated that large particle, colloids and biopolymers (such as PN and PS) and high valent cations contributed much to the formation and morphology of DM, and also the irremovable fouling of the DM.

3.5. The retention effect of the DM

Table 4 showed the concentrations of pollutants and foulants in the DMBR influent, mixed liquor and the effluent. The formed DM showed a certain retention effect, as evidenced by a concentration difference of 25 mg/L, 0.1 mg/L and 0.1 mg/L for COD, NH_3–H, and TP, respectively, between mixed liquor and the effluent. The result was in accordance with a previous study, which reported that the DM alone could remove a part of pollutants, with COD, NH_3-N and TP removal in the ranges of 7.0–15.4%, 1.4–6.7% and 3.5–9.4%, respectively [14]. The phenomenon might be due to the fact that COD were largely involved in particulates and colloids while NH_3–H and TP were mainly in dissolved form. So, the well-formed DM could enhance the treatment performance to a certain extent in DMBR [34,35], which was mainly controlled by the characteristics of DM and the existing form of pollutants, such as suspended or dissolved form. Potential membrane foulants such as proteins (PN)

Table 4
Concentrations of water quality parameters in different water samples.

Parameter	Influent	Mixed liquor	Effluent
COD (mg/L)	163.6 ± 40.9	38.9 ± 8.5	14.8 ± 2.4
NH_3–N (mg/L)	30.4 ± 5.0	0.5 ± 0.2	0.4 ± 0.2
TP (mg/L)	3.5 ± 0.5	2.1 ± 0.3	2.0 ± 0.3
PN (mg/L)	23.2 ± 3.5	8.4 ± 1.2	8.2 ± 1.0
PS (mg/L)	4.7 ± 0.5	1.9 ± 0.4	1.4 ± 0.3
PN/PS	4.9	4.4	5.9

Note: PN=proteins, PS=polysaccharides. Values are given as mean ± standard deviation, number of measurement: n=30 for turbidity, n=13 for COD, n=22 for NH_3–N and TP, n=5 for PN and PS.

