Development of Membrane Testing Protocols for Characterisation of RO and NF Membranes

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Abstract

The CSIRO Flagship Cluster project Advanced Membrane Technologies for Water Treatment is a collaboration of nine Australian Universities and the CSIRO looking at improving the energy efficiency of desalination of seawater using membrane processes. One of the initial aims of the cluster is to develop a standardised suite of tools and techniques for the characterisation of membranes for seawater desalination. Measures used to assess membrane separations are speed, selectivity and stability. These three performance measures depend upon the physical and chemical properties of the membrane, the feedwater and the type of filtration process being used (ie. Dead end batch filtration versus continuous crossflow filtration). Our proposed testing protocol will cover three main categories; transport properties, pore characteristics and surface properties. The transport properties of membranes are strongly related to the pore and surface characteristics, however no general predictive capability exists yet that is widely accepted in the literature.

Keywords: Desalination, reverse osmosis, nanofiltration, seawater, fouling, natural organic matter.

1. Introduction:

This work has arisen from research relating to the CSIRO Water for a Healthy Country Flagship Program. Under this program a CSIRO Flagship Cluster was launched in May 2007 to investigate technological improvements to membrane desalination. The project involves nine Australian universities and a number of research groups within the CSIRO, and has been established to investigate novel modifications to membrane surfaces, in order to reduce the energy demand of desalination associated with fouling of membranes.

In order to develop new fouling resistant membranes it is important to understand the critical parameters which determine fouling phenomena. The usual performance measures used to assess membrane separations are speed, selectivity and stability. Speed is also known as the membrane flux, a property which describes how quickly a given volume of feedwater passes through the membrane. Flux is controlled by hydraulic permeability, the thickness of the membrane layer, available membrane surface area, the transmembrane pressure (TMP) and the viscosity of the fluid passing through the membrane. As the membrane becomes fouled, flow restrictions occur because of a number of phenomena. These include concentration polarization, cake buildup and pore plugging. Whilst a number of researchers have focused on the effect of colloidal deposition on membrane surfaces [1-3], there is an enormous amount of work currently underway looking at the fouling effect of natural organic matter (NOM) and complexes of NOM and divalent metal ions [4-9].

The selectivity is how well the membrane discriminates between various components in the feedwater. The solute rejection behaviour of membranes is different according to the specific characteristics of the solute and solvent. Again, there are a range of models available to describe such behaviour, most based on the Donnan exclusion approach [10, 11].

Membrane stability is how long the previous two performance measures are able to be maintained at a desirable level. To a large extent this is related to the pore characteristics of the membrane both on the surface and throughout the thickness of the membrane. The pore characteristics of a membrane include pore size distribution, surface porosity and pore shape. However, two membranes with essentially the same pore size can display markedly different water permeabilities and solute rejection characteristics. This can be because of variations in pore tortuosity and surface chemistry. The determination of pore characteristics is an important aspect of membrane assessment, especially when used in conjunction with surface characterization techniques.

2. Membrane Fouling and Flux Decline

The characterisation of membrane fouling is generally conducted by measuring the flux decline over time for a given feedwater. Flux decline data is then analysed to determine the fouling mechanism using one or more of a number of classic fouling models. These models are usually based on a generalised version of Darcy's Law:

$$Q = \frac{\Delta P - \sigma_0 \Delta \pi}{\mu(R_m + R_p)} A \quad (1)$$

Where Q is filtrate flowrate, μ is solution viscosity, ΔP is transmembrane pressure, R_m is clean membrane resistance, R_p is the resistance of the cake or deposit on the surface of the membrane, A is filtration area and σ_0 and $\Delta \pi$ are osmotic reflection coefficient and osmotic pressure difference across the membrane. Using Darcy's Law as a basis, a number of membrane fouling phenomena can be modelled such as complete pore blockage, intermediate pore blockage, pore constriction and cake filtration [12].

In the case of fouling by feedwaters with natural organic matter (NOM), there is significant evidence to suggest that there is a transition of fouling modes between pore blockage and cake filtration [5, 12]. Ho and Zydney [12] put forward a combined pore blockage and cake filtration model which describes this transition in fouling behaviour, from deposition of foulants causing reduction in filtration area through to the development of fouling layers. The filtrate flowrate given by the combined pore blockage and cake filtration model is calculated according to:

$$Q = Q_0 \left[\exp\left(-\frac{\alpha \Delta P C_b}{\mu R_m} t\right) + \int_0^t \frac{\alpha \Delta P C_b}{\mu(R_m + R_p)} \exp\left(-\frac{\alpha \Delta P C_b}{\mu R_m} t_p\right) dt_p \right] \quad (2)$$

Where Q_0 is clean membrane flowrate, α is a pore blockage parameter, C_b is concentration of foulant in the feed, t is time and t_p is the time at which the deposit is established and begins to grow [12]. The cake or deposit resistance, R_p , as a function of time is described by:

$$R_p = (R_m + R_{p0}) \sqrt{1 + \frac{2f'R'\Delta PC_b}{\mu(R_m + R_{p0})^2} (t - t_p)} - R_m \quad (3)$$

Where R_{p0} is the resistance of the initial deposit, f' is fraction of foulant that actually contributes to the deposit with regard to foulant convected to the surface of the membrane and R' is specific resistance of the cake layer. The combined cake filtration and pore blockage model, as described by equations 2 and 3, has been used successfully to predict the fouling behaviour of model polysaccharide solutions [13], NOM fouling of ultrafiltration membranes [14] as well as surface modified nanofiltration membranes [15].

