

Recent development in membrane science and its industrial applications

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The word membrane comes from Latin word, “membrana” that means a skin (Jones, 1987). Today’s word “membrane” has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi permeable properties. Physically a membrane could be solid or liquid. Its function is as a separation agent that very selective based on the difference of diffusivity coefficient, electric current or solubility.

Actually membrane has become an integral part of our daily lives. All cells composing living things, including ours are surrounded with membrane. Biological membranes (membrane cells) are very selective that transfer only particular species.

Synthetic membrane history began in 1748 when French Abble Nollet demonstrated semi-permeability for the first time, that animal bladder was more semi-permeable to water than to wine. One century later, Fick published his phenome-

nological law of diffusion, which we still use today as a first-order description of diffusion through membranes. He was also the first man to prepare and study artificial semi-permeable membranes. These membranes were made from an ether-alcohol solution of cellulose called “colloidion”. After that many researches were done and many inventions were found such as dialysis, different permeability of gases at rubber, osmotic pressure, and Donan’s ion equilibrium phenomena.

Sartorius Werke GmbH, Germany manufactured industrial scale membranes, microfiltration membranes, for the first time in 1950. Before that, membranes were developed in small scale for laboratory applications (Lonsdate, *et al.*, 1982). However, the most fundamental breakthrough in membrane technology came in late 1950s when Loeb and Sourirajan discovered very thin membranes for reverse osmosis, the asymmetric membranes.

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Nowadays membrane applications spread over various industries: metal industries (metal recovery, pollution control, air enriching for combustion), food and biotechnology industries (separation, purification, sterilization and byproduct recovery), leather and textile industries (sensible heat recovery, pollution control and chemicals recovery). Other industries that also use membrane technology are pulp and paper industries (replacing evaporation process, pollution control, fiber and chemicals recovery), and chemical process industries (organic material separation, gas separation, recovery and recycle chemicals). Medical sector including health-pharmaceutical-and medical industries (artificial organs, control release (pharmaceutical), blood fractionation, sterilization and water purification), and waste treatment (separation of salt or other minerals and deionization).

Generally, there are several processes to synthesize membrane, some of them are sintering, stretching, track-etching, phase inversion, and coating. There are several ways to classify membranes. Based on their materials, membranes are classified as polymeric membrane, liquid membrane, solid (ceramics) membrane and ion exchange membrane. Based on their configuration, membranes are classified as flat (sheet) membrane, spiral wound, tubular, and emulsion. Based on what they do and how they perform, membranes are classified as fine filtration (microfiltration/MF, ultrafiltration/UF, nanofiltration/NF, and reverse osmosis/RO), dialysis, electro dialysis (ED), gas separation (GS), carried-mediated transport, control release, membrane electrode, and pervaporation (PV).

Membrane processes

Membrane processes discussed in this paper are classified based on various driving forces, some use pressure difference (microfiltration, ultrafiltration, reverse osmosis, and piezodialysis), while others use other driving forces such as concentration difference (gas separation, pervaporation, liquid membrane and dialysis), thermal (membrane distillation, thermo osmosis)

and electric (electrodialysis).

The principal advantages of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness. Membrane-based separation is a result of different rate of transfer between each substance in membrane and not a result of phase equilibrium or mechanically based separation. Therefore, there is no need to add additive material such as extractor and adsorber to proceed the separation. Then we can say that membrane technology is "clean technology", in which no additive materials, which may be potential pollutants, are needed.

One of the major advantages of membrane technology is low energy consumption. As discussed elsewhere in this paper, membrane-based separation is not a result of phase equilibrium that takes a lot of energy to achieve and maintain. It also means that the process could be done in normal conditions where no phase change occurs. Phase change may affect the quality of materials and products. Therefore, membrane technology is suitable for the pharmaceutical, biochemical and food industries.

Designs of membrane module are very simple, compact and easy-to-use. In addition, not much auxiliary equipment is needed. There is a unique phenomenon in membrane where the scale of process and operating costs are related proportionally. This phenomenon may be caused by the modular-nature of membrane. This nature distinguishes membrane processes from other processes such as distillation, in which an increase in the process scale is followed by a decrease in cost until economical condition is reached. Not only in cost spent, but also in operating condition. Adding several modules including its auxiliary to existing system can do scaling up membrane processes.

Besides the advantages described above, membrane processes also possess several disadvantages, such as flux optimization and selectivity, material sensitivity, fouling and dependability. Until now there have been several studies conducted to overcome the disadvantages and

drawbacks in membrane processes.

Flux and selectivity problems arise as an increase in flux is usually followed by a decrease in selectivity, while we aim at increasing both. Therefore membrane processes are suitable for very selective separation in which flux is not concerned such as that carried out in pharmaceutical industries.

The dependability problems arise as the characteristics of membrane differ from each other. It is due to the different characteristics of each membrane that a direct scale up of membrane processes is virtually impossible. Before a process is applied in an industrial scale, it is suggested to have a laboratory assessment of the membrane. In this way we may have better prediction on process performance.

