

Forward Osmosis

Original

Forward Osmosis / Camilleri-Rumbau, Maria Salud; Nguyen, Xuan Tung; Sanahuja-Embuena, Victoria; Frauholz, Jan; Yangali Quintanilla, Victor Augusto; Tiraferri, Alberto; Petrinic, Irena; Helix-Nielsen, Claus - In: Experimental Methods for Membrane Applications in Desalination and Water Treatment / Salinas-Rodríguez S. G., Villacorte L. O.. - ELETTRONICO. - London : IWA Publishing, 2024. - ISBN 9781789062977. - pp. 71-96 [10.2166/9781789062977_0071]

Availability:

This version is available at: 11583/2984827 since: 2024-01-04T08:33:28Z

Publisher:

IWA Publishing

Published

DOI:10.2166/9781789062977_0071

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Chapter 4

Forward Osmosis

Maria Salud Camilleri-Rumbau, Aquaporin, Denmark/Eurecat, Spain

Xuan Tung Nguyen, Aquaporin, Singapore

Victoria Sanahuja-Embuena, Aquaporin, Denmark

Jan Frauholz, Aquaporin, Denmark/RWTH Aachen, Germany

Victor Augusto Yangali Quintanilla, Grundfos, Denmark

Alberto Tiraferri, Politecnico di Torino, Italy

Irena Petrinic, University of Maribor, Slovenia

Claus Hélix-Nielsen, Technical University of Denmark, Denmark

The learning objectives of this chapter are the following:

- To define principles of forward osmosis
- To define and apply forward osmosis parameters for assessing performance
- To present and discuss the basic equations governing forward osmosis performance using typical experimental modes
- To understand the theoretical background of forward osmosis performance and performance prediction using modeling tools.

4.1 INTRODUCTION: PRINCIPLES OF FORWARD OSMOSIS

Forward osmosis (FO) is an osmotically driven membrane technique which allows the separation of water from a feed solution through a semi-permeable membrane using osmotic pressure gradient as a driving force. Although during the last decade there have

© 2024 The Authors. This is an Open Access book chapter distributed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (CC BY-NC-ND 4.0), (<https://creativecommons.org/licenses/by-nc-nd/4.0/>). The chapter is from the book *Experimental Methods for Membrane Applications in Desalination and Water Treatment*, Sergio G. Salinas-Rodriguez, Loreen O. Villacorte (Eds).

Experimental Methods for Membrane Applications

been important advances in FO in terms of material development and processes, the few commercially available products and best practices for effluent processing makes the standardization of the FO applicability challenging.

In terms of materials used for fabrication of FO membranes, cellulose acetate (CTA) membranes and thin film composite (TFC) polyamide (PA) membranes are the most widely known, both being commercially available (Xiao *et al.*, 2017). New approaches using new materials for FO purposes have also been developed. To name a few, these are double-skinned membranes, membranes obtained by layer-by-layer techniques, mixed organic-inorganic membranes and aquaporin-based membranes, which consist of TFC PA with embedded aquaporins (Suwaileh *et al.*, 2020).

Despite FO being a developing technology, in the recent years, there has been an increasing interest for its use in industry. This opens countless opportunities for further developing membrane configurations that can be used in an industrial setting. In terms of applications, FO is a versatile membrane technique with a broad applicability spectrum within the water treatment sector (desalination, municipal wastewater, industrial wastewater, potable and non-potable water reuse, etc.), the management of process water (biorefineries, pharmaceutical processes, etc.) and food and beverage processes (concentration of flavours and aromas, juices, etc.).

Regarding membrane performance, FO relies on the osmotic pressure of the two solutions separated by the semi-permeable membrane. The pass of water is allowed due to osmotic gradient resulting in a concentrating process for the lower osmotic pressure solution (known as feed) and a dilution process for the higher osmotic pressure solution (known as draw solution). As for any other membrane-based process, water flux (J_w) and forward solute rejection (R) can be obtained from experimental data (see section 4.3.1); while a parameter known as reverse solute flux (J_s), unique for FO, allows to track the loss of draw solute into the feed solution.

During FO processing, concentration polarization can severely affect membrane performance in both feed and draw sides of the membrane. Both external concentration polarization (ECP) at the feed side of the membrane as well as internal concentration polarization (ICP) at the draw side of the membrane, play a detrimental role that cannot be overlooked when interpreting the FO process performance and when evaluating its applicability (see section 4.3.2. for more details). Concentration polarization can act in combination with fouling, scaling and/or a combination of both fouling mechanisms, to decrease the net driving force available for mass transport.

With this Chapter, the authors have put together the most relevant experimental practices in the FO field in order to guide researchers and engineers towards getting hands-on experiences in FO.

4.2 MATERIALS AND EXPERIMENTAL SET-UP

4.2.1 Membrane configurations

Membranes for FO processes and generally for liquid-liquid separations, can be found commercially either as flat-sheets or hollow tubes. The modules of these can be classified, similarly as done for other membrane processes, in four module types: plate-and-frame, spiral-wound, hollow fiber and tubular. The first two types are made of flat-sheet membranes, while the last two types are composed of hollow tube membranes.

Plate-and-frame modules are the simplest module configuration where membrane sheets are mounted in frames closely together. The feed solution to be treated passes alongside the sheets surface and it gets collected at the end as a concentrated retentate, while the permeate is collected in its own channel. Spiral-wound are membrane sheets rolled in alternating order together with turbulence promoting plastic grids, called spacers. The feed solution is introduced at one end of the module and flows axially on the active layer and feed spacer side of the membrane. The permeate is collected in the envelope and led to the permeate channel which is centrally located. Hollow fiber modules consist oppositely of tubes, packed closely together and placed inside a vessel. Here, the feed solution passes through the lumen of the hollow fiber, permeates through the membrane towards the shell side and exits the module. When their inner diameter rises to 5 mm or above, and the module packing density significantly decreases, the module is known as a tubular module.

There are intrinsic advantages and disadvantages of using each module configuration and their usage would depend on the intended process application. For example, plate-and-frame and tubular configurations are usually used with extremely high-particulate streams and/or high-viscosity solutions. The simplicity of the plate-and-frame configuration allows for high cross-flow velocities, reducing fouling by increasing longitudinal shear stress. Additionally, these membranes can be easily cleaned which increases the lifetime of the membrane. However, this module type is expensive to manufacture, and the packing density is low, which increases the membrane installation footprint considerably. Similarly, tubular modules can be more tolerant to fouling and clogging due to the large inner diameter of their hollow tube and the possibility of operating at high cross-flow velocities. However, it suffers from the same disadvantages as its counterpart, the plate-and-frame module due to a low packing density. Spiral-wound and hollow fiber configurations are thus the most commonly used module configurations for membrane-based liquid-liquid separation and FO processes, as they can cover a broad range of applications by balancing effectiveness and price.

4.2.2 Experimental modes

In general, there are three main experimental modes, regardless of process configuration being single-stage or multi-stage, that can be defined when working with FO membrane processes:

- Single pass mode
- Batch-batch mode
- Semi-batch mode

Experimental Methods for Membrane Applications

The main differences between these operational modes are related to how the feed and draw solutions are being processed within the membrane module. For example, in single pass mode, the feed and draw solutions enter the module and have a unidirectional contact area across the membrane, where the solutions are not recirculated. The feed recovery or concentration is achieved in one pass. Oppositely, in batch mode, both feed and draw solutions are recirculated to their respective holding tanks. This means that the feed solution gets increasingly concentrated in the feed tank, while the draw solution gets diluted with time. During semi-batch mode operations, one of the two solutions, either feed or draw solutions, are run in a batch mode while the other solution runs in single pass mode. Typically, the feed will run in a batch mode, allowing for continuous concentration during processing, while the draw solution will run in single pass to minimize loss in FO performance due to dilution of the draw solution.

The advantages of the operational modes above depend on the type of feed, on the process that needs to be undertaken, and on the objective of the FO system. For instance, during food valuable concentration processes, a semi-batch mode will be preferred, while a batch-batch mode might be preferred during concentration of secondary effluent by using sea water brine as a draw solution.

Test setup – Semi-batch mode (feed in batch mode vs. draw in single pass mode)

Figure 1 shows the schematic outline of a semi-batch FO setup. The draw solution will become diluted during the feed concentration process. The draw outlet can be discarded to the drain. The feed solution will be continuously recirculated to the FO membrane module and thus concentrated.

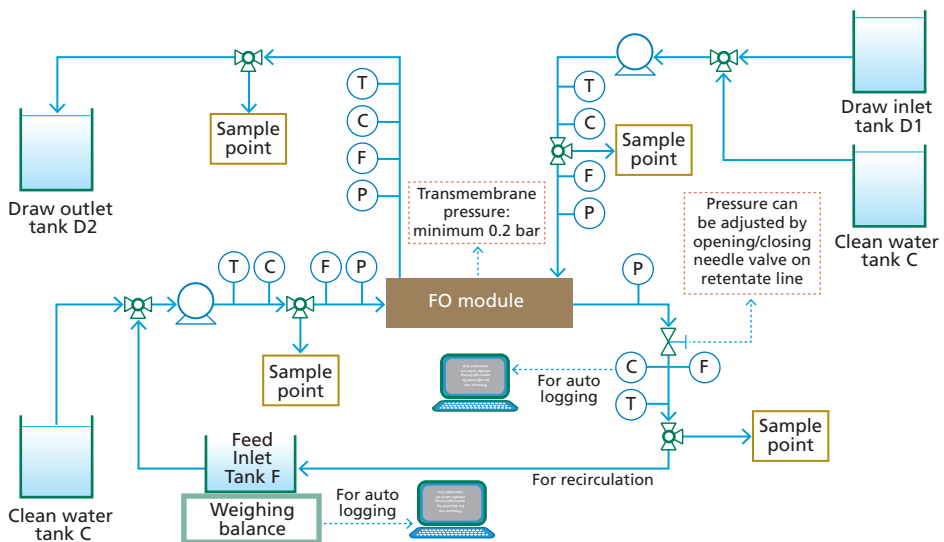


Figure 1 Setup for FO semi-batch operation

Recommendations for running an FO application test:

1. To select the type and strength of the draw solution, refer to section 4.2.3.
2. Start the feed pump to fill in the system. Afterwards, start the draw pump and adjust to the operating conditions as indicated by the FO membrane/FO system manufacturers, always ensuring that the system operating conditions are in agreement with the membrane manufacturer operating limits. Ensure removal of air in the system. The operating conditions can be modified during the application test. For example, the feed inflow can be increased to enhance shear on the membrane surface and delay fouling, while the draw inflow can be increased if flux (J_w) falls below 1 L/m²h.
3. TMP must always be kept positive where possible. For this, it is crucial to monitor that the feed inlet and outlet pressure readings do not overcome the maximum TMP and inlet pressure specified by the membrane module manufacturer. See more details on the effects of negative TMP in section 4.3.3.
4. To be able to calculate compound mass balances, weight of samples taken from the feed inlet, feed outlet and draw outlet should be considered throughout the concentration process. This will allow monitoring of J_w and water recovery values accurately during the FO process.

For further recommendations on process parameters and constraints, refer to Table 1.

Table 1 Process parameters to be considered during FO application test

Process parameter	Process values - considerations
Recommended (and maximum) application flow rates, L/h	Refer to FO membrane/system manufacturer's recommendations.
Minimum feed outlet flow, L/h	Refer to FO membrane/system manufacturer's recommendations. The user needs to make sure that the feed outlet has a minimum flow to avoid module damage.
TMP, bar	Refer to FO membrane/system manufacturer's recommendations. Generally, it should be around or just above 0 bar.
Feed and draw inlet pressure, bar	Refer to manufacturer's recommendations on pressure tolerance for the specific FO product.
Recommended (and maximum) temperature, °C	Refer to manufacturer's recommendations. Generally, the FO module should be able to run feed and draw solutions at room temperature. Be aware that increases in operating temperature could affect FO performance, e.g., increased J_w and J_s . The module temperature tolerance should not be surpassed. Refer also to manufacturer's recommendations for CIP procedures.

Data collection during the application test

The data to be collected during the test is shown in Table 2. For detailed calculations, refer to equations on 'Typical parameters and phenomena' in section 4.3.1.

Experimental Methods for Membrane Applications

Table 2 Process parameters to be measured during the semi-batch application test and where to make the related readings

Purpose/calculated values	Process parameters	Where to measure
Water flux (J_w)	Flow/Weight	Feed bulk
TMP	Pressure	Feed inlet/outlet, draw inlet/outlet
Feed inlet pressure	Pressure	Feed inlet
Maintain stable temperature (T)	Temperature	Feed outlet (if measuring conductivity at feed outlet)
Osmotic pressure (indirect measurement)	Conductivity	Feed outlet
Ensure minimum feed outlet flow	Flow	Feed outlet

4.2.3. Draw solutions: properties, regeneration, types and selection criteria

The performance of FO applications depends on the draw solution, which provides the driving force for water permeation. An adequate choice of draw solute agent can maximize the water flux (J_w) and the water recovery of the system. In addition, the reverse solute flux (J_s) can be reduced and the regeneration costs can be lowered, which usually represents the largest operational costs in FO applications. Therefore, this subsection will give a short summary of the most important properties of draw agents, their influence on the membrane performance, available draw regeneration methods, and discuss advantages and disadvantages of different classes/types of draw agents. Eventually, guidelines regarding the selection of suitable draw solutes are given.

Main properties of a draw solution

Osmotic pressure

The driving force in forward osmosis processes is provided by the difference in osmotic pressure across the active layer of the membrane, as defined as follows:

$$\Pi = -\frac{RT}{V_m} \cdot \ln(a_w) = -\frac{RT}{V_m} \cdot \ln(\gamma_w \chi_w) \quad \text{Eq. 1}$$

Where R is the gas constant, T the temperature, V_m the partial molar volume of water, a_w the water activity, γ_w the activity coefficient, and χ_w the mole fraction.

In practice, assumptions are made to simplify osmotic pressures estimation, often also due to unknown activity coefficients. In very dilute solutions the solvent activity coefficient can be assumed to be close to 1, resulting in the validity of the van't Hoff equation, as follows:

$$\Pi = c_m RT \quad \text{Eq. 2}$$

where c_m is the osmotic concentration (osmolarity). The osmolarity is the molar concentration of osmotic active solutes. For a salt solution, such as NaCl which dissociates into two ions, the osmolarity equals twice the molarity assuming complete dissociation.

Even though the van't Hoff's equation is formally only valid for very dilute solutions, it often provides acceptable accuracy for salt-based draw solutions, especially if direct measurements of the osmolarity (e.g., freezing-point or vapor pressure osmometry) are available. In comparison, prediction of osmotic pressures of organics, polymers, or other draw solutes can lead to significant deviations.

Diffusivity and viscosity

In most technical applications, the draw solution is applied on the support layer side of the membrane leading inevitably to driving force losses due to concentration polarization effects (see section 4.3.2). Besides the properties of the membrane (structural parameter), the extent of ICP is mainly related to the draw solution concentration and diffusivity. The use of a higher draw concentration, hence nominal driving force, does not correlate with a linear increase in the water flux. A higher draw concentration leads to larger relative driving force losses due to stronger ICP related to the convective transport of draw solutes away from the active layer. Since the transport of draw solutes towards the active layer is diffusive only, the diffusivity of the draw agent significantly influences the extent of polarization effects. Diffusivity depends mainly on the solution's viscosity and the diffusion coefficient. Overall, draw solutions of low viscosity and high diffusion coefficient are the best choice when considering FO system productivity.

Regeneration of draw solutions

Continuous FO processes require a reconcentration of the diluted draw solution. Up to now, the regeneration process remains the bottleneck in the draw solution selection. Among the most studied draw regeneration methods are membrane-based processes, such as reverse osmosis (RO), nanofiltration (NF), and membrane distillation, as well as evaporative technologies and electrodialysis. While pressure-driven membrane processes are limited in achievable osmotic pressures due to allowable pressure, the evaporation of water is highly energy intensive. This has led to ideas for the implementation of FO within applications that do not require a draw regeneration. Important to mention are (so-called direct) FO processes using seawater or a concentrated fertilizer as draw solution, which may be discarded or beneficially used once diluted, to avoid costly regeneration. Furthermore, novel types of draw solutions have been designed to overcome existing challenges in draw regeneration. These so-called responsive draw solutions exploit drastic changes in physical and chemical properties of the draw agent provided by external stimuli, such as heat or pH, enabling a practical and efficient draw regeneration. Please note that the energy required for draw agent regeneration is always somewhat related to its target osmotic pressure due to thermodynamics considerations, thus simplicity of regeneration should not be confused with cost of regeneration and the two issues should be considered separately and simultaneously to design a feasible and effective FO system.

Types of draw solutes

In theory, any water-soluble component exhibiting an osmotic pressure can be used as a draw solute. Considering the above-described influence of draw properties on the process performance, small solutes of high osmotic pressures (high solubilities) are preferred. A variety of different draw solutes including salts, small organic molecules (e.g., sugars), volatile organic compounds, nanoparticles, polymers, or hydrogels have been investigated up to now.

Experimental Methods for Membrane Applications

Among the most studied and applied draw solutes are inorganic and organic salts offering the advantages of high osmotic pressures, low viscosities, high diffusivity, electrical charge, and low toxicity. As a result, salt-based draw solution can reach a high water flux, exhibit comparable low driving force losses, enable a hazard-free operation and simple regeneration by pressure-driven membrane processes such as reverse osmosis. Most salts are inexpensive, available as food grade quality, and their replenishment costs are low.

Due to the larger variety of salts, salt-based draw solutions can be selected with regard to the specific process requirements. For example, multivalent ions of higher molecular weights can be selected for food and beverage application to minimize the reverse solute flux into the product stream. Furthermore, studies indicate that the rejection of feed compounds can be enhanced by selecting an appropriate draw solute.

Worth mentioning is sodium chloride (NaCl), one of the most studied draw solutes. It is often used as a benchmark draw agent to evaluate membrane and process performance. Many membrane manufacturers and published articles use the specific reverse solute flux (J_s/J_w) of NaCl as key characteristic to account for the membrane's selectivity for water transport.

Besides the comparable high reverse solute flux of salts, their regeneration remains the bottleneck of salt-based draw solutions due to osmotic pressure limitation. Novel approaches such as osmotically-assisted reverse osmosis (OARO) may enable higher draw concentrations in the future (Peters and Hankins, 2020).

To exceed the osmotic pressure limitation of conventional draw solutes, a variety of responsive draw solutes which can switch solubility properties by external stimuli were studied. Among the most studied responsive draw solutions are thermo- and CO₂-responsive draw agents. Thermo-responsive draw solutions exploit temperature-dependent miscibility gaps between water and polymers or ionic liquids. By exceeding the lower critical solution temperature, the diluted draw solution separates into two phases whereof one phase is rich in draw agent and the other is water-rich. CO₂-responsive draw solutions undergo acid base reaction and are often amine-based. Amines can react reversibly with CO₂ and form bicarbonate salts which can be used as draw agents. Upon heating or purging with inert gas, the diluted amine bicarbonate draw solute decomposes into either a water-insoluble liquid or gaseous amines such as trimethylamine or ammonia. Disadvantages of responsive draw solutions are related to the costs, toxicity (amines), or low membrane performance due to severe ICP (polymers).

Selection of draw solutes

The right choice of draw agent depends on the specific application and feed stream, the target recovery, the process configuration, availability and costs of different energy forms (electrical, waste heat, ...), space requirements, commercial assessment, as well as further considerations. The following guidance can assist in selecting an adequate draw agent:

1. Osmotic pressure of the draw solution
 - Too low osmotic pressure of the draw solution induces low membrane performance, prolonging the process time or requiring larger membrane areas. Both may contribute to target compound losses from the feed solution as well as draw solute contamination of the feed solution.
 - Too high osmotic pressures can accelerate membrane fouling and scaling. Regeneration costs can increase due to dissipation of osmotic potential.
 - Rule of thumb: ratio in osmotic pressure between the draw solution and concentrate should not be below 1.1 - 1.2
2. Draw regeneration method:
 - The draw regeneration process is often limiting the choice of draw type and strength
 - Reverse osmosis:
 - RO is the most energy efficient process to regenerate draw solutions
 - Limited by hydraulic pressure (65 bar, high-pressure RO: 120 bar)
 - Osmotically-assisted reverse osmosis is not established but can overcome osmotic pressure limitations
 - Evaporators
 - Energy intense regeneration with no limitations regarding osmotic pressures
 - Corrosive draw solutes (e.g., chlorides) can drastically increase the CAPEX due to material requirements and should be avoided
 - Electrodialysis
 - High CAPEX
 - Limited to ionic draw solutes
 - Energy efficient at low osmotic pressure range
 - Membrane distillation
 - Energy intensive regeneration, but often low grade heat sources can be used
 - Not-yet-established technology due to currently low performance and specific current limitations related to module configurations, fouling/scaling, and long-term stability
 - Responsive draw recovery
 - Still under development, offering the potential to concentrate draw solution to high osmotic pressures
 - Energy intensive, but often enabling the utilization of low-grade heat sources
3. Applications:
 - Food and beverage
 - Only food-approved draw solutes are applicable (sugars, salts)
 - Multivalent ions and agent of higher molecular weight can reduce unwanted reverse solute flux
 - Target compound rejection can be increased by selecting draw solutes which are already present in the feed stream
 - Wastewater concentration
 - Lower concentration of draw agents may be beneficial to reduce fouling propensity
 - Target compound rejection can be increased by selecting draw solutes which are already present in the feed stream

4.3 EXPERIMENTAL METHODS

4.3.1. Typical parameters and phenomena

The most important process parameters are the water flux J_w , the reverse solute flux J_s , the specific reverse solute flux J_s/J_w , the recovery, and the rejection (both forward and reverse).

The water flux J_w is defined as the areal permeation rate of water as follows:

$$J_w = \frac{Q_{\text{permeate}}}{A_{\text{membrane}}} = \frac{Q_{\text{feed}} - Q_{\text{concentrate}}}{A_{\text{membrane}}} = \frac{Q_{\text{draw out}} - Q_{\text{draw in}}}{A_{\text{membrane}}} \quad \text{Eq. 3}$$

Where Q is the flow rate and the active membrane area (A) is in the denominator. As seen above, J_w can be calculated based on the difference in feed in- and outlet flow rates as well as

based on the difference on the draw side. Its unit is L/m²h. In batch operation, J_w can be determined by measuring the change in feed or draw weight under the assumption that only water permeates the membrane.

The reverse solute flux J_s is defined as follows:

$$J_s = \frac{m_{\text{solute}}}{A_{\text{membrane}}} \quad \text{Eq. 4}$$

Where the mass flux of draw solute is in the numerator and the active membrane area (A) is in the denominator. The reverse solute flux is determined by measuring the draw solute concentration in the concentrate stream. Depending on the feed composition, an appropriate measurement of draw solute concentration, such as conductivity, ICP-OES, or HPLC, can be used. The reverse solute flux is usually given in g/m²h.

The specific reverse solute flux J_s/J_w is defined as the ratio between J_s and J_w . It is a measure of the selectivity for water permeation over draw solute transport given in g/L.

The transmembrane pressure (TMP) is defined as the average hydraulic pressure between the feed side and the the draw side of the membrane, given as follows:

$$TMP = \frac{(P_{\text{feed}} + P_{\text{feed out}}) - (P_{\text{draw in}} + P_{\text{draw out}})}{2} \quad \text{Eq. 5}$$

The recovery (Rec) defines the ratio of the volume of recovered water to the volume of feed solution. In single-pass operation the membrane recovery is defined by using the permeate and feed flow rates as follows:

$$\text{Rec}_{\text{membrane}} = \left(\frac{Q_{\text{permeate}}}{Q_{\text{feed}}} \right) \times 100\% = \left(1 - \frac{Q_{\text{concentrate}}}{Q_{\text{feed}}} \right) \cdot 100\% = \left(\frac{Q_{\text{draw out}} - Q_{\text{draw in}}}{Q_{\text{feed}}} \right) \cdot 100\% \quad \text{Eq. 6}$$

In batch processes where the feed solution is constantly concentrated, the recovery is defined as follows:

$$\text{Rec}(t) = \left(1 - \frac{V_{\text{feed}}(t)}{V_{\text{feed}}(t_0)} \right) \times 100\% \quad \text{Eq. 7}$$

Assuming only water to permeate the membrane and a constant density of the feed solution $\rho_{\text{feed}(t)}$ allows calculating the recovery by weights instead of volumes.

