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Forward Osmosis as a Pre-Treatment Step for Seawater Dilution and Wastewater Reclamation

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Abstract

This chapter presents the exploration of the combined process of wastewater reclamation and seawater dilution using forward osmosis (FO). Wastewater and seawater are the two most abundant water sources that are free of the hydrological cycle and could serve as an alternative potable water source. Forward osmosis was chosen as the an ideal pre-treatment step to dilute seawater prior to desalination at relatively lower energy demand and low fouling propensity. Membrane fouling behavior was studied and investigated using different feed compositions bearing fractions of effluent organic matter (EfOM). The negative surface charge of all organic foulants was reduced by the adsorption of calcium ions. Filtration of feed streams containing single, simple organic foulants revealed that alginate (polysaccharides) and bovine serum albumin (BSA) resulted in significant loss in process performance as a result of permeate flux reduction. The complex mixture of alginate, BSA and humic acid caused severe loss in membrane performance due to dominant favorable synergistic interactions between foulants and between foulants and membrane surface. The forward osmosis process presents a viable alternative for a simple and effective seawater dilution step using wastewater as the feed solution. Process performance can be improved by selecting a foulant resistant membrane with matching flux.

Keywords: desalination, fouling, forward osmosis, membrane, seawater, wastewater

1. Introduction

Water forms part of the fundamentals of human existence, however; growth in human population and current extreme climatic conditions have resulted in many parts of the world (particularly arid areas) faced with minimal or no access to water supply. Statistics and research have predicted that over the next decade the impact of water crisis will increase fourfold.

It has been shown that developing countries are the most affected and about 80–90% of all diseases and 30% of all deaths result from exposure to poor quality drinking water [1, 2]. The lack of good quality water has adverse impacts on essential factors of human survival such as food and energy supply. Adequate supply of good quality water and affordable energy sources are vital to sustaining good public health and growing economic rate. Thus, there is a growing awareness among governments and corporations that the future prosperity of societies is intimately tied to the availability of fresh and safe drinking water [3, 4]. The possibility of wastewater reuse instead of disposing it has received increasing attention over the past decades as a viable solution towards minimizing the effect of water scarcity. Past studies have provided a baseline information that wastewater, brackish water, and seawater have great potential to augment shortage water supply, however; the energy expenditure and equipment required for purification of such water streams has limited their potential in many parts of the world [2, 5]. The reuse of wastewater for other applications rather than drinking purpose is already established and examples include the irrigation of golf courses or industrial cooling [6].

Thus water reuse and desalination technologies have been identified as promising strategies to provide safe drinking water to water-stressed communities [2]. Desalination and wastewater reclamation using pressure-driven membrane processes such as nanofiltration (NF) and reverse osmosis (RO) processes have been elaborately applied to produce potable water from brackish and seawater as well as treated wastewater effluent [7]. Pressure-driven membrane processes such as RO and NF rely on the use external hydraulic pressure to overcome the osmotic pressure of the feed solution and produce purified permeate water [8]. The applied pressure is the driving force for mass transport through the membrane. The over-arching advantage of RO is that it produces high quality permeate water that in most cases ready for use. However, there are several inherent drawbacks such as its heavy reliance on hydraulic pressure, large concentrate volumes, and high membrane fouling propensity have greatly restricted its sustainable development in recent times, especially in developing countries, due to the soaring oil and electricity prices [9].

Normally wastewater is composed of a wide range of pollutants and substances which could negatively affect human and aquatic life. The nature of the compounds found in reclaimed water may be of concern in drinking water, but not in water intended for landscape irrigation and other peripheral uses. Among the constituents of wastewater is effluent organic matter (EfOM) which comprises of a range of low- to high-molecular-weight organic compounds such as polysaccharides, proteins, humic and fulvic acids, organic acids and lipids [1, 10]. And it has been repeatedly reported that among the different EfOM components; humic acids, polysaccharides and proteins were responsible for extensive membrane fouling [11]. The chemical complexity and heterogeneous nature of wastewater present a challenge to developing a proper understanding on the key role of the interactions between the different kinds of organic compounds in permeate flux decline as well as fouling layer formation. And numerous findings have attributed the observed difficulty in treating wastewater to the synergistic effects between co-existing organic species [1, 12].

Thus, major efforts have been made to design water treatment technologies that are environmentally friendly, energy-saving and have greater permeate water recoveries with high produced water quality [13]. Innovative membrane separation processes such as forward osmosis (FO) have shown great potential for application in seawater dilution, wastewater treatment and reclamation [14]. Several advantages make the forward osmosis process a more attractive alternative compared to other techniques and they include low energy utilization, lower membrane fouling propensity, simplicity as well as the good rejection of a wide variety of foulants compared to pressure-driven membrane processes [13, 15]. The forward osmosis can also be fitted as an additional step to pressure-driven processes resulting in hybrid processes with potentially improved water recovery and energy savings [16, 17].

Thus, this work seeks to develop insight into the performance of a forward osmosis process as a pre-treatment step for seawater dilution. Significant focus was directed to developing a proper mechanistic understanding of forward osmosis membrane fouling behavior during seawater dilution and wastewater reclamation; where the fouling processes are more complex compared to simple feed and draw solutions. Combined wastewater reclamation and seawater dilution have the potential of fouling both sides of the membrane and thus hugely impacting the process performance. This is due to altered foulant-membrane and foulant-foulant interactions as well as more severe internal concentration polarization effects.

1.1. Forward osmosis membrane processes for water treatment

The main driving force in a forward osmosis membrane separation process is the chemical potential difference between the two solutions across a semi-permeable membrane; that is: pure water diffuses from an impaired source (feed solution) through a semi-permeable membrane to a solution of higher solute concentration (draw solution) induced by osmotic pressure difference. Forward osmosis has inherent potential advantages that highlight it as a promising alternative to pressure-driven membrane separation technologies [16]. These advantages include low energy consumption due to minimal or non-use of external hydraulic pressure. As a result of utilizing low external hydraulic pressure, the subsequent fouling cake layer is much less compressed and can be easily detached by simple physical cleaning methods. Thus, many of the possible forward osmosis applications can be performed with low-quality feed water, including domestic and industrial wastewater/wastewater effluent. Osmotic driven processes can also be integrated to pressure-driven membrane counter-parts such as reverse osmosis to form FO-RO hybrids aimed at improving process performance and lowering energy utilization. However, energy expenditure can only be reduced when forward osmosis is situated before reverse osmosis, as a pre-treatment step to reduce reverse osmosis fouling and scaling; subsequently minimizing the intensity of hydraulic pressure applied to treat water. Thus, in pure thermodynamic terms energy saving is not possible in a closed-loop FO-RO unit. Forward osmosis also has a high rejection of a wider range of inorganic and organic contaminants. In addition, the claimed lower membrane fouling

propensity when compared to pressure-driven membrane processes is yet to be proven at high fluxes in real practice. Its process further presents the ability to recover and reuse the osmotic agent [17].

Forward osmosis has found application in a variety of fields such as the production of nutrient-rich drinks that are used as part of life-saving equipment in life boats. The process has also been applied in food processing, in emergencies such as natural disasters as an osmotic concentration of liquid foods [18–26]. As previously stated, it is a robust membrane separation technique that boasts of good rejection of a broad range of pollutants and foulants and dissolved ions. It is therefore for these reasons that it's being researched and improved for water treatment applications such as seawater desalination [27–29], wastewater reclamation [30–33], industrial wastewater treatment [34], brine concentration [35], osmotic membrane bioreactors [36] and the use of the salinity gradient for power generation or osmotic dilution prior to reverse osmosis seawater desalination (using impaired water as feed and seawater as draw solution) [37].

Some of the recent performed research studies in water treatment include comparing the impacts of membrane surfaces (such as the asymmetric polyamide thin-film composite and cellulose triacetate) and system operating conditions on the performance of forward osmosis membranes for membrane desalination of produced water using a standard method and system operating conditions similar to those applied in the operation of industrial-scale spiral wound reverse osmosis membranes conducted by Coday et al. [1, 38]. They found that rejection of inorganic solutes was greater than 94% and dissolved organic carbon was higher than 93%. However, the rejection of total nitrogen (TN) was poor, recording a moderate 63%. Duong and co-workers, [39] evaluated the performance of the forward osmosis process in treating stable oil–water emulsions. Their study demonstrated that FO was successful in the treatment of a wide range of oil–water emulsions from low to very high concentrations of up to 200,000 ppm. Water was separated from oily feeds containing 500 ppm or 200,000 ppm emulsified oil at a relatively high flux of $16.5 \pm 1.2 \text{ L m}^{-2} \text{ h}^{-1}$ or $11.8 \pm 1.6 \text{ L m}^{-2} \text{ h}^{-1}$, respectively, using a thin film composite membrane at a draw solution concentration of 1 M NaCl. The membrane managed to achieve an oil rejection of 99.88% and producing permeate water with negligible oil concentrations.

The forward osmosis process was used for the dilution of concentrated fertilizer solution which was then applied for fertigation purposes [35, 40]. Furthermore, the idea of combining wastewater treatment and desalination using FO-RO hybrid system was also proposed and investigated [41–43]. Hancock et al. [44] piloted a forward osmosis process scale during simultaneous seawater desalination and wastewater reclamation and subsequently evaluating its performance. A commercial spiral wound forward osmosis membrane element was tested continuously for 1300 h of processing 900,000 L of wastewater effluent and producing 10,000 L of treated water through a hybrid FO-RO process. Water flux was maintained at a relatively constant rate of $5.7 \pm 0.2 \text{ L m}^{-2} \text{ h}^{-1}$ with membrane bioreactor permeate feed and seawater draw solution. Test of sample fluorescence showed that the forward osmosis membrane and the hybrid process provided a strong rejection of protein-like species associated with wastewater effluent. There was also 99.9% removal of orthophosphate and dissolved

organic carbon and more than 96% rejection of nitrate. However, as briefly stated, most forward osmosis applications are still restricted to small-scale laboratory experiments. More elaborate studies and conceptual proofs are required to turn its promising performance into a fully-fledged water treatment process.

1.2. Challenges and progress in water reuse and desalination technologies

The process of water desalination requires high electrical power input to achieve high water recoveries, which implies high capital and overall operational costs. It is believed that the cost of saline water desalination including infrastructure, maintenance and energy are very exceeded those needed for other common alternatives such as treating surface water and or ground water. The heavy energy demand of this process remains the hindrance to its extensive application. The theoretical value of about 0.86 kWh of energy is required to desalinate 1 m³ of salt water (34,500 ppm) which is equal to 3 kJ kg⁻¹. However, in reality this value is normally inflated 5 to 26 times depending on the type of process used. Thus, clearly; it is necessary to make attempts to reduce the energy demand of process as much as possible [45].

The other aspects of saline water desalination include environmental impacts that need consideration. Thus, the disposal of saline concentrate into the water bodies also represents a huge environmental issue when using RO desalination technology. Recent years have seen stricter regulation being established in to protect receiving water bodies, aquatic life, and public drinking water sources by reducing total dissolved solids in brine that could be discharged into waterways. So it can be concluded that the combined treatment of wastewater and seawater could lead to double (heavy) membrane fouling, but; eliminating the use of pressured membrane process where the cake layer can be easily compacted eases the fouling irreversibility [46, 47]. This provides more motivation to explore forward osmosis processes that inherently have low membrane fouling propensity due to the absence of applied hydraulic pressure.

1.3. Determining factors of the forward osmosis membrane process

Permeate flux rate is commonly used as one of the primary performance indicators for membrane-based processes and is influenced by several factors that can be generally categorized as membrane properties, reverse salt diffusion and concentration polarization, feed water quality (and fouling) and operating conditions [48].

1.3.1. Membrane properties

The efficiency of an FO processes is directly linked to its membrane which in –turn is defined by its intrinsic separation properties stemming from the material used in its synthesis or preparation. The most used membrane performance parameters include the pure water permeability (A), solute rejection (R), solute permeability coefficient (B) and structural parameter (S). The membrane water permeability (A) is defined as the transport/passage of water through the membrane per unit driving force. The ability of a membrane to partially or completely retain solutes while allowing free passage of water molecules is referred as solute rejection (R),

whilst the solute permeability coefficient (B) is described as the transport of a particular solute through the membrane per unit driving force at given water flux. The structural parameter (S) is a factor that defines the influence of membrane support thickness, porosity and tortuosity on mass transfer in the support layer [49, 50]. Membranes commonly used for osmotically driven filtration processes are characterized by an asymmetric structure defined by a dense thin top selective layer usually followed by a porous sub-layer. Ideally, a membrane needs to be freely permeable to the solvent (water) and completely retain the solute. Therefore, water permeability describes the extent to which water is able to percolate through the membrane's structure (Eq. 1), which is usually determined using hydraulic pressure.

$$A = \frac{J_w}{\Delta P} = \frac{V_{perm}}{A_m \Delta t \Delta P} \quad (1)$$

Where A_m represents the membrane's effective surface area (m^2), V_{perm} is the volume of the permeated water (L), Δt is the time elapsed during the permeation (h) and ΔP is the pressure difference across the membrane (bar).

The water transport across an osmotic membrane is generally described according to:

$$J_w = A(\Delta P - \Delta \pi) \quad (2)$$

Where A is the membrane water permeability ($L h^{-1} bar^{-1}$), ΔP is the pressure difference across the membrane (bar), $\Delta \pi$ is the osmotic pressure differential across the membrane (bar). The osmotic pressure of a solution can be calculated from the Morse equation. This equation is derived from the van't Hoff work (Eq. 3) on osmotic pressure and only applies to solutions with dilute concentrations (i.e. $< 0.5 M$). This equation indicates that osmotic pressure is linearly proportional to the solute concentration, (i.e. the higher the solute concentration, the higher the osmotic pressure of the solution).

$$\pi = imRT = i\left(\frac{n}{v}\right)RT \quad (3)$$

Where: i is the van't Hoff factor, (defines the number of ions produced during dissociation of a solute in an aqueous solution), m is the molarity of the solute which is equal to the ratio of the number of solute moles (mol) to the volume of the solution (L), R is the universal gas constant ($8.3145 J K^{-1} mol^{-1}$), T is the absolute temperature (K).

