MASS TRANSFER OPERATIONS: HYBRID MEMBRANE PROCESSES

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Contents

Summary

Among the various technical options offered by Chemical Engineering for a sustainable industrial growth, membrane science and technology provide today some of the most interesting and concrete solutions for design, rationalization, and optimization of innovative production cycles. The attractive prospects are related to the possibility of integrating various membrane units in different industrial cycles, with important overall benefits in terms of product quality, plant compactness, environmental impact, and energetic aspects. In the following are presented some successful and interesting examples of membrane processes integrated into industrial practice or hybridized with conventional schemes

1. Introduction

In the frame of a globalized market, Chemical Engineering faces today the crucial challenge to find sustainable solutions to the increasing demand for raw materials, energy and tailored-made products. Within the more and more stringent constraints of legislative and social rules, answers might be found in the rational integration and implementation of innovative technologies and approaches, able to increase process performance, save energy, reduce costs, minimize environmental impact. In this respect, membrane science and technology contributed to significant innovations in both processes and products since the 1980s, because they are flexible processing techniques, able to maximize phase contact, to integrate conversion and separation processes with improved efficiency and with significant lower energy requirement compared to conventional techniques.

Membrane technology is today recognized as key factor for a sustainable growth in many industrial segments. Some of the basic properties of membrane operations, such as simplicity in concept and operation, modularity for an easy scale-up, and reduced energy demand, make them potentially attractive for a more rational utilization of raw materials and wastes minimization.

Various membrane operations are available today for a wide spectrum of industrial applications, and most of them can be considered as well accepted unit operations, as in the case of pressure-driven processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO); electrodialysis (ED) is another example of a mature technology.

Membrane operations show potential in molecular separations, clarifications, fractionations, concentrations, etc. in the liquid phase, in the gas phase, or in suspensions, so covering practically all existing aspects of process engineering.

Although membranes already represent the standard in various sectors (desalination, water treatment, gas separation etc.), their utilization as hybrid systems – in combination with other conventional techniques or integrated with different membrane operations – is considered the way forward more widespread and rationale applications.

The synergic interactions that can be achieved make hybrid membrane systems advantageous in many industrial processes, where they can be eventually integrated with other traditional unit operations, so optimizing their global performance.

As suggested by the several and excellent examples pertaining to water treatment processes, hybrid or integrated systems give today the concrete possibility to reduce the environmentally harmful effects, to decrease the energetic requirements, and to recycle and reuse by-products streams so approaching the concept of Zero Liquid Discharge. Additional cases in which hybrid membrane systems have increased their industrial relevance are presented.

2. Hybrid Membrane Desalination Systems

2.1. MSF/RO Systems

The integration of thermal desalination and membrane operations as hybrid desalination systems with power generation is currently considered as viable alternative to dual purpose plants based on traditional and energetically-extensive processes, such as Multistage Flash evaporators (MSF) or Multiple Effect Distillation (MED).

RO plants do not involve changes of phase and, therefore, they require a half to a third of energy with respect to MSF plants. In most cases, MSF and RO are operated in parallel and independently with the aim to increase the overall water recovery factors (Figure 1). This simple and traditional hybridization concept in which the permeate from RO units is blended to distillate from thermal MSF has been implemented in Saudi Arabia dual-purpose plants (Jeddah, Yanbu-Medina).If MSF is fed by the brine of RO, the water recovery factor can increase up to about 30%.

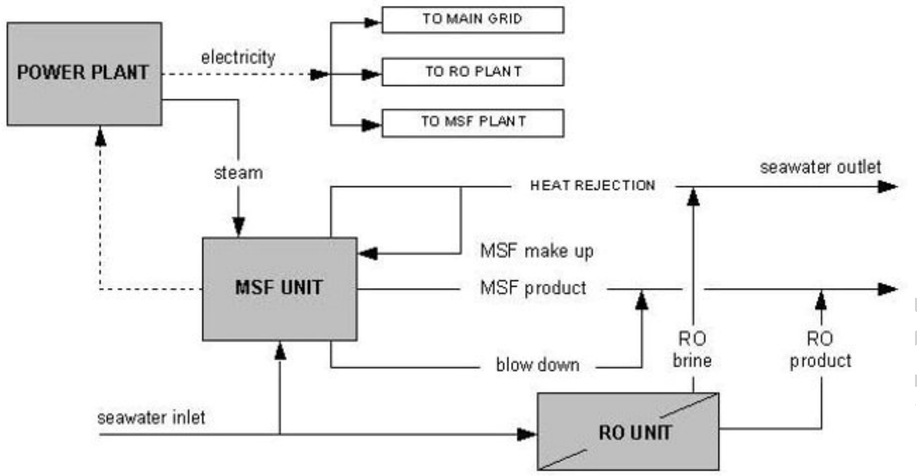

Figure 1. Hybrid MSF/RO plant with thermal and membrane units operating in parallel.

