An anaerobic membrane bioreactor – membrane distillation hybrid system for energy recovery and water reuse: Removal performance of organic carbon, nutrients, and trace organic contaminants

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ABSTRACT

In this study, a direct contact membrane distillation (MD) unit was integrated with an anaerobic membrane bioreactor (AnMBR) to simultaneously recover energy and produce high quality water for reuse from wastewater. Results show that AnMBR could produce 0.3 – 0.5 L/g COD_{added} biogas with a stable methane content of approximately 65%. By integrating MD with AnMBR, bulk organic matter and phosphate were almost completely removed. The removal of the 26 selected trace organic contaminants by AnMBR was compound specific, but the MD process could complement AnMBR removal, leading to an overall efficiency from 76% to complete removal by the integrated system. The results also show that, due to complete retention, organic matter (such as humic-like and protein-like substances) and inorganic salts accumulated in the MD feed solution and therefore resulted in significant fouling of the MD unit. As a result, the water flux of the MD process decreased continuously. Nevertheless, membrane pore wetting was not observed throughout the operation.

Key words: anaerobic membrane bioreactor (AnMBR); membrane distillation (MD); trace organic contaminants (TrOCs); energy recovery; wastewater treatment and reuse.

1 Introduction

Water scarcity driven by population growth, climate change, and environmental pollution has prompted the development of new technologies, such as membrane distillation (MD), and the improvement of existing ones, such as membrane bioreactor (MBR) for wastewater treatment and reuse (Shannon et al., 2008). MBR integrates the membrane separation process with biological treatment to produce high standard water for recycling applications (Nguyen et al., 2012; Huang and Lee, 2015; Jegatheesan et al., 2016; Judd, 2016). Previous studies have demonstrated the capacity of MBR for wastewater treatment and reuse regarding both basic water quality parameters and high removal efficiency of a broad range of trace organic contaminants (TrOCs) (Tadkaew et al., 2011; Boonyaroj et al., 2012; Navaratna et al., 2012; Wijekoon et al., 2013; Di Bella et al., 2015; Prasertkulsak et al., 2016).

The widespread occurrence of TrOCs in municipal and industrial wastewater is of significant concern to water reuse (Acuña et al., 2015; Huerta et al., 2016). TrOCs include a diverse range of emerging chemicals that are widely used in our modern society for health care, agriculture, aquaculture, live stocking, and industrial production. They are continuously released into the environment either accidentally through agricultural and industrial activities or inevitably through human and livestock excretion. TrOCs are ubiquitously detected in wastewater and sewage-impacted water bodies at trace levels up to a few micrograms per litre (μg/L) (Osorio et al., 2012). Although the impact of long-term exposure to low concentrations of TrOCs on human health is still largely unknown, ecological data to date have evidenced their chronic effects on a range of sensitive aquatic organisms, such as fish and reptiles (Schwarzenbach et al., 2006; Guillén et al., 2012). Thus, adequate removal of TrOCs is essential for water reuse applications and environmental protection (Luo et al., 2014).

MBR can be operated in aerobic or anaerobic conditions according to the presence or absence of oxygen in the biological reactor (Huang et al., 2015). Recent studies have focused mostly on aerobic MBR systems as they can be readily deployed for wastewater treatment and reuse. There is also a growing interest in the development of anaerobic MBR (AnMBR) for energy efficient wastewater treatment and reuse (Stuckey, 2012). Compared to aerobic MBR, which requires significant energy input for aeration, AnMBR is more energy-efficient and can even be an energy positive system by producing biogas for beneficial usage. However, AnMBR often has a lower treatment capacity to remove nutrients and TrOCs in comparison with aerobic MBR. Recent studies have demonstrated that some TrOCs (such as carbamazapine, atrazine, and diclofenac) are poorly removed by AnMBR due to their resistance to biodegradation (Monsalvo et al., 2014; Wijekoon et al., 2015). As a result, it is necessary to complement AnMBR with an additional treatment process to achieve a suitable product water quality for reuse.

MD is a thermally driven membrane separation process and has been recognized as an emerging technology in wastewater treatment and reuse (Wijekoon et al., 2014a; Wijekoon et al., 2014b; Nguyen et al., 2016). During MD operation, water in the vapour form transports under a partial vapour pressure gradient across a microporous and hydrophobic membrane from a high temperatue solution to a low temperature solution. MD can utilize low-grade waste heat and solar thermal that is otherwise unusable by other means. Thus, MD can potentially be used for the futher purification of wastewater effluents, particulalry after anaerobic treatment where thermal heat from the combustion of produced biogas can be utilised as energy input to the MD process. Kim et al. (2015) has demonstrated that MD could further treat effluent from an anaerobic moving bed biofilm reactor by achieving complete rejection of phosphorus and more than 98% rejection of dissolved organic carbon. Similarly, Jacob et al. (2015) reported 90% rejection of chemical oxygen demand (COD) and ammonia from AnMBR effluent by MD. Nevertheless, data from these previous studies were from batch test experiments and little is known about the MD performance when simultaneously operated with AnMBR.

This study aimed to investigate the performance of an integrated AnMBR-MD system for water reuse and energy recovery from wastewater. The hybrid system performance was examined in terms of biogas production, biomass characteristics, contaminant removal, and membrane fouling. Removal of organic matter, nutrients, and TrOCs by both the AnMBR and MD processes were evaluated. Fouling behavior of the MD membrane was delinated.

2 Materials and methods

2.1 Synthetic wastewater and trace organic contaminants

A synthetic solution, simulating high strength domestic wastewater, was used and was prepared daily to consist of 4000 mg/L glucose, 750 mg/L peptone, 2250 mg/L sodium acetate, 175 mg/L potassium dihydrogen phosphate, 175 mg/L magnesium chloride, and 175 mg/L urea. Key physicochemical properties of the synthetic wastewater were determined every four days throughout the experiment. In particular, the synthetic wastewater contained 6252.3 mg/L COD, 166.8 mg/L total nitrogen (TN), 195.4 orthophosphate (PO_4^{3-}), and 34.7 mg/L ammonium (NH_4^+). The electrical conductivity and pH of the synthetic wastewater were 4.01 ± 0.9 mS/cm and 7.0 ± 0.2, respectively. It is noteworthy that anaerobic treatment is not viable for biogas production from low strength wastewater due to the low methane production over heating requirement ratio. As a result, it is necessary to pre-concentrate municipal wastewater to increase the COD content by processes such as forward osmosis prior to anaerobic treatment (Ansari et al., 2016). Thus, the synthetic wastewater with higher strength than typical municipal wastewater was used in this study.

