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Membrane technologies for water treatment and agroindustrial sectors

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Abstract

Although water is essential for human survival and progress, it is distributed very unevenly and with a different purity over the surface of the earth. A variety of contaminants can be present in raw water, depending on its origin. The size of these contaminants ranges from the micrometer (e.g. bacteria) to the tenths of a nanometer order (ions). Membrane processes like microfiltration, ultrafiltration, nanofiltration and reverse osmosis could be a solution for an advanced physical treatment of water for drinking purposes as well as for agroindustrial sectors. Many applications are well assessed and are expanding very quickly; however, to obtain an ever-growing performance, it is necessary to prepare membranes with tailored structure and transport properties. Characterisation methods play also a role of paramount importance for the selection of the more appropriate membrane for the above-mentioned applications. In this work the main membrane preparation techniques and characterisation methods will be reviewed and discussed. ***To cite this article: A. Bottino et al., C. R. Chimie 12 (2009).***

Résumé

Bien que l'eau soit essentielle pour la vie et le progrès humain, elle n'est pas distribuée d'une façon homogène ; en outre, elle est présente sur la surface de la planète à des niveaux différents de pureté. Une variété de substances contaminantes peut être présente dans l'eau avant de la traiter, en fonction de ses origines. Les dimensions des particules contaminantes peuvent être comprises entre le micromètre (comme les bactéries) et l'ordre du dixième de nanomètre (ions). Les systèmes membranaires, comme la microfiltration, l'ultrafiltration et l'osmose inverse, peuvent représenter des solutions à appliquer dans le traitement physique avancé des eaux, pour la potabilisation aussi bien que pour son utilisation dans les secteurs agricole et industriel. Beaucoup d'applications sont déjà utilisées et leur diffusion est très rapide ; pourtant, afin d'obtenir une performance toujours meilleure, il est indispensable de préparer des membranes ayant une structure et une capacité de transport adaptées aux différents usages. Les techniques de caractérisation ont un rôle remarquable dans le processus de sélection de la membrane la plus adapte pour une certaine application. Les techniques et les méthodes de préparation et caractérisation des membranes seront illustrées et approfondies par cette étude. ***Pour citer cet article : A. Bottino et al., C. R. Chimie 12 (2009).***

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1. Introduction

Although water is essential for human survival and progress it is distributed very unevenly and with a different purity over the surface of the Earth. Based on how the water is to be used, it can be classified into: (*i*) water for industrial purposes; (*ii*) water for agricultural use; and (*iii*) water for human consumption. Table 1 contains a list of water contaminants. The size of these contaminants ranges from the micrometer (e.g. bacteria) to the tenths of a nanometer order (ions). In order to meet the requirements stated by either the regulations in force or the end-user, water has to be treated with an appropriate group of technologies.

In traditional drinking water treatments before network distribution, raw water is firstly pre-disinfected with a chemical oxidant (usually NaOCl), secondly clarified (usually after adding flocculants), thirdly filtered through sand and finally post-disinfected. It has been revealed that traditional water treatments are ineffective in removing some contaminants and that during the disinfection step new harmful compounds can be produced (e.g. trichloromethane from the reaction between chlorine and natural organic matter). Membrane processes could be a solution for an advanced physical treatment of water for drinking purposes other than for wastewater recovery [1,2].

Different membrane processes with a different separation range are available [3,4]. Table 2 shows the applications of membrane processes in water treatments. Microfiltration (MF) and ultrafiltration (UF) are low-pressure processes (0.1–2 bar for MF, and 2–10 bar for UF) that effectively remove microorganisms and suspended solids (MF) and colloids (UF). A primary disinfection of water can be provided by MF and UF without using chemicals such as chlorine. A first application of MF for this purpose was carried out in recent years in USA on water contaminated by pathogens like Cryptosporidium and Giardia which became resistant to traditional disinfection treatment. Nanofiltration (NF) and reverse osmosis (RO) work at higher pressure (8–20 bar for NF and 10–80 bar for RO). Nanofiltration is a relatively young membrane process which is effective for water softening through the removal of magnesium and calcium ions and for removing some simple organic compounds. NF could also be used with success to remove the by-products (trihalomethanes) formed during the conventional disinfection treatments. The application of RO for desalting brackish water and seawater is well known, but this process can be also used for the removal of low molecular weight organic compounds either of natural or synthetic origin from water. The different membrane processes can substitute single purification steps in traditional water treatment plants or can be opportunely combined to make an integrated membrane process.

Table 1
Water contaminants.

Pathogenic organism	Inorganic contaminants	Organic compounds
Bacteria, enteric viruses, protozoa and other organisms	Metals, asbestos, cyanide fluoride, nitrite, nitrate sulphate	Natural organic matter (NOM), Synthetic organic contaminants (SOCs)

USA and Japan are the main developers of membrane technology while European companies play a greater role in marketing and selling membrane and equipment. According to a series of market research reports prepared by BCC Research [5], the global market for microfiltration (MF) membranes used in liquid separations was estimated at $792 million in 2005 and is expected to reach $1.2 billion in 2010 with an average annual growth rate (AAGR) of 9.4%. Large potential MF markets are in wastewater treatment, and sales of membrane bioreactors (MBRs) [6] using MF modules are expected to approach $363 million in 2010 with respect to an estimated $216.6 million in 2005. Thus the global MBR market is believed to rise at an AAGR of 10.9% which is faster than world MF growth and other membrane separation process such as RO (estimated $1.9 billion in 2005, expected $3 billion in 2010, AAGR 10.3%).

Nevertheless a wider diffusion of membrane processes is still limited mainly by technological and economical factors. From an economical point of view the cost of some types of membrane (especially those based on ceramic materials) is still high and the costs increase as the desired water quality increases. MF and UF are cheaper than NF and RO even though, over the last few years, the cost of a RO plant has decreased due to a greater diffusion of this technology for water desalination.

Table 2
Membrane used in membrane processes for water treatments.

Membrane process	Application	Membrane type	Material
Microfiltration	Sterilisation Removal of suspended solids and colloids	Porous-symmetrical or asymmetrical	Ceramic Polymeric Metallic
Ultrafiltration	Removal of viruses and macromolecules	Porous-symmetrical or asymmetrical	Polymeric Ceramic
Nanofiltration	Removal of organic compounds and some dissolved salts	Dense or nanoporous asymmetrical	Polymeric
Reverse osmosis	Removal of salts	Dense composite or skinned	Polymeric

On the other hand, each new potential application of membrane processes requires an individual study of the suitable membrane material (chemical stability in aggressive environments such as chlorine containing water, antifouling properties) and of the operating conditions (control of fouling phenomena and scaling). Fouling can be due to metal oxides, organic or inorganic colloids, bacteria or other microorganisms, while scaling is due to the presence of high levels of calcium sulphate, carbonate or fluoride or of silica or magnesium hydroxide.

The research effort on membrane preparation is now focused on solving these problems and the challenges of academic and industrial research are the synthesis of membranes with high chemical stability for wastewater recovery, the development of membranes and modules with antifouling properties, the preparation of large membrane surfaces with homogeneous characteristics and minimising energy consumption during applications by an appropriate study of the membrane module and equipment. In order to improve the performance of the membrane process in the production of drinking water a suitable choice of the membrane material and structure, the module configuration, pre-treatments and the operational modes to recover the initial membrane performance are essential.

2. Survey of membranes for water treatment

Membrane preparation methods are widely discussed in the literature and although there is a high number of membrane retailers, industrial membrane preparation is handled by a limited number of industries. Organic polymer membranes are widely used for all the membrane processes while ceramic and metallic membranes are mainly limited to MF and UF. Membranes can be prepared with different geometries. Table 3 compares different membrane geometries. Ceramic membranes are mainly used in a tubular multichannel configuration.

3. Membrane preparation methods

There are several techniques and materials available to prepare membranes [7,8]. Table 4 reports some of the materials that are currently used in industrial membrane manufacturing, along with the type of membrane that can be prepared. Obviously the type of membrane prepared depends on the type of synthesis and in some cases on the operating conditions adopted.

The attention of both membrane producers and researchers is focused on the study of both traditional and novel materials, on the preparation of antifouling membranes and on developing methods to produce large membrane surfaces with homogeneous characteristics (scale up from the laboratory membrane to the module). For the preparation of a membrane with antifouling properties the recent research trend is moving in two directions: (a) starting from materials with antifouling properties; and (b) providing antifouling properties through chemical treatments of the membrane after synthesis or after module realisation. Some of the preparation techniques will be briefly discussed.

3.1. Sintering

This technique is mainly used to prepare UF and MF ceramic or metallic membranes. Particles of the

Table 3
Comparison of the different membrane configurations.

Membrane geometry	Suspended solids tolerance	Control of fouling	Cleaning easiness	Packing density	Cost for unit of volume
Tubular	Good	Excellent	Excellent	Low–medium	Medium–high
Spiral-wound	Low	Limited	Medium	High	Low
Hollow fibre (external feed)	Scant (good)	Scant (good)	Scant (good)	Excellent	High (low)
Flat	Medium	Good	Medium	Medium	Medium–low

Table 4
Main materials used for commercial membranes manufacturing.

Material	MF	UF	NF	RO
Cellulose acetate	•	•	•	•
Cellulose nitrate	•			
Polyacrylonitrile		•		
Aromatic polyamide			•	•
Polybenzimidazole			•	•
Polybenzimidazolone			•	•
Special polymers (polyether, polyurea, etc.)			•	•
Polycarbonate	•			
Polyethersulfone	•	•		
Polypropylene	•			
Polysulfone	•	•		
Sulfonated PSf		•		•
Polytetrafluoroethylene	•			
Polyvinylidenefluoride	•	•		
α-Al_2O_3	•	•		
α-Al_2O_3/γ-Al_2O_3			•	
γ-Al_2O_3/TiO_2/ZrO_2	•	•		
Stainless steel	•			

material are pressed and heated at or below the melting temperature. The membrane structure is symmetric and the pore size ranges from some micrometers to a few tenths of micrometers.

3.2. Stretching of semi-crystalline polymer foils or hollow fibres

This technique is used to produce MF polymeric membranes. When a semi-crystalline polymer is stretched perpendicular to the axis of crystallite orientation, reproducible microchannels are formed. CELGARD® is an example of a polypropylene (PP) membrane obtained through a monodirectional drawing while Gore-Tex® (made from polytetrafluoroethylene, PTFE) is the result of an orthogonal bi-directional stretching. The stretching can be carried out on the cold foil of dense polymer or after the membrane is swollen in a solvent, or by alternating cold and hot stretching.

3.3. Track-etching of irradiated foils

This method is used for making MF polymeric membranes. A thin dense polymer film is exposed to a collimated beam of radiation to break bonds in the polymer chains. The foil is then dipped in a bath to etch the damaged polymer and form pores. The technique is generally used to produce polycarbonate MF membranes that are mainly used for laboratory applications.

3.4. Phase inversion

This is the main technique used to prepare polymeric membranes. In the thermal phase inversion a polymer is dissolved in a hot solvent and cast to form a film. Through cooling, a de-mixing process takes place and a porous structure is obtained. This production process is used to produce PP membranes both as a film and as a hollow fibre. In the wet phase inversion method, a polymer is dissolved in a solvent and cast to form a film which is then dipped in a coagulation bath where the membrane precipitates. A non-woven fabric is often used as casting support to improve mechanical properties of the membrane. The phase inversion technique may be used for a large variety of polymers. Through this technique, membranes with different structures (symmetrical and asymmetrical), geometry (flat sheet, tube, "spaghetti", hollow fibre), porosity and separation properties can be obtained by operating properly on the preparative parameters. Additives are often incorporated into the casting solution to favour pore formation through their dissolution during membrane formation in the coagulation bath. Insoluble additives (like, for example, fine inorganic particles) are also used to obtain membranes with novel characteristics due to the presence of the additive in the polymeric structure. Adding insoluble additives is a very recent and simple approach for improving or modifying the characteristics of a polymeric membrane through an intimate dispersion of inorganic particles in the membrane porous structure. Annealing post-treatments are employed to reduce pore size in order to obtain skinned membrane with high salt retention.

