Characterization of a hybrid powdered activated carbon-dynamic membrane bioreactor (PAC-DMBR) process with high flux by gravity flow: operational performance and sludge properties

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Abstract: Three PAC-DMBRs were developed for wastewater treatment under different PAC dosages with biomass concentrations averaged at 2.5, 3.5 and 5.0 g/L. The DMBRs could be continuously operated at 40-100 L/m^{2}h, while higher fluxes were obtained within the PAC-DMBRs with hydraulic retention times varying in 4-10 h. A dose of 1 g/L PAC brought about obvious improvement in the sludge particle size distribution, settling, flocculating and dewatering properties due to the formation of biological PAC, and the sludge properties were further improved at a higher PAC dose (3 g/L). The addition of PAC notably shortened the DM formation time after air backwashing and enhanced pollutant removal. Moreover, under a long solid retention time (approximately 150 d), the concentrations of both soluble and bound extracellular polymeric substances (EPS) decreased substantially because of the adsorption and biodegradation effects of the biological PAC. No obvious impact on biomass activity was observed with PAC addition.

Keywords: PAC-DMBR hybrid process; powdered activated carbon; wastewater treatment; sludge property; filtration resistance

1. Introduction

The widespread application of membrane bioreactor (MBR) in wastewater treatment and reuse has been hampered by several issues, such as the high investment cost caused by membrane installation and significant operating and maintenance costs of membrane fouling control. As a result, many efforts were made to operate the MBRs with cost-effective membrane material, reduced energy demand and effective membrane cleaning protocols (Guo et al., 2012; Ersahin et al., 2012). Under these conditions, an emerging membrane-based water treatment process, named a dynamic membrane bioreactor (DMBR), garnered significant research attention and was considered as a potential substitute to conventional MBRs (Kiso et al., 2000; Fan and Huang, 2002; Chu et al., 2010; Hu et al., 2016).

When filtering the solutions containing suspended particles, such as the activated sludge, the dynamic membrane can be formed on the underlining large pore size support material (such as non-wave cloth, nylon and stainless steel mesh) instead of the MF/UF membrane used in the MBRs. This dynamic membrane is an effective in-situ sludge cake layer with a good solid/liquid separation effect rather than support material; moreover, the filtration process can mainly be achieved by gravity flow with water heads in the range of 0.1-2.0 m, flux of more than 20 L/m^2h, mesh pore size of 30-100 μm, biomass concentration of 3-30 g/L, solid retention time (SRT) from several days to infinite, and hydraulic retention time (HRT) of several hours (Ersahin et al., 2012). Meanwhile, the dynamic membrane can more conveniently be cleaned because commonly adopted physical cleaning methods (such as air backwash) are sufficient for recovery of DM filterability (Chu et al., 2010; Alibardi et al., 2014).

The research and application of the DMBR covered the following aspects: (1) process performance (Kiso et al., 2000; Fan and Huang, 2002), (2) the development and optimization of a hybrid system (Fuchs et al., 2005; Chu et al., 2010; Loderer et al., 2012), (3) feasibility for treating different types of waters and wastes at a large scale (Yu et al., 2012; Xiong et al., 2014; Liu et al., 2016), (4) the formation process

and mechanism of the DM and its affecting factors (Liu et al., 2009; Liang et al., 2013), and (5) characterization of the DM layer (An et al., 2009; Chu et al., 2014). The research results improved the understanding and optimization of the DMBR process, and, more importantly, noted the key role of the well-formed DM layer in determining the stable operation of the DMBR (Ersahin, et al., 2012; Liang et al., 2013).

As reported, the formation process of the dynamic membrane can be divided into several stages (including DM layer formation, stable filtration and cleaning for DM regeneration) (Liu et al., 2009). During the first stage, the effluent quality was generally poor and the effluent can contain a high SS concentration due to the passage of sludge flocs through the coarse mesh pores, which could last for several minutes to hours (Xiong et al., 2014). However, after the formation of the DM, excellent filtration performance that is comparable to MF/UF can be obtained during the stable operation period (Ersahin et al., 2012) until the physical cleaning stage is reached due to the continuous accumulation of potential foulants on the formed DM layer. Therefore, the approach for optimally lowering the DM formation time (the unstable period) and prolonging the stable operation stage is crucial to the practical operation of the DMBR process (Hu et al., 2016).

Recently, several additives (such as PAC and diatomite) were tentatively added into the DMBR to develop the emerging hybrid DMBR system (Chu et al., 2010; Jamal Khan et al., 2012; Chu et al., 2014), which was verified to possess the potential to enhance the quick formation of the DM, modify the DM structure and simultaneously improve the effluent quality as noted in PAC-MBR studies (Satyawali and Balakrishnan, 2009b; Hu et al., 2014). The underlying reason for the associated benefits in the PAC-MBR system was attributed to the formation of biological PAC with synergistic effects of simultaneous adsorption, biodegradation and bio-regeneration (Satyawali and Balakrishnan, 2009b; Jamal Khan, 2012). However, because little work has been performed in the hybrid PAC-DMBR compared to in PAC-MBR, some issues still need to be clarified, such as the changes in activated sludge and DM layer properties, process performance enhancement after PAC addition, and the behaviors and effects of potential fouling-causing substances.

Thus, the objective of this study was to investigate the influence of PAC addition on the hybrid PAC-DMBR process performance, sludge properties and behaviors of EPS under the high flux continuous operation mode by gravity flow. Various analytical methods were adopted, including sludge particle size distribution (PSD) analysis, the extraction and measurement of extracellular polymeric substance (EPS), excitation-emission microscopy (EEM) spectroscopy analysis, gel permeate chromatography (GPC) analysis, and specific oxygen utilization rate (SOUR) measurement. This work would assist with understanding the emerging hybrid PAC-DMBR process and advance its potential practical applications.

