Recent Progress in Reverse Osmosis (RO) Science and Technology

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ABSTRACT

While writing a book on reverse osmosis, it was realized that there had been remarkable progress in recent years in reverse osmosis science and technology. This is a brief summary in which many aspects of RO are discussed, including membrane material and membrane fabrication, membrane characterization, membrane transport, RO module, RO system design, economics, membrane fouling, RO applications and RO/NF membranes for nonaqueous system.

Keywords: Reverse osmosis, membrane, fabrication, fouling, applications

1.0 HISTORY OF RO THEORY AND CHARACTERIZATION

It was more than fifty years ago when the first reverse osmosis membrane was announced by Loeb and Sourirajan [1]. Soon after the announcement, Sourirajan wrote a book to tell how he launched his reverse osmosis research [2]. According to the book, the invention of the Loeb-Sourirajan RO membrane for seawater desalination was made on the basis of the Preferential Sorption-Capillary Flow (PS-CF) model. As the name of the model implies, pores are required for the transport of water through the RO membrane. The Solution-Diffusion model (S-D model) was then presented by Lonsdale [3] and it has soon become the mainstream of the RO transport model. Since Lonsdale regarded the pores as the defects of the nonporous semi-permeable membrane, S-D model has been used for a long time to justify the nonexistence of pores in the perfect dense layer of the RO membrane. Several other transport models have also been presented since then but they were all based on either the presence or absence of the pore.

Nowadays, the derivations of transport equations for RO transport are hardly found in the literature. On the other hand, the membrane characterization techniques were making remarkable progress. In nineteen-sixties and seventies, the only characterization tool was Scanning Electron Microscope (SEM) that did not allow the resolution below 10 nm when the polymeric membrane surface was investigated [4]. Needless to say that it was impossible to observe the sub-nanometer pores and for this reason the top skin layer was generally thought to be dense and homogeneous. Much later, however, the investigation of RO membranes by Small-Angle Neutron Scattering (SANS) [5] and positron annihilation spectroscopy (PALS) [6] allowed to study the morphology of RO membrane more in detail, and many of them came to the
conclusion that there are two distinctive groups of pores, i.e. the “network” and “aggregate” pores.

As the industrial membrane fabrication method shifted from the phase inversion technique of cellulose acetate membrane to in-situ polymerization of thin film composite (TFC) polyamide membrane, so did the membranes as the object of membrane characterization. Nowadays most of the characterization methods are applied to TFC polyamide membranes.

At almost the same time, progress was also made in the membrane transport theory. Instead of interpreting the experimental data of membrane performance by a set of simple transport equations, it is more fashionable nowadays to use the molecular dynamics (MD), by which the structure of the polymeric membrane and the material transport through the membrane are simulated by a set of computer software [7]. It is particularly interesting to note that many of the MD simulation studies have resulted in the polymeric membrane structure with bi- or multi-modal pore size distributions.

2.0 MEMBRANE FABRICATION

Many cellulosic materials were tested for RO membranes prepared by the phase inversion technique soon after the announcement of the cellulose acetate membrane for desalination. Cellulose acetates of different acetyl contents were tested. Other cellulose esters and ethers and their blends were also tested [8]. Synthetic polymers including polybenzimidazole [9], polyamide [10], polyamide hydrazide [10], and sulfonated polyphenylene oxides [11] were used for RO membrane fabrication. Among those, only cellulose acetate of about 2.5 acetyl content could survive in the commercial market. But cellulose acetate had a serious drawback of hydrolysis at low and high pH.

Cellulose acetate membrane was therefore practically replaced by the thin film composite membrane developed by Cadotte at Filmtech [12] for the reason that TFC membrane fabricated by in-situ polymerization of polyamine and polyacetyl chloride on the surface of the substrate polysulfone membrane is superior to cellulose acetate membrane in performance as well as pH stability. However, TFC membrane is susceptible to chlorine that is often used in disinfection of RO feed solution. For further improvement of RO performance and chlorine stability, many different combinations of polyamine and polyacetyl chloride have been tested [13]. It should be noted that despite of a large amount of work reported on the fabrication of TFC membranes only few monomers other than polyamine and polyacetyl chloride were used for in-situ polymerization.