In food and beverage processes, concentration factors (CF) are often used instead of recovery, where CF is:

$$\text{CF} = \frac{1}{1 - \frac{R}{100\%}} \quad \text{Eq. 8}$$

The average **membrane forward rejection** R of a compound i (moving forward from the feed to the draw side) is commonly defined using the concentration ratio between permeate and feed. To take the concentration difference between incoming feed and outgoing concentrate stream into consideration, the average concentration on the feed side of the membrane is often used:

$$R_i = \left(1 - \frac{c_{i,\text{permeate}}}{\frac{c_{i,\text{concentrate}} + c_{i,\text{feed}}}{2}} \right) \times 100\% \quad \text{Eq. 9}$$

In contrast to most other membrane applications, the permeate concentration cannot be directly measured due to its dilution by the draw. Therefore, its average must be calculated based on a mass balance of component i on the draw side.

Taking the draw flow rate into consideration leads to:

$$c_{i,\text{permeate}} \times Q_{\text{permeate}} = c_{i,\text{draw out}} \times Q_{\text{draw out}} - c_{i,\text{draw in}} \times Q_{\text{draw in}}$$

Inserting equation 1 (J_w) and rearranging leads to:

$$c_{i,\text{permeate}} = \frac{c_{i,\text{draw out}} \times Q_{\text{draw out}} - c_{i,\text{draw in}} \times Q_{\text{draw in}}}{J_w \times A_{\text{membrane}}} \quad \text{Eq. 10}$$

While in (draw) batch operation the ingoing target solute concentration in the draw solution needs to be considered, in single-pass operation $C_{i,\text{draw in}}$ is in most cases negligible.

The achieved membrane forward rejection depends on the membrane type, operation conditions (e.g., flow rates of draw and feed solutions), the water flux, as well as the recovery, and it is different for different compounds.

Experimental Methods for Membrane Applications

It is important to note that the above membrane rejection calculations consider the observed rejection and not the real compound rejection, as it is calculated considering:

- 1) The total mass that has passed through the membrane during the entire pass and the average J_w (or entire time in batch mode) and not the mass that is passing across the membrane in each location along the module (or at any given time in batch mode);
- 2) The feed or draw bulk concentration and therefore not considering the higher compound concentrations reached at the active layer interface due to the polarization phenomena. Larger molecules are often better rejected than smaller ones. In addition, uncharged organic molecules show lower rejection than charged molecules due to missing electrostatic repulsion. Even during batch concentration processes the rejection may change significantly as shown in the case of urea (Figure 2).

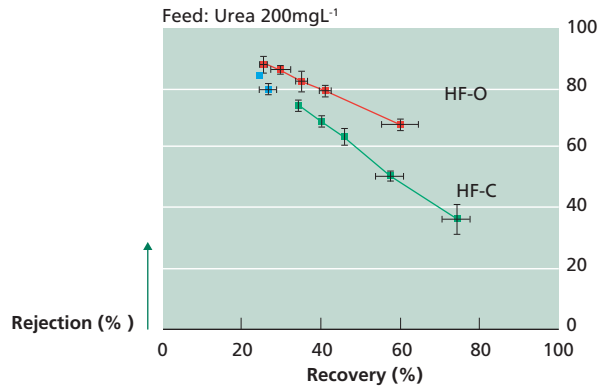


Figure 2 Urea rejection variation with recovery rate for HF-C (chlorinated membranes) and HF-O (non-modified membranes). Adapted from Sanahuja-Embuena *et al.* (2019).

4.3.2 FO process design constraints and considerations

To design a specific FO process and experimental setup, users are strongly advised to refer to the manufacturer's FO module datasheet to understand the operating limits of the given modules. It is also recommended that the user reads any other documentation provided by the FO manufacturer.

Concentration polarization (ECP/ICP)

As seen in Figure 3, concentration polarization occurs on both sides of the membrane due to the permeation of water concentrating the feed solution while diluting the draw solution. A distinction is made between external concentration polarization (ECP) on the active layer side of the membrane and polarization effects in the membrane's support layer referred to as internal concentration polarization (ICP). Depending on the membrane orientation, i.e. FO mode (where the feed solution is in contact with the active layer) or PRO mode (where feed solution is in contact with the membrane support layer), these polarization effects can either be dilutive or concentrative. In most applications, the draw solution is applied on the support layer side leading to dilutive ICP and concentrative ECP.

Concentration polarization reduces the difference in osmotic pressure across the active layer and leads inevitably to driving force losses for water permeation. Besides driving force losses, concentrative ECP increases the risk of membrane fouling and scaling. Lower water fluxes as well as turbulent flow conditions can contribute to reducing these risks.

The intensity of dilutive ICP depends on the porosity, tortuosity, and thickness of the support layer (see structural parameter in section 4.4.1) as well as on the diffusivity of the draw solutes and the water flux. Since draw solutes diffuse against the convective water flux, draw solutions of low viscosity and high diffusion coefficients can mitigate dilutive ICP (see draw solution in section 4.2.3). Additionally, highly porous, and thin support layers can lower the extent of driving force losses.

AL-DS membrane orientation can significantly decrease dilutive CP of the draw solution. Since concentrative CP of feed solutes in the support layer is increased, this membrane configuration might only be beneficial in specific applications, where the feed presents low fouling potential).

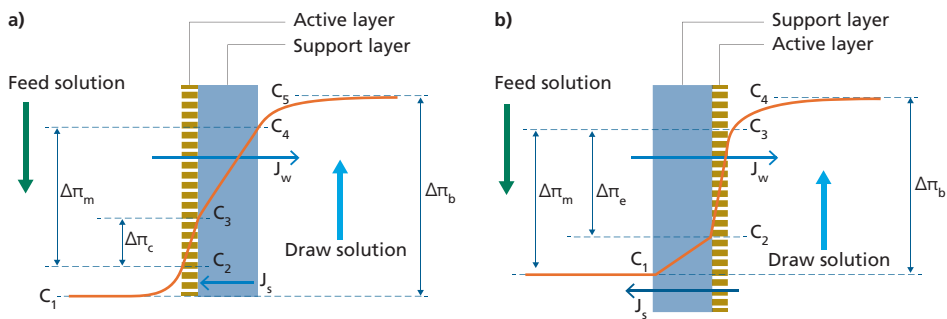


Figure 3 ECP and ICP at a) AL-FS mode, and b) AL-DS mode. Adapted from Wang and Liu (2021).

Pressure limit

Pressure limit is one of many important factors to consider as it affects the choice of flow rate and cross flow velocity sent into each element. This typically already translates into the recommended flow rate range on both feed and draw side. In addition, how much water is transported into the draw solution side is primarily a function of draw solution flow rate and concentration. Even at low draw solution inlet flow, high osmotic pressure difference may result in a large water permeation rate and hence a higher flow rate on the draw side.

System projections are therefore useful to predict the behavior of pressure drop on both feed and draw lines. However, calculating pressure drops in a system can be complicated as this will depend on several factors such as module geometry, array configuration and liquid properties among other factors. Few considerations need thus to be taken when projecting: 1) permissible pressures given by membrane manufacturer should not be exceeded, 2) TMP

Experimental Methods for Membrane Applications

usually increases during batch concentration (e.g., viscosity increase of feed, feed outflow rate increases due to a lower J_w), or in continuous mode due to fouling, 3) system arrays require special considerations such as accounting for local changes in pressure drops, pressure build-up when more-than-one modules are connected in series, draw solution fed in the system in series or in parallel, etc.

Flow rate limit

Flow rate limit, by extension, is determined by the maximum pressure limit of the module. Flow rate should be selected within manufacturer's recommendation in order not to exceed pressure limit. In addition, users are advised to check for any minimum feed reject flow requirement by manufacturers. In a batch process or semi-batch, feed and bleed process, recovery of feed is time-dependent and not flow-dependent. It is therefore possible to maintain as high cross-flow velocity as possible, while staying within pressure limit, to minimize risks of fouling and scaling. This is especially so when feed streams contain medium to high degree of foulants. In a single-pass continuous process, recovery of the feed is flow-dependent. Designers of the FO process should determine, through projection, whether concentrate flow rate at the last in-series element is below recommendation.

Moreover, draw flow rate in operation should be carefully selected and monitored because it influences transmembrane pressure, permeation flux across FO membrane, and the concentration of draw agent and of possible compounds permeated from the feed side. Usually, for polyamide-based FO membrane, manufacturers may recommend a safe limit of negative TMP, beyond which there poses a risk of delamination of polyamide active layer. Having a high draw flow rate increases the overall permeation. However, an excessively high draw flow rate might raise pressure on the draw solution side and result in a high chance that the negative TMP limit is exceeded.

Flow direction

Flow direction, whether counter-current or co-current, is also a tool available for FO process designers. In co-current operation, feed and draw solutions enter the module through the same end of the module, leading to a constantly reducing driving force along the module length. Counter-current operation enables to maintain a more constant osmotic pressure difference along the lengths of the module (see Figure 4). Additionally, counter-current operation maximizes the average water flux across the FO module or system and the permeate recovery, while minimizing local differences in water flux. This means that the difference between water flux across FO membrane across inlet and outlet of FO system is less for counter-current, as compared to co-current flow direction.

It should however be noted that the selection of the flow mode (i.e., co-current or counter-current) depends on module type. For spiral wound or some plate-and-frame module type, flow path is designed to be in cross flow, where feed and draw solutions are perpendicular to each other. For hollow fiber and tubular membrane type, flow path can be selected to be counter-current or co-current.

Conventionally, a counter-current flow path is the preferred option in most applications and experimental setups as it allows maximization of the driving force.

In practice, FO process designers should pay attention to ease of filling up the shell side chamber in counter current mode, assuming that the module is mounted vertically (i.e., feed side flow is upwards and draw side flow is downwards). Modules of larger size which are mounted vertically may however require ingoing streams to enter on the bottom side of the module to remove any trapped air from the module. In such a case, if the draw inlet flow rate is too small, partial filling of shell chamber may occur resulting in underutilized membrane area. In this specific case, operating in co-current operation may be advantageous even though process performance is reduced.

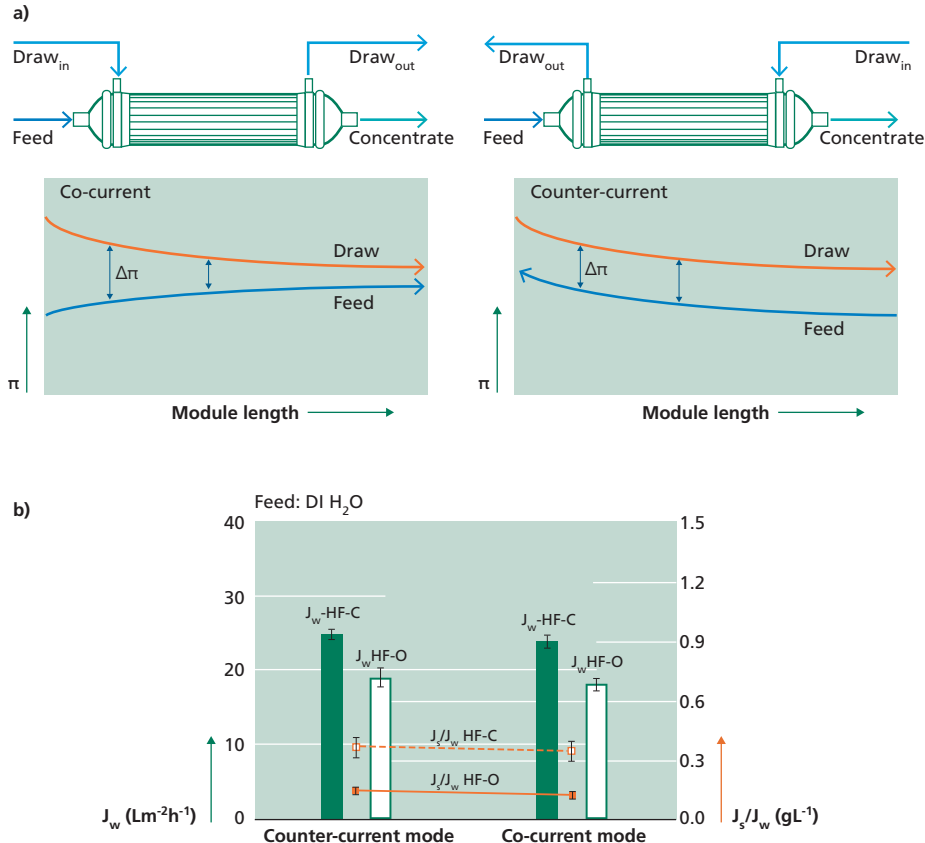


Figure 4 a) Driving force for counter-current and co-current flow direction; b) J_w and J_s/J_w for HF-C (chlorinated membranes) and HF-O (non-modified membranes) in co-current and counter-current when DI water was used as FS. Operating conditions were: Feed flow rate was $100 \text{ L}\cdot\text{h}^{-1}$, draw flow rate was $25 \text{ L}\cdot\text{h}^{-1}$, draw concentration was 1 M NaCl and TMP was 0.2 bar . ($n = 2$). Adapted from: Sanahuja-Embuena *et al.* (2019).

Limiting flux

Lastly, water permeation limit or design flux limit is a major factor affecting the FO design. On the one hand, this is related to feasible feed inlet flow rate for FO module and system. A lower FO feed inlet flow rate limit by manufacturers' recommendation or by system design

Experimental Methods for Membrane Applications

indicates lower maximum design flux limit. However, this is in fact generally related to fouling potential and reversibility of fouling.

While there is no consensus on what design flux limit for FO membrane should be, there are research reports indicating limiting flux to be between 10-20 LMH and designed flux for reversible fouling to be 5-15 LMH. Here, limiting flux is defined to be the starting flux value at which there is decline of flux over time at constant osmotic driving force difference. Design flux is defined to be the starting flux at which there is minimal flux decline and there is flux restoration upon cleaning if there is any flux decline over time. These flux values vary depending on membrane type and feed quality or foulants present in feed.

Water permeation limits may be controlled by draw inlet flow rate and draw inlet concentration. As mentioned above, a higher draw inlet flow rate means less dilution effect on the draw side, allowing osmotic driving force to be sustained from inlet to outlet of module. This comes with the drawback of having a higher pressure drop on the draw side.

A higher draw inlet concentration means higher osmotic driving force across entire FO modules or system, at the same draw inlet flow rate. The disadvantage is the high likelihood of exceeding design or limit FO flux at certain sections of FO membrane within a module or system. This may lead to sustained high ECP in those regions, increased likelihood of fouling and scaling and premature module failure.

4.3.3 Best practices

Transmembrane Pressure (TMP)

Most forward osmosis membrane suppliers recommend running FO processes under low positive transmembrane pressure. The positive TMP can hinder the transport of draw solutes towards the feed solution due to the pressure gradient, which helps in preventing the immediate contamination of feed solution by draw solutes in the event of membrane breakage or defects on the selective layer. In the case of small defects on the polyamide layer, a positive TMP will also be beneficial. However, a positive TMP may also aid the transport of feed solutes into the draw solution and thus, the quality of the selective layer would need to be checked. A tight and highly cross-linked polyamide layer should not be significantly or drastically affected by slight positive and negative TMPs, and if this happens, it may be a sign of membrane deterioration.

Nevertheless, a negative TMP should be strictly avoided, even for brief periods of time, due to the polyamide layer configuration (where the layer is on the lumen side of the membrane). When a negative TMP is applied, the pressure gradient direction can cause the delamination of the polyamide layer, and consequently, the breakage of the membrane.

During the FO module operation, pressure losses from inlet to outlet for both feed and draw side are expected, regardless of the flow mode selected (i.e., counter-current or co-current), which could provoke negative TMP at the feed outlet or draw inlet locations. It is therefore of paramount importance to maintain a positive TMP at the feed outlet ensuring following the manufacturing guidelines on pressure limits.

In summary, since FO is a virtually pressure-less membrane process, membranes are not designed for high hydraulic pressures on either side of the membrane. Therefore, commonly recommended TMPs are around 0.2 bar. Allowable pressures given by the membrane manufacturers should not be exceeded to ensure safe operation. Here, pressure relief valves in the experimental setup can protect the membrane from maloperation.

Avoiding 'over-recovery'

High recoveries of feed solution can lead to the precipitation and deposition of feed particles on the membrane (fouling and scaling). While membrane fouling is characterized by the deposition of (mainly organic) suspended solids, scaling refers to the precipitation and crystallization due to exceeding salt solubilities. In process configuration consisting of serial connected FO modules, fouling will occur in the first stages while scaling usually occurs in the consequent stages.