Other major problems are material sensitivity and fouling. Polymeric membranes have limited stability (chemically, physically, and biologically), which restrict the conditions of membrane processes applied. Nowadays, there are efforts to invent materials, which may overcome these constraints. Fouling causes a decline in performance of membrane processes, in which flux (performance) is very high initially but then decline drastically as materials of foulant accumulate on membrane surface. Solutions to the problem may lie in the hydrodynamic of the process and pretreatment processes.

Membrane industry and market potential

Membrane-based market industry covers the membrane itself and its module, including additional equipment and the systems. Commercial success is one of indicator showing the important role played by membrane technology in various applications. The benefits in membrane process applications include reduced operating costs relative to competitive technology, saving of product, recovery of by-products, savings of water, energy, chemical, etc. In effluent reduction applications, savings in transport and disposal cost become important (Srikanth, 2000). Membranes and membrane processes are used in four main areas, which are, in the separation of molecular and particulate mixtures, in the controlled

release of active agents, in membrane reactors and artificial organs, and in energy storage and conversion systems. Membrane has become a multi billion-dollar business and is still growing fast. The worldwide membrane market in 1998 particularly in sales of membrane and modules reached more than 4 billion USD. While sales of membrane system reached more than 15 billion USD (Strathmann, 2001). Figure 1 shows annual sales of membrane and modules for various membrane processes. It can be seen that the sales were increased over the years and reached a value of approximately 4500 million USD in 1998.

From the applications view, approximately 40% of membrane sales are destined for water and wastewater applications, while food and beverage processing combined with pharmaceuticals and medical applications account for another 40% of sales and the use of membranes in chemical and industrial gas production is growing (Wiesner and Chellam, 1999). The total membrane market is unevenly distributed, 75% of the market share belongs to USA, Japan and Western Europe (Srikanth). The development of membrane market is determined by energy costs, required product quality, environmental protection needs, new medical therapies, and the availability of new and better membranes and membrane processes (Strathmann, 2001).

Some applications of membrane processes, such as water desalination or wastewater treatment, have high industrial relevance. However, in these applications the membrane processes compete with conventional water desalination or water treatment techniques, such as multistage flash evaporation or biological sewage treatment plants. In other applications of high commercial relevance, such as in hemodialysis or in fuel cells, membranes are key components, and no economic alternative technique that could compete with membrane is currently available. There are other applications, such as the production of ultrapure water, where membrane processes compete with conventional techniques, but have a clear advantage. There are also a large number of membrane applications of lower industrial relevance, such as

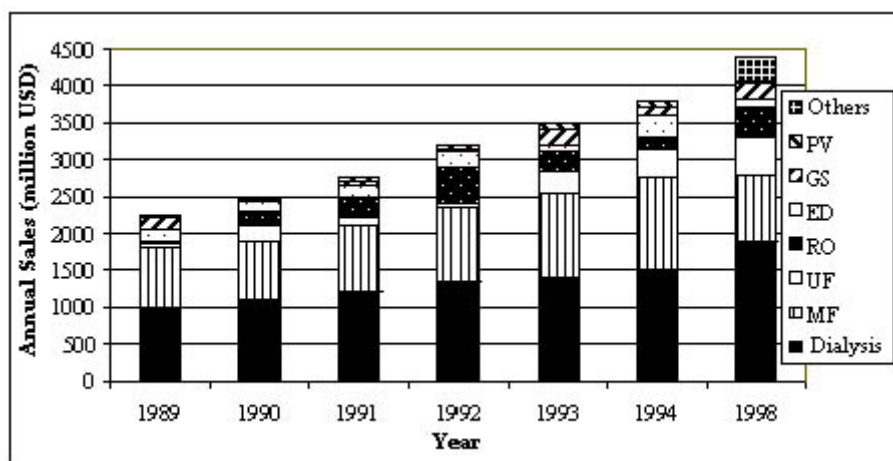


Figure 1. Annual sales of membrane and membrane modules for various membranes processes worldwide.

Note: All data only cover membrane and modules membrane sales, and do not include sales of support system (Strathmann, 2001; Manem and Sanderson, 1996)

the dehydration of organic solvents by pervaporation or the recovery of organic vapors from waste air streams by gas and vapor permeation membranes. In certain biosensors and diagnostic devices, membranes are key components, but in terms of the total costs of the final device, the cost of the membranes in these devices is negligibly low. Therefore, this application is often of lesser interest to the membrane producing industry (Strathmann, 2001). As the membrane market has grown, the scale of membrane facilities has become more ambitious. The first UF facility for potable water treatment, inaugurated in 1988 at Aubergenville, France, had a design capacity of 160 m³/day. Today, facilities' exceeding 100,000 m³/day is being planned (Wiesner and Chellam, 1999).

In spite of impressive sales and growth rate of the industry, the use of membranes in industrial-scale separation process is not without technical and economic problems. Technical problems are related to insufficient membrane selectivities, relatively poor transmembrane fluxes, general process operating problems, and lack application know-how. Economic problems originate from

the multitude of different membrane products and processes with very different price structure in a wide range of applications, which are distributed by a great number of sales companies, very often as individual products (Mallevalle *et al*, 1996).

In future, the largest market for membrane will continue to be water treatment, with sales to manufactures of consumer water purification equipment becoming more important. The primary group of customers (electric utilities, industrial water users and municipal water works) will continue to dominate demand in this sector, but this segment is rapidly maturing and sales are increasingly dependent upon replacements for existing systems. In addition, as both the physical and chemical means of cleaning membranes continue to improve, the average life span of the membranes is lengthening, thus reducing replacement sales (Wiesner and Chellam, 1999).

Emerging processes (Strathmann, 2001)

Development of improved membranes and membrane materials Significant progress has been made during recent years in the develop-

ment of new membranes and their applications. New inorganic and organic materials, super molecular structures with specific binding properties, are used as membrane materials. For the separation of gases, especially oxygen/nitrogen and methane/carbon dioxide, new glassy polymers and inorganic materials such as zeolites are used to produce membranes with better selectivity and higher fluxes. For the separation of enantiomers, carrier-facilitated transport membranes are produced using molecular imprint techniques. In reverse osmosis, membranes with better chemical stability and higher fluxes are now available. Surface-modified membranes with better compatibility and affinity membranes for the removal of endotoxins or other toxic components from blood may soon be available. The recent development in membrane technology have been assisted by new research tools, such as atomic force microscopy, acoustic time-domain reflectometry, molecular dynamic simulations, and computer-aided process design.

High-performance reverse-osmosis membranes The Nitto Denko Corporation has led the progress that has been made in improving reverse-osmosis seawater desalination membranes during the last 20 years, which shows the salt rejection in excess of 99.5% and the water flux of various membranes by a factor of 3. The reason for this significant progress is based on the preparation technique of the barrier layer of the composite membrane, which has many folds, with the result, that the surface of the actual barrier layer is about three times larger than the area of the support structure.

Stabilization of supported liquid membranes One of the shortcomings of today's supported liquid membranes is their short useful life. In thin membranes the solvent or carrier can be lost within several hours, which makes the membrane useless. The stability of liquid membranes can be increased drastically up to 1000 hours by placing a thin polymer layer on top of the liquid membrane.

Preparation of composite hollow fiber by the triple-nozzle spinneret Asymmetric hollow

fiber or capillary membranes with a denser skin on the in- or outside of the fibers are generally made by a phase-inversion process. Dip-coating process is mostly used to produce composite hollow fiber membrane although it require additional production step. A triple-nozzle spinneret was developed for the preparation of composite hollow-fiber membranes. The main advantage of composite hollow fibers made in one step with the triple-nozzle spinneret compared to those made by dip-coating is a simplified production process because it can be done in a single production step. Generally, higher fluxes are also obtained in the single-step production, since pore penetration, which is often a problem with dip-coating, is avoided.

Inorganic membranes for gas and vapor separation with high selectivity Historically, inorganic membranes are produced by a slip-coating and sintering procedure based on metal oxides such as $\alpha\text{-Al}_2\text{O}_3$. These membranes can be considered as state-of-the-art structures and are used today in micro- and ultrafiltration. An interesting recent development is the preparation of zeolite membranes. Because of the unique properties of zeolite crystals such as molecular sieving, ion exchange, selective adsorption, and catalysis, these membranes have a large number of potential applications in gas and vapor separation and in membrane reactors and chemical sensors. Dense inorganic membranes based on palladium and palladium alloys have been used for many years for the selective transport of hydrogen. However, their large-scale industrial applications are limited due to high price of the metal. Dense ceramic membranes based on perovskites exhibit high mixed electronic and oxygen ion conductivity, and are widely studied for applications in solid oxide fuel cells, oxygen sensors, and membrane reactors. An increasingly important research area is related to nanoporous ceramic membranes with well-defined pore structures prepared by template-assisted, self-assembling methods. Furthermore, an increasing amount of research effort is concentrated on the development of proton-conducting membranes for high-temperature applications in fuel cells and

membrane reactors.

Development of improved membrane modules The overall performance of the state-of-the-art membrane modules, such as the plate-and-frame, the spiral-wound, and the hollow-fiber and capillary membrane modules has been improved gradually over recent years, and production costs have been reduced significantly. However, only very few completely new module concepts have been developed. Two exceptions are the so-called transversal flow capillary membrane module and the spiral-type tubular module. The transversal flow module is used mainly in dialysis. The characteristics of these modules are straight membrane capillaries and axial flow through the fiber lumen and the shell. In spite of the poor flow distribution, and thus mass transfer, at the shell-side membrane surface, this type of module is preferred because of its high packing density and low production costs. Spiral-type tubular membrane module involves flow around a curved tube at a sufficiently high velocity so as to produce centrifugal instabilities and secondary flow from the membrane surface to the center of the tube, and results in a substantial increase in flux. However, higher production costs and poor performance of the spiral-type membrane modules have so far limited any large-scale industrial applications.

Development of novel membrane processes and applications New membrane processes that give a large breakthrough in its applications are demineralization by electrodeionization technique, new application in biomedical science, and application in fuel cells. Actually, a significant development has been made in another process, for example, in controlling waste gas emission by membrane contactor and membrane reactor, for both chemical as well as biological conversion. Development in membrane reactor for dehydrogenating reaction, esterification, and enzymatic reaction, seem very prospective that has been developed for a long time, however, until today its industrial application has not been seen yet. It is the same as membrane contactor for emission control. Typical study and empirical data show a large potential of this process; however, its ap-

plication has also not been seen yet.