Currently, TFC polyamide membrane manufactured by Dow-Filmtech and Toray is dominating in the commercial RO market except for the RO membrane based on cellulose triacetate (Toyobo).

Stimulated by the success of the incorporation of zeolite in TFC polyamide membrane [14] and also by the report that water flux in the carbon nanotube (CNT) membrane is orders of magnitude higher than in the polymeric membrane [15], it has become rather fashionable during the past decade to develop thin film nanocomposite (TFN) membranes with fillers such as zeolite, clay [16], TiO$_2$ nanoparticles [17], CNTs [18], graphene and graphene oxide [19]. The performance has been improved by TFN membranes but not as much as by orders of magnitude, as expected.
At present, there is one TFN RO membrane (LG) in the commercial market. Another ambitious attempt to increase the RO membrane flux is based on the aquaporin protein function. Currently, aquaporin containing TFN membrane is in a pilot plant testing [20]. Despite many works on TFN membranes, mathematical formula to predict the effect of nano-filler incorporation is not available, while MD simulation was attempted to know the effect of incorporating CNT [21].

One interesting but very challenging area is the development of inorganic RO membrane. It was attempted a long time ago based on the sol-gel method, which did not lead to any fruitful results due to the large size of particles that surrounded the pore. It was shown by MD simulation that the flux of inorganic RO membrane may become very high [22] and a new approach is adopted to make inorganic membrane of high performance by fabricating an ultrathin zeolite membrane. When a practical inorganic RO membrane is developed, it has tremendous potential to revolutionize RO membrane technology, since it will allow the separation of organic mixtures as well as the operation at high temperatures.

3.0 CHARACTERIZATION

This is the most advanced field of RO membrane research. In early days RO publications were mostly on membrane fabrication, performance testing and data analysis by using transport models. Nowadays, publication is almost impossible unless membranes are characterized by a number of sophisticated instruments due to the progress made in the characterization technique and the availability of relatively inexpensive characterization instruments. Most of the research institutions possess an excellent characterization facility. Among the instruments, the most popular ones are Scanning electron microscopy (SEM) for investigation of surface and cross-sectional morphology, atomic force microscopy (AFM) for measuring surface roughness, Fourier Transform Infrared (FTIR) spectroscopy for confirmation of nanofiller grafting, X-ray photoelectron spectroscopy (XPS) for the measurement of atomic composition at the surface, thermogravimetric analysis (TGA) for the weight loss due to polymer decomposition, tensile strength measurement for the evaluation of mechanical strength, contact angle measurement for evaluating the surface hydrophobicity and zeta potential measurement for knowing the surface charge.

Moreover, transmission electron microscopy (TEM) is used to show the hollow structure of carbon and clay nanotubes and wide angle X-ray diffraction (WAX) is for confirming the presence of crystalline fillers. Positron annihilation life time spectroscopy (PALS) is very important tool to measure the size and size distribution of free volume (pore) [17] but it is less popular since the equipment is very expensive. Other less popular but potentially useful characterization techniques are electron paramagnetic resonance (EPR) [23] and Raman spectroscopy [24]. It should also be noted that pore size and pore size distribution can now be evaluated from the SEM image by using a computer software and electron dispersive X-ray spectroscopy (EDX) is also attached to SEM, which enables the evaluation of atomic composition either lateral or cross-sectional direction of the membrane by elemental mapping [25].
4.0 TRANSPORT

As already mentioned, many models and equations for the membrane transport were presented in early days of RO research. Those equations are a set of simple analytical equations that could predict the RO performance under different operating conditions. Recently, software for molecular dynamics (MD) simulation have been used to investigate the detailed structure of the membrane and the movement of solvent and solute in the membrane. The simulation however does not allow easy prediction of RO performance under different operating conditions.

5.0 MODULE

Soon after the discovery of the cellulose acetate membrane was announced, four types of RO modules were designed and constructed. They are plate and frame, tubular, hollow fiber and spiral wound module. After the withdrawal of Du Pont’s polyamide hollow fiber module, spiral wound module, in which polyamide TFC membrane is housed, is dominating particularly for seawater desalination by RO. The module diameter has been increased from 4 inch to 8 inch to enhance the module productivity and even the module with 16-inch diameter was constructed [26]. But still 8-inch diameter is the most popular choice. The improvement of module performance is usually made by designing a new spacer to improve the turbulence near the membrane surface while minimizing the pressure drop.

