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**Assessing the removal of organic micropollutants by a novel baffled osmotic membrane
bioreactor-microfiltration hybrid system**

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Abstract

A novel approach was employed to study removal of organic micropollutants (OMPs) in a baffled osmotic membrane bioreactor-microfiltration (OMBR-MF) hybrid system under oxic–anoxic conditions. The performance of OMBR-MF system was examined employing three different draw solutes (DS), and three model OMPs. The highest forward osmosis (FO) membrane rejection was attained with atenolol (100 %) due to its higher molar mass and positive charge. With inorganic DS caffeine (94-100 %) revealed highest removal followed by atenolol (89-96 %) and atrazine (16-40 %) respectively. All three OMPs exhibited higher removal with organic DS as compared to inorganic DS. Significant anoxic removal was observed for atrazine under very different redox conditions with extended anoxic cycle time. This can be linked with possible development of different microbial consortia responsible for diverse enzymes secretion. Overall, the OMBR-MF process showed effective removal of total organic carbon (98%) and nutrients (phosphate 97% and total nitrogen 85%), respectively.

Keywords: Biofouling; Microfiltration (MF); Osmotic membrane bioreactor (OMBR); Organic micropollutants (OMPs); Salinity build-up.

1. Introduction

With rapidly growing world's population, climate change and extensive industrialization pressure is increasing on the limited fresh water resources (Kim et al., 2017). Increased water scarcity led to advancement of many technologies that utilize alternative water sources, such as domestic sewage. This can help in protecting environment and ease water paucity by indirect and direct reuse of impaired water (Luo et al., 2016). Nevertheless, wastewater treatment processes facing some issues, specifically regarding organic micropollutant removal (Nguyen et al., 2016). Removal of OMPs from wastewater by current physico-chemical technologies is prohibitively expensive (Singhal & Perez-Garcia, 2016). Wastewater treatment facilities using conventional activated sludge treatment are ineffective and inconsistent of degrading the wide range of organic micropollutants that could potentially pose risks to humans and the environment (Holloway et al., 2014; Singhal & Perez-Garcia, 2016).

Therefore, main concern to reclaimed water application is unpredictable and usually limited OMPs removal by traditional wastewater treatment processes (Luo et al., 2016). Novel OMPs removal or destruction options are activated carbon, ultraviolet (UV) disinfection and advanced oxidation processes (AOP). Also, membrane bioreactor (MBR), reverse osmosis (RO), nanofiltration (NF) and more recently, forward osmosis (FO) have been used extensively. In various studies it was found that the removal efficiency mostly depends on OMPs hydrophilicity, surface charge, and bio degradability (Besha et al., 2017; Coday et al., 2014; Luo et al., 2016). Advanced treatment processes based on MBR technologies can achieve higher and more consistent micropollutants removal compared to conventional systems (Besha et al., 2017). It has been investigated that MBR process efficiently remove moderately biodegradable and hydrophobic OMPs to conventional process (Park et al., 2015). Although MBR effectively removes some of the OMPs like ibuprofen, it cannot be

used as an absolute barrier to effectively remove some poorly biodegradable OMPs (Alturki et al., 2012; Besha et al., 2017). In fact, MBR could not remove hydrophilic OMPs very well due to their persistent nature and low bio-adsorption on sludge (Luo et al., 2017b).

More recently research effort has been dedicated to the development of an innovative osmotic membrane bioreactor (OMBR) process, which uniting activated sludge process with forward osmosis (FO) membrane (Luo et al., 2015b; Nguyen et al., 2015). FO membrane appeared as a robust alternative for the indirect and direct potable reuse applications and a good barrier to OMPs in the bioreactor thereby aiding their consequent biodegradation (Coday et al., 2014). OMBRs have many advantages such as higher quality product water, lower fouling propensity than conventional membrane processes and better energy efficiency. However, the salt accumulation in the mixed liquor due to the reverse salt flux (RSF) from the draw solution (DS) and the osmotic concentration of the feed solution leads to a reduced driving force for permeate flux and also affect the biological activity inside the reactor (Lay et al., 2010; Luo et al., 2015a; Nguyen et al., 2015; Pathak et al., 2017; Qiu & Ting, 2013).

Nitrogen compounds are nutrients limiting sewage treatment and they can cause a variety of problems, including a reduction in concentrations of dissolved oxygen in water sources which can lead the death of fish and also bring about eutrophication (Derakhshan et al., 2018). Nitrogen removal by simultaneous nitrification/denitrification (SND) requires a separate anoxic tank in the process with circulation of the mixed liquor from the anoxic tank and membrane tank in a MBR plant. Circulation of the mixed liquor suspension accounts for 10-15% of total energy consumption in current MBRs. Kimura et al. (2007) proposed a baffled membrane bioreactor that can eliminate the energy needed for the mixed liquor circulation. In our previous work, Pathak et al. (2017) successfully demonstrated the performance of a novel baffled OMBR in which baffles are inserted in the reaction tank and feed water is drawn through FO membranes. By utilizing this method, SND can be promoted in a single reactor.

As a result, sludge recirculation pump and anoxic tank mixer can be omitted (Pathak et al., 2017).