Electrodeionization and the use of bipolar membranes Electrodeionization are used for the production of deionized water of high quality by combining conventional ion-exchange techniques with electrodialysis. The process can be operated continuously without chemical regeneration of the ion-exchange resin. The only disadvantage of the process is the relatively poor current utilization. Bipolar membranes are used today in combination with regular ion-exchange membranes for the production of acid and bases from the corresponding salts in a process referred to as electrodialytic water dissociation. A bipolar membrane consisting of a cation- and an anion-exchange layer arranged in parallel between two electrodes. As in electrodialysis, up to 100 cell units can be stacked between two electrodes. Electrodialytic water dissociation is a very energy efficient way. However, there are still severe problems, such as salt leakage into the products and low current utilization at high concentrations of the acid and bases.

Membrane contactors In membrane contactors the membrane functions as a barrier between two phases that avoids mixing but does not control the transport rate of different components between the phases. The membrane pores are sufficiently small that capillary forces prevent direct mixing of the two phases. A key advantage of membrane contactors is a large mass-transfer area in a relatively small device. A typical large-scale application of a liquid/gas contactor is the removal or delivery of dissolved gases from or to a liquid, for example, the blood oxygenation during open-heart surgery, the removal of oxygen during the production of ultrapure water, and the separation of olefin/paraffin gas mixtures.

Membrane reactors A membrane reactor is a device that utilizes the properties of a membrane to improve the efficiency of chemical or biochemical reactions. Various forms of membrane reactors are applied mainly in catalytic and enzymatic reactions. In the simplest form of a membrane reactor the membrane is used as a contactor that separates the catalyst from the reaction

medium. The membrane merely provides a large exchange area between the catalyst and the reaction medium, but performs no separation function. It is often used in cell culture and fermentation processes such as the enzymatic degradation of pectin in fruit juice. In the second type of membrane reactor the membrane shows the selective mass-transport properties, and is used to shift the equilibrium of a chemical reaction by selectivity removing the reaction products, for example, in dehydrogenation or oxygenation reactions such as the dehydrogenation of n-butane. The third type of membrane reactor combines the membrane contactor and separation function, such as in enzyme catalyzed deesterification reactions.

Membranes for fuel cells / electrolysis (Srikanth) One breakthrough in the application of ionic conducting polymer membranes is the proton exchange membrane fuel cell, a device that converts chemical energy directly into electrical energy without burning. As the electrochemical combination of hydrogen (the fuel) and oxygen produce water, the fuel cell is environmentally clean and is expected to replace the gasoline engine or rechargeable battery in the automobiles.

Synthetic membranes in medical applications Biomedical applications are by far the most relevant use of synthetic membranes. Membranes are used in medical devices such as hemodialysers, blood oxygenators, and controlled drug-delivery systems. There is, however, a substantial effort focused on the development of the membrane for the next generation of artificial organs, such as the artificial liver or artificial pancreas. In this device, as in other novel vehicles for the delivery of cell and gene therapy, synthetic membranes are combined with living cells to form so-called biohybrid organs.

Breakthrough in industrial application

Membrane processes cover a wide-range of application from (waste) water treatment to medical application. For some application, membranes play an important role in which other technologies are not capable such as in medical

sector (hemodialysis) and energy sector (fuel cell). Table 1 shows a list of selected industrial applications of membrane processes.

From Table 1, it can be seen that pressure-driven membrane processes dominate the application rather than other driving-force membrane processes. Yet, it does not mean that other driving-force membrane processes are not having part in

Table 1. Selected Industrial Applications of Membrane Processes (Mulder, 1996; Rautenbach and Albrecht, 1989; Wenten)

Industrial Sector	Membrane Processes
Drinking water	NF, UF, RO
Demineralized water	RO, ED, EDI
Wastewater Treatment	
Direct (physical)	MF, NF, RO, ED
MBR	MF, UF
Food Industry	
Dairy	UF, RO, ED
Meat	UF, RO
Fruit and vegetables	RO
Grain milling	UF
Sugar	UF, RO, ED, MF, NF
Beverages	
Fruit juice	MF, UF, RO
Wine and brewery	MF, UF, RO, PV
Tea factories	MF, UF, NF
Biotechnology	
Enzyme purification	UF
Concentration of fermentation broth	MF
SCP harvesting	MF, UF
Membrane reactor	UF
Marine biotechnology	MF, UF
Medical	
Control release	UF
Hemodialysis	RO, UF
Chemical industry	
Gas separation	
Hydrogen recovery	GS
CO ₂ separation	GS
Vapor-liquid separation	
Ethanol dehydration	PV
Organic recovery	PV
Chlor-alkali process	Membrane electrolysis
Energy	
Fuel-cell	Proton exchange membrane

industrial sectors. GS (gas separation) and PV (pervaporation), which are concentration-driven membrane process, are used in chemical industry sector for gas separation and vapor-liquid separation. In USA and EU, the most important sector that using membrane technology is food industry especially dairy sector. Membranes are used for desalting and concentration of whey, and also for conversion of milk into cheese and preparation of egg white and egg yolk. Fruit and vegetable processing also utilized membrane technology resulted in high energy saving. Beverage industry also an important sectors in which to apply membrane process particularly for separation of alcohol from beer. In sugar sector, membranes are used in almost 20% of the potential application in Netherlands (Rachwal *et al.*, 1994). In chemical industry, beside listed in table above, electrocoat paint recovery still the biggest industry sector that utilizes membrane-based processes particularly UF. Other sector that predominant for UF application is pure water supply for semiconductor industry. High-demand for ultra-high purity chemicals in same industry also fulfilled by the availability of chemical-resistant membrane. In biotechnology, purification of enzyme can be accomplished using UF. In medical sector, membranes play a key role particularly in hemodialysis and control release process. Water-oil separation now also become a potential application for UF especially in metal cleaning and wool scouring processes (Nuner and Peinemann, 2001).

Membrane technology also makes a breakthrough in water treatment. A revolutionary water treatment process was accomplished by corporate membrane into the treatment process resulting in high effluent quality. Water treatment has become an important issue regarding to the fact of the scarcity of clean water sources. A huge supply of water that covers the earth in form of ocean can not fulfilled the needs of water readily considering conventional desalination process that must be done before it can be used as potable water. Desalination with distillation process popular in 1970's is not attractive anymore because of its high capital cost and wide space demand. In

area with high minerals content, distillation process are also susceptible to corrosion.

Conventional water treatments are not capable in producing potable water that fulfilled the requirement of water quality standard that becoming more stringent nowadays. An advanced water treatment like ozonation and activated carbon can improve water quality but on other hand add in a difficulty in operation and cost. Membrane technology offers one or two simple steps to overcome it. Membrane as highly selective layer is capable to separate microorganisms' pathogen completely. Membranes are also capable of reducing hardness, controlling color, and removing inorganic and organic compounds. Four membrane processes have direct application for potable water treatments are RO, NF, UF, and MF. These pressure-driven processes differ in the size of the membrane pores, types of constituents removed, and the way removal is achieved (Manem and Sanderson, 1996). Water with low quality is acceptable to be processed by membrane. In space demand, membrane processes require a smaller space compared with conventional technology. A number of examples from well-known and emerging application of membrane processes in the drinking water industry are desalination using RO, softening using NF, and production of drinking water from surface water, backwash water and nitrate removal using ED (Saxena and Bhardwaj, 2001B.) .

The development of membrane science and technology offers various membrane materials. Membrane for potable water production commonly made from organic polymer (Manem and Sanderson, 1996B.) but ceramic materials also can be used (Bottino, *et al.*, 2001). PVDF (polyvinylidene fluoride) as one of fluorocarbon material is suitable to use as membrane-produce potable water because of its resistance against various oxidants (Saxena and Bhardwaj, 2001A., 2001B; Rachwal, *et al.*, 1994). PVDF membrane is a hydrophobic membrane and can easily integrate with other technology i.e. pulsed UV light, chlorine dioxide, etc. These integrated systems economically fulfilled the SWTR (Surface Water

Treatment Rule) and DBP (Disinfection By Product) regulations (Saxena and Bhardwaj, 2001B).

Modules configuration mostly used are spiral wound and hollow fiber. HFMF (hollow fiber microfiltration) can be used to produce potable water for small community (300,000-gph equivalent to 3000 peoples). Nowadays, HFMF become Best Available Technology (BAT) to supply small community by treated surface water/ground water resulted in accomplishment of requirement stated by SWDA (Safe Water Drinking Act). HFMF can operate with dead-end mode or some degree of circulation. For surface water treatment, it can achieve a flux range 35-50 gallon per feet quadrate per day (Saxena and Bhardwaj, 2001B). In various treated water, MF PVDF 0,1 micron with outside-in configuration can achieved flux of 75 gph (Saxena and Bhardwaj, 2001B) with 0.3 bar pressure operation for clean membrane and 2 bar for fouled-membrane. High quality, less than 0.05 NTU drinking water can be assured by intact MF membranes, which essentially remove 100% of *Cryptosporidium* and *Giardia* and exceed SWTR log removal requirements (Saxena and Bhardwaj, 2001A).

MF and UF started to be used for water treatment since 1980s. Applications of MF and UF as low-pressure membrane process begin to increase rapidly in 1994. This is caused by the lowering cost of processes and also a decrease in energy consumption, which can be attained to less than 1 kWh/m³ for 1-10 bar operation pressure (Rachwal *et al.*, 1994). Before the year 1994, the capacities of all MF and UF factories are less than 3 million gallon per day. Nowadays with the growing of understanding and the availability of the technology, a new facility of membrane with capacity 2 – 10 million gallon per day is being built in US (U.S. Water News Online, 1999). RO and ED now become the chosen methods for desalting seawater to produce potable water. RO particularly have emerged as an effective solution to transform saline, brackish, and contaminated water into usable and/or potable product (Manem and Sanderson, 1996C). In 1988, 49,4% of total desalination factories worldwide is using RO

(Saxena and Bhardwaj, 2001). Seawater desalination processes for drinking water purposes is widely practiced in Middle East and claimed to be 2/3 of desalting capacity in the world. However, the largest plant of RO is located in Yuma, Arizona with the capacity of 660 million gpd followed by a plant in Saudi Arabian (Saxena and Bhardwaj, 2001). RO plants installed in Bahrain desalinate highly brackish water, although the cost is relatively high compared with the cost of treating fresh water by conventional means, it is certainly an economically feasible alternative to transporting water over long distance (Mallevalle *et al.*, 1996).

