Fouling and Cleaning in Osmotically Driven Membranes

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Abstract

Fouling is a phenomenon that occurs in all membrane processes. It is a complex problem, which limits the full operation of this technology. Fouling in pressure-driven membranes (PDMs) has been studied extensively, and the occurrence is well understood in that methods of mitigation have been proposed; however, limitations still occur for their full implementation. The use of osmotically driven membranes (ODMs) for water treatment is an emerging technology, which has shown some advantages such as low hydraulic pressure operation, high solute rejection and high recovery over PDMs. However, like in PDMs, fouling still presents a challenge. This chapter is aimed at evaluating the impact of fouling on the ODM performance, exploring the factors and mechanisms governing the fouling behaviour, developing approaches for mitigating fouling, elucidating the effect of membrane fouling and providing mitigation strategies as well as the causes of fouling in ODMs.

Keywords: membrane fouling, fouling mitigation, forward osmosis, pressure retarded osmosis, pretreatment

1. Introduction

The use of osmotically driven membranes (ODMs), such as forward osmosis (FO), pressure retarded osmosis (PRO), direct osmotic concentration (DOC) and osmotic dilution (ODN), for water treatment is an emerging technology that has shown some advantages such as low hydraulic pressure operation and hence low energy consumption, high solute rejection and high recovery over pressure-driven membranes (PDMs) [1–5]. The ODMs are seen to gradually outperform the conventional PDMs. For instance, Mi and Elimelech [6], in their review, noted that forward osmosis is said to consume only about 20% of the electrical energy required by other processes such as desalination. These processes could use low quality heat like the waste heat from power plants as their energy inputs. The advantage associated with it has been the higher recovery, and because of this, less discharge of brine to the environment is noticeable [6].

Until recently, the focus of most studies has been on PDMs; however, a shift in research is being noticed and more research is emerging regarding the application of ODMs. However, the studies on ODMs published has been intensified mainly on issues such as choice of draw solutions, membrane properties and other factors relating to the application of ODMs. Fouling mechanisms in these membranes has, on the contrary, received less attention. On the other hand, fouling in PDMs has been studied extensively and methods of mitigation and control are being adopted for their implementation [6].

Fouling is a phenomenon that occurs in all membrane processes. It is a complex problem that limits the full operation of this technology. Fouling can be caused by the accumulation of suspended particles or colloids, organic molecules and also soluble inorganic compounds, microorganisms, or a combinations of all these on the membrane [7]. Different substances have been identified to cause fouling in membranes and as such, this can result in different fouling mechanisms in the membranes. For example, fouling could occur as a result of the deposition of foulants onto the surface of the membrane thus forming a cake layer. This phenomenon is commonly referred to as external fouling. It could occur within the pores of the membrane. In this instance, the foulant sizes could be relatively smaller than the pores of the membranes, hence penetrates the pores of the membrane thereby leading to pore blocking. This type of fouling is called internal fouling [7].

Fouling occurs in all membrane operations, however, the tendency and its behaviour varies due to the mode of operation, the nature of the membranes and the nature of the foulants. Mi and Elimelech [8] studied the chemical and physical aspects of organic fouling of FO membranes using alginate, bovine serum albumin (BSA), and Aldrich humic acid (AHA) as the exemplary organic foulants. In that study, the effect of chemical and physical interactions such as intermolecular adhesion forces, calcium binding and the membranes initial permeate flux were investigated. Similarly, the membrane orientation on organic fouling of FO membranes was investigated. They observed that there was a relationship between organic fouling and intermolecular adhesion, thus indicating that foulant-foulant interaction is an important aspect that can determine the rate and level of fouling, therefore emphasising that the main factors that control membrane fouling differ from foulant to foulant [8].

Studies on the fouling in ODMs have revealed that fouling propensity within the ODMs is lower as compared to PDMs [2, 3, 9, 10]. The lower fouling propensity is said to be so in the case, whereby the active layer of the membrane is arranged to face the feed solution containing the foulant. In addition, the low flux conditions and lack of applied pressure in the FO process have been highlighted as some of the reasons for this occurrence. However, internal concentration polarisation (ICP) could still occur within the membrane [10]. Therefore, ICP is one of the major drawbacks of ODMs especially in FO [3].

Factors such as draw solutions, hydrodynamics and operating conditions and feed water characteristics could impact fouling in different ways. The effect of these factors, if properly managed, will help mitigate fouling propensity on the membrane. The configuration of the membranes can also affect membrane performance significantly. Tang et al. [3] studied the coupled effects of internal concentration polarisation and fouling on flux behaviour of FO membranes during humic acid filtration. They found that the membrane orientation plays an important role. In their observation, ICP occurred more when the active layer faced the draw solution (AL-facing-DS) as compared to when the membrane active layer faced the feed water (AL-facing-FW). This leads to a dilutive ICP in the FO support layer [3]. However, a more substantial flux stability is said to be achieved by the AL-facing FW as against the dilutions of the bulk draw solution and membrane fouling.

Thus, understanding the phenomenon of fouling in ODMs will provide more information that could lead to the development of new FO membranes with reduced ICP and high water permeability. The aim of this review is to evaluate the impact of fouling on the ODMs performance and to explore the factors and mechanisms governing the fouling behaviour. Further, it aims to develop approaches for mitigating fouling and to further elucidate the effect of membrane fouling and mitigation strategies. The causes of fouling in ODMs will also be described. The performance of FO membranes is defined by three parameters; the pure water permeability coefficient, solute permeability coefficient and the structural parameter. The solute permeability describes mass transport across the membrane active layer while the structural parameter governs the transport phenomena across the membrane support layer. The aforementioned parameters are used to describe the permeate water and solute fluxes of FO processes [11].

2. Fouling in membranes

The fouling phenomenon in PDMs and ODMS differs in some ways. In PDMs, factors that affect membrane fouling can be classified into three categories: membrane properties, operating parameters and the nature of the waste water to be treated. In ODMs, there could be additional factors to the aforementioned, such as the membrane orientation and the type of draw solutions [12–14]. The driving force for PDM systems is pressure. Hence, the relationship between pressure and flux is positive. A rise in pressure causes a rise in flux; however, for a feed mixture there is a point where a further increase in pressure results in a minimal increase in flux. This is because the particles of the component being rejected by the membrane accumulates on the membrane surface and obstructs the passage of the solvent through the membrane. If the process is allowed to continue to run, the rejected layer on the membrane surface grows thicker and becomes more and more resistant to solvent flow and this results in the flux dropping. At this point, it is said that the membrane is fouled and it is no longer economically justifiable to continue to run because the added energy to the system does not recover or even maintain flux [15, 16].

On the other hand, ODM systems use the osmotic pressure gradient, which is the chemical potential difference between the feed water and the concentrated draw solution as its driving force. With this application, the use of external pressure is not needed [3, 10, 17, 18]. As a result of this, the system is said to be more economically viable due to its significantly low energy consumption [19]. This advantage has attracted the application of ODMs in seawater desalination, wastewater reclamation and in liquid food processing. However, like PDMs, a decline in flux always results, due to the severe internal concentration polarisation that always occurs in the porous membrane support [9, 17, 20, 21].

Fouling in membranes could occur internally or externally on the membrane. The extent of fouling in membranes depends on the type of separation and the type of membrane used to carry out the separation. Fouling leads to an overall increase in membrane resistance for mass transport, and hence affects the performance of membranes by a gradual decrease in flux and a decrease in rejection. The effect of this is seen in the deterioration of the membrane properties and as such results in high costs of operation and cleaning of the membranes to restore its initial flux [22].

The orientation of ODMs could be in two ways; active layer-feed solution (AL-FS) and the active layer-draw (AL-DS) solution. Hence, the nature of fouling differs with orientation [17]. The AL-FS mode is reported to be the FO mode (normal), while the AL-DS is the (PRO) reversed AF [23]. AL-FS orientation is when the active layer of the membrane faces the feed solution; and the AL-DS is when the active layer of the membrane faces the draw solution [14]. The type of fouling that will occur in the membrane will depend on the orientation of the membrane. The AL-DS could also be referred to as external fouling because solutes from the feed solution accumulate on the membrane surface thus forming a cake layer with time. This is similar to that formed in PDMs. On the other hand, in the AL-DS orientation, complications arise because other fouling mechanisms, such as pore blocking, could occur in addition to the cake layer formation. The occurrence of this is however dependent on the type and nature of foulants. Smaller sized particles will find their way into the pores of the membranes, thereby causing the membrane pores to be become blocked and therefore, internal fouling occurs. However, if it contains larger particles, these foulants will remain on the surface of the membrane and are thus deposited on the membrane surface hence blocking the pores leading to external fouling. If the feed solution contains a mixture of both sizes of foulants, both types of fouling could be occurring within the membrane [7, 23].

Both orientations affect the performance of the membrane in different ways. The AL-DS orientation has shown to have a lower initial flux, however, a higher fouling resistance, while the AL-FS has a higher initial flux but is less prone to fouling. However, it can be immensely affected by dilutive ICP. Therefore, ODM membranes are faced either with a more severe dilutive ICP in AL-FS or having much greater fouling tendencies in AL-DS, and therefore a balance must be reached in order to obtain optimum performance carrying out mitigating measures [17]. However, Chen et al. [23] reported in their study that the effect of fouling is more enhanced in PRO membranes. The purpose for this is the fact that PRO membranes are composed of a denser or thicker structure than the FO membranes to enable them to withstand the high pressure loading. Therefore, the denser structure contributes to the fouling tendencies.

Mi and Elimelech [6] studied the organic fouling of forward osmosis membranes. The main aim of that study was to examine organic fouling and the cleaning methods that will follow in the FO. Two types of membranes were used; polyamide and cellulose acetate (PA and CA) with alginate as the model foulant. Again, they used atomic force measurement (AFM) to detect the role of membrane materials in determining membrane fouling and cleaning behaviour.

They found that the PA was prone to more fouling propensity. The PA membrane surface were said to contain some adhesive sites even though lower as compared to those from the CA. The higher fouling in the PA membranes were due to the fact that the PA membranes caused more adsorption, thereby leading to a more severe fouling at an early stage [6].

Furthermore, Mi and Elimelech [6], in the same study, considered the flux behaviour in RO and FO and found that similar flux patterns were obtained in membrane types; however, the flux recovery was different. A higher flux was recovered from FO than the RO. The reason for this occurrence was attributed to the fact that the fouling layer formed on the FO membrane was less compact due to a lack of hydraulic pressure application [6].

Xie et al. [24], in their study on the role of pressure in organic fouling in FO and RO, used alginate as the foulant, while varying the contribution pressure in terms of osmotic and hydraulic. From that study, two possible mechanisms of fouling were identified which were permeation drag force and compression of foulants. The fouling thickness that was observed by them was in the decreasing order of FO < PFO < R O. They arrived at the same conclusion that hydraulic pressure plays a significant part in the compression of the fouling layer to a great extent [24]. The drag force was the only applied force in FO; however, this did not necessarily mean that fouling will not occur in the FO membranes.

As stated earlier, different factors are responsible for fouling in membranes. One dominant factor is the nature of contaminants that can be found in the wastewater, for example, colloidal particles or particulate matter, dissolved organics, chemical reactants, micro-organisms and other microbial substances [17]. Foulants are colloidal materials with different properties, which interact with the membrane thereby causing fouling. They can be grouped into four categories: organic precipitates, inorganic precipitates, biological and particulates [13, 25]. Hence, the type of fouling can be grouped based on the foulant type, e.g., inorganic (scaling), organic and biofouling [22].

2.1. Inorganic fouling

Inorganic fouling normally results from the deposition and accumulation of inorganic matter and other precipitates such as metal hydroxides and silica on the surface of the membrane. Inorganic fouling will foul the membrane both on the surface and internally. The precipitates are formed when the concentration of the chemical species is more than their saturation concentrations. This tends to happen on the membrane surface where accumulations of particles occur due to retention on the membranes. The result of this will be a decline in flux [17, 26].

Mi and Elimelech [27], in their study on the gypsum scaling and cleaning in FO, reported a decline in flux in both RO and FO modes. About 96% of the flux was recovered in the FO mode following a water rinse only without the use of any chemical cleaning agent. In the RO mode, however, the flux recovered was 10% lower than that of FO. Similarly, the same authors, Mi and Elimelech [26], reported in their study for silica scaling and scaling reversibility in FO, a decline in flux both in the FO and RO mode. However, 100% flux was recovered in the FO and only 80% in the RO modes. They concluded, after characterising the fouled membrane, that scaling on the membrane originated from the monosilicic acid deposition on the membrane surface, which was followed by polymerisation (the formation of a soft amorphous silica gel layer that hardened with time by a continuous dehydration). Again, on the use of the AFM force measurement, it was revealed that the membrane surface roughness played a crucial part by increasing the adhesion force between the membrane and the silica gel layer, thereby considerably reducing the cleaning efficiency of the membrane [26].

The combination of alginate, which is the main component of polysaccharides with calcium ions in water, could lead to a more pronounced decline in flux due to the formation of a cake layer or gel layer. Chun et al. [28] reported that inorganic scaling, which was caused by calcium and phosphate and the interactions with other organic constituents in the feed solutions used, were the main cause of the reduction in flux of the membrane [28]. The cleaning of the inorganic scaling was, however, poor after using both physical and chemical methods. On further characterisation of the membrane, it was confirmed that gypsum and organic components that were present in the feed solution might have formed a gel layer (calcium bridging), thereby enhancing the fouling layer rigidity [17, 28]. Silica scaling is said to be difficult to be removed physically, while other types of the NOM foulants can be easily removed.

2.2. Organic fouling

The adsorption of organic matter such as humic substances, protein, and grease onto the membrane surfaces is referred to as organic fouling. These organic substances can be hydrophobic, hydrophilic or transphilic in nature. The mechanisms of organic fouling are complicated due to the wide variety of organic foulants existing in natural waters. These organic matters, commonly known as natural organic matter (NOM), are prevalent in most natural water sources such as run-offs, rivers, seawater and ground water [17].

NOM which are terrestrially derived are known as autochthonous NOM. There are also the microbially derived and wastewater NOM. Each of these organic fractions foul membranes differently because of different hydrophobicity, molecular weight size and charge density. However, microbially derived NOM are found to be the worst foulants. Fouling from these fractions is found to be most problematic and severe [29]. A study by Bessiere et al. [30] on the effect of NOM on fouling shows that hydrophilic components of NOM are responsible for the rapid but reversible fouling on the membrane. **Figure 2** elaborates concentration polarisation that could occur in FO membranes. The hydrophobic components were found to be responsible for the slow but irreversible fouling on the membrane. The hydrophilic components were small compared to the hydrophobic components. Both of these components are adsorbed on the membrane material.

The size of NOM plays a great role on the fouling of the membrane. Because NOM adsorbs onto the membrane, small NOM enter the pore of the membrane and get adsorbed on the wall of the pore channel resulting in pore narrowing. Larger NOM components get trapped at the entrance of the membrane pores and block the entrance to the pore channel resulting in cake layer formation as filtration progresses [31]. Fan et al. [32] found that the fouling order of hydrophobic membranes by NOM material is as follows; hydrophilic neutrals > hydrophobic acids > transphilic acids. Again, Chun et al. [17], in their study, noted that hydrophilic, H-bond acceptor, non-H-bond-donor and neutrally charged membranes are said to be resistant to organic fouling; however, hydrophobic and rougher membranes are more prone to fouling by NOM [17].

For ODM systems, a strong correlation has been established between organic fouling and intermolecular adhesion forces. For example, Mi and Elimelech [8] studied the chemical and physical aspects of organic fouling of FO membranes and found a strong correlation between organic fouling and intermolecular adhesion forces, which indicated that foulant-foulant interaction played an important role in determining the extent of the fouling [8]. They used the AFM. Adhesion force measurement was used to elucidate the impact of membrane material fouling. They found that the small adhesive sites on the membrane played a significant role in organic fouling formation [8]. They concluded that permeation drag, hydrodynamic shear force and calcium binding were the main contributing factors that govern organic fouling development [8, 17].

Colloidal matter in a suspension can be charged and depending on the charge of both the membrane and the particle, adhesion or repulsion will occur. The charge of the particles can be altered by adjusting the pH of the suspension. pH adjustment changes the electrostatic interaction between the membrane and particle from attractive to repulsive or from repulsive to attractive [33]. The effect of the ionic strength of colloidal particles on fouling was also studied by Singh and Song [34]. The study found that increasing the ionic strength of colloidal matter and its concentration in the feed solution increases the fouling potential of the water linearly.

2.3. Biofouling

Biofouling in simple terms can be defined as biological fouling. It is a net resultant of microbial attachment to the membranes and the consequent growth and discharge of biopolymers that are connected with this microbial activity. The foulants in biofouling include proteins, organics, organic acids, polysaccharide fats, etc. [14]. Biofoulants in this section will be divided into humic materials and micro-organisms (bacteria) [35]. The attached communities of bacteria in aquatic systems are encased in a glycocalyx matrix that is polysaccharide in nature. This matrix material mediates adhesion. The biofilm is made up of single cells and micro colonies that are enclosed in a hydrated, predominantly anionic exopolymer matrix. The attachment of bacteria to surfaces is irreversible and it results from a secretion by the bacteria itself which is a matrix of extracellular polymeric substances in which the bacteria cells are embedded upon [36].

This adhesion of microbial cells to the membrane surface is the beginning of membrane biofouling. Subsequent to attachment of microbial, a biofilm layer is formed, which has a composition that is vast in diversity of different micro-organisms which could be bacteria, algae, protozoa, fungi, etc. [36]. Basically, three steps are involved in the formation of the biofilm; adsorption of the organic species and other suspended species on the wet membrane, transportation of microbial cells to the formed film and finally, the microbial cells then attach themselves on the membrane surface. The growth and metabolism as well as the biofilm of the attached organisms are then developed [37].

