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**Review Article**

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# Decontamination of water by RO process

**Raaz Maheshwari*[1] and N S Nathawat[2]**

[1]Department of Chemistry, SBRMGC, Nagaur, Rajasthan, India
[2]Department of English, SBDTC, Lakshman Garh, Rajasthan, India
*E-mail: drraazgreenchemacs@gmail.com

## ABSTRACT

Two of the greatest challenges facing the 21st century involve sustainable supplies of clean water and energy, too highly interrelated resources at affordable cost. Membrane technology is expected to continue owing to energy efficiency. However, there is need for improve membranes that have higher flux, are more selective and less prone to various types of fouling, and a more resistant to chemical environment, especially chlorine, of these processes. The article summarizes the Indian water problems and reviews the innovative state-of-the-art reverse osmosis technology existing deficiencies and the opportunities to resolve them.

**Key words:** Reverse osmosis; Electro dialysis; Foiling; Osmotic Pressure; Salt rejection

## Introduction

It has been widely recognized that the depletion of conventional energy resources combine with their environmental impact pose major issues for our society and new technologies must be developed to achieve a sustainable source of energy. It is not so well appreciated that there is an analogous situation in meeting the world's need for water; and this problem is already spreading worldwide. As in the case of energy, new technology is the key to current and future needs, and many companies are investigating heavily to meet these challenges. The ultimate source of this energy is the Sun and the only problem is in capturing solar energy in an efficient and economical way. There is lot of water on the planet, but increasingly this water is of inadequate quality (purity) for human consumption or other beneficial (industrial or agricultural) purposes.

Thus, advance technologies for water purification are the essential part of meeting the current and future needs for water. Membrane process in today's scenario has emerged as a viable means for water purification with desalination. Reverse osmosis being the most common example, but not the only example. Because of their energy efficiency, membranes will grow in importance compared to other technologies. This combined with the growing need to purify more and more water represents a growth opportunity for membrane technology. As membranes are of major interest in polymeric, this represents an opportunity for polymer science. The purpose of the article is to review the current state of polymeric membranes for water purification and to identify areas where improvements are needed. Further background can be found for water purification in number of books and reviews.

## Background

Less than 1 % of all the fresh water on earth is usable by humans. Most fresh water inaccessibly locked in polar ice caps or permanent mountain snow cover. Fresh water only constitutes 2.5 % of the earth's water; the vast majority is salt water. (97%) in the ocean and the smaller remainder is brackish water found in estuaries and salty underground aquifers. Of all the fresh water that humans consume, 70% is used for irrigation, 20% is allocated for industries and only 10% finds domestic use. Clearly, the latter figure is not sufficient to provide drinking water to 1.2 million people across the world. 3.4 million People die each year in India from a water related disease, which is almost the entire city of Los Angeles.

Freshwater availability is also in inextricably linked to energy production. Webber recently described the vicious cycle linking water purification and energy production.[3] Delivery of 1 million gallons of clean water from a lake or a river requires 1.4 megawatt – hours of energy; desalination raises that figure to 9.8-16.5 megawatt-hours for the same amount of clean water derived from sea water. ! Megawatt-hour of electricity produced using coal or oil, however, requires 25 thousand- 60 thousand gallons of water to make the same amount of electricity. Gasoline vehicles consume 7-14 gallons of water for every 100 miles they travel; more "environmental-friendly" vehicles technologies consume even more water. Development of energetically efficient methods of water purification will be key to finding solutions within this cycle. Agriculture consumes 70% of all human fresh water withdrawals. Water shortages, therefore, will limit food production and place pressure on food imports. The growing population, as noted, will also drive up the demand for food. Increased energy cost contributes to elevated fertilizer cost, which in turn, raises total prices. The link between water and food supplies can be illustrated by examining how much water is consumed during the production of various food products. A single hamburger for example, requires 635 gallons water. A glass of milk requires 53 gallons, a single egg requires nearly 36 gallons, and a slice of bread requires 10.5 gallons.[11]