Technology for wastewater treatment that might provide several advantages compared with conventional biological process alone is membrane bioreactor. Membrane bioreactor (MBR) can be defined as the combination of two basic processes, biological degradation and membrane separation. Biological process commonly used for wastewater treatment combined with membrane process is activated sludge process. Currently, the majority of installed MBR system are being used for the treatment of wastewater from the automotive, cosmetic, metal fabrication, food and beverage processing, landfill leachate, and other industries (Adham and Gaggiardo, 1998). MBR can be categorized into three types that are MBR for biomass separation, MBR for aeration, and MBR for pollutants extraction. Submerged membrane bioreactor for biomass separation is a breakthrough in membrane bioreactor field for industrial wastewater treatment that for the first time was introduced by Yamamoto (1989). The submerged MBR system should be distinguished from other MBR system, in this system membrane is installed inside biological reactor. The driving force for submerged MBR is the pressure gradient that limits the pressure up to 1 atm. This pressure gradient can be applied only by a suction pump. Energy consumption is low because there is no re-circulation pump. Study which was done by Yamamoto have succeed to treat waste water with an aerobic system and stable flux of about 0.1 kg COD/kg MLSS.day F/M ratio, critical

organic loading from 3 to 4 kg COD/m³.day and a very low power consumption of about 0.007 kWh/m³.day. In the same manner as the other membrane bioreactor processes is compared to conventional biological process, this technology have a main advantage in high-quality effluents (BOD/TSS < 5 ppm), disinfected, a very low excess sludge production, high biodegradation efficiency and a relatively small place necessity. Therefore, in the future, this technology has a large potential to be applied in several water and waste water treatment. The key of this technology is to overcome washout biomass (that to be a problem in conventional process), because in MBR, hydraulic retention time (HRT) and sludge retention time (SRT) are independent.

In the way of using MBR for water reuse, the application can be seen in several developed countries such as in Japan and USA. The factor that makes MBR become an attractive alternative is the superiority of this technology in producing a very low excess sludge or even zero sludge production and it has been properly proven. The membrane bioreactor process is probably the best technology for water recycling inside buildings requiring compact system and excellent water quality. Two different systems are experiencing large commercial success: UBIS in Japan (Lambert, 1983; Rouillet, 1989) and Cycle-let in the United States (Irwin, 1989,1990). The Ultra Biological System (UBIS) is a membrane bioreactor system where aerobic-activated sludge reactor combined with membrane unit. This UBIS system is installed in more than 40 buildings and produces more than 5000 m³/day (Manem and Sanderson, 1996). The Cycle-let is also a membrane bioreactor system, which is based on the combination of a two-phase biological treatment system (anoxic and oxic) with tubular organic membranes. Activated carbon for color removal and ozone for disinfection are used to finish and improve the water quality. Today, the Cycle-let is installed in more than 30 installations in USA. Wastewater treatment and recycling in apartment buildings is also performed in Europe, where the Lyonnaise des Eaux group developed an MBR

process using a ceramic tubular-type membrane. In Japan, the population relies on three domestic wastewater treatment categories: public sewage, on-site treatment tanks, and collected human excreta treatment system, which is also called the "night-soil" treatment system (Magara and Itoh, 1991). Magara *et al.* (1994) reported that there are about 1200 night-soil treatment system across Japan that treat more than 42 million population equivalents of night soil and 30 million population equivalent of on-site treatment tank sludge. The technology of membrane bioreactor can treat this high concentration effluent. Several pilot studies have been reported and at least six full-scale plants are under operation with the Activated Sludge and Membrane Complex System (AMEX) technology (Rouillet, 1989) (Manem and Sanderson, 1996).

EDI (electrodeionization) is a continuous chemical-free deionization process that relies on the same fundamental principle as for mixed-bed ion exchange. An EDI stack consists of diluted compartments concentrated compartments and electrode compartments. The diluted compartments are filled with mixed-bed ion-exchange resins, which enhance the transport toward the ion-exchange membranes under the force of a direct current. The later configuration, both diluted compartments and concentrated compartments are filled with mixed-bed ion-exchange resins. Since the concentration of ions is reduced in the diluted compartment and is increased in the concentrated compartment, the process can be used for either purification or concentration.

The concept of electrodeionization (EDI) process has been extensively recognized since the mid-1950s. Walters *et al* (1955) investigated a batch EDI process for concentrating radioactive aqueous wastes, based on electrolytic regeneration of ion-exchange resins, and proposed an ionic conduction mechanism through mixed-bed ion-exchange resins in contact with dilute solution. In the late 1950s and early 1960s, Glueckauf (1959) investigated theory, design, and operating parameters of the EDI process. The proposed theoretical model involved the diffusive transfer from the

flowing solution to the ion-exchange resin beads combined with the electrolytic transfer of ions along the chain of ion-exchange beads. Sammons and Watts (1960) evaluated multi-cell EDI module and quantified the relationships among solution concentration, flow rate and applied current.