Although FO is generally considered a low fouling propensity membrane technology which can handle more difficult-to-treat feed stream, fouling and scaling will ultimately reduce the membrane performance. Indications are a reduced water flux, increased pressure drops on the feed side of the membrane, as well as reduced rejections. Besides an appropriate pre-treatment of the feed solution to remove suspended solids, frequent cleaning-in-place (CIP) can mitigate the deposition of solids on the membrane surface and performance detriment. Scaling should be prevented by estimating the scaling risk of a certain feed composition by using the Scaling Index and avoiding working at water recoveries that could provoke severe compound precipitation.

4.4 DATA ANALYSIS: BASIC FO PROCESS DESIGN

4.4.1 FO Fundamental Equations

In a typical FO process, the equation for water flux flowing from feed side to draw side is given by:

$$J_w = A \left[(P_F - P_D) - (\pi_D^m - \pi_F^m) \right] \quad \text{Eq. 11}$$

Where J_w is water permeation flux, A is the water permeability, P_F and P_D is hydraulic pressure of feed side and draw side respectively, and π is osmotic pressure of draw side and feed side at membrane surface, respectively. In FO operation, hydraulic pressure difference tends to be zero or close to zero.

The salt flux equation is given by:

$$J_s = B (C_D^m - C_F^m) = B \Delta C_m \quad \text{Eq. 12}$$

where J_s is salt flux from draw to feed, B is the salt permeability, and C is solute concentration in draw and feed solution at membrane surface, respectively.

Experimental Methods for Membrane Applications

The salt transport across the FO membrane is also described by the convection-diffusion model with a diffusive term proportionally related to solute concentration gradient and a convective term related to water permeate flux across the membrane in the opposite direction.

$$J_s = D \frac{dC(x)}{dx} - J_w C(x) \quad \text{Eq. 13}$$

Where D is the solute diffusion coefficient. The solution of the transport equations above differ depending on the orientation of the membrane.

In active layer facing feed side (AL-FS) mode or FO mode, water permeates from feed side into the support layer on the draw side, leading to dilutive internal and external concentration polarization (i.e., ICP and ECP, respectively). On the feed side, the convective water flux carries solutes from bulk feed solution to membrane surface, at which they are rejected and accumulate, causing concentrative ECP. The solution of the convective-diffusive equation above, for AL-FS mode, become:

$$\Delta C_{m,ALDS} = \frac{C_D^b \exp\left[-\frac{J_w}{k_D}\right] - C_F^b \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right] - \exp\left[-\frac{J_w}{k_D}\right] \right\}} \quad \text{Eq. 14}$$

For active layer facing draw side (AL-DS) mode or PRO mode, water permeates from feed side with solutes that are rejected and accumulate across the support layer, resulting in concentrative ICP and ECP on the feed side. On the draw side, there is dilutive ECP as pure water permeates into the draw side. The solution of the convective-diffusive equation above, for AL-FS mode, becomes:

$$\Delta C_{m,ALDS} = \frac{C_D^b \exp\left[-\frac{J_w}{k_D}\right] - C_F^b \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right]}{1 + \frac{B}{J_w} \left\{ \exp\left[J_w \left(\frac{1}{k_F} + \frac{S}{D_F}\right)\right] - \exp\left[-\frac{J_w}{k_D}\right] \right\}} \quad \text{Eq. 15}$$

Where k is mass transfer coefficient, and the term ' $\exp(-J_w/k_D)$ ' indicates external concentration polarization in general whereas the term $\exp[J_w(1/k_F + S/D_F)]$ denotes internal concentration polarization with S being structural parameter of membrane, consisting of porosity and tortuosity term used in modifying solute diffusion coefficient from the bulk solution to the inside support layer.

The mass transfer coefficient k value is dependent on the type of membrane form factor and module. In general, mass transfer coefficient is:

$$k = \frac{Sh \times D}{d_h} \quad \text{Eq. 16}$$

where Sh is Sherwood number and d_h is hydraulic diameter, both being geometry-dependent.

Combining above stated equations, one is able to calculate the expected water permeation, J_w , and reverse solute flux, J_s , of a FO membrane, given its bulk feed and draw solution characteristics and some basic hydrodynamic information to obtain mass transfer coefficients.

4.4.2 FO Module Mass Balance

To simulate transport inside a membrane module, mass balance equations should be considered. In addition, the effect of volume change due to dissolved solute should also be taken into account. This means the differential term of density and concentration of solute cannot be neglected.

Typically, mass balance equations for pressure, velocity and concentration along module length can be established. For instance, the velocity and concentration differential equation on the feed side can be seen below for a rectangular flat plate channel type.

$$\frac{dv^F}{dx} = \frac{\left[-J_w \times \rho^w + J_s - \frac{d\rho^F}{dc^F} \times J_s \right] \times \frac{1}{H}}{\rho^{F,bulk} - \frac{d\rho^F}{dc^F} \times c^F} \quad \text{Eq. 17}$$

$$\frac{dc^F}{dx} = \frac{-c^F \times \frac{dv^F}{dx} + \frac{1}{H} \times J_s}{v^F} \quad \text{Eq. 18}$$

Where ρ^w is density of pure water, v^F is the differential term to account for volume change with solute concentration and H is the height of flat plate flow channel. In other geometries, such as for hollow fiber or tubular types, these terms are referred to inner diameter of hollow fiber (this assumes an inside out FO module with active layer being on the lumen side).

Similarly, the velocity and concentration differential equation on the draw side for a rectangular flat plate channel type can be seen below.

$$\frac{dv^D}{dx} = \frac{\left[J_w \times \rho^w - J_s + \frac{d\rho^D}{dc^D} \times J_s \right] \times \frac{1}{H}}{\rho^D - \frac{d\rho^D}{dc^D} \times c^D} \quad \text{Eq. 19}$$

$$\frac{dc^D}{dx} = \frac{-c^D \times \frac{dv^D}{dx} + \frac{1}{H} \times J_s}{v^D} \quad \text{Eq. 20}$$

Experimental Methods for Membrane Applications

For a hollow fiber bundle, the H hydraulic radius term becomes the following for lumen and shell respectively:

$$H_{\text{lumen}} = 4/d_i \quad \text{Eq. 21}$$

$$H_{\text{shell}} = (4 \times n \times d_i) / (n \times d_o^2 - D_i^2) \quad \text{Eq. 22}$$

where d_i is fiber inner diameter, d_o is fiber outer diameter, D_i is shell housing inner diameter and n is the total number of fibers.

Similarly, the velocity and concentration differential equation on the draw side for a rectangular flat plate channel type can be seen below.

$$\frac{dv^D}{dx} = \frac{\left[J_w \times \rho^w - J_s + \frac{d\rho^D}{dc^D} \times J_s \right] \times \frac{1}{H}}{\rho^D - \frac{d\rho^D}{dc^D} \times c^D} \quad \text{Eq. 23}$$

$$\frac{dc^D}{dx} = \frac{-c^D \times \frac{dv^D}{dx} + \frac{1}{H} \times J_s}{v^D} \quad \text{Eq. 24}$$

It should be noted that the sign of the velocity differential equation is reversed in the event of counter current flow.

The pressure drop equation across the module strongly depends on the type of module used. As an example, for the hollow fiber form factor, the analogy of flow through a packed bed with the Ergun equation could be used to model pressure drop across the tube bundle on the shell side.

$$\frac{dP^D}{dx} = \theta \times \alpha \times \left[\frac{150 \cdot (1-\varepsilon)^2 \times \mu^D \times v^D}{\varepsilon^3 \times d_o^2} + \frac{1.75 \times (1-\varepsilon) \times \rho^D \times v^{D^2}}{\varepsilon^2 \times d_o} \right] \quad \text{Eq. 25}$$

where θ is empirical pressure drop correction factor and α is flow direction (1 for counter current, and -1 for co-current). ε is packing density of hollow fiber bundle, μ is fluid dynamic viscosity, ρ is fluid density, and v is fluid velocity. D denotes draw solution side, which typically flows on the shell side of a hollow fiber module.

Meanwhile, the Hagen-Poiseuille model for pressure drop across cylindrical tube is used for the lumen side pressure drop:

$$\frac{dP^F}{dx} = \frac{32 \times \mu^F \times v^F}{d_i^2} \quad \text{Eq. 26}$$

where P is pressure, F denotes the feed solution side, which typically flows on the lumen side of a hollow fiber bundle, μ is fluid dynamic viscosity, v is fluid velocity and d_i is the fiber inner diameter.