The 100 MGD desalination plant in Fujairah (United Arab Emirates), the largest hybrid installation in the world, combines a 62.5 MGD MSF and 37.5 MGD SWRO units. The cogeneration plant produces 500 MW of electrical energy. The flexibility of hybrid desalination plants well support the needs of this country, where the demand of water is nearly constant throughout the whole year while the power demand drops by about 40% during the winter season. In this case, the RO system helps to improve the load duration curve.

The power plant comprises 4 gas turbines each rated 109 MW and 4 heat recovery steam generators (380 t/h at 68 bar and 537°C) supplying 2 steam turbine generators. The expanded steam serves the MSF units. Seawater desalination process is designed for feed water with 40 000 ppm TDS and temperature in the range of 22-35°C. The thermal line of the plant includes 5 MSF units each of 12.5 MGD capacity, with performance ratio of 8 and top brine temperature in the range of 107-109°C. The RO plant is dimensioned for a recovery factor of 43% in the first pass (18 trains), and for a recovery rate of 90% in the second pass.

2.2. NF/MSF Systems

Application of nanofiltration as seawater pre-treatment results in the reduction of salt concentration and removal of most of the hardness ions (Ca^{2+}, Mg^{2+}) and co-ions (SO_4^{2-}, HCO_3^{-}) which are responsible for the formation of precipitate (scaling) on the heat transfer surfaces of thermal desalination processes. Pre-treatment of raw seawater by nanofiltration gives the possibility to safely increase the top brine temperature (TBT) of thermal desalination units above their present TBT limit. An increase of TBT results in the enhancement of water production and performance ratio.

A hybridized NF/MSF pilot plant was operated successfully in Al-Jubail up to a top brine temperature (TBT) of 130ºC, which is the design TBT limit of the unit, without injection of scale control additive for a period of 1200 h and the product recovery was increased up to 70% compared to 35% obtained from conventional operated MSF desalination plants (Figure 2).

It is expected that higher TBT can be attainable (up to 160°C), leading to high-efficiency dual-purpose plants at increased production of water and power.

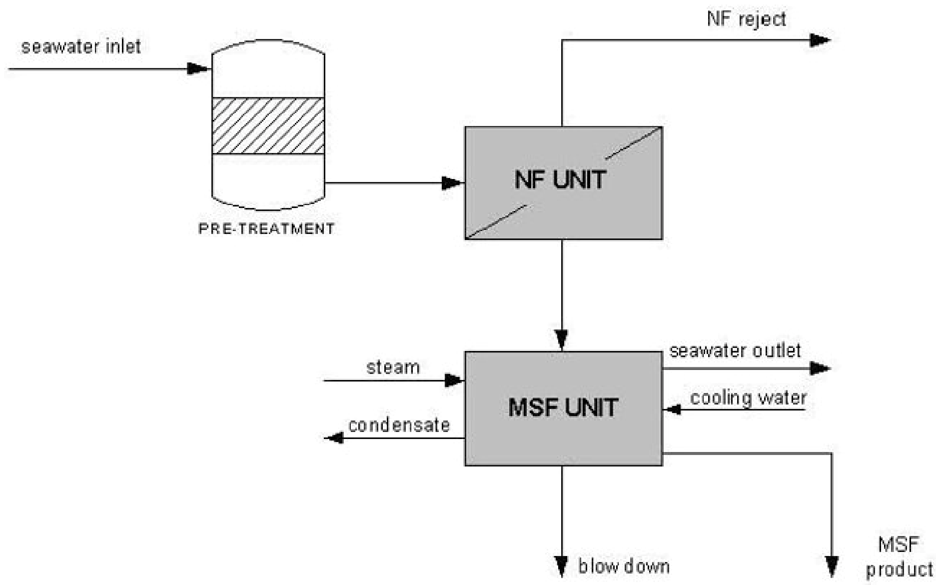

Figure 2. Hybrid NF/MSF desalination system.