An extended investigation of operating conditions and performance of the EDI process has been conducted by Matejka (1971) for high-purity water production from brackish or tap water. Several researchers were also actively studying EDI process (Korngold, 1976; Kedem and Maoz, 1976; Govindan and Narayanan, 1981; Ganzi *et al.*, 1992; Neumeister *et al.*, 1996; and Wang *et al.*, 2000). During this time, numerous patents were granted for various types of EDI device and its applications (White, 1992; Oren *et al.*, 1992; Giuffrida and Ganzi, 1993; Ganzi, 1993; Sugo *et al.*, 1994; Ganzi, 1994).

Millipore introduced the first commercial-ly available module and component systems in 1987 under the trade name Ionpure CDI (Korngold, 1976). There are presently two sizes of EDI modules available from U.S. Filter. So-called "industrial" module can have 30-240 diluting compartments and are capable of flow rates of 2.0-64.0 gpm (0.45-14.5 m³/h). The smaller versions, "compact" EDI modules, typically have 10-40 diluted compartments and are capable of flow rates of 0.5-4.0 gpm (0.1-0.9 m³/h). U.S. Filter is dominant manufacturer of industrial size EDI. Millipore Corporation fabricates low-flow EDI device (under trade name Elix) for laboratory water purification applications. Recently, other companies (Christ Ltd., Electropure Inc., Elga Ltd., Glegg Water Conditioning, Ionics Inc., and Osmonic Inc.) have begun to offer EDI units. Because of inherent process limitations, the EDI process may be not competitive with conventional technologies. These limitations include: (1) A mixed-bed ion-exchange resins in stack compartments is a good filter media; (2) Anion-exchange resin tends to adsorb negative charged-colloids; (3) Precipitation of inorganic components occur at high pH regions; (4) Quaternary amine is converted into tertiary amine or union-

ized group; (5) Channeling due to the stack design is not proper. In addition, the technology is labor intensive to assemble and requires a multitude of thin compartments. The inability to produce excellent ion-exchange membranes results in the loss of electrical efficiency.

Limited success in overcoming the challenges mentioned above has been reported. New membranes have been developed but are not cost effective. Hence, carefully pressure control is much more effective to minimize electrical efficiency loss due to convective transport across ion-exchange membranes. In order to reduce scale formation, Tessier *et al* (Gallagher, 1996) proposed the addition of scaling agent into concentrate and electrode rinse in the concentration range of 1 to 40 ppm. Special techniques for introducing and removing ion-exchange resins and other particulates from an assembled EDI stack to reduce labor cost also have been patented by Parsi *et al* (Parsi *et al.*, 1993)

Since the initial commercialization in 1987, EDI systems have been applied worldwide to meet the need of high purity water, such as in pharmaceuticals, semiconductors, power, and high quality optics industries. Limited ability of existing technology to reduce especially the need of high water production cost effectively and environment friendly offers a significant market opportunity for the commercialization of EDI systems.

Although electrodeionization is mainly applied to ultrapure water production, it is increasingly used in a wide variety of applications. Some systems have been installed for wastewater treatment (Ganzi *et al.*, 1992; Donovan). There may also be EDI applications for starch processing (Widiasa, 2002), recovery of citric acid from fermentation broth (Sutrisna, 2002). Millipore Corporation has continued to apply EDI to specialty separations in the pharmaceutical industry.

The backshock process

The performance of membrane in cross-flow membrane filtration is strongly influenced by the build up of a fouling layer that finally may completely plug the porous membrane surface.

Jonsson *et al.* showed that for MF membranes, the pore blocking type of membrane fouling is by far the most predominant. Two approaches have mainly been used to increase the fluxes in MF: applying high crossflow velocities (2-6 m/s) and, the use of backflush technique. In backflush technique, the direction of the permeate flow through the membrane is periodically reversed. However, high velocities are energy demanding, and give problems with too high-pressure losses in the membrane modules; backflushing also reduces the effective operation time, and gives a loss of permeate to the feed solution.

Very short backflush intervals were reported by APV passilac where the backflush duration is 1-5 seconds, and they are performed 1-10 times per minute at a pressure difference of 1-10 bar. This generally means that backflushing accounts for about 10-20% of the total operation time, by which the product flux may improve up to 100%; however, the negative flux during backflushing has to be taken into account. Since the impact of backflushing in industrial application is very limited, because of its fundamental limitation, i.e. loss of permeate and operation time, the backflush process needs adequate optimisation.

The backflush process is optimized both for the duration of the backflush and for the backflush interval. The improvement of the product rate upon backflushing is mainly a function of the backflush pressure and the interval between two backflushes. A novel backflush technique with a high frequency and extremely short duration times has been introduced. It was found that extremely good results could be obtained using very short backflush time (typically 0.06 second) with an interval time of maximum 5 seconds, preferably 1 to 3 seconds. Since the effective backflush time is very short and the backflush pressure is relatively high (typically 1 bar over the feed pressure) the name "backshock" is introduced. The loss of permeate during backshocking is very low and hardly affects the net permeate flow.