Another area of improvement is the end-cap that prevents the telescoping effect of the spiral wound membrane and also bypassing of feed solution between the outer surface of rolled membrane leaf and the inner surface of the module. It is important to know the flow velocity, flow direction and concentration of the feed solution inside the spacer filled channel. Many studies have been conducted either by computational fluid dynamics (CFD) [27] or experimental observations using module imaging by particle image velocimetry [28] or by nuclear magnetic resonance (NMR) [29].

6.0 SYSTEM

Recent development in the RO system is mostly in the design of hybrid systems. RO-Evaporator is known to reduce the energy consumption caused by evaporation of water. In RO-UF and RO-MF hybrid systems, UF and MF are used for the pretreatment of feed seawater that is fed to RO. These hybrid systems are gaining popularity to replace the conventional water pretreatment facility. RO-NF hybrid system is also used to remove divalent cations from the feed for RO.

Recently, combining emerging membrane technology such as forward osmosis (FO) and pressure retarded osmosis (PRO) with RO to alleviate the energy consumption in seawater desalination has been proposed as the new hybrid systems. One of such examples is to draw water from waste water into seawater, used as the draw solution, in FO, before diluted seawater is desalinated by RO [30].

In NF-FO-RO, brackish water is first treated by NF to produce desalinated water, then the concentrated brackish water is used in FO as the draw solution [31]. In the hybrid system RO-PRO, the concentrated brine is supplied to the PRO as the draw solution, while solution of low salinity, e.g. wastewater is supplied to PRO as the feed solution [32]. There are two advantages of this hybrid system. One
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It is known that the energy consumption as well as the water production cost of RO is less than desalination processes such as multi-stage flash (MSF) or multi-effect distillation (MED). The energy consumption of seawater desalination and the total water cost were 3-4 kWh/m³ and 0.5-1.2 US$/m³, respectively, in the year 2013 [34]. Development of RO membranes and modules with improved performance and the construction of larger desalination plant have further contributed to the reduction of water production cost. Water production cost depends on many factors and therefore changes from one site to the other.

Shrivastava et al. [35] analyzed the energy consumption in seawater desalination by RO and concluded that the thermodynamic energy required to demix salt and water was about 50% of the total energy requirement. On the other hand, energy required for the flow of water through the membrane was about 15%. The latter energy consumption can be reduced by improved water flux through the RO membrane, which however does not contribute to the reduction of the total energy consumption very much. For the desalination of brackish water, energy consumption of water flow through the membrane is about 30%, since the thermodynamic energy requirement is lower than seawater.

8.0 FOULING

It has been known for a long time that the membrane fouling prevents the wider application of membrane separation processes. Therefore, many researchers attempted to find the cause of fouling and also to mitigate membrane fouling. The research on fouling mitigation has been done mostly by membrane surface modification.

Another important method is the pretreatment of the feed solution. The conventional method of pretreatment involves perchlorination, pH adjustment, flocculation and coagulation, prevention of scale formation by antiscalant. But nowadays the use of UF and MF membranes is becoming more common for the pretreatment of feed seawater, as already mentioned. Typically, the membranes for pretreatment of feed are made of polyethersulfone (PES) and polyvinylidene fluoride (PVDF) and their modified versions, with molecular weight cut-off (MWCO) of 100 to 150 k and pore size of 0.02 to 0.1 μm [36].

9.0 MEMBRANES FOR ORGANIC SOLVENT TREATMENT

Separation processes play a key role in the chemical and pharmaceutical industries, where the chemical synthesis is often performed in organic solvents. The high-valued products have to be separated from the organic
solvent. As well, the organic solvent has to be recovered after the products are removed. Many conventional separation processes can be used for these purposes. Distillation, evaporation, adsorption, extraction and chromatography are the examples. Recently, more attentions are focused on membrane separation due to the substantially lower energy requirement [37] than the conventional processes. The thermal damage of the heat sensitive product molecules due to the room temperature operation of the membrane process is another reason.