2.3. MF and UF as Pretreatment Processes

Feed water for RO desalination plants needs extensive pre-treatment in order to prevent the damages related to membrane fouling. At present, the conventional pre-treatment still remains the preferred approach because of the lower investment cost and relative lack in experience of implementing low-pressure membrane operations. Due to the advancement in microfiltration and ultrafiltration technologies, their implementation for water filtration was drastically expanded since 2000, and several hundred systems have been started up for municipal drinking water systems worldwide. Microfiltration is a low energy-consuming technique extensively used to remove suspended solids and to lower Chemical Oxygen Demand (COD)/Biochemical Oxygen Demand (BOD) and Silt Density Index (SDI) to values below 5. Ultrafiltration, retains suspended solids, bacteria, macromolecules and colloids; despite of the larger pressure gradient with respect to MF, this membrane separation method remains competitive against conventional pretreatments.

The growth of membrane filtration market has been exponential in the 1990s: in 1995 it was estimated that less than 25 MGD installed capacity was in operation in North America; five years later that number has grown to about 400 MGD. In 2006, the updated technical market research report from BCC Research estimated the global market for microfiltration (MF) membranes used in liquid separations at $792 million in 2005, rising at an average annual growth rate (AAGR) of 9.4% through the forecast period, to more than $1.2 billion.

With the introduction of modern ultrafiltration (UF) and microfiltration technologies, it is expected that these membrane filtration processes would provide the optimum pretreatment technology for reverse osmosis (RO) applications. These expectations have been realized in the reclamation of municipal wastewater. Practically, all new wastewater reclamation systems that use RO for salinity reduction apply UF or MF technology as a pretreatment step before RO (Figure 3). Effectiveness of membrane pretreatment in producing better quality RO feed water is proven and well documented. In a wastewater reclamation process with integrated membrane pretreatment, the benefits of significantly lower fouling rates of RO membranes, low cost of chemicals and disposal of pretreatment waste stream, outweighs the higher cost membrane pretreatment equipment.

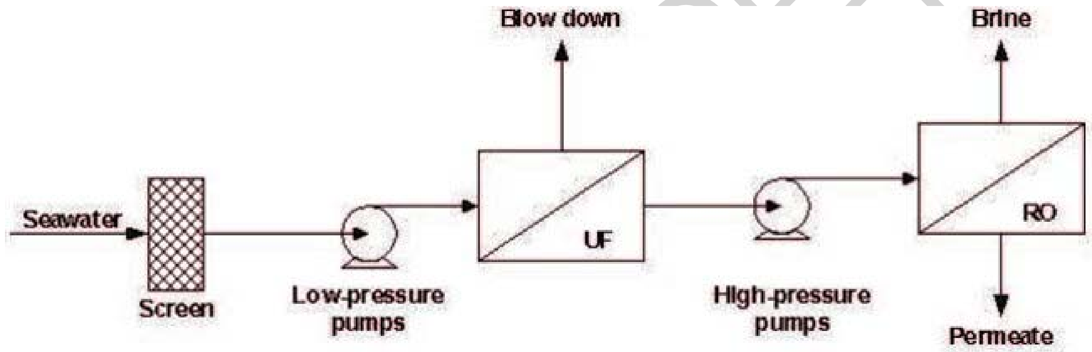

Figure 3. Seawater desalination: UF pretreatment to RO trains

3. Integrated Membrane Systems in Agrofood Industry

In agrofood industry, integrated membrane processes are today proposed for the production of high quality fruit juice concentrate. Flowsheet in Figure 4 offers a practical example of this kind of application. Ultrafiltration is used in order to separate fruit juices into the serum and the pulp (clarification). The clarified juices are pre-concentrated to 20–25°Brix by Reverse Osmosis, and the Reverse Osmosis retentates can be concentrated up to 60-70°Brix by Osmotic Distillation. The UF retentate could be submitted to a pasteurization process and then added to the final OD concentrate. The stability of the antioxidant activity (TAA) during juice processing is of interest since they play an important role in reducing the risk of free radical related oxidative damage associated with a number of diseases. Analysis showed that the content of ascorbic acid, phenolics and total antioxidant, besides anthocyanins and Vitamin C, did not decrease significantly during the processing.