A set of 26 TrOCs was selected for study. These TrOCs represent four major groups of chemicals of emerging concern that are ubiquitously present in domestic wastewater, including pharmaceuticals and personal care products, endocrine disruptors, industrial chemicals, and pesticides. Key physicochemical properties of these TrOCs are summarized in Table S1, Supplementary Data. Based on their effective octanol – water partition coefficient (i.e. Log D) at solution pH 7, the 26 TrOCs could be categorized as hydrophobic (i.e. Log D > 3.2) and hydrophilic (i.e. Log D < 3.2) (Tadkaew et al., 2011). A stock solution containing 10 mg/L of each TrOC compound was prepared in pure methanol and then stored at -18 °C in the dark. The TrOC stock solution was added daily to the synthetic wastewater described above to obtain a concentration of 2 µg/L of each compound.

2.2 Anaerobic membrane bioreactor – membrane distillation

A lab-scale AnMBR-MD system was used in this study (Figure 1). This system consisted of a feed reservoir, an anaerobic bioreactor with a working volume of 20 L, a biogas collector, an external membrane module, and an effluent reservoir. A peristaltic pump (Masterflex L/s, USA) controlled by a water level controller was employed to feed the synthetic wastewater into the bioreactor. A proportional-integral-derivative temperature controller (Neslab RTE7, ThermoScientific, USA) equipped with a plastic coil was used to maintain the bioreactor temperature at 35 ± 1 °C. A Tedlar sampling bag was connected to the bioreactor for biogas collection and subsequent biogas composition analysis using a biogas meter (Biogas 5000, Geotech, UK) as described in a previous study (Nghiem et al., 2014). A ceramic microfiltration (MF) membrane module (NGK, Japan) in stainless steel housing was externally integrated with the bioreactor. The normalized pore size and effective area of the MF membrane was 1 µm and 0.09 m^2, respectively. A peristaltic pump (Masterflex L/s, USA) was applied to circulate digested sludge from the bioreactor to the external MF membrane module and then back to the bioreactor. At the same time, an industrial grade peristaltic pump (ProMinent, Australia) was employed to circulate digested sludge from the bottom to the top of the bioreactor for sludge mixture. The bioreactor and all pipelines involved in this system were wrapped with insulation foam to minimise heat loss. Detailed description of the AnMBR system is also available elsewhere (Song et al., 2016).

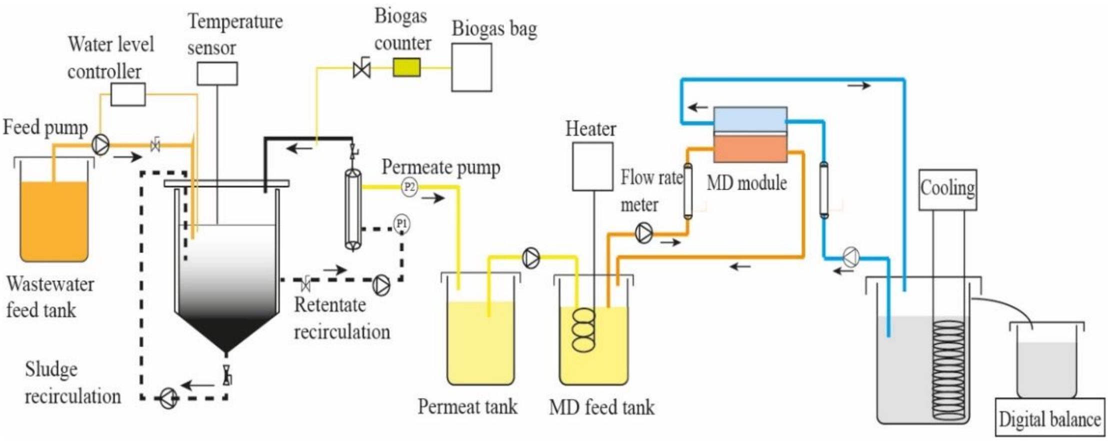

Figure 1: Schematic diagram of the laboratory scale AnMBR-MD hybrid system.

A direct contact MD system was integrated with AnMBR as a post-treatment step (Figure 1). The MD system comprised of a feed reservoir, a plate-and-frame membrane module, a distillate reservoir, and two identical gear pumps (Micropump, Vancouver, WA). A separate MD feed reservoir with a working volume constant at 10 L was set to ensure a continuous feed supply. A peristaltic pump controlled by a water level controller was used to transfer the AnMBR effluent to the MD feed reservoir. The membrane module was made of acrylic plastic and consisted of two identical semi-cells. Each cell was engraved with a flow channel of 142 mm long, 91 mm wide and 3 mm deep. A hydrophobic microporous membrane from Porous Membrane Technology (Ningbo, China) was used. The membrane was composed of a thin polytetrafluorethylene (PTFE) layer on the top of a polypropylene (PP) support layer and had a thickness, nominal pore size, and porosity of 60 µm, 0.2 µm, and 80%, respectively. The feed and distillate temperatures were maintained at 45 ± 1 °C and 20 ± 1 °C, respectively, using two temperature controllers (Neslab RTE7, Thermo Scientific, USA). The overflowing distillate was weighed by a digital balance connected to a computer for determining the MD water flux.

2.3 *Experimental protocol*

Digested sludge from a full-scale wastewater treatment plant was used to inoculate the bioreactor. AnMBR was acclimatized to the synthetic wastewater and laboratory conditions for over three months. Once stable operation had been achieved as indicated by the removal of organic matter (i.e. > 97% total organic carbon (TOC) and COD removal), TrOCs were introduced to the synthetic wastewater. After obtaining 10 L effluent, the MD system was integrated downstream with AnMBR to form an AnMBR-MD hybrid system (Figure 1).

The AnMBR-MD hybrid system was continuously operated for 30 days. A peristaltic pump was used to extract water from the bioreactor through the MF membrane with a permeate flux of 2 L/m^{2}h in a cycle of 14 min suction and 1 min relaxation. The relaxation time was provided to reduce the MF membrane fouling. To maintain a constant working volume of the bioreactor, the feed flowrate was set at 3.5 mL/min, which resulted in the hydraulic retention time (HRT) of AnMBR at approximately 4 days. Hydraulic backwash was conducted every two days using AnMBR effluent to maintain the water flux. Mixed liquor (650 mL) was taken weekly for biomass characterization, resulting in an operating sludge retention time of approximately 215 days. Sodium bicarbonate was added to maintain the mixed liquor pH at 7. AnMBR effluent was continuously pumped to the MD feed reservoir to maintain its working volume at 10 L. Deionized water (2 L) was used as the MD distillate. Both MD feed and distillate were circulated to the membrane cell with a cross-flow rate of 1 L/min (corresponding to a cross-flow velocity of 6.1 cm/s). The MD membrane was replaced every ten days to maintain a desirable water production and provide samples for membrane fouling investigation.

2.4 Analytical methods

2.4.1 Analysis of basic water quality parameter

Aqueous samples from the AnMBR feed, bioreactor, AnMBR effluent, MD feed, and MD distillate were collected every three days for water quality analysis. Specifically, TOC and TN concentrations were measured using a TOC/TN-V$_{CSH}$ analyser (Shimadzu, Japan). COD was quantified by using high range digestion vials (Hatch, USA) following the standard dichromate method. The removal rates of TOC, TN, and COD by the AnMBR and MD processes were quantified based on the method described in the following section for TrOCs. A Flow Injection Analysis system (QuikChem 8500, Lachat, CO) was used to detect NH_4^+ and PO_4^{3-} concentrations. Electrical conductivity and pH were monitored by an Orion 4 Star Plus portable pH/conductivity meter (Thermo Scientific, USA).

2.4.2 Analysis of trace organic contaminants

Aqueous samples were collected in duplicate every five days for TrOC analysis according to a method reported by Tadkaew et al. (2011). Briefly, this method involved solid phase extraction (SPE), liquid chromatography, and quantitative determination by tandem mass spectrometry with electrospray ionisation. Before SPE, most samples were spiked with a surrogate standard solution containing 50 ng of an isotopically labelled version of each compound except for oxybenzone, chlorpyrifos, fenofibrate, propylparaben, phenylphenol, sucralose and aspartame, which were quantified by external dilution. Hydrophilic/lipophilic balance cartridges (Waters, Millford, MA, USA) were used for TrOC extraction after being preconditioned with 5 mL methyl tert-butyl ether (MTBE), 5 mL methanol, and 10 mL reagent water. Compounds were eluted from cartridges into centrifuge tubes using 5 mL methanol and 5 mL methanol/MTBE blend (v/v = 1/9). Resultant extracts were concentrated to approximately 100 µL by nitrogen stream and then diluted to 1 mL with methanol before being analysed using a high performance liquid chromatography (Agilent, Palo Alto, CA) and a triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with a turbo-V ion source and employed in both positive and negative electro-spray modes. The limit of quantification of propylparaben and phenylphenol was 20 ng/L while that of all other compounds was 5 ng/L (Table S2).

The removal of TrOC by AnMBR is defined as:

$$R_{AnMBR} = \frac{C_{Wastewater} - C_{Effluent}}{C_{Wastewater}} \times 100\% \qquad (1)$$

Where $C_{Wastewater}$ and $C_{Effluent}$ are the measured TrOC concentrations in the synthetic wastewater and AnMBR effluent, respectively. To calculate the removal of TrOCs by MD, it is necessary to take into account the dilution of the MD permeate by the initial water in the distillate loop of the DCMD process. Thus, the following equation is used:

$$R_{MD} = \frac{C_{MDF} - C *_{MDE}}{C_{MDF}} \times 100\% \qquad (2)$$

C_{MDF} is the measured TrOC concentration in the MD feed; $C*_{MDE}$ is the calculated TrOC concentration in the MD permeate before being diluted with the existing distillate. $C*_{MDE}$ is obtained via a mass balance calculation.

$$C*_{MD} = \frac{M_{MD}}{V_{MD}} \qquad (3)$$

$$\mathrm{M}_{\mathrm{MD}} = \left(\mathrm{C}_{\mathrm{Distillate(t)}} - \mathrm{C}_{\mathrm{Distillate(t-\Delta t)}}\right)\mathrm{V}_{\mathrm{Distillate}} + \frac{\left(\mathrm{C}_{\mathrm{Distillate(t)}} + \mathrm{C}_{\mathrm{Distillate(t-\Delta t)}}\right)}{2}\mathrm{V}_{\mathrm{MD}} \qquad (4)$$

where M_{MD} is the mass of the TrOC passing through the MD membrane between time $t - \Delta t$ and t; $C_{Distillate(t)}$ and $C_{Distillate(t-\Delta t)}$ are TrOC concentrations measured in MD distillate at time $t - \Delta t$ and t, respectively; $V_{Distillate}$ is the effective volume of the distillate (2 L); V_{MD} is the volume of excessive distillate between time $t - \Delta t$ and t, which can be determined by the MD water flux.

Finally, the removal of TrOCs by the AnMBR-MD hybrid system is calculated as:

$$R_{AnMBR-MD} = \frac{C_{Wastewater} - C*_{MDE}}{C_{Wastewater}} \times 100\% \qquad (5)$$

The fate of TrOCs in the sludge (i.e. solid phase) was not investigated because sludge is completely retained by MF cannot reach the MD process.

2.4.3 Biomass characteristics

Oxidation reduction potential (ORP) was measured using WP-80D dual pH-mV meter (TPS, Australia). Mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solids (MLVSS) concentrations and alkalinity were measured according to the Standard Methods for Examination of Water and Wastewater.