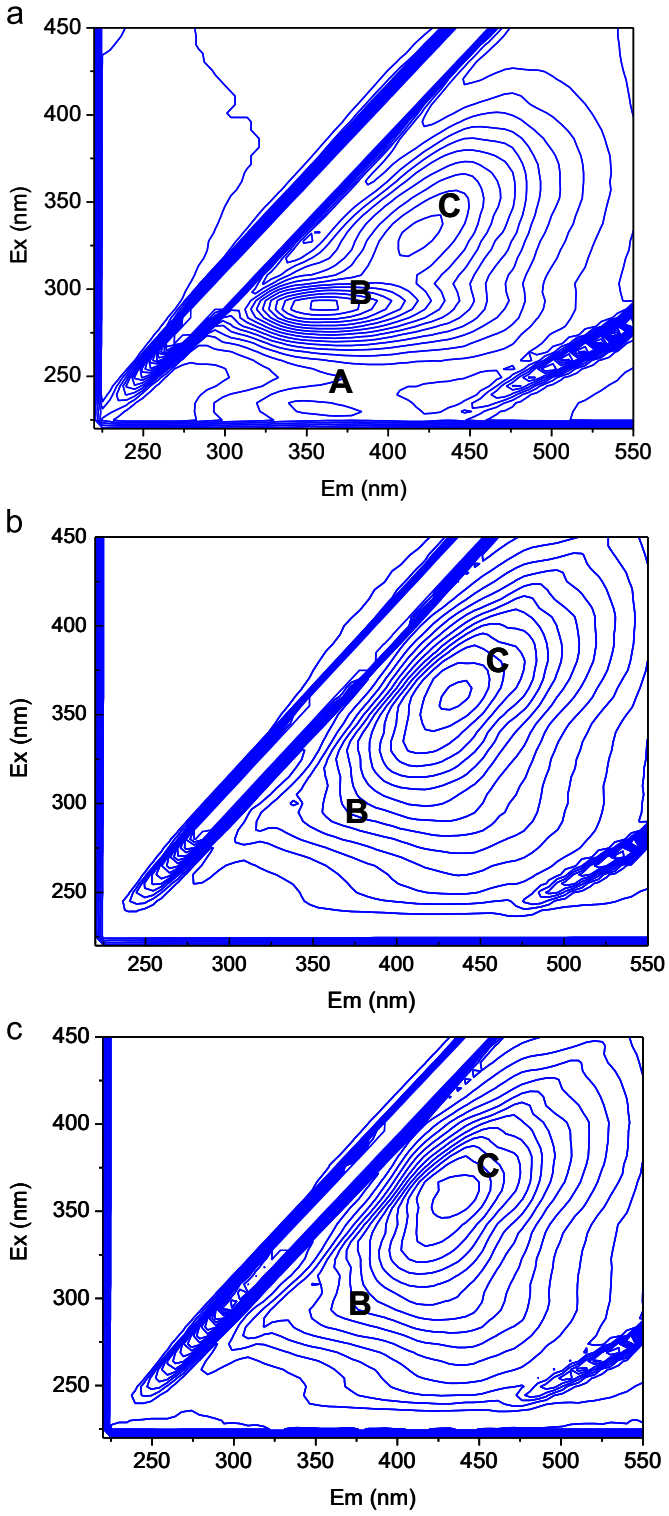

Fig. 7. EEM fluorescence spectra of (a) influent, (b) SEPS and (c) effluent.

and polysaccharides (PS), were also measured and presented in Table 4. By comparing the concentrations of PN and PS in the influent and effluent, it was found that the removals of PN and PS were 65% and 70%, respectively. Also, the mixed liquor and effluent showed a little difference in the content of PN and PS. About 0.2 mg/L and 0.5 mg/L of PN and PS were retained by the DM, accounting for 1% and 11% of the total amount. The observation was consistent with the statement of one recent study, which indicated that the content of EPS, particularly carbohydrates, controlled the fouling rate of the DM [26]. Additionally, about 34% and 19% of PN and PS permeated as effluent organics, which indicated the important effects of biopolymers (mainly SEPS) in mixed liquor on the DM fouling and effluent quality.

To reflect the fluorescent properties of the organic substances such as proteins and humic substances, 3D EEM spectroscopy was applied for characterizing the influent, effluent and EPS samples. Measurements of EEM fluorescence spectra were carried out several times, and similar results were obtained, so typical spectra were presented in Fig. 7. Two peaks (Peak B and Peak C) could be detected in the influent, SEPS and effluent samples though Peak B was not so evident in the SEPS and effluent samples. Another peak (Peak A) was only observed in the influent samples. Peak A was identified at the Ex/Em of 230–240 nm/345–355 nm, which was related to aromatic protein-like substances, while Peak B, located at the Ex/Em of 280–290 nm/340–355 nm was reported as tryptophan protein-like substances. Peak C around 325–400 nm/420–440 nm was attributed to humic acid-like substances [36]. Similar results were reported in an anaerobic DMBR that three peaks were detected in the influent while two peaks were observed in the effluent, and also the study confirmed that the fluorescent protein-like and humic acid-like substances were partly removed during the biological treatment [37].

For the influent sample, Peak B were the main components with a high fluorescence intensity (FI), while Peak A and Peak C also existed, albeit, the FI was lower. The effluent and SEPS showed similar EEM spectra but quite different from that of the influent as evident by a high FI of Peak C and low FI of Peak B. This difference could be due to the fact that SEPS did not only originate from the influent but also related to the microbial products of biomass. Moreover, fluorescent substances in the effluent were more related to those of SEPS, which were suspended in mixed liquor and could move freely in the bioreactor. By careful comparison, it was found that the FI of Peak B and Peak C in SEPS were a little higher than that of the effluent, indicating that a little amount of fluorescent organics (protein-like substances and humic acid-like substances) was rejected by the DM as foulants.

