TUTORIAL :

Membrane Technology and Processes for Pressure-Driven Systems : Theory and Application

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Abstract: The first section of this course outlines some commonly accepted theories of fluid transport mechanism through porous and dense materials. The second part addresses some practical applications related to water treatment that involves use of membrane processes in dry and hot environment.

Note: This document was prepared based on information available in the Prior Art. This article is not a research paper; rather, it encompasses some information that is aimed to introduce chemists and chemical engineers to the field of membrane materials and processes.

Introduction

This work is an introduction to the use of membrane processes in the field of filtration, separation and purification. Over the past four decades, membrane technology has had increasing interest due to its attractive properties in retention efficiency, scalability, space/energy/cost saving benefits and adaptability to other conventional processes. For practical applications, membrane technology is now replacing or combined with rapid mix, flocculation and sedimentation steps to produce drinkable water. It is also a good substitute to space and energy consuming distillation techniques used in beverage, chemical, and pharmaceutical industries. Another example is the replacement of costly cryogenic operations for gas recovery in fuels applications. Indeed, membrane-based processes offer unmatched performances to concentrate, purify and separate components of mixed systems at levels that competitive technologies can hardly reach. This course has been designed with some emphasis on the use of membrane materials for the treatment of water. A presentation of major membrane processes utilized to treat liquid streams is reviewed along with phenomenological description of fluid transport through dense and porous materials. The tutorial ends with the study of two practical cases of drinkable water production via membrane techniques by researcher groups from Cyprus and Jordan.

I) Conventional Method and Membrane Processes Used for Water Treatment

1.2 CONVENTIONAL METHOD FOR DRINKING WATER TREATMENT

<u>WATER TREATMENT PLANT</u>:

Surface Water ⇨ Coarse Screen ⇨ Rapid Mix (30 sec) ⇨

Coagulation (30 min.) ⇨ Flocculation (30 min) ⇨ Sedimentation basin (4hrs) ⇨

Granular media filtration ⇨ Chemical disinfection ⇨ Drinking water

ISSUES:

Cost (equipment, maintenance, energy)

Safety (Not 100% below 30 microns / Not 100% effective against bacteria, viruses (e.g: Cryptosporidium)

Heavy process – too many steps!

1.2 INTRODUCTION OF MEMBRANE TECHNOLOGY FOR SURFACE WATER TREATMENT

Membrane treatment of surface or ground water is significantly faster and easier to operate than conventional methods as it only involves the four following steps:

Surface Water ⇨Screen ⇨UF/RO membrane ⇨Disinfection ⇨Drinking water

II) Ultrafiltration (UF), Nanofiltration (NF), Reverse Osmosis (RO) modules

From microfiltration to Reverse Osmosis

TYPE →	Reverse Osmosis (RO)	Nanofiltration (NF)	Ultra/Micro filtration (UF and MF)
PORE SIZE →	**0.1 - 2 nm**	**2 - 50 nm**	**50 - 100 nm (UF)** **100 nm – 10 µm (MF)**
MATERIAL →	**Cellulose acetate** **Polyamide** Polysulfone/**Polyamide**	**Cellulose acetate** **Polyamide** PVDF/**Polyamide**	**polyvinylidene fluoride** **Nylon** **Polyacrylonitrile**

III) Fluid Transport Through UF, NF and RO Membranes: Theory and Applications [1,2]

3.1 EFFECT OF PRESSURE DROP AND CONCENTRATION DIFFERENCE

Driving force → Fluxes ↓	Pressure Drop	Concentration Difference
Solvent Flow	**Permeability (Darcy's law)**	**Osmosis**
Solute flux	**Ultra/Nano Filtration**	**Diffusion**

3.2 EXPRESSION OF OSMOTIC PRESSURE AND VAN'T HOFF LAW

A semi-permeable membrane is defined as a material that can retain a solute and allow its solvent to pass through. When such membrane separates a solvent (phase A), solvent/solute (phase B) system, a displacement of solvent is seen from phase A to phase B. This phenomenum creates an excess of pressure in phase B compartment, $\Delta\pi$, that is termed osmotic pressure.

Van't Hoff law demonstrates that for dilute ideal solutions $\Delta\pi = RT\,\Delta C + \ldots$
Where R: ideal gas constant, T: temperature, and C: solute concentration
And the expression of flux through the membrane, Ji, for both solvent and solute can be defined as follows:
$J1 = lv\ \Delta P$, where lv: the hydraulic permeability and ΔP: pressure drop across the membrane

$J2 = D\,\Delta C/L$ (Fick law) gives $J2 = [D/L \times \Delta\pi/RT] = D/LRT \times \Delta\pi = \omega \times \Delta\pi$,
where ω: solute permeability, L:membrane thickness, D: diffusion coefficient

J1: solvent flux and J2: solute flux

3.3 EXPRESSION OF SOLVENT TRANSPORT (DARCY'S LAW) & SOLUTE DIFFUSION

Darcy's law expresses in its simplest form the linear relationship that exists between the flux of a pure fluid across a microporous or dense membrane and the pressure drop applied to it:
$J1 = lp\ \Delta P$, with lp: hydraulic permeability.

But when a solvent/solute system is used Darcy's equation is slightly modified to include the counter pressure produced by osmotic effect: $Js = lp\ (\Delta P - \sigma\,\Delta\pi)$,
where Js is the **solvent** flux and σ: reflection coefficient
(σ =1 yields no solute penetration ; σ =2 solute can penetrