

MASS TRANSFER OPERATION–MEMBRANE SEPARATIONS

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Keywords: Membrane technology, chemical and process engineering, process design, integrated systems, sustainable growth, process intensification, nanotechnologies, tailored materials, advanced molecular separations and chemical conversions.

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Summary

Because of its intrinsic properties that well fit the requirements of process intensification strategy, membrane technology has well established applications in most of the industrial processes ranging from water desalination, wastewater treatments, agro-food, chemical and petrol chemical industry, etc. In particular, integrated membrane systems are today recognized as an interesting tool for a better rationalization of numerous industrial cycles. However, a good understanding of the materials properties and transport mechanisms, as well as the development of innovative materials with improved properties, is a key issue for the further applications of this

technology. Appropriate module design, hydrodynamic studies, and, in general, engineering analysis are also relevant aspects for their large-scale applications.

In this work, an overview on the fundamentals and applications, including basic process design, modules configuration, and choice of materials, of some specific membrane processes (reverse osmosis, nanofiltration, ultrafiltration, microfiltration, electrodialysis, gas separation, pervaporation and vapor permeation, membrane contactors and catalytic membrane reactors), also integrated, is presented.

1. Introduction

A membrane is thin interphase that restricts the passage of different components in a specific mode and over a wide range of particle sizes and molecular weights, from ions to macromolecules.

Synthetic membranes may be manufactured as solid or liquid phase, using organic or inorganic materials; they may be homogeneous or heterogeneous, symmetrical or asymmetrical, porous or dense, electrically neutral or charged; they may exhibit isotropic or anisotropic properties.

The efficiency of a membrane basically is determined by two parameters: permeability (the rate at which a given component is transported through the membrane) and selectivity (the ability to separate in specific way a given component from others).

The transport of different species through a membrane is a non-equilibrium process, and the separation of the different components is due to differences in their transport rate.

In a membrane separation process, the transport rate of a component can be activated by various driving forces such as gradients in concentration, pressure, temperature or electrical potential.

In many membrane operations more than one driving force is involved (e.g. pressure and concentration in gas separation, concentration and electrical potential in electrodialysis, etc.), but all these parameters can be included in one thermodynamic function, the electrochemical potential η (which includes the chemical potential). For a single component i transported, the flux J_i can be described by a semi-empirical equation [1]:

$$J_i = -L \cdot \frac{d\eta_i}{dx} \quad (1)$$

where $\frac{d\eta_i}{dx}$ is the gradient in electrochemical potential of the component i and L is a phenomenological coefficient.

In multi-component systems, driving forces and fluxes are interdependent, giving rise to complex interactions; not far from equilibrium, linear equations derived from

irreversible thermodynamics suggest that,

$$J_i = -L_{ij} \cdot \frac{d\eta_i}{dx} \quad (2)$$

where L_{ij} is a proportionality coefficients.

Membrane can have two different configurations: flat sheet or tubular (Figure 1).

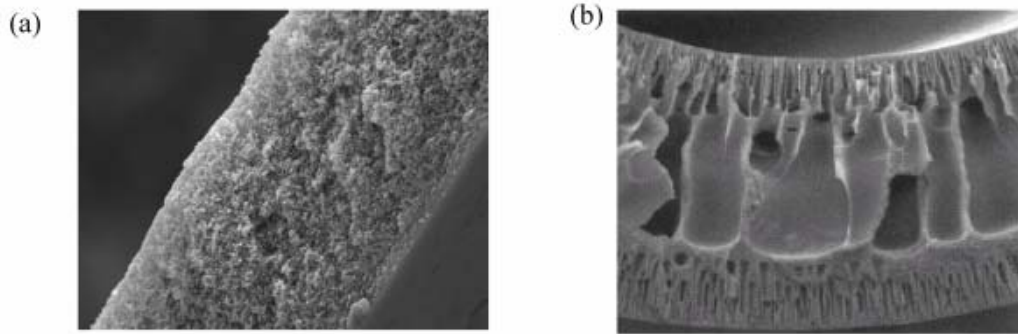


Figure 1: Scanning electron microscopy (SEM) images of the cross section of a flat sheet [2] (a) and of a hollow fiber [3] (b) membrane prepared from a modified polyetheretherketone known as PEEK-WC.

Tubular membranes can be distinguished in: hollow fibers (fiber diameter below 0.5 mm), capillary (fiber diameter comprised between 0.5 and 10 mm) and tubular (fiber diameter > 10mm).

