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Insight into the Effect of Organic and Inorganic Draw Solutes on the Flux Stability and Sludge Characteristics in the Osmotic Membrane Bioreactor

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Abstract:

In this study, chloride based ($CaCl_2$ and $MgCl_2$) and acetate based (NaOAc and MgOAc) salts in comparison with NaCl were investigated as draw solutions (DS) to evaluate their viability in the osmotic membrane bioreactor (OMBR). Membrane distillation was coupled with an OMBR setup to develop a hybrid OMBR-MD system, for the production of clean water and DS recovery. Results demonstrate that organic DS were able to mitigate the salinity buildup in the bioreactor as compared to inorganic salts. Prolonged filtration runs were observed with $MgCl_2$ and MgOAc in contrast with other draw solutes at the same molar concentration. Significant membrane fouling was observed with NaOAc while rapid flux decline due to increased salinity build-up was witnessed with NaCl and $CaCl_2$. Improved characteristics of mixed liquor in terms of sludge filterability, particle size, and biomass growth along with the degradation of soluble microbial products (SMP) were found with organic DS.

Keywords:

Osmotic membrane bioreactor, membrane distillation, draw solutes, reverse solute transport, salinity buildup.

1. Introduction:

In contrast to conventional membrane bioreactor (MBR), having either submerged micro- or ultra-filtration membranes under high suction force and resulting in rapid membrane fouling, the osmotic membrane bioreactor (OMBR) configuration extracts water osmotically from a low saline sludge into a highly concentrated draw solution (DS) and mitigates the problem of intensive biofouling. It also increases the removal of small particles, trace organic compounds (TrOCs) and dissolved species with less consumption of energy (Achilli et al., 2009; Holloway et al., 2014a; Wang et al., 2016a). Therefore, a conventional MBR running with either micro- or ultra-filtration membranes can be replaced with an appropriate DS-assisted osmotic MBR. In spite of the good rejection properties of OMBR, the FO membrane also causes limitations in parallel such as lower membrane flux, internal concentration polarization (ICP), reverse transport of solute into the bioreactor from the DS side. The later combine with those solutes of the feed wastewater rejected by the membrane and results in a progressive build-up of salinity within the bioreactor (Aftab et al., 2015; Qiu and Yen-Peng Ting, 2013; Wang et al., 2016a).

FO membranes are also prone to fouling mechanism, though this is relatively low when compared to fouling in a conventional MBR due to avoidance of the suction force requirement and lower operating flux conditions (Lutchmiah et al., 2014; Wang et al., 2016b; Yuan et al., 2015; Q. Zhang et al., 2014). Nevertheless, running under FO mode, with the active layer facing the mixed liquor, membrane fouling still occurs. Direct contact of mixed liquor containing a variety of microorganisms including organic and inorganic foulants (i.e. a highly complex feed) with FO membrane, not only leads to decline of the water permeability as membrane resistance increases but also raises the external concentration polarization (ECP) (Qiu and Yen-Peng Ting, 2013; Wang et al., 2016b; Yuan et al., 2015). Production of extra polymeric substances (EPS) and an altered bacterial community within the bioreactor plays a vital role in biofouling development (Qiu and Yen-Peng Ting, 2013; Q. Zhang et al., 2014). Nguyen et al. (2016a) recently introduced moving carriers to reduce suspended solids within the bioreactor to mitigate the problem of biofouling, while aeration intensity and modification of membrane surface were also found to be advantageous in lowering the fouling intensity in the OMBR (Li et al., 2016; Qiu and Yen-Peng Ting, 2013; Q. Zhang et al., 2014).

Mixed liquor suspended solids can be retained by the membrane in a conventional MBR, but a substantial volume of particles may still be permitted into the effluent across the membrane. That’s why, negligible amount of salt accumulation in a conventional MBR is observed. However, high retention MBR systems (HRMBR) can hold the maximum dissolved solids and colloidal particles. This rejection not only provides a highly precise effluent quality, but also raises the salt level with potentially adverse impacts on microbial growth and biological treatment. The biochemical and physical properties of the microorganisms required for biological treatment are also affected by a high saline condition (Reid et al., 2006). Microorganisms in domestic wastewater are generally not immune to halophilic conditions; thus, it is difficult for them to bear the osmotic stress exerted by a saline environment. Especially some microorganisms, like denitrifying bacteria, are apparently more sensitive under osmotic stress (Lay et al., 2010). Moreover, accumulated salinity eventually increases the amount of soluble microbial products (SMP) and extra polymeric substances (EPS) in the mixed liquor, resulting in membrane fouling and flux reduction (Wang et al., 2014). The high retention behaviour of the FO membrane aiding reverse transport of draw solute further compounds the situation of feed solute accumulation, which consequently leads to build-up of the salinity content within the bioreactor (Aftab et al., 2015; Ge et al., 2012). This exalted saline condition is consequently an integral concern that high retention MBRs may have to deal with.

Various researchers have introduced a number of tactics to cope with the challenge of salinity build-up throughout the OMBR process. Coupling of electrodialysis and a UF/MF unit with the OMBR process has been implemented as a solution to alleviate high salinity within the bioreactor (Lu and He, 2015; Qiu and Yen-Peng Ting, 2013). The MF/UF technology coupled with the OMBR is not only capable of reducing the high saline content of mixed liquor, but also permits the enriched nutrients such as phosphorus to be mined for direct recovery from the bioreactor (Holloway et al., 2014b; Wang et al., 2014). Development of new salts (mixtures) or the use of alternative draw solutions instead of conventional ones are emerging as another effective strategy that promises to alleviate the salinity content. Nguyen et al., (2016a, 2015) used different mixtures (organic and surfactant) with inorganic salt to create a novel DS which dramatically lowered the salinity in the bioreactor. Lower leakage of organic salts from the DS into the reactor and their biodegradable nature results in a lower salt accumulation. Additionally, the leakage of organic salts increases the carbon content as a food for microorganisms and is also beneficial for the production of methane gas in anaerobic processes (Ansari et al., 2015; Qiu and Yen-Peng Ting, 2013). Divalent inorganic salts also show relatively lower salinity buildup and better flux performance, as compared to monovalent salts (Achilli et al., 2010; Nguyen et al., 2015). In reference to these previous studies, the complete spectrum of membrane fouling and sludge characteristics across organic and inorganic DS in OMBR still requires further investigation.

In the present research work, the performance of two divalent inorganic ($CaCl_2$ and $MgCl_2$) and two organic (NaOAc) and (MgOAc) draw solutions were investigated in OMBR operation. The commonly used sodium chloride (NaCl) was used as a bench mark to compare its performance with these salts. A cross-flow direct contact membrane distillation (DCMD) process was used for the recovery of draw solute and the production of pure water. An OMBR setup integrated with the DCMD process as a hybrid OMBR-MD (FOMBR-MD) system was continuously operated for the draw solutions until fouling of the membrane occurred. The study aimed to investigate the effect of salinity build-up by different salts on mixed liquor characteristics, membrane fouling, flux stability and pollutants removal efficiency.

2. Materials and methods

2.1. Description of experimental set-up:

A laboratory-scale hybrid OMBR-MD setup was used for this research work (**Error! Reference source not found.**). The system consisted of a feed tank, a bioreactor having a submerged FO membrane module, a draw tank and a direct contact membrane distillation (DCMD) unit for the recovery of draw solutes and the production of pure water.

On the OMBR side, a feed tank was placed on a top loading balance (UX6200H, Shimadzu, Japan) attached to a computer to determine the flux of the FO membrane. A peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA) attached with a relay unit (Omron Floatless Level Switch, 61F, Japan) was installed to feed the bioreactor. A plate and frame-type FO membrane module which was made of acrylic sheet with a length, width and height of 30, 30 and 1.5 cm respectively was submerged in the bioreactor. The module was also provided with 10 baffles each of 0.6 cm thickness to increase the contact time of DS with in the module. A flat sheet cellulose triacetate (CTA) FO membrane from Hydration Technology Innovations (HTI) USA with an effective membrane area of 0.12 m^2 was attached to the module to seal the DS flow channel. The membrane active layer was facing the feed side (AL-FS) during the OMBR operation, as this configuration cause less fouling in comparison with the active side facing DS (AL-DS) (Aftab et al., 2015). Continuous dissolved oxygen of 3-4 mg/L was provided for the active growth of microorganisms as well as facilitating membrane scouring by using an air pump. Conductivity in the bioreactor was monitored by using an in-line conductivity meter. A peristaltic pump (Cole Parmer, 77200-62, Masterflex, USA) was used for the circulation of DS with a cross-flow velocity of 500 mL/min from the draw tank to the FO membrane module.

Draw tank was used for integration of OMBR and MD systems to make hybrid OMBR-MD system. Draw tank not only collected the treated water from OMBR side but also served as a feed reservoir for MD side. DCMD unit comprised of acrylic flat sheet module for hydrophobic membrane having two flow channels. Hydrophobic flat sheet microporous polytetrafluoroethylene (PTFE) membrane from Porous Membrane Technology (Ningbo, China) with an effective area of 0.005 m^2 was used for the DCMD set-up.