Extracellular polymeric substances (EPS) are high molecular weight secretions of micro-organisms that are made up of organic substances such as polysaccharide, protein, nucleic acids and lipids. EPS offer a binding base for biofilm to the membrane surface. They contribute to the mechanical stability of the biofilm and to the organisation of the biofilm community. Once the biofouling has been established, other organic and inorganic materials contribute to the building of the fouling mass [38]. EPS promotes the adhesion of microbial to surfaces by changing the physicochemical characteristics of the biofilm fouled membrane surface such as its charge, hydrophobicity and roughness. The EPS offers building blocks between the membrane pore and microbial cells. High concentration of EPS contributes greater binding capacity. EPS aggregates are comprised of charged groups, and they therefore have both wetting and cross-linking characteristics which contains both hydrophobic and hydrophilic sites on their structure. This enables them to be able to adhere to both hydrophilic and hydrophobic surfaces. The factor that makes biofouling very complex to understand and plan against is the fact that EPS have flexibility and rearrangement characteristics. This means EPS structure will rearrange themselves so that they are able to stick to any surface [37].

Biofouling is one of the most difficult fouling to control as there is a large range of biofoulants that could be present in a particular aqueous system at a particular time for a particular feed solution [17]. Other types of fouling are easily mitigated by the use of chemical and physical pre-treatment. Like other fouling mechanisms, it causes significant losses in flux it is reported that it can cause a 10–15% decline in the membrane performance of the start-up values under the applied operational conditions [17]. Further impacts of biofouling are observed in membrane biodegradation which can lead to an increased salt passage as well as raising energy requirements. Consequently, a higher operating and maintenance cost and possibly shortening of membrane lifetime will be the overall impact [17].

Bogler et al. [14] reported that biofouling in FO has a lower influence on permeate water flux than that in PDM membranes. The same hydrodynamic conditions, feed concentration, membrane type and bacterial concentration were used to test for biofouling in RO and FO membranes, and it was found that there was a 10% decrease in flux as compared to the 30% in RO membranes after 24 h. However, the influence of biofilm in FO has been considered to be more complicated than in RO. This is due to the fact that the additional phenomenon that occurs is unique to membrane systems, which are driven by osmotic force [14]. According to Bogler et al. [14], there is an interaction between the reverse solute and the biofilm by the draw solution especially when it contains divalent cations as calcium [14]. Again, the biofilm formed on the FO membrane is more loosed and thicker than that formed in RO membrane. This was said to enhance CP instead of the additional hydraulic resistance as the main reason for permeate water flux reduction [14].

3. Concentration polarisation in ODMs

The major challenge in bringing about a deep knowledge that will aid to understand membrane fouling is the difficulties in the identification of the actual foulants, and distinction between the indicators of fouling and effect of CP. CP is the occurrence in membrane processes, whereby the concentration of solute near the membrane surface is very different from that of the bulk solution [7, 39, 40]. In membrane systems, using hydraulic pressure, the liquid is passed through the membrane and the particles accumulates near the membrane surface thereby forming a thin layer. In the layer, the particles get stuck in the transverse direction which is close to the membrane surface such that retained particles on the stationary layer provides an added resistance to the permeate flow. The resistance therefore depends on the total number of particles formed on the layer and on as well as the spatial distribution. The stationary layer containing retained particles is called concentration polarisation (CP) and is inherent to all cross flow filtration processes [41]. The retained solutes/particles diffuse back to the bulk solution. However, the rate of permeation in membrane systems is higher than the rate at which the rejected solutes diffuse back to the bulk solution. This results in a higher solute concentration at the membrane surface than in the bulk solution. As filtration progresses, the concentration of the particles on the membrane surface becomes so high that a gel layer is formed which acts as a secondary barrier to permeate flux [42].

The effect of the CP is noticeable during membrane operation by the reduction of permeate flux as well as decline in the effective driving force across the membrane, leading to further fouling of the membrane. This influence occurs both in PDMs and ODMs. A similar scenario is observed with the ODM membranes; however, because the driving force here is osmotic pressure, a difference in CP mechanism is noticed. It has been emphasised that in ODMs, CP could occur as internal concentration polarisation (ICP) or external concentration polarisation (ECP) of the membrane (see **Figure 1**) [7, 17, 21, 39]. **Figure 1** shows that the solutes on the draw side decreases while those on the feed side increases, as a result a concentration gradient is formed and as such, a reduction in the osmotic pressure difference between the two solutions is enriched as shown in **Figure 1B**. The result of this is seen in the build-up of CP, which thus reduces flux flow.

ICP occurs within the membrane porous support layer, while ECP occurs on both sides of the membrane surfaces [17, 39]. The orientation of the membranes plays a vital role with regards to the type of CP that will occur on the membrane and it should be noted that CP is contributed by both convective and reverse solute diffusion (RSD) [21, 39]. The effect of ICP is more pronounced on the membranes than that of ECP. The reason is attributed to the fact that there is an axial flow of salt solution within the asymmetric FO membrane, which is the solute that enters and exits the porous support layer. To further validate and understand the nature of CP, both ECP and ICP have been elucidated and categorised as concentrative external concentration polarisation (CECP) and diluted external concentration polarisation (DECP) for ECP and diluted ICP (DCIP) (**Figure 2**).

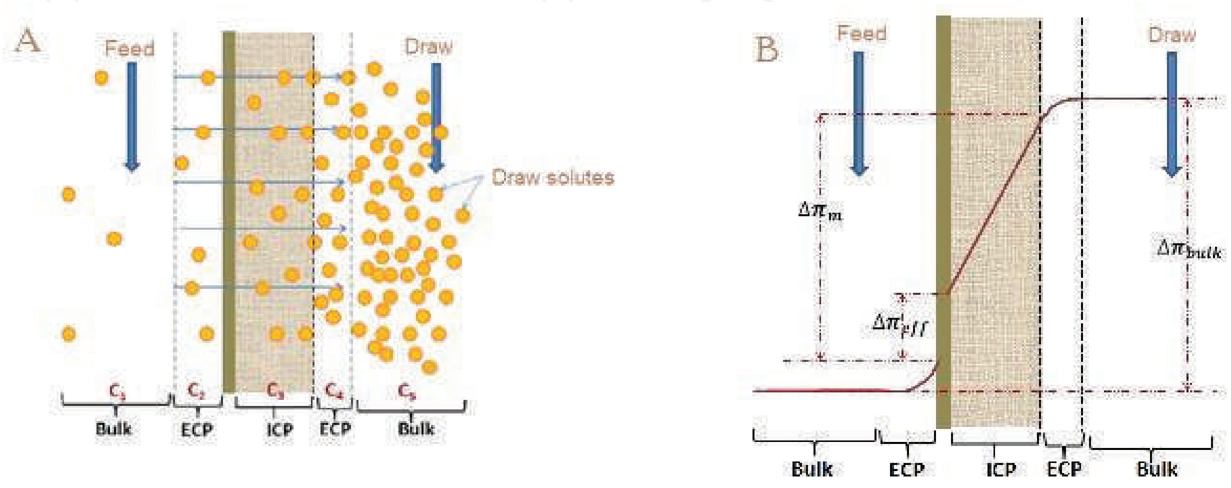

Figure 1. Schematic representation of (A) concentration polarisation on FO membranes (B) osmotic pressure difference due to effects of CP [43].

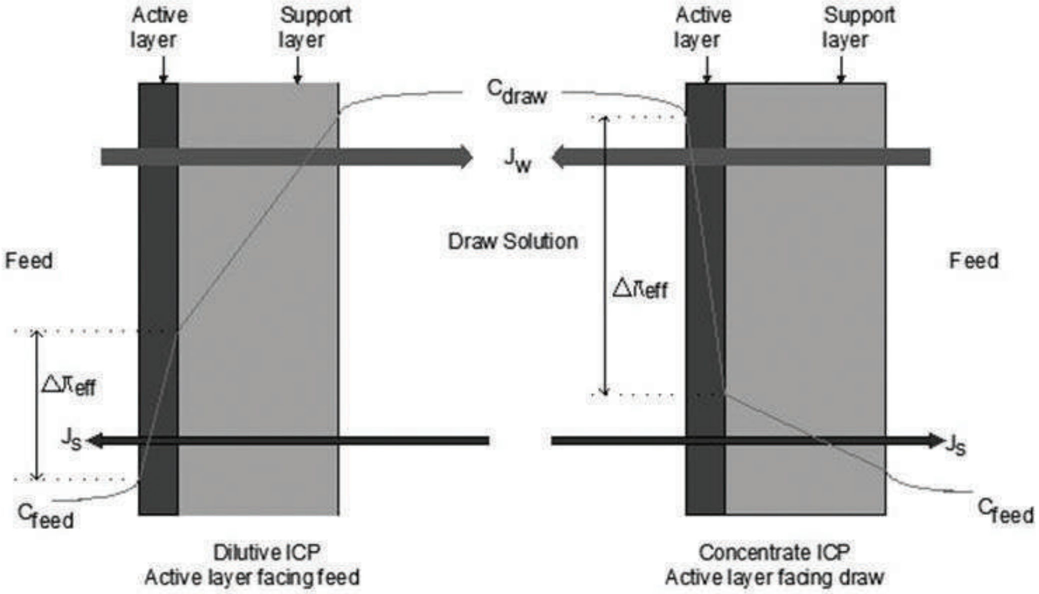

Figure 2. Schematic representation of DECP and DICP on a porous support layer [17].

The logical explanation for this is the fact that the drawn solution is greatly diluted by the permeate water within the porous support of the membrane [39]. Therefore, CECP occurs when the active layer of the membrane faces the feed solution and as such, there is accumulation of the solutes thereby increasing the feed concentration while DECP occurs when the active layer of the membrane faces the draw solution, hence dilution. The outcome of this is seen in the effective osmotic pressure of the feed solution increasing from the bulk solution to the membrane surface and that of the draw solution decreasing from the draw bulk solution to the to the membrane surface. This can be seen in the equation of FO which describes the permeate flux as seen in (Eq. (1)).

$$\mathrm{Jw} = \mathrm{A} * \Delta\pi = (\pi_{\mathrm{D,m}} - \pi_{\mathrm{F,m}}) \tag{1}$$

where Jw is the permeate flux; A is the pure water permeability coefficient; $\pi_{F,m}$ is the osmotic pressure of feed solution on the membrane surface; $\pi_{D,m}$ is the osmotic pressure of draw solution on the membrane surface.

Equation (1), above which describes the flux in FO, was first modified by McCutcheon and Elimelech [44].

$$\frac{\pi\mathrm{f, m}}{\pi\mathrm{f, b}} = \exp\frac{\mathrm{Jw}}{\mathrm{K}} \tag{2}$$

$$\frac{\pi\mathrm{D, m}}{\pi\mathrm{D, b}} = \exp\frac{\mathrm{Jw}}{\mathrm{K}} \tag{3}$$

Where Jw is the permeate flux and k is the mass transfer coefficient. k is related to the Sherwood number (Sh), solute diffusion coefficient and hydraulic diameter of the flow channel

$$k = Sh * \frac{D}{d_h} \quad (4)$$

Depending on the flow regime, *Sh* is calculated using either Eqs. (5) and (6).

$$sh = 1.85 * \left(Re * Sc * \frac{d}{L}\right)^{0.33} \text{ (laminar flow } Re \leq 2100\text{)} \quad (5)$$

$$sh = 0.04 * Re^{0.75} Sc^{0.33} \text{ (turbulent flow } Re > 2100\text{)} \quad (6)$$

However, if the salt back diffusion across the membrane does not take place, then the permeate flux [Eq. (1)] is modified by taking CECP and DECP into consideration the equation can be transformed to Eq. (7).

$$Jw = A * \left(\pi D, b * \exp\left(-\frac{Jw}{Kd}\right) - \pi F, b * \exp\left(\frac{Jw}{Kf}\right)\right) \quad (7)$$

Equation (7) describes ECP in FO; however, ECP effect on flux decline is not as pronounced as that of ICP. The impact of ICP on the membrane is more prominent on the membrane. Therefore, to account for ICP that occurs in the membrane, the equation is modified [1].

Apparently, due to the nature of most membranes being asymmetric and comprising of a thin selective layer and a thick, non-elective layer, Eq. (7) cannot be used to describe ICP porous support layer. This being due to the fact that the osmotic pressure of a solution can be established only at the interface with the selective layer. Noted also is the fact that asymmetric structure of the membrane.

The asymmetric structure of the membrane is made such that one of the boundary layers is within the support layer which then results in ICP [1]. Therefore, to justify for the porous layer, an effective mass transfer coefficient (K_{eff}) is defined as shown in Eq. (8) [1].

$$K_{eff} = \frac{D_s \epsilon}{\tau \delta} = \frac{D_s \epsilon}{\tau t} \quad (8)$$

Where D_s is the diffusivity of the solute, δ is the thickness of the boundary layer ε, τ, and t are the porosity, tortuosity, and thickness of the porous support layer of the membrane.

In normal mode of FO, Eq. (7) is modified to:

$$Jw = A * \left[\pi D, b * \exp\left(-\frac{Jw}{Kdeff}\right) - \pi F, b * \exp\left(\frac{Jw}{Kf}\right)\right] \quad (9)$$

According to Chun et al. [17], the effect of ECP is suffered on all membrane processes. The effect of CP is experienced more on the interface because it is more in contact with the bulk solution. This is due to the fact that the layer interface becomes polarised. Transport of water and other solutes within this interface is merely on advection and molecular diffusion [17]. Because, it is only a minimal amount of the solute that is able to penetrate through the dense selective layer, back diffusion occurs with an accumulation of solute within the porous layer which leads to the formation of ICP effect [17]. Like PDMs, enhanced cake layer concentration

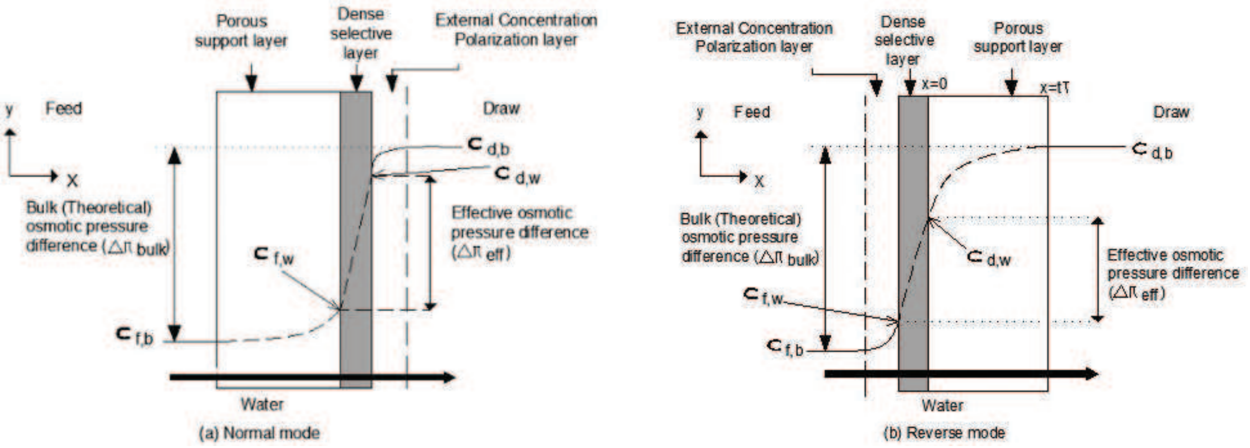

Figure 3. Schematic representation of (a) and (b) shows the different membrane orientation. (a) The normal mode and (b) reverse mode adapted from [24].

polarisation could be formed on the membrane surface. This can happen when the flux is significantly high and thus leads to the formation of a porous fouling layer on the membrane surface such that solute diffusion inside this layer becomes seriously hindered [21, 45]. The effects of Enhanced CP can be expressed through a mass transfer coefficient as shown in Eq. (10) [21].

$$\mathrm{KECP} = \frac{\mathrm{Dml}.\varepsilon \mathrm{la}}{\delta \mathrm{la}.\tau \mathrm{la}} \tag{10}$$

where D_{ml} is diffusion coefficient of the solutes inside the fouling layer; εla is porosity and δla the thickness and τla is the tortuosity of the fouling layer, respectively.

She et al. [39], in his review, outlined the main equations that described both ICP and ECP in ODMs. He noted that the actual solute concentration at the support-active layer interface and that on the active layer surface were not the same with that of the bulk solution.

Xie et al. [24] modified the film models to predict flux behaviour in FO considering its external and internal concentration polarisation. They tested the membranes in two modes; the normal and the reverse. In the normal mode, the dense selective layer faced the DS while the porous layer faced the feed solution; while in the reverse mode, the dense selective layer faced the feed solution while the porous layer faced the draw solution [24]. This is illustrated in **Figure 3**. From their study, they expected the FO to have a greater flux, considering the fact that the influence of ICP in the FS was lesser than in the DS. According to them, the FO process should be preferably operated in the normal mode, this is also the mode implemented which is obtainable commercially as FO membrane for FO processes [24].

4. Membrane materials

One factor that is now increasingly being considered in membrane materials is the material's susceptibility to fouling. Some of the properties of the membrane that affect fouling are charge, roughness and pore size. Membrane material and its properties play an important role in the type of fouling that will occur in ODMs [8]. Knowledge of the nature of the membrane helps in the identification and understanding the fouling mechanism occurring in the membrane.

The development of membranes that can be used for FO has remained a challenge till date. ODMs can be made either by modifying an existing NF or RO membranes or by the development of new membranes with specific design for FO applications [22]. The latter is said to be simple, effective to some extent and cost efficient. Membranes used in RO or NF are made up of a non-porous active layer and a porous support layer and are made from thin-film polymerisation on a polysulfone layer supported by nonwoven fabrics However, they suffer from ICP and thus reduces the effective driving force [7, 22, 46].

The phase inversion and membrane process formation is one way to modify the membranes to improve its properties. These membranes are fabricated with a thin and porous support layer that can reduce ICP effect, while at the same time maintaining a thin and dense selective layer for adequate water flux and salt rejection [46]. Loeb and Sourirajan [47] were the first to use the phase inversion method to fabricate asymmetric polymeric membranes viz. cellulose triacetate (CTA). Ever since, cellulose acetate (CA) has become a popular material for different separation applications [46]. Relatively high hydrophilicity that favours flux and low fouling propensity has been associated with the use of CA. In addition, CA has shown high mechanical strength and availability. The other commonly available membrane type is the polyamide (PA). This is also referred to as the thin film composite (TFC) membrane. This membrane has an asymmetric structure with a dense thin film as well a thick porous support layer. This membrane is said to offer a higher flux and salt rejection and can be operated over a wide range of temperature. Early attempts in using the RO membrane as FO, however, failed due to CP that occurred in the membranes hence reducing flux. Wang et al. [48] further defined asymmetric membranes as consisting of a 0.1–1 μm thick dense layer supported by a highly porous, 100–200 μm thick support layer. The dense layer provides the selectivity of membrane. Hence, the separation properties chemical nature, thickness of the skin layer and pore sizes that are normally between 0.4 and 1 nm [48].