However, most of RO works are for desalination and water treatment except for very few that are dealing with the treatment of organic solvents. The reason is that the size of organic solvents is larger than water molecules, which makes the separation by the size exclusion of the solute less effective. Moreover, the electrostatic repulsive force working between the membrane and the solute is much weaker in the organic solvent due to the solvent’s low dielectric constant. Therefore, the charged solute will pass through the pore even when the pore is only slightly larger than the solute. The development of RO membrane for organic solvent remains as one of the future challenges.

Compared with RO, a vast amount of papers have been published on the so-called organic solvent nanofiltration (OSN) [37]. Polymeric membranes for the treatment of organic liquids are fabricated either by the phase inversion technique or by thin film coating on a substrate membrane. For coating various methods such as in-situ polymerization, dip-coating and layer by layer assembly of cation and anion are employed. Nanoparticles are also added to the membrane to fabricate the mixed matrix membrane. Particularly, inorganic membranes play an important role in the treatment of organic liquids because they do not swell in the organic environment. OSN can be used for the following purposes.

Solute enrichment: Solute is separated from solvent to obtain a high-value solute or to recover the solvent. OSN is an excellent alternative to distillation due to mild operating conditions.

Solvent recovery: A large amount of solvent is used in organic synthesis and the solvent is lost unless it is recovered. As well, purification of industrial products often requires a large volume of solvent. Reduction in the amount of solvent used in the industry by solvent recovery is thus necessary.

Solvent exchange: In solvent exchange, the solution changes from being rich in solvent A to solvent B. The main advantage of using OSN in solvent exchange is that a high boiling solvent A can be changed to low boiling solvent B without applying heat.

Purification: After product enrichment, the purification is necessary to obtain high-value products. In fact, the purification process accounts for up to 90% of the total production coast. It should be emphasized that purification is different from solute enrichment because high selectivity is required among different solute species, i.e. the membrane should exhibit high selectivity for one major product component over the other contaminants. In this respect, the current OSN membrane’s selectivity is not necessarily high enough and improvement of membrane is needed to compete with the conventional purification processes such as chromatography and recrystallization.

The commercial applications of OSN are not as much as RO applications for the treatment of aqueous solutions such as wastewater.
treatment and desalination. But it has tremendous potential to become a very important separation process once an appropriate membrane is developed.

10.0 RO APPLICATIONS

The areas of RO applications have not changed since the implementation of RO process. They are mainly in the production of drinking and ultrapure water, production of water for irrigation, for food processing, for the treatment of large amount of wastewater produced in enhanced oil recovery and oil production from tar sand, and the treatment of wastewater produced from the mining industry. Applications in water treatment in space [38] and decontamination of radioactive water [39] are gaining importance.

11.0 CONCLUSION

As a result of this survey, the following conclusions can be drawn:

1) Advanced characterization instruments detected heterogeneity in membrane morphology.
2) The theoretical study of membrane transport made by MD simulation, instead of deriving model equations, enables to reach deeper understanding of the RO membrane structure and membrane transport. However, it is not easy to predict the effect of operational parameters on the membrane performance by MD.
3) MD simulation played a leading role in the research of thin film nanocomposite membrane. However, the impact of the nanocomposite membrane on the membrane industry remains to be seen.
4) Enormous progress in the membrane characterization method contributed to materials science of membrane.
5) The size of the membrane module tends to grow as the RO plant size increases. In the meantime, fluid dynamic simulation and particle imaging technology contributed to better understanding of fluid flow and particle distribution in the membrane module.
6) Design and construction of RO hybrid systems is being attempted to reduce the energy consumption.
7) The water production cost of RO desalination kept decreasing due to the increase in the module size, by adoption of pressure exchanger and improvement of membrane performance. It was said however, that further increase in membrane flux would contribute to cost saving only marginally.
8) To reduce the membrane fouling, the conventional pretreatment system is gradually replaced by NF, UF and MF,
9) Almost all RO applications predicted when RO process was implemented could have been achieved. The applications are now widely spreading.
10) The application of RO for the treatment of organic liquid remains to be seen. In this respect, the development of inorganic RO membrane is very important.
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REFERENCES


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