3.5. Interfacial polymerisation

This procedure is used to prepare polymeric nanofiltration and reverse osmosis membranes. Two monomers dissolved in immiscible liquids (e.g. water and an organic compound) are used. A porous (UF) membrane is first impregnated with the aqueous solution of the first monomer and then put in contact with the organic solution of the second monomer. The rapid polymerisation reaction at the interface between the two solutions (corresponding to the surface of the porous membrane) creates a thin (few tenths of a nanometer) polymer film. Various types of monomers are used for making a variety of thin polymer films with a very high salt retention and permeability.

3.6. Membrane surface modifications

Surface modification techniques are frequently used to give the polymeric membrane surface some desired properties, such as a given degree of hydrophylicity, which improves the fouling resistance of the membrane. There are several surface modification methods (chemical oxidation, plasma treatment, polymer grafting, etc.).

3.7. Sol–gel and slipcasting

These techniques are used for the preparation of asymmetrical UF ceramic membranes (or NF ones, at experimental production level) through the deposition of a mesoporous film on the surface of a macroporous ceramic support [9]. The sol–gel technique is based on inorganic polymerisation reaction where hydrolysis and condensation of a precursor lead to a macromolecular network that is first dried and then fired or sintered to form the membrane. The precursor is usually an alkoxide or a metal salt. The film deposition on the macroporous support can be also made, starting from a slurry of oxide particles.

4. Membrane characterisation

Table 5 resumes the main techniques used for membrane characterisation along with the measured characteristics and the kind of information (morphology or performance related parameter) supplied. Some of these techniques are well assessed while other methods are not yet standardised and harmonised [3]. There are different moments in which the characterisation techniques are applied. A researcher uses the greatest number of characterisation techniques after membrane synthesis to find the preparative conditions that lead to a membrane with the best performance. Manufacturers use some techniques to test membrane integrity and the module (seals and leaks). End-users monitor membrane performance using some techniques before and during the membrane application. Further characterisations can be carried out on the membrane at the end of its life to investigate the cause of its degradation (chemical, physical) or loss of performance (fouling, pore plugging).

Characterisation techniques can be classified into static and dynamic techniques. Dynamic techniques are of fundamental importance to investigate membrane performance. Static methods mainly give information on the membrane morphology and structure. Some characterisation techniques involve membrane destruction. Non-destructive techniques are more suitable to monitor the membrane performance also during its use.

4.1. Flux

Flux measurements represent a fundamental step in membrane characterisation. The fluid is generally pure water or a dilute solution containing a model species (solute, macromolecule, particle, etc., see retention below) and the results depend on the operating conditions (pressure, temperature, velocity at the

Table 5
Membrane characterisation techniques.

Method	Characteristic	Typology	Morphology	Performance
Gas adsorption/desorption	Pore size distribution	Static Non-destructive	•	
Electron microscopy	Top layer thickness Surface porosity Pore size distribution Qualitative structure analysis	Static Destructive	•	
Flux measurements	Hydraulic pore radius Pure water flux	Dynamic Non-destructive		•
Retention and selective permeation	Retention Cut-off value	Dynamic Non-destructive		•
Bubble pressure method and liquid displacement method	Pore size distribution	Dynamic Non-destructive	•	•
Permporometry	Pore size distribution	Dynamic Non-destructive	•	•
Burst pressure	Maximum pressure Membrane compaction	Destructive		
Contact angle	Hydrofilicity or hydrofobicity	Static Non-destructive	•	•

membrane surface) that must consequently be well defined. The flux method is applicable to both organic and inorganic membranes, for any basic geometry (flat or tubular) and module configuration (spiral-wound, multichannel, hollow fibre).

Flux measurements are also useful for supplying an appraisal of the fouling tendency of the membrane (by comparing the fluxes before and after a given application) as well as proper information on the effectiveness of a given detergent to remove foulants from the membrane surface (by comparing the fluxes before and after membrane cleaning).

4.2. *Retention and molecular weight cut-off*

Retention measurements exploit the membrane separation properties for ions, solutes, macromolecules or suspended solids present in the feed. The retention method (like the flux technique) is applicable to any type of membrane. Different model solutions are used depending on the type of membrane process considered. For RO and NF very low molecular weight solutes (generally NaCl, $MgSO_4$, glucose and sucrose) are used. A very good RO membrane would have a NaCl rejection greater than 99.7%. Model solutions of electrolytes are sometimes used at different pH to characterise NF membranes. Molecular Weight Cut-Off (MWCO, corresponding to the molecular weight of the macromolecule with a 90% retention) is a commonly used parameter to characterise UF (preferably using macromolecules of different molecular weight alone, rather than in a mixture). Microorganisms (e.g. *Pseudomonas diminuta*) or latex particles of a known size can be normally used for MF membrane characterisation.

4.3. *Bubble point and porosimetry (gas–liquid and liquid–liquid displacement methods)*

These methods are all based on the intrusion of a liquid inside or through the membrane pores and the interpretation is based on the Young–Laplace equation. They are of great importance because the results of these techniques are directly linked to membrane performance since they give information on the open or passing pores.

Bubble point measurements are used to determine the largest membrane pore (maximum pore size). The membrane pores are filled with a liquid which also covers the membrane surface and the pressure of a gas on the opposite side of the membrane is then increased. The bubble pressure corresponds to the gas pressure necessary to observe the first gas bubble. The most important factor is the surface tension of the liquid which fills the membrane. The greater the surface tension for a given pore size is, the lower the pressure needed. With the air–water pair the method is substantially limited to the characterisation of MF membranes. Bubble pressure is used by manufacturers to obtain information on membrane integrity, and by end-users who want know about the membrane status when it is new, or after storage or use. By further increasing the gas pressure, pores of progressively lower sizes are emptied and the gas flow passing through the membrane is measured for any given pressure increase, allowing for the pore size distribution of MF membrane to be calculated. Liquid–liquid displacement porosimetry seems to be a more suitable method for characterising UF membranes since pore size distribution can be evaluated without the need of high pressures, as the interfacial tension between two immiscible liquids are lower that the interfacial tension between the gas and the liquid. The comparison between pore size distribution of the membrane before and after a given application supplies important information of the fouling tendency.

4.4. *Pressure based test*

Pressure Decay Test (PDT) consists of putting the membrane at a pressure below the bubble pressure (usually at 80% of the bubble pressure) and monitoring the pressure decay against the time. If the pressure decay is faster than the decay trend registered after the membrane module installation then some membranes in the module do not work correctly and are probably damaged. This test is widely used for testing MF and UF membrane integrity.

Monitoring of the trans-membrane pressure (other than the permeate flux) during a given application can give information on the progressive fouling or eventual deterioration of the membrane.

4.5. *Electron and atomic force microscopy*

Electron Microscopy (EM) is a powerful tool to characterise membrane. Scanning Electron Microscopy (SEM) gives important information on the overall membrane structure. Transmission Electron Microscopy (TEM) has a greater resolution than SEM and is consequently more useful to investigate the skin selective layer of the asymmetric membrane, but the sample preparation is more difficult and delicate than for SEM observations. Both the instruments can be equipped with an EDS probe for a semi-quantitative elemental analysis and a Back Scattering detector for the compositional and topographic information.

Atomic Force Microscopy (AFM) gives a topographical map of the membrane surface. The basic advantage of this technique is that no membrane preparation is necessary and consequently the risks of artefacts due to this operation are considerably reduced.

5. Conclusions

Membrane technology applications are expanding very quickly. Many applications are well assessed but improving their performance and reducing their costs requires the use of new and better materials, preparation techniques for improving membrane life, chemical resistance and to produce large membrane surfaces with homogeneous characteristic. The role played by the characterisation techniques is therefore essential. Much work has to be made in order to standardise some of the membrane manufacturing and testing techniques.

Many characterisation techniques are used for controlling membrane performance during its use in order to test membrane integrity in real time.

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