2.4.4 Fluorescence excitation – emission matrix spectroscopy

A two-dimensional fluorescence spectrophotometer (Perkin-Elmer LS-55) was used to measure the fluorescence intensity of aqueous samples with excitation wavelengths between 240 and 450 nm and emission wavelengths between 290 and 580 nm (in 5 nm increments). Fluorophores detected in the excitation-emission-intensity matrix (EEM) were assigned to specific dissolved organic matter fractions (Luo et al., 2017). All samples were diluted to the same TOC concentration of 5 mg/L for resolving and comparing EEM spectra.

2.4.5 Membrane autopsy

A scanning electron microscopy (SEM) coupled with energy dispersion spectrometry (EDS) (JCM-600, JEOL, Tokyo, Japan) was used to identify the morphology and composition of the fouling layer on the MD membrane surface every ten days. Membrane samples were air-dried in a desiccator before being coated with an ultra-thin gold layer with a sputter coater (SPI Module, West Chester, PA) for SEM imaging. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy (IRAffinity-1, Shimadzu, Kyoto, Japan) was also used to probe the chemical composition of the fouling layer. The measured spectrum ranged between 600 and 4000 cm^{-1} with 2 cm^{-1} resolution. Each scan was performed 20 times. A background correction was conducted before each measurement. Membrane hydrophobicity was measured by contact angle measurements using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) based on the standard sessile drop method. Ten water droplets were applied to each membrane sample and contact angles on both sides of the droplet were analysed.

3 Results and discussion

3.1 Biological stability of AnMBR

Stable biomass characteristics were achieved during AnMBR operation (Table 1). The MLSS and MLVSS concentrations in the bioreactor were stabilized at approximately 10 and 5 g/L respectively, corresponding to a constant MLVSS/MLSS ratio of 0.5. This result confirms the operational stability of the anaerobic bioreactor. It has been reported that the effective biological treatment of AnMBR could be achieved with the MLVSS/MLSS ratio of 0.4 – 0.9 under a wide range of operational conditions, such as HRT and SRT (Baek et al., 2010; Huang et al., 2011; Zhang et al., 2015). The mixed liquor alkalinity was stable at 2216 ± 220 mg $CaCO_3$/L. A relatively high ORP (-190 ± 14 mV) was observed in this study compared to conventional anaerobic treatment processes (Hafuka et al., 2016). The high ORP value observed here was possibly because of the circulation of biomass to the external membrane module and regular mixed liquor sampling for ORP measurement.

Table 1: Key characteristics of the mixed liquor during AnMBR operation (mean value ± standard deviation from four measurements over 30 days)

Parameter	Value
MLSS (g/L)	10 ± 1
MLVSS (g/L)	4.9 ± 0.9
MLVSS/MLSS	0.5 ± 0.1
Alkalinity (mg $CaCO_3$/L)	2216 ± 220
Conductivity (mS/cm)	6.7 ± 0.2
ORP (mV)	-190 ± 14

A stable performance of AnMBR was also observed in terms of biogas production (Figure 2) and organic removal (Table 2). During AnMBR operation, biogas production was stabilized in the range from 0.3 to 0.5 L/g COD_{added} with the methane content at approximately 65% (Figure 2). This observation is consistent with previous studies (Wijekoon et al., 2015; Song et al., 2016), suggesting an effective biodegradation of organic substances by anaerobic digesters. Indeed, near complete removal of both TOC and COD could be achieved by AnMBR (Table 2).

Despite the excellent capacity for the removal of organic matter, AnMBR exhibited a low nutrient (i.e., nitrogen and phosphorus) removal (Table 2). Indeed, the low removal of nutrients is a major concern in terms of the development and practical application of AnMBR (Liu et al., 2016). Biological nutrient removal by microbial assimilation in AnMBR is limited due to the slow biomass growth in anaerobic digesters (Smith et al., 2012). On the other hand, NH_4^+ is generated from N-bearing organic compounds during anaerobic treatment (Chen et al., 2016). Thus, only small TN removal (10 – 30%) by AnMBR was observed in this study while NH_4^+ in the effluent was about ten times higher than that in the influent. The anaerobic process also liberates phosphorus from P-bearing organic in the form of PO_4^{3-}. As a result, PO_4^{3-} concentration in the effluent was also higher than that in the influent (Table 2).

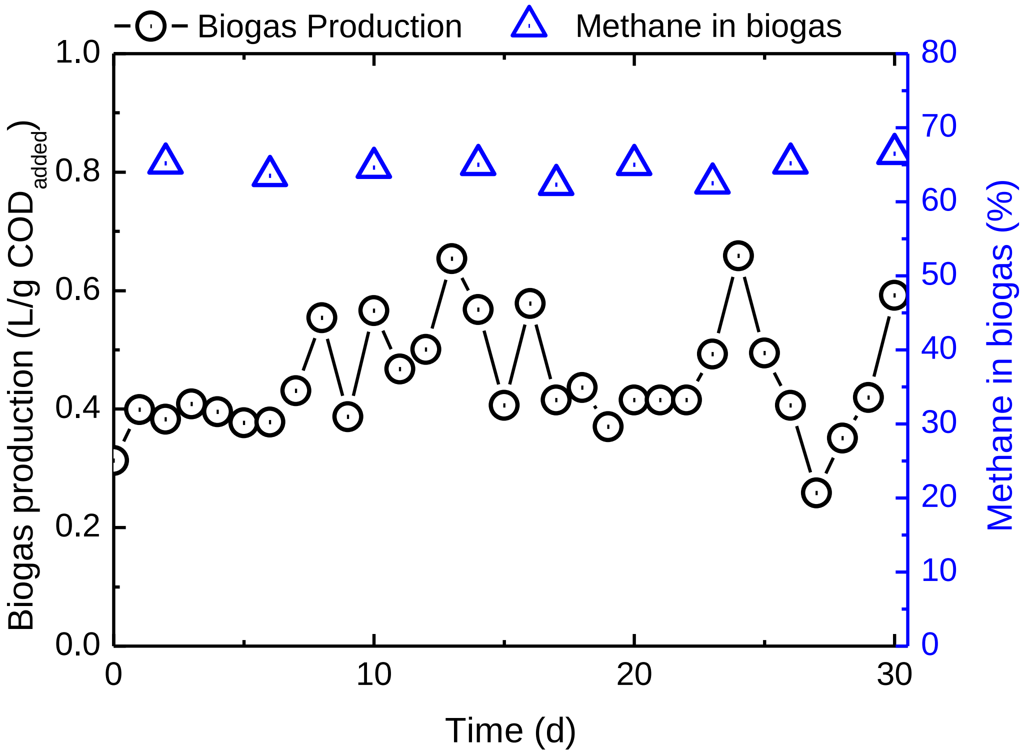

Figure 2: Biogas production and its methane fraction during AnMBR operation. Experimental conditions: HRT = 4 d; bioreactor temperature = 35 ± 1 °C; mixed liquor pH = 6.8 ± 0.2 (controlled by adding $NaHCO_3$). No extra sludge was withdrawn except for mixed liquor sampling (650 mL per week).