Fig. 1

Two peristaltic pumps (Cole Parmer, 77200-62, Masterflex, USA) were used for the circulation of feed i.e., DS and permeate in a countercurrent manner through each channel providing the same circulation velocity on both sides. To heat the feed solution for the hot MD side, a heater containing a stainless-steel heat exchanging coil immersed in a hot water reservoir was used. Two temperature sensing devices (SANHNG-TPM-900, China) were installed to measure the temperature of the incoming and exit temperature of the feed side (i.e. hot side). HACH (sensION, USA) TDS meter was used to measure the TDS of feed i.e., DS. Permeate passes through the chiller to maintain a temperature gradient between the cold and hot side. An-line TDS meter with a temperature sensor (KOMATSU, China) was installed on the cold side (i.e. permeate side) to record effluent TDS and temperature. The permeate tank was placed on a top loading balance (UX6200H, Shimadzu, Japan) attached to a computer to measure the flux of the MD membrane.

2.2. Draw Solutions and Feed:

Nawaz et al. (2013) found that divalent salts ($CaCl_2$ and $MgCl_2$) were more supportive to the growth of the microbial community as compared to monovalent salts. Commonly used divalent $CaCl_2$ and $MgCl_2$ were selected as inorganic DS for this study to operate in the OMBR system. Divalent salts, due to their large hydrated radii, produce better flux performance and lower reverse salt transport in comparison with monovalent salts (NaCl) (Holloway et al., 2015; Khanzada et al., 2016; Nguyen et al., 2015). Similarly, sodium acetate (CH_3COONa or NaOAc) and magnesium acetate ((Mg $(C_2H_3O_2)_2$) or MgOAc) were carefully chosen as organic draw solutes due to their ability to control salinity. Such acetate salts are highly degradable and are capable of achieving a stabilized flux as they have a lower reverse salt flux than NaCl (Ansari et al., 2015; Bowden et al., 2012). Performance of these four salts was investigated against the commonly used draw solute NaCl in the OMBR system at 0.25 M concentration of each DS.

A synthetically prepared feed solution was used to simulate the domestic wastewater. The composition of the synthetic wastewater included glucose, ammonium chloride, and potassium dihydrogen orthophosphate and trace nutrients as reported in **Table 1**.

Table 1

2.3. Operational protocol:

A bioreactor with a 4.5 liter working volume and with a submerged FO membrane module was continuously aerated. Activated sludge having 7-8 g/L MLSS from the National University of Sciences and Technology (NUST) Membrane Bioreactor (MBR) Plant, Islamabad was used as a seed sludge for OMBR-MD continuous operation. Sludge was further acclimatized with the synthetic wastewater used in this study for two weeks, prior to feeding the OMBR-MD system. New sludge was taken from the MBR plant every time for each DS, as the reverse solute of previous DS into the sludge suspension may interfere with the performance of the next DS. Initial hydraulic retention times (HRTs) of five different DS were in the range of 7- 10 hrs as per initial water fluxes of FO membrane. The HRT increased over time as a function of decrease in water flux. The OMBR system was operated at a constant solids retention time (SRT) of 20 days under each DS condition. Maintenance of SRT was also helpful to alleviate the salinity build-up in the bioreactor (to a certain extent) that is beneficial for biomass growth (Aftab et al., 2015; Luo et al., 2016). To concentrate the DS continuously, the MD system was run parallel to the OMBR system with an initial circulating velocity of 1000 mL/min on both sides (i.e. hot and cold side). A suitable temperature on a trial and error basis was selected for every DS recovery on the hot side and 10^{o}C was maintained on the cold side throughout the study. Behaviour of the water transfer rate on the MD side was dependent on the water flux of the FO side. The water transfer rate of the MD side was adjusted on a daily basis to match with the transfer rate of the OMBR side by changing the circulating velocity of the MD system. Luo et al. (2016) reported that the FO membrane flux was adjusted with a RO system by changing the hydraulic pressure. Additionally, the velocities of both sides remained identical throughout the study. TDS in the draw tank was continuously measured to maintain a 0.25M concentration of each DS.

To stabilize the condition of increasing TDS concentration in the draw tank, the circulating velocity was reduced. Whenever the TDS concentration in the draw tank decreased due to the salt deposition on the hot side, the MD membrane was flushed with DI water. During flushing process, DI water was circulated on both sides of the MD membrane with a cross flow velocity of 20 cm/s at 25^{o}C for one hour. After flushing, the MD system was again attached to the OMBR setup to achieve a continuous recovery of draw solute and thus maintain TDS concentration in the draw tank. The OMBR-MD system operation was terminated when the flux of the FO membrane declined to 20% of the initial flux.

2.4. Analytical Methods:

For each salt, sludge characteristics were observed in term of mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), capillary suction time (CST) and particle size distribution (PSD). The treatment analysis was accomplished in terms of chemical oxygen demand (COD), Phosphate-P (PO_4^{3-}P) and Ammonium-N (NH_4^+-N). All these analyses were performed as per Standard Methods (APHA et al., 2012).

Mean particle size of the sludge floc was measured by using a particle size analyzer (LA-300, HORIBA, Japan). A CST apparatus (304B-CST, Triton, Canada) was used to analyze the filterability and conditioning of sludge in terms of capillary suction time (CST). In this process, water is removed from the sludge by using a standard filter paper and the rate at which water permeates through the paper depends on sludge dewaterability. Two electrodes are positioned at a standard interval from the funnel; the time, taken by the water front to travel between these two poles is the capillary suction time.

2.5. EPS extraction and quantification:

The cation exchange resin method was used to extract the Extracellular Polymeric Substances from the sludge (FrØlund et al., 1996). Concentrations of proteins and polysaccharides were used to measure the concentration of soluble microbial products (SMP) and extracellular polymeric substances (EPS). A standard curve for protein (PN) was developed by using various concentrations of Bovine Serum Albumin (BSA). The Lowery method utilizing Folin-Ciocalteu's phenol regent was used to measure the concentration of protein (PN), using a spectrophotometer (T60-UV/VIS, PG-Instrument, UK) where absorption was measured at the wavelength of 750 nm (Lowry et al., 1951). Concentrations of carbohydrate or polysaccharide

(PS) were measured by using the Dubois method (Phenol-Sulfuric Acid), where a wavelength of 470 nm was used to measure the absorption of solution (Dubois et al., 1956). Standard curves of PS were developed using analytical grade glucose.

3. Results and discussion:

3.1. Process performance or OMBR system:

3.1.1 Water Flux:

Fig. 2a illustrates the normalized water flux as a function of time for each draw solution. However, among the five different DS, $CaCl_2$ and NaCl produced the highest initial flux followed by NaOAc, $MgCl_2$ and MgOAc respectively at a constant molar concentration. These results correlated well with previous findings (Achilli et al., 2010; Ansari et al., 2015; Bowden et al., 2012).

Providing high salt rejection (>98%) by the MD membrane, a minute decrease in DS concentration was observed at the end of each filtration run. So the decrease in water flux was due to either membrane fouling or by raised salinity level in the bioreactor. The decline in flux for each inorganic salt (NaCl, $CaCl_2$ and $MaCl_2$) was actually due to the accumulation of salt, as a result of which salinity level rose within the bioreactor. A rapid decline of water flux was observed with NaCl (**Fig.2a**) within 12 days of filtration run while the filtration runs with $CaCl_2$ and $MaCl_2$ as DS ended within 16 and 21 days, respectively at the same molar concentrations. These results were mainly attributed to the values of specific reverse salt diffusion (**Table 2**) of each DS. Achilli et al. (2010) and Bowden et al. (2012) found that specific reverse salt diffusion (Js/Jw: reverse salt flux (Js) and water flux (Jw)), is a valuable parameter for DS performance. Independent of the concentration, the values of specific reverse salt diffusion (Js/Jw) remain relatively constant for each salt and this ratio is helpful for the estimation of reverse salt transport during the FO process: lower values of Js/Jw indicates minimum salt loss or less reverse transport of solute. (Achilli et al., 2010; Bowden et al., 2012; Phillip et al., 2010). Draw solutions that exhibit higher ratios of specific reverse salt diffusion are reflected in lower efficiencies of the process in term of water flux and decrease in membrane selectivity due to the effect of internal concentration polarization (ICP) at the supporting layer of the FO membrane (Achilli et al., 2010; Ansari et al., 2015; Hancock and Cath, 2009).

Table 2

Moreover, the salinity build-up in the bioreactor (to be discussed in section 3.1.2) decreased the osmotic pressure gradient between DS and feed solution (FS) (Aftab et al., 2015), which resulted in a relatively rapid flux drop in the case of $CaCl_2$ and NaCl in comparison with $MgCl_2$. A sticky, gel-like fouling layer was observed at the end of the filtration run for each of the inorganic DS. This fouling layer on the surface of the membrane was due to an enhanced release of SMP (Soluble microbial products), due to an increased osmotic stress on the FS side; this has also been reported elsewhere (Aftab et al., 2015; Zhang et al., 2014b). A DS producing a more saline stress condition in the bioreactor results in a rapid flux decline, due to a higher Js/Jw ratio.

On the other hand, a prolonged and stable filtration run was observed (**Fig. 2a**) for both the organic draw solutions (MgOAc and NaOAc) as compared to the inorganic salts. Considerably lower salinity build-up resulted for each organic DS, as each exhibited significantly lower values of Js/Jw (**Error! Reference source not found.**) in contrast with the inorganic DS. In the case of the organic DS, flux decline resulted mainly from membrane fouling rather than from salt accumulation within the reactor. A significantly prolonged filtration run of 24 days was observed with MgOAc as compared to 19 days for NaOAc at the same molar concentration. Even with less salinity build-up, NaOAc has a noticeable decline in flux (Error! Reference source not found.**a**) in comparison with $MgCl_2$ because of severe membrane fouling. Attachment of biomass on the membrane surface was observed at the end of the filtration run with MgOAc and NaOAc, as the reverse organic salt flux (the acetate ion) acted as a carbon/food source for microbial growth and resulted in biofilm formation on the membrane surface as reported earlier by Ansari et al., 2015 and Luo et al., 2016. The EPS of biomass attached on the membrane surface implies that NaOAc causes more severe fouling than MgOAc and other inorganic salts, and for that reason a rapid decline in water flux was observed for NaOAc. The attached biomass for NaOAc contains higher PN content within the EPS and also exhibits higher hydrophobicity, resulting in severe membrane fouling (Liu and Fang, 2003).

Fig. 2

3.1.2. Mixed Liquor Conductivity:

A natural phenomenon associated with the OMBR system is the accumulation of salts within the bioreactor, both due to the high salt rejection of the FO membrane and the reverse transport of draw solute acting as a major source for salinity build-up. An elevated TDS concentration within the bioreactor decreases the driving force for water flux, as the osmotic gradient decreases between the feed and DS side (Holloway et al., 2014a). The trend of mix liquor conductivity within the bioreactor as a function of time is shown in (**Fig. 2b**) for each DS. Significantly less salinity build-up was observed in the bioreactor with Na-Ace and Mg-Ace, as expressed by the electrical conductivity (mS/cm). In the case of organic DS, the conductivity increases from approximately 0.8 to 9 mS/cm and from 0.7 to 6.8 mS/cm with NaOAc and MgOAc, respectively. Due to the low salt accumulation in the bioreactor, lower decrease in osmotic gradient was observed and this resulted in prolonged filtration runs for both organic DS at similar molar concentrations as compared to $CaCl_2$ and NaCl (**Fig. 2a**). The specific reverse salt diffusion (or ratio of reverse salt flux to the water flux) as reported in **Error! Reference source not found.** also meant that, due to lower ratios of Js/Jw for the organic salts, a low reverse salt flux was produced which resulted in less salinity build-up in the bioreactor as compared to inorganic salts (Achilli et al., 2010; Bowden et al., 2012).

These results were also attributed to the size, in terms of hydrated diameter of the respective anions and cations of DS investigated in this study. Achilli et al. (2010) found that the draw solutions with a larger hydrated size of anions produced lower reverse salt flux, irrespective of the size of their corresponding cations. The acetate ion (CH_3COO^-) with both of its corresponding cations (Mg^{2+} and Na^+) gave the lowest specific reverse salute diffusion (Js/Jw) as compared to the inorganic salts having a chloride ion (Cl^-). These results were credited to the larger hydrated diameter of acetate ions in comparison to the chloride ions.

On the other hand, when we consider only organic salts, NaOAc produces a slightly higher conductivity and a more rapid decline in flux, as compared to MgOAc as shown in **Fig. 2a and b**. This is actually due to the smaller hydrated diameter of the sodium ion (Na^+) in comparison with that of the magnesium ion (Mg^{2+}); because of smaller hydrated radii, monovalent ions can be more easily diffused across the FO membrane from the DS side to the FS side as compared to divalent ions (Nguyen et al., 2016b). Similar behaviour was observed in the case of inorganic draw solutions for NaCl and $MgCl_2$. The inorganic DS have the same anions but differed in their impact on water flux and conductivity, and this was due to the dissimilarity in the size of their hydrated cations. Additionally, a further difference was observed between $CaCl_2$ and $MgCl_2$; the conductivity increased from 0.86 to 21.02 mS/cm, as compared to $MgCl_2$ for which it increased from 0.66 to 13.78 mS/cm. The reason behind this difference was the higher reverse solute flux of $CaCl_2$, due to a smaller hydrated diameter of calcium ion (Ca^{2+}) compared to the magnesium ion (Mg^{2+}) (Achilli et al., 2010; Nguyen et al., 2016b). The effect of the salt accumulation on sludge characteristics and removal efficiencies will be discussed in later sections.

3.2. Organic and nutrients removal:

3.2.1. Build-up and removal of organic matter:

Regardless of the draw solute, the high retention characteristics of the FO membrane and the reverse salt flux of each DS resulted in the accumulation of organic content within the bioreactor. Error! Reference source not found. represents the build-up of organic content in the bio-tank and the removal efficiency in the permeate for each DS. More than 98% removal of COD was observed in the permeate for each DS, as reported in **Table 3,** because of the synergistic effect of both the dual barriers of high retention membranes (FO and MD) and the biological treatment. Accumulation of COD within the bioreactor was observed with both organic and inorganic draw solutions, which is consistent with the previous studies (Aftab et al., 2015; Luo et al., 2016; Qiu and Yen-Peng Ting, 2013).

For each inorganic draw solution (NaCl, $CalC_2$ and $MgCl_2$) a much higher level of COD (organic matter) build-up within the bioreactor (Error! Reference source not found.) was witnessed as compared to organic salts. $CaCl_2$, with the highest reverse salt flux and salinity build-up, produced the highest organic accumulation. Similar behaviour was also observed with NaCl. An increased concentration of organic content in the bio-tank reflects the decrease in biodegradation of organics by the microbial consortium. The majority of microbes involved in wastewater treatment processes, such as the activated sludge process, are non-halophilic in nature. These microbial communities do not possess the ability to survive in highly saline environments. Osmotic stress on the feed side compels the intercellular water to move outside; this subsequently causes cell dehydration, which results in cell plasmolysis and deteriorates the cell activity for microbes (Lay et al., 2010; Yogalakshmi and Joseph, 2010). Hence, the deteriorating conditions gradually lead to accumulation of the organic matter within the bioreactor. This accumulation actually initiated the gathering of non-biodegradable dissolved organic matter (DOM) in the bio-tank (Qiu and Ting, 2013). Elevated salinity not only deteriorates the metabolic activity of the bacterial community, it also increases the level of DOM which can be attributed to the release of soluble microbial products (to be discussed in section 3.3.2) within the activated sludge (Luo et al., 2016; Qiu and Ting, 2013; Yogalakshmi and Joseph, 2010).

Fig. 3

Likewise, both organic draw solutions also show the accumulation of COD in the bio-tank (Error! Reference source not found.**)**. However, as discussed earlier (section 3.1), the lower reverse salt diffusion of organic DS mitigates the problem of high salt accumulation, while on the other hand providing additional carbon source for bacterial growth. These results were attributed to the organic nature of the acetate ion as reported elsewhere (Ansari et al., 2015; Luo et al., 2016), resulting in accumulation of organic content in bioreactor. The readily degradable nature of organic draw solutions, credited to their osmoprotectant features, reduces the osmotic stress on microbial consortium (Oh et al., 2008). However, this reduced osmotic stress on the feed side also enhances the microbial growth by providing an additional carbon source (Ansari et al., 2015).

Table 3

3.2.2. Biological removal of Nutrients:

3.2.2.1. Phosphate enrichment and removal:

The OMBR performance in terms of phosphate (PO_4^{3-}-P) removal was evaluated for the five different draw solutions and the results are shown in **Fig. 4**. Due to the high retention properties of the FO membrane, substantial enrichment of phosphate was observed within the bioreactor for each DS. A much lower phosphate concentration was witnessed in the bio-tank during the filtration runs with the organic as compared to the inorganic draw solutes. As shown in **Fig. 4**, with an average influent phosphate of roughly 10 mg/L, the phosphate concentration in the mixed liquor rose to 20 mg/L with organic DS. This accumulation was credited to an effective FO membrane rejection, due to a negatively charged and larger hydrated diameter of the ortho-phosphate ion (Luo et al., 2016, 2015). In addition to this, a lower buildup of phosphate with organic DS 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 phosphorus accumulating organisms

(PAOs). Increased bacterial growth was observed due to lower salinity buildup (section 3.1.2) and lower osmotic stress on the feed side with the readily degradable acetate ion as reverse solute. Hence, higher bacterial activity lowers the phosphate accumulation in the bioreactor when using organic DS.

However, the salinity buildup in the case of inorganic draw solutions generates a detrimental condition for 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). In this context, high phosphate enrichment was observed for inorganic DS when compared to organic salts (**Fig. 4**). **Fig. 4** shows that using $CaCl_2$, phosphate accumulated up to 37 mg/L at the end of the filtration run, and a similar trend was also witnessed with NaCl and $MgCl_2$ i.e., phosphate concentration up to 30 mg/L. A higher concentration of chloride ions (Cl^-) also inhibits the performance of PAOs, which in turn reduces the phosphate removal, as reported elsewhere (Bassin et al., 2011). Therefore, this increased amount of phosphate accumulation was actually due to the high retention features of the FO membrane and the salinity buildup in the bio-tank (Aftab et al., 2015; Lay et al., 2010; Qiu and Ting, 2014). Despite the accumulated phosphate within the bioreactor, more than 99% removal of phosphate was achieved in the permeate for each salt because of the dual membrane barriers presented by the FO and the MD.

Fig. 4

3.2.2.2. Nitrogen removal:

Nitrification is a very sensitive process, as microbes (nitrifiers) involved in this process are slow growing and highly susceptible to environmental circumstances such as DO concentration, pH, temperature and salinity (Lay et al., 2010). It was also reported that lower removal of biological nitrogen is generally due to deprived nitrification. **Fig. 5** demonstrates the buildup of ammonium-N for each salt used as a DS at the same molar concentration. With high saline stress due to salt accumulation in the bio-tank, buildup of NH_4^+-N was also observed for each inorganic draw solute. These trends with NH_4^+-N are also consistent with previous studies (Aftab et al., 2015; Luo et al., 2015; Qiu and Ting, 2013). This increased concentration of NH_4^+-N within the bio-tank was accompanied by its transfer into the draw tank as reported in **Table 3**. The removal efficiency of NH_4^+-N in the draw tank decreased noticeably from 98 to 72% with $CaCl_2$ and from 98% to 79% for NaCl. $MgCl_2$ also showed a similar behaviour. These results were ascribed to the inhibition of bacterial activity for ammonia oxidizing bacteria (AOBs), by high saline stress (Qiu and Ting, 2013).

Fig. 5

In the permeate, more than 98% of NH_4^+-N removal was achieved for each draw solute in the study. Although small amounts of NH_4^+-N were transferred to the draw tank across the FO membrane, it was further rejected by a high retention MD membrane.

In contrast to the previous results for inorganic DS, a continuous decline in the concentration of NH_4^+-N within the bioreactor was observed **(Fig. 5**) throughout the filtration runs for both the organic DS. A very small amount of NH_4^+-N was observed in the draw tank at the start of the filtration run with both organic DS, which was further reduced to a negligible value. Luo et al. (2016) also reported that degradation of NH_4^+-N increased in the mixed liquor with increased biomass activity in the OMBR. The acetate ion as a reverse transported solute provides a source of carbon for bacterial growth, due to its readily degradable nature. This provides a suitable environment to microorganisms for their growth and microbial activity which increases the rate of NH_4^+-N removal.

3.3. Biomass Characteristics:

In MBR operations, the characteristics of the biomass play an important role in biological treatment. It not only governs the productivity of biological treatment, but also effects the membrane filtration processes (Holloway et al., 2014a; Lay et al., 2010).

3.3.1. Behaviour of suspended solids:

Concentration of MLSS and MLVSS as a function of time is shown in **Fig. 6a and b.** A highly saline environment adversely affects the MLSS and MLVSS as it decreases their concentration continuously throughout the filtration run for inorganic DS. Increased osmotic stress due to salinity build-up inhibits the growth of microorganisms as biomass starts to decay within the salty environment (Luo et al., 2016; Tadkaew et al., 2013). The MLVSS/MLSS ratio decreased from 0.83 to 0.74, 0.80 to 0.75 and 0.79 to 0.69 for $CaCl_2$, $MgCl_2$ and NaCl, respectively throughout the filtration run. These results infer the decrease or death of biomass due to increased levels of salinity in the bio-tank for each inorganic draw solute. Luo et al. (2015) also reported that, due to increased osmotic stress on the feed side, a reduction in MLVSS/MLSS ratio was observed which decreased the concentration of active biomass in the sludge. An active biomass decline in the mixed liquor not only reduces the biological treatment process, it also affects the characteristics of the sludge. On the contrary, when using organic DS at the same molar concentration in the OMBR-MD system, completely different trends were observed as compared to inorganic DS. In **Fig. 6a and b**, a rise in the concentration of MLSS and MLVSS with organic salts was observed as a function of time. An increase in MLVSS/MLSS ratio from 0.82 to 0.91 and from 0.78 to 0.85 was observed with the use of NaOAc and MgOAc as DS, respectively, indicating the increase in biomass growth within the bio-tank. This increase in the concentration of active biomass was accredited to the reverse transport of acetate ion (CH_3COO^-) (Ansari et al., 2015; Luo et al., 2016). The readily degradable nature of the acetate ion not only provides the additional organic substrate but also lowers the osmotic stress for the growth of microbes, resulting in the increase of active biomass.

Fig. 6

3.3.2. Organic foulants:

While discussing organic foulants, soluble microbial products (SMP) and extracellular polymeric substances (EPS) feature as the most conspicuous agents liable for the fouling of the membrane (Luo et al., 2015; Xie et al., 2014). SMP and EPS are both heterogeneous and generally comprise of proteins, humic acid, lipids, carbohydrates and nucleic acid. Proteins and carbohydrates are the dominant components found naturally in extracted SMP and EPS. So, the sum of proteins and carbohydrates was used to represent SMP and EPS. **Fig. 6c and d** compares the temporal concentrations of SMP and EPS for each of the organic and inorganic salts employed as DS in the OMBR-MD setup.

Salt accumulation within the bioreactor (section 3.2) increases the osmotic stress on microbial activity, due to which a conspicuous increase in the concentration of SMP was observed **(Fig. 6c)** with chlorides of Na, Ca and Mg. These observations are consistent with previously reported results, for which salinity build-up in the bio-tank resulted in an increased concentration of SMP in the supernatant of the OMBR (Luo et al., 2015; Reid et al., 2006). This increase was attributed to the accelerated endogenous respiration, which is accompanied by the release of organic cellular components from cell lysis and by cell secretions (Reid et al., 2006). It was also reported that this rapid increase in SMP fraction was due to the addition of the chloride ions. Luo et al. (2015) also reported that accumulation of intermediate and unmetabolized constituents, due to partial degradation of organic material in high saline environments, led to an increase in the amount of SMP in mixed liquor. Moreover, increased salinity within the bio-tank could also accelerate the solubility of carbohydrate and protein contents of SMP, which might be an additional cause for the increased SMP contents in supernatant (Zhang et al., 2014b).

Along with an increase in the supernatant SMP concentration when using the inorganic salts, a decrease in the concentration of EPS was observed, as shown in **Fig. 6d**. This was due to salinity buildup within the bioreactor. Lin et al. (2014) reported that environmental stresses and unfavorable conditions in the bioreactor can disturb the contents of EPS; under such conditions, cell lysis and death of the biomass is expected, causing the release of carbohydrates and proteins into the supernatant. Increased saline stress within the bioreactor due to a high salt concentration can also elevate the risk of EPS extraction from sludge flocs (Zhang et al., 2014b), as a result of which an increase in the concentration of SMP was observed (**Fig. 6c**). The observed decrease in EPS concentration was also credited to the high solubility of EPS fragments (carbohydrates and proteins) with the increase in the salinity of the mixed liquor, as reported elsewhere (Luo et al., 2015). Both released and extracted fractions of EPS were highly soluble because of salt accumulation, which further resulted in a decrease in EPS and an increase in SMP production.

On the other hand, no significant change in the concentration of EPS was found (**Fig. 6d**) when using organic salts as draw solution. This is because of the stabilized microbial growth, which in turn is due to the reverse transported acetate ions providing a source of organic content within the bioreactor. Increased microbial growth balanced the hydrolysis and release of EPS concentration, as reported elsewhere (Luo et al., 2016). Additionally, degradation of SMP content in the supernatant with the use of organic DS was also observed, as shown in **Fig. 6c**. SMP degradation was probably due to the enhanced microbial activity in the bioreactor, as a result of which a decrease in the concentration of SMP in the mixed liquor was found. Menniti and Morgenroth (2010) similarly observed that SMP produced by the retained compounds in a bioreactor operation is readily degradable. The methane producing properties of acetate also reduce the production of SMP (Barker and Stuckey, 1999). Thus, an increased biomass activity, due to reverse acetate flux, degrades the SMP contents of the mixed liquor in the bioreactor.

3.3.3. Sludge filterability and floc size:

Sludge filterability in terms of capillary suction time (CST) was observed for each organic and inorganic salt, as reported in **Table 4**. An increase in capillary suction time means a reduction in filterability of the sludge, as observed when inorganic salts were employed as draw solution in the OMBR system. A deteriorated sludge filterability can be credited to the accumulation of SMP contents with the buildup of salinity level in the bio-tank (Reid et al., 2006). In the case of $CaCl_2$ and $MgCl_2$, the CST increased from 22 to 45 s and from 25 to 37 s, respectively. With regards to the floc size of suspended sludge, it decreased with the increase of salt accumulation when using salts of chloride as DS. **Table 4** shows the decrease in mean particle size that was evaluated on the basis of the percent volume of particles. The drop in particle size with salts of chloride (NaCl, $CaCl_2$ and $MgCl_2$) was attributed to the decrease in the amount of filamentous bacteria in activated sludge flocs with increased salinity (Jang et al., 2013); these filamentous organisms are the backbone of sludge flocs contributing to the development of larger flocs. Zhang et al. (2014b) also reported that increased saline stress has a detrimental effect on floc strength and the flocculation of activated sludge. The extraction of EPS from flocs (section 3.3.2) because of cell lysis, and the production of more SMP in the supernatant with the increased salinity, may also deteriorate the settling and flocculating properties of mixed liquor (Barker and Stuckey, 1999; Lin et al., 2014; Zhang et al., 2014b). So, in the case of inorganic DS, a smaller particle size might be the reason for an increased CST, reducing the sludge filterability.

Table 4

On the contrary, an increase in particle size was observed **(Table 4)** in the case of organic draw solutes. Salts of acetate (NaOAc and MgOAc) actually act as a source of carbon that increases the microbial growth in sludge. As already discussed, with an increased biomass activity, degradation of SMP also increased and stabilized EPS production was observed. No change in EPS confirms the increase in mean particle size, because stabilized EPS content increases the stability of floc size, as reported elsewhere (Lin et al., 2014; Zhang et al., 2014b). Particle size increased from 14.18 to 25.64 µm with NaOAc and from 16.91 to 23.20 µm with MgOAc; this was correspondingly accompanied by a decrease in CST **(Table 4)** with organic draw solutes exhibiting enhanced microbial growth and an improved filterability. By considering these results, we came to the conclusion that an increased saline stress within the bio-tank not only decreased the floc size, it also increased the CST due to cell autolysis and dehydration. On the other hand, an increase in particle size and a reduction in CST were observed with the employment of organic salts as DS in the OMBR system.

4. Conclusions

This study of OMBR appraised the flux performance of organic and inorganic DS, and the effect of reverse salt diffusion on mixed liquor characteristics. Improved sludge characteristics with an increase in filterability and enhanced flocculation were achieved with organic DS particularly with MgOAc (organic DS). Moreover, stabilized and prolonged filtration runs were observed with MgOAc followed by $MgCl_2$ (inorganic) as DS. Significant fouling with NaOAc was observed due to dense biofilm formation. Chloride based salts inhibited the biological growth, resulted in accumulation of phosphates and ammonium salts as well as showed relatively poor removal efficiency of pollutants.

Supplementary Data:

Supplementary data **Fig. S1**, **Fig. S2, Fig. S3** and **Table S1.**

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Table Captions:

Table 1: Composition of synthetic wastewater.

Table 2: Specific reverse salt diffusion (Js/Jw) for draw solutions (DS) at same molar concentrations.

Table 3: Concentration and Removal % of contaminants in Inlet, Draw Solution and Permeate.

Table 4: Sludge filterability and floc size for each draw solution.

Table 1: Composition of synthetic wastewater.

Composition	Formula	Unit	Concentration
Glucose	$C_6H_{12}O_6$	mg/L	308.4
Ammonium Chloride	NH_4Cl	mg/L	114.6
Potassium Phosphate	KH_2PO_4	mg/L	44.0
Magnesium Sulfate	$MgSO_4.7H_2O$	mg/L	2.92
Calcium Chloride	$CaCl_2$	mg/L	2.92
Ferric Chloride	$FeCl_3$	mg/L	0.88
Manganese Chloride	$MnCl_2.4H_2O$	mg/L	0.60
Sodium Bicarbonate	$NaHCO_3$	mg/L	69.71

Table 2*:* Specific reverse salt diffusion (Js/Jw) for draw solutions (DS) at same molar concentration.

Draw Solution	Concentration (moles/L)	Concentration (g/L)	Osmotic Pressure (MPa)	Specific Salt diffusion Js/Jw (g/L)[a]
$Mg(CH_3COO)_2$	0.25	35.6	1.04	0.11
CH_3COONa	0.25	20.52	1.08	0.26
$MgCl_2$	0.25	23.81	1.64	0.59
$CaCl_2$	0.25	27.75	1.72	0.83
NaCl	0.25	14.61	1.15	0.74

[a] Data from Achilli et al., (2010) and Bowden et al., (2012)

Table 3: Concentration and Removal % of contaminants in Inlet, Draw Solution and Permeate.

Salts	COD			
	Inlet (mg/L)	**Draw solution (mg/L)**	**Permeate (mg/L)**	**Removal (%)**
NaCl	302.29 ± 12.08	-	4.30 ± 1.41	98.57 ± 0.48
$CaCl_2$	305.22 ± 10.41	-	4.26 ± 1.36	98.59 ± 0.47
$MgCl_2$	301.27 ± 10.36	-	4.00 ± 1.97	98.67 ± 0.65
CH_3COONa	305.7 ± 11.17	-	4.05 ± 1.41	98.68 ± 0.45
$Mg(CH_3COO)_2$	300.92 ± 7.26	-	3.27 ± 1.36	98.91 ± 0.45
Salts	**Ammonium-N**			
	Inlet (mg/L)	**Draw solution (mg/L)**	**Permeate (mg/L)**	**Removal (%)**
NaCl	30.34 ± 1.02	3.94 ± 2.15	0.40 ± 0.25	98.69 ± 0.81
$CaCl_2$	30.31 ± 1.76	5.03 ± 2.49	0.33 ± 0.11	98.80 ± 0.41
$MgCl_2$	29.38 ± 1.40	3.24 ± 1.30	0.42 ± 018	98.55 ± 0.63
CH_3COONa	30.17 ± 1.60	0.68 ± 0.38	0.24 ± 0.08	>99
$Mg(CH_3COO)_2$	29.8 ± 0.90	0.84 ± 0.37	0.18 ± 0.12	>99
Salts	**Phosphate-P**			
	Inlet (mg/L)	**Draw solution (mg/L)**	**Permeate (mg/L)**	**Removal (%)**
NaCl	10.83 ± 1.54	1.09 ± 0.55	0.09 ± 0.02	>99
$CaCl_2$	10.67 ± 1.44	1.06 ± 0.61	0.10 ± 0.03	>99
$MgCl_2$	10.31 ± 1.09	0.89 ± 0.35	0.10 ± 0.01	>99
CH_3COONa	10.70 ± 0.66	0.75 ± 0.24	0.11 ± 0.05	>99
$Mg(CH_3COO)_2$	10.58 ± 0.44	0.78 ± 0.20	0.08 ± 0.05	>99

Table 4: Sludge filterability and floc size for draw solutions (DS)

Salts	**CST (s)**		**Floc Size (µm)**	
	Beginning	End	Beginning	End
NaCl	26	42	15.44	6.88
$MgCl_2$	25	37	13.96	9.81
$CaCl_2$	22	45	14.42	5.23
CH_3COONa	27	16	14.18	25.64
$Mg(CH_3COO)_2$	25	19	16.91	23.2

Figure Captions:

Fig. 1: Process flow diagram of the hybrid OMBR-MD system.

Fig. 2: Variations in (a) Normalized water flux of FO membrane and (b) conductivity (mS/cm) of mixed liquor in the OMBR.

Fig. 3: Concentration of COD in bio-tank supernatant with different DS in the OMBR-MD system.

Fig. 4: Concentration of PO_4^{3-}-P in bio-tank supernatant with different DS in the OMBR-MD system.

Fig. 5: Concentration of NH_4^+-N in bio-tank supernatant with different DS in the OMBR-MD system.

Fig. 6: Temporal variations in the concentration of (a) mixed liquor suspended solids (MLSS), (b) mixed liquor volatile suspended solids (MLVSS), (c) soluble microbial products (SMP), and (d) extracellular polymeric substance (EPS) with different DS in the OMBR-MD system.

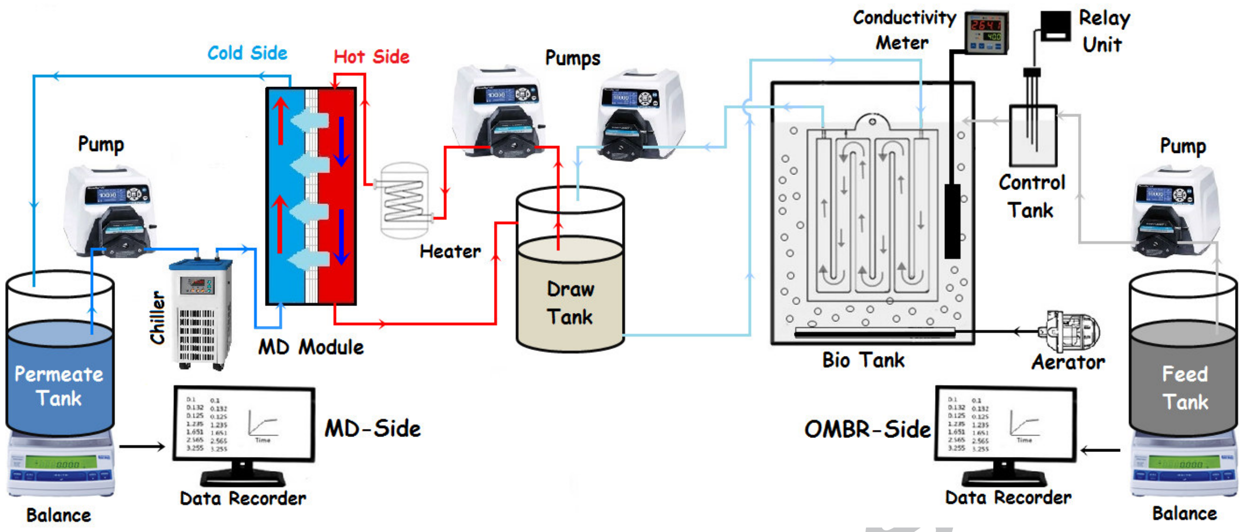


Fig. 1: Process flow diagram of the hybrid OMBR-MD system.

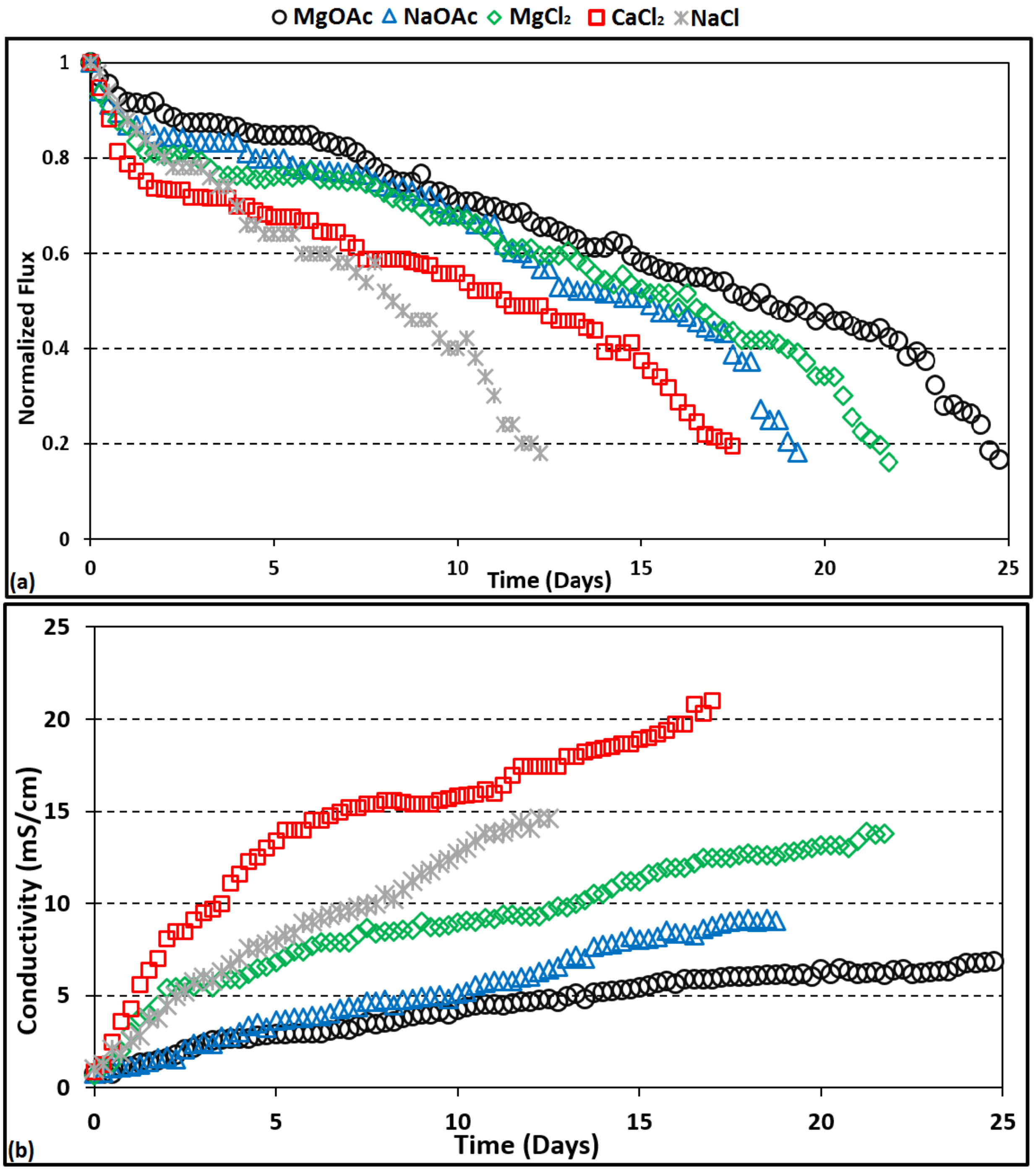


Fig.2: Variations in (a) Normalized water flux of FO membrane and (b) conductivity (mS/cm) of mixed liquor in the OMBR.

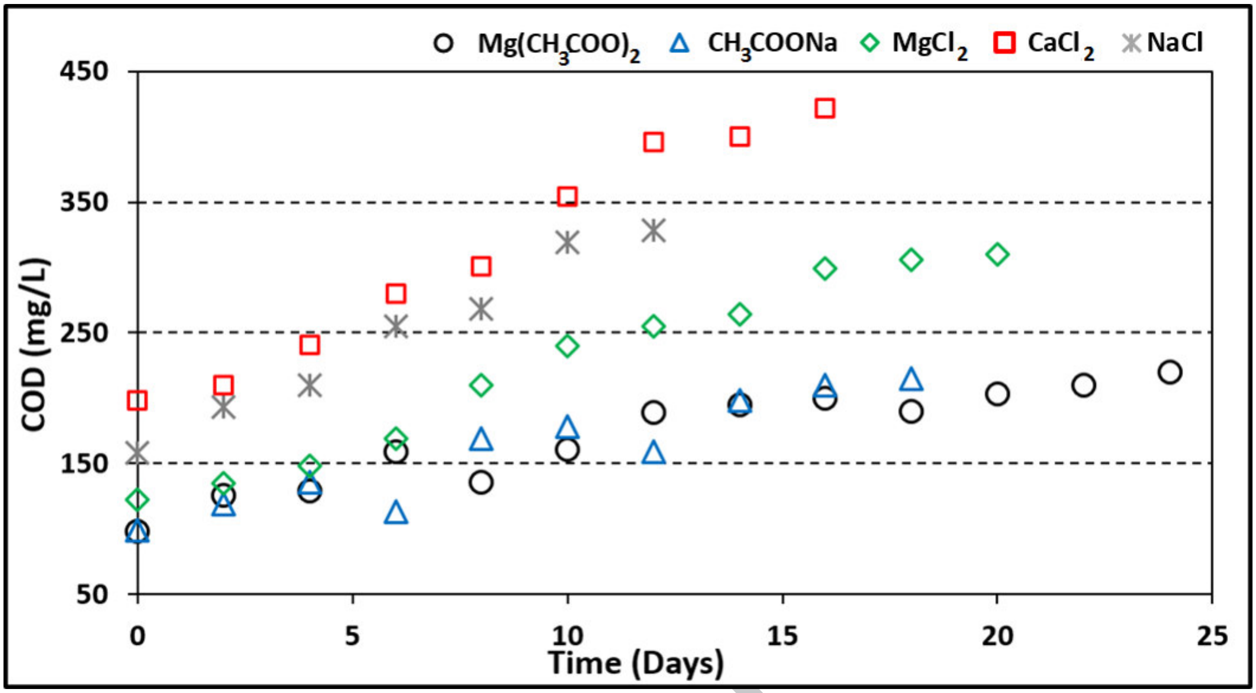


Fig. 3: Concentration of COD in bio-tank supernatent for each draw solution.