This paper investigated the technical feasibility of a baffled OMBR-MF hybrid system for wastewater treatment applications, in particular the efficiency of OMPs removal under oxic-anoxic conditions. This study also evaluated carbonaceous organic removal and nutrient removal in a baffled OMBR-MF system employing inorganic and organic draw solutes. The baffled OMBR-MF system performance was investigated in terms of permeate flux and salt accumulation, analysing growth of biofouling layer and microbial activity using confocal laser scanning microscopy (CLSM), extracellular polymeric substances (EPS) and floc size analysis respectively. Lastly, three model OMPs were analysed to evaluate the feasibility for wastewater reuse.

2. Materials and methods

2.1 FO and MF membrane characteristics

The Hydration Technology Innovations (HTI) (Albany, OR, USA) made Cellulose triacetate (CTA) FO membranes was employed in this work (Kim et al., 2017). FO membrane area was 0.0264 m². The submerged FO membrane module was custom designed and fabricated using stainless steel (SS). The hollow-fiber micro-filtration (MF) membrane (Uniqflux Membranes LLP, India) was employed in this study. The MF membrane had 0.1 m² area and a nominal pore size of 0.33 µm respectively.

2.2 Feed solutions

All the chemicals used in this research were of reagent grade (Sigma Aldrich Saudi Arabia). The feed to the OMBR-MF hybrid system was a simulated sewage consisting of 300 mg/L glucose, 50 mg/L yeast, 15 mg/L KH₂PO₄, 10 mg/L FeSO₄, 60 mg/L (NH₄)₂SO₄, and 30 mg/L urea. The simulated sewage was prepared from stock solution providing 350 mg/L

chemical oxygen demand (COD), 16 mg/L ammonium nitrogen ($\text{NH}_4\text{-N}$), 28 mg/L total nitrogen (TN) and 3.5 mg/L phosphate ($\text{PO}_4\text{-P}$).

In lab-scale baffled OMBR-MF hybrid system three OMPs removal was examined. Atenolol, atrazine and caffeine were supplied by Sigma Aldrich (Saudi Arabia). All three OMPs commonly exist in sewage and considered as persistent to conventional activated sludge process. Atenolol is a beta-blocker retaining both electron donating groups ($-\text{OR}$, $-\text{CH}$) and electron withdrawing group ($-\text{CONH}_2$). Similarly atrazine is a herbicide also has electron donating group ($-\text{NHR}$) and electron withdrawing group ($-\text{Cl}$). Wei et al. (2016) reported that caffeine being a stimulant and its removal was too less in the beginning and it would need longer adaptation time even though cyclic structure has strong electron donating group ($-\text{R}$).

2.3 Draw solutions

The DS employed in this study were prepared to make 0.75 M by dissolving respective salts of three different chemicals sodium chloride (NaCl), potassium chloride (KCl) and sodium acetate (CH_3COONa or NaOAc) in deionized (DI) water. The chemicals used in this study were reagent grade procured from Sigma-Aldrich, Saudi Arabia. NaCl and KCl were selected as inorganic DS and NaOAc was chosen as organic DS to compare the performance of baffled OMBR between inorganic and organic draw solutes. NaCl is commonly used inorganic ionic salt draw solute in most of all OMBR studies. KCl is inorganic salt with high water flux. These solutes are ideal for minimizing ICP and creating high osmotic pressures. Both NaCl and KCl possess high solubilities in water and no toxicity. The use of organic based draw solutes such as salts of NaOAc exhibits significantly lower reverse salt flux than that for inorganic DS. Additionally, organic DS are biodegradable and do not contribute toward salinity build-up in the bioreactor (Achilli et al., 2010; Bowden et al., 2012; Yap et al., 2012). Thermodynamic properties of DS were determined at temperature of 20 °C using

OLI Stream Analyzer (OLI System Inc., Morris Plains, NJ, USA) and provided in **Table 1**. The osmotic pressure of 0.75 M NaCl, KCl and NaOAc were 34.08, 32.45 and 30.38 atm respectively. The corresponding diffusivities were 1.32×10^{-9} m²/s, 1.61×10^{-9} m²/s and 1.07×10^{-9} m²/s for NaCl, KCl and NaOAc respectively.

2.4 Baffled osmotic membrane bioreactor-microfiltration (OMBR-MF) experimental set-up and operation

A lab-scale baffled OMBR-MF system was used in this study and a schematic of the system is shown **Fig.1**. The OMBR-MF system comprised of a feed tank, a plexiglass baffled bioreactor into which FO membrane cell was immersed and a hollow fibre MF membrane module, a concentrated DS reservoir and a diluted DS reservoir. The incorporation of the MF module was to alleviate salinity build-up as well as to maintain constant hydraulic retention time (HRT) by adjusting the MF flux as the FO flux decreases with time during continuous operation. The bioreactor tank (i.e., 24.5 cm length * 15.5 cm width * 40 cm height) had an effective volume of 10.5 L. The concept and operating details of the baffled reactor are discussed elsewhere (Kimura et al., 2007; Pathak et al., 2017). The seed sludge was collected from the wastewater treatment plant (WWTP) in the King Abdullah University of Science and Technology (KAUST)-Thuwal, Saudi Arabia. The sludge was acclimatized for two weeks prior to adding into the baffled OMBR-MF system. The OMBR-MF hybrid system was continuously operated for 7 days for each DS employed in this study under similar operating conditions. The mixed liquor suspended sludge (MLSS) was initially adjusted to 3-3.5 g/L. Throughout the operation, 70 d solids retention time (SRT) was maintained by wasting measured quantity of sludge from the bioreactor. By employing the level controller, the oxic cycle time was set 0.5 h (level controller leg 0.5 cm above the baffle tip) and anoxic cycle time 1.5 h (level controller leg 1.5 cm below the baffle tip) can be adjusted accordingly. The air diffuser was installed inside the oxic zone and 3 LPM airflow rate was maintained.

