Nanofiltration Membranes in Desalination – From Fundamental to Applications

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Abstract

Desalination, by definition, refers to the process of removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be inferred as removal of various inorganic ions from solution with the final target so as to produce clean and potable water. Nanofiltration (NF) as a subset of membrane processes have found wide application within this purview of desalination. Through the development of a good predictive modelling for nanofiltration membrane processes, it is possible to utilise the model for the purpose of membrane characterisation, process modelling, optimisation, membrane design and applications. The integrated usage of the modelling work has enabled the work on various aspects of research and development work from fundamental understanding of the separation phenomena, design and optimization of desalination processes down to practical and real applications in desalination and other relevant relevant applications. Future work will need to stress on solving the existing industrial problems that hinders further development of NF membranes. Thus a good collaboration between academia and industry should be strongly encouraged.

Keywords: Nanofiltration, Modelling, Synthesis, Optimum, Application

Introduction

The nanofiltration (NF) membrane is a type of pressure-driven membrane with properties in between reverse osmosis (RO) and ultrafiltration (UF) membranes. NF offers several advantages such as low operation pressure, high flux, high retention of multivalent anion salts and an organic molecular above 300, relatively low investment and low operation and maintenance costs. Because of these advantages, the applications of NF worldwide have increased [1]. The history of NF dates back to the 1970s when RO membranes with a reasonable water flux operating at relatively low pressures were developed. Hence, the high pressures traditionally used in RO resulted in a considerable energy cost. Thus, membranes with lower rejections of dissolved components, but with higher water permeability, would be a great improvement for separation technology. Such low-pressure RO membranes became known as NF membranes [2]. By the second half of the 1980s, NF had become established, and the first applications were reported [3,4].

Desalination, by definition, refers to the process of removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be inferred as removal of various inorganic ions from solution with the final target so as to produce clean and potable water. Nanofiltration (NF) as a subset of membrane processes have found wide application within this purview of desalination. NF for example has been used in a desalination plant as pre-treatment to both reverse osmosis (RO) and thermal processes, resulting in enhanced production of desalted seawater and reduced cost, yet remains an environmentally friendly process [5]. Pre-treatment of seawater feed to RO/thermal processes using nanofiltration prevents scaling by removal of scale forming hardness ions, prevents membrane fouling in RO processes by removal of turbidity and bacteria and is expected to lower the required pressure to operate RO plant by reducing seawater feed TDS [6].

Our research work aims at looking at a broader yet innovative means of enhancing the NF role within the desalination process. The main theme of the research work is the development of predictive modelling for nanofiltration membrane with its concurrent utilisation for characterisation, process modelling, optimisation, membrane design and applications. The innovation in this works comes from the integrated usage of the modelling work in various aspects of research and development work from fundamental understanding of the separation phenomena, design and optimization of desalination processes down to practical and real applications in desalination and other relevant relevant applications. The work in this area by the author and collaborators has been cited extensively by various researchers (more than 500 citations) and the the number of scientific papers published ranked among the top 10 in the world in the area of Nanofiltration (ISI Citation Report 2007).

The objectives of this paper is to describe in further details some of the research work that has been carried out pertaining to nanofiltration. The emphasis of our work has always been in trying to develop a fundamental understanding of the separation phenomena and correlate these understanding to the intended applications.

Process Modelling For Nanofiltration Membrane

A good predictive model will allow users to obtain membrane characteristics, predict process performance as well as optimize the process. The ability to develop such modelling techniques successfully will result in a smaller number of experiments and subsequently save time and money in the development stage of a process [7].

The framework of the model has been initiated in various studies in the late 90’s based on the extended Nernst-Planck equation in conjunction with Donnan equilibrium [8,9]. The model was termed Donnan-Steric-Pore model (DSPM) and has been widely accepted as one of the most effective model for predicting the behaviour of ionic rejections in nanofiltration membranes. The work has been extended by a modified Donnan-Steric-Pore model (DSPM) to predict the rejection of mixture of charged ions in NF membrane based on the extended Nernst-Planck equation with the incorporation of charge and steric effects for the transport of ions inside the membrane and incorporation of concentration polarization effect for mixture of charged ions [10,11]. With this approach, the permeate flux can be calculated based on the concentration of ions solutes at the membrane surface.