The novel backflush technique known as backshock technique in combination with the use of reversed asymmetric membrane structures

allows filtration at extremely low crossflow velocities with very stable permeate fluxes. A hollow fiber membrane made of a very pressure-stable polymer, with a rather thick skin layer on the outside of the fiber (pore sizes around 0.6 μm) and a very open structure (pore sizes up to 20 μm) at the inner surface, is used for clarification of fermentation broth (brewing process). Since the largest pores are in contact with the feed (beer), the yeast cell can partially penetrate into the porous structure. Without any backshock at all, this would lead to very low fluxes but the very frequent backshock prevents the membrane from definitive clogging, and enables a filtration process with an extremely stable flux level (Figure 2).

The fouling layer as such is very likely present inside the porous structure of the membrane and controlled by the backshock technology. Since the fouling layer is deposited during the first few seconds, and the shear stresses both in the flow channel and at the pore entrance have a significant effect on how proteins are denaturated and adsorbed at the membrane surface, a hydraulic cleaning of the membrane surface is performed every few (1-5) seconds using a pressure of less than 0.1 seconds. As a result of the extremely short durations, the loss of permeate during backshocking is negligible. In addition, it is found that very good transmissions of high MW components could be obtained in combination with a very low turbidity of the feed.

Figure 2. Comparison between normal and reverse asymmetric membranes in combination with backshock (backshock duration is 0.1 s, interval is 5 s, crossflow velocity is 0.5 m/s; TMP = 0.2 bar (normal) and 0.05 bar (reverse asymmetric); the backshock was stopped after 72 hours)

Future industrial prospect

Intensive researches and development in membrane area are related closely to the rapid growth of membrane technology. It is certainly not easy to predict the future of this technology. However, below are presented some facts that can roughly describe the future trend of this technology.

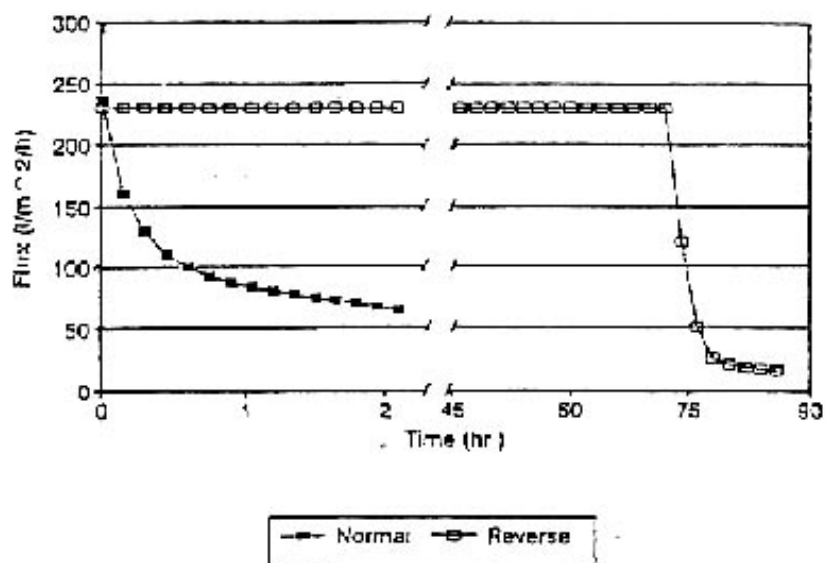


Figure 2. Comparison between normal and reverse asymmetric membranes in combination with backshock (backshock duration is 0.1 s, interval is 5 s, crossflow velocity is 0.5 m/s; TMP = 0.2 bar (normal) and 0.05 bar (reverse asymmetric); the backshock was stopped after 72 hours)

Firstly, current rapid development in alternatives of membrane materials, membrane production processes and the increase of membrane production, and followed by the membrane quality enhancement. Consequently, membrane price tends to decrease and the process is more economical. This is causing wider membrane technology implementation especially in application that requires high productivity and low cost as in water and wastewater treatment.

Secondly, for high-pressure and large capacity membrane processes like high-pressure reverse osmosis, energy recovery units have already been developed. This allows 70% energy recovery, so that the process becomes less expensive.

Thirdly, ultra low-pressure membrane with high productivity has also been developed; hence reverse osmosis process that used to operate on high pressure (60-80 bars) could operate on lower pressure (\approx 20 bars). This condition obviously lowers the energy consumption. Moreover, process system and equipment specification become simpler.

Next, the fourth factor deals with the environmental conservation fee. With refers to environmental regulation, industry that produce waste has to pay an environmental fee, amount to the production capacity or waste volume produced. Since membrane technology is a clean technology, it produces minimum waste or even none. In addition, membrane technology is one of the waste treatment technologies that improve waste quality or even better than that conditioned in the Industrial WasteWater Standard. It is a technology that can reuse water. Application in starch industry at PT. Raya Sugarindo, Indonesia, not only recovers tapioca but also produces (reuses) high quality water used for process water.

In Indonesia particularly, membrane technology still looks exclusive and expensive. Besides, there are some inhibiting factors such as the unstandardized membrane and laboratory assessment requirement that resists the widening of membrane application. As mentioned in the beginning of this discussion, membrane based processes also possess several disadvantage, such as

flux optimization and selectivity, material sensitivity, fouling, and dependability. Until now there have been several studies conducted to overcome the disadvantages and drawbacks in membrane processes. For example, researches dealing with hydrodynamic techniques as one alternative way to overcome fouling.

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