The combined cake and pore blockage model does suffer the limitation of under predicting flux decline for long filtration times. This can be overcome by incorporating the role of intermolecular repulsion between foulant and membrane, as well as hydrodynamic forces (i.e. inertial lift and shear), which act on foulants in the feed. Hence foulants can only deposit on the surface of the membrane if the drag force and attractive intermolecular forces can overcome the repulsive and hydrodynamic forces. This resistance to deposition is defined as back transport and can be included in the fouling models [12, 16, 17].

3. Development of Membrane Testing Protocol

3.1 Primary Characterisation: DEF versus crossflow filtration

Membrane flux is usually measured in a laboratory environment using either a dead end flow (DEF) cell or a crossflow unit. The DEF apparatus, also known as a stirred cell, uses a stirrer bar positioned close to the membrane surface to decrease the rate and extent of concentration polarization and cake buildup during filtration tests. The TMP is applied to the cell by application of a gas blanket. The benefits of DEF are relatively quick processing times, minimal equipment and feedwater requirements and potential for longer membrane usage compared to other techniques.

The alternative to this technique are crossflow cells, which can be either flat sheet or hollow fibre. The benefits of crossflow filtration are better control of concentration polarization and cake buildup, potential for continuous operation, ease of scale-up and easier cleaning of membranes. However, the crossflow technique requires significantly more ancillary equipment as well as larger amounts of feedwater compared to the DEF technique.

Tansel and coworkers [18] found that clean water permeability of the same membrane was slightly higher in cross flow mode than for DEF. This may be because of slightly higher compaction of the membrane in DEF, as the water molecules are forced through the membrane perpendicular to the surface, rather than sweeping across the surface as in crossflow filtration. However, in the same study [18] the specific flux of ionic solutions were found to be greater in DEF, whilst crossflow filtration showed somewhat better ion rejection characteristics. This may be attributed to the hydrated radii of ions in solution, with those ions having weaker hydration shells more likely to pass through the membrane in DEF mode.

In a comparative study of fouling behaviour using a number of different test cell designs (RO, UF, CF and DEF), it was found that, whilst the DEF cell could substantially reduce membrane

testing time, the dissolved organic carbon rejection was significantly different to that of the other test cells [19]. In contradiction to these findings a study by Koyuncu and coworkers [20] determined that for nanofiltration membranes, there was no difference in permeate quality or flux decline between the crossflow and DEF experiments. For RO membranes flux decline was slightly higher for crossflow filtration compared to DEF at an equivalent recovery of 75%.

Overall the application of each mode of testing is a balance between applying a process which more closely mimics industrial applications, compared to a process which is significantly less equipment and feedwater intensive.

3.2 Secondary Characterisation: Surface and internal pore measurement

There are three main approaches to pore characterization. These are visualization, flow and fluid intrusion and solute rejection methods. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) will continue to be essential tools in the analysis of surface pore characteristics. However, these techniques are limited in that they are only able to measure the properties of the membrane surface. Fluid intrusion methods measure internal porosity but suffer from problems because of membrane swelling, pore imperfections or lack of information on internal pore structure, requiring assumptions to be made that cannot necessarily be confirmed by experiment [21]. Whilst the limitation of the hydraulic permeability technique is that pore length and tortuosity must be assumed or measured using other characterisation methods, it is the most simple of the fluid intrusion methods and has the benefit that it can be performed as part of normal membrane flux experiments.

Solute rejection methods for pore size characterisation suffer from the assumption that rejection is based on size alone, and that parameters such as particle morphology and surface charge are unimportant. Clearly this is not the case as many researchers have found that the surface chemistry of membranes, as well as pH, ionic strength and temperature of feedwater all play a role in solute rejection [8, 23, 23]. Despite this, molecular weight cut off (MWCO) remains a popular method for membrane manufacturers to describe the characteristics of their products. Hence the MWCO technique is recommended for assessment of membranes in order to make comparisons of test results with data reported by manufacturers.

In order to more accurately determine the internal 3-dimensional porous structure of membranes a number of new techniques are emerging. With Positron Anihilation Lifetime Spectroscopy (PALS) positrons are injected into the sample and form a positronium (positron-electron bound state). The ortho state of the positronium is trapped in vacancies within the sample. The lifetime of the ortho-positronium relates to the void sizes and the probability relates to the void concentrations [24]. This is a very powerful technique which can be enormously useful in determination of internal porosity of membranes [25, 26].

3.3 The importance of surface properties and feedwater chemistry

The surface properties of membranes can have an enormous affect on the fouling behavior of these materials. Important characteristics are surface roughness, hydrophobicity/hydrophilicity, surface charge and solute-membrane affinity.