Table 2: Removal of bulk organic matter and nutrients by AnMBR (mean value ± standard deviation from ten measurements over 30 days)

Parameters	**Influent concentration (mg/L)**	**Effluent concentration (mg/L)**	**Removal (%)**
TOC	2118.0 ± 66.5	26.5 ± 6.6	98.7 ± 0.3
COD	6252.3 ± 108.7	101.5 ± 22.9	98.4 ± 0.4
TN	166.8 ± 7.0	132.5 ± 16.9	20.4 ± 11.0
PO_4^{3-}	195.4 ± 11.4	213.7 ± 38.7	–
NH_4^+	34.7 ± 2.3	346.3 ± 37.0	–

3.2 Performance of the MD process integrated with AnMBR

3.2.1 Removal of bulk organic matter and nutrients

The MD process could complement AnMBR by further enhancing the removal of organic substances and phosphate (Figure 3). By integrating MD with AnMBR, complete and near complete removal of COD and phosphate was achieved, respectively (Figure 3a and b). This is because the MD process can offer complete rejection of non-volatile substances (Chen et al., 2016). As a result, a considerable accumulation of COD and PO_4^{3-} in the MD feed solution was observed, which consequently resulted in significant fouling to the MD membrane as discussed in the section 3.2.3.

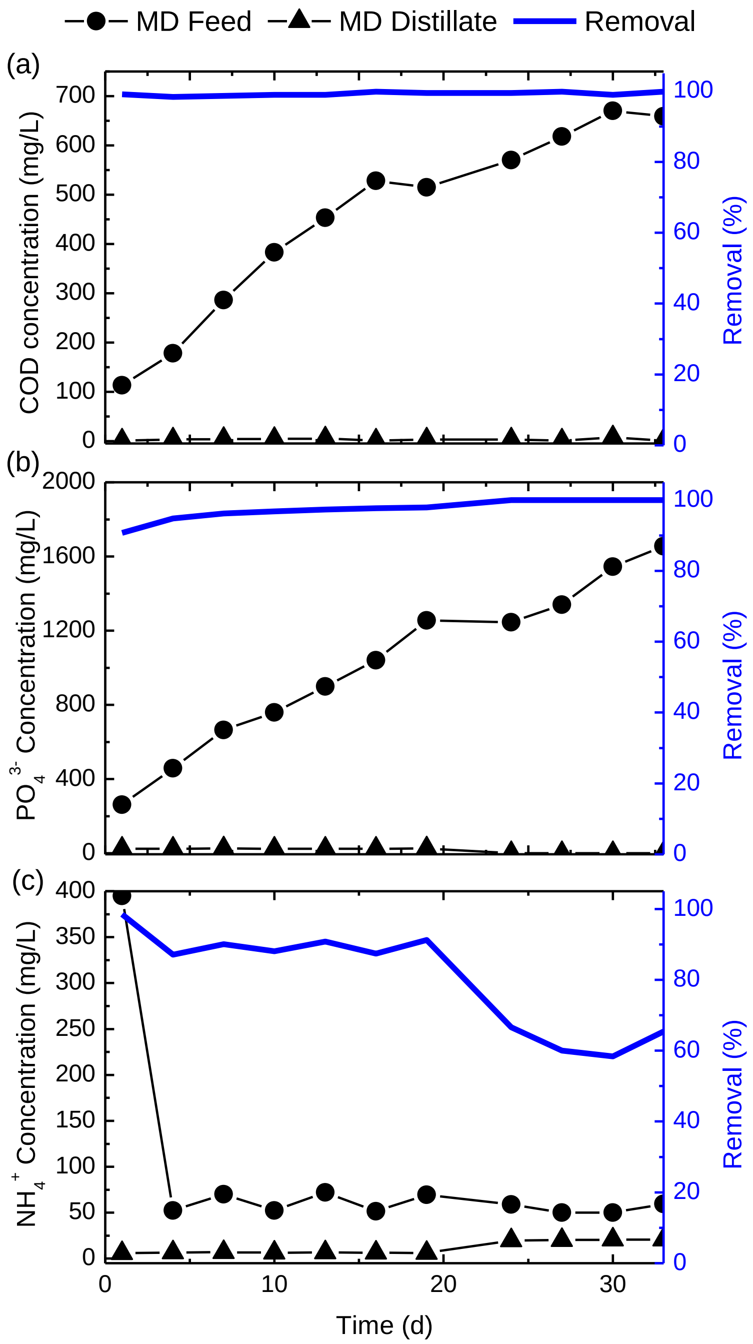

Figure 3: Distribution and removal of (a) COD, (b) PO_4^{3-} and (c) NH_4^+ by the MD process subsequently integrated with AnMBR. MD membrane was replaced every ten days. Operation condition of MD: feed temperature = 45 ± 1 ° C; distillate temperature = 20 ± 1 °C; feed working volume = 2 L; feed and distillate flow rate = 1 mL/min (i.e. cross-flow velocity = 6.1 cm/s). AnMBR effluent was continuously replenished to

maintain the working volume of the MD feed at 10 L. Operation conditions of AnMBR are summarized in the caption of Figure 2.