The oxic zone pH was varying in the range of 6.86-7.35 and for the anoxic zone pH variation was observed from 7.18-7.67 respectively. The continuous-flow experiments were conducted in active layer facing feed side (AL-FS) mode using the CTA-FO membrane. The HRT of the combined baffled OMBR-MF system was set at about 30 h by adjusting MF permeate as FO flux decreased. The concentrated DS was refilled twice a day and the diluted DS tank was emptied. Salinity build up in the OMBR mixed liquor was measured by conductivity meter. The pH, total dissolved solids (TDS) and conductivity of the mixed liquor, permeate and DS were measured at regular intervals (HACH, Germany). The OMBR-MF hybrid system was operated from day 1 to 7, day 10 to 16 and day 19 to 25 using KCl, NaCl and NaOAc DS respectively. At end of each run FO operation was ceased and reactor was operated solely with MF membrane in order to reduce salinity to initial value. In the beginning of each run new CTA-FO membrane and new DS was employed.

OMPs removal in the reactor and MF can be obtained using Eq. (1). Since FO utilized DS, OMPs removal in FO should be calculated in a different way using Eq. (2) (Cui et al., 2014).

$$R_{OMPs} = \left(1 - \frac{C_{OMPs}}{C_{OMPs,f}}\right) \times 100\% \quad (1)$$

$$R_{FO,OMPs} = \left(1 - \frac{C_{D,OMPs} \times V_D / V_P}{C_{OMPs,f}}\right) \times 100\% \quad (2)$$

Where, R_{OMPs} is the removal efficiency for organic micropollutants in the reactor or MF membrane, $R_{FO,OMPs}$ is the removal efficiency for organic micropollutants in FO, C_{OMPs} is the concentration of OMPs in the MF permeate or the reactor (mmol/L), $C_{D,OMPs}$ is the concentration of OMPs in DS (mmol/L), $C_{OMPs,f}$ is the concentration of organic micropollutants in feed solution (mmol/L), V_D is the volume of DS (L) and V_P is the volume of the FO permeate (L).

2.5 Analytical methods

2.5.1 Biological parameters and basic water quality parameters

Total organic carbon (TOC) concentration was measured with a TOC analyzer (TOC-V-CSH, Shimadzu, Japan). The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) in the bioreactor were measured using APHA, AWWA, WEF (1998) standards. The concentration of dissolved oxygen (DO) was measured by using a DO meter (Vernier, USA). Chemical oxygen demand (COD) of wastewater was analysed according to standard methods (APHA, 1998). $\text{NH}_4\text{-N}$, TN and $\text{PO}_4\text{-P}$ were measured using Hach TNTplusTM reagent vials and HACH® Spectrophotometer DR5000. Samples were diluted as necessary to minimize chloride and other ion interferences. Mean particle size of the sludge flocs was measured by using a particle size analyzer (Malvern Mastersizer, UK).

2.5.2 EPS extraction and quantification

The formaldehyde-NaOH method was used to extract the extracellular polymeric substances (EPS) from the sludge (Zhang et al., 1999). The extracted samples were analysed for protein (PN) and polysaccharide (PS) concentrations, following the modified Lowry method (Sigma, Australia) and Anthrone-sulfuric acid method (Raunkjær et al., 1994), respectively. Standard curves of PN and PS were developed using various concentrations of Bovine Serum Albumin (BSA) and glucose, respectively.

Liquid chromatography-organic carbon detection (LC-OCD) developed based on size-exclusion chromatography (SEC) was utilized to characterize the water-soluble organic carbon (OC) such as polysaccharides and proteins found in EPS.

2.5.3 Confocal laser scanning microscopy (CLSM)

The fouled FO membranes were removed from the bioreactor at the end of each experimental run with all three DS. For each sample, the membrane was cut into 1.0 cm x 1.5 cm membrane coupons to ensure the representativeness of results. The fouled membrane samples were stained with a mixed dye for both live and dead bacteria (LIVE/DEAD BacLight from Molecular Probes company), which consisting of SYTO 9 and Propidium iodide dyes. After staining, the membrane coupons were kept at ambient temperature under dark for half an hour.

2.5.4 LC-MS for organic micropollutants measurement

OMPs analysis was performed by following same protocol as mentioned in previous work (Wei et al., 2016). For each OMP analysis 50 ml sample was aliquoted. This OMP sample was spiked with the corresponding isotopes and then concentrated using solid phase extraction device (Dione Autotrace 280) followed by evaporation. The OMP concentration was measured using liquid chromatography-mass spectroscopy (LC-MS) (Agilent Technology 1260 Infinity Liquid Chromatography unit, USA and AB SCIEX QTRAP 5500 mass spectrometer, Applied Biosystems, USA).

3. Results and discussion

3.1 Process performance of OMBR system

Fig. 2 (a) illustrates the variation of FO and MF water flux as a function of time for each draw solution and salt accumulation in the mixed liquor. Among the three different DS, KCl produced the highest permeate flux (7.95-6.5 LMH (litres per square meter per hour)) followed by NaCl (7.46-6.0 LMH) and then NaOAC (7.1-2.6 LMH) at a similar molar concentration. This can be attributed to the osmotic pressure difference and corresponding diffusivity of the different DS tested.

At 0.75 M DS concentration, the osmotic pressure of NaCl is 34.1 bar and for KCl is 32.5 bars, respectively. However, the diffusivity of KCl ($1.61 \times 10^{-9} \text{ m}^2/\text{s}$) is much higher than NaCl ($1.32 \times 10^{-9} \text{ m}^2/\text{s}$), which justifies the higher initial water flux for KCl DS (7.95 LMH) than other two DS NaCl (7.46 LMH) and NaOAc (7.06 LMH). Furthermore, the viscosity of KCl is also less than NaCl. NaOAc has a lower osmotic pressure and diffusivity and higher viscosity, which is linked to the lowest initial water flux among the three DS employed in this study. Moreover, it has been reported that the small diffusion coefficient of NaOAc was responsible for severe internal concentration polarisation within the FO membrane support layer thus lowering the water flux (Luo et al., 2016). A significant permeate flux decline within seven days of the experiment was observed for NaOAc DS.

The normalised water flux of all three DS is shown in **Fig. 2 (b)**, where a decrease with time is observed for all three DS. The flux decline trend is much quicker for NaOAc DS followed by KCl and NaCl, respectively. The SRSF from the draw side to the feed is another significant and unique aspect in osmotically driven membrane operations (Alturki et al., 2012). Specific reverse salt flux (SRSF) is defined as the ratio of reverse salt flux (RSF) of draw solutes and water flux is a valuable parameter for DS performance in FO process. Independent of the concentration, the values of SRSF remain relatively constant for each salt. Lower values of SRSF indicate minimum salt loss or less reverse transport of solute (Achilli et al., 2010; Bowden et al., 2012; Siddique et al., 2017). SRSF of NaCl, KCl and NaOAc were 0.74, 1.14 and 0.26 g/L respectively (Data adapted from Siddique et al. (2017); Bowden et al., (2012) and Achilli et al. (2010)). The SRSF value is the lowest for NaOAc (0.26 g/L) among the three DS. Basically, organic DS NaOAc showed very low RSF due to its large molar mass and so lower diffusion coefficient. Much lower salt accumulation in a reactor with NaOAc can be linked to low water flux exhibited by organic DS as compared to other two inorganic DS NaCl and KCl. The rapid flux declined can also be attributed to the

severe membrane fouling. NaOAc being an organic DS, can support the microbial growth on the membrane surface thereby promoting an additional barrier to the water permeation. In another OMBR study, it was also observed that using NaOAc as an organic DS the RSF from draw side to the reactor could provide carbon source (acetate) for bacteria which contributed to severe FO membrane fouling. Further, in comparison to inorganic DS NaCl less salt accumulation was noticed in the reaction tank for NaOAc DS (Luo et al., 2016). The SRSF is the highest for KCl manifested by the increased salinity in the bioreactor followed by NaCl DS. The hydrated diameter for K is lower than Na (Achilli et al., 2010) which also leads to more SRSF (1.14 g/L) for KCl as compared to other two Na based DS. As a result NaCl showed relatively less flux decline and salinity increase in the bioreactor during one week process.

In this experiment reactor TDS increased from about 470-2500 mg/L for KCl, 485-1882 mg/L for NaCl followed by NaOAc at 476-971 mg/L (**Fig. 2(a)**). The lower TDS increase was observed for NaOAc due to its low SRSF (0.26 g/L) as compared to KCl (1.14 g/L) and NaCl (0.75 g/L). Lower RSF which allowed less amount of NaOAc to accumulate in the bioreactor. Moreover, NaOAc is an organic DS so it can easily be consumed by microbes. NaOAc is widely used as an external carbon source in wastewater treatment specifically to enhance denitrification. This means biomass is capable of oxidising acetate (electron donor) more readily and use carbon and energy for metabolism which is not possible with other inorganic DS. Thus, the combined effects of low RSF (0.26 g/L) as well as consumption of acetate ion as a substrate by microbes led to less salinity build up when NaOAc was employed as DS. For the 0.75 M NaCl employed, salinity increased from 0.49 g/L to 1.88 g/L which is similar to observations in another OMBR study reporting a salinity increase from 0.17 g/L to 4.13 g/L in one week OMBR operation with 1 M NaCl (Alturki et al., 2012). In

the present study, incorporation of a MF membrane unit was therefore done to alleviate salt accumulation in the mixed liquor.

3.2 Organic-micropollutants (OMPs) removal

The removal of organic micropollutants is mainly directed by the interaction between physical rejection by the FO membrane and biological degradation in the reactor (Eyvaz et al., 2016). **Fig. 3** shows the rejection rate of OMPs in oxic and anoxic reactors as well as by MF and FO membranes during one week of continuous operation. The OMBR-MF hybrid system exhibited excellent removal for all OMPs ranging between 93-100 % respectively. These results are in agreement with previous OMBRs studies showing high removal of OMPs by this system (Holloway et al., 2014; Luo et al., 2017b). In fact, due to great rejection by FO membrane followed by adsorption onto the biomass which provides extended detention time in the OMBR tank might have facilitated improved biodegradation of OMPs (Wang et al., 2016).