4.4.3 FO Design Considerations

For the batch or feed-and-bleed type of system, feed solution is re-circulated and water extraction happens over time. Sensors may be installed to automate the feed-and-bleed or cycle shutdown operation. In such a system, because the feed side is being concentrated, water flux will start high and decrease over the course of a cycle, assuming that draw inlet flow rate and concentration are constant. Care should be taken to ensure that initial flux is below design flux limit for the given process, and final flux is non-zero so that cycle time is still productive and reverse salt flux into feed batch is minimized.

For a single pass process where the FO feed outlet is expected to reach a desired concentration factor, the number of modules and their array should be designed to achieve recovery outcome, while balancing all design constraints above.

For instance, FO modules may be arranged in parallel to sub-divide flow to be within recommended flow rate. FO modules, and hence membrane area, may be added in series to achieve recovery in single pass, while design flux limit is obeyed. For the same flow rate extraction requirement, added area means lower operating flux, ensuring that it is within design limit. The maximum number of modules in series is dictated by pressure drop across the system, while the maximum number of lines of modules in parallel is dictated by the minimum FO outlet flow rate for each line.

One way to circumvent minimum FO outlet flow rate being below limit is to implement multi-stage design. That means, the flow rate of multiple lines of FO modules of the so-called first stage are combined and redistributed over a smaller number of lines in the second stage. This allows more flow per module when recovery is at the highest point and by design, above module limit by manufacturers' recommendation.

Lastly, it should be noted that process limits should be considered for both flushing or cleaning process as well as FO process. In the former, cross flow velocity on the feed side is highest, and on the later cross flow velocity on the draw side is highest. It should be ensured that design considerations are met for both operation types for successful commissioning of a FO system.

Other design considerations

Beside technical considerations, there are other parameters that FO process designers should pay attention to as it influences the operating cost of such a system. Most directly, increasing the number of FO modules used will increase the cost of membrane replacement and initial capital investment on the system. This will also increase the hold-up volume and volume of flushing water or chemicals required for the cleaning process, even though this tends to take a small fraction of overall operating cost.

If operating flux is still within design flux limit, increasing draw solute concentration results in less membrane required and reduces membrane initial investment. However, this would result in increased reverse salt flux from draw to feed side, increased salt passage into draw regeneration permeate stream and increased energy cost of draw regeneration step.

4.5 APPLICATION EXAMPLES

Textile industry application of FO for lowering water footprint

Textile production is estimated to be responsible for about 20% of global clean water pollution from dyeing and finishing products (Morlet *et al.*, 2017). Given the increasing need for the textile industry to lower the environmental impact it is necessary not only to design appropriate wastewater treatment technologies but also to enable reuse and recycling of water. Here FO can be used for water reclamation using concentrated dyeing salt solutions where the diluted dyeing salt solutions can be used in the dyeing baths directly (see Figure 5).

Following the study of Sheldon *et al.*, (2019) it was evaluated the potential of dye solutions as a novel draw solution by screening, assessing and identifying suitable reactive dyes, e.g., Reactive Black 5 and Basic Blue 41 GRL dyeing solutions were investigated as draw solutions in FO with a dye-to-salt 1:10 mass ratio, see Figure 1. Synthetic seawater (SSW) and two types of textile wastewater (TWW1 and TWW2) were evaluated as feed solutions for water reclamation. Reactive Black 5 and Basic Blue 41 GRL were diluted 10 and 5 times respectively.

With Reactive Black 5 as draw solution and SSW as feed solution a water recovery of 75% was achieved. Using TWW1 and TWW2 as draw solutions, water recovery was around 30%. Using Basic Blue 41 GRL with SSW, TWW1, and TWW2 as feed solutions, water recoveries of 50%, 20% and 20%, respectively, were achieved. The average reverse solute fluxes were between 0.06 and 0.34 g/m²h. Results indicated the potential of FO in the textile industry leading to substantial water savings.

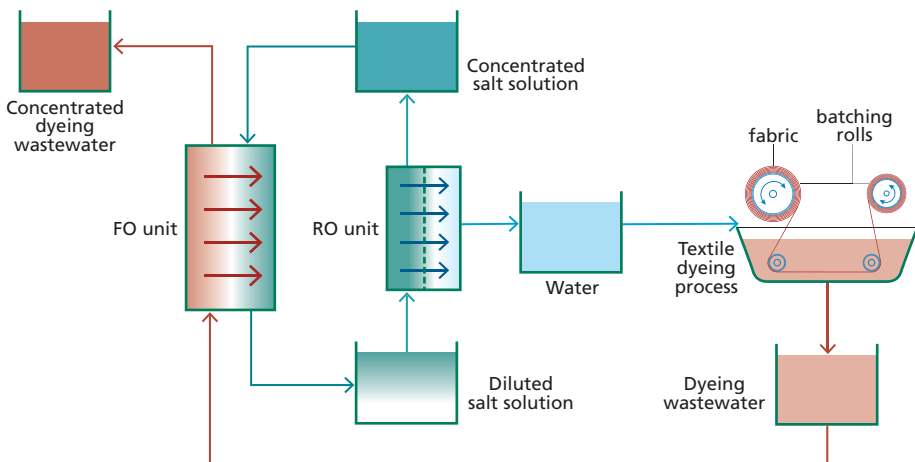


Figure 5 Implementing forward osmosis (FO) into the textile wastewater treatment process can provide high value to an industry segment which is a large consumer of fresh water and one of the biggest polluters. The scheme shows the FO process integrated in a textile wastewater treatment plant using inorganic salt as a draw solution. For using the salt solution as a draw solution there is an integrated reverse osmosis unit for the reuse of the diluted salt.

Concentrating distillery wastewater for subsequent antioxidant retrieval

Alcohol distillation from sugarcane molasses constitutes an important industry in several countries. Molasses-based distillation is a water intensive method with a freshwater consumption in the range of 9-21 L per alcohol and concomitant wastewater production of 7-15 L per L alcohol (Gol, 2014). The resulting wastewater has a high organic load, low pH, and high total dissolved solids. About 2% (w/v) of the wastewater is melanoidins, a product of Maillard reaction obtained from reducing sugars and amino acids during distillation. From a classical wastewater treatment point of view this makes this particular stream problematic as melanoids are not readily biodegradable. However, melanoidins have antioxidant properties which could be a valuable sub-product. The high organic load and the high total dissolved solids makes separation based on classical filtration challenging but due to the inherently low fouling potential FO has attracted attention as a method for up-concentration of this potential antioxidant source.

Singh *et al.* (2018) studied the concentration of distillery wastewater by FO with magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) as draw solution. They used a 10% v/v melanoidins model feed solution to optimize the operational parameters. Subsequently they achieved 85-90% melanoidins rejections with as-received distillery wastewater and 3M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as draw solution. The water flux was $2.8 \text{ L m}^{-2} \text{ h}^{-1}$ with water recovery over 24 h was around 70% which is significantly higher than reported for RO (35-45%). However, further investigations on membrane fouling and draw solution recovery are required to establish the superiority of FO over RO for the concentration of this type of wastewater.

Concentrating electroplating wastewater

Chromium plating and chromate processes are widespread technologies for electroplating of pristine or nickel-coated plastics as chromium and chromate endow surfaces with special properties such as hardness and corrosion resistance (Korzenowski *et al.*, 2018; Sorme *et al.*, 2002). In this process, large quantities of wastewaters, residues, and sludge is generated which can be categorized as problematic waste requiring extensive waste treatment (Sorme *et al.* 2002).

In the study of Bratovic *et al.* (2022) FO was investigated for concentration of hexavalent chromium (Cr(VI)) in electroplating wastewater from processing plastics to enable the reuse of recovered Cr(VI) in the plating baths, see Figure 6. The feed solution was chromium galvanic wastewater, while the draw solution was an underground brine (close to the factory location) with osmotic pressures of 28 and 226.8 bar, respectively.