To attain optimum performance of ODM membranes, their selection and fabrication should be based on the following characteristics:

1. The membrane should be dense, ultrathin, have uniform active surface layers, high solute rejection and high permeate flux rate.
2. It should have a thin, porous supporting layer as well as be strong enough to provide mechanical strength to the membrane. The thin layer should help curb ICP and hence increase the membrane flux.
3. Finally, the membrane material should have high hydrophilicity tendency to enhance water flux and reduced membrane fouling [49].

The hydrophobicity of the membrane material plays a major role in membrane fouling. Hydrophobic interaction can be described as “like attracts like.” The similar chemical structures owned by both the membranes and the solutes tend to have a natural tendency to be attracted to each other. Hydrophobic attraction is a result of the van der Waals forces, which occur between molecules [50]. Hydrophobic adhesion is a crucial mechanism for fouling which dominated by NOM due to the fact that high molecular weight NOM offers a higher potential for hydrophobic adhesion because of their charge density. Other factors that affect the strength of the adhesion to membrane surfaces are membrane surface roughness and membrane pore size [51]. A study by Bendinger et al. [52] showed that most foulants that are hydrophobic and slightly hydrophilic adhere better on hydrophobic surfaces than on hydrophilic surfaces. Only highly hydrophilic foulants attach stronger on hydrophilic material. Extremely hydrophobic materials do not adhere too well on the hydrophobic and hydrophilic material.

Hydrophilic membranes have higher fouling resistance than hydrophobic membranes. This means that hydrophobic membranes can be impregnated with water-soluble materials such as poly-vinyl pyrrolidone or poly-vinyl methyl ether. However, this is mostly at the polymer formulation stage [53]. The FO membrane surface roughness does not vary significantly from those of a typical RO and nanofiltration membrane (NF) [6]. The rough and large pore size membranes are shown to be more prone to fouling than the smooth, small pore membranes. This is because the bigger pores are more accessible to foulants. The nature and the extent of the fouling are determined by the specific physical and chemical characteristics of the each component as well as the membrane [6].

In RO membranes, it is expected that the porous support layer material should be thick enough to be able to withstand the high pressures involved, but for FO membranes, which uses osmotic pressures, the thickness of the support layer could be reduced since mechanical strength is not an issue here. Therefore, modifications can be made to reduce the thickness and adjust the structure of the support layer to mitigate the CP phenomenon [19]. The modification of membranes is potentially one of the suitable ways to mitigate and prevent fouling. Therefore, attempts have been made to modify the singly skinned asymmetric FO membranes into a double-skinned membrane structure. This is made such that it contains a porous support, which can be sandwiched between the two rejection skins [10, 46]. The single skinned asymmetric FO membranes face a dilemma of either experiencing more severe dilutive ICP in AL-FS or having much higher fouling propensity in AL-DS [10].

Also, some FO membranes are modified from RO/NF membranes. Hence, they are composed of asymmetric structures which are characterised by a dense active layer on top of a porous support layer. This main separation and structural properties of the active support layer governs both the water and solute transportation. This further enhances the membrane fouling behaviour.

Membranes made up of superior separation properties and structural properties such as the higher water permeability, selectivity and smaller structural parameter could provide much higher water flux [49]. However, an increase in the membrane fouling could be observed due to the enhanced hydrodynamic drag force. Therefore, a balance between mechanical strength and porosity of the membrane is needed. The mechanical strength of the membranes should be reduced so as to increase the porosity and tortuosity [22]. McCutcheon and Elimelech [49], in their study, removed the backing fabric support layer (thickness of 80–120 μm) of commercial RO membranes (overall thickness of 200 μm) and the FO water flux of the modified membranes was improved by a factor of 5.

Pore wettability of the membrane is tied to its ease to wet easily with water. Therefore, for FO membranes, it is important that the pore wettability is improved because the presence of un-wetted pore regions may block the water flux and significantly intensify ICP [22]. The use of a highly hydrophilic polymer, like polydopamine (PDA), to coat the membranes has been demonstrated to be an effective technique in the improvement of the wettability. It has been reported that the wettability can be increased ten folds after coating with FDA [22, 54, 55].

5. Fouling mitigation

Membrane fouling mitigation deals mainly with the management or minimization of the effect of membrane fouling since fouling itself cannot be completely avoided in membrane filtration [56]. Membrane fouling can be controlled and managed at different stages. These include feed pre-treatment to reduce the fouling tendencies, and improve on its antifouling properties. Others such as membrane cleaning and optimisation of operating conditions could further be of benefit also [50].

5.1. Hydrodynamic/operating conditions

Hydrodynamic condition controls the rate of particle deposition on the membrane. According to She et al. [7], most of the conclusions drawn regarding fouling mechanisms in PDMs can also be drawn on ODMs. The operating conditions and properties of the membrane play an important role in the mass transport of the ODMs. Cath et al. [1], in their study, supported the fact that the effect of operating conditions is more noticeable in ODMs than in PDMs. They reiterated that newly developed ODMs are tested under varying temperatures, draw solution compositions and as well the concentrations, flow rates and pressure [1, 48]. Hence, optimum operating conditions should be established to serve as a basis of comparison. Like in PDMs, severe fouling could occur at a higher water flux and lower cross flow velocity. Cross flow velocity has been the most common and widely used method to control fouling at the membrane surface; however, it cannot certainly prevent internal fouling. High cross flow velocity influences membrane fouling through CP and mass transfer near the membrane surface [7, 50].

High cross-flow velocity creates mixing on the membrane surface thereby improving the mass transfer coefficient, but the increase in mass transfer coefficient is different for different feed solutions [57]. At the membrane surface for any filtration system, rejected particles accumulate in a boundary layer. According to Fick’s law, particles in the boundary layer collide with each other more frequently thereby improving particle diffusion from the boundary layer to the bulk solution. This diffusion can be improved by what is called shear-induced diffusion. This is achieved by causing movement of the liquid close to the boundary layer. When the movement of the liquid is increased, the particle collision becomes vigorous and the particle diffusivity is increased. Shear-induced diffusion of particles is highest at the membrane surface or at the boundary layer because of the high particle density in that region [57]. The membrane orientation should also be considered, because AL-FS is preferred due to low fouling propensity, however, the ICP is more prone in this orientation.

Hydrodynamic conditions in PDMs mostly refers to initial permeate flux, transmembrane pressure and turbulence at the membrane surface. Initial flux is the flux at the beginning of filtration and is usually high because at this stage the membrane is clean. Due to high initial flux, particles in a suspension are dragged towards the membrane surface faster than they are diffused/dispersed back into the bulk solution. Therefore, more particles are deposited on the membrane during high initial flux [58].

The study by Hwang et al. [59] showed that high initial flux, results in a large number of particles being simultaneously transported towards the membrane surface. The simultaneous arrival of these particles on the membrane surface was found to be the factor that benefits flux because entry to the membrane pore is hindered and particles only deposit on the membrane surface rather than the membrane internals. The opposite was found for a low initial flux. The finding of Hwang et al. [59] was also confirmed by Wang and Tarabara [60].

For most PDM systems, the effect of aeration as a means to mitigate fouling has been extensively studied especially for membrane bioreactors [61]. The introduction of aeration to cross flow velocity helps to reduce fouling on the membrane surface. This concept has not been widely researched on ODMs. Therefore, there is the need to investigate the effect of aeration on fouling in ODMs.

5.2. Temperature

Temperature of the solution is one of the parameters that can be altered to reduce the effects of fouling. However, this parameter is not often used for fouling control particularly in water treatment [62]. For FO processes, factors such as osmotic pressure, fluid viscosity, mass transfer and mineral solubility depends on temperature, hence it needs to be maintained so that the membrane performance is not altered [62]. Zhao and Zou [62] elaborated that at a higher temperature there is a higher initial permeate flux, higher water recovery and higher concentration factors, and since temperature effect can significantly impact on the membrane, it is important that this parameter is optimised.

Salahi et al. [63] found that when the temperature of the feed water (oily wastewater) used in their study was increased by 20°C, there was an increase in flux of about 60%. This was attributed to an increase in the diffusion rate as the temperature was raised. The flux increase was attributed to the combined effects as listed by She et al. [7] to be (1) a decrease in solution viscosity which can reduce the membrane resistance and as such can cause an increase in the water permeability, (2) an increment in the solute diffusivity which also can increase the mass transfer around the boundary layer and thus leading to a reduction in CP most importantly, ICP and (3) finally an increment in the osmotic pressure thereby increasing the effective driving force. The effect of temperature on ODM fouling was outlined to be through the influence of hydrodynamic conditions such as mass transfer of foulants and initial flux thermodynamic conditions such as osmotic pressure of the solution, solubility and stability of the foulant and finally the interaction of the foulants and the membrane [7].

Kim et al. [64], in the study of the fouling types and mechanisms in a FO membrane processes, under raised temperature, found that flux due to organic fouling was more pronounced when the draw solution was increased. This increase was attributed to the increased permeation drag at increased initial flux level. However, on increasing the feed solution, less fouling was observed because of the organic back diffusion from membrane surface and the increase in the organic solubility [64]. The same authors, Kim et al. [64], in their study observed that membrane fouling became more enhanced when the initial flux was increased to a certain critical flux as temperature for both the feed and DS was increased. This was because organic convection by permeation drag dominated the fouling mechanism. At critical flux, only localised deposition on the membrane occurs, because the rate at which particles deposit on the membrane surface is almost equal to the rate at which they are diffused back into the solution [65]. However, if the process is operated above the critical flux, enhanced fouling is observed on the membrane.

5.3. Feed pretreatment

The feed water to be treated, in most cases, are made up of various components which might include divalent ions, humic substance, alginate, silica and a host of others. These particles could accumulate on the porous membrane structure thereby causing severe decline in membrane permeate flux [23]. The extent to which the feed water is pre-treated depends on the quality of the water; hence, this factor is also dependent on the sources of the water. Pretreatment of feed can be divided into two: physical and chemical. Physical pretreatment involves the use of mechanical filtration such screening, cartridge filters, sand filters or membrane filtration while chemical pretreatment involves the addition of scale inhibitors, coagulants, disinfectants and polyelectrolytes [26].

Extensive studies regarding feed pretreatment in PDMs especially for NF and RO membranes have been investigated extensively, basically for removal of particulate matter [27]. Ultrafiltration (UF) and microfiltration (MF) membranes are used as feed pretreatment to most NF and RO processes due to their porosity. At other times even NF membranes can be used as pretreatment method. The permeates from these membranes have been presented to have low turbidity and silt density index thus increasing recovery in the RO process. For instance, Mi and Elimelech [27] compared three pretreatment technologies; powdered activated carbon (PAC), addition of coagulants such ferric chloride and pretreatment using UF before RO desalination.

The use of NF as pre-treatment to ODM systems however has not been comprehensively studied and remains a crucial aspect for further investigations. Chen et al. [23] studied the first systematic investigation on the use of a loose NF to pretreat feed wastewater in practical PRO practice. They found that the low pressure NF was able to mitigate the fouling potential from multivalent ions and organic matters. Thus, they found the NF method of pretreatment as cost effective. However, the low-pressure NF was able to mitigate the fouling potential from multivalent ions and organic matters, but silica scaling was still predominant, hence, they recommended further investigation. This comparison was made based on a previous study of theirs. That study made use of retentate from a RO unit of a municipal water recycling plant as the main feed stream for an osmotic power generation. Two pre-treatment methods were used: anti-scaling and pH adjustment. The pH adjustment was accompanied by water flushing and 100% by air bubbling thereby resulting in an increased flux [43].

Chemical pre-treatment, on the other hand, involves the addition of chemicals to the feed water. The addition of chemicals for pH adjustment, prevention of scaling and fouling is also used for the pre-treatment of feed to RO processes. This however, in most cases still requires a physical method to be used alongside. For example, a membrane filtration process could be used to pre-treat the feed water and thereafter the chemicals could be added. The advantage presented in following this path is the reduction in chemical consumption. Chlorination, however, should be added to the feed water independent of the pre-treatment method that is being employed. This is to prevent biofouling of the membrane [26]. Nonetheless, after the chlorination, a dechlorination of the feed has to be considered since most of the membranes are susceptible to chlorine attacks.

The addition of coagulants and flocculants causes the dissolve matter to adsorb on the hydroxides and also to cause the agglomeration of colloidal matter. The use of the coagulants aids in reducing the fouling potential on the membrane and also provides a better quality feed water to the RO [26]. The addition of antiscaling agents is considered as one of the pre-treatment methods as well. The precipitation of salts on the membrane surface is referred to as scaling and it is caused by super saturation. It reduces membranes productivity and as well the recovering of water. Different scale inhibitors can be used as antiscalant. These inhibitors control the scaling caused by sulphates, carbonates and calcium fluoride [26].

5.4. Selection of draw solutes

One of the key factors in ODMs is the selection of the right draw solution (DS). The knowledge on the various types of DS used is needful to understand the crucial issues that are related with FO such as CP and mass transport [11]. The following factors should be considered in the selection of DS in ODMs; the solution should produce a substantial amount of osmotic pressure, it should not be expensive ant toxic to the environment and easily regenerated [5, 11, 17, 66]. The commonly used DS is NaCl, because of its high water solubility and it is relatively easy to reconcentrate using desalination processes [17, 66]. Other low molecular weight salts used as DS in recent times include; $MgCl_2$, $CaCl_2$, KCl, Mg_2SO_4. Others such as sucrose, glucose, 2-methylimidazole-based compounds have also been used. Further still, magnetic particles, thermolytic inorganic salts for example ammonia-carbon dioxide and hydrogels have all been tried as DS. It is expected that these solutions should provide a high osmotic pressure and at the same time be easily regenerated and recovered [17].

Cai and Hu [5] reviewed draw solutes used in FO, where they categorise DS into two, namely responsive and non-responsive. The non-responsive solutes were defined as those which when a stimuli such as temperature, pH and others were added to them, no significant change was observed in their water affinity. While on the contrary, the responsive DS were those that, upon exposure to a stimulus, underwent a significant change in their water affinity and thereby accompanied by phase transitions between two states with different water affinities [5].

There is a general perspective regarding the increase in the concentration of the draw solution. Increasing the DS concentration leads to an increase in initial water flux and as such an increase in membrane fouling. The occurrence has been attributed to the effect of increase in hydraulic drag force which is a result of the higher flux that promotes foulant deposition on the membrane [3, 8, 11]. The effect of increasing the DS concentration also influences the RSD by elevating it from the FS to the DS thereby increasing fouling also [67]. She et al. [68] reiterated in their study how RSD influences the deposition of solutes on the membrane surface. The result of this is a change in the feed water chemistry and thus may cause more severe fouling. In that study, they observed that greater alginate fouling occurred on the FO membrane when the DS contained higher concentration of divalent ions of Ca^{2+} and Mg^{2+}. They attributed that the RSD enhanced organic fouling relates to the nature of the DS and to the rate of its diffusion into the feed solution and its ability to interact with the foulant [68]. Therefore, the type and nature of the DS can affect the membrane fouling and the water chemistry too. It was observed that divalent ions in DS, as mentioned above, could influence an additional fouling which is more than the DS even without the specific ions at the same initial water flux level. This occurs as a result of the strong attraction between the ions (foulants) in the solution and the specific ions after they reversely diffuse from DS into FS.

She et al. [39] studied the relationship between reverse and forward solute diffusion to membrane fouling in ODMs. The types of DS used were; NaCl, $MgCl_2$, $CaCl_2$ and $Ca(NO_3)_2$ to reiterate the connection that exists between RSD and forward solute diffusion (FSD). They found that the extent of fouling for the chosen DS was in the order of $Ca(NO_3)_2 > CaCl_2 > MgCl_2 > NaCl$. They concluded that NaCl DS had the highest RSD, this was followed by $Ca(NO_3)_2$ DS, then $CaCl_2$ and finally the least was $MgCl_2$ DS. According to them, the order of the RSD was consistent with the order of their solute permeability. Therefore, the RSD of divalent ions impacted more on the feed solution thus leading to an alginate membrane fouling. Fouling propensity was in the order $Ca(NO_3)_2 > CaCl_2 >> MgCl_2 > NaCl$. Even though a greater amount of NaCl was reversing, the effect of fouling was limited using the NaCl, reason been that the Na^+ did not interact with the alginate. This was related to the cation and anion of the DS and rate of its reverse diffusion.

6. Membrane cleaning

Membrane cleaning is an integral and an important part of membrane processes [16]. Cleaning could be done either hydraulically or chemically. Membrane cleaning becomes necessary when avoiding irreversible fouling of the membrane. The longer the membrane is allowed to operate in its fouled state, the harder it becomes to remove the foulants from the membrane. It, therefore, becomes necessary to use chemicals or greater force to recover a highly fouled membrane.

Physical and chemical methods of cleaning can be employed for fouled membranes. Physical method is also referred to as the hydraulic method. It employs the use of mechanical forces to displace and remove the fouling agents from the membrane surface [69]. These methods of cleaning are typically used in the cleaning in place (CIP) situations. Series of studies have been carried out for the cleaning of ODM membranes using physical methods such as membrane surface flushing and membrane backwashing [7, 16]. The surface washing (forward washing) is achieved when the cross flow velocity is increased on the membrane surface to remove the deposited foulants [13]. Backwashing involves pumping permeate water at a high cross-flow velocity in the opposite direction from which the feed comes in. It is a reversed filtration process in which the permeate of backwashing solution is flushed through the membrane back to the concentrate side. These methods have both shown to be effective against the membrane fouling under different of conditions.

Mi and Elimelech [6] determined the efficiency of surface flushing to investigate the reversibility of FO and RO membranes fouled with organic foulants. Their findings indicate that fouling in FO was more easily reversible than in RO. The reason was due to the hydraulic compaction imposed on the RO membrane which was absent in the FO membranes. It is recommended that for higher recovery of flux, backwashing should be combined with surface flushing. Both surface flushing and backwashing are limited to the fact that only the surface foulants are removed. The internal foulants within the membrane remains after the whole procedure; however, backwashing is moderately successful in removing internal clogging material from the membrane internals.

For FO and PRO membranes, osmotic backwashing has been developed for these processes. The process employs the use of high salinity water to replace the feed solution while a lower salinity water is used to replace the draw solution. Just like in PDMs, the water permeation direction is in the reverse form, thereby creating a negative water flux. The action of this results in the breaking of the foulants away from the membrane [7]. Even though success of osmotic backwashing has been reported by many researchers on recovering of flux, a few others have contrary views where efficiency of osmotic backwashing for water flux recovery was low [7].

When a fouled membrane can no longer be completely removed by physical cleaning, the membrane is irreversibly fouled and therefore, chemical cleaning is required. Caution is however to be employed when cleaning the membranes chemically because the membranes can also be damaged by the chemicals used for membrane cleaning [26, 70]. The choice of chemicals for membrane cleaning must be able to completely dissolve the foulants on the membrane but not damage the membrane itself [69].

Chemical cleaning is a reaction between the chemicals and the foulants on the membrane surface. The process involves mass transfer of the chemicals to the fouling layer and the products of the reaction are dispensed back to the bulk liquid phase. Effectiveness of the chemical cleaning is improved by hydrodynamic conditions that promote contact between the cleaning chemicals and the fouling layer on the membrane surface [50].

The recovery of flux through cleaning has been enumerated to be more in FO than RO membranes. The reason is due to the fact that most fouling in FO is more reversible than that in PDMs [28]. This has extensively been studied by Mi and Elimelech [6], Mi and Elimelech [27] where they carried out chemical and physical cleaning on alginate, bovine serum albumin (BSA) and Aldrich humic acid (AHA) as model organic foulants. They reported a fouling reversibility in the FO and attributed that to the less compacted organic fouling layer formed due to the absence of hydraulic pressure. Another study on the efficiency of physical cleaning in inorganic scaling experiments was also carried out by Zhao and Zou [62] under different temperatures of 25, 35 and 45°C. Membranes were cleaned by the use of water at a cross flow velocity of 33.3 cm/s for 20 min, thus no chemicals were used. Their findings revealed that the higher temperature resulted in higher initial permeate fluxes, higher water recoveries and higher concentration factors. However, more compressed solutes were deposited on the membrane surface and thus the membrane cleaning efficiency was affected [62].

Air scouring induces shear force at the membrane surface as the air bubbles rise travelling adjacent to the membrane surface. The mechanisms responsible for the shear force in the membrane surface are fall film effect and wake effect. These are a net result of the quick rise of air bubbles and the feed solution. Air scouring generates localised cross-flow conditions along the membrane surface thereby reducing the deposition of particles and the development of a cake layer on the membrane surface [61].

7. Conclusion

Fouling in ODM membranes was the main objective of this book chapter. Despite the recognition that ODMs have received in applications in various industries, the use of this this technology is still limited by fouling, thus hindering its overall performance. The information on the fouling mechanisms is still limited and thus needs to be examined critically. This book chapter provides vital information on the impact of fouling on ODMs performance and it explored the factors and mechanisms governing fouling in ODMs. Further still, the effects of membrane fouling were expounded and approaches on the mitigation and cleaning of the membranes were outlined.

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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 ± 1.2 Lm^{-2} h^{-1} or 11.8 ± 1.6 Lm^{-2} 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 ± 0.2 Lm^{-2} 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 m^3 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.

$$A = \frac{J_w}{\Delta P} = \frac{V_{perm}}{A_m \, \Delta t \, \Delta P} \tag{1}$$

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:

$$J_w = A(\Delta P - \Delta \pi) \tag{2}$$

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).

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

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):

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_p} \tag{4}$$

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 NH_3–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 are 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 $Al_2(SO4)_3$ 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 cm^2 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	$\times 10^{-7}$ 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 $CaCl_2$. 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*		

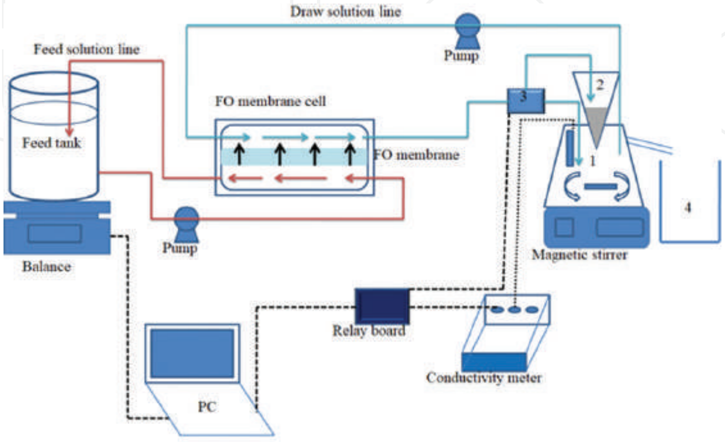
*The concentrations of the single foulants were kept the same in their mixtures (100, 80, 20 and 200 mg/L for bovine serum albumin; BSA, alginate; ALG, octanoic acid; OA and humic acid; HA, respectively.

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.



1. Draw solution tank, 2. Filter funnel with salt, 3. 3-way valve, 4. Draw over-flow vessel

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 (± 0.87) $Lm^{-2}\ h^{-1}$. 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.

$$\zeta = \frac{\Delta V \eta \sigma}{\Delta P \varepsilon\, \varepsilon_o} \tag{5}$$

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 ($C^2N^{-1}\ m^{-2}$). The permittivity is defined as $\varepsilon = \varepsilon_0.D$, where ε_0 is permittivity of vacuum = 8.85×10^{-12} ($C^2N^{-1}\ m^{-2}$) 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,

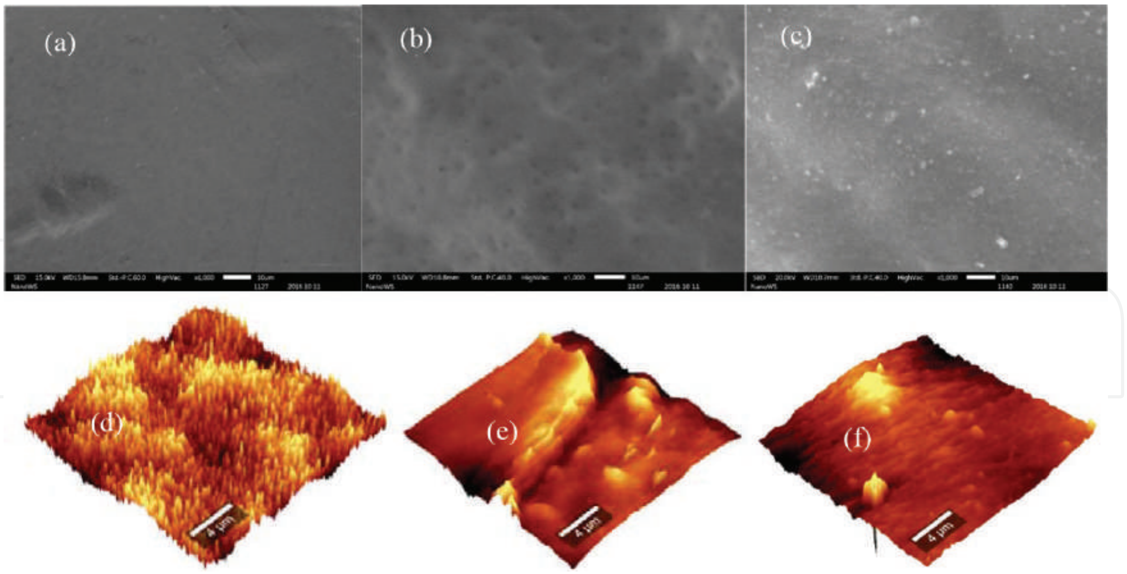


Figure 2. Clean and fouled membrane surface morphology and topology: (a) SEM image of clean TFC membrane, (b) image of membrane fouled with Alg + BSA, (c) image of membrane fouled with Alg + BSA + HA, (d)–(f) corresponding AFM micrographs.

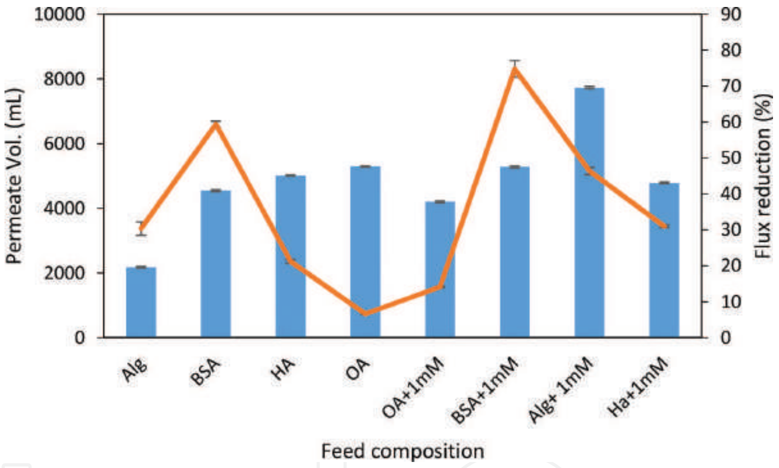


Figure 3. Recorded permeate volumes and flux declines during seawater dilution suing simple feed streams.

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 though 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

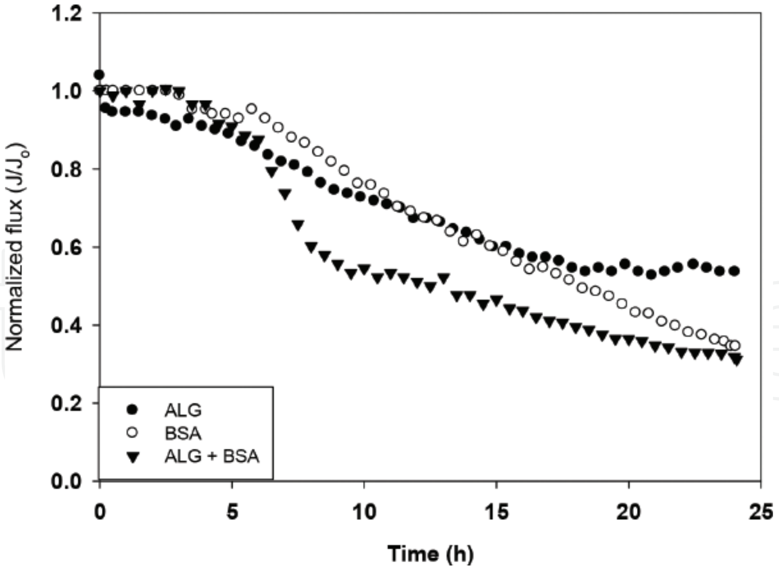


Figure 4. Membrane permeate flux decline pattern during co-foulant (Alg + BSA) feed stream filtration.

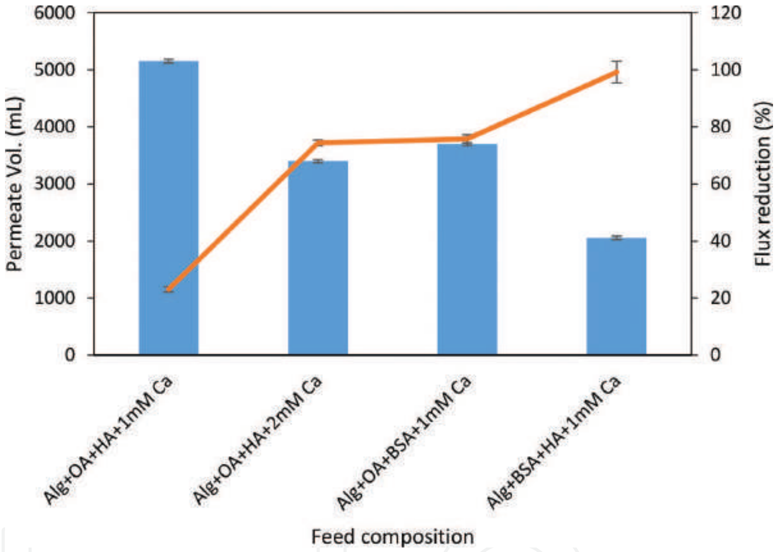


Figure 5. Permeate volumes and permeate flux loss during seawater dilution using complex feed streams.

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

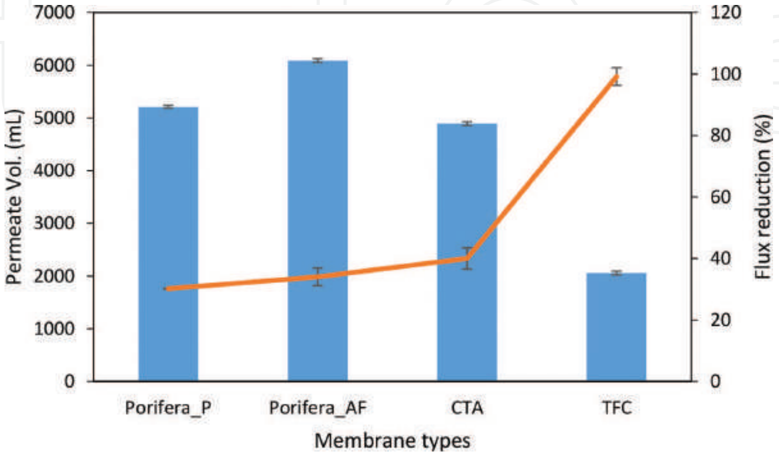


Figure 6. Performance of FO membranes used to filter complex feed streams. Porifera P represents the plain membrane while Porifera AF was modified to induce anti-fouling properties.

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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Applications of Reverse and Forward Osmosis Processes in Wastewater Treatment: Evaluation of Membrane Fouling

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Additional information is available at the end of the chapter

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Abstract

Although reverse osmosis (RO) process is widely used for wastewater reclamation, it requires high amount of energy that has a major effect on the economic effectiveness of the process. Furthermore, RO membranes are susceptible to fouling, which further limits their effectiveness and increases the costs due to the need for frequent cleaning. Consequently, the use of osmotically driven membrane separation processes such as forward osmosis (FO) has gained increasing consideration, although its uptake in wastewater remediation is still low. This is because the FO process, unlike the RO process, is operated by the osmotic gradient between the feed and draw solutions; therefore, it requires minimal or no hydraulic pressure. Hence, it has unique advantages, such as possibility of low fouling, and high water recovery. Nonetheless, the long-standing problem of membrane fouling still remains a major challenge even in the performance of FO processes especially when treating raw wastewaters, which have various contaminants. Furthermore, the mechanism of fouling in FO process has been found to be different from an RO process, and there is need for further studies to elucidate the differences of FO and RO fouling. These aspects are evaluated in this review.

Keywords: forward osmosis, membrane fouling, osmotic pressure, reverse osmosis, wastewater

1. Introduction

For many centuries, water has been considered a renewable, unlimited resource. However, in recent decades, the awareness that fresh water is not unlimited has arisen. The two major issues around water management are, thus, water scarcity and escalating pollution. Indeed, water pollution has put a potential strain on the existing water sources resulting in scarcity of fresh water. This has been occasioned by the rapid growth in global human population, thus increasing the demand; enhanced industrial and agricultural activity leading to rampant pollution of water sources; as well as climate change resulting in water scarcity through droughts. All these issues suggest the need for a more rational use of water resources [1]. The use of alternative sources of water such as seawater desalination and the reuse of wastewater after appropriate treatment is therefore necessary. Furthermore, the protection of natural water resources and development of new technologies for water and wastewater treatment for reuse are key priorities of the twenty-first century.

Wastewater reuse offers an opportunity to reduce demand on existing water resources [2]. This is because wastewater represents a suitable water source that can be used after appropriate treatment to reduce the fresh water demand and to lower the environmental impact of wastewater discharge [3]. Consequently, effluent from municipal wastewater treatment plants (MWWTPs) is a potential source of recycled water; however, to ensure its approval by the target population, microbial, physical, and chemical pollutants need to be removed using appropriate treatment technologies [4, 5].

Conventional municipal wastewater treatment processes rely on physicochemical and biological processes. However, with increasing contamination of wastewater by organic micropollutants and microbial contaminants, the current treatment technologies are often not successful in meeting the stringent standards. The reduction or complete removal of refractory organic contaminants from wastewater is important from the viewpoint of wastewater reclamation, recycling, and reuse [5]; however, conventional municipal wastewater treatment is inefficient especially in the removal of biorecalcitrant organic micropollutants and some resistant microorganisms.

There is therefore a pressing need to develop alternative wastewater remediation technologies that are capable of complete removal of organic micropollutants; have the provision of effective disinfection; are capable of utilization of minimum resources such as energy; are economically viable; and are environmentally friendly [6]. Suitable technologies should be able to enhance water recovery as well as extract biomass from the wastewater for reuse [7]. Membrane-based technologies have gained increasing prominence for wastewater remediation. Although low pressure processes such as microfiltration (MF) and ultrafiltration (UF) have been employed to treat secondary wastewater effluent, these technologies are not effective in removing emerging micropollutants and trace metals from wastewater, thus limiting the potential application of the reclaimed wastewaters. Consequently, the use of high pressure processes such as nanofiltration (NF) and reverse osmosis (RO) have been explored. However, they too suffer limitations such as high energy demand and severe membrane fouling, which ultimately increases the operating costs. This has prompted the exploration of osmotic pressure–driven membrane processes (ODMPs) such as forward osmosis (FO) as a suitable alternative to overcome these concerns [8]. This chapter presents the water scarcity and pollution challenge, applications of membrane-based processes (RO and FO) for wastewater remediation, and recent developments in addressing membrane fouling in RO and FO processes.