However, this equation does not hold for solutions with higher concentrations (usually $> 0.5 M$). When computing the osmotic pressure of concentrated draw solutions other factors such as solution viscosity come into play [51]. In addition to water permeability property, a membrane has to have selectivity for solutes and is expressed by a rejection coefficient (R):

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \quad (4)$$

Where the solute concentrations on the feed and permeate, are represented by C_f and C_p respectively. Water permeability (A) and solute rejection (R) are membrane characteristics

which are mainly linked to the active layer, that is; the active layer should permit water molecules to diffuse across while retaining solutes and other unwanted substances.

1.3.2. Draw solution

A draw solution is described as the solution of higher solute concentration and osmotic potential, relative to the feed solution, such that net pure water is induced through the membrane from the less concentrated impaired water to the draw solution to dilute it [52–55]. Different varieties of draw solutions have been evaluated for forward osmosis processes with the aim to achieve a low energy separation method for clean water production. And currently reverse osmosis is the best option for post-treatment of FO treated water, it can be used to separate the draw solution to produce clean potable water. However, there are still concerns about its reliance on hydraulic pressure which translates to high energy demand. Thus, FO draw solute regeneration can be made less energy intensive through the use of low grade energy sources but there can be some gains in energy depending on the type of energy used. In a closed loop FO-RO hybrid set-up, the energy utilization will always be higher than that of just reverse osmosis. But, when fouling in reverse osmosis is reduced then the practical energy consumption of FO-RO hybrid might be lower than just reverse osmosis.

Several fundamental criteria are considered when selecting draw solutions and are as follows: (i) the solute must have a high osmotic efficiency which results from high solubility in water and relatively low molecular weight; (ii) the osmotic agent must also be easily and economically separated from the diluted draw solution to yield potable water without being used up in the process; and (iii) the osmotic agents should ideally be inert, stable, neutral or near neutral pH, and nontoxic. Furthermore, the draw solutions should not be toxic to the membrane's physical structural integrity [52, 54]. Therefore, this makes finding the appropriate draw solution a systematic task. The solutes used to generate osmotic pressure for osmotic processes can be put into four major categories: inorganic solutes, thermolytic/volatile solutes, organic solutes, and polymer-based macro-solutes [56–59].

Inorganic salts are by far the most used draw solutes in FO and PRO research and this is down to abundant availability, affordability, and the ability to generate high osmotic pressures that induce high membrane flux [57, 58].

Thermolytic salts, on the other hand, are considered a unique kind of draw solutes, constituting of highly soluble gases and or volatile solutes that can produce high osmotic pressures and can be easily recovered [59]. This presents the opportunity to evaporate and regenerate the draw solute via the use low temperatures from poor quality heat sources (e.g., power plants) [60, 61]. The $\text{NH}_3\text{--CO}_2$ mixture has received extensive attention as a potential thermolytic draw solution. In the case of high draw solution concentrations can be created through manipulating the ratio of NH_3 to CO_2 [59, 62]. Application of thermal processes, heating to around 58°C is required to boil away the NH_3 and CO_2 and produce clean permeate water. These gases (NH_3 and CO_2) are then re-combined to produce thermolytic salt and utilized again to generate osmotic pressure. However, the small hydration ions of NH_4^+ compared to those of divalent cations (Ca^{2+} and Mg^{2+}) lead to high reverse salt diffusion rate from the draw

solution side to the feed water which greatly reduces the effective driving force. The need to apply a significant amount of thermal energy to boil away NH_3 and CO_2 stands as a major hindrance to the development of this draw solution.

It is for these concerns that recent studies have emphasized on polymer-based macro-solutes as potential osmotic agents, which allow easier recovery using low-pressure filtration processes such as ultrafiltration [63, 64]. However, the efficient use of ultrafiltration in the separation can have counter-effects, the accumulation of osmotic agents on the membrane can lead to a build-up of osmotic pressure that can lower the efficiency of the separation process. One outstanding advantage is that the polymer's molecular configuration and size can be tailored to produce draw solutions that give high osmotic pressure and desirable performance.

The lack of ideal draw solutes in forward osmosis is just but one drawback, the non-existent of cheap and simple draw solute separation strategies from the diluted draw solution to produce clean usable water is an area of paramount importance. Thus, attempts have been made recently towards the design of negatively charged super-paramagnetic nanoparticles that can be used in the recovery of an $\text{Al}_2(\text{SO}_4)_3$ draw solute through coagulation [63, 65]. These previous research work have given an insight that future studies should combine the synthesis of novel, easily separable draw solutes, with novel and effective draw solute recovery technologies.

1.3.3. Feed water quality and osmotic gradient

The performance of the FO process is highly linked to the feed water composition. The targeted feed streams for the FO process include brackish water, seawater, treated wastewater effluent and industrial wastewater [20, 26, 27, 66, 67]. These are impaired water types composed dissolved substances or compounds that can induce membrane fouling and cause a severe decline in permeate flow [23, 24, 68–71]. Therefore, the sustainability of membrane permeate flux during FO operation is hugely influenced by feed water composition (foulant type, concentration and physicochemical properties) as well as the feed solution chemistry (i.e. solution pH, ionic strength and cationic species concentration) [65, 69–72]. The high osmotic pressure of seawater can lower the effective osmotic gradient or driving force, subsequently lowering water recovery which subsequently implies that the direct use of seawater as a feed stream in pressure-driven membrane processes such as RO amounts to huge energy consumptions.

Permeate flux is one performance indicator for a membrane-based process and is primarily dependent on the applied osmotic gradient. Therefore, the use of ideal draw solution that can generate high osmotic pressure ($\Delta\pi$) is critical for advancing FO technology [73]. The osmotic pressure difference is a result of the solute content of both the feed and draw solutions. A higher draw solution concentration gives a large osmotic pressure potential which in turn induces high permeate rates. The relationship between draw solution concentration and permeate flux is not linear mostly due to reverse diffusion of the osmotic agent and concentration polarization which are inherent phenomena of forward osmosis [37].

1.3.4. Operational conditions

Conducting a forward osmosis filtration tests involves the optimization of external operating parameters which have a huge role on the overall performance of the system. They include hydrodynamic parameters such as initial flux and cross-flow velocity as well as temperature. The aforementioned conditions strongly impact the output of an FO process, for example; it has been revealed that a higher cross-flow velocity minimizes the boundary layer thickness and concentration polarization, thus; subsequently lowering membrane fouling rate and enhancing water recovery [74]. Feed water composition and operational temperature can also hugely impact the performance of an FO membrane process. Operating temperature is closely linked to mass transfer, salt solubility, membrane fouling and concentration polarization, regardless of being a difficult parameter to monitor in practice, temperature is one critical operating condition [75–77]. Zhao and Zou, [40] observed increased water fluxes and recovery when higher operating temperatures were applied during filtration which they attributed to the decrease in permeate viscosity and an increase in osmotic pressure (and thus driving force), water permeability and mass transfer. Similar observations were made by Xie et al. [72] they found that the water permeability (A) values for different forward osmosis membranes increased with increasing temperature. However, in addition to increased water fluxes, the solute permeability coefficient (B) value was enhanced as well leading to higher reverse salt diffusion rates. The membrane structure factor, S was found to be unaffected by elevation in operating temperatures.

1.3.5. Membrane fouling

Membrane fouling is a broad term that describes the deposition and eventual accumulation of all kinds of substances on the membrane surface resulting from complex physical and chemical interactions between foulants and membrane. Fouling occurs when unwanted substances in the feed water block membrane pores or form an extra cake layer that generates resistance towards permeate flow through the membrane [75, 76, 78, 79]. Any membrane process using impaired water sources are subject to fouling. The fouling process in forward osmosis is said to be reversible due to the lack of pressure on the feed side, as a result foulants loosely bind to the membrane surface; however, the coupled occurrence of membrane fouling and concentration polarization lead to a severe decline in permeate flux [71]. There are four reported types of fouling often encountered in osmotic membrane filtration: inorganic fouling (scaling), biological fouling, colloidal fouling and organic fouling. Large quantities of research have been dedicated to understanding the subject of membrane fouling in osmotic membranes [77, 78, 80]. As partially highlighted, membrane fouling is linked to membrane and foulant's physicochemical properties [81]. Therefore, in summary, it can be stated that the eventual deposition of foulants on the membrane surface depends on the interplay of many factors that can be grouped into feed-water characteristics, hydrodynamic conditions and membrane properties. Attempts to investigate the fundamentals of membrane fouling have shown that the general mechanisms of fouling in osmotic membranes include adsorption, chemical interactions between solutes and membrane, gel formation and bacterial formation [75, 76, 79, 82, 83].

1.4. Challenges of the forward osmosis membrane process

Despite the various potentially attractive advantages of the FO process, it is still yards away from matching reverse osmosis mainly due to the number of obstacles that need to be resolved before its practical real-world implementation [53, 54]. Some of the efforts directed to advancing the forward osmosis technology include conducting systematic experimental research to solve challenging problems including identification of new draw solutes that will be capable of generating higher osmotic pressure, but are still easily separated from the diluted bulk draw solution at lower energy consumption [61, 64]; in addition to this there is the need of tailoring membranes that will decrease the effect of internal concentration polarization (ICP) which mostly occur in the porous support layer of current forward osmosis membranes and significantly reduces water flux because the diffusion of solutes is hindered and hydrodynamic force cannot effectively mix solutions inside the porous support layer [84].

More strategic progress in membrane and draw solute design need to be made for practical up-scaling of the FO technology. However, the subject of membrane fouling has not been fully understood and developed, but is essential to the significant improvement and viability of osmotically driven membrane processes in water treatment. Investigation of FO membrane fouling needs to be emphasized particularly at sufficiently high fluxes that allow economic sustainability. Even though the fouling propensity in forward osmosis is often stated to be relatively mild compared to reverse osmosis [85–88], there remains a need to effectively minimize fouling in order to increase process performance and prolong membrane lifespan. Membrane fouling does not only lead to a decline in permeate water flux, but also deteriorates the permeate water quality and consequently inflates the operating and membrane replacement costs. This is also the subject of interest in this work; therefore, the next sections will be expanding the discussion on the effect of membrane fouling on membrane flux loss in a forward osmosis processes, as well as potential alleviation remedies.

2. Combined wastewater reclamation and seawater dilution

The forward osmosis membrane process was then used to dilute seawater using simulated secondary treated wastewater effluent as feed solution in a laboratory scale setting. The system performance in recovering water was evaluated. Membrane fouling and fouling behavior were investigated.

2.1. Materials and methods

Sodium alginic acid salt, humic acid, bovine serum albumin and octanoic acid were used to as model organic foulants representing common polysaccharides, part natural organic matter (humic substances), proteins and fatty acids respectively in wastewater. These organic macromolecules have been reported to be the major components of organic fouling during membrane-based filtration systems [89, 90]. Alginate had an average molecular weight of 12–80 kDa. Stock solutions of 2 g/L were prepared by dissolving alginate powder in deionized (DI) water

by mixing vigorously for 24 hours then kept at 4°C. The stock solution was stored for a maximum of 12 h before use. The molecular weight of humic acid ranged from 12 to 80 kDa as indicated by the supplier, and was prepared by dissolving 2 g/L in deionized water and vigorously stirred for 24 h after which, it was diluted to the desired concentration. Bovine serum albumin received in a powder form with a molecular weight of approximately 66 kDa. It was stored at 4°C upon delivery and was prepared by dissolving 1 g/L in deionized water over 24 h. Octanoic acid was received in a liquid form and was stored at room temperature. Stock solutions were prepared by mixing 1 g/L with deionized water and its pH was adjusted to around 6.7 using 0.05 M NaOH prior to addition to the feed solution. These model organic compounds were all supplied by Sigma-Aldrich (St Louis, MO) and were used as received. They were selected for this particular work because they are functionally similar to the organic foulants in wastewater effluent, so the observed fouling behavior and mechanisms might be comparable to real water effluent treatment using the FO process. However, the simulated wastewater used in this work does not contain particles, nor all the mentioned organic fractions, so real one on one translations could be difficult.

Three types of forward osmosis membranes were used in this work; cellulose triacetate membrane, thin film composite and Porifera membrane. The first two were supplied by Hydration Technologies, Inc. (Albany, OR) while the Porifera membrane was supplied under a confidentiality agreement. The cellulose triacetate membrane possesses an asymmetric structure made of a cellulose acetate skin layer supported by embedded polyester mesh. The thin film composite had a polyamide surface modification while the Porifera membrane was modified to be resilient to fouling (anti-fouling modification). Both the cellulose triacetate and Porifera membranes were stored in ultrapure water at 4°C prior to use. While the thin film membrane was stored in special packaging away from direct light and was soaked in ultrapure water for a minimum of 3 h before use.

The pure water permeability coefficient (A) of the forward osmosis membranes was determined in a laboratory-scale cross-flow reverse osmosis set-up. The effective membrane area was 49 cm² and the cross-flow velocity was fixed at 10 cm s⁻¹. Initially, the membrane permeate flux was equilibrated with deionized water at an applied pressure, ΔP , of 8 bar (116 psi), until the permeate flux reached a steady value. After equilibration, the volumetric permeate flux was measured at applied pressures ranging from 2 to 12 bar (29 to 174 psi) in increments of 2 bar (29 psi). The membrane's water permeability coefficient (A) is given by the slope of water flux plotted against applied pressure [65], using Eq.1.1.

The membranes' intrinsic separation parameters determined using equations Eq. 1–4 are presented in **Table 1**. And it is shown that the traditional flat sheet CTA membrane had the lowest pure water permeability (A) and highest salt permeability coefficient (B), with corresponding with a rather lower salt rejection. The thin-film composite membrane (TFC) had significantly increased pure water permeability compared to cellulose triacetate. It also recorded the lowest salt permeability coefficient (B) which translated to a high salt rejection (R). The novel Porifera membrane had the highest pure water permeability (A) and a high salt rejection almost similar to that of the thin film composite membrane. There was no clear correlation between the membrane structural factors and the other parameters. However, the superior

	A	B	R	S
	L/m ² h bar	×10 ⁻⁷ m/s	%	μm
CTA	0.61	1.5	88.5	663
TFC	1.17	0.2	98.2	1227
POR	1.89	1.3	96.0	344

Table 1. Forward osmosis membrane intrinsic separation properties.

performance of thin film composite and Porifera membranes compared to the cellulose triacetate membrane was demonstrated, based on their respective *A*, *B* and *R* values (**Table 1**). These values also confirm the improvement made in water permeability and solute rejection of thin film composite membranes [86, 87, 91].