Results show that the highest FO membrane rejection was attained with atenolol (100 %) employing all three DS. Atenolol possess highest molar mass (266.3 g/mol) compared to the other two OMPs can be attributed to highset rejection (Kim et al., 2017). Alturki et al. (2012) reported in their OMBR study that almost all OMPs having larger than 266 g/mol molar mass revealed outstanding removal efficiency. Wang et al. (2016) noticed that typically hydrophilic OMPs with more than 200 g/mol molar mass could be effectively detained by FO membrane. They attributed this improved OMPs removal either due to the size exclusion or adsorption phenomena. Moreover, atrazine and caffeine have neutral charge while atenolol has positive charge (Kim et al., 2017). Holloway et al. (2014) also noticed high FO rejection for atenolol with similar CTA membrane for sewage treatment in bench scale and pilot scale studies. Under neutral pH and ambient conditions of this study CTA FO membrane remained

relatively uncharged. However, positively charged atenolol has higher molar mass and hydrated diameter as compared to two neutral OMPs employed in this study. Thus, steric hindrance would have predominantly affected OMPs transfer and rejection (Holloway et al., 2014; Kim et al., 2017). Moreover, it has been postulated that membrane fouling leads to membrane pore blocking. This further inhibited OMPs partitioning through the membrane due to its adsorption to the biofouling layer (Holloway et al., 2014). This can be attributed with the results obtained in present study as a thick biofilm for NaOAc > NaCl > KCl provided high rejection of all three studied OMPs, respectively.

Due to high retention capacity of FO membrane, OMPs could have detained in the reactor for much longer than actual HRT. Subsequently, the increased retention time could facilitate further biological degradation (Alturki et al., 2012). Caffeine is readily and completely biodegradable compound (Dorival-García et al., 2013) and it showed high removal in bioreactor more than 94 % with all three DS. Trinh et al. (2016) have examined effect of salinity shock on OMPs removal efficiency in MBR study. They have observed that in 24 h time after introducing the salinity shock of 20 g/L, 97 % caffeine removal efficiency was achieved. Authors have reported that caffeine removal was slightly reduced under high salinity conditions. In another MBR study caffeine removal efficiency was found to range between 96–99% regardless of its exposure to simulated hazardous events such as ammonia shock or aeration failure (Phan et al., 2015a). Higher caffeine removal can be related to the fact that caffeine is easily biotransformable compound and its biotransformation is thus maintained by the subset of organisms or metabolic processes not impacted by the shocks (Phan et al., 2015a; Trinh et al., 2016). When KCl DS was employed anoxic zone achieved higher caffeine removal 98 % as compared to oxic zone (94 %). Atenolol showed more than 90 % removal for both oxic and anoxic in this study with all three DS. Employing NaCl DS in anoxic zone 96 % atenolol removal was obtained as compared to 89 % in oxic zone. Other

literatures also reported that MBRs achieved high and stable removal (>90%) of eight pharmaceuticals and personal care products (PCPs) including atenolol and caffeine (Phan et al., 2015a; Phan et al., 2015b; Trinh et al., 2016). Atenolol and caffeine are hydrophilic and thus biodegradation is thought to be the major removal mechanism during biological treatment processes (Phan et al., 2015b). Phan et al. (2014) also reported good removal of the atenolol and caffeine which can be attributed to the existence of anoxic tanks. Park et al. (2009) reported that in a constructed wetland relatively high atenolol (95 %) removal efficiency was achieved. The presence of amide functional group in atenolol is thought to make it amenable to biodegradation via mediated hydrolysis reactions under anoxic conditions, as the pond was relatively stagnant with longer hydraulic residence time. In our study DO level variation with extended anoxic conditions might have created favourable conditions for higher micropollutant removal.

Atrazine removal in the oxic and anoxic reactors varied in the range of 22-40% and 16-51% respectively for all three DS. Further, in comparison to caffeine and atenolol inferior removal of atrazine can also be attributed to its persistent nature towards biodegradation. Alturki et al. (2012) examined OMPs removal using OMBR and they reported that certain micropollutants such as diuron, triamterene, simazine including atrazine were too persistent to biodegradation and less than 50% removal efficiency could have been achieved. Luo et al. (2015a) previously reported that low removal of OMPs could be referred either to the absence of electron donating group (EDG) or presence of strong electron withdrawing group (EWG), such as $-\text{Cl}$, $-\text{NH}_2$ and $-\text{NO}_2$ bonds attached to benzene ring structure. Atrazine possess halide ($-\text{Cl}$) the electron withdrawing functional group attached to the cyclic ring responsible for inferior biological process performance in our study (Luo et al., 2017a). Phan et al. (2014) in their MBR study observed < 20 % atrazine removal when operated at internal recirculation ratio of 3 and at 25 d SRT. They also reported that atrazine and ametryn are both triazine

compounds, but only ametryn was well removed (80%), possibly because of the presence of –Cl (strong EWG) in atrazine but not in ametryn. Despite its recalcitrant nature, due to their extended retention in the bioreactor, biodegradation was still the most prevalent removal mechanism of hydrophilic atrazine in OMBR–MF hybrid system.