2. The RO and FO membrane processes

2.1. Principle of operation of RO and FO membranes

In the FO process, an osmotic pressure gradient across the semipermeable membrane drives water from a dilute feed solution (FS) to a concentrated draw solution (DS) [9]. In this way, the DS generates greater osmotic pressure and drives water from the feed through the membrane while rejecting solutes, thus separating the water from the diluted DS [10]. The RO process, on the other hand, employs hydraulic pressure to effect the permeation of water through a semipermeable membrane. The principle of operation of RO and FO processes is shown in **Figure 1**. The ideal semipermeable membrane for use in RO and FO processes should possess the following attributes: high water flux and salt rejection, less fouling propensity, and high chemical and thermal stability, among others [10]. The FO process has been shown to have a lower propensity to fouling and consequently, a higher reversibility of fouling than RO, and this is attributed to the lack of applied hydraulic pressure. Subsequently, FO can be used to treat low-quality feed waters such as municipal wastewater and landfill leachate, among

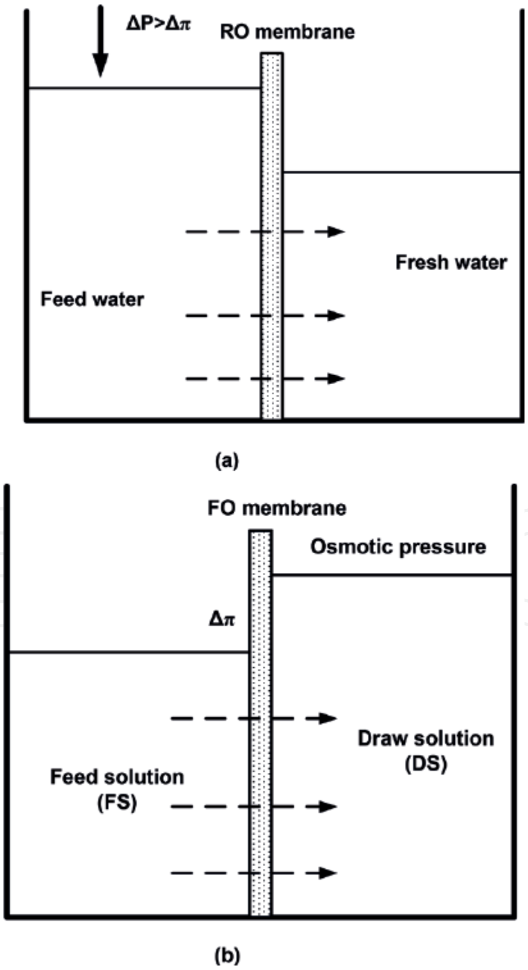

Figure 1. Working principle of (a) RO and (b) FO processes.

others [11]. Nevertheless, even in an FO-based separation process, energy is still required to extract clean water from the DS and to reuse the DS [12].

The general equation used to describe water flux across the RO and FO membrane (J_w) is calculated using Darcy's law [9]:

$$J_w = A_w \times (\sigma\,\Delta\pi - \Delta P) \tag{1}$$

where A_w is the membrane pure water permeability coefficient, ΔP is the applied hydrostatic pressure, $\Delta\pi$ is the differential osmotic pressure, and σ is the reflection coefficient indicating the rejection capability of a membrane (for an ideal membrane σ =1). Therefore, in FO, ΔP is zero thus making the water flux to be directly proportional to the difference in osmotic pressure, while for RO, $\Delta P > \Delta\pi$. This relationship is illustrated in **Figure 2**.

Despite not using hydraulic pressure, the FO process can produce permeate quality that is close to that produced by RO and superior permeate quality than that of microfiltration (MF) and ultrafiltration (UF) membranes [7]. Moreover, the FO process has benefits including high

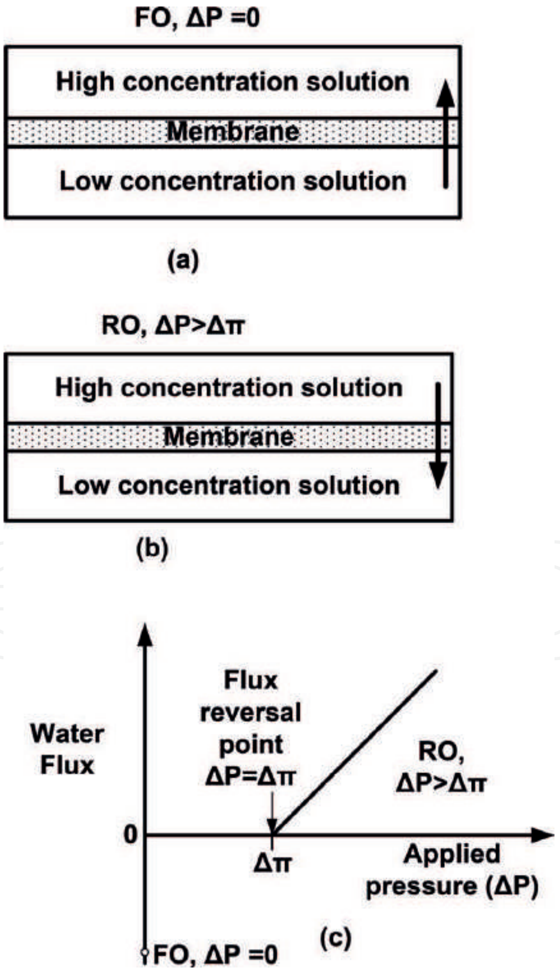

Figure 2. Schematic representation of FO (a) and RO processes (b) and a plot of water flux versus applied pressure for both processes (c). Adapted from [13].

rejection of a wide range of pollutants without using hydraulic pressure and hence the reduced energy expenditure and low membrane fouling tendency (more reversible fouling) [14]. For instance, a study by Altaee and colleagues [15] reported that the total power consumption by the FO process was 2–4% that of the RO-FO process, which shows that the use of FO can lead to significant reduction in energy expenditure. It is due to these unique advantages of FO membranes that they have been employed in many applications such as desalination of seawater, wastewater remediation, food and pharmaceutical processing, as well as renewable osmotic energy production [16].

However, notwithstanding these advantages of FO, it still suffers from the challenges faced by RO, mainly membrane fouling that results in reduced permeate quality and quantity as well as increased operational cost [17]. Developing an understanding of fouling behavior in FO is needed since it has been found that the fouling factors and mechanism of fouling in FO are different from those of an RO process [18]. Consequently, further research is required to understand the fouling behavior of FO and RO membranes to enable the development of tailored fouling controls [19].

2.2. Applications of RO and FO membranes in wastewater treatment

The FO and RO processes have been used to treat a variety of wastewaters such as municipal wastewater [14, 16, 18, 20], oily wastewater [21, 22], produced water [23], tannery wastewater [24], dairy wastewater [25], olive mill wastewater [26], as well as synthetic wastewater [8, 27]. In some of these studies, it has been reported that FO membranes could perform better than RO membranes. For instance, a comparative study by Cui and coworkers [28] on the removal of organic micropollutants (phenol, aniline, and nitrobenzene) reported that FO membranes achieved rejections of over 72%, which the authors observed that cannot be attained by commercial or lab-synthesized RO membranes. The FO and RO membranes can also be used in combination with other processes to increase the performance effectiveness. For instance, the use of combined MBR-RO and MBR-FO systems considerably improves the performance in wastewater treatment. Since the MBR alone is not effective in the removal of color and salts, the combination with RO and FO membranes allows for effective removal of these constituents [29]. Qui and colleagues [30] recently investigated the use of a biofilm-forward osmosis membrane bioreactor (BF-FOMBR) and reported that the process achieved very high removal efficiency of organic matter and nitrogen within a hydraulic retention time of 2 h. Furthermore, a significant reduction in FO membrane fouling was achieved (24.7–54.5%) due to decreased bacterial attachment and colonization of the membranes. A summary of the recent studies and the performance attained is shown in **Table 1**.

2.3. Limitations of RO and FO membranes

The use of membrane-based processes for wastewater treatment has been driven by the need to enhance water recovery, reduce energy consumption, and improve sustainability in application [31]. Consequently, membrane-based wastewater reclamation is considered a promising solution to supplement water supply and alleviate water shortage [18]. The RO process has received wide attention; however, it requires high hydraulic pressure, thus making it

Wastewater	Membrane type	Performance	Reference
Activated sludge	Cellulose triacetate Polyamide thin-film composite membranes (FO)	96% COD rejection.	[20]
Produced water	Cellulose triacetate Polyamide thin-film composite membranes (FO)	90% rejection of neutral hydrophobic compounds.	[23]
Oily wastewater	Hybrid forward osmosis membrane distillation (FO-MD) system	Water recovery of 90%. Almost complete rejection of oil and NaCl.	[21]
Soybean oil/water emulsion	Thin-film composite (TFC) FO membranes	Oil rejection of 99.9%.	[22]
Municipal wastewater	Superhydrophilic sulfonated poly-phenylenesulfone (sPPSU) polymer matrix TFC membranes (FO)	85% water recovery.	[16]
Municipal wastewater	FO membranes	A 5% flux decline in the absence of suspended solids and a 20% flux decline in the presence of suspended solids.	[18]
Synthetic urban runoff	Cellulose triacetate FO membrane	Rejection of trace metals (98–100%); phosphorus (97–100%); nitrate (52–94%). A 70% water recovery.	[27]
Synthetic wastewater	Cellulose triacetate (CTA) membranes (FO)	Rejection of pollutants in the wastewater (> 97%).	[8]
Municipal wastewater	Cellulose triacetate (CTA) membrane (FO)	89.2% removal efficiency of NH_4^+-N.	[14]
Tannery wastewater	ESPA-1 RO membranes	>98% rejection of COD and salts.	[24]
Dairy wastewater	TFC HR SW 2540 spiral RO membranes	99.9% TOC rejection and 99.5% conductivity reduction.	[25]
Olive mill wastewater	XLE and BW30 RO membranes	96.3% COD rejection.	[26]

Table 1. Studies on the application of RO and FO membranes in wastewater treatment.

energy intensive and costly due to the resulting membrane fouling and replacement. It is due to these concerns that in recent times the FO process has become an attractive alternative to RO due to the fact that it utilizes an osmotic pressure gradient as driving force for separation and also has additional merits such as lower energy consumption, less susceptibility to membrane fouling, and higher water recovery [32, 33]. Furthermore, FO membranes consistently reject a range of pollutants in municipal wastewater (chemical and biological contaminants), making FO an appropriate technology for wastewater remediation for reuse [20]; however, its application in wastewater treatment is still low [34]. Nevertheless, fouling still remains a formidable challenge even in FO processes limiting long-term operation, leading to flux decay and shortening of membrane lifespan [35].

3. Membrane fouling

3.1. Categories of membrane fouling

Membrane fouling arises from the accumulation of pollutants on the membrane surface leading to a reduction in flux. It has far-reaching implications since it affects the permeate quality and increases the operating costs such as process downtime leading to production losses, cleaning chemicals, energy and labor requirements, and eventually membrane replacements [36, 37]. The magnitude of membrane fouling depends on the physicochemical properties of the membrane and the wastewater composition. For instance, hydrophilic, low roughness, and neutral charge membranes present a high resistance to fouling [20]. In terms of location of foulants, fouling can be divided into surface fouling and internal fouling depending on the location of the foulants. Surface fouling is more frequent in high pressure membranes such as RO due to their compact and nonporous nature. On the other hand, based on foulant types, fouling can also be divided into biofouling, organic fouling, inorganic scaling, and colloidal fouling [20, 38].

a. Biofouling

This is the adhesion of microorganisms on the membrane surface leading to the formation of a biofilm. It occurs through the reversible attachment of planktonic bacteria, cell growth, and extracellular polymeric substance (EPS) production leading to the formation of biofilms [20]. Therefore, the two main components of biofilms are bacteria and EPS, which are excreted by bacteria. Biofouling is regarded as one of the most formidable forms of membrane fouling since bacteria reproduce on the membrane surface, thus enhancing the biofilm that leads to additional fouling [39]. This is because microorganisms are present in many water systems and they readily adhere to membrane surfaces and multiply.

b. Organic fouling

This arises from the adsorption or deposition of organic matter such as humic substances, polysaccharides, proteins, lipids, nucleic acids and amino acids, organic acids, and cell components on the membranes. It is the most common fouling experienced in wastewater treatment using membrane bioreactors (MBRs). The organics often become precursors of biofouling [40]. Effluent organic matter in wastewater arises from three sources: natural organic matters (NOMs), synthetic organic compounds (SOCs), and soluble microbial products (SMPs).

c. Inorganic scaling

This entails the chemical or biological deposition of inorganic substances on the membrane surface or within the pores, thus preventing permeation of water. It occurs when the concentration of some ions (such as metal sulfates and carbonates) in the water is high enough to exceed the equilibrium solubility product and hence become supersaturated leading to the deposition of the ions [13]. In fact, if the feed water is not well pretreated due to improper design of coagulation or oxidation processes, it may lead to the introduction of metal hydroxides into the fouling matrix, which causes significant challenges in chemical cleaning to enhance water flux.

d. Colloidal fouling

This refers to the deposition of fine suspended particles (colloids) on the membranes. Colloidal foulants can be divided into two types: inorganic foulants and organic macromolecules. Colloidal fouling leads to substantial flux decline resulting from the deposition of thick or less porous fouling layers composed of particulate matter. Consequently, this hinders back diffusion of salts that permeate water flux from the DS, thus increasing the salt concentration on the membrane surface.

A detailed analysis of the different modes of fouling in FO and RO membranes can be found in recent studies by Chun and colleagues [13] and by Jiang and coworkers [38], respectively. In addition, the following factors play a major role in fouling: the characteristics of the fouling matter, the chemistry of the DS and FS, the membrane properties (hydrophilicity and surface roughness), and hydrodynamic conditions, and they have been discussed in the literature [36].

3.2. Comparison of fouling in RO and FO membranes

Understanding the mechanisms of fouling is essential for improving membrane performance especially in FO membranes where very little has been done. For instance, the driving force for membrane separation plays a significant role in membrane fouling. It influences the fouling layer structure as well as the fouling reversibility. It has been reported that although the extent of compaction resulting from the permeate drag force is similar in FO and RO fouling layers, however, higher compressibility of foulants occurs under hydraulic pressure in RO processes. Therefore, in RO, there are two compaction mechanisms involved: compression of foulants and permeate drag force, whereas in FO, only the permeate drag force is predominant. These mechanisms reinforce one another, resulting in dense, compact, and irreversible fouling layers in RO [11].

Furthermore, in the RO processes, the hydraulic pressure–driving force remains constant during operation and hence the fouling effect can be readily determined. On the other hand, the fouling properties of FO process are different because of the changing osmotic pressure difference, accompanied by changes in concentration polarization. This makes it difficult to use the FO flux to accurately show the actual effect of membrane fouling [36]. Moreover, permeate flux and transmembrane pressure are commonly used to indicate membrane fouling in RO membranes, but these are not used in the FO process [36]. Additionally, in terms of transport, in the FO process, permeate water transports from the FS to DS; hence, the DS is diluted and FS concentrated steadily. Subsequently, the osmotic pressure decreases, leading to permeate flux decline along the membrane channel. However, in the RO processes, the concentration of the FS is only observed along the membrane channel [41]. Overall, studies have shown that the lack of hydraulic pressure in the FO system has a positive effect in that the membrane fouling generated is in most cases reversible and the water flux can be almost fully recovered using hydraulic washing, thus eliminating the use of chemical cleaning [37].

It has also been reported that membrane fouling in FO is less severe than in RO membranes. For instance, Yu and colleagues [42] compared the fouling propensity in RO and FO membranes treating activated sludge effluent and reported that the membrane fouling based on flux reduction was lower in FO membranes than in RO membranes. However, despite this, it is still necessary to pretreat the wastewater to prevent excessive fouling of FO membranes and decelerate membrane degradation [23]. A comparative study on the fouling of FO and RO membranes using polysaccharides (alginate, xanthan, and pullulan) depicted that alginate and xanthan resulted in more pronounced fouling in RO than in FO. Similarly, the study reported that polysaccharides naturally produced by marine bacteria improved the permeate flux instead of causing fouling in FO membranes [32]. Tow and coworkers, on the other hand, observed similarities in fouling in FO and RO membranes in terms of swelling and wrinkling of the fouling matter. They suggested that this could be leveraged to develop cleaning protocols for both FO and RO membranes [43]. In another study, Kwan and colleagues [44] evaluated biofouling in FO and RO membranes under similar hydrodynamic conditions and observed significant differences such as the following: (i) water flux decline was significantly lower in FO than in RO and (ii) biofilms in FO were loosely organized and in a thick layer, whereas in RO, they were tightly packed (due to hydraulic pressure). Consequently, the more packed biofilms in RO resulted in high resistance to water flow leading to higher flux decline. In another study, organic fouling has been reported to be dominant in RO membranes used for the treatment of municipal wastewater [45]. **Table 2** summarizes some of the recent studies on membrane fouling in RO and FO membranes.

Nevertheless, the fouling mechanism is complex and depends on numerous aspects such as water quality, process conditions, module design, and membrane properties, among others. It is therefore imperative to consider these factors in process design and development to mitigate fouling [9]. Moreover, the fouling behavior in the FO processes is unique because both sides of the FO membrane are involved [13], whereby there is membrane fouling and a drop in driving force [46]. A comprehensive evaluation of mass transport and fouling in FO and other ODMPs has been provided by She and colleagues [19].

3.3. Characterization of membrane foulants

Characterization of the fouling layer is important to enable the evaluation of membrane fouling especially the interaction of foulants with membranes and the composition of fouling matter.

Process	Water matrix	Type of fouling	Reference
FO, PFO, and RO	Sodium alginate	Organic fouling	[11]
FO and RO	Alginate, xanthan, and pullulan	Organic fouling	[32]
FO and RO	Activated sludge	Organic fouling	[42]
FO	Municipal wastewater	Cake layer formation	[46]
RO and FO	Alginate and methylene blue dye	Organic fouling	[43]
RO	Municipal wastewater	Organic fouling and inorganic scaling	[45]
FO and RO	Synthetic wastewater containing *Pseudomonas aeruginosa*	Biofouling	[44]

Table 2. Studies on membrane fouling in RO and FO membranes.