The different simulated fractions of effluent organic matter were fixed into the following concentrations: 200 mg/L, 100 mg/L, 80 mg/L and 20 mg/L for humic acid (HA), bovine serum albumin (BSA), alginate (Alg), and octanoic acid (OA) respectively. The total feed ionic strength was fixed at 20 mM using 17 mM NaCl and 1 mM CaCl₂. The fouling characteristics and potential of the model organic foulants were determined by conducting single foulant experiments for all four model foulants. Possible synergistic effects between foulants were investigated by preparing mixtures of two or more foulants that were then used to conduct fouling tests. The different feed solutions used to investigate thin film membrane fouling behavior are listed in **Table 2**.

2.2. Laboratory test unit

Laboratory filtration tests were performed using a self-assembled forward osmosis cross-flow set-up. It consisted of two closed loops dedicated to the feed and draw solution streams. These solutions were pumped past the cross-flow membrane cell and circulated using variable speed pumps (Cole-Palmer, USA). The cross-flow membrane cell was custom built with equally structured channels on both sides of the membrane. Each channel had the dimensions of 250, 50 and 1 mm for length, width and depth respectively. A polypropylene diamond spacer mesh was added on either side of the TFC membrane to create turbulence and mimic real membrane filtration processes. The change in feed solution weight was monitored over time through a weighing balance (Ohaus, USA) connected to a computer for data logging. These changes in feed water weight over time were used to calculate the water flux during membrane filtration tests.

During filtration, the permeate water gradually dilutes draw solution which decreases its concentration and in-turns reduces the osmotic drive force across the membrane. To prevent this effect, the concentration of the draw solution was maintained at a constant value using a real-time conductivity based program using a Consort conductivity meter (C3310 model, Turnhout, Belgium). Varying amounts of dry salt were dosed into the draw solution triggered by a decline in conductivity [92]. The schematic of the laboratory scale FO cross-flow unit is illustrated in **Figure 1**.

A program-controlled (LabVIEW software, National Instruments, UK) 3-way valve was installed on the draw solution return tube just before it enters the draw solution tank (**Figure 1**).

Feed solution composition	Ionic strength (mM)	Draw solution concentration (m)
100 mg/L BSA	20 mM (20 mM NaCl)	0.52 M NaCl
80 mg/L Alg		
20 mg/L OA		
200 mg/L HA		
BSA + Alg*	20 (17 mM NaCl +1 mM CaCl ₂)	
Alg + HA + OA*		
Alg + OA + BSA*		
Alg + HA + BSA*		
Alg + HA + OA*		

*The concentrations of the single foulants were kept the same in their mixtures (100, 80, 20 and 200 mg/L for bovine serum albumin; BSA, alginate; ALG, octanoic acid; OA and humic acid; HA, respectively).

Table 2. Feed solution composition, ionic strength and draw solution concentration.

The valve temporally directs (at set intervals) the draw solution into a filter funnel containing dry solid salt (NaCl) after being triggered by a decline in draw solution conductivity. The dissolved salt then dripped into the bulk draw solution to correct the dropping solution conductivity and keep the draw solute concentration constant [50, 92].

2.3. Seawater dilution testing protocols

Membrane filtration tests were performed with the high-performance polyamide modified thin film composite forward osmosis membrane characterized by a hydrophilic surface using synthetic seawater as a draw solution. Particular emphasis was made on studying the effect of foulant synergy on permeate flux loss during wastewater effluent treatment. Furthermore, the effect of different membrane surfaces on fouling behavior was investigated using two additional forward osmosis membranes.

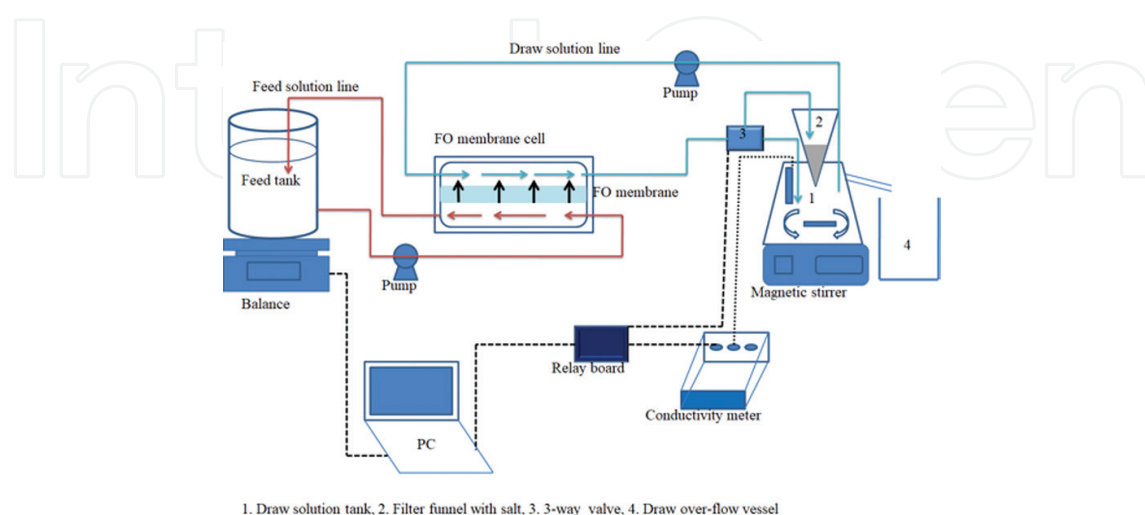


Figure 1. Schematic of the laboratory scale forward osmosis cross-flow test unit.

In all fouling tests, sodium chloride (0.5 M) was used to induce permeation across the membrane (as a draw solution). Before conducting each filtration test, a baseline experiment was conducted, where a feed solution containing only the salt solution was filtered for the same duration as the foulant-bearing feed streams. This was performed to isolate flux decline due to due to foulant deposition and cake layer formation from that caused by internal concentration polarization. After the baseline test the membrane was flushed with large amounts of deionized water to wash-off the salt on its surface. Filtration tests were then performed with feed solutions bearing the different single compounds (alginate, humic acid, bovine serum albumin and octanoic acid) or their combinations. After each fouling test; the forward osmosis system was flushed with deionized water at high cross-flow velocity to clean the remnants of the previous test from the tubing system. The feed solution volume was fixed at 10 L while the re-concentrated draw solution volume was 1 L.

The thin film composite membrane was used as the primary membrane for all the filtration tests and its performance and fouling behavior was compared to that of cellulose triacetate and Porifera using the feed solutions that resulted in the most severe permeate flux loss. The concentration of the draw solution was fixed at 0.5 M NaCl for all experimental tests and was adjusted accordingly for the other membranes (cellulose triacetate and Porifera) to achieve an initial permeate flux of $13.5 (\pm 0.87) \text{ L m}^{-2} \text{ h}^{-1}$. Filtration tests were conducted for 24 h. The active layer-facing-feed solution (FO mode) configuration was used during tests. The cross-flow velocity was fixed at 10 cm s^{-1} .