The current and future pressure on water supplies, low cost, high efficiency means of water purification from a variety of sources that have not been traditionally exist to provide large volumes of water needs with desalination. And the high osmotic pressure of sea water makes desalination and energy-intensive process with current technology. Brackish water does not require as much desalination and may represent energetically favorable source. Many other non traditional sources do not require as much desalination and may represent energetically favorable source. Petroleum refining produces large volume of waste water that contains residual oil and refining bi-products. Each barrel of refined oil generates 7-10 barrels of waste water. Each of these sources may be important contributors to water for human consumption, but each has unique separation requirements. Membranes represent energetically efficient solution for carrying out many of these separations.

## Membrane Basics

Before discussing details of water purification via membrane technology, it is important to recognize how the membrane fits into a typical water purification process such as desalination.

### Membrane separations as a Unit Operation

A simplified flow diagram for a membrane-based water purification process is shown in figure 1. In this example there are two membrane separation steps; a membrane pretreatment unit for removal of particulates and other macromolecules followed by reverse osmosis (RO) unit for salt removal and the flow diagram indicates several other process steps related to microbial control (chlorine addition), pH control, particle flocculation, dechlorination (to protect the reverse osmosis membrane), and scaling control. The membrane technologies of primary interest are pressure driven processes where a pressurized feed is supplied to membrane unit to produce purified permeate (product) and some these membrane processes use cross-flow geometry whereby a retentive (or concentrate) containing high level of total dissolve solids (TDS) is also produced.

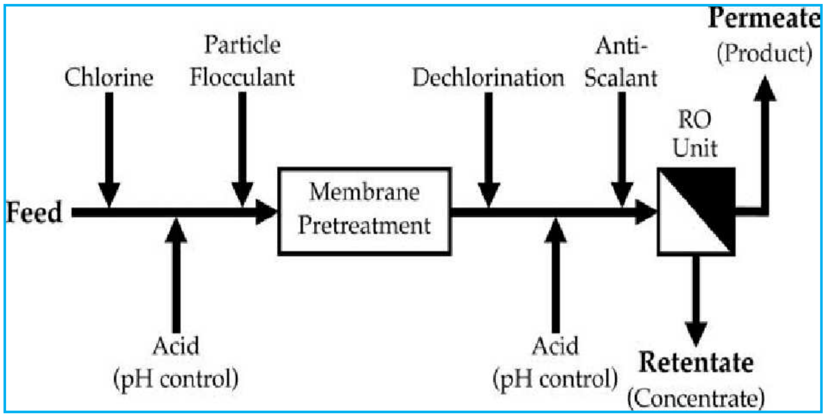


**Figure.1 Simplified process flow diagram of a water purification process involving two applications of membrane technology; one for pre treatment and the other for salt removal via reverse osmosis.**

### Osmotic Pressure

Dissolved solutes in the aqueous feed create an osmotic pressure, thermodynamically defines in terms of the activity of solvent (water) in the solution

$$\pi = -(RT/V_w) \ln a_w \qquad (1)$$

Where Vw is the partial molar volume of the solvent, R is the gas constant, T is the absolute temperature, and Aw is the activity of the solution. For sufficiently dilute solution, equation (1) simplifies to well known van't Hoff equation

$$\pi = C_sRT \qquad (2)$$

Where $C_s$ is the molar concentration of the solute to accomplish purification using a semi permeable membrane, the applied trans-membrane pressure difference must be greater than the osmotic pressure difference between the feed and the permeates solution. The flux of water through the membrane can, therefore be positive (in the direction of the solution of the lower solution concentration) or negative (in the direction of the solution of higher concentration) depending upon the applied pressure difference as illustrated in figure 2.

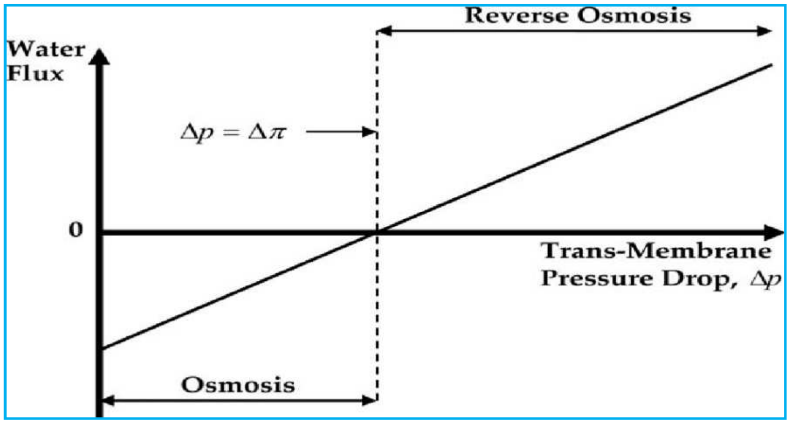


**Figure.2 Membrane flux versus an applied pressure for cellulose acetate membrane pressure difference, with a given osmotic pressure difference.**

**Table.1 Osmotic Pressure for Typical Feed Solutions (25 8C)**[28]

| Solute or Solution | Total Dissolved Solids (mg/L) | Molar Concentration (mol/L) | Osmotic Pressure (psi) | Osmotic Pressure (bar) |
|---|---|---|---|---|
| Brackish Water | 2,000–5,000 | – | 15–40 | 1.0–2.7 |
| Seawater | 32,000 | – | 340 | 23.4 |
| NaCl | 2,000 | 34.2 | 22.8 | 1.7 |
| NaCl | 35,000 | 598.9 | 398 | 27.4 |
| $NaHCO_3$ | 1,000 | 11.9 | 12.8 | 0.883 |
| $NaSO_4$ | 1,000 | 7.1 | 6.0 | 0.41 |
| $MgSO_4$ | 1,000 | 8.3 | 3.6 | 0.25 |
| $MgCl_2$ | 1,000 | 10.5 | 9.7 | 0.67 |
| $CaCl_2$ | 1,000 | 9.0 | 8.3 | 0.57 |
| Sucrose | 1,000 | 2.9 | 1.05 | 0.0724 |
| Dextrose | 1,000 | 5.5 | 2.0 | 0.14 |

The data in the table 1 represents the reasonable range of osmotic pressure to the expected for water purification application and it is important to note that osmotic pressure is highly dependent on the salinity and the composition of the solution. Note that the osmotic pressure is sensitive to the total concentration of species (ions and molecules) in solution.;Therefore, in table 1, the brackish water sample with a TDS of 2000 mg $L^{-1}$ solution of sodium chloride. This is due to the presence of heavier ions (in terms of molar mass) in the brackish water sample.

## Membrane Characteristics

Membranes are generally classified as isotropic or anisotropic. Isotropic membranes are uniform in composition and physical nature varies across the cross-section of the membrane. Isotropic membranes are non uniform over the membrane cross-section, and they typically consist of layers which vary in structure and / or chemical composition. Isotropic membranes can be divided into various sub categories. For example, for isotropic membranes may be micro porous. Micro porous membranes are often prepared from rigid polymeric materials with large voids that create interconnected pores. The most common micro porous membranes are phase inversion membranes. These are produced by casting a film from a solution of polymer and solvent and immuring the cast film in non solvent for the polymer and most polymers used in such applications are hydrophobic, so what is the most common non solvent. Upon contact with water, the polymer precipitates to form the membrane. Another type of micro porous membrane is the track / etched membrane and this type od membrane is prepared by irradiating a polymer film with charge particle that attack a polymer chain, leaving damaged molecules behind. This film is then passed through an etching solution, and the damaged molecules dissolve to produce cylindrical pores many if which are perpendicular to the membrane surface. A less common micro porous is an expanded / film membrane. These are oriented crystalline polymers with voids created by extrusion and stretching process. Isotropic membranes can also be dense films which either lack pores or contain pores that are so small as to render the membrane effectively non porous and these films are prepared by solution casting followed by solvent evaporation or melt extrusion.