Process	Characterization technique	Water matrix	Reference
RO and FO	Fouling visualization apparatus	Alginate gel and methylene blue dye	[43]
RO and FO	CLSM	Sodium alginate	[11]
FO	SEM and LC-OCD	Synthetic wastewater	[33]
FO	SEM, FTIR, EDS	Oily wastewater	[37]
FO and OMBR	SEM, FTIR, EEM, EDX	Municipal wastewater	[14]
FO and RO	AFM and contact angle	Activated sludge	[42]
RO	FTIR, EEM	Municipal wastewater	[45]

Table 3. Studies on characterization techniques for RO and FO membranes.

This provides insight into the fouling mitigation strategies that can be adopted. Furthermore, a classification of fouling into chemical, physical, and microbiological enables also the identification of the appropriate techniques for characterization. Physical characterization can be performed by visual examination using environmental scanning electron microscopy (ESEM) and atomic force microscopy (AFM). Chemical characterization can be done using Fourier transform infrared (FTIR) and excitation emission matrix (EEM) analyses to determine the organic composition; energy dispersive X-ray spectroscopy (EDS) to determine the elemental composition of the fouling layer; evaluation of zeta potential to determine the surface charge and membrane hydrophilicity; and liquid chromatography with organic carbon detection (LC-OCD) to determine the different fractions of dissolved organic carbon. On the other hand, microbiological characterization can be accomplished using adenosine triphosphate (ATP) measurements, EPS quantification, and CLSM analysis for biofilm visualization and thickness estimation [8, 13, 14, 20]. More details can be found in a recent work by Li and coworkers [47] who reviewed the use of membrane fouling research methods to study fouling in RO and FO membranes. They also identified the main foulants involved in the various types of membrane fouling; however, they did not evaluate the mitigation strategies for membrane fouling. **Table 3** shows some of the studies that have been conducted and the characterization of membrane foulants.

4. Addressing membrane fouling

Municipal wastewater contains a variety of contaminants such as organic matter, inorganic matter, and microorganisms that can lead to membrane fouling [14]. Since membrane fouling is inevitable, it is imperative to develop strategies to address this challenge. Approaches for tackling fouling are twofold: (i) fouling mitigation through membrane and module development and optimization of hydrodynamic conditions and (ii) adapting cleaning approaches [48]. These strategies can further be broken down into the following: feed pretreatment, membrane monitoring and cleaning, membrane surface modification, or the use of novel membrane materials [38].

4.1. Feed pretreatment

It involves improving the feed water quality to minimize contaminant concentration prior to membrane filtration. It is aimed at ensuring reliable membrane operation and prolonging the membrane lifespan. Some of the most commonly used pretreatment technologies for RO include UF [49], coagulation/flocculation, and MF. In fact, FO can also be used as a pretreatment for RO because the former does not require hydraulic pressure and hence reduces the overall energy required and process costs by decreasing RO membrane fouling, minimizing the cleaning frequencies, and also increasing the water recovery [49, 50]. Nanofiltration has also been employed as a pretreatment for RO membranes. This is reported to have resulted in an increase in water recovery and water flux and also a reduction in RO membrane scaling and thus contributing to lowering the operating costs [51]. In another study on the treatment of geothermal water, NF was used as pretreatment for RO to reduce the concentration of divalent ions [52]. Combined pretreatment technologies have also been employed such as the use of ozonation, ceramic MF, and biological activated carbon (BAC) together as pretreatment for RO as reported by Zhang et al. [53]. In this combination, ozonation increased the oxidation of organic matter leading to its dissolution and facilitating removal by the ceramic MF and BAC prior to treatment by RO.

4.2. Membrane monitoring and cleaning

It entails the in situ monitoring of the membrane performance to evaluate the extent of fouling so as to conduct cleaning timeously. Some of the proven effective cleaning approaches of FO membranes include hydraulic cleaning and osmotic backwashing [23]. Osmotic backwash entails the reversed flow of water from the permeate side to the feed side based on the osmotic pressure difference. Lotfi and coworkers [33] observed that physical cleaning of FO membranes was effective leading to almost full restoration of the initial flux. In addition, treatment of oily wastewater using FO membranes indicated that osmotic backwashing resulted in over 95% water flux recovery and performed better than chemical cleaning using oxidants and acids [37]. Bell and colleagues employed chemically enhanced osmotic backwashing to clean FO membranes. The study showed that the cleaning removed cations and anions from the membrane surface but only slightly improving the water flux [23]. Similarly, Yu and colleagues demonstrated that during treatment of activated sludge using FO membranes, the flux was fully recovered using osmotic backwashing rather than cleaning by changing the cross-flow velocity or air scouring. They concluded that osmotic backwashing is a more efficient way to clean the FO membrane. A study by Wang and colleagues [54] investigated the chemical cleaning of FO membranes using different chemicals. They reported that disodium-ethylene-diamine-tetra-acetate (EDTA-2Na), sodium dodecyl sulfate (SDS), NaOH, HCl, and citric acid were not effective in removing the foulants after severe fouling; on the other hand, 0.5% hydrogen peroxide applied for 6 h at 25°C resulted in 95% recovery of permeability suggesting that almost all the foulants were removed. **Table 4** provides a summary of strategies employed in cleaning RO and FO membranes.

However, implementing costly cleaning protocols such as air scouring or chemical cleaning may be detrimental to the economic sustainability of the FO process. Therefore, it is necessary

Process	Cleaning strategy	Performance	Reference
TFC-FO	Water rinsing without using chemicals	97% water flux recovery.	[22]
FO	Hydraulic cleaning (cross-flow rate of 800 mL/min for 15 min)	90% water flux recovery.	[33]
FO	Hydraulic cleaning (cross-flow velocity 33 cm/s for 30 min) Osmotic backwash	75–80% flux recovery using hydraulic cleaning and 95% flux recovery using osmotic backwash.	[37]
FO OMBR	Hydraulic cleaning (cross-flow velocity of 10 cm/s for 60 min)	49.37% flux recovery in FO and 10.60% flux recovery in OMBR.	[14]
	Chemical cleaning (1% NaClO, 0.8% EDTA, and 0.1% sodium dodecyl sulfate (SDS) in sequence. Each lasted for 60 min.)	58–67% flux recovery in FO and 2–18.5% flux recovery in OMBR.	[14]
RO and FO	Hydraulic cleaning (cross-flow velocity of 25 cm/s for 60 min)	After hydraulic cleaning, the foulant peels off the membranes in both RO and FO.	[43]
FO, PFO, and RO	Hydraulic cleaning (cross-flow velocity 17 cm/s for 30 min)	Flux recovery: FO (99%); PFO (58%); and RO (10%).	[11]
FO and RO	Physical cleaning (cross-flow velocity of 8.5–25.5 cm/s for 1 min) Osmotic backwashing (1 min)	75% flux recovery by physical cleaning; 99.9% flux recovery by osmotic backwashing.	[42]
FO	Chemical cleaning (0.5% hydrogen peroxide for 6 h)	More than 95% recovery of permeability.	[54]

Table 4. Cleaning strategies employed for RO and FO membranes.

to explore proven strategies such as osmotic backwash, which has recently been demonstrated to successfully clean fouled FO membranes and has been extensively studied in the RO literature. This will allow for sustainable operation without use of chemicals [48]. In addition, real-time monitoring of the membrane process can provide useful information essential for efficient cleaning. To overcome the limitations of the individual cleaning methods, it is necessary to explore the use of multiple methods to take advantage of synergy in the use of multiple cleaning strategies such as a combination of osmotic backwashing and surface backwashing to further improve the performance of FO membrane [42]. For instance, a study by Sun and colleagues [14] showed that even in cases of severe membrane fouling, the use of hydraulic and chemical cleaning resulted in effective recovery of water permeability.

4.3. Membrane surface modification and the use of novel materials

It is based on the fact that membrane properties such as smoothness and hydrophilicity greatly influence performance. For instance, smooth surface and hydrophilic membranes are less prone to fouling compared to those with rough and hydrophobic surfaces. In addition to surface modification, the development of novel membrane materials with unique characteristics tailored to meet specific applications is another promising avenue. These novel materials include carbon nanotubes, zwitterionic materials, and metal oxide nanoparticles [38]. Li and coworkers [10] reviewed developments in materials and strategies for enhancing properties and performances of RO and FO membranes. They noted that surface modification of RO and FO membranes has received wide attention due to it being less costly and easy to perform compared to developing novel polymeric materials. However, surface modification may also have adverse effects such as pore blockage on the membrane active layer when some modifiers such as polyelectrolytes may promote concentration polarization and consequently reduce water flux. Asadollahi and colleagues [55] have recently also reviewed the enhancement of the performance of RO membranes through surface modification. They reported that the fact that membrane fouling has a strong dependence on membrane surface morphology and properties makes surface modification using physical and chemical methods a key tool to address membrane fouling. However, they also observed that surface modification has its demerits too such as the following: (i) it increases the membrane resistance, thus impeding permeation and reducing the water flux and (ii) the stability of surface modifiers during membrane cleaning and long-term operation has not been well studied. A study by Kochkodan and Hilal [56] evaluated the surface modification of polymeric membranes targeting the control of biofouling. The authors reported that generally high membrane hydrophilicity, smooth membrane surface, and the use of bactericidal or charged particles on the membrane surface result in a reduction in membrane biofouling. However, the challenge of developing membranes that can overcome the complexities of biofouling without having adverse effects still remains.

Therefore, understanding the mechanisms of fouling in membranes is paramount to develop the appropriate mitigation strategies. As an example, recently, Tow and colleagues [43] developed a fouling visualization apparatus to elucidate the mechanisms of organic fouling and cleaning in RO and FO processes. They identified one internal fouling mechanism that is unique to FO membranes based on vapor phase formation within the membrane. They further reported that although the use of feed spacers is advantageous in reducing the rate of fouling, it may also obstruct cleaning by preventing pieces of detached gel from flowing downstream.

5. Future perspectives

The performance of the FO process can be improved through its integration with other technologies to take advantage of the unique strengths of the individual processes. As an example, the FO-MD hybrid process has been employed for oily wastewater treatment [21]. The findings indicated that water recovery of greater than 90% was attained even at high salinities and also almost complete rejection of oil and sodium chloride. In another study [57], the FO-MD process was also applied for raw sewage; water recovery of 80% was achieved, and removal efficiency for trace organics was 91–98%. In addition, the use of FO-ED hybrid system for the treatment of secondary municipal wastewater resulted in treated water that met potable water standards (low concentration of TOC, carbonate, and low conductivity) [58]. Another promising hybrid process is the combination of FO and RO (FO-RO). Based on the unique advantages of RO and FO processes, it is important to exploit these to solve the challenges of wastewater remediation and even desalination. For instance, the potential of FO to reduce the

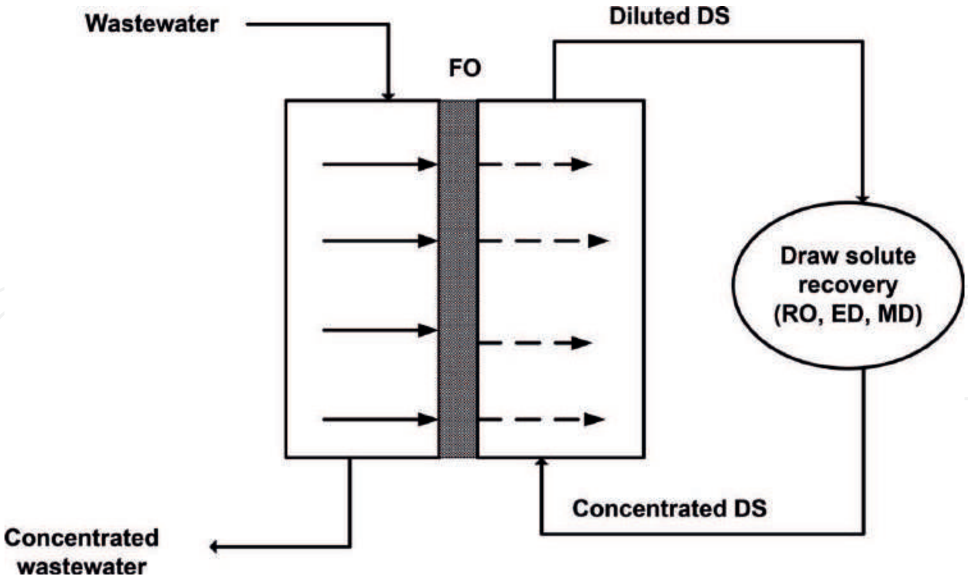

Figure 3. FO-based hybrid technologies (FO-MD, FO-RO, and FO-ED). Adapted from [63].

energy consumption of RO is very important. This can be done using an FO-RO hybrid process in which FO is implemented as a pretreatment step before RO. Furthermore, this FO-RO hybrid has the additional benefit of being a double-barrier protection leading to high-quality treated water [48]. Linares and coworkers [59] have recently shown that hybrid FO-RO systems are economically advantageous compared to other technologies for desalination or even wastewater treatment and recovery systems. Another integrated technology is the coupling of FO and microbial osmotic fuel cell (MOFC), which was performed by Werner and coworkers [60]. The key benefits reported were that the system could simultaneously treat wastewater treatment and desalinate seawater within the same reactor [60]. Furthermore, the integration of FO and conventional MBR can result in reduced energy consumption [61]. A coupled forward osmosis and microbial desalination cell (FO-MDC) was employed to simultaneously treat wastewater and desalinate seawater and the COD removals were satisfactory as well as high levels of desalination were achieved [62]. Therefore, these hybrid systems can greatly improve FO performance and increase its feasibility for commercial application. However, before the integrated processes can be implemented, there is a need for detailed studies on the energy consumption to determine their economic viability [34]. **Figure 3** shows a schematic representation of some of the FO-based hybrid technologies.

6. Conclusions

The review has provided insights into the use of forward osmosis either individually or in combination with other processes for wastewater treatment. Forward osmosis is gaining wide acceptability and application because of its unique advantages such as not requiring hydraulic pressure and less fouling propensity compared to conventional pressure-driven membrane processes. Inasmuch as the literature has indicated that the lack of hydraulic pressure in FO processes alters the extent of membrane fouling; further studies are required especially on how this influences the cleaning strategies to be adopted. Furthermore, it is necessary to develop new FO membranes taking into account the effect of the membranes on fouling and cleaning behavior. It is also imperative to explore the synergy in the use of multiple cleaning strategies such as a combination of osmotic backwashing and surface backwashing to further improve the performance of FO membrane.

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Chapter 12

Membrane Gas Absorption Processes: Applications, Design and Perspectives

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Additional information is available at the end of the chapter

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Abstract

Membrane gas absorption (MGA) is one of the most attractive technologies among the osmotically driven membrane processes because of its configurational advantages with respect to the conventional absorption systems that use packed bed columns for different industrial applications. Nowadays, membrane gas absorption is used in industrial wastewater treatment, CO_2 absorption from greenhouse gases, treatment of flue-gas and off-gas streams, which contain SO_2, H_2S, NH_3 or HCl, upgrading and desulphurization of biogas from anaerobic digesters and landfills and acid gas removal of natural gas and olefin-paraffin separation in the petrochemical industry, among other applications. In this framework, the advantages of membrane gas absorption over packed bed processes are related to the decreasing of installation surface requirements through compact process design and easy operation modes. These aspects will increase the applications of these types of processes in the mid-term. Nevertheless, the main design criteria of this technology have been poorly addressed in the literature. This chapter summarizes the fundamental aspects of transport phenomena that drive these processes, as well as the main conceptual aspects, to propose a correct design through an overview of the current status of this technology and its potential applications, challenges and future trends.

Keywords: membrane gas absorption processes, gas-filled membrane absorption processes

1. Introduction

In a membrane contactor, the separation process integrates the mass transfer with the conventional phase contacting operation. Thus, membrane contactor operations can be designed with the same phenomenological approach of conventional extraction or absorption processes [1].

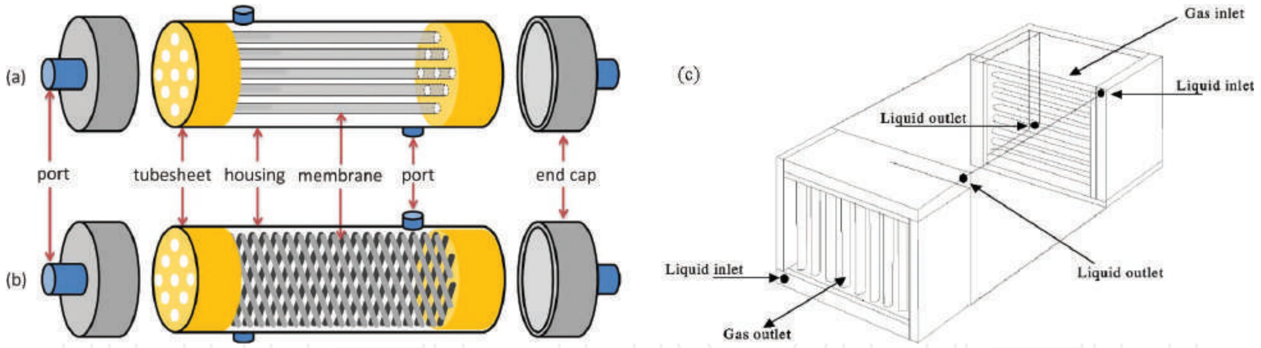

Figure 1. Hollow fiber membrane modules with (a) parallel, (b) crisscross and (c) transversal flow membrane arrangement [1, 2].

One of the most important aspects to be considered in the design of these membrane processes is the maximization of the contact surface area available for the mass transport through an interface, maintaining low pressure drop in the membrane modules. In this way, hollow fiber modules represent the most common geometrical configuration in membrane contactor processes because of their high value of contact surface area per volumetric unit, complemented with a relatively low pressure drop.

As phase contactors, these types of modules are conformed by a bundle of porous hollow fibers, which are arranged in a housing. Thus, one of the phases is circulated into the lumen side; meanwhile, the other phase flows through the shell side. However, the design of a membrane absorber cannot be based on the same hollow fiber modules used in filtration processes, which respond to other design criteria. **Figure 1** shows an outline of three different arrangements of hollow fiber modules [1, 2].

The geometrical arrangements described in **Figure 1** are not exclusive of membrane contactors, and it is used in other membrane processes such as filtration (MF, UF and NF), forward/reverse osmosis (FO, RO) and dialysis [2]. **Figure 1a** and **b** shows conventional arrangements designed from filtration applications. **Figure 1c** shows a transversal flow configuration specially designed for gas-liquid contactor duties [1]. This module involves a rectangular housing where the gas flow is perpendicular to the fibers, and the absorption liquid is circulated though the lumen.