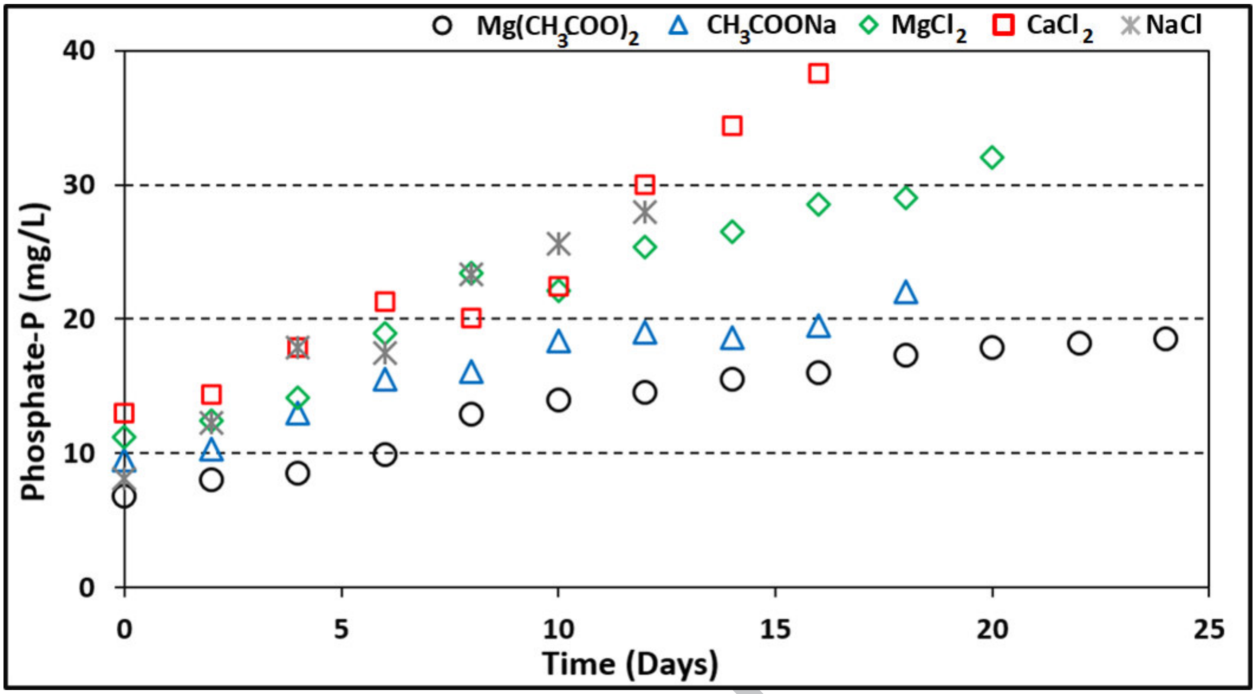


Fig. 4: Concentration of PO_4^{3-}P in bio-tank supernatent for each draw solution.

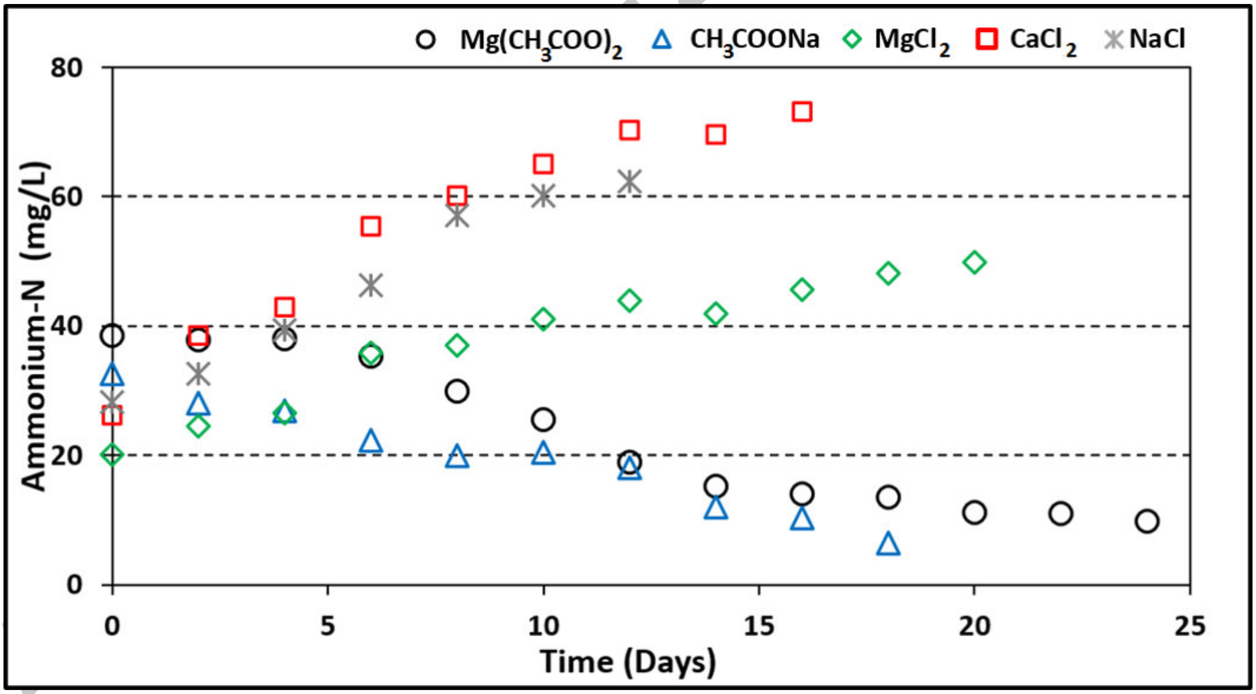


Fig. 5: Concentration of NH_4^+-N in bio-tank supernatant for each draw solution.

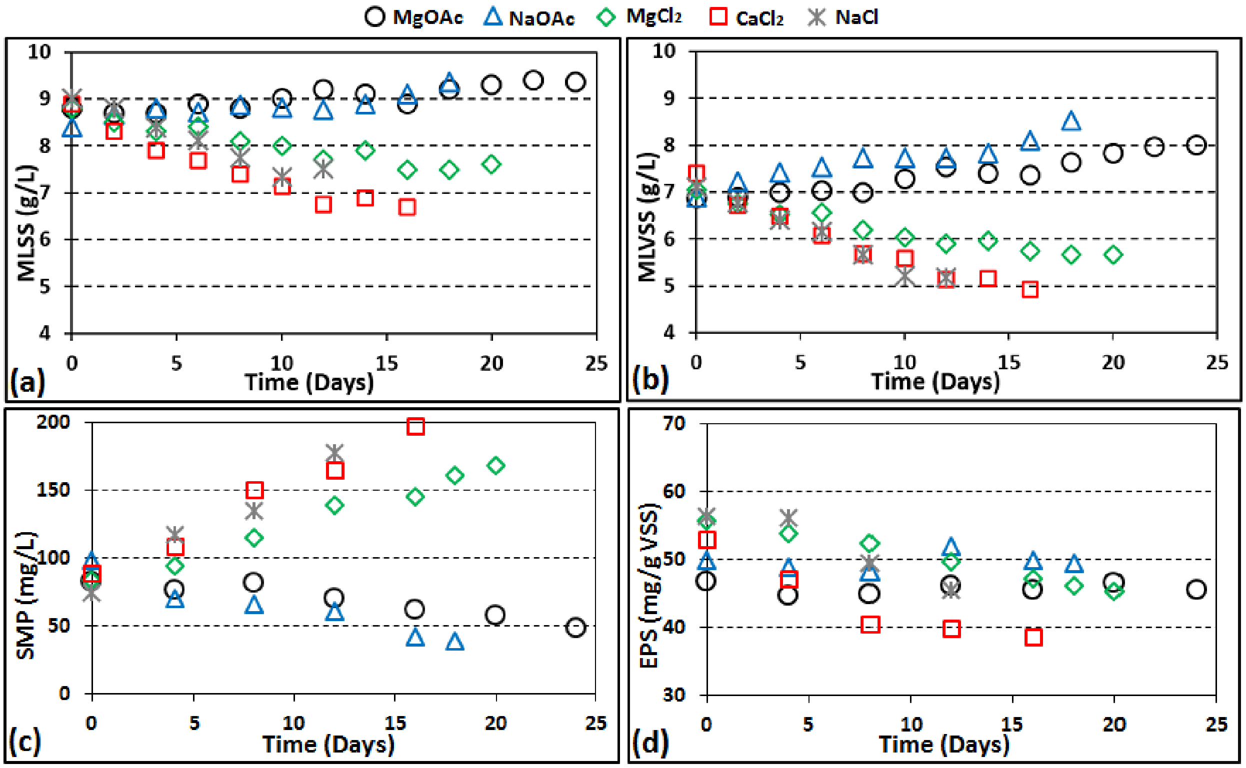


Fig. 6: Temporal variations in the concentration of (a) mixed liquor suspended solids (MLSS), (b) mixed liquor volatile suspended solids (MLVSS), (c) soluble microbial products (SMP), and (d) extracellular polymeric substance (EPS) with different DS in the OMBR-MD system.

Supplementary Data

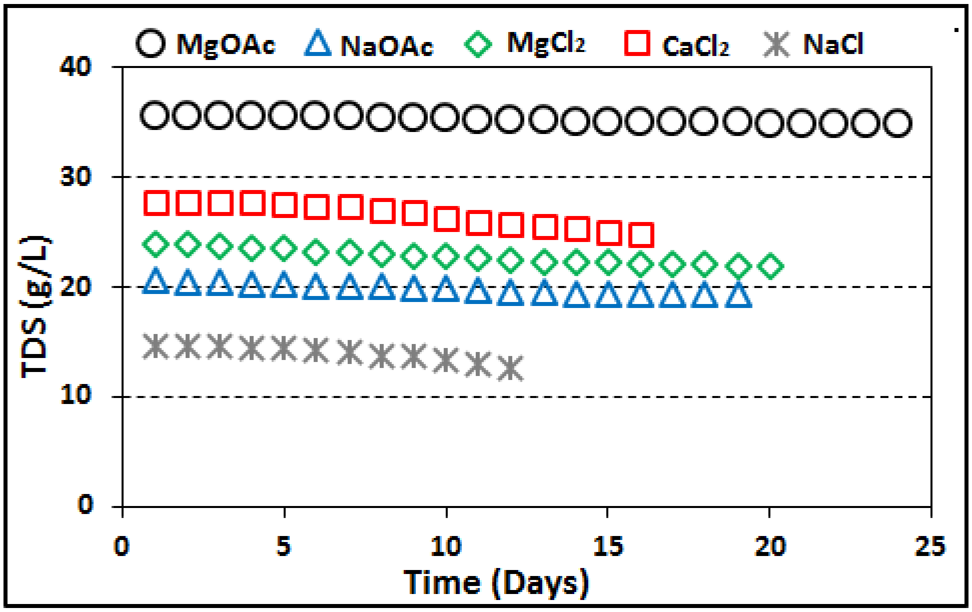


Fig. S1: TDS concentration in draw tank for each salts. Conductivity or TDS concentration remains almost constant for each draw solute, as MD membrane reject more than 98% of salts. At a same molar concentration filtration run for each draw solution completed when the initial water flux declined upto 20% of the initial flux. To match the water transfer rate of MD and FO membrane, techniques of forward flushing of MD membrane and reduction of circulating velocity was applied on MD side (section 2.3), as MD system is dependent on OMBR setup.