When NaCl and NaOAc DS was employed, 40% and 51% atrazine removal was observed in the anoxic zone in the baffled reactor compared to 30% and 39 % removal in oxic zone respectively. In this study due to the extended anoxic period (1.5 h) relatively better anoxic conditions prevailed evidenced by too low DO concentration in anoxic zone of baffled OMBR (DO profile was shown in our previous work). Hai et al. (2014) reported that near-anoxic conditions (DO = 0.5 mg/L) can be a favourable operating regime for the removal of the persistent OMPs such as carbamazepine possess strong EWG groups such as N=O and NH₂ which was similar like halide (-Cl) group in atrazine. In another study Derakhshan et al. (2018) elucidated very high (74 %) biodegradation of atrazine in the anoxic moving bed biofilm reactor under nitrate reduction conditions. They reported that atrazine biodegradation was improved (74 %) in the presence of nitrates in comparison with absence of nitrate that showed only 10 % atrazine removal. In addition atrazine and nitrate compete for reduction by denitrifying bacteria, nonetheless both molecules simultaneously reduced though denitrifying bacteria prefer nitrate to atrazine as an electron acceptor. Also, anoxic mixed biofilm culture was suitable for the atrazine degradation therefore atrazine removal mechanism in this system was co-metabolism. In our study relatively high atrazine removal in anoxic zone could also be attributed to the existence of attached biomass on to the outer baffle wall as well to the inside wall of the reactor in anoxic zone. Further, oxic-anoxic cycle variation must have created very different DO levels in the baffled reactor with extended anoxic cycle time. This might have created different redox conditions that could be responsible for the growth of different microbial consortia inside attached biomass leading to the excretion of diverse

enzymes. Thus, varying degree of biodegradation was observed with atrazine micropollutant in oxic and anoxic zones respectively (Phan et al., 2014). Future work has been planned to address microbial community dynamics in oxic and anoxic zone in the baffled bioreactor to elucidate its impact on OMPs removal.

3.3 Carbonaceous organics and phosphorous removal

The hybrid OMBR-MF system, with an integrated MF unit to alleviate salt accumulation resulted in an almost complete removal in terms of TOC regardless of DS used due to the high retention characteristics of the FO membrane, longer HRT and SRT (**Fig. 4 (a)**). Average concentrations of TOC in the diluted KCl, NaCl and NaOAc DS were 1.59 ± 0.60 , 1.95 ± 0.47 and 1.27 ± 0.27 mg/L, respectively, representing removal efficiencies of 98, 98 and 99 %. Other OMBR studies have reported 98-99 % global TOC removal. As FO membrane has very high pollutant selectivity, insignificant seepage of TOC into the DS was noticed during the OMBR process (Achilli et al., 2009; Qiu & Ting, 2014; Tan & Ng, 2008). In our study, a similar performance by OMBR process was achieved.

The OMBR performance in terms of phosphate ($\text{PO}_4\text{-P}$) removal was evaluated for all three DS (**Fig. 4 (b)**). Due to the high retention properties of the FO membrane, substantial enrichment of phosphate within the bioreactor was anticipated for each DS. An accumulation was reported in other OMBR studies and related to the effective FO membrane rejection based on a negatively charged and large hydrated diameter of the ortho-phosphate ion (Luo et al., 2016). With an average influent phosphate concentration of 3.53 ± 0.29 mg/L, the concentration in the mixed liquor was found to be 1.13 ± 0.16 mg/L (**Fig. 4 (b)**). However, the salinity build-up in the case of the inorganic DS generated a detrimental condition for phosphorous accumulating organisms (PAOs). It is generally hypothesized that salt accumulation within the cells not only adversely affects the sensitivity of PAOs but also reduces the phosphate accumulating ability of microbes increasing the osmotic stress within

the cells (Lay et al., 2010; Luo et al., 2016). A reasonable overall phosphate removal (68%) in mixed liquor under strict anoxic conditions was the result of higher biomass activity. Aftab et al. (2015) also reported a lower accumulation of phosphate due to increased microbial activity resulting in higher phosphate consumption, this latter fulfilling the nutrient demand of PAOs with the incorporation of MF membrane. The FO process achieved more than 97 % removal of phosphate for each DS due to excellent rejection offered by FO membrane.

3.4 Simultaneous nitrification-denitrification (SND) in OMBR-MF hybrid system

Nitrification of ammonia in domestic wastewater is first required before it can be further denitrified into molecular nitrogen. However, nitrification remains a limiting step in SND process due to high DO and longer SRT requirement (Kimura & Watanabe, 2005; Tan & Ng, 2008). **Fig. 5** (a) and (b) show the removal of $\text{NH}_4\text{-N}$ and TN for all three DS at the same molar concentration. Nitrification is a very sensitive process, as the nitrifying microbes involved in the process are slow growing and highly susceptible to the process conditions such as DO concentration and increased salt concentration (Lay et al., 2010). Permeate quality showed that more than 98% of $\text{NH}_4\text{-N}$ removal was achieved for all DS. Almost complete nitrification was achieved in this study and can be attributed to sufficient oxygen availability and maintaining longer SRT of 70 d. Hence limitation in nitrification was not observed (Tan & Ng, 2008). The trend of $\text{NH}_4\text{-N}$ build-up was observed for inorganic draw solutes in previous studies with high saline stress in the bio-tank (Luo et al., 2015b; Qiu & Ting, 2013). Recently Siddique et al. (2017) noticed $\text{NH}_4\text{-N}$ accumulation in the bioreactor using inorganic DS. The main reason for $\text{NH}_4\text{-N}$ accumulation was reported as high salinity (7-10 g/L) build up in the reactor. Holloway et al. (2015) also observed $\text{NH}_4\text{-N}$ accumulation for about 3 weeks due to high salinity build up (3-8 g/L) in the bioreactor. Elevated salt concentrations had adversely affected microbial community and salinity build up (up to 8 g/L) was the major cause for loss of nitrification. In the same study in next the phase when