The interface will be stabilized at the entrance of the pores on the lumen or on the shell side depending on the surface interaction between the membrane material and the contacted phases. Hollow fibers can be made in different types of materials such as hydrophobic and hydrophilic polymers [3, 4], ceramics [5] and metals [6]. Currently, hydrophobic membranes are widely used in gas-liquid contacting processes because of their larger contact area than the hydrophilic membranes [7].

2. Theory

Membrane gas absorption (and stripping) process is a gas-liquid contacting operation [8–10]. The core in the membrane gas absorption process is a microporous hollow fiber membrane.

The gas stream is fed along one side of the membrane; at the same time, absorption liquid is flowing at the other side of the membrane [1].

In the membrane absorption process, a hydrophobic or hydrophilic hollow fiber contactor is used to separate a feed solution containing a solute from the receiving gas phase. In the case of the stripping process, the solute to transfer is contained in the gas phase. The hydrophobic or hydrophilic character of the membrane determines the penetration of liquid solution or gas phase into the membrane pores, which are filled with liquid or gas. Thus, solute transfer through the membrane is achieved according to the following sequence of steps, which are presented in **Figure 2**:

1. Solute transfer through a boundary layer of gas phase at the membrane surface;
2. Solute gas transfer through the air gap that fills the pores;
3. Phase equilibrium between the feed solution at the membrane surface and the gas phase retained in the membrane pores for a hydrophobic membrane;
4. Mass transport of absorbed solute into the bulk receiving liquid phase.

For the stripping process, the solute will be transferred from the gas phase into the liquid phase. Moreover, two modes of operation are possible in gas/liquid contactors, according to the application: wetted mode and dry (or non-wetted) mode. Wetted mode occurs when the pores are filled with liquid, for example, if the liquid phase is aqueous and a hydrophilic membrane is used. Conversely, a hydrophobic membrane would operate in the dry mode in this case because the pores would be filled with gas. Dry mode is usually preferred in order to take advantage of the higher diffusivity in the gas; however, the wetted mode may be preferred if there is a fast or instantaneous liquid phase reaction; as a result, the gas phase resistance controls [10].

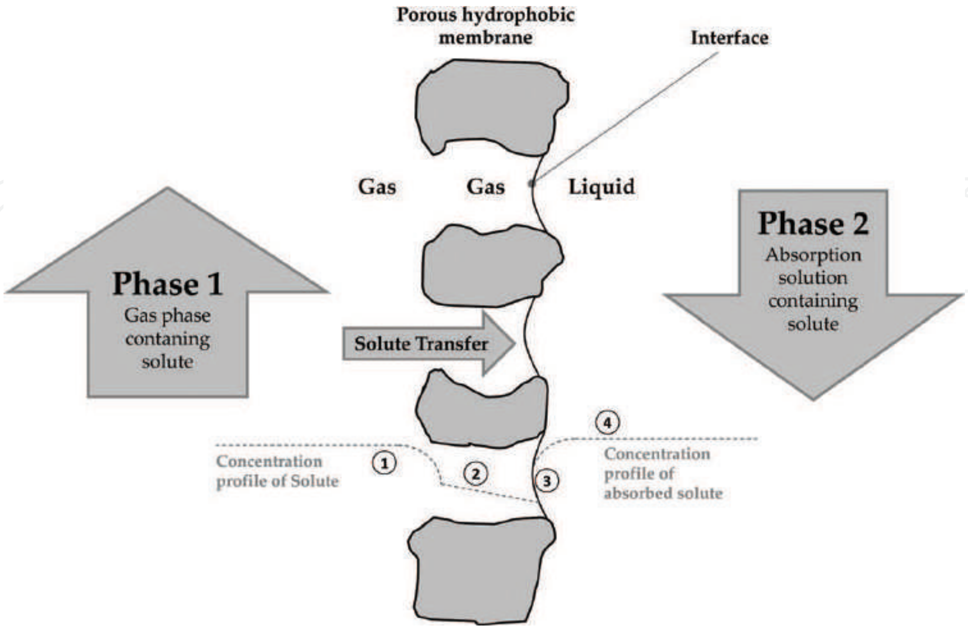

Figure 2. Outline of the membrane absorption process in a hydrophobic membrane.

This transfer of solute in the membrane absorption process can be described by means of a model based on a resistances-in-series approach applied on the proximities of the membrane [10, 11]. The overall solute transfer through the porous membrane can be described by the following equation.

$$N_i = KA\Delta C^i_{ml} \tag{1}$$

where N_i is the flux of solute transferred from the gas phase to the absorption phase, K is the overall mass transfer coefficient, A is the surface area available for mass transfer and $\Delta C_{ml}{}^{i}$ is the logarithmic mean driving force in the absorption phase expressed by:

$$\Delta C^i_{ml} = \frac{\left(C^i_L - C^{i*}_L\right)_1 - \left(C^i_L - C^{i*}_L\right)_2}{\ln\left[\frac{\left(C^i_L - C^{i*}_L\right)_1}{\left(C^i_L - C^{i*}_L\right)_2}\right]} \tag{2}$$

$C_L{}^{i*}$ represents the pseudo-equilibrium concentration of solute in the absorption solution phase, which can be estimated by the following distribution equation:

$$C^{i*}_L = C_L \frac{y_i}{m_i} \tag{3}$$

In Eq. (3), C_L is the total concentration of the liquid phase and m_i is the partition constant (H_i/P) in mol of solute in the gas phase per mol of solute in the liquid phase, which represents the liquid feed-gas equilibrium that could be described by Henry's law for each solute transferred [11] as follows:

$$Py_i = H_i \ x_i \tag{4}$$

here, P is the total pressure, y_i is the mol fraction of solute in the gas phase, x_i is the mol fraction of solute in the liquid phase and H_i is the Henry's constant of solute i. The overall mass transfer coefficient can be represented as a global resistance, which involves the contribution of individual mass transfer steps [10, 12, 13]. Thus, the overall mass transfer coefficient K can be estimated by means of a resistances-in-series approach applied in the proximities of the membrane according to the following equation:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{d_{in}}{m_i k_m d_{ml}} + \frac{d_{in}}{m_i k_G d_{out}} \tag{5}$$

For the driving force based on liquid phase and the gas phase flowing by the shell side and liquid phase by the lumen side. In the case of hydrophilic membranes, the overall mass transfer can be expressed by:

$$\frac{1}{K} = \frac{d_{out}}{k_L d_{in}} + \frac{d_{out}}{k_m d_{ml}} + \frac{1}{m_i k_G} \tag{6}$$

where k_L is the local mass transfer coefficient in the boundary layer of the liquid phase, k_m is the local mass transfer coefficient through the phase in the membrane pores, k_G is the local mass transfer coefficient in the boundary layer of the gas phase, d_{in} is the internal diameter of the fiber, d_{out} is the external diameter of the fiber and d_{ml} is the mean logarithmic diameter of the fiber. The resistances-in-series model is based on one-phase diffusion (i.e., liquid phase) with the assumption the overall mass transfer resistance only occurs in the liquid phase. This assumption is valid since the estimation of the mass transfer resistance in the absorption phase is lower than 4%, using the Hatta method [14]. The local mass transfer coefficient at both sides of the membrane (lumen and shell sides) can be estimated by means of a specific correlation [12, 15], which considers the geometry and the dimensionless Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers of the system. The correlation of mass transfer coefficient of each boundary layer depends on the circulation configuration of the phase in the membrane contactor. **Table 1** shows a summary for different correlations published in the literature.

On the other hand, inside the membrane pores, the local mass transfer coefficient for the retained phase can be described by molecular diffusion [18] according to the low estimated value of the dimensionless Knudsen number [21], close to 0.002. Thus, the local mass transfer coefficient in the gas pores can be estimated as follows:

$$k_m = \frac{D_{AB}\varepsilon}{\tau e} \tag{7}$$

Here, D_{AB} is the diffusion coefficient of the solute A in the phase B, which fills the membrane pores, ε is the porosity of the fibers, τ is the tortuosity of the fibers and e is the fibers thickness. The physical properties of this system, such as diffusion coefficients, viscosity and density of both phases must be established by using different theoretical or empirical relationships as function of system properties (absolute pressure, temperature and composition).

Correlation	Configuration	Observation	Reference	Eq. N°
$Sh = \alpha\left(\frac{d_{in}}{L}\mathrm{Re}Sc\right)^{0.33}$	Lumen side	The value of coefficient α can be 1.86, 1.64 (empirical) or 1.62 (theoretical). Characteristic length is d_{in}.	[16]	(7)
$Sh = 1.25\left(\frac{d_h}{L}\mathrm{Re}\right)^{0.93}Sc^{0.33}$	Shell side, parallel flow	$0 < \mathrm{Re} < 500$; $0.03 < \phi < 0.26$ Characteristic length is d_h.	[16]	(8)
$Sh = 0.022\mathrm{Re}^{0.6}Sc^{0.33}$	Shell side, parallel flow	Characteristic length is d_h.	[17]	(9)
$Sh = \beta(1-\varphi)\left(\frac{d_h}{L}\right)\mathrm{Re}^{0.6}Sc^{0.33}$	Shell side, parallel flow	β = 5.85 for hydrophobic membranes and 6.1 for hydrophilic membranes. $0 < \mathrm{Re} < 500$; $0.04 < \phi < 0.4$ Characteristic length is d_h	[18]	(10)
$Sh = 17.4(1-\varphi)\left(\frac{d_h}{L}\right)\mathrm{Re}^{0.6}Sc^{0.33}$	Shell side, parallel flow	$0 < \mathrm{Re} < 100$; $0.25 < \phi < 0.48$ Characteristic length is d_h	[19, 20]	(11)
$Sh = 0.9\mathrm{Re}^{0.4}Sc^{0.33}$	Shell side, cross flow	$1 < \mathrm{Re} < 25$; $\phi = 0.03$ Characteristic length is d_{out}	[16]	(12)

Note: d_h is the hydraulic diameter (4*[flow surface area]/[wetted perimeter]). Φ is the fiber packing fraction.

Table 1. Mass transfer correlations for local coefficients in different membrane module configurations.

3. Comparison between MGA and conventional packed columns

Mass transfer equipment can be sized as a relation between the number of transfer units (NTU) and the height (or length) of transfer units (HTU). The NTU value is determined by operational parameters such as stream flow rates, solutes concentration and equilibrium constant value of solutes, while HTU is defined by the equipment characteristics such as mass transfer area, stream velocities and mass transfer coefficients values. Thus, the height or length of a mass transfer equipment can be estimated as follows [13].

$$Z = HTU \cdot NTU \tag{8}$$

In terms of comparing the conventional packed columns and hollow fiber membrane contactors, the main difference of sizing will be HTU value, since this parameter depends on equipment dimensions and hydrodynamic characteristics. The HTU parameter can be estimated as shown in the following Eq. [22].

$$HTU = \frac{v}{Ka} \tag{9}$$

where v is the velocity of the stream flow rate and a is the specific transfer area (mass transfer area per equipment volume, m^2/m^3). Different studies have been conducted to compare *Ka* values for conventional mass transfer equipment and membrane modules applied to different absorption applications.

Table 2 shows that the *Ka* values for membrane modules can be 10 times higher than *Ka* values observed in conventional packed towers. Furthermore, the gas and liquid streams are independent in the membrane module; therefore, the gas flow can be increased without changing the liquid flow and vice versa. These altered flows will not cause flooding, as they might in a packed tower [8].

Application	*Ka* value for membrane module	*Ka* value for conventional absorption packed tower	Reference
Absorption of SO_2 in water from air	$0.10–0.13\ s^{-1}$	$0.01–0.04\ s^{-1}$	[22]
Absorption of CO_2 in water from air	$0.12–0.25\ s^{-1}$	$0.01–0.18\ s^{-1}$	[22]
Absorption of CO_2 in monoethanolamine aqueous solution from air	$1.3–4.0$ kmol/(m^3hkPa)	$1.1–1.2$ kmol/(m^3hkPa)	[23]
Absorption of CO_2 from flue gas	$4.3\ s^{-1}$	$0.47\ s^{-1}$	[1]
Absorption of CO_2 in monoethanolamine aqueous solution from flue gas	$8.93 \times 10^{-4}–7.53 \times 10^{-3}$ mol/(m^3sPa)	2.25×10^{-4} mol/(m^3sPa)	[24]
Absorption of CO_2 in diethanolamine aqueous solution from air	$0.126–0.43\ s^{-1}$	$0.05\ s^{-1}$	[25]

Table 2. Comparison of *Ka* values between MGA modules and conventional absorption equipment.

4. MGA applications

There is a large body of literature on membrane absorption because this process can be applied to the same cases of most gas absorption processes with conventional dispersive contactors such as packed columns or spray towers. Thus, the use of membrane absorption can be justified when the use of membrane contactor modules involves clear operational and economic advantages over conventional dispersive contactors [1]. In some cases, this suitability is related to the treatment of smaller volume of gases.

Among the most studied cases are the absorption of CO_2 and its recovery from flue-, bio-, and off gases, the removal of SO_2, CO, H_2S, NH_3, HCN, HCl and VOCs from different streams, the upgrading and desulfurization of biogas produced from anaerobic digesters and landfills, the removal of acid gas from fuel gas mixtures and natural gas, the removal of mercury from natural gas, flue gas and glycol overheads, the separation of olefin-paraffin in petrochemical industry and the removal of specific compounds in indoor air [1, 4].

In the following sections, a summarized description of the main applications is presented in order to show the broad range of cases using different absorbents.

4.1. Absorption of CO_2 from flue gas

Nowadays, the reduction of greenhouse gases is probably the main challenge for scientists and engineers facing the unprecedented increase in the concentrations of these compounds, mainly represented by CO_2. In this framework, the absorption of CO_2 from flue gas becomes the most studied application of membrane gas absorption (MGA) processes because this process seems to be a promising alternative to the conventional dispersive absorption systems.

In this application, the selection of the membrane material represents a key parameter for the successful implementation of the process. Currently, typical membranes for gas–liquid contacting processes are prepared from polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluorethylene (PTFE) and polysulfone (PS). Among these materials, PTFE shows high hydrophobicity, good mechanical properties and high chemical stability [7, 26]. Different geometrical configurations of membrane contactors have been tested and reported in the literature [7, 27]. The performance of the CO_2 absorption will be more or less affected by the flow mode depending on the contactor geometry and the operation conditions. However, there are some issues that have to be taken into account in this application, when the gas mixture flows inside the lumen, because membrane pores can be plugged by the impurities present in the flue gas [28]. Thus, in the majority of studies, the absorbent flows inside the fibers and the flue gas stream flows in the shell side [7].

On the other hand, the major advancement in the CO_2 absorption has been carried out in the search of more efficient absorber solutions. Thereby, the main aspects that are to be taken into account in the selection of the absorber involve the nature of the process (physical or chemical) and its properties such as the regeneration capacity, viscosity, surface tension and its compatibility with the membrane material. The most commonly used absorber in membrane gas absorption of CO_2 is monoethanolamine (MEA), but there is a wide variety of absorbers such as amine solutions, alcohol-amine solutions as well as their blends [7], and more recently, other compounds such as ionic liquids [29]; the finding of a suitable CO_2 absorber has to match all these aspects. For the most common single absorbents, the CO_2 absorption performance order is NaOH > tetraethylenepentamine (TEPA) > triethylenetetramine (TETA) > diethylenetriamine (DETA) > amino acid potassium (GLY) > monoethanolamine (MEA) > diethanolamine (DEA) > diisopropanolamine (DIPA) > 2-amino-2-methylpropanol (AMP) > triethanolamine (TEA) > methyldiethanolamine (MDEA) > K_2CO_3. Meanwhile, the regeneration performance order is TEA > MDEA > DEA > AMP > DIPA > MEA > NaOH [7].

Recent studies [29, 30] involve the use of ionic liquids as absorbers in membrane absorption systems. Ionic liquids are salts that remain in liquid phase at temperatures lower than 100°C. These compounds are constituted by a relatively large organic cation and a smaller inorganic or organic anion, and they are considered a novel class of 'designer solvents', which show unique properties. Among these properties, their ionic nature and negligible vapor pressure are probably the most particular characteristics. These compounds, mainly based on imidazolium, ammonium, phosphonium, pyridinium, and pyrrolidinium cations, are being used as solvents, electrolytes and reaction media in different chemical processes. Ionic liquids have been studied for use as good gas absorbers [31], particularly of CO_2 [32]. 1-Butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF_4]) and 1-(3-aminopropyl)-3-methyl-imidazolium tetrafluoroborate ([apmim][BF_4]) have been tested as absorbers of CO_2 in a membrane absorption system [29]. A much higher absorption was obtained with [apmim][BF4], but this ionic liquid was difficult to be regenerated under vacuum. Meanwhile, the less effective [bmim][BF_4] could be completely regenerated. More recent studies [30] involve the tests of membrane absorption using an amino acid-functionalized protic ionic liquid (monoethanolamine glycinate or [MEA][GLY]), which could be a potential substitute for the conventional chemical absorbent. Nevertheless, further research is necessary to find task-specific ionic liquids with lower viscosities and good absorption and regeneration capacities.

4.2. Removal of SO_2

The removal of SO_2 from gas streams was another pioneering application of hollow fiber absorption systems [22]. One of the first membrane absorption experiments using hollow fiber contactors for the simultaneous absorption of SO_2 and CO_2 considered the use of solutions of Na_2SO_3 [33]. The removal of SO_2 from flue gas has been intensively studied using different types of absorbers such as aqueous solutions of Na_2SO_3, Na_2CO_3, $NaHCO_3$ and NaOH [4]. Thus, different well-known chemical reactions can be considered depending on the absorber selected:

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O \tag{10}$$

$$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2 \tag{11}$$

$$SO_2 + 2NaHCO_3 \rightarrow Na_2SO_3 + H_2O + 2CO_2 \tag{12}$$

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3 \tag{13}$$

From these four chemical reactions, Park et al. [4] report that an aqueous solution of Na_2CO_3 proved to be the most efficient absorber when the feed SO_2 concentration was 400 ppm.