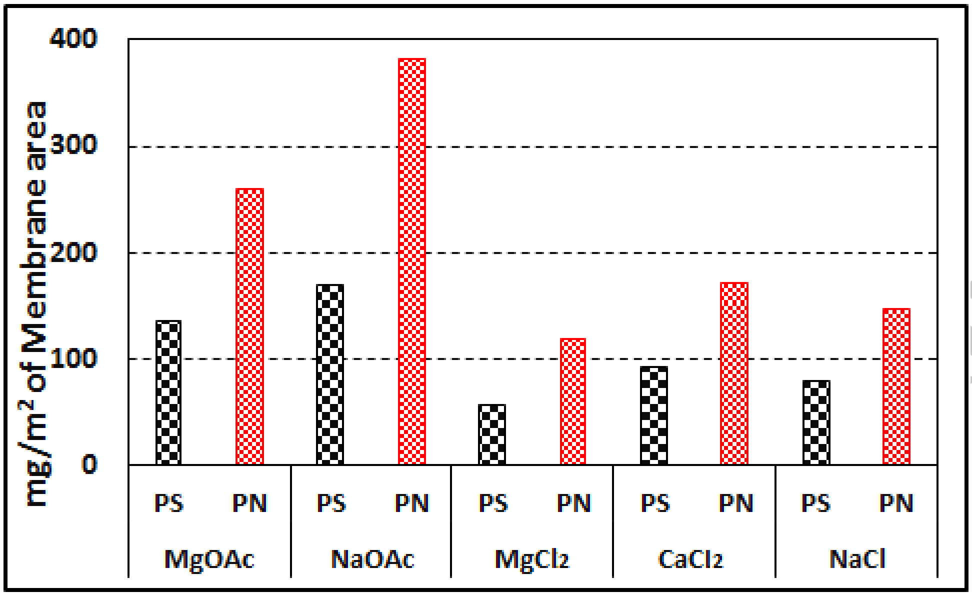


Fig. S2: Protein and carbohydrate contents in fouling layer found on the surface of FO membrane

Biomass deposition on membrane surface is shown in Fig. S3 below in terms of g/m^2 of membrane area.

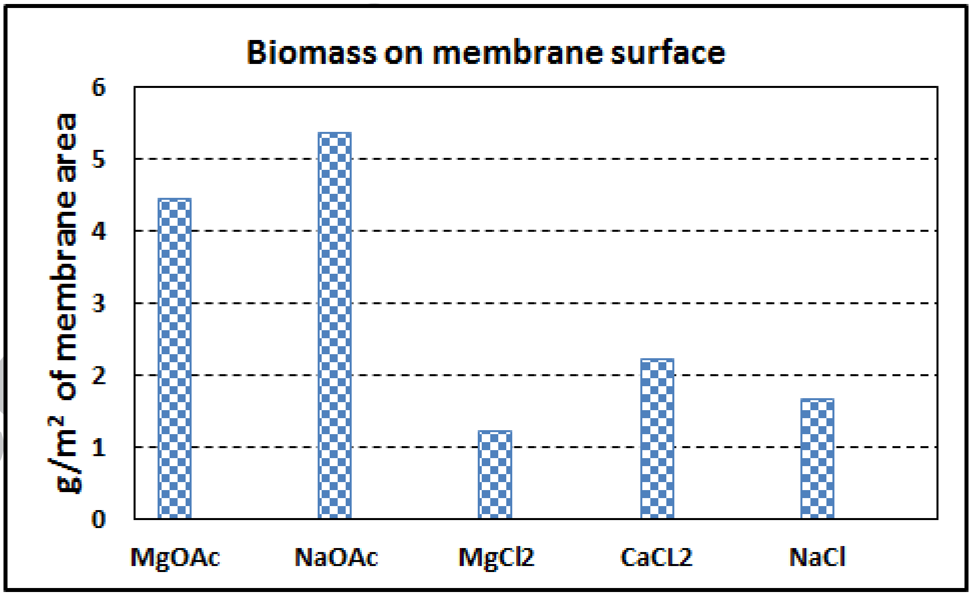


Figure S3: Deposition of biomass on the surface of membrane

It shows relatively increased deposition of biomass on the membrane surface with Organic salts. Deposition of excess biomass due to NaOAc as DS is responsible for relatively faster flux decline as compared to MgOAc as reported in Fig. 2. Also, Fig. S2 of supplementary data also shows increased value of EPS in attached biomass for NaOAc and MgOAc. However, the elevated salinity in bio-tank with the use of inorganic salts was dominant in terms of membrane fouling by severely affecting the water flux as compared to that of organic salts.

Table S1 : Hydrated diameter of ions used in this study.

Ions	Hydrated diameter (picometer)[a]
Anions	
Cl^-	300
$CH3COO^-$	450
Cations	
Na^+	450
Ca^{2+}	600
Mg^{2+}	800

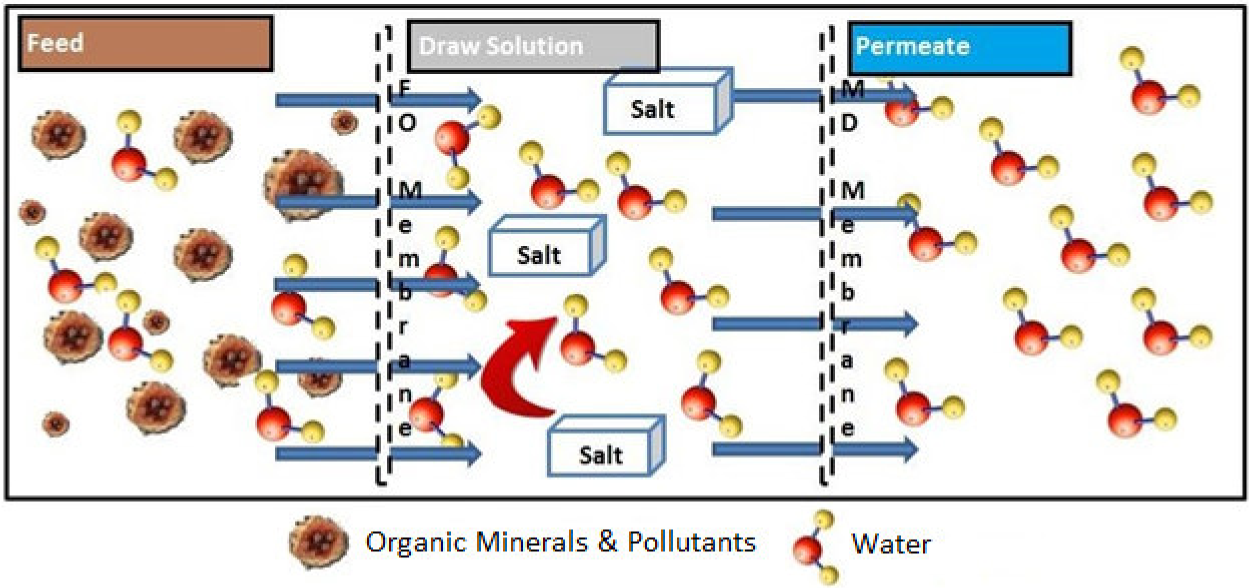
[a] Data from Achilli et al., (2010) and Kielland., (1937)

References:

Achilli, A., Cath, T.Y., Childress, A.E., 2010. Selection of inorganic-based draw solutions for forward osmosis applications. J. Memb. Sci. 364, 233–241. doi:10.1016/j.memsci.2010.08.010

Kielland, J., 1937. Individual activity coefficients of ions in aqueous solutions. J. Am. Chem. Soc. 59, 1675–1678. doi:10.1021/ja01288a032

Graphical abstract:



Highlights:

Increased salinity buildup and rapid flux decline was observed with NaCl and $CaCl_2$.

Acetate-based DS were found useful for the degradation of soluble microbial products.

Build-up of COD, NH_4^+-N and PO_4^{3-}P in bioreactor increased with chloride based salts.

98% removal of contaminants observed in permeate for each DS due to dual barriers.

Organic DS results into particle size enlargement and increased sludge filterability.