Baseline and FO filtrations were performed using Aquaporin Inside(R) membrane hollow fibre FO (AIM™ HFFO) modules with a sequence of baseline, filtration (1.5h) and cleaning (30 min with DI water) steps. During the initial filtration (F1), the water flux decreased on average from an initial value of 28.7 LMH at 46.7 % water recovery to 18.5 LMH. For the second filtration (F2) the water flux decreased from 20.1 LMH at 28.4 % water recovery to 16.8 LMH. The corresponding feed solution (wastewater) volume reduction factors were 1.9 and 1.4 with a concomitant Cr(VI) concentration factor of 1.6 and 1.3 for F1 and F2, respectively. After 1.5 h of filtration, the Cr(VI) rejection was 99.7 % and 95.8 % for F1 and F2, respectively. As the AIM™ HFFO membrane is negatively charged electrostatic repulsion

Experimental Methods for Membrane Applications

between the membrane surface and the negative ions (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) will contribute to the rejection of Cr(VI). The appearance of Cr(VI) in the draw solution indicated a loss of membrane integrity which was ascribed to chemical degradation of the membrane due to oxidation from Cr(VI). Local guidelines for standard chromium discharge from industrial wastewater into the environment is $0.5\text{--}1\text{ mg L}^{-1}$. Since the diluted brine draw solution contained 0.07 gL^{-1} and 0.65 gL^{-1} of Cr(VI) for F1 and F2 respectively, it cannot be directly discharged into the salt groundwater resource.

In conclusion, brine-driven FO could concentrate chromium galvanic wastewater taking advantage of the high chemical potential gradient provided by the high salinity brine, but the membrane material must be adapted to withstand harsh environments.

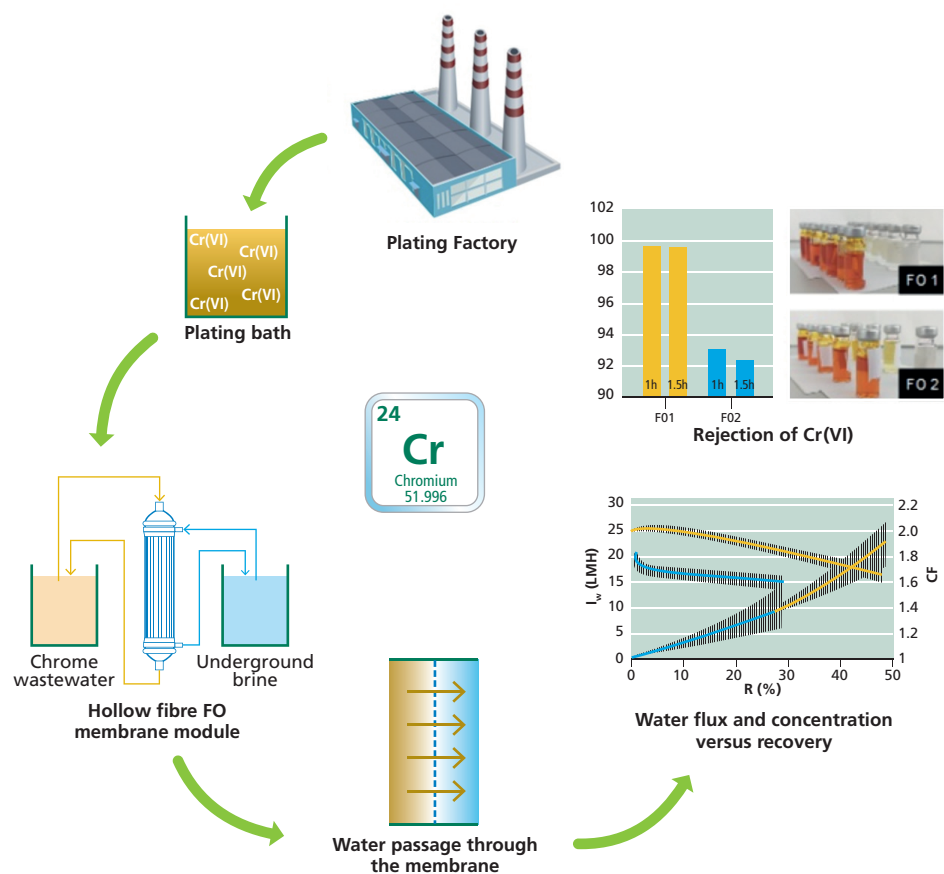


Figure 6 FO tests using Aquaporin Inside membrane hollow fibre FO (AIM™ HFFO) modules for concentration of hexavalent chromium (Cr(VI)) in electroplating wastewater from processing plastics to enable the reuse of recovered Cr(VI) in the plating baths. Chromium galvanic wastewater was used as feed solution while the draw solution was underground brine close to the factory location. The results show that FO can be used in this type of application, but the membrane material must be adapted to withstand harsh environments (Bratovic *et al*, 2022)

4.6 OUTLOOK

FO is a relatively new technology which presents numerous advantages, especially when a direct FO system can be implemented (i.e., draw solution is available and regeneration is not needed) or when the resulting feed concentrate can bring an added value to the final product. However, FO presents the drawbacks of a developing technology. These are mainly the scarce availability of FO membrane manufacturers, the development of materials which ensure a high water flux, high compound rejection, withstand harsh environments, high selectivity to water and a reduced concentration polarization. The unique system design characteristics required by the FO technology (i.e., draw solution regeneration and membrane configurations) also involve an additional level of system complexity. The availability of non-expensive draw solutions with the desired characteristics and the suitability of these in those applications that require high safety levels, such as in food and pharma industries, are also challenging. However, overall, FO technology can still bring unique advantages in niche applications, although more research in membrane materials and processing are needed to fully understand its capabilities in industry.

4.7 REFERENCES

- Baker, R. W. (2004). *Membrane Technology and Applications*. John Wiley & Sons, Ltd. DOI:10.1002/0470020393
- Bratovic, A., Buksek, H., Helix-Nielsen, C., Petrinic, I., Concentrating hexavalent chromium electroplating wastewater for recovery and reuse by forward osmosis using underground brine as draw solution *Chemical Engineering Journal*, 431, #133918, 2022.
- Gol, 2014. Report by Principal Scientific Advisor to Government of India. Electronic source. <http://psa.gov.in/publications-reports/opportunities-green-chemistryinitiatives-molasses-based-distilleries-2014>
- Im Sung-Ju, Lee H., Jang A. (2021). Effects of co-existence of organic matter and microplastics on the rejection of PFCs by forward osmosis membrane. *Environmental Research*, 194, 110597
- Jørgensen, M. K., Keiding K., Christensen, M.L. (2014). On the reversibility of cake buildup and compression in a membrane bioreactor. *Journal of Membrane Science*, 455, 152-161
- Korzenowski C., Rodrigues M.A.S., Bresciani L., Bernardes A.M., Ferreira J.Z., Purification of spent chromium bath by membrane electrolysis, *J. Hazard. Mater.* 152 (3) (2008) 960–967.
- Morlet, A., Opsomer, R., Herrmann, S., Balmont, L., Gillet, C., and Fuchs, L. (2017). *A new textiles economy: Redesigning fashion's future*. Ellen MacArthur Foundation.
- Mulder, M. (1996). *Basic Principles of Membrane Technology*. Springer. DOI: 10.1007/978-94-009-1766-8
- Peters, Christian D. and Hankins, Nicholas P. (2020). The synergy between osmotically assisted reverse osmosis (OARO) and the use of thermo-responsive draw solutions for energy efficient, zero-liquid discharge desalination, *Desalination*, Volume 493, 114630
- Sanahuja-Embuena, V.; Khensir, G.; Yusuf, M.; Andersen, M.F.; Nguyen, X.T.; Trzaskus, K.; Pinelo, M.; Helix-Nielsen, C. Role of Operating Conditions in a Pilot Scale Investigation of Hollow Fiber Forward Osmosis Membrane Modules. *Membranes* 2019, 9, 66. <https://doi.org/10.3390/membranes9060066>
- Sheldon *et al.* *Water Sci Technol* (2019) 80 (6): 1053–1062
- Singh *et al.* *Water Research* 130 (2018) 271-280
- Sorme L. and Lagerkvist R., Sources of heavy metals in urban wastewater in Stockholm, *Sci. Total Environ.* 298 (1-3) (2002) 131–145.
- Suwaileh W., Pathak, N., Shon H., Hilal N., Forward osmosis membranes and processes: A comprehensive review of research trends and future outlook, *Desalination*, Volume 485, 2020, 114455, ISSN 0011-9164, <https://doi.org/10.1016/j.desal.2020.114455>.
- Wang J, Liu X (2021) Forward osmosis technology for water treatment: Recent advances and future perspectives. *Journal of Cleaner Production* 280: 124354 DOI <https://doi.org/10.1016/j.jclepro.2020.124354>
- Xiao, T., Nghiem, L. D., Song, J., Bao, R., Li, X. & He, T. (2017). Phenol rejection by cellulose triacetate and thin film composite forward osmosis membranes. *Separation and Purification Technology*, 186 45-54.