One of these alternatives is the dual alkali process [1], which involves the production of sodium bisulfite that can be reused on site. This process can be described by means of the reactions 19 and 20 that explain the absorption and regeneration step, respectively:

$$2NaHSO_3 + Na_2CO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2 \tag{14}$$

Klaassen et al. [1] described pilot-scale experiments in a potato starch production plant of AVEBE (the Netherlands) where the combustion of H_2S containing biogas in a steam boiler results in flue gas containing SO_2. Thus, sulfur dioxide was recovered as bisulfite from the flue gas and it can be reused in the starch production process according to the description given in **Figure 3**.

This installation was successfully tested with as capacity of 120 m^3/h obtaining a SO_2 recovery of over 95% for two production sessions of 6 months each. Problems related to the variation in the gas flow rate, changes in the SO_2 concentration or membrane fouling were not observed.

4.3. Absorption of CO

The absorption of CO from N_2-CO mixtures has been reported in the literature [34] using a hollow fiber module containing porous polypropylene fibers (Celgard X-20) and an ammoniacal cuprous chloride solution as receiving phase. Thus, the preferential absorption of carbon monoxide can be driven by the following reaction:

$$CO + CuCl \overset{NH_4Cl}{\Longleftrightarrow} \left[Cu(NH_4Cl)_3CO\right]^+ Cl^- \tag{15}$$

This process shows a very high selectivity and the permeation rate seems to be controlled by the mass transfer in the liquid phase at moderate liquid flow rates and by the chemical reaction

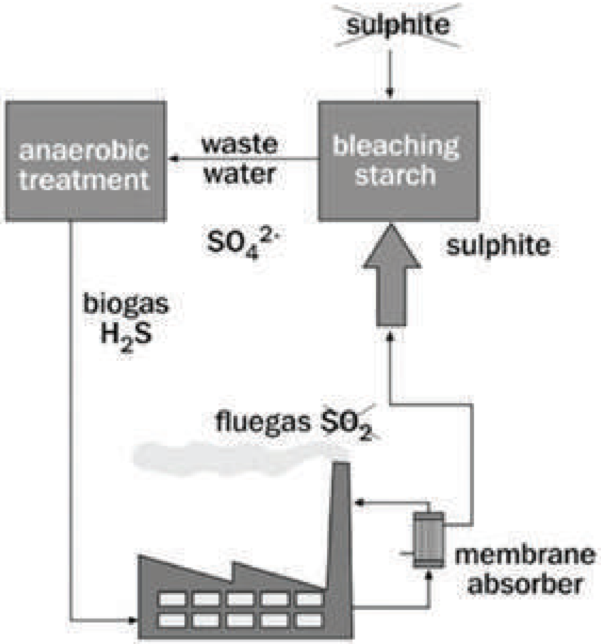

Figure 3. Scheme of the membrane gas absorption process for SO_2 removal and reuse [1].

at higher liquid flow rates. The selected polypropylene membranes seem to show a good chemical resistance to the solutes present in the absorption solution.

4.4. Elimination of H_2S

One of the major impurities of natural gas, refinery gas and coal gas is the hydrogen sulfide (H_2S) contained. Furthermore, it is an important indoor and outdoor air contaminant. This compound is toxic and corrosive and one of the main sources of acid rain [3]. Furthermore, this gas can be produced by sulfate-reducing bacteria under anaerobic conditions contributing to foul odors.

The most common processes to remove H_2S from gas streams are the gas absorption systems using water or different types of aqueous solutions such as sodium hydroxide, sodium carbonate [3], monoethanolamine (MEA) or diethaloamine [35] and ferric solutions of ethylenediaminetriacetic acid (EDTA) and hydroxyethylethylenediaminetriacetic acid (HEDTA) [36] and, more recently, ionic liquids [37].

The use of asymmetric hollow fiber membrane modules for absorption of H_2S has been studied by Li et al. [3], who tested two different hollow fiber membrane modules prepared from polysulfone or polyethersulfone hollow fibers with an outer edge thin layer and a 10% NaOH solution as absorbent. In this system, the presence of the membrane involves a significant increase of mass transfer resistance and the H_2S transfer could be increased if the structural membrane properties, such as porosity, are improved.

On the other hand, a further application considers the removal of H_2S from air using demineralized water (pH 7) for odor control [38]. Porous polypropylene hollow fiber modules with different geometrical parameters were used in this application obtaining 89% of removal for inlet concentrations of 100 ppmv when the gas stream was circulated through the lumen and the water through the shell of the membrane contactor. Fluid dynamic and geometrical aspects have to be considered to operate under the optimal conditions.

4.5. Removal of Hg from industrial gas streams

The removal of Hg from gas streams has also been analyzed using different types of hollow fiber membranes in transversal and shell-tube configurations and several oxidizing liquid solutions [39]. Mercury can be present in the atmosphere due to several industrial activities such as incineration of industrial and domestic waste and natural gas production, and its removal from gaseous streams can be complex because of its low concentration, which is common in the sub-ppm range. Thus, this application requires high gas/liquid flow ratio, and the liquid stream can be suitably circulated through the lumen of the hollow fibers.

Some oxidizing liquids tested to capture Hg from gas streams are H_2O_2/H_2SO_4, $K_2Cr_2O_7$, $K_2S_2O_8$, $Na_2S_2O_8$ + $AgNO_3$ as a catalyst, $KMnO_4$, NaClOx (saturated) and Cl_2 gas [39]. This oxidative membrane absorption process needs chemically resistant hollow fibers, and polytetrafluoroethylene (PTFE) seems to be the suitable membrane material because it shows stable behavior in contact with the oxidizing solutions [39].

4.6. Other applications

Other applications consider the use of a variant of the membrane absorption system called gas-filled membrane absorption. This configuration process is explained in detail in Section 6 and couples the stripping and absorption steps in a single membrane contactor. Thus, a compact design can be proposed, and the gas phase is confined into the membrane pores as an effective supported gas membrane. This system has been studied for the removal of NH_3 from wastewaters and aqueous streams [40], the extraction of SO_2 during the sulfite quantification in wines [41] and the elimination of HCN from pharmaceutical wastewaters [42], plating waters or its recovery from cyanidation solutions in the mining industry [11, 43]. **Figure 4** summarizes the treated and receiving streams in each one of these applications as well as the circulation configuration used in the abovementioned studies.

These three different applications of the GFMA process can involve the recovery of the specie transferred through the membrane and captured in the absorber phase. Thus, the NH_3 removal involves the saturation of the solute $(NH_4)_2SO_4$ or $(NH_4)Cl$ formed in the receiving solution to recover it as by-products. The SO_2 removal from wine involves the indirect quantification of the sulfite content in the absorber, and the elimination of HCN from a cyanidation solution involves the recovery of cyanide from the basic absorber to be reused in the same process.

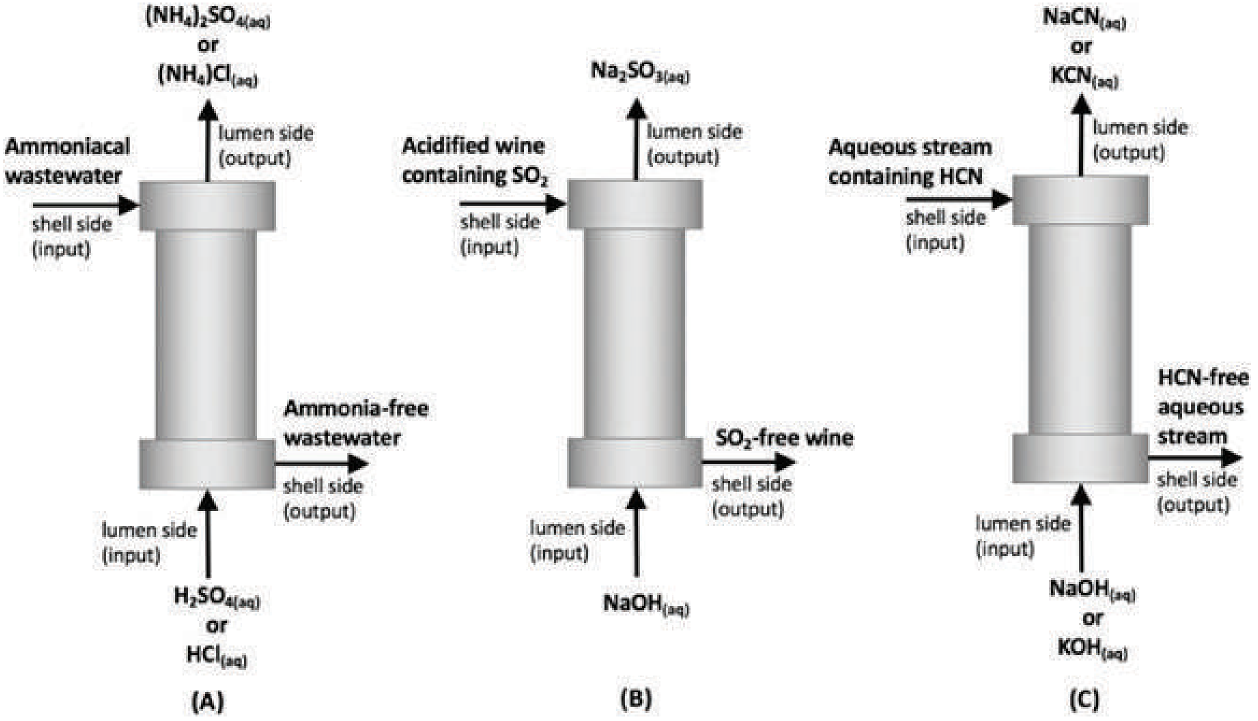

Figure 4. Outline of the input and output streams in GFMA processes for (a) NH_3 removal from wastewater [40], (b) absorption of SO_2 from wine samples [41] and (c) HCN recovery from cyanidation solutions [11].

5. Aspects of design

The design of a membrane gas absorption process is mainly focused on the mass transfer area required to ensure the absorption efficiency established. This area must be estimated by Eq. (1) according to the solute transferred from the gas phase into the liquid phase (N_i), which is defined by the mass balance (operational equation) in the process. In this context, the total area will be defined by the operational conditions (solute concentrations) and the mass transfer coefficient. When experimental results determine the absorption time, the total area required to transfer a solute flow can be estimated using Eq. (1). However, there are current limitations with respect to the modules size available, where the LiquiCel Extra Flow with center baffle module has the largest size, capable of treating a maximum liquid flow rate of 125 m^3/h, having a total transfer area of 373 m^2 [44]. In cases of large absorption times, the total area required could increase over the unitary area specified for one module forced to include an arrangement of hollow fiber membrane contactors modules in series and parallel configuration. In this scenario, one of the first analyses of the optimum hollow fiber membrane contactor arrangement was performed by Prasad and Sirkar [45], who estimated the number of membrane modules needed to treat 2 L/s of feed flow rate of an aqueous solution containing 4-cyanothiazole, which is treated with benzene to recover 98.3% of solute. For this purpose, the researchers proposed an arrangement using a LiquiCel hollow fiber membrane contactor module of 61 × 5.08 cm, 11,000 fibers and 4.6 m^2 of transfer area. Different arrangement of in series-parallel configuration was assessed in order to obtain a minimum number of total membrane modules needed to achieve the extraction efficiency of 4-cyanothiazole. Thus, the arrangement that determined the minimum number of membrane modules was 15 modules in series with 5 parallel configurations giving a total amount of membrane modules equal to 75. Nevertheless, the expected total pressure drop for each parallel configuration (containing 15 in series modules) was estimated on 3684 kPa; instead an arrangement of 5 in series modules with 34 parallel configuration minimizes the pressure drop (144 kPa), ensuring the 4-cyanothiazole extraction, although the total membranes modules required are 136. Hence, a conclusion of this study is that the optimum arrangement depends on a technical and economic analysis, considering the energy consumption determined by the pressure drop and the capital cost based on the total membrane modules defined.

Even though the arrangement analysis performed by Prasad and Sirkar [45] includes the pressure drop as a main parameter for design purposes, this study did not take into account the maximum permissible pressure by membrane module, having typical values around of 7.0 bar (700 kPa) at ambient temperature. In this regard, the first arrangement proposed by Prasad and Sirkar [45] involves to feed in the first membrane module of each parallel configuration at feed pressure of around 35 bar. This value is much higher than the maximum permissible pressure specified by commercial hollow fiber membrane contactors modules. This limitation of membrane contactors modules was included in a design analysis for a hydrogen cyanide recovery process using a gas-filled membrane absorption process (GFMA) [43]. In this study, the optimum configuration estimated was 39 hollow fiber membrane contactors [44] in-series to treat 60 m^3/h of cyanide solution to reach 90% of cyanide extraction. According to the maximum permissible feed pressure for membrane module (720 kPa) and the drop pressure for each membrane module

(27.58 kPa), the maximum stages of membrane modules-in-series were 16, forcing the inclusion of intermediate pumping stages. Therefore, the maximum permissible pressure for feed solution limits the total stages of membrane modules in-series, increasing the auxiliary equipment for an industrial plant design. In this scenario, the industrial modules available could limit the application of a membrane gas absorption process, especially for high flow rate requirements.

Summing up, the industrial design for a membrane gas absorption process must include an analysis of the optimum arrangement of in-series modules in parallel configuration, considering the pressure drop for each in-series circuit, the total membrane modules and the maximum permissible feed pressure for each module.

6. Gas-filled membrane absorption

The gas-filled membrane absorption process has been developed to perform the absorption and stripping stages in only one step of hollow fiber membrane contactor [28]. In this process, a hydrophobic hollow fiber contactor is used to separate a feed solution containing a volatile solute (stripping phase) from the receiving phase of absorption solution. The hydrophobic character of the membrane avoids the penetration of aqueous solutions into the membrane pores, which are filled with air. Thus, solute transfer through the membrane is achieved according to the following sequence of steps, which are presented in **Figure 5**:

1. Solute transfer through a boundary layer of feed solution to be treated at the membrane surface;
2. Phase equilibrium between the feed solution at the membrane surface and the gas phase (air) retained in the membrane pores;
3. Solute gas transfer through the air gap that fills the pores;
4. Phase equilibrium between the gas filling the pores and the receiving absorption solution at the membrane surface. In this step, the solute can be absorbed or can react into a new product;
5. Mass transport of absorbed solute into the bulk receiving solution.

The GFMA process has been applied to extract or recover solutes of interest, such as ammonia from wastewater [40, 46], SO_2 from wine [41, 47] and HCN from different wastewaters [11], [42, 48, 49]. These studies have shown high recoveries of volatile solutes (>90%), producing a concentrate product in the absorption solution. Moreover, a technical and economic study was carried out, comparing the GFMA process to recover HCN in gold mining and the conventional process, which uses stripping and absorption stage, separately, in packed towers [43]. This study estimated operational and capital cost reduction at about 10 and 20%, respectively, for the GFMA process, due to the saving on energy consumption (pumping vs. air blow in the towers) and footprint reduction.

Therefore, the GFMA process is an intensified membrane gas absorption process, which is capable of performing stripping and absorption stages in a single step. It is worth mentioning

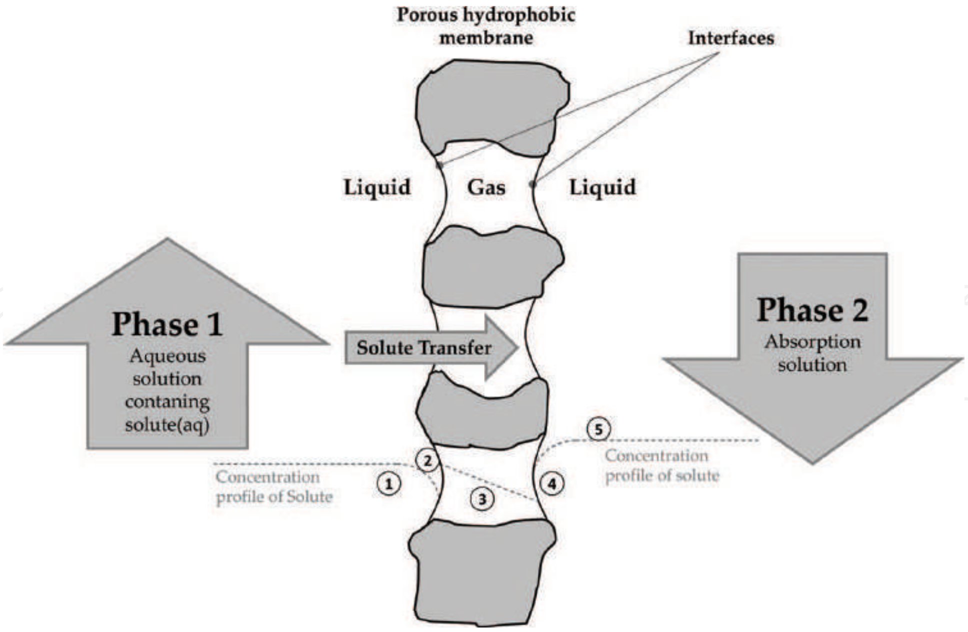

Figure 5. Scheme of the gas-filled membrane absorption process, which shows two gas-liquid interfaces at the pore entrances.

that the design aspects of a GFMA process are similar to the membrane gas absorption process commented upon earlier, taking into account the differences in physical properties on each phase.

7. Challenges and future trends

In this chapter, the most common applications of gas membrane absorption processes are described. Nowadays, these operations are applied in a wide range of fields and can be related to relevant environmental, technical and economic challenges. Nevertheless, the processes under study are currently using modules, which were originally designed for other purposes. Thus, the newest tools for industrial design such as 3D printing, the use of novel materials for membrane preparation and module fabrication, such as specific polymers or their blends, and the use of other absorbers, such as ionic liquids, could enhance the design of further operations according to the precepts of the process intensification; this would allow the design of safer, cleaner and cheaper operations, which are implemented in more efficient and compact units.

On the other hand, the well-known specific surface area into the membrane modules may enhance some procedures and processes at laboratory scale that need high reproducibility, such as analytical techniques [41] or the preparation of specific materials [50].

There is a broad spectrum of new applications, such as biorefineries or the production of bio-based materials that could require a major development of the membrane absorption processes as efficient separation techniques.

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