GFC has been widely applied for separating organic substances based on a differential permeation process to acquire useful information regarding MW distribution. Fig. 8 demonstrates the MW distributions of the organic matter in the influent, effluent and SEPS samples. All the samples showed broad and similar MW distributions, containing a little part of high MW substances with a retention time near 7.5 min, and a large amount of moderate to low MW substances with a retention time between 10 min and 20 min. By comparison, it was found that the DM showed certain retention of large and low MW substances as evidenced by the

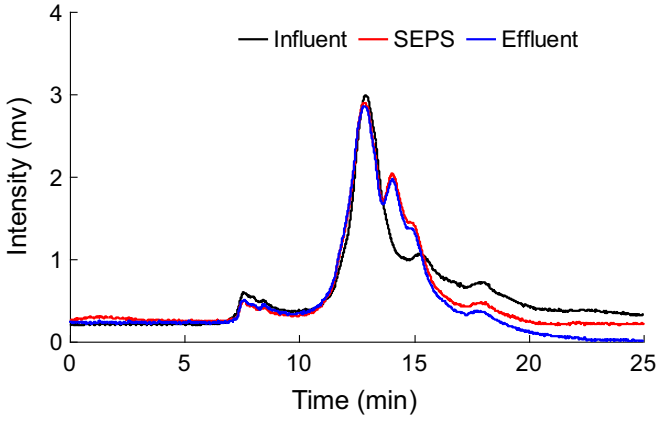

Fig. 8. Molecular weight distribution of dissolved organic matter in influent, SEPS and effluent.

peak near 7.5 min and more than 15 min. A little retention effect on moderate MW substances was observed evidenced by the peak near 13 min, which might be related to the other characteristics of organics such as hydrophobicity. Also, it was detected that more moderate to low MW substances existed in the SEPS and effluent than those in influent as indicated by the peaks around 14 min, which might stem from microbial products. In one recent study the same GFC analysis was also employed to characterize the DOM from a bio-diatomite DMBR. Three major peaks in the MW order of 80 kDa, 800–2500 Da and 37 Da were observed in the raw water, however in the mixed liquor and effluent peaks of high and low molecular substances almost disappeared and peak of moderate molecular substances decreased by about 40%, and also a new peak emerged [11]. The main difference in retention effect of the studies might come from the differences in raw water quality, bioreactor operation and the effects of bio-diatomite addition (such as enhanced biodegradation and adsorption). So the addition of PAC, diatomite, kaolin and other additives [12–14], which recently caused much attention from the researchers, was highly appreciate due to their positive effects on the formation and structure of DM, also more importantly on enhancing pollutant removal and the retention effect of the DM.

The GFC chromatogram of the SEPS and effluent were almost the same except for a little difference in the peak intensity, which further confirmed that SEPS had a significant impact on the effluent properties and that the DM could retain DOM to a certain extent. Although the retention effect of DM was not as significant as that found in conventional MBR and particles enhanced DMBR [12–14,38], more attention should be paid to these biopolymers because during long-term operation the retained foulants might contribute to the blocking of DM and cause accumulation of irremovable fouling due to their gelling nature [39]. However, as verified in this study if efficient physical cleaning method (such as the combination of air backwashing and surface brushing) was adopted for DM regeneration, these membrane fouling substances could be efficiently removed and showed no obvious impact on stable operation of the DMBR due to the retention effect and easy regeneration of the DM.

4. Conclusions

The DMBR process was characterized in this study as a three-stage operational cycle including DM formation, stable operation, and physical cleaning for DM regeneration. Using the relatively smaller pore size nylon mesh as support material brought about low effluent turbidity at the start of the operation and therefore much shortened the time for DM formation. Periodical bottom aeration was also found to be suitable to keep a good condition for maintaining a stable flux and effective removal of pollutants. In addition to air backwashing, the function of surface brushing was identified as to remove the irremovable fouling so that the filtration flux could be well recovered for efficient DM regeneration. The DM layer showed its retention effect to accumulate various inorganic and organic substances from the mixed liquor in the DMBR, which resulted in a much different morphological and physical structure of the cake sludge from the activated sludge. As many of these substances belong to membrane foulants, they should be effectively removed at the final stage of the operational cycle. The understanding on the operational cycle of the DMBR can assist the rational design of the process toward its stable operation.