the system was operated with UF membrane in parallel to FO better $\text{NH}_4\text{-N}$ removal was achieved throughout the operation due to low salinity level (1 g/L) employing UF subsystem. In contrast to the previous results (Holloway et al., 2015; Siddique et al., 2017) a high removal of $\text{NH}_4\text{-N}$ within the bioreactor was observed (**Fig. 5 (a)**) throughout the operation with both the inorganic and organic DS. Compared to other OMBR studies, incorporating MF membrane in the bioreactor mitigated salinity build-up (0.9 to 2.4 g/L), and good nitrification was achieved due to the high SRT and sufficient aeration employed in the present study. In another OMBR-MF hybrid study salinity build up to 5 mS/cm in the bioreactor was effectively controlled by combining MF membrane in comparison to 50 mS/cm in the conventional OMBR without MF membrane. In this study 98 % $\text{NH}_4\text{-N}$ removal was achieved using CTA-FO membrane (Wang et al., 2014b).

Overall TN removal efficiencies in the reactor were 73 % at a low aeration rate of 2-3 L air/min. TN removal was > 84 % in the FO permeate for all DS. Remarkable denitrification achieved in the baffled OMBR-MF hybrid system was possibly due to the FO membrane rejection of nitrite/nitrate species, which prolonged their retention in the bioreactor, thus facilitating their removal during the anoxic cycle under very low DO concentration.

3.5 Fouling behaviour in OMBR-MF hybrid system

3.5.1 SMP and EPS measurement

It is well known that the SMP and EPS play important roles in membrane fouling. SMP and EPS are both heterogeneous and generally comprise a range of organics mainly polysaccharides, proteins, humic acid, glycolipids and deoxyribonucleic acid (DNA) (Wang et al., 2014a). The different fractions of organics in OMBR mixed liquor supernatant were analysed by LC-OCD (integration values for chromatograph are shown in **Table 2**. The biopolymer ratio was around 1 %, 6 % and 23 %, respectively in supernatant of KCl, NaCl

and NaOAc, respectively. The humic substance ratio at MW 1000 g/mol was 2, 2 and 8 % in the supernatant of KCl, NaCl and NaOAc, respectively. Zhang et al. (2012b) also reported in their OMBR study higher humic concentration as compared to the conventional MBR. Further, this difference may stem from the high retention by FO membranes of the humic substances. The biopolymer percentage trend indicates there is an increasing amount of biofilm growth on the FO membranes and SMP formation in the order NaOAc > NaCl > KCl as a DS.

Proteins and polysaccharides content in the mixed liquor EPS were extracted as per the details mentioned in section 2.5.2. Total amount of protein and polysaccharide to volatile suspended solid ratio in the mixed liquor were 16.1, 15.4 and 14.2 mg/g VSS for KCl, NaCl and NaOAc DS, respectively. Further, protein like substances contributed more to the EPS than polysaccharide in all three DS examined. Proteins in EPS have been reported to have a strong positive influence on the hydrophobicity of microbial flocs and hence affect membrane fouling positively. Zhang et al. (2012a) also suggested that one of the main contributing factors to the biofouling was bound proteins content in EPS and its impact on sludge hydrophobicity.

3.5.2 Organic foulant on FO membrane

In order to describe foulant morphology on the FO membrane surface CLSM analysis was performed for all three DS tested. The CLSM images (not included in this revised manuscript) have shown that the average biofilm thickness at the end of each test run (7 days) was 84 μm , 94 μm and 113 μm for KCl, NaCl and NaOAc, respectively. However, attachment of a thick biofouling layer (113 μm) on the membrane surface was observed at the end of the filtration run with NaOAc which may add to the hydraulic resistance. In fact, the reverse organic salt flux (the acetate ion) acted as a carbon/food source for microbial growth

resulting in a thick biofilm formation on the membrane surface, as described by Ansari et al. (2015).

To get a better understanding of the foulants characteristics on the FO membrane surface, fouled membrane coupons were prepared after experiments and sonicated to extract and recover the foulants for LC-OCD analysis. The biopolymer and humic substances are considered as major fouling contributors. The foulant layer comprised of biopolymers (5, 6 and 12 % with KCl, NaCl and NaOAc DS respectively) followed by humic substances. This can be correlated with increasing fouling layer thickness for NaOAc > NaCl > KCl.

The particle volume distributions of sludge granules in the OMBR-MF system with different DS were measured, with results shown in **Fig. 6**. The sludge granules size distribution (in volume) was found to increase in the order KCl > NaCl > NaOAc, with average volume sizes of 144.94, 130.86 and 122.39 μm with three DS respectively. The larger floc size favoured a reduction of membrane fouling, which agreed with the variations of fouling layer thickness with three DS. Al-Halbouni et al. (2008) reported the positive effect of larger flocs who argue that large microbial flocs have a lower impact on membrane fouling. This is due to large flocs restricts other foulants once porous cake layer is established on the membrane (Le-Clech et al., 2006). In a recent OMBR study, an increase in particle size was observed for organic DS as acetate salts (NaOAc and MgOAc) (Siddique et al., 2017). In this study, however, floc size was found to decrease with NaOAc in addition to substrate COD reduction from 350 mg/L to 200 mg/L when NaOAc DS was used. The SRSF from NaOAc DS was 0.26 g/L that could supplement essential substrate requirement, however the organic load of system could not have delivered sufficient food for bacterial growth because of the low water flux (7.06 to 2.61 LMH) provided by the organic solute NaOAc (Eyvaz et al., 2016). Hence, the food to the microorganism (F/M) ratio might have been reduced or may have fluctuated as compared to the other two inorganic DS. This could be the possible reason for the low EPS quantity into

the mixed liquor as evidenced by slightly less EPS content with NaOAc DS, subsequently resulting in the smaller floc size for NaOAc as compared to the other two DS.

However, thick biofouling layer (113 μm) with NaOAc should not be confused with smaller NaOAc average particle size (122.39 μm) among three DS. The possible explanation could be low reverse salt flux (RSF) from NaOAc DS in the first instance had to pass through active layer of FO membrane. Organic DS as a food source was easily available to the microbes attached to the membrane surface. Microbes were easily proliferated due to this favourable conditions as compared to inorganic DS thereby accelerated biofilm growth. When acetate ions reached to the reactor mixed liquor available food would be insufficiently led to lower F/M ratio consequently smaller floc size was observed.

4. Conclusions

This study investigated OMPs removal, flux performance and fouling behaviour employing three different DS in a novel hybrid baffled OMBR-MF system. With inorganic DS caffeine showed higher removal (94-100 %) as compared to atenolol (89-96 %) and atrazine (16-40 %) respectively. Atrazine as a refractory compound exhibited significant anoxic removal with alterations in redox conditions in anoxic zone and due to probably different microbial community proliferation. The organic DS NaOAc showed maximum biofilm thickness due to readily available acetate from RSF supporting microorganisms growth on the membrane surface as compared to the other two inorganic DS.

Appendix A. Supplementary data

"E-supplementary data for this work can be found in e-version of this paper online"

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Table Captions:

Table 1. Characteristics of draw solution (DS) used in OMBR-MF system.

Table 2. Different fractions of soluble microbial products in the initial reactor mixed liquor and different DS mixed liquors at the end of the experiment.

Figure Captions:

Fig. 1 Schematic of lab scale baffled OMBR-MF combined system.

Fig. 2 Variations of (a) Water flux and (b) normalised flux with time in baffled OMBR-MF hybrid system using three different DS. (feed: synthetic wastewater; draw solution: 0.75 M KCl, NaCl and NaOAC; temperature: 20 ± 5 °C; membrane orientation: active layer facing the feed solution; 7 days operation for each DS).

Fig. 3. Variations of OMPs removal in baffled OMBR-MF hybrid system using different DS.

Fig. 4 Variations of (a) TOC and (b) $\text{PO}_4\text{-P}$ removal in baffled OMBR-MF hybrid system using different DS.

Fig. 5 Variations of (a) $\text{NH}_4\text{-N}$ and (b) TN removal in OMBR-MF hybrid system using different DS.

Fig. 6. Particle size distribution of sludge granules in baffled OMBR-MF hybrid system employing different DS.

Table 1. Characteristics of draw solution (DS) used in OMBR-MF system

Chemicals	Potassium chloride	Sodium chloride	Sodium acetate
Formula	KCl	NaCl	CH ₃ COONa
Molecular weight (g/mol)	74.6	58.5	74.6
Concentration (M)	0.75	0.75	0.75
Osmotic pressure (atm)	32.45	34.08	30.38
Diffusivity ($\times 10^{-9} \text{ m}^2/\text{s}$)	1.61	1.32	1.07
Viscosity (cP)	0.99	1.07	1.31

Thermodynamic properties were determined at temperature of 20 °C by using OLI Stream Analyzer.

Table 2. Different fractions of soluble microbial products in the initial reactor mixed liquor and different DS mixed liquors at the end of the experiment

Approximate molecular weights (g/mol):							
			>> 20,000	~1000	~300-500	< 350	< 350
		DOC	Biopolymers	Humic substances	Building blocks	LMW neutrals	LMW acids
Initial Reactor	mgC/L	9.25	0.22	0.05	0.19	0.26	< 0.01
	% DOC	100 %	2 %	1 %	2 %	3 %	--
KCl DS	mgC/L	18.58	0.12	0.34	1.30	2.24	0.20
	% DOC	100 %	1 %	2 %	7 %	12 %	1.00 %
NaCl DS	mgC/L	17.66	1.00	0.40	0.56	2.86	0.56
	% DOC	100 %	6 %	2 %	3 %	16 %	3 %
NaOAc DS	mgC/L	10.10	2.28	0.78	1.76	3.46	1.80
	% DOC	100 %	23 %	8 %	17 %	34 %	18 %

Fig. 1

Fig. 2

Fig. 3

Fig. 4 (a) and (b)

Fig 5 (a) and (b)

Fig. 6

HIGHLIGHTS

- A hybrid OMBR-MF examined for OMPs and nutrient removal from simulated sewage.
- Performance of inorganic and organic draw solutes in OMBR-MF system assessed.
- Baffled OMBR-MF achieved high removal for nutrient and OMPs.
- Persistent OMP like atrazine exhibited high anoxic removal compared to oxic.
- Atenolol showed highest forward osmosis rejection due to high molar mass.
- Large microbial flocs contributed to lower membrane fouling propensity.