The removal of NH_4^+ by the MD process was nearly 90% within the first 20 days of operation, but gradually decreased thereafter to approximately 60% on day 30 (Figure 3c). This decrease can be attributed to conversion to ammonia (NH_3) at a high feed temperature of 45 °C. Ammonia is a highly volatile species and can be readily transported through the MD membrane (Kim et al., 2015). As a result, a small but clearly discernible increase in NH_4^+ concentration in the distillate was observed due to ammonia transport through the MD membrane by volatilisation. In addition, NH_4^+ stripping (i.e. ammonia volatilisation) from the feed solution also occurred as evidenced by its sharp decline and then constant feed concentration despite its moderate rejection (60 – 90%) by the MD process. Results reported here indicate the need to control ammonia volatilisation and to further remove it from the product water when MD is utilized to purify the AnMBR effluent.

3.2.2 Water flux

Water flux of the MD process decreased continuously when used to purify the AnMBR effluent (Figure 4). The observed flux decline can be attributed to salt accumulation in the feed solution, and more importantly, membrane fouling. The feed conductivity increased considerably from approximately 3 to 55 mS/cm over 30 days of continuous operation (Figure 4). As a result, a small decrease in the initial water flux due to the increase in feed salinity was observed after replacing a new MD membrane every 10 days. This observation also suggested a significant role for membrane fouling in the water flux decline of the MD process. Membrane fouling could reduce the water flux by restricting the active membrane area for water vapour transport. In addition, the fouling layer may result in lowering the membrane surface hydrophobicity as indicated by a decrease in the contact angle from 135 ± 10° for the pristine membrane to less than 60° when the membrane was replaced. Nevertheless, pore wetting did not occur to the MD membrane as evidenced by the consistently low distillate conductivity throughout the experiment (Figure 4).

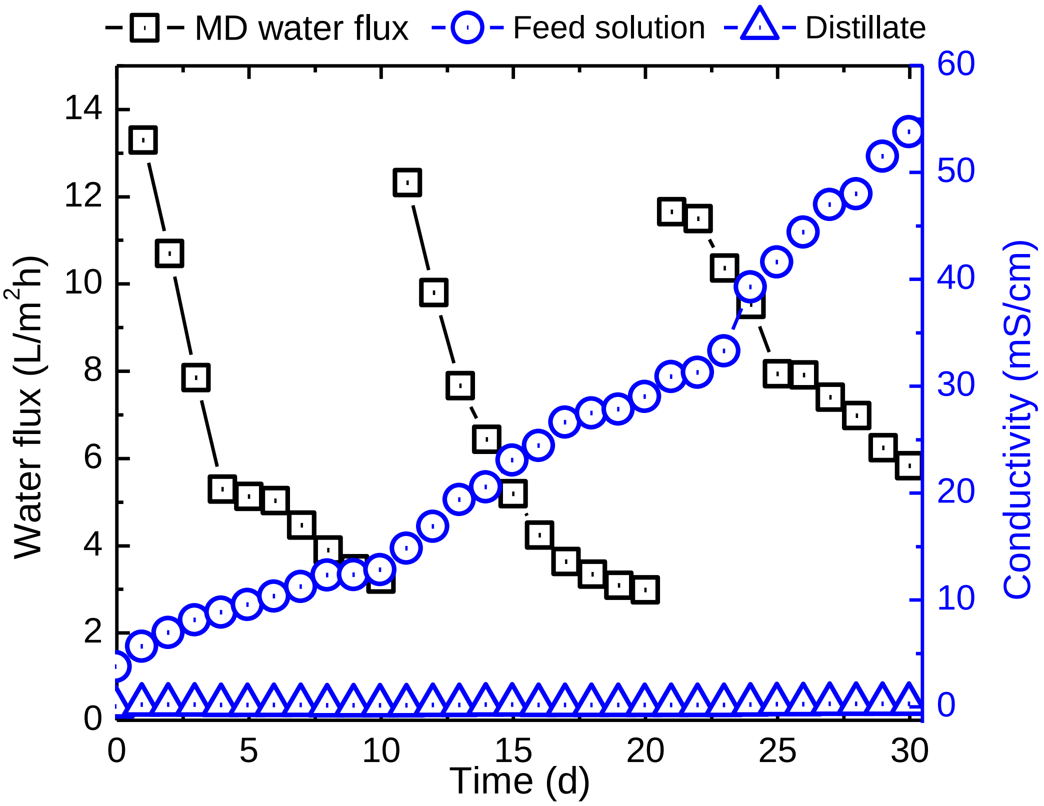

Figure 4: Water flux and the variation of the feed and distillate conductivity when the MD process was used to treat AnMBR effluent. Experimental conditions are summarized in the captions of Figures 2 and 3.

3.2.3 Membrane fouling characterisation

Membrane fouling layers were characterised to identify the fouling behaviour of the MD membrane for treating AnMBR effluent. A homogeneous cake layer was observed on each membrane surface after every 10 days of operation (Figure 5). The cake layer consisted of mainly carbon, oxygen, ferrous, sodium, chloride, magnesium, calcium, and phosphorus, suggesting the occurrence of both organic (biological) and inorganic fouling on the MD membrane surface. Indeed, inorganic crystals were visualized on the membrane surface through the SEM images and could be attributed to phosphate precipitates, such as calcium/magnesium phosphate and struvite given the accumulation of phosphate (Figure 3b) and inorganic salts in the feed solution (Figures 4).