There are main two types of anisotropic membranes: phase separation membranes and thin film composite membranes. An isotropic phase separation membrane is often called Loeb/Sourirajan membranes, referring to the people who are credited with initially developing them. Such membranes are produced by phase inversion techniques such as those described above, except that the pore sizes and porosity vary across the membrane thickness and it often consist of a rather denser layer of polymer on the surface of an increasingly porous layer and the thin film composite membranes are both chemically and structurally heterogeneous and they usually consist of highly porous substrate coated with a thin dense film of different polymer. They can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment. The description above of anisotropic and isotropic membranes refers to flat sheet configurations. However membranes can also be produced as hollow fibers. Like flat sheets these fibers can either be isotropic or anisotropic and they can be dense or porous. One advantage of hollow fiber membrane is that they have more surface area per unit volume than flat sheet membranes.

**Reverse Osmosis Membranes**

There are at least 4 requirements for a commercially viable reverse osmosis membrane system for desalination. First, the membranes must be made from a polymer that intrinsic characteristics are capable of giving adequately high water permeation and low salt permeation rates. Second, to achieve the high flux needed, the membrane layer that does the abrasion must be made very thin, viz., about 100 nm in thickness. However, the membrane needs to have sufficient mechanical integrity to be assembled into a module and to with stand the driving pressure in pores, that is, several times the osmotic pressure of the salt solution to be purified. Thin dense layer (skin) over laying a porous support structure, has proven to be the ideal way to meet these opposing requirements as stated in figure 3.

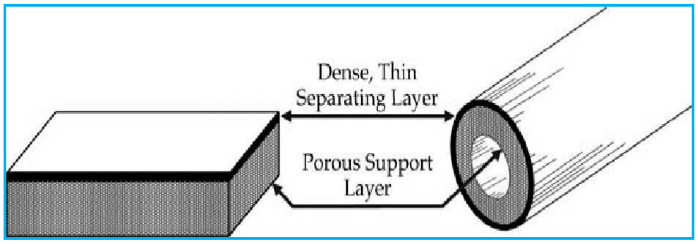


**Figure 3 Schematics for flat sheet (left) or hollow fibers (right) where each has a dense, thin selective separating layer supported by a porous layer**

Third, these membranes must be assembled in a way that provides a high membrane area per unit volume of the pressure vessel and there 4 types of membrane modules that have found some commercial utility: tubular, plate and frame, hollow fibers and spiral wounds as illustrated in figure 4.

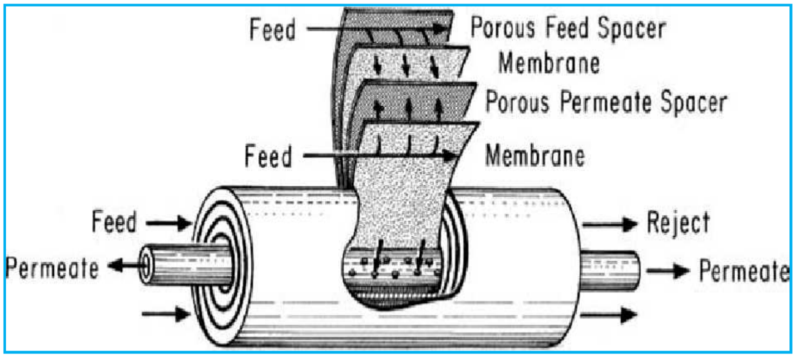


**Figure 4 Spiral wound module**

The following sub sections review the development of membranes that meet most of the above requirements, the current state of art and some of the possibilities for the next generation membranes and the last half century has seen remarkable evaluations of the membrane technologies for this purpose.

The first commercially useful reverse osmosis membranes were made from cellulose acetate. Cellulose acetate films were capable of much higher salt rejection than other polymer considers. The break through that made reverse osmosis viable process, and ultimately membrane separation of gases was the discovery of Loeb & Souriagam. Figure 5 shows the flux and rejection characteristics of experimental asymmetric cellulose acetate.

As the degree of acetylation of the cellulose acetate increases, membranes made from them exhibit higher salt rejection but the flux decreases. Some of the best membranes reported consist of blends of 39.8 wt% acetatylat polymer with small amount of cellulose acetate butyrate sea water salt rejection of 99.0-99.5 % with, which is close to the theoretical limit, were achieved but fluxes were modest and they also have an advantage as their resistant to the chlorine added disinfect the feed water which is advantageous for application with significant bacterial content. However, these membranes do hydrolyze overtime; the rate is at minimum in the pH range of 4-6.

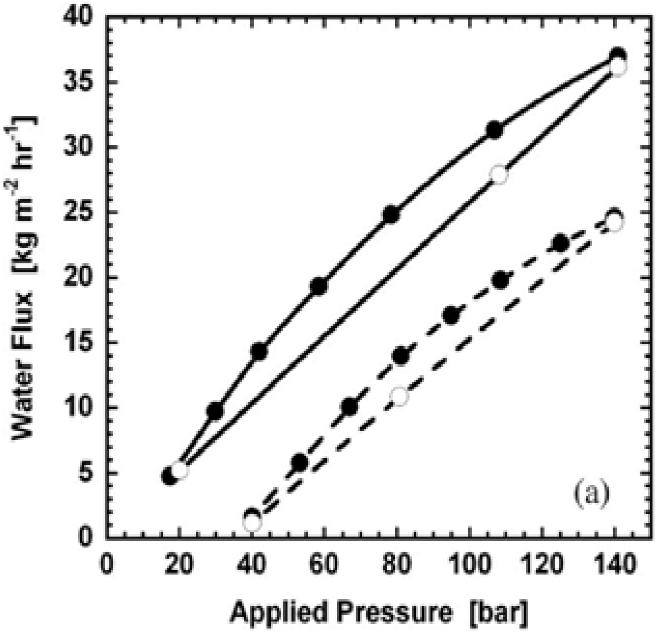


**Figure 5(a) Water Flux versus applied pressure for a cellulose acetate membrane**

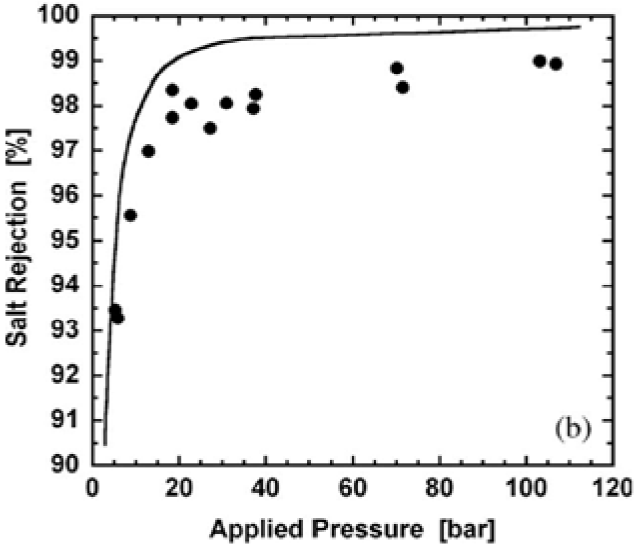
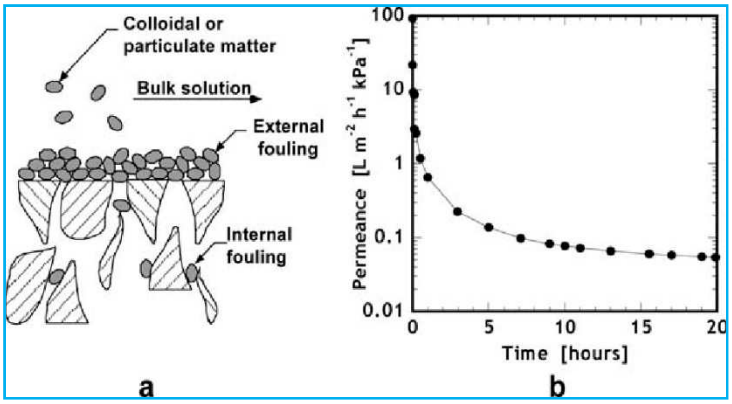


**Figure 5 (b) Predicted salt rejections based on water and salt permeability measurements and Experimental data.**

**Ways of preventing foiling of membranes**

Fouling is the deposition of colloidal or particulate matter in a membrane's pores or on its surface that leads to the changes in membrane transport characteristics as shown in figure 6. As water containing particulates, colloids, macro molecules, or microbes is filtered through a membrane, and the foreign material deposits inside the porous structure and onto the surface of the membrane, creating a cake layer which drastically reduces water flux and affects overall membrane rejection performance figure 6.



Because of foiling, the flux declines which results in significant increases in the cost of membrane operations due to the required membrane cleaning, periodic membrane replacement and increase energy input to achieve high flux.
Different kind of membranes experience different kinds of foiling. For example, pore flow membrane are subjected to surface foiling caused by particulates adsorption to the membrane's surface while internal foiling is the result of foulant entrainment in the membrane pores. Non porous reverse osmosis membranes, in contrast, undergo surface fouling only. Internal foiling is largely irreversible entrained in the membrane cannot be easily removed, even with harsh chemical or mechanical cleaning. Surface foiling may be reversible or irreversible. Reversible surface fouling consist of foulants that may be removed by cleaning and some particulates, especially after extended exposure to the membrane surface, are so strongly adsorbed to the membrane surface that they cannot be removed, constituting irreversible surface fouling.

Surface modification has developed as a popular means of reducing the fouling propensity of many types of membranes. Surface modification aims to change the surface property of the membrane while maintaining its selective structure while reducing fouling, flux is maintained at a high level, resistant to fouling also lessens the need to clean the membranes. Cleaning can be accomplished in many ways as such as through back pulsing, gas sparging, increasing share at the membranes of surface or UV radiation. Chemical agents such as ozone, acids, bases or chlorine may be used. But these compounds may pose environmental consequences or even degrade the membrane structure. In water treatment hydrophilic membranes show reduce fouling because of its affinity for water and water is strongly bound to a highly hydrophilic membrane surface; and foulants interact only with the water layer and not with the membrane surface and to increase the surface hydrophilicity of a membrane, two types of surface modification appears, may be coated or grafted.
Grafting of hydrophilic changes may be used as an alternative to the dense coating layer but foulants may still be able to find their way inside the membrane structure. Hydrophilic polymers can be grafted directly to membrane surface by a variety of methods. Chemical grafting to the surface provide a more stable structure than simple adsorption of hydrophilic polymers to the membranes. Grafting can be achieved by inducting polymerization from the membrane surface or by tethering polymer chains to the surface. Photo – initiated graft polymerization as been used to attach a variety of monomers to the polyethersulfone membrane by inducing radical in the PES backbone and grafting by photo polymerization has been carried out in membrane architecture other than the flat sheet such as micro porous membranes.[12]

## Other Membrane Processes

### Forward Osmosis

Water can be purified from a process known as Forward Osmosis whereby water from the feed solution is driven through the membrane by a draw solution of lower solvent chemical potential, thus, the driving force for water transport is the Osmotic Pressure difference across the membrane. So, it's a process used to extract high quality water from low quality feed water using a semi-permeable membrane and high osmotic pressure solution. As long as an effective, easily removable, and recyclable draw solvent can be used, for what Osmosis desalination could potentially be less energy intensive process than RO. One critical challenge is the design of membrane itself. Specifically, the challenge is to design the membrane that reduces both internal and external concentration polarization, where the former is believed to be of a greater challenge. Of course, as is the case with the most membrane base separations, membranes with high flux and high rejections are required. Furthermore, fouling issues are also applied to forward osmosis system. These issues represent areas where development in polymer science and membrane design could aid the development of forward osmosis technology.

**Power Generation**

Purification of water consumes energy; however, in principle it is possible to turn this surround and generate power using the differences in salinity of two bodies of water. This concept was first proposed by Loeb & was termed pressure-retarded osmosis. Many areas exist where industrial water (such as sewage or treatment plants) discharge substantial volume of fresh or low salinity water into the ocean; such locations could be ideal for prototype salinity gradient systems to do this requires membrane based generating system. If fresh water and salt water streams are allowed to flow across flow past a reversible osmosis membrane, there will be tendency for the fresh water to permeate through the membrane into the salt water (osmosis) at a flux equal to $-A\Delta\pi$ or the $\Delta p = 0$.If their salt solution is pressurizes to $\Delta p<\Delta\pi$, osmosis still occurs but the volume flow across the membrane against the pressure can do work.

$$\text{Water flux} = A\,[\Delta p-\Delta\pi]$$

The theoretical power generation per unit area for a membrane is given by;

$$\text{Theoretical power} = \text{flux}\ \Delta p = A\,[\Delta p-\Delta\pi]\,\Delta p$$

The potential power will be of parabolic form when plotted $\Delta p$, and goes to zero when $\Delta p=0$ or $\Delta p=\Delta\pi$, and the maximum power generation possible occurs when $\Delta p = (1/2)\ \pi$ and is $A(\Delta\pi)^2/4$.

**Electrodialysis**

Desalination of power generation could be accomplished using electrodialysis and reverse electrodialysis. It is generally accepted that electrodialysis as a desalination process, is limited to brackish or ultra high purity water application due to high level of energy that would be used in sea water technology. Electrodialysis and reverse electrodialysis rely on the implementation of both cationic and anionic membranes where cationic membranes have negative fixed charge group and anionic membranes have positive fixed charge group. Membranes for both processes must be able to transport ions with very high selectivity to either purify water or regenerate electric power efficiently. Membranes must have low electrical resistance and high ion selectivity; both of this characteristic membrane has been shown to be dependent on membrane charge density.

## Summary and Conclusion

The global challenge of providing safe water for human use, agriculture and manufacturing for an ever-growing a shifting population poses an opportunity for innovation in polymer chemistry, physics and engineering. In many ways, the supply of energy is intimately connected to that of water as pointed out here. And because of their energy efficiency another advantage, membrane processes will become the dominant technology for water purification. However, to meet the needs of the future, better membranes and a membrane processes must be developed.

In nearly all cases, water purification process would benefit from membranes with higher productivity and selectivity; both are determined by membrane structure. The physical morphology of all practical membranes is complex. Better ways are needed to control and analyze their structure and assess its impact on transport of water, solutes and particulate matter. For membranes, which function by pore flow mechanisms, the selectivity of the membrane is determined by the size, distribution and interconnectivity of these pores plus surface and charge interactions. For membranes which function by a solution diffusion mechanism, there must be an extremely thin dense layer to achieve a high Flux but with few defects to realize the intrinsic selectivity of the polymer. There is dearth of systematic studies of the relation between transport behavior and polymer molecule structure. The polymer literature has not been addressed at any level fundamental issue of characterization and behavior of thin films with thickness of the order of 100 nm or less in an aqueous environment. These layers must be supported on some form of porous substrate made of the same or a different polymer. Understanding and optimizing polymer morphology of these types would pay huge dividends.

Membranes are also prone to fouling via a variety of mechanisms; biofouling processes are the most troublesome. Solving, at least managing would have huge impact for society. Contemporary approaches include grafting polymer chains to the membrane surface, addition of highly permeable coatings, manipulation of surface charge. Innovations in these or other approaches are critically needed. Increased membrane durability or life-time is another way to affordability. The polymer used must be robust enough to survive aggressive environment for years.

This includes operating over a wide range of ph and conditions where hydrolysis reactions and many forms of undesirable biologically driven chemistry are possible. One particular problem is the resistance used to disinfect water and curb bio-fouling.

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