Successful application of integrated membrane operations in fruit juice concentration has been developed by the Australian company (Wingara Wine Group, Melbourne). A hybrid pilot plant where UF/RO and OD are integrated has been realized. It consists of UF and RO pretreatment stages, an OD unit and a single-stage brine evaporator. This pilot plant concentrates fresh juices up to 65–70_Brix and has a capacity of 50 l/h. Being athermal, OD allows concentrating without product deterioration or loss of flavors.

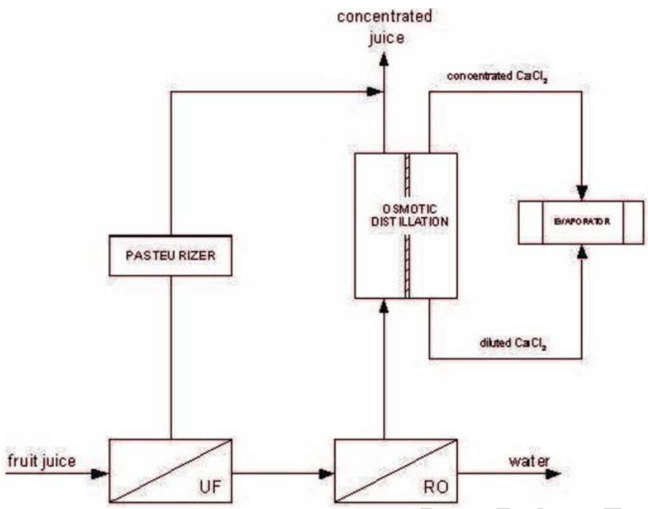

Figure 4. Integrated membrane system for fruit juice concentration.

Gas-Liquid Membrane Contactors (GLMC) are today used to transfer soluble gases, to/from an aqueous stream, in a variety of applications in the food and beverage industries. Liqui-Cel®, Extra-Flow™ Membrane Contactor manufactured by Celgard, Inc. of Charlotte, NC is, at present, the most popular GLMC module available for agrofood industrial applications.

For instance, N_2 introduction is requested to lower CO_2 content into “smooth” beer. Direct injection leads to highly undesirable turbulence that knocks CO_2 out of solution; with the Celgard technology, nitrogen could be introduced at low pressure (30-45 psi), a level that is actually lower than the 60 psi pressure needed to move the beer around.

Since 1993, a bubble-free membrane-based carbonation line has processed about 112 gal/min of beverage by membrane contactors having a total interfacial area of 193 m^2 (Pepsi bottling plant in West Virginia).

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Bibliography

Al-Sofi M.A.K., Hassan A.M., Mustafa G.M., Dalvi A.G.I., Kither M.N.M. (1998). Nanofiltration as a means of achieving higher TBT of 120°C in MSF. *Desalination* 118, 123–129 [Potentialities of nanofiltration as softening process integrated to MSF]

Bernardo P., Criscuoli A., Clarizia G., Barbieri G., Drioli E., Fleres G., Picciotti M. (2004). Applications of membrane unit operations in ethylene process. *Clean Tech. Environ. Policy* 6, 78–95 [Possible integration of membrane contactors and catalytic membrane reactors in the ethylene process]

Bonchio M., Carraro M., Scorrano G., Fontananova E., Drioli E. (2003). Heterogeneous Photooxidation of Alchols in Water by Photocatalytic Membranes Incorporating Decatungstate, *Advanced Synthesis & Catalysis*. 345, 1119-1126 [The incorporation of decatungstate in polymeric membranes provides new heterogeneous photocatalysts for the oxidation of organic substrates]

Carraro M., Gardan M., Scorrano G., Drioli E., Fontananova E., Bonchio M. (2006). Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon® membranes embedding a fluorous-tagged decatungstate: the importance of being fluorous. *Chemical Communications* 43, 4533–4535 [The improved performance of decatungstate heterogenized on hydrophobic fluorous hyflon]

Cassano A., Adzet J., Molinari R., Buonomenna M.G., Roig J., Drioli E. (2003) Membrane treatment by nanofiltration of exhausted vegetable tannin liquors from the leather industry. *Water Research* 37, 2426–2434 [Technical aspects of NF treatment of wastes from leather industry]

Fontananova E., Donato L., Drioli E., Lopez L., Favia P., d'Agostino R. (2006). Heterogenization of polyoxometalates on the surface of plasma modified polymeric membranes. *Chemistry of Materials* 18, 1561-1568 [Membranes are modified by plasma treatments on the surface to graft N-containing polar groups that are able to act as binding sites with phosphotungstic acid]