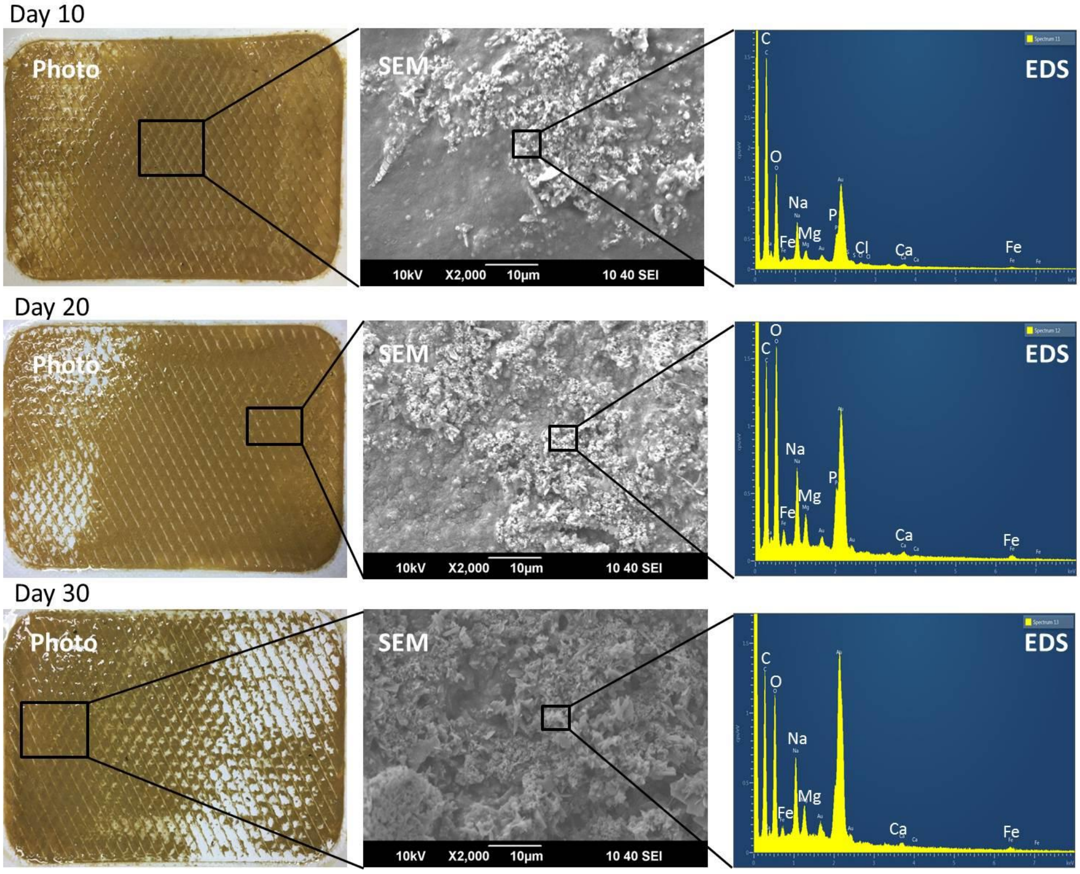

Figure 5: SEM images and EDS analyses of the fouled MD membranes. The MD membrane was replaced every ten days for fouling characterization. Operating conditions of MD were described in the caption of Figure 3.

Organic membrane fouling could also be evidenced by the ATR-FTIR measurement (Figure 6a). Compared to the pristine MD membrane, all fouled MD membranes exhibited distinctive adsorption peaks at 1653 cm^{-1}, which usually associates with alkene (C=C) in aliphatic structures and/or amide I (C=O) bonds, and at 1543 cm^{-1}, representing amide II (C-N-H) bonds. The three fouled membranes also showed a sharp peak at 1032 cm^{-1}, indicating carbonyl (C=O) bonds of polysaccharides. These results indicated that protein and polysaccharides were major components contributing to the organic fouling of the MD membrane. EEM analysis identified a significant accumulation of humic-like ($\lambda_{ex/em}$=300-370/400-500 nm) and protein-like substances ($\lambda_{ex/em}$=275-290/330-370 nm) in the MD feed solution due to their high rejection by the MD membrane (Figure 6b).

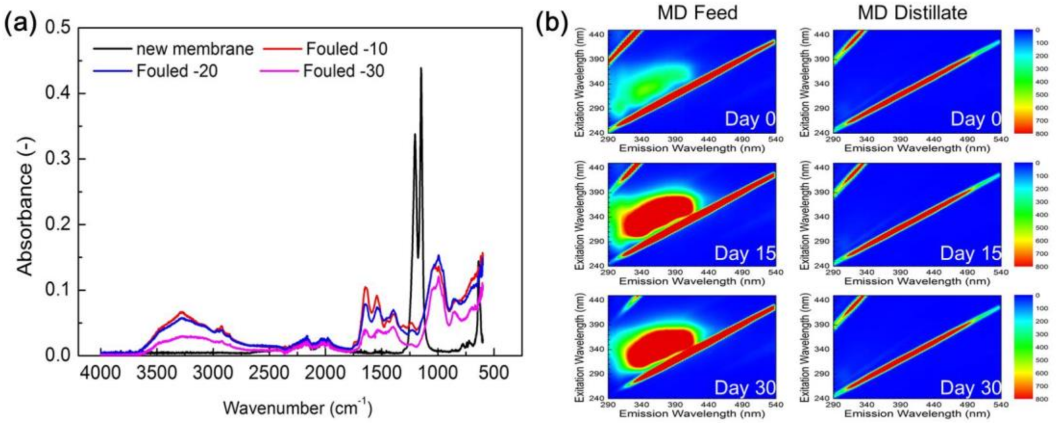

Figure 6: (a) ATR-FTIR adsorption spectra and (b) Fluorescence excitation and emission matrix (EEM) spectra for MD feed and MD distillate during AnMBR-MD operation. MD membrane was replaced every ten days for fouling characterization and named as fouled-10 d, fouled-20 d, and fouled-30 d, respectively.

3.3 TrOC removal by AnMBR integrated with MD

The role of the AnMBR and MD processes for TrOC removal in the integrated system was elucidated (Figure 7). In this study, the removal of TrOCs by AnMBR varied significantly from approximately 15.1% (i.e. primidone) to 94.2% (i.e. trimethoprim), depending on their molecular properties, such as hydrophobicity and molecular structures. Indeed, previous studies have demonstrated that TrOC removal by MBR is largely governed by their molecular properties, regardless of the presence or absence of oxygen in the bioreactor (Tadkaew et al., 2011; Wijekoon et al., 2015). In particular, the removal of ketoprofen, primidone, ibuprofen, diclofenac, carbamazepine, gemfibrozil, simazine, atrazine, and diuron by AnMBR alone was only in the range of 15 – 25%. The low biodegradability of these compounds under anaerobic conditions could be attributed to the presence of electron withdrawing groups, such as chloro, amide, and nitro in their molecular structures (Wijekoon et al., 2015). In addition, these compounds were relatively hydrophilic with Log D values lower than 3.2 (at solution pH = 7). As a result, they did not adsorb significantly to the sludge phase and biodegradation was their predominant removal mechanism from the aqueous phase.