Recent [11] work has been extended by modifying the DSPM-DE model to include the osmotic effect due to the high concentration of salt solutions in desalination applications. The modified model has been found to be able to predict the rejection and flux of single salts solutions such as NaCl, Na_2SO_4, and $MgCl_2$ at higher concentration ranging from 5000 – 2000 ppm, which are the typical concentrations in sea waters. The concentration of salts used in the study was generally higher than in previous reported studies. The concentrations were chosen to represent typical ions concentrations in seawater environment. At such higher concentration, the osmotic pressure difference lead to flux decline, which was quite significant when compared to the pure water flux. The osmotic pressure was calculated using the Pitzer equation as well as Vant Hoff equation. It was found that both equations managed to estimate the osmotic pressure difference with negligible difference for the range of concentrations used in this study. The Vant Hoff equation was then incorporated into the DSPM-DE model to allow for prediction of permeate flux in addition to salt rejections. The DSPM-DE model was able to predict the permeate fluxes and rejections with reasonable agreement for some of the salts by just using fitting parameters obtained using the NaCl rejection data.

Applications For Optimization And Economic Assessment

A good predictive model will the allow the users to use it for the purpose of process modelling, optimization and economic assessment of an NF system for various applications such as diafiltration of dyes solution and removal of divalent salts [12,13]. In addition it is also possible to use the model to identify optimum membrane properties [14] as well as selecting the most suitable membranes among the commercially available membranes for the specific intended application [15].

To illustrate an example, the model in conjunction with a cost model has been used to look at the cost impact (capital and operating cost) of an NF system [13]. By using an economic assessment model for NF processes, the two most important factors determining the performance of NF membranes which are λ (the ratio of solute radius and membrane pore radius) and ζ (the ratio of membrane charge effective density to bulk concentration) were examined. The optimal conditions for minimum operation cost and optimal operating pressure were also determined. Detailed cost analysis reveals both capital and operating cost were not affected by the variation of ζ. However, decreasing the membrane pore size will increase costs. It was found that up to 30% of the capital and operating costs in recovering sodium sulphate solution can be saved by using looser membrane compared to the tight membrane structure. Similarly for desalination application [16], the overall cost study shows that lowest system cost will be obtained for the membrane with the largest pore size provided that the required minimum rejection can be achieved. The effective charge density may also affect the overall cost and it should be considered as well for membrane selection.

Through a sensitivity study using the model, an optimum NF membrane configurational structure can also be achieved and it has been shown to be possible to produce the membranes with the desired characteristics by using the interfacial polymerization technique [17]. Atomic force miscroscope has been used to confirmed the presence of nanopores and the results showed that the NF membranes can be tailor-made to achieve the optimum characteristics that will lead to lower cost and optimum configuration.

Membrane Synthesis And Development

The results from the predictive model lead us to the next challenge which is to develop optimum NF membranes for specific application of interest. One of the main techniques to produce NF membranes is through the interfacial polymerization technique. The technique has been used to produce commercially successful NF membranes such as the NF-45 membrane by Dow [18]. Membranes produced using this technique are considered thin film composite membranes due to the thin layer deposited on top of the support structure. Thus, by understanding the variation of properties during the interfacial polymerization process, it would lead toward better NF membranes for future applications.

In one study [19], five NF membranes were produced through interfacial polymerization under different conditions of reactions, namely varying reaction time, as well as monomer concentrations. The membranes were then imaged using atomic force microscope (AFM). AFM images provided information on the average pore size, pore size distribution, and surface roughness. For some of the membranes, discrete pore sizes were visible. Increasing the reaction time resulted in decreasing water permeabilities but based on AFM imaging the pore size was of similar value. Increasing the monomer concentration also resulted in decreasing water permeabilities. However, based on AFM imaging the pore size differs considerably. Additional permeation experiments were also carried out using NaCl and Na_2SO_4 solutions with membranes identified as NF. By fitting the rejection data using a model such as the Donnansteric- pore model, the variation in effective charge density of the membranes was also determined. The ability to tailor composite NF membranes with the right properties will significantly improve membrane performance.