2.3.1. Characterization techniques

The membrane's electrokinetic properties were investigated via streaming potential measurements which were performed using a SurPASS Electrokinetic Analyzer, (Anton Paar GmbH, Austria). This enabled the determination of membrane surface charge. Measurements were conducted using 0.01 mol/L KCl aqueous solutions as an electrolyte solution at 23°C and a pH of about 5.9. Surface zeta potentials were then derived from the measured streaming potentials according to the Helmholtz–Smoluchowski equation (Eq. 5) [93]. The presented data are average values of three different samples of each membrane type.

$$\zeta = \frac{\Delta V \eta \sigma}{\Delta P \epsilon \epsilon_0} \quad (5)$$

Where ΔV is the measured streaming potential, η is the electrolyte viscosity (Pa s), electrolyte's electrical conductivity (S/m), ΔP is the applied pressure and ϵ is the permittivity of water ($\text{C}^2\text{N}^{-1} \text{ m}^{-2}$). The permittivity is defined as $\epsilon = \epsilon_0 D$, where ϵ_0 is permittivity of vacuum = $8.85 \times 10^{-12} \text{ (C}^2\text{N}^{-1} \text{ m}^{-2}\text{)}$ and D the dielectric constant of water = 78.55 at 25°C .

Membrane surface morphology as well as the structural arrangement of fouling layers was assessed using scanning electron microscopy (SEM); using a JEOL IT300 scanning electron microscope (Tokyo, Japan.). Small dried membrane pieces were cut and attached to sample holders using a carbon tape. The sample holder with the membrane pieces was coated with either gold or carbon to provide electrical conductivity and prevent charging during imaging. Analysis was performed at different desired magnifications and working distances.

The topology and roughness of clean and used membranes were studied using an atomic force microscope (AFM: Alpha300, Germany). The average hydrodynamic diameter of the organic aggregates in the different aqueous solutions was measured using the dynamic light scattering (DLS) technique (Malvern nanosizer, Malvern Instruments, UK).

3. Results and discussions

3.1. Feed solution properties

Dynamic light scattering (DLS) measurements provide information on the particle size distribution of a suspension. And it was used in this study to monitor macro-aggregate formation during mixed foulant fouling to gain more insight into foulant-foulant interactions. The intensity of the scattered light is a strong function of the particle size and bigger aggregates cause more scattering which is translated to a larger intensity peak. The role of divalent cations (particularly Ca^{2+}) on organic fouling has been well studied and widely reported using surrogate organic compounds [94]. Their presence has been associated with intense fouling caused by organic foulants via charge neutralization, complexation and forming calcium bridges [95, 96]. In this study, the concentration of Na^+ was 17 mM and that of Ca^{2+} was fixed to 1 mM. **Table 3** presents hydrodynamic diameters for single foulants and their different combinations. And according to the recorded values, it demonstrated that the cations had a significant influence on the physicochemical properties of the individual and combined foulants. The changes in particle sizes were conspicuous, there was clear aggregation of macromolecules when calcium ions were introduced. This trend

Feed sample	Zeta potential (mv)	Hydrodynamic diameter (nm)
Alg*	-54 ± 3	66 ± 4
HA*	-48 ± 3	213 ± 10
BSA*	-10 ± 1	4
Alg	-14 ± 1	261 ± 8
HA	-27 ± 1	199 ± 2
BSA	-2	8
OA	—	—
Alg + BSA	-20 ± 3	349 ± 15
Alg + HA + OA	-19 ± 2	603 ± 19
HA + BSA + OA	-13 ± 1	377 ± 11
HA + BSA + Alg	-19 ± 5	—
HA + BSA + Alg + OA	—	—

*Measured zeta potential and hydrodynamic diameters in the absence of cations.

Table 3. Measured foulant zeta potentials and average hydrodynamic diameters in the different feed solutions.

was further supported by the surface charge reduction of the aggregates upon exposure to electrolyte solutions. The foulant-cation complexation was more prominent in humic acid and alginate because of the abundant presence of carboxylic acid groups; ionization of carboxylic acids gives carboxylate anions that in turn complex with the positive Na^+ and Ca^{2+} to form aggregates.

The influence of these ions on the fouling potential of each foulant was found to be different. Alginate fouling was consistent with the observed physicochemical (charge and particle size) changes; however, a noticeable deviation was observed with humic acid which resulted in less fouling even in the presence of calcium ions. A possible explanation for this anomalous observation lies on the HA- Ca^{2+} ratio used for the purposes of this study; there were insufficient calcium ions to complex with humic acid macromolecules. Also, Na^+ competed with the Ca^{2+} for the negatively charged HA carboxylate ions.

All three primary foulants were found to exhibit a negative surface charge. Alginate and humic acid had the highest negative charges in solution which can be attributed mainly due to the abundant presence of negative carboxylate groups. Therefore, they had prominent interaction with the cations as evidenced by the large reduction in negative charges in the presence of cations. The determination of both surface charge and hydrodynamic diameter of octanoic acid was unsuccessful. The BSA molecules had the lowest zeta potential values (**Table 3**) and were least influenced by the cations.

The reported zeta potential and hydrodynamic sizes for mixed foulants cannot be tied down to a single factor but rather a combined influence of cationic species' concentrations, molecular size and shape as well as organic-organic interactions. Therefore, the values presented here are averages of a range of sizes and they should be viewed with some reservation. Thus, the discussion is based on qualitative observations rather than on quantitative data. However, the changes in the measured hydrodynamic diameters are in accordance with earlier reported studies on the influence of Na^+ and Ca^{2+} on organic foulants [16, 97], and it was found that the aggregate size followed this order: BSA < humic acid < alginate.

3.2. Membrane surface morphology

Scanning electron and atomic force microscopy analysis of the membrane's feed side gave the micrographs presented in **Figure 2**. The membrane surface appeared to be covered by a thick, loose and flexible fouling layer after filtration of the mixtures of alginate and BSA (**Figure 2(b)**) and that of alginate, BSA and humic acid (**Figure 2(c)**). An indication of heavy foulant deposition during seawater dilution. The fouling layer appears loose and detached which is typical of FO membrane fouling due to the lack of external hydraulic pressure. AFM images show a relatively rough thin film composite membrane in **Figure 2(d)**. The images in **Figure 2(e)** and **(f)** show completely different topologies which suggest the presence of a cake layer on the surface of the membrane.