For applications on large scale, membranes are efficiently packed in small and compact units or modules. Different typologies of module design are today available: flat membranes climbed on plate-and-frame (Figure 2) and spiral-wound modules (Figure 3); hollow fibers, capillary and tubular membranes assembled in modules having tubular geometry (Figure 4).

Properties of the different module configuration	Plate and frame	Spiral wound	Tubular	Capillary	Hollow fiber
Representative packing density (m ² /m ³)	100-400	300-1000	< 300	600-1200	Up to 30000
Capital cost	high	med-high	High	Low	low
Fouling tendency	low to moderate	med-high	Low	High	very high
Ease of cleaning	good	poor to good	good to excellent	Poor	poor
Operating cost	high	moderate	High	Low	low

Table 1: Properties of different module configurations

Plate-and-frame modules make use of flat-sheet membranes (in sandwich configuration) separated by support plates. These modules have low packing densities and are correspondingly expensive; they are for examples used to produce potable water in small-scale applications (Table 1).

Spiral-wound modules allow the efficient packaging of flat-sheet membrane in a convenient cylindrical form. They consist in an arrangement of two rectangular membranes placed back to back and sealed on three sides. They are rolled around a collector tube connected to the fourth side which remains open. The solution to be treated is brought to one end of this cylinder and the product circulates between both membranes to the collector tube. A spiral-wound module is contained in a pressure vessel assembly, consisting of a cylindrical housing for the modules, a plumbing to connect the modules together in series and a plumbing to connect the feed inlet, product and concentrate outlet. These modules have a good density, but cleaning is difficult. Modules composed by tubular membranes generally contain up to 30 tubes, normally supported within stainless steel vessels; with this module design, the feed and permeate channels can be easily cleaned. The major advantage of the tubular configuration is that the tube diameter is large enough to promote turbulent flow under most conditions without an excessive pressure drop. On the other hand, the low module packing density represents a serious disadvantage.

Capillary and hollow fiber modules have the highest membrane surface area per element; however, due to the high density packaging, these modules appear to be very sensitive to the feed stream quality in terms of fouling potential.