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References

[1] H. Chu, Y. Zhang, X. Zhou, Y. Zhao, B. Dong, H. Zhang, Dynamic membrane bioreactor for wastewater treatment: Operation, critical flux, and dynamic membrane structure, J. Membr. Sci. 450 (2014) 265–271.
[2] W. Fuchs, C. Resch, M. Kernstock, M. Mayer, P. Schoeberl, R. Braun, Influence of operational conditions on the performance of a mesh filter activated sludge process, Water Res. 39 (5) (2005) 803–810.
[3] M.E. Ersahin, H. Ozgun, J.B. van Lier, Effect of support material properties on dynamic membrane filtration performance, Sep. Sci. Technol. 48 (15) (2013) 2263–2269.
[4] C. Loderer, A. WÖrle, W. Fuchs, Influence of different mesh filter module configurations on effluent quality and long-term filtration performance, Environ. Sci. Technol. 46 (7) (2012) 3844–3850.
[5] D. Jeison, I. Días, J.B. van Lier, Anaerobic membrane bioreactors: are membranes really necessary? Electron. J. Biotechnol. 11 (4) (2008) 1–2.
[6] M. Walker, C.J. Banks, S. Heaven, Development of a coarse membrane bioreactor for two-stage anaerobic digestion of biodegradable municipal solid waste, Water Sci. Technol. 59 (4) (2009) 729–735.
[7] M.E. Ersahin, H. Ozgun, Y. Tao, J.B. van Lier, Applicability of dynamic membrane technology in anaerobic membrane bioreactors, Water Res. 48 (2014) 420–429.
[8] L. Alibardi, R. Cossu, M. Saleem, A. Spagni, Development and permeability of a dynamic membrane for anaerobic wastewater treatment, Bioresour. Technol. 161 (2014) 236–244.
[9] J. Xiong, D. Fu, R.P. Singh, Self-adaptive dynamic membrane module with a high flux and stable operation for the municipal wastewater treatment, J. Membr. Sci. 471 (2014) 308–318.
[10] M.E. Ersahin, H. Ozgun, R.K. Dereli, L. Ozurk, K. Roest, J.B. Van Lier, A review on dynamic membrane filtration: materials, applications and future perspectives, Bioresour. Technol. 122 (2012) 196–206.
[11] H. Chu, D. Cao, B. Dong, Z. Qiang, Bio-diatomite dynamic membrane reactor for micro-polluted surface water treatment, Water Res. 44 (5) (2010) 1573–1579.
[12] H. Chu, B. Dong, Y. Zhang, X. Zhou, Gravity filtration performances of the bio-diatomite dynamic membrane reactor for slightly polluted surface water purification, Water Sci. Technol. 66 (5) (2012) 1139–1146.
[13] H. Chu, Y. Zhang, B. Dong, X. Zhou, D. Cao, Z. Qiang, Z. Yu, H. Wang, Pretreatment of micro-polluted surface water with a biologically enhanced PAC-diatomite dynamic membrane reactor to produce drinking water, Desalin. Water Treat. 40 (1–3) (2012) 84–91.
[14] H. Chu, Y. Zhang, X. Zhou, B. Dong, Bio-enhanced powder-activated carbon dynamic membrane reactor for municipal wastewater treatment, J. Membr. Sci. 433 (2013) 126–134.
[15] B. Fan, X. Huang, Characteristics of a self-forming dynamic membrane coupled with a bioreactor for municipal wastewater treatment, Environ. Sci. Technol. 36 (2002) 5245–5251.
[16] M. Ye, H. Zhang, Q. Wei, H. Lei, F. Yang, X. Zhang, Study on the suitable thickness of a PAC-precoated dynamic membrane coupled with a bioreactor for municipal wastewater treatment, Desalination 194 (2006) 108–120.
[17] Y. Kiso, Y.J. Jung, K.S. Min, W. Wang, M. Simase, T. Yamada, K.S. Min, Coupling of sequencing batch reactor and mesh filtration: operational parameters and wastewater treatment performance, Water Res. 39 (2005) 4887–4898.
[18] Z. Yu, H. Chu, D. Cao, Y. Ma, B. Dong, Y. Wei, Pilot-scale hybrid bio-diatomite/dynamic membrane reactor for slightly polluted raw water purification, Desalination 285 (2012) 73–82.
[19] H. Chu, D. Cao, W. Jin, B. Dong, Characteristics of bio-diatomite dynamic membrane process for municipal wastewater treatment, J. Membr. Sci. 325 (2008) 271–276.
[20] W.J. Gao, H.J. Lin, K.T. Leung, H. Schraft, B.Q. Liao, Structure of cake layer in a submerged anaerobic membrane bioreactor, J. Membr. Sci. 374 (2011) 110–120.
[21] Y. Hu, X.C. Wang, Y. Zhang, Y. Li, H. Chen, P. Jin, Characteristics of an A^2O-MBR system for reclaimed water production under constant flux at low TMP, J. Membr. Sci. 431 (2013) 156–162.
[22] E.F. Hartree, Determination of protein: a modification of the Lowry method that gives linear photometric response, Anal. Biochem. 48 (2) (1972) 422–427.
[23] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem. 28 (1956) 350–356.
[24] Chinese NEPA, Water and Wastewater Monitoring Methods, 4th ed., Chinese Environmental Science Publishing House, Beijing, China, 2002.
[25] F.G. Meng, H.M. Zhang, F.L. Yang, L.F. Liu, Characterization of cake layer in