3.3. Fouling characteristics of single foulants

Filtration tests using feed streams containing single, simple organic compounds yielded varying membrane performances as shown in **Figure 3**. The feed streams containing humic acid,

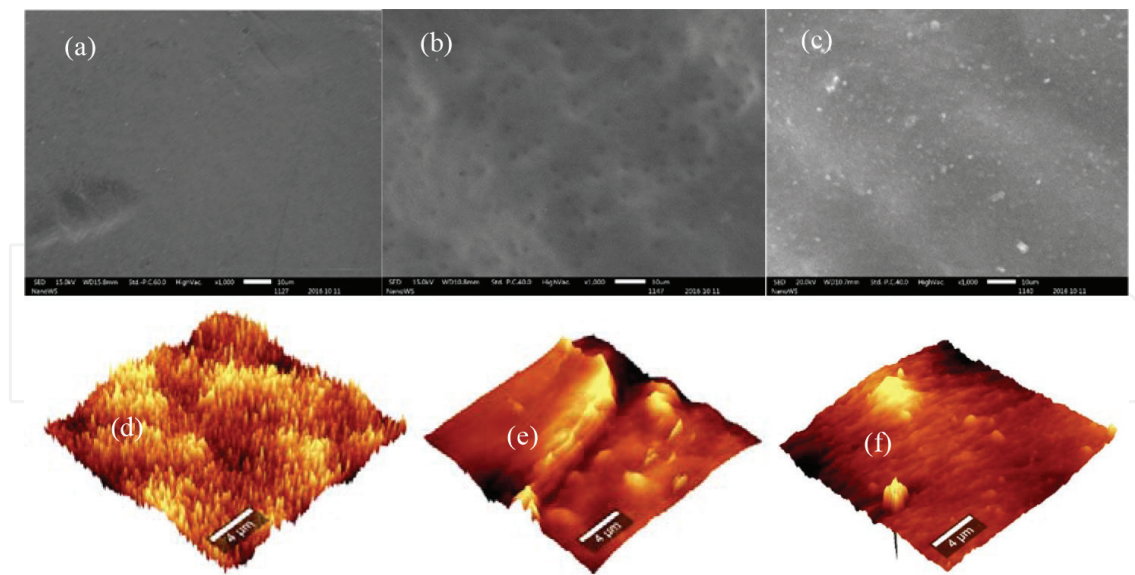


Figure 2. Clean and fouled membrane surface morphology and topology: (a) SEM image of clean TFC membrane, (b) image of membrane fouled with Alg + BSA, (c) image of membrane fouled with Alg + BSA + HA, (d)–(f) corresponding AFM micrographs.

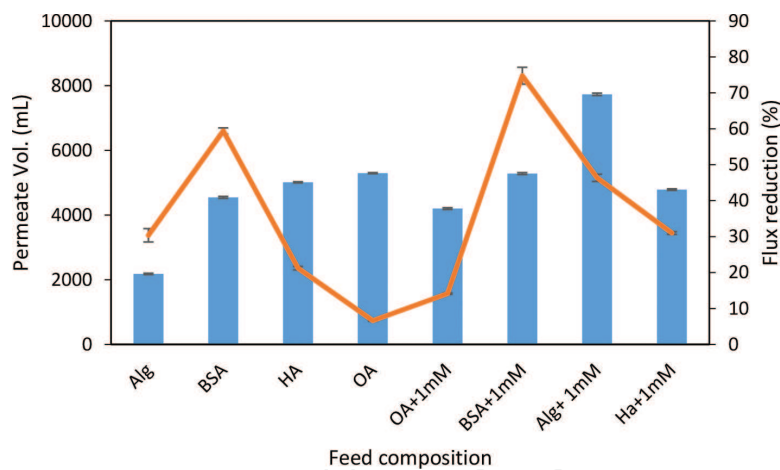


Figure 3. Recorded permeate volumes and flux declines during seawater dilution using simple feed streams.

alginate and octanoic acid recorded the highest water recovery of above 50%. A slight decline in water recovery was observed when the membrane was used to filtrate the feed solution containing bovine serum albumin recording a 40% recovery. The addition of 1 mM CaCl_2 to the feed solutions had a significant influence on membrane performance; particularly, on the feed solutions containing BSA and alginate which correlated to their flux reduction. That is, the calcium ions improved cross-linking of ionized alginate macromolecules forming an organized gel layer that was easily deposited on the membrane surface, creating an extra resistance layer to water permeation. This observation is supported the measured alginate aggregate sizes in **Table 3**, which showed an increase in aggregate size in the presence of Ca^{2+} . The same phenomenon is expected for humic acid, however, the resulting cake layer is porous and offered little resistance to permeate flow, so permeate flux remained the same.

There was a further loss in permeate recovery for the BSA bearing feed solution, the presence of Ca^{2+} enhanced its affinity for the membrane surface. The macromolecular size was reduced to almost neutral values leading to subsequent weakened electrostatic repulsions from the negative membrane surface leading to its multilayer adsorption. Permeate flux reduction patterns correlated to the recorded permeate water recovery rates. The feed solutions containing humic and octanoic acids had the lowest permeate flux reduction with and without calcium ions. The BSA feed exhibited the highest permeate flux loss reduction of 60% before the addition of calcium ions. Permeate flux reduction increased by 16% when Ca^{2+} was added to the alginate feed solution, rising from 30 to 46%. These results revealed that the FO process had an average performance for simple, single foulants bearing feed streams. And humic and octanoic acid had no significant influence on permeate flux unlike, polysaccharides (alginate) and proteins (BSA) that dominated permeate flux loss [95]. The next section investigates the interactions between co-foulants when they co-exist in the same feed solution in an attempt to underpin foulant-foulant interactions.

3.4. Influence of co-foulants on flux

The two fractions that caused the most significant permeate flux decline (alginate and BSA) in the previous section were combined and tested for their impact on permeate flux loss. The resulting fouling trend was compared to those observed during filtration of single foulants as depicted by **Figure 4**. And it can be seen that the co-existence of alginate and BSA resulted in more permeate flux loss. The flux decline curve is similar to that of BSA alone, characterized by the first stable flux region followed by a rapid flux loss rate until a semi-steady flux point was reached. This indicates that BSA macromolecules had a dominant effect on the formation of the combined fouling layer. According to the measured surface charge results the two foulants should electrostatically repel each other due to the negative surface charges; however, hydrophobic interactions among the foulants appear to be dominant in the formation of alginate-BSA aggregates as supported by the increase in sizes when the two foulants are present in the same feed solution (**Table 3**). It is thought that the BSA molecules became integrated into the alginate-calcium complexes [98, 99], and since there were favorable interactions that promoted BSA attachment onto the membrane surface; the alginate aggregates were sort of “functionalized” and easily deposited to form the fouling layer shown in **Figure 2(b)**. It can therefore be concluded that the addition of alginate to BSA enhanced permeate flux loss (fouling), which implies the dominant presence of synergistic interactions between the proteins and polysaccharides.

3.5. Filtration tests with complex feed solutions

The feed streams were made more complex by mixing three organic compounds in one feed solution. When the feed solution containing alginate, humic and octanoic acid was filtrated using the TFC membrane, a 51% water recovery was recorded and initial permeate flux was reduced by 30% after 24 h (**Figure 5**). This result was beyond expectations since alginate and humic acid in the presence Ca^{2+} have been reported to worsen fouling due to the formation of HA-Ca^{2+} , Alg-Ca^{2+} and Alg-HA complexes, as the formed fouling layers act to increase

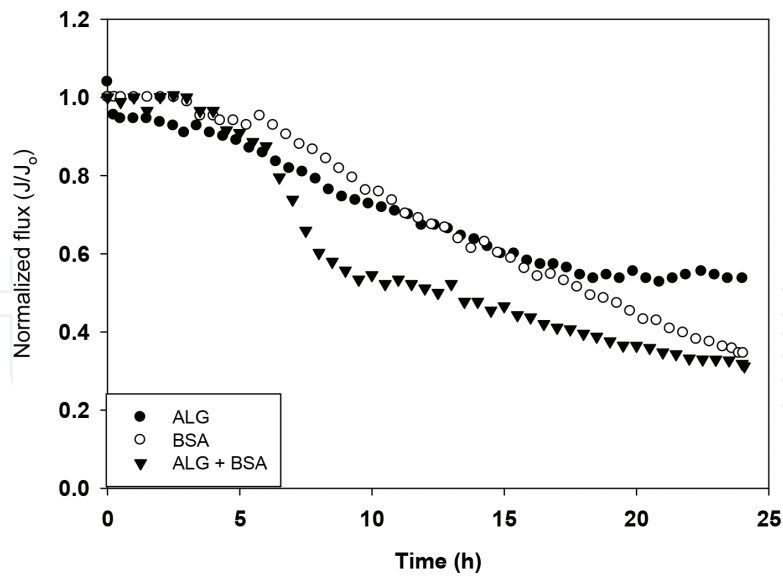


Figure 4. Membrane permeate flux decline pattern during co-foulant (Alg + BSA) feed stream filtration.