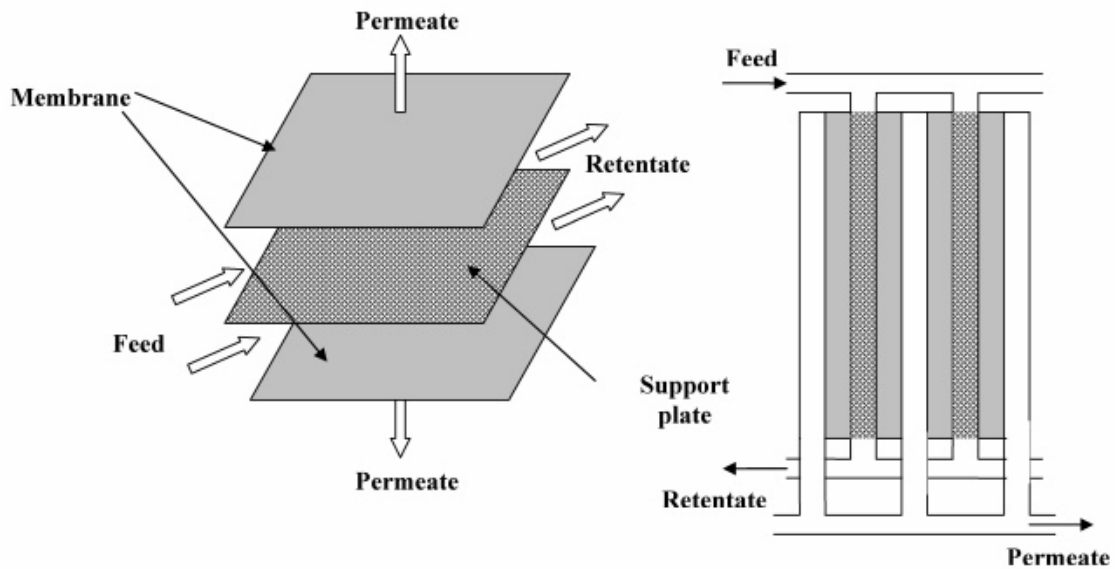


Figure 2: Scheme of a plate and frame membrane module

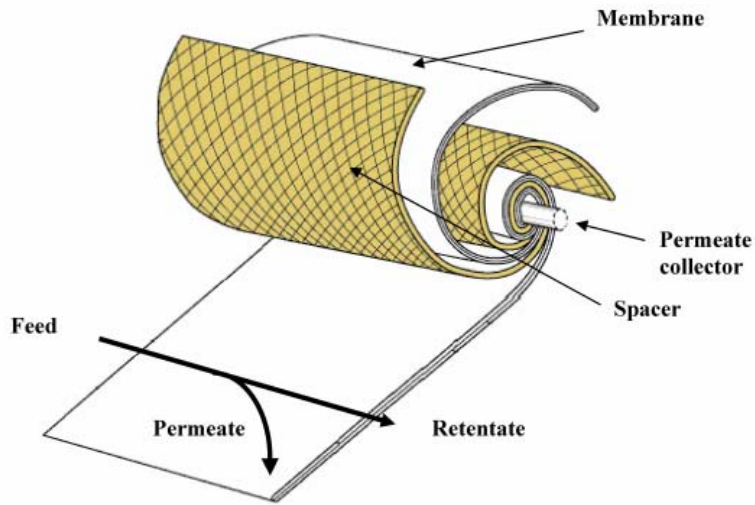


Figure 3: Scheme of a spiral wound module

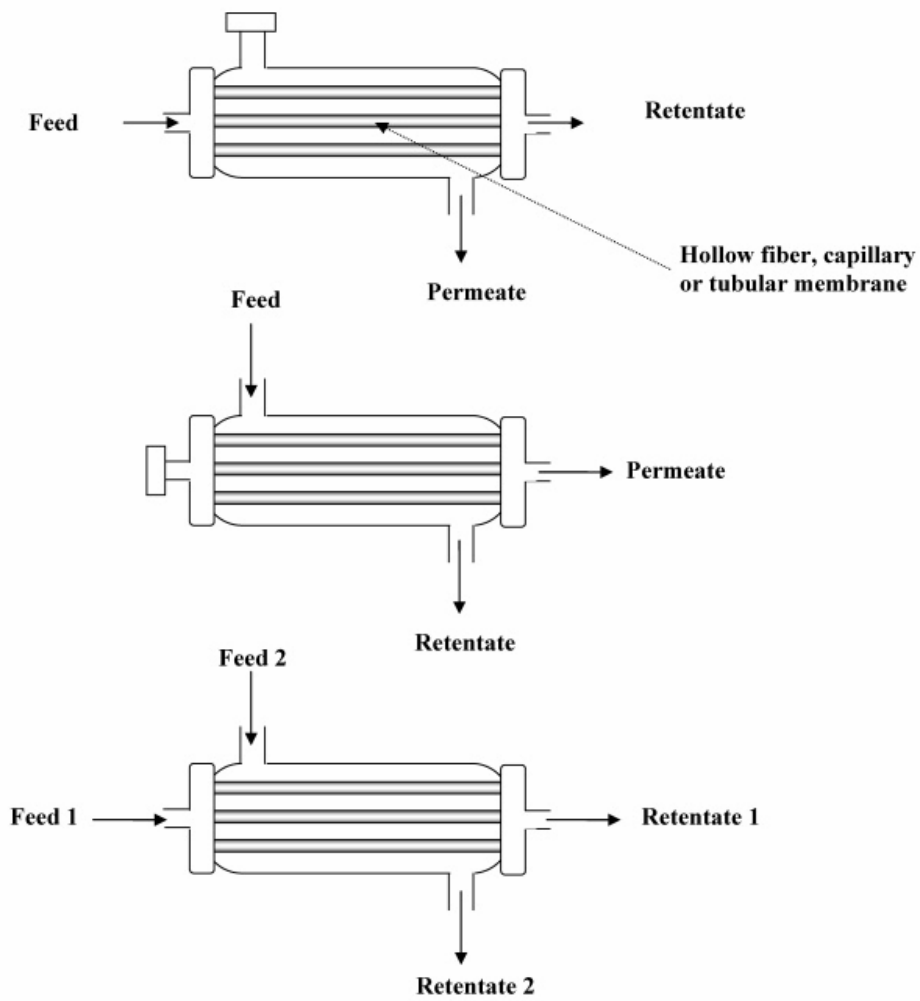


Figure 4: Scheme of tubular modules with different operative design

In a membrane separation process two main operative design are possible: cross-flow and dead-end

A schematic representation of a cross-flow and a dead-end membrane separation stage is reported in figure 5.