Surface roughness is typically characterised using techniques such as AFM and SEM and researchers have found strong links between surface morphology and fouling potential of membranes [1, 2, 27]. Typically a material can be characterized as hydrophobic or hydrophilic according to a contact angle measurement [1, 28]. However, membrane surface roughness can create an apparent contact angle, related to the microscopic geometric morphology of the surface. This can often be very different to the intrinsic contact angle measured from a completely smooth sample of the same materials used to manufacture the membrane [28]. Tanaguchi et al. [29] provide a method for compensating for this surface roughness using AFM results. Similarly, standard contact angle measurements must be made on a dry membrane, which may not be representative of performance under real solution conditions. An alternative is the captive bubble technique where the contact angle is measured between an air bubble and a membrane in a solution environment [30].

Surface charge is also important for determination of the potential for attraction and/or rejection of fouling species in feedwater. High energy surfaces are more hydrophilic and contain charged surface groups, whilst hydrophobic and non-polar surfaces are lower energy. Surface charge resulting from the ionizable groups on the membrane surface can be measured using streaming potential techniques [2, 31, 32]. This method has been applied to membranes only recently and there is a significant scope for further studies into characterization of membranes using streaming potential. As an example, Figure 1 shows preliminary streaming potential data that we have obtained using a GE Osmonics AK membrane.

Fig 1 Apparent zeta potential of GE Osmonics AK membrane, measured in a 5 mmol/litre sodium chloride solution..

Overall it will be important to investigate all aspects of membrane surface characterization, including contact angle, surface roughness and streaming potential with regard to different feedwater compositions. By far the greatest challenge will be to develop suitable techniques for assessment of solute-membrane affinity, with a major aspect of this being the development of appropriate model solutions for reproducible membrane fouling experiments.

4. Model Solutions for Membrane Fouling Studies

Developing model solutions to study membrane fouling for seawater desalination can be much more difficult than one would expect. Seawater has a complex inorganic and organic chemistry which varies with the location and with the depth the sample is taken [33, 34]. Whilst the industry standard for reporting salt rejection is to use sodium as a single solute, a more important measure would be to determine the change in solute rejection from a sodium only system, to mixtures of sodium and calcium (i.e. monovalent and divalent ions). As an example, Figure 2 shows rejection data determined using a DEF for a GE Osmonics AK (low energy) membrane. These results clearly show that the rejection of sodium ions decreases in the presence of competing ions such as calcium. Expanding further, it is also important to build up information on a number of binary and multiple ion systems in order to understand the interactions of different species which make up the chemistry of seawater on membrane solute rejection.

Fig 2 Sodium Ion Rejection from a GE Osmonics AK membrane when both a pure sodium chloride feed is used (34 mmol/L) and a mixed sodium chloride (20mmol/L) and calcium chloride (5 mmol/L) feed is used.

With regard to fouling behaviour, a large number of researchers have investigated the effect of NOM on membrane fouling and there have been a number of approaches as to the model solutions used to characterise membrane fouling behaviour. Humic substances are of greatest

interest because of their relatively large concentration in natural waters and their high fouling potential. The most popular technique for model solution synthesis is to purify and dissolve a commercially available humic acid [4, 8, 9, 23, 29, 35-38]. Other researchers have isolated humic substances from natural water sources [8, 9], which is only useful if a standard humic acid can be tested alongside the local humic substance. Further to this some researchers have focussed on the fouling by polysaccharides, another important component of NOM [7, 39, 40]. A major consideration for the development of model NOM solutions for seawater desalination is how the chemistry of NOM in seawater is different from that found in river and lake systems, which have been the focus of previous membrane fouling studies. Whilst only 10-20% of seawater NOM has been fully characterised [32, 41], it is understood that humic substances in seawater can have a significant aquatic origin (i.e. algae and micororganisms rather than terrestrial plant matter) which can make the humic acids more aliphatic and change the H/C ratio of the compounds [34]. We do not yet know how the complexation and fouling mechanisms may differ between humic substances from terrestrial and aquatic sources and this could potentially be an important avenue of investigation.

5. Conclusions

The development of an appropriate membrane testing protocol is an essential component of the CSIRO Membrane Desalination project. The testing protocol will provide a framework for direct comparison of the physical and chemical characteristic of newly developed membrane materials. As a result of this literature review, we have developed a preliminary testing protocol as follows:

- Primary characterisation of speed and selectivity will use dead end filtration for rapid analysis, supported by crossflow filtration work for data validation. This primary characterization includes the evaluation of flux and rejection data for model seawater (32,000 mg/L as NaCl) and brackish water (2,000 mg/L NaCl) solutions. Both sodium chloride and mixed sodium/calcium ion solutions will be tested across a range of pH values and operating pressures.
- Further tests of membrane stability will be conducted using crossflow systems to estimate changes in flux and rejection when a foulant such as alginic acid or humic acid is present. We still have considerable work to do to determine the most realistic foulant.
- Membrane pore characteristics will be evaluated using PALS analysis
- Surface roughness will be evaluated using AFM measurements.
- A combination of captive bubble contact angle and streaming potential measurements will allow the determination of membrane surface chemistry and membrane-solute affinity.

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