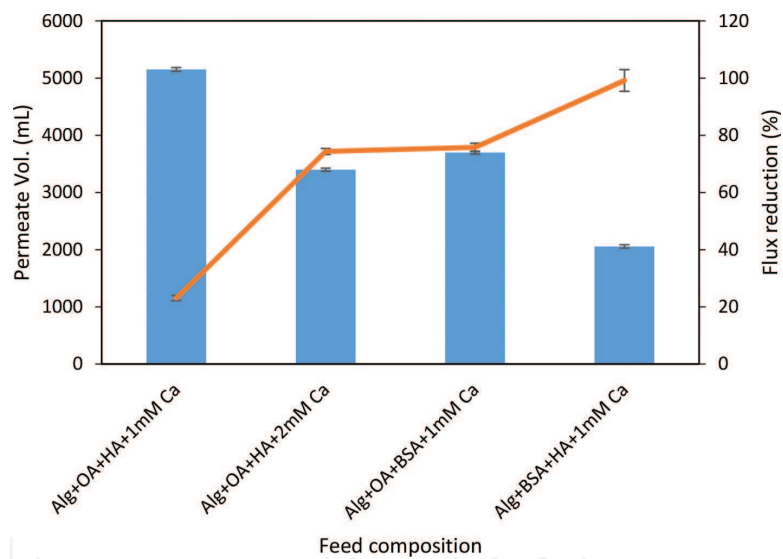


Figure 5. Permeate volumes and permeate flux loss during seawater dilution using complex feed streams.

resistance to permeate flow [100]. The explanation for this could be that the Ca^{2+} concentration was ineffective in causing complete complexation of the foulants (80 mg/L Alg and 200 mg/L HA), thus aggregate formation was in significant and the foulants remained in the bulk solution rather than being deposited. And it also suggests that the cake layer formation during foulant deposition was dominated by humic acid macromolecules which formed a loose porous layer such that permeate flow rate was not significantly lowered. This explanation is backed by the flux reduction and water recovery in the presence of 2 mM Ca^{2+} which shows a 15% reduction in water recovery and a 74% permeate flux loss. The calcium ions interacted with the alginate and humic acid macromolecules to form a thick compact cake layer that offered resistance to permeate flow.

The presence of proteins (BSA) in the feed solution containing alginate and octanoic acid reduced water recovery (37%) and increased flux reduction by 75%. Interestingly, the mixture of alginate, BSA and humic acid resulted in poor process performance with a water recovery of 20% and almost no permeation after 16 hours of filtration. This suggests that there were favorable interactions between the foulants that led to excessive deposition rate onto the membrane surface, resulting in a thick and resistant cake layer which enhanced reverse solute diffusion contributing into flux loss. The differences observed in the permeate flux reductions can be attributed to the various foulant-foulant and organics-membrane interactions during filtration, which then leads to different fouling layer properties.

These results demonstrated that the performance of the FO membrane in treating heavily impaired water using seawater as a draw solution. There was severe flux loss when polysaccharides, humic substances and proteins co-existed in the same feed solution. This is the most likely, occurrence in secondary treated wastewater. However, the organic foulants exist in lower concentrations than what was used in this experiments (worst case scenario). Thus, the combined wastewater-seawater dilution process promises to be a simple and effective water recovery process that might be hindered by membrane fouling. But the resulting fouling layer can be easily washed-off using physical cleaning methods [101, 102].

3.6. Influence of membrane surface

The performance of the commercial thin film composite membrane was compared to that of the low flux cellulose triacetate membrane and two custom-made Porifera membranes using the most complex feed solutions. Average water recovery for the three membranes was above 50% (Figure 6). The Porifera membranes had superior performance at the same operating conditions and initial permeate flux, followed by the cellulose triacetate membrane. The observed varying performances are due to differences in surface properties and functionalities. The rough polyamide layer of the TFC membrane was highly susceptible to protein deposition and foulant adhesion. Whilst, the smooth cellulose triacetate surface is resilient

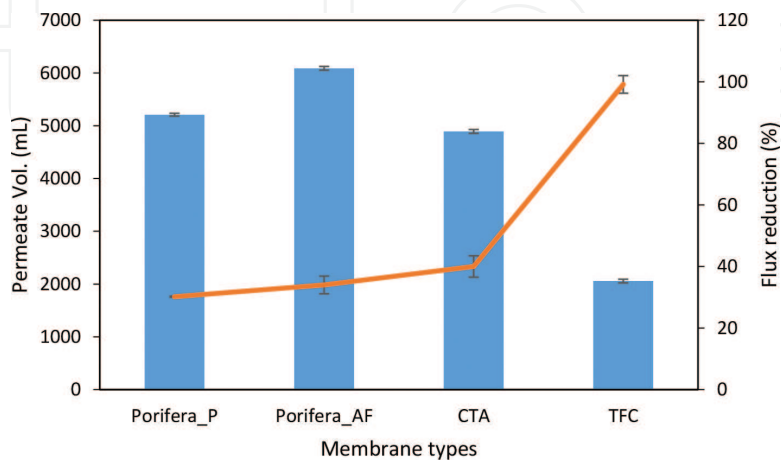


Figure 6. Performance of FO membranes used to filter complex feed streams. Porifera P represents the plain membrane while Porifera AF was modified to induce anti-fouling properties.

to foulant deposition [103]. Therefore, seawater dilution using wastewater can be further improved by choosing a foulant resistant membrane with a matching flux.

4. Summary

The on-going water shortage has opened an opportunity for wastewater and seawater to be explored as alternative water sources to supplement water supply due to the diminishing natural fresh water sources. However, extensive treatment procedures are required to make these water streams suitable for either domestic, industrial or even agricultural purposes, thus forward osmosis membrane process was identified as an ideal candidate to lower the osmotic pressure of seawater prior to desalination using wastewater as a feed source. The fouling behavior of the membrane process was studied. And the results revealed that proteins and polysaccharides had a dominant role in governing permeate flux loss. The presence of divalent cations, especially Ca^{2+} exacerbated the fouling process. Filtration tests demonstrated that there were favorable electrostatic and hydrophobic interactions among foulants and membrane surface that promoted foulant deposition and cake layer formation. The forward osmosis process had an average performance in treating heavily impaired feed water streams under exaggerated conditions. This implies that an even better performance can be expected for real water samples where foulant content is lower. It was also found that the process performance can be improved by selecting/using foulant resistant membranes.

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