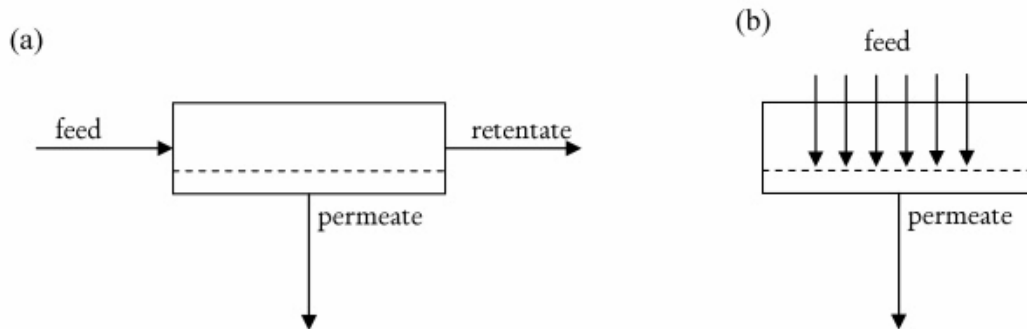


Figure 5: Schematic drawing of a membrane separation stage: cross-flow (a) and dead-end (b)

In the cross-flow mode, the feed stream flows parallel to the membrane and is separated into two streams: the retentate (or concentrate) and the permeate.

In the dead-end the feed is forced perpendicularly the membrane leading to a concentrate phase (retentate) and a permeate. This operative modality is characterized by a higher tendency to fouling phenomena than cross-flow mode, and so cross-flow operation is generally preferred for industrial applications [4, 5].

If the product stream coming from a single-stage design does not meet the requested level of purity, the retentate and/or permeate stream has to be treated in a multi-stage membrane process or cascade operation (Figures 6 and 7).

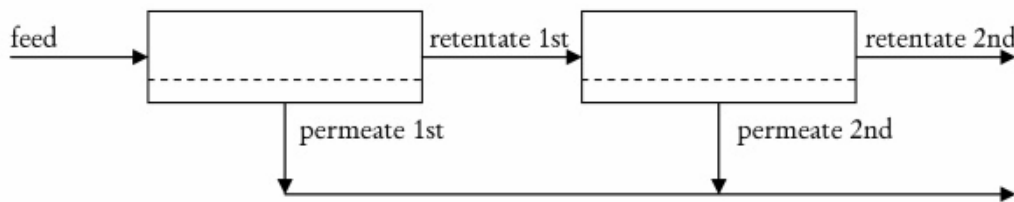


Figure 6: Two stage membrane separation system

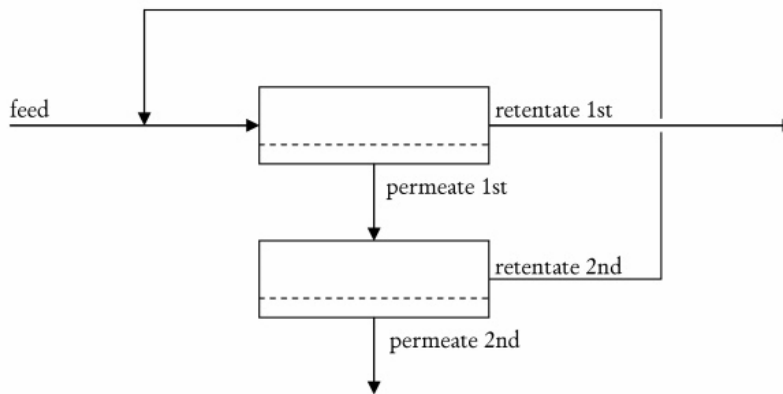


Figure 7: Two pass membrane separation system

2. An overview on the most industrialized membrane separation processes and emerging applications

Membrane operations, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, compatibility between different membrane operations in integrated systems, low energetic requirement, good stability under operative conditions, advanced control, easy scale-up and elevated flexibility, are today used in a large number of industrial applications.

The total annual market for membranes and membrane equipments is forecast to grow from \$ 6.3 billion worldwide in 2004 to over \$ 8.4 billion in 2007 [6]. The membrane industry is therefore an important economic factor; however, it is significant to realize that this market is extremely heterogeneous with a multitude of segments. Presently, water and wastewater treatment is the most relevant membrane application followed by food and beverage processing and drug and medical application. Catalytic membrane reactors, enantiospecific membrane separation processes and fuel cells can be considered emerging applications.