submerged membrane bioreactor, Environ. Sci. Technol. 41 (2007) 4065–4070.
[26] S. Liang, L. Qu, F. Meng, X. Han, J. Zhang, Effect of sludge properties on the filtration characteristics of self-forming dynamic membranes (SFDMs) in aerobic bioreactors: Formation time, filtration resistance, and fouling propensity, J. Membr. Sci. 436 (2013) 186–194.
[27] L. Chu, S. Li, Filtration capability and operational characteristics of dynamic membrane bioreactor for municipal wastewater treatment, Sep. Purif. Technol. 51 (2006) 173–179.
[28] Y. Wu, X. Huang, W. Zuo, Effect of mesh pore size on performance of a self-forming dynamic membrane coupled bioreactor for domestic wastewater treatment, in: Proceedings of the Fifth International Membrane Science & Technology Conference, Sydney, Australia, November 10–14 2003.
[29] T. Miyoshi, T. Tsuyuhara, R. Ogyu, K. Kimura, Y. Watanabe, Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, Water Res. 43 (2009) 5109–5118.
[30] X. Ren, H.K. Shon, N. Jang, Y.G. Lee, M. Bae, J. Lee, K. Cho, I.S. Kim, Novel membrane bioreactor (MBR) coupled with a non-woven fabric filter for household wastewater treatment, Water Res. 44 (2010) 751–760.
[31] M. Kumar, S.S. Adham, W.R. Pearce, Investigation of seawater reverse osmosis fouling and its relationship to pretreatment type, Environ. Sci. Technol. 40 (2006) 2037–2044.
[32] A.R. Badireddy, B.R. Korpol, S. Chellam, P.L. Gassman, M.H. Engelhard, A.S. Lea, K.M. Rosso, Spectroscopic characterization of extracellular polymeric substances from *Escherichia coli and Serratia marcescens*: suppression using subinhibitory concentrations of bismuth thiols, Biomacromolecules 9 (2008) 3079–3089.
[33] M.J. Higgins, J.T. Novak, Characterization of exocellular protein and its role in bioflocculation, J. Environ. Eng.: ASCE 123 (1997) 479–485.
[34] Y. Wu, X. Huang, X. Wen, F. Chen, Function of dynamic membrane in self-forming dynamic membrane coupled bioreactor, Water Sci. Technol. 51 (6–7) (2005) 107–114.
[35] F. Li, J. Chen, C. Deng, The kinetics of cross flow dynamic membrane bioreactor, Water SA 32 (2) (2006) 199–203.
[36] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter, Environ. Sci. Technol. 37 (2003) 5701–5710.
[37] Y. An, Z. Wang, Z. Wu, D. Yang, Q. Zhou, Characterization of membrane foulants in an anaerobic non-woven fabric membrane bioreactor for municipal wastewater treatment, Chem. Eng. J. 155 (3) (2009) 709–715.
[38] S. Rosenberger, C. Laabs, B. Lesjean, R. Gnirss, G. Amy, M. Jekel, J.-C. Schrotter, Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment, Water Res. 40 (2006) 710–720.
[39] D. Okamura, Y. Mori, T. Hashimoto, K. Hori, Identification of biofoulant of membrane bioreactors in soluble microbial products, Water Res. 43 (2009) 4356–4362.