Gryaznov V. (1999). Membrane catalysis. *Catalysis Today* 51, 391-395 [An overview on the catalytic membrane processes with emphasis on hydrogenation and dehydrogenation reactions]

Helal A.M., El-Nashar A.M., Al-Katheeri E.S., Al Malek S.A. (2004). Optimal design of hybrid RO/MSF desalination plants. Part II: Results and discussion. *Desalination* 160, 13-27 [This paper provides some technical data on the possible combination of thermal and membrane desalination technologies]

Jiao B., Cassano A., Drioli E. (2004). Recent advances on membrane processes for the concentration of fruit juices: a review Journal of Food Engineering 63, 303–324 [A review on the potentialities of membrane operations in agrofood industry]

Kujawski W. (2000). Application of Pervaporation and Vapor Permeation in Environmental Protection, *Polish Journal of Environmental Studies* 9, 13-26 [A survey on the applications of pervaporation at industrial level]

Larmine J., Andrews D. (2000) Fuel Cell Systems Explained. John Wiley & Sons, Ltd.: Chichester [An introductive book to fuel cells world]

Ludwig H. (2003). Hybrid systems in seawater desalination-practical design aspects, status and development perspectives. Desalination 157, 31-32 [A technical and economical assessment on hybrid desalination systems]

Melin T., Jefferson B., Bixio D., Thoeye C., De Wilde W., De Koning J., van der Graaft J., Wintgens T. (2006). Membrane bioreactor technology for wastewater treatment and reuse, *Desalination* 187, 271-282 [Potentiality and perspectives of MBR in municipal water treatment]

Miachon S., Dalmon J.-A. (2004). Catalysis in membrane reactors: what about the catalyst?. *Topics in Catalysis* 29, 59-65 [Role and properties of the catalysts in membrane reactors]

Osman A. H.(2005). Overview of hybrid desalination systems — current status and future prospects. *Desalination* 186, 207–214 [A comprehensive review about the hybrid systems in seawater desalination]

Paul D., Sikdar S.K. (1998). Clean production with membrane technology. *Clean Products and Processes* 1, 39–48 [Membrane applications for a sustainable and eco-friendly industrial development]

Tanaka K., Yoshikawa R., Ying C., Kita H., Okamoto K. (2001). Application of zeolite membranes to esterification reactions. *Catalysis Today* 67, 121–125 [Potentialities and performance of zeolite membrane reactors in esterification process]

Biographical Sketches

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Professor of Chemistry and Electrochemistry at the School of Engineering of the University of Naples (since 1968) and Full Professor at the School of Engineering of the University of Calabria (since 1981).

- Dean of the School of Engineering of the University of Calabria (1982-1985).
- Director of the Institute on Membrane Technology of the National Research Council (former Research Institute on Membranes and Modelling of Chemical Reactors - IRMERC) (since 1993).
- President of the European Society of Membrane Science and Technology (1982 - 1998).
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- Doctorate *Honoris Causa* in Chemistry and Chemical Technology from Russian Academy of Science (February 1992).
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Author of more than 450 scientific papers and 14 patents in the field of Membrane Science and Technology:

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Researcher at the Department of Chemical Engineering and Materials of the University of Calabria. Since 1999 he is associate researcher at the Institute on Membrane Technology (ITM-CNR) of the Italian Research National Council, where he developed his expertise on membrane science and technology.

His present research interests concern: development of membrane crystallization devices and advanced membrane contactors, design and optimization of integrated membrane desalination systems, implementation of new brine disposal strategies, development of membrane bio-reactors for hepatocyte cells culture.

He is co-author of the book "Membrane Contactors: fundamentals, applications and potentialities" (Elsevier, 2005), author of more than 30 papers in international journals, and several proceedings of international scientific conferences and workshops. Dr. Curcio received the European Membrane Society Award for the best published paper in Membrane Science and Engineering on 2004.

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Graduated *cum laude* in Chemistry at the University of Calabria (Rende (CS), Italy) in 2001.

Contract Researcher at the Engineering Faculty of the University of Calabria and at the Institute on membrane Technology (ITM-CNR) (since 2001).

Research interests: membrane preparation and application in membrane reactor, membrane contactor, fuel cell and stereoselective recognition in membrane separation processes.

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Author of about 20 research papers in international journals and numerous presentations in international scientific meetings on membrane science and technology.

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