The possibility of combining properties of organic and inorganic materials was also explored in order to develop a more robust membranes. The presence of finely dispersed inorganic particles in the polymer matrix has proven to be very useful in the improvement of membrane performance. Many new types of organic/inorganic hybrid materials have the potential to combine the desired properties of inorganic and organic systems, improving the mechanical and thermal properties of inorganic ones with the flexibility and ductility of organic polymers [20]. These hybrid materials can be readily prepared by using a sol-gel process, which offers several advantages over other techniques.

In our recent work [21,22,23] Hybrid organic–inorganic membranes were fabricated using sol–gel technique using poly(methyl methacrylate) (PMMA) and tetraethyl orthosilicate (TEOS) with 80/20 (w/w) ratios with THF solvent. The thin films were then characterized using FTIR, SEM, EDX, DSC, TGA, water permeability and also its molecular weight cut-off. From the preliminary characterization, the hybrid membrane was found to have nano and ultra scale tight pore ranges. FT-IR spectroscopy uncovered all the signature peaks characteristic of silicate structures in the near-surface regions. Fingerprints of Si O Si groups in cyclic and linear molecular substructures are present. The SEM image clearly shows that hybrid membranes have homogenous and smooth surface. EDX analysis shows the composition of particles in the membrane. DSC analysis of the membrane shows interesting phenomenon regarding glass transition temperature (T_g). The hybrid membrane was found to have higher T_g than pure PMMA. From TGA analysis, the hybrid membranes were observed to have higher thermal stability than pure PMMA.

Process Applications

Similarly the application of the models and membranes in areas such as wastewater treatment and seawater desalination has been succesful and resulted in the development of inherent principles for the selection of membranes, process conditions and economic assessment for NF system. The applications studied include removal of divalent ions from seawater [24,25], heavy metals from leachate [26] and electroless plating solutions [27]. Another important work is in creating a value added product as a result of a desalination application in a palm oil mill effluent treatment [28,29]. The retentate and permeate of such processes were utilised succesfully to produce enzymes and itaconic acids respectively through biotechnological means. This findings will augur well in the effort to balance environmental concerns with cost-effective treatment and value-added usage of the resulting waste.

Future Works

There are many interesting challenges ahead in order to make nanofiltration process more efficient technically and economically. Process prediction will play a very important role in ensuring that the fundamental understanding of the separation phenomena will be applied towards solving the existing problems during the application of NF membranes. A recent work [30] discussed several key unresolved problems that slow down large-scale applications. They have identified six challenges for nanofiltration where solutions are still scarce: (1) avoiding membrane fouling, and possibilities to remediate, (2) improving the separation between solutes that can be achieved, (3) further treatment of concentrates, (4) chemical resistance and limited lifetime of membranes, (5) insufficient rejection of pollutants in water treatment, and (6) the need for modelling and simulation tools. Some of our works that have been discussed in this paper are directly related to the challenges mentioned. Therefore, our future works will specifically focus on:

- Improving the predictive model to take into account the effect of fouling and long term process operation,
- Validating the model with real industrial data and using the model for process optimization within a desalination plant,

- Developing or modifying existing membranes towards better selectivity, process performance and fouling resistance
- Finding niche applications within desalination or other related processes.

One important component that has to be addressed is the need for collaboration between academia and industry. We would therefore encourage any interested parties from the industry to jointly collaborate with us towards finding a better solution for the future.

Conclusions

Through the development of a good predictive modelling for nanofiltration membrane processes, it is possible to utilise the model for the purpose of membrane characterisation, process modelling, optimisation, membrane design and applications. The integrated usage of the modelling work has allowed us to work on various aspects of research and development work from fundamental understanding of the separation phenomena, design and optimization of desalination processes down to practical and real applications in desalination and other relevant relevant applications. Future work will need to stress on solving the existing industrial problems that hinders further development of NF membranes. Thus a good collaboration between academia and industry should be strongly encouraged.

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