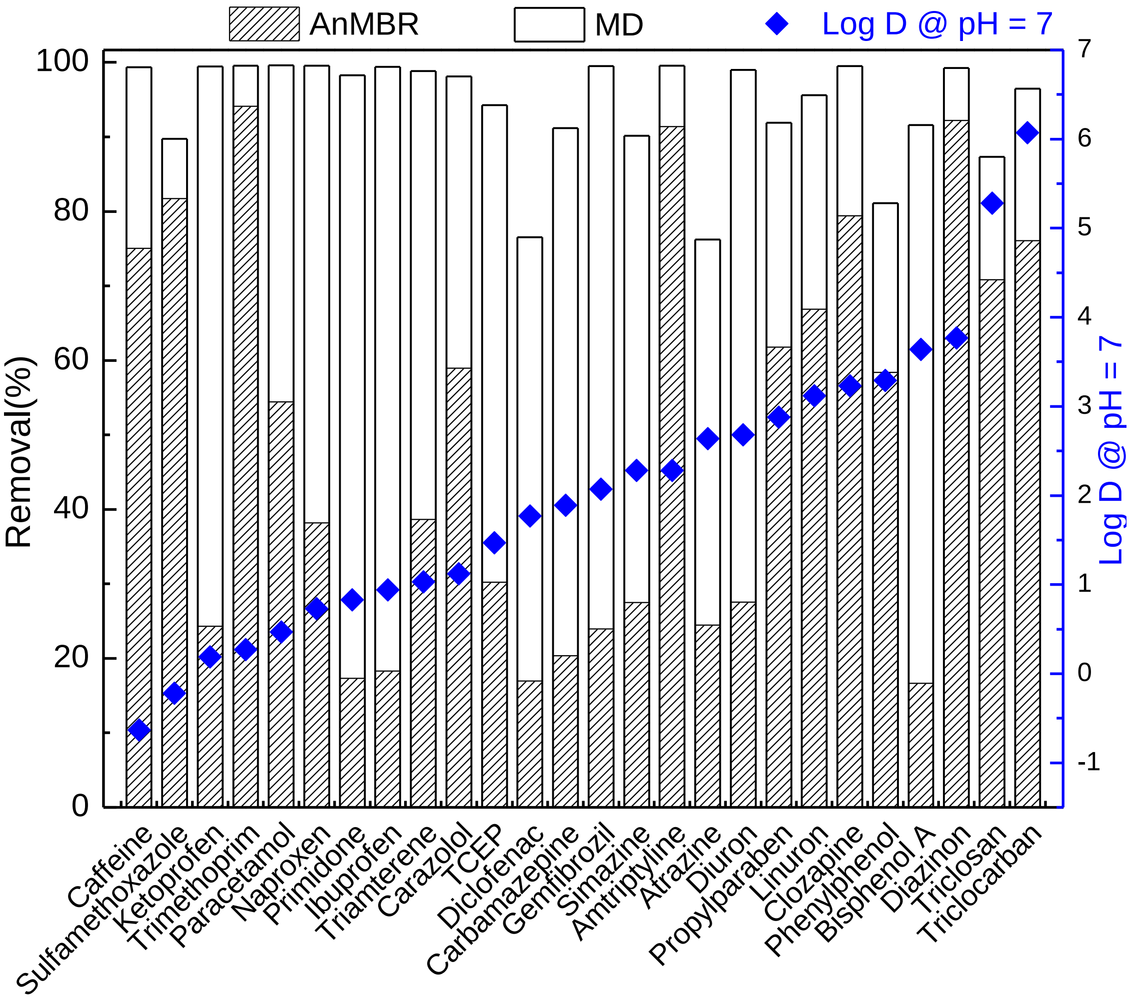

Figure 7: TrOC removal by AnMBR integrated with MD. TrOCs are listed in the order of increasing hydrophobicity. Based on their effective octanol-water partition coefficient (Log D) at solution pH of 7, the 26 TrOCs investigated were classified as hydrophobic (Log D > 3.2) and hydrophilic (Log D < 3.2). Average removal rates from six measurements (once every five days) were shown with standard deviation in the range of 0.1 – 24%. Experimental conditions are summarized in the caption of Figure 2.

Several TrOCs were removed by AnMBR by over 70%. These TrOCs included caffeine, sulfamethoxazole, trimethoprim, amtriptyline, linuron, clozapine, diazinon, triclosan, and triclocarban (Figure 7). Given the relatively low hydrophobicity of caffeine, sulfamethoxazole, trimethoprim, and amitriptyline, their effective removal by AnMBR could be attributed to the high intrinsic biodegradability with the presence of electron donation groups, such as amine and hydroxyl, in their molecular structures (Tadkaew et al., 2011). By contrast, linuron, clozapine, diazinon, triclosan, and triclocarban were highly hydrophobic with Log D values higher than 3.2 (at pH = 7). Thus, these compounds could effectively be retained by anaerobic digesters and thus facilitate their biodegradation and hinder their permeation through the MF membrane.

Although TrOC removal by AnMBR was highly variable and strongly dependent on the specific molecular properties of each compound, the MD process could consistently enhance the overall TrOC removal. Indeed, the MD process could effectively reject all TrOCs selected in this study (Figure S1, Supplementary Data). As a result, over 76% removal of all TrOCs could be achieved by the integrated AnMBR-MD system (Figure 7). The role of MD in this hybrid system for TrOC removal was most significant for these compounds (such as, primidone, ibuprofen, diclofenac, and bisphenol A) that were poorly removed by AnMBR.

4 Conclusion

Results reported here suggest that the MD process could complement very well with AnMBR for energy and water recovery. AnMBR could produce 0.3 – 0.5 L/g COD_{added} biogas (approximately 65% methane). By integrating MD with AnMBR, high removal of organic matter and nutrients could be achieved. The high retention capacity of the MD membrane resulted in significant phosphate accumulation in the feed solution, thereby producing an opportunity for phosphorus recovery from AnMBR effluent. The synergy between the biological treatment and the MD membrane rejection contributed to 76% to complete removal of all 26 selected TrOCs by the integrated AnMBR-MD system. Further research is necessary to address the issue of MD membrane fouling when it is coupled with AnMBR for phosphorus recovery and water reuse applications.

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