2. Materials and methods

2.1. Experimental PAC-DMBR setups and operation

Three identical PAC-DMBRs (Fig. S1 in Supplementary material), each with an effective volume of 15 L, were located at a local wastewater treatment plant (WWTP) in Xi'an, China. During the startup period, PAC at different dosages (0, 1, and 3 g/L) was added into the PAC-DMBRs, which were named PAC-DMBR1, PAC-DMBR2 and PAC-DMBR3, respectively. The commercial PAC, which has a mean particle size distribution of 30 μm, was used as additive. In each bioreactor, one flat-sheet DM module was vertically immersed with a double-sided effective filtration area of 0.04 m^2. The configuration of the DM module can be observed in Fig. S2 in Supplementary material. The DM module consisted of PVC plates and two layers of support material. The inner layer was stainless steel mesh (10 mm pore size), and the outer layer was nylon mesh (75 μm pore size). Air diffusers were installed at the bottom of the four corners in the reactors. Air pumps were used to continuously supply oxygen for biomass demand as well as to induce circulation flow in the reactor. The dissolved oxygen (DO) concentrations in the PAC-DMBRs were in the range of 2.0-6.0 mg/L.

The inoculation sludge was obtained from the local WWTP. After two weeks of acclimation, the sludge was placed into the DMBRs. Meanwhile, the PAC, after

cleaning with deionized water, was dosed into the PAC-DMBR2 and PAC-DMBR3. Then, the DMBRs were operated in parallel. After a short startup period (first 4 operational cycles), all PAC-DMBRs entered the stable operation period (subsequent 4 operational cycles) and the total experimental time was approximately one month from April to May 2016. No sludge was discharged, expect a little amount of sludge (approximately 100 ml daily) was regularly sampled for sludge property measurements. As a result, the SRT was as long as approximately 150 d. The MLSS concentrations for three systems after PAC addition were averaged at 2500, 3500 and 5000 mg/L.

Real domestic wastewater (main parameters shown in Section 3.1.2) was fed into the PAC-DMBRs by submersible pumps with a water temperature of 20-25℃ and pH of 7.2-8.0. The effluent was continuously withdrawn by a 10 cm water level difference between the bioreactor and effluent port. The flux decreased gradually with time in the constant pressure operation mode. When the flux dropped to 10% of the initial flux, a physical cleaning method (air backwashing with a flow rate of 72 L/min for 2 min) was applied for permeability recovery (Hu et al., 2016). The initial fluxes in PAC-DMBRs were near 500 L/m^2h, and the immediate membrane fluxes after the DM formation were approximately 180-250 L/m^2h, while the end fluxes for air backwashing were approximately 50 L/m^2h. As a result, the minimum HRT at the starting point was less than 1 h, while, after the DM formation, the HRT varied in the range of 1.5-7.5 h.

2.2. Analytical methods

2.2.1 EPS extraction and analysis

EPS (soluble EPS and bound EPS) was extracted from the sludge samples in the PAC-DMBRs according to the previously used thermal treatment method (Hu et al., 2013). The analysis of the extracted EPS samples was performed for proteins using the modified Lowry method with bovine serum albumin (BSA) as the standard (Hartree, 1972) and for polysaccharides using the phenol-sulfuric acid method with glucose as the standard (Dubois et al., 1956).

2.2.2 Particle size distribution (PSD) analysis

The PSD of PAC and sludge samples in the PAC-DMBRs was analyzed using a laser granularity distribution analyzer (LS 230/SVM+, Beckman Coulter Corporation, USA) with a detection range of 0.4-2000 μm. Each sample was measured three times with a standard deviation below 5% and typical profiles were plotted and reported.

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

The 3D-EEM fluorescence spectra of the dissolved organic matter were measured using an FP-6500 spectroflurometer (Jasco Corporation, Japan). The excitation wavelengths increased from 220 to 450 nm at 5 nm steps, while for each excitation wavelength, the emission was detected from 220 to 550 nm in 5 nm steps. The scan speed was set at 2000 nm/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 were presented.

2.2.4 Gel filtration chromatography (GFC) analysis

The molecular weight distribution (MWD) of dissolved organics in water samples was determined according to the reference (Hu et al., 2016). A GFC analyzer (LC-2010A, Shimadzu Corporation, Japan) installed with a Zenix SEC-100 type gel column (Sepax Technologies Corporation, USA), and a UV detector (SPD-10, Shimadzu Corporation, Japan) was utilized. Sodium phosphate buffer (150 mM, including Na_2HPO_4 and NaH_2PO_4) was employed as the eluent at a flow rate of 1.0 mL/min. The dissolved organic matter in samples was obtained by filtering through a 0.22 μm filter, and the injection volume was 50 μL for effluent and SEPS and much lower (5 μL) for BEPS.

2.2.5. Specific oxygen utilization rate measurement

The specific oxygen utilization rates (SOUR) of heterotrophic bacteria, ammonium oxidizers and nitrite oxidizers in the sludge samples, namely, $(SOUR)_H$, $(SOUR)_{NH3}$ and $(SOUR)_{NO2}$, were determined to indicate the microbial activities according the reported method (Liu et al., 2004).

2.2.6 Other analysis

Chemical oxygen demand (COD), UV_{254}, ammonia (NH_3-N), total phosphorus (TP), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in the bioreactor were measured according to the Standard Methods (Chinese NEPA, 2002). Turbidity was measured with a turbidity meter (ET266020, Lovibond Corporation, Germany), color with a colorimeter (SD9011B, China), 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. The capillary suction time (CST) was with a CST meter (DPDFC-10A, China).

The supernatant COD of the activated sludge was characterized by evaluating soluble COD (CODs) and colloidal COD (CODc) according to the reported method (Meng et al., 2007). Microscopy observation of the sludge samples was captured by a digital camera (N90i, Nikon Corporation, Japan) that was attached to a microscope. The photography of the membrane modules was taken using an SLR camera (EPM2, Olympus Corporation, Japan).

3. Results and discussion

3.1 Operational performance

3.1.1. Filtration performance of the PAC-DMBRs

As mentioned before, because the PAC-DMBRs were operated under a constant pressure mode by gravity flow with a low water head averaged at 10 cm, the gradual decline of membrane flux could be expected. Fig. 1 (a) and (b) showed the variation profiles of flux and effluent turbidity during eight consecutive operational cycles in the PAC-DMBRs. During the first four cycles (the startup period), the initial flux was as high as 500 L/m^2h, but it quickly declined to 30-40 L/m^2h during 24 h, which was the predetermined termination flux and approximately 10% of the initial flux. The

three systems showed a similar evolution trend for flux, although slightly higher flux was achieved in PAC-DMBR1. Additionally, it was commonly recognized that effluent turbidity falling below 1 NTU or effluent SS equal to zero could be regarded as an indicator for the formation of the DM layer. While it was noted that at the initial stage, although the effluent turbidity decreased rapidly to 1-2 NTU, a long time (several hours) was needed for a further drop to below 1 NTU, indicating a long time for the DM formation in all PAC-DMBRs. During the startup period, the inoculation sludge from MBR process was not acclimatized to the DMBR process, and there were many fine particles in the inoculation sludge as the mean particle size of the inoculation sludge (<30 μm) was lower that the pore size of the nylon mesh (approximately 75 μm). The high levels of fine sludge flocs, small PAC particles, and colloids in the reactors would pass through the DM layer to affect effluent turbidity, reduce the porosity of the DM layer and cause potential fouling problems. Using large pore size meshes (75-150 μm), a similar DM formation time in the range of several hours to days was reported (Fan and Huang et al., 2002; Xiong et al., 2014; Ersahin et al., 2014). During the startup period, the harsh hydraulic selection effect caused the loss of small size particles, especially the short time after air backwashing with a high permeate flux (approximately 500 L/m^{2}h). As a result, it was expected that only large particles could be retained in the bioreactor and the mean particle size of activated sludge would substantially increase afterwards to improve the DM layer permeability.

As expected, during the subsequent four operational cycles (the stable operation period), the variations in the flux and turbidity were different from the startup period. The fluxes showed a slow declining tendency to the end of the cycle (40-50 L/m^{2}h), and a longer stable operation time was achieved with the operational flux between 40-100 L/m^{2}h, which was much higher than those applied in the conventional MBRs. Moreover, the operational cycles were prolonged to the range of 70-100 h, indicating that long-term stable operation of the DMBRs could be possible. Moreover, the stable operational fluxes were in the following order: PAC-DMBR3> PAC-DMBR2> PAC-DMBR1. In detail, the stable fluxes in PAC-DMBR3 were 5 and 15 L/m^{2}h higher than those in PAC-DMBR2 and PAC-DMBR1, respectively. At this stage, the

effluent turbidity dropped quickly below 1 NTU within 5-20 min, indicating a quick formation of the DM layer in DMBRs. Additionally, it was noted that the DM layer formation time in PAC-DMBR2 and PAC-DMBR3 was generally shorter than that in PAC-DMBR1; moreover, the effluent turbidity in PAC-DMBR3 could decrease to near 0.1 NTU lower than the minimum values detected in the other two DMBRs. The results indicated that PAC addition, under the current low dosage (such as 3 g/L), could shorten the unstable period after air backwashing as well as enhance the quick formation and permeability of the DM layer. This finding was in accordance with the previous PAC-MBR and PAC-DMBR studies (Satyawali and Balakrishnan 2009a; Remy et al., 2009).

From Fig. 1. (c) and Table 1, the filtration resistance distributions in three systems were further demonstrated. It was supposed that there was no irremovable fouling (such as pore blocking) after physical cleaning because the flux could be almost completely recovered, as shown in Fig. 1 (a), which is quite different from the MBRs. As a result, the total filtration resistance (R_t) was the sum of the supporting mesh resistance (R_m) and the DM layer resistance (R_c). During the startup period (the first four cycles), R_c and R_t in PAC-DMBR1 were obviously lower than those in the other two systems, which was considered to be caused by the addition of PAC into the bioreactor as the mean particle size of PAC (Fig. S3 in Supplementary material) was much lower than the pore size of the nylon mesh. Specific PAC levles that were not effectively combined with sludge flocs would behave as foulants, blocking the pores of the formed DM layer. However, after the formation of biological PAC, the structure and permeability of the DM layer could be modified and less dissociated PAC was observed. As a result, the R_c and R_t in PAC-DMBR2 and PAC-DMBR3, respectively, were lower than those in PAC-DMBR1 at the stable operation stage (subsequent four cycles), resulting in more favorable filtration performance, as in the results obtained in other PAC-MBR systems (Jamal Khan et al., 2012; Hu et al., 2014). The potential mechanism might include the modification of sludge properties (such as increase in PSD and others properties) and enhancement of the formation of a more porous and less compressible cake layer, as demonstrated by other researchers (Remy

et al., 2009; Remy et al., 2010; Skouteris et al., 2015) and in Fig. S2 in Supplementary material, which shows the obviously different DM layer structures in three PAC-DMBR systems.

Fig. 1

Table 1

3.1.2 Pollutant removal by the PAC-DMBRs

During the stable operation period, the treatment performance of common pollutants (including COD, UV_{254}, NH_3-N, TP and color) by the PAC-DMBRs was measured and is shown in Table 2. It was noted that high removal of all pollutants, except for TP were obtained, and the averaged COD, NH_3-N and color values in the effluent were below 25 mg/L, 1 mg/L and 20 c.u., respectively, in all systems. In these aerobic bioreactors, TP removal was low with removal efficiency that was lower than 30% because the anoxic or anaerobic environment hardly existed for the survival of polyphosphate accumulation organisms. The results were in accordance with those achieved in a hybrid diatomite-DMBR process in which biological degradation was observed as the main mechanism for pollutant removal, while the retention effect of the DM was quite limited (Chu et al, 2010).

Comparing the different PAC-DMBR systems, it was found that with increasing PAC dosage, the removals of COD, UV_{254}, NH_3-N and color were obviously enhanced, except for TP. It was attributed to the following reasons: the adsorption and flocculation effects of the PAC to remove various pollutants and PAC adopted as the biological carrier benefiting for the enrichment and growth of heterotrophic bacteria, nitrifying bacteria and other microorganisms (Hu et al., 2014; Jamal Khan et al., 2012).

Table 2

3.2 Sludge properties analysis

3.2.1 Morphological analysis

To investigate the effects of the PAC dosage on sludge properties, the morphology of the sludge samples (including microscopy observation and PSD measurement) during the stable operation period was firstly analyzed. From Fig. S4 in Supplementary material, it was noted that activated sludge in PAC-DMBR1 was porous and loosely distributed. While in PAC-DMBR2 and PAC-DMBR3, PAC particles were well-combined within the flocs and were severed as the skeleton for the compact sludge flocs formation, although little uncombined PAC in PAC-DMBR3 was found to be located out of the sludge floc. This observation verified that the biological PAC was present due to the interactions between PAC and sludge flocs; also, the strength of the activated sludge could be improved by PAC addition.

Fig. 2 compared the PSD of inoculation sludge and sludge samples from the bioreactors. The mean PSD values of activated sludge from three PAC-DMBRs were 50.7, 59.4 and 52.8 μm, respectively, which were much higher than the mean PSD of inoculation sludge (26.1 μm). Compared to the PAC-DMBR2, the slightly lower mean PSD of activated sludge in PAC-DMBR3 might be caused by the existence of a certain amount of uncombined PAC particles as their mean PSD (29.4 μm) was not as high as that of the biological PAC. The phenomena were also observed by previous researchers. Using PAC with a volume mean diameter of 24.5 μm, Ng et al. (2006) observed that the sludge particle size increased at a PAC concentration of 1 g/L, but it decreased at higher concentrations of 3 and 5 g/L. The reason could be related to the following factors, such as the relative size of PAC and sludge particles, PAC dosage, and operational parameters (aeration intensity) (Satyawali and Balakrishnan, 2009a). The difference in sludge morphology/structure was observed through the above analysis, which was expected to affect the structure and permeability of the formed DM layer as discussed in Section 3.1.1.

Fig. 2

3.2.2 Flocculating, settling and dewatering abilities

Table 3 illustrates the comparison of various sludge properties in the PAC-DMBRs. With the increase in the PAC dosage, the MLSS increases from 2.5-3.5 g/L in

PAC-DMBR1 to 4.5-5.5 g/L in PAC-DMBR3; however, the settling velocity (SV_{30}) did not rise significantly, resulting in a decrease tendency for sludge volume index (SVI). It was indicated that adding PAC could improve the settling properties of the activated sludge as the biological PAC showed a more compact structure with an incompressible nature and higher density comparing to the activated sludge alone (Hu et al., 2014). Moreover, due to the adsorption and flocculating effect of the PAC particles, the supernatant turbidity, CODc and CODs all declined with increasing PAC dosage, allowing for better sludge flocculating properties to be detected in PAC-DMBR2 and PAC-DMBR3. The results were similar to those obtained in a PAC-MBR, showing the higher adsorption capacity of the fine colloids and solutes in the bulk mixture by PAC addition (Ng et al, 2006). Lastly, CST was analyzed to reflect the dewatering ability of activated sludge, while it was noted that lower values were detected in PAC-DMBR2 and PAC-DMBR3. Iversen et al. (2009) attributed the CST improvement in a MBR to the removal of large amounts of dissolved organic carbon and the change in the flocs due to the incorporation of PAC particles.

The results showed that PAC addition could enhance the flocculating, settling and dewatering properties of the activated sludge. Furthermore, it was previously claimed that adding PAC could enhance the adsorption and degradation of some slow biodegradable/the bio-refractory substances and protect the microorganisms from a toxic environment, simultaneous adsorption and biodegradation rather than a single biological process reflected the advantage of PAC combined systems (Ng et al., 2013). So it was noted the potential application of PAC-DMBR process could be extended to treat wastewater or waste containing recalcitrant substances as explored in PAC-MBR system, which has been applied for the removal of a large number of pollutants including persistent xenobiotics and trace organic contaminants (TrOCs), residual organic matter (ROM) and other refractory organics (Skouteris et al., 2015).

Table 3

3.2.3 Microbial activity analysis

In the aerobic bioreactor, specific oxygen utilization rate (SOUR) measurement was the commonly used method to determine the activities of aerobic microorganisms (including heterotrophic bacteria, ammonium oxidizers and nitrite oxidizers), using $(SOUR)_H$, $(SOUR)_{NO2}$ and $(SOUR)_{NH3}$ to indicate their respective activities.

From Fig. 3, it was noted that microbial activities in three PAC-DMBRs showed no obvious difference, with the $(SOUR)_H$, $(SOUR)_{NO2}$ and $(SOUR)_{NH3}$ of 8-10 (mg/g.h), 2-3 (mg/g.h) and 3-4 (mg/g.h), respectively, indicating that at the present dosage (less than 3 g/L) PAC demonstrated no inhibition effect on microorganisms. Similarly, Jamal Khan and Visvanathan (2008) showed that in a MBR process treating synthetic municipal wastewater, the total SOUR of activated sludge was in the range of 15-25 (mg/g.h). However, when operating a PAC-MBR process to treat high strength distillery wastewater, lower values of the total SOUR, ranging from 4 (mg/g.h) to 12 (mg/g.h), was reported. It was attributed to the presence of toxicity imparting components; however, during the stable operation periods the PAC-MBR system always showed higher SOUR values compared to the non-PAC MBR system (Satyawali and Balakrishnan, 2009a). The results from this work showed that low dosage of PAC would not affect the microbial activities of aerobic microorganisms.

Fig. 3

3.3 EPS properties analysis

3.3.1 EPS concentration

EPS are the pool of complex organic compounds (such as polysaccharides, proteins and humics) produced from substrate metabolism and biomass decay, causing the aggregation of cells into flocs and granules. EPS can be in bound and soluble form (Ni et al., 2011). EPS could cause fouling issues in the MBRs (Guo et al., 2012), while in DMBRs it would result in the blocking of DM layer and physical irremovable fouling (Chu et al., 2014; Hu et al., 2016). Due to its dual effects on both sludge properties and DM filterability, EPS properties in PAC-DMBRs were further investigated.

Fig. 4 present the concentrations of two types of EPS (SEPS and BEPS) and their main components (polysaccharides and proteins) in the PAC-DMBRs during the stable operation period. As shown in Fig. 4(a), all polysaccharides, proteins and SEPS obviously decreased with increasing PAC dosage. From Fig. 4(b), it was further observed that BEPS in PAC-DMBR1 and PAC-DMBR2 were almost the same, but they were a little higher than those in PAC-DMBR3 (especially for proteins).

It was considered that, first, the PAC with a large specific area would adsorb SEPS from the sludge supernatant; then, part would settle down at the bottom of the bioreactor due to the increase in PAC density while the others would combine with sludge particles to from large size flocs (Skouteris et al., 2015), which could be the main reasons for the SEPS concentration reduction after PAC addition.

Further, it was supposed that the adsorbed organics would be tightly combined within the biological PAC and not be easily detached and released into the bioreactor again. These adsorbed organics could be utilized as the substrate for biodegradation and enhance the growth of attached biomass (Ng et al., 2013; Hu et al., 2014). On the other hand, the adsorbed organics would be hardly extracted by the common EPS extraction method due to the close interaction between the organics and PAC. Furthermore, as noted by other researchers, itias inevitable that the adsorption capacity of PAC will decrease with operation time. Thus frequent discharge of a certain amount of saturated PAC and low-dose PAC replenishment could secure a desirable system performance (Nguyen et al., 2012; Nguyen et al., 2013; Skouteris et al., 2015). However, in this work, no subsequent addition of PAC was performed after initial PAC dosing, but constant lower EPS concentrations were detected in PAC-DMBR2 and PAC-DMBR3 compared to PAC-DMBR1, so it was claimed that the biodegradation effects of the added PAC was more predominant rather that the saturation of the PAC.

The potential effects of EPS on the DM filterability in DMBRs were reported by recent researchers (Liang et al., 2013; Chu et al., 2014; Hu et al., 2016). The authors noted that the BEPS and polysaccharide content in BEPS had a significant impact on the fouling propensity of the DM and filtration resistance, while SEPS was mainly

responsible for the reduction of DM porosity and physical irremovable fouling during long term operation. The different fouling behaviors between SEPS and BEPS were possibly due to their differences in concentration, component, an existing form in sludge and other properties (such as molecular weight). As the PAC could adsorb organics (such as SEPS) from sludge supernatant, so less soluble or colloidal organics existed in activated sludge with PAC addition would improve the filterability as verified in this study. On the other hand, the same level of BEPS and polysaccharides concentrations in three DMBRs indicated that no harmful effect was detected with PAC addition regarding the influence of BEPS on filterability. Additionally, the adsorbed organic (EPS) together with PAC would serve as the skeleton for large sludge particle formation and strengthen the floc structure, which would eventually increase the incompressibility and porosity of the DM layer and thus enhancing the membrane flux (Kim et al., 1998). Above analysis indicated the effects of PAC addition on the EPS properties, and their potential relationships with the DM filtration performances.

Fig. 4

3.3.2 MWD by the GPC analysis

The molecular weight distribution (MWD) of dissolved organics (samples of the effluent, SEPS and BEPS) from the PAC-DMBRs was analyzed using the GPC measurement and shown in Fig. S5 of Supplementary material. Obviously, the effluent and SEPS samples showed a quite similar MWD profiles with a relatively narrow distribution with the elution time from 10 min to 20 min (covering the high, intermediate and low MW organics), which were different from those of BEPS presenting a widespread MWD containing all four categories of different MW organics.

Comparing the samples in different PAC-DMBRs, it was found that variations of the peak intensities of various MW organics in the effluent SEPS and BEPS samples followed the subsequent order: PAC-DMBR1> PAC-DMBR2> PAC-DMBR3, which was closely related to their EPS concentrations as discussed in Section 3.3.1. Taking

the SEPS samples for example, the WMD analysis gave the clear evidence that adding PAC-reduced concentrations of SEPS within a broad MW, while higher dosage seemed to be more effective. In a PAC-DMBR system, it was reported that at 0.2 g/LPAC, only compounds below 6000 Da were somewhat adsorbed. At higher doses, adsorption was significant and occurred in the entire molecular weight range. It was considered that the extent of adsorption and adsorbed components strongly depended on both the PAC concentration and competition between high and low molecular weight components (Satyawali and Balakrishnan, 2009b). As expected, SEPS in PAC-DMBR3 showed a much lower intensity of a WMD profile compared to other two systems due to the higher PAC dosage.

Commonly in MBRs, it was recognized that SEPS played an important role in determining the effluent water quality (such as organic concentrations and MWD) (Ni et al., 2011). It was also found in this study that the MWD profiles of effluent and SEPS samples were almost the same, except for a small difference in peak intensity, which probably resulted from the biodegradation and retention effects of the DM layer (Hu et al., 2016). From the BEPS MWD profile it was noted that various MW organics existed (especially for macro and low MW organics); the difference in WMD profiles between SEPS and BEPS was closely related to their different original source as previously reported (Wang et al., 2010; Ni et al, 2011).

3.3.3 Fluorescent property by EEM analysis

EEM spectroscopy was used to further analyze the fluorescent properties of dissolved organics in the effluent and EPS. As shown in Fig. 5 and Table 4, four fluorescence peaks, namely peak A (230 nm/310–350 nm), peak B (275–290 nm/335–370 nm), peak C (310–350 nm/405–440 nm) and peak D (250 nm/410–415 nm), respectively, were observed. Peak A represented aromatic protein-like substances, peak B reflected tryptophan protein-like substances while peaks C and D showed the existences of humic acid-like and fulvic acid-like substances, respectively (Chen et al., 2003).

The results indicated that dissolved organics in effluent and SEPS samples showed similar fluorescent properties in terms of the spectra shape (peaks B, C and and D) and fluorescent intensity (FI), which was different from those of BEPS samples, which contained peaks A, B and C. For the FI of effluent samples in different PAC-DMBRs, there was a notable difference, as the FI of peaks B, C and D all decreased from PAC-DMBR1 to PAC-DMBR3. The same trends were also noted for SEPS and BEPS in different bioreactors.

The four fluorescent peaks represent two types of organics, namely proteins and humics, which were different in hydrophobicity, MWD and biodegradability (Wang et al., 2010). Furthermore, as discussed in Section 3.3.2, the organic in EPS samples had a broad MW distribution, but it also contains considerable organics with lower MW (intermediate and low MW substances). The more hydrophobic, lower MWD and biodegradability humic acid-like and fulvic acid-like substances (as peaks C and D) in EPS would be preferentially removed through PAC adsoprtion. Moreover, more hydrophilic, relatively higher MWD and biodegradability proteins-like substances (peaks A and B) would be more easily removed by the biomass degradation during the biological treatment. Thus, after addition in the bioreactor, PAC was thought to first perform as an absorbent to absorb humic acid-like and fulvic acid-like substances as well as protein-like substances; if so, these PAC particles would incorporate with sludge flocs to form large biological PAC. Under this condition, the adsorbed organics could be further used as substrate for the growth of surrounding biomass, allowing the adsorption and biodegradation capacity to determine the balance between the adsorption and biodegradation effects of the biological PAC. These tradeoffs have also been noted in the potential problem of PAC saturation with foulants (Remy et al., 2010). Apparently, the retention time of refractory organics in the bioreactor would be extended after PAC adsorption, and then biodegradation would be enhanced by possible cultivatation of a particular biomass during long term operation (Satyawali and Balakrishnan, 2009b). The analysis gave an explanation of the variations in fluorescent organics in the PAC-DMBRs, indicating that their removals could be potentially enhanced by the adsorption and biodegradation effects of the PAC in

PAC-DMBRs, although more attention was still needed to verify the mechanisms in depth.

Fig. 5

Table 4

4. Conclusions

The PAC-DMBRs effectively enhanced the system performance with the DM formation time of 5 to 20 min. The stable flux in PAC-DMBR3 was 15 and 5 L/m^2h higher than those in PAC-DMBR1 and PAC-DMBR2, and the lowest R_c ($5.4\times10^{10}\ m^{-1}$) and R_t values ($6.1\times10^{10}\ m^{-1}$) were noted. By increasing the PAC dosage, the removal of COD, UV_{254}, NH_3-N and color were obviously enhanced. Biological PAC formation improved sludge properties, and the adsorption and biodegradation effects of the biological PAC also changed the EPS properties, indicating that additives that could modify sludge properties might also be promising in developing hybrid DMBRs.

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Figure captions and Tables

Fig. 1. Filtration performance of PAC-DMBRs: (a) flux; (b) effluent turbidity and (c) cake layer resistance (R_c).

Fig. 2. PSD of activated sludge samples in the PAC-DMBRs.

Fig. 3. Microbial activity reflected by SOUR of activated sludge.

Fig. 4. EPS content in activated sludge: (a) SEPS and (b) BEPS.

Fig. 5. EEM fluorescence spectra samples from PAC-DMBRs.

Table 1 Filtration resistance distribution of the PAC-DMBR hybrid process

Table 2 Pollutants removal by the PAC-DMBRs.

Table 3 Properties of the activated sludge in the PAC-DMBRs.

Table 4 Fluorescent properties of effluent and EPS samples.

Table 1 Filtration resistance distribution of the PAC-DMBR hybrid process

Filtration resistances	1st-4th operational cycles			5th-8th operational cycles		
	DMBR1	DMBR2	DMBR3	DMBR1	DMBR2	DMBR3
R_m ($10^{10}m^{-1}$)	0.73	0.69	0.71	0.73	0.69	0.71
R_c ($10^{10}m^{-1}$)	6.00	7.10	6.54	6.95	6.03	5.37
R_t ($10^{10}m^{-1}$)	6.72	7.78	7.25	7.67	6.71	6.08
R_c/R_t (%)	89.29	91.26	90.21	90.61	89.87	88.32

Table 2 Pollutants removal by the PAC-DMBRs.

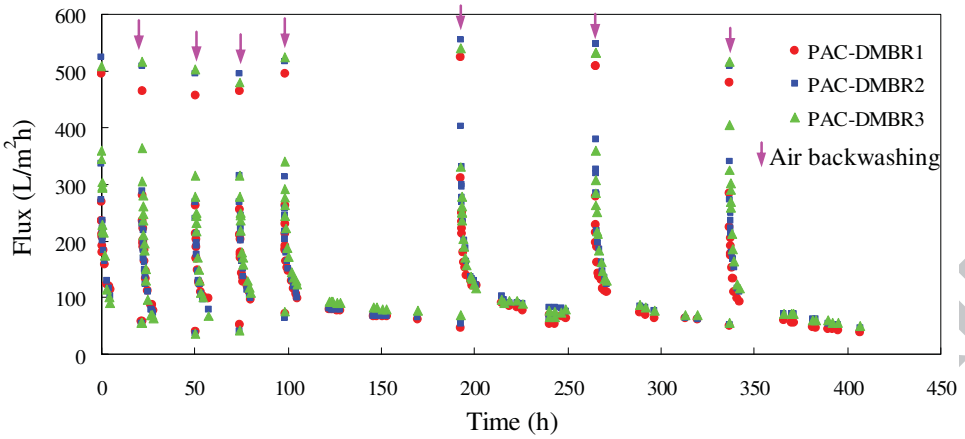
Parameters	Influent	Effluent		
		PAC-DMBR1	PAC-DMBR2	PAC-DMBR3
COD (mg/L)	196.8±66.8	21.8±14.0	20.0±13.4	19.0±14.6
UV_{254} (cm^{-1})	0.17±0.07	0.10±0.01	0.08±0.01	0.07±0.01
NH_3-N (mg/L)	25.2±4.3	0.64±0.15	0.53±0.21	0.55±0.14
TP (mg/L)	3.3±0.37	2.41±0.25	2.42±0.26	2.38±0.14
Color (c.u.)	128.7±26.3	17.5±3.0	13.2±3.5	9.2±4.3

Table 3 Properties of the activated sludge in the PAC-DMBRs.

Parameters	PAC-DMBR1	PAC-DMBR2	PAC-DMBR3
MLSS (mg/L)	2.5-3.5	3.5-4.5	4.5-5.5
SV_{30} (%)	36.8	44.6	42.9
SVI (mL/g)	104.2	102.1	94.2
Supernatant turbidity (NTU)	3.0	2.8	2.5
Supernatant CODc (mg/L)	27.1	23.5	22.7
Supernatant CODs (mg/L)	37.6	32.2	31.5
CST (s)	30.1	19.9	20.9

Table 4 Fluorescent properties of effluent and EPS samples.

	Aromatic protein -like substances (Peak A)		Tryptophan protein-like substances (Peak B)		Humic acid-like substances (Peak C)		Fulvic acid-like substances (Peak D)	
	Ex/Em	FI	Ex/Em	FI	Ex/Em	FI	Ex/Em	FI
Effluent1	-	-	275/370	126	320/410	86	250/410	170
Effluent2	-	-	280/350	73	330/415	55	250/415	99
Effluent3	-	-	-	-	-	-	-	-
SEPS1	-	-	275/370	128	310/405	88	250/415	172
SEPS2	-	-	280/345	75	330/410	60	250/410	108
SEPS3	-	-	-	-	-	-	-	-
BEPS1	230/345	1324	290/355	2144	350/440	274		
BEPS2	230/310	1600	285/350	1763	340/435	200	-	-
BEPS3	230/325	1088	285/335	828	320/420	157	-	-



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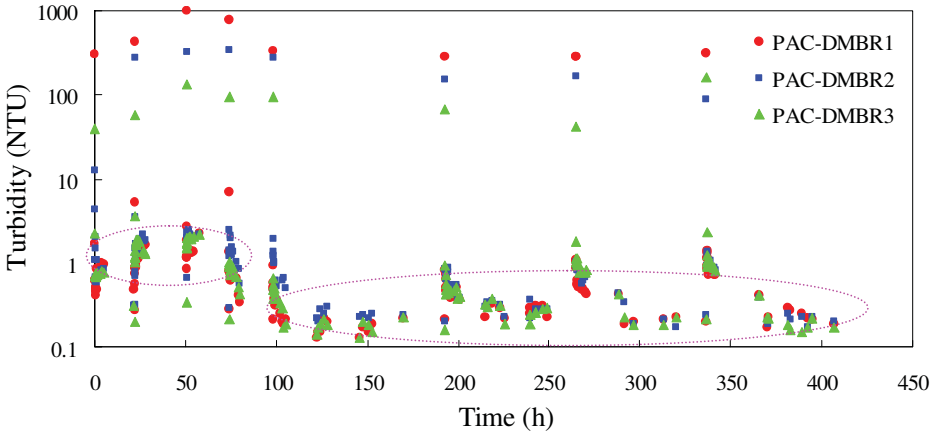

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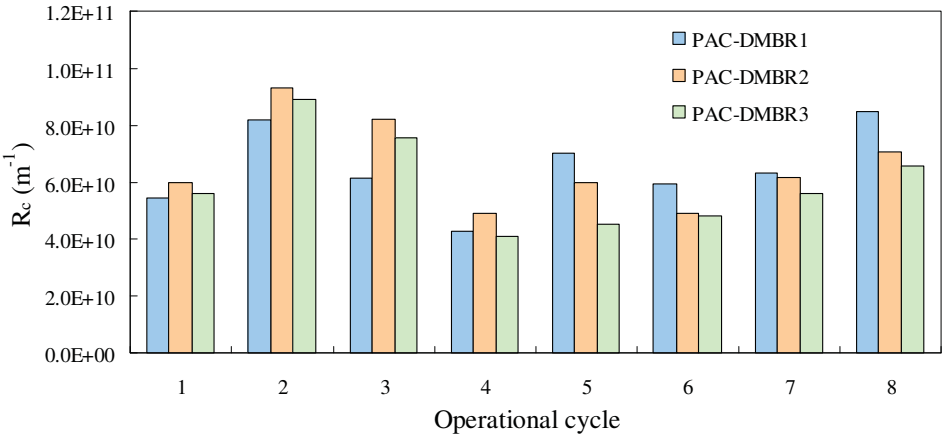


(c)

Fig. 1. Filtration performance of PAC-DMBRs: (a) flux; (b) effluent turbidity and (c) cake layer resistance (R_c).

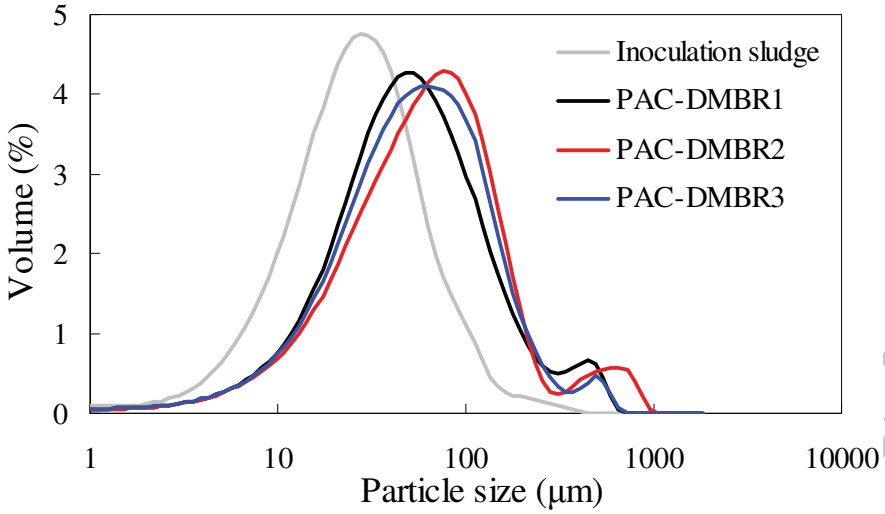


Fig. 2. PSD of activated sludge samples in the PAC-DMBRs.

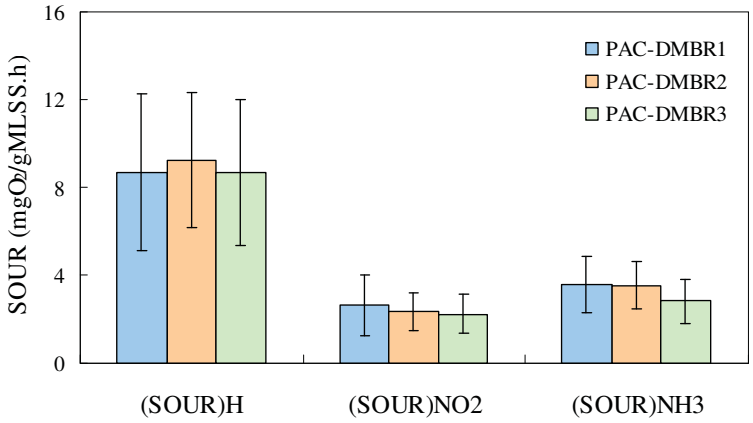
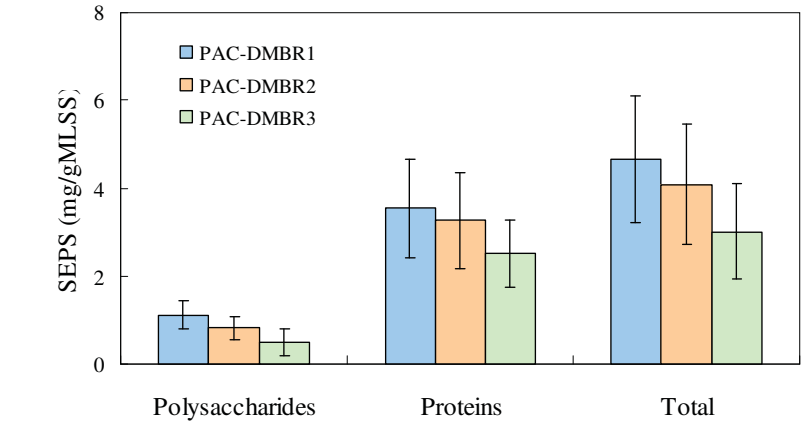
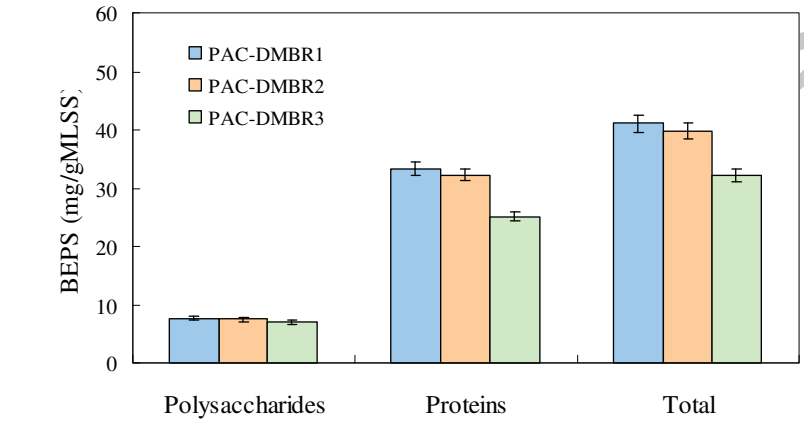


Fig. 3. Microbial activity reflected by SOUR of activated sludge.



(a)



(b)

Fig. 4. EPS content in activated sludge: (a) SEPS and (b) BEPS.

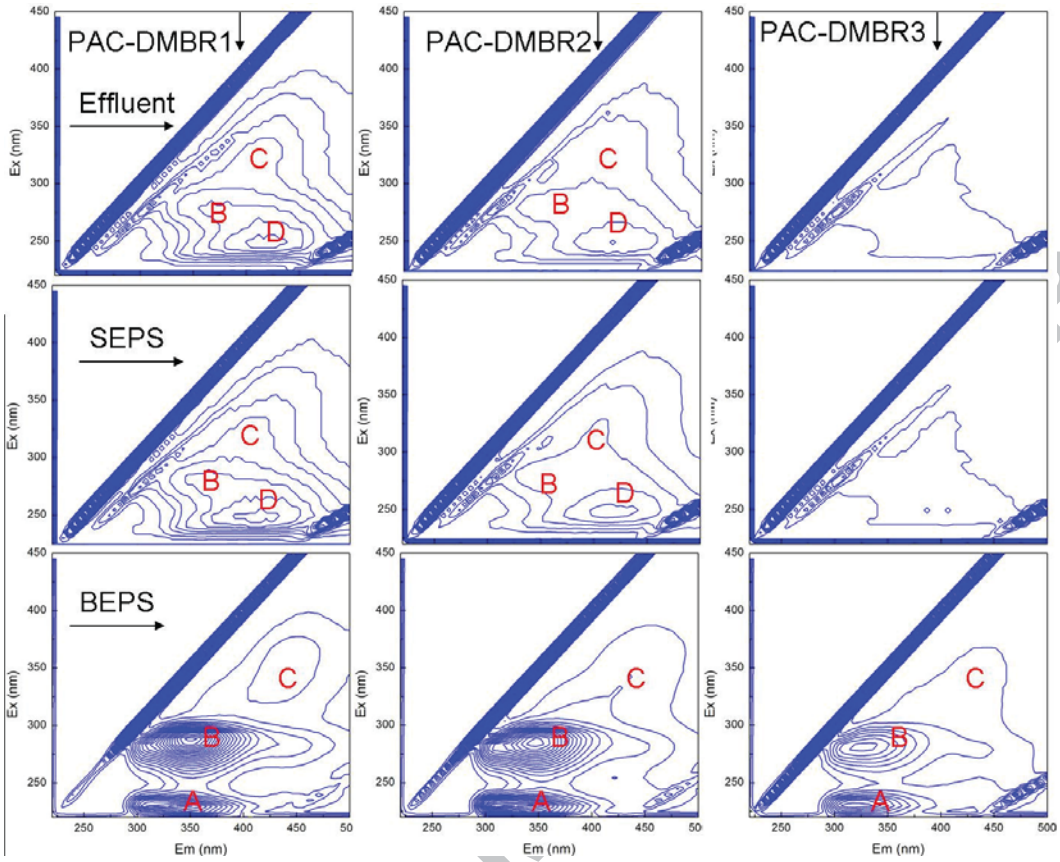


Fig. 5. EEM fluorescence spectra samples from PAC-DMBRs.

Highlights

The emerging PAC-DMBR hybrid process were developed and investigated
PAC-DMBRs showed high fluxes (40-100L/m^2h) with long operational cycles of 70-100h
PAC addition improved the process performance, sludge and EPS properties
Enhanced performance was attributed to the synergistic effects of biological PAC