The vast majority of membrane materials are nowadays polymeric, although the demand for non polymeric materials for special applications, including ceramic, metal and composite types, registers a rapid growth. Typical examples are zeolite membranes applied to promote the molecular separation and the catalytic act [7,8] ceramic membranes for high temperature applications [9], and perovskite type membranes for oxygen separation and catalytic reactors for syngas production and the partial oxidation of hydrocarbons [10, 11, 12, 13].

The growing interest towards membrane science and technology is evident. At the 9th World Filtration Congress held in New Orleans (23-24 April, 2004 - Louisiana, USA) most of the scientific communications were held concerning applications of membrane systems in various production sectors. A confirmation of the industrial interest and strategic role for membrane operations, has been the presence of almost 200 exhibitors connected with the membrane world at the 9th edition ofACHEMA (19-24 May, 2003 - Frankfurt am Main, Germany), the world's largest exhibition for chemical engineering, environmental technology and biotechnology. A further evidence of the increasing

interest on membrane systems is the presence of numerous research projects in this field, approved, in progress or carried out in the latest years, with the financial support from the European Union. In particular, a Network of Excellence: “Expanding membrane macroscale applications by exploring nanoscale material properties (NanoMemPro)”, has been recently approved in the 6th Framework Programme (2002-2006) of the EU, and is now in progress. Significant transformations in the European membrane industry are also confirming the maturity of the membrane operation in various industrial areas. Danish Separation Systems (DSS) acquisition by Alfa Laval (2002), Nadir and Microdyn merging in the Advanced Separation Technologies Group Membranes (2003), Osmonics and Ionics (2005) acquisition by General Electrics (GE) are some consolidations which are taking place in industry.

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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).
- Chairman of the Working Party on Membranes of the European Federation of Chemical Engineering (since 1985).
- Doctorate *Honoris Causa* in Chemistry and Chemical Technology from Russian Academy of Science (February 1992).
- Honorary Professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China (Sept. 1991).
- Honorary Founding President of the European Membrane Society (from 1999).
- Honorary Member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow (from 1999).
- Patron Member of the Indian Membrane Society.
- Member of the Advisor Board of the UNESCO Center on Membrane Science and Technology at the New South Wales University, Australia.
- Member of the European Communities Chemistry Council (E.C.C.C.).
- Member of Executive Council of the European Federation of Chem. Engineering (from 1996)
- Member of the Interim Board of Governors of the Middle East Desalination Research Center, Oman, Muscat (1994 - 1996); Member and Moderator of the Research Advisory Council of the Middle East Desalination Research Center, Oman, Muscat (from May 1997)
- Member of the NATO/CCMS Pilot Study on "Clean Products and Processes"
- International Scientific Counselor of the Membrane Industry Association of China
- Member of the Editorial Boards of the: *Chemical Engineering and Processing* Elsevier; *Desalination* – Elsevier; *Journal of Membrane Science* – Elsevier; *Journal of Molecular Catalysis* (1982–1992) – Elsevier; *Chemical Engineering and Technology Journal* - Wiley-VCH; *Industrial & Engineering Chemistry Research* (from Jan. 2002) – American Chemical Society; *Journal of Clean Products and Processes* - Springer-Verlag; *Acqua-Aria* – Arti poligrafiche europee; *Chimica Oggi* - TeknoScienze; *La Chimica e L'Industria* - Editrice di chimica; *Orizzonti Tecnologici* - CESVITEC; *Water Treatment* - China Ocean Press; *Anales de Fisica* - La Sociedad; *Russian Journal of Physical Chemistry* - MAIK Nauka, *Interperiodica Publ.*; *Journal of Separation and Purification Technology* - Childwall University Press; *Membrane Science and Technology* – Lanzhou (China)

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He received his Degree and Ph.D in Chemical Engineering at the University of Calabria in 1999 and 2005, respectively.

He is Researcher at the Department of Chemical Engineering and Materials of the University of Calabria. Since 1999 he is in the research staff of 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 optimisation 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 about 30 publications in referred 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

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Enrica Fontananova

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.

Tutor of Chemistry at the Engineering Faculty of the University of Calabria (since 2001).

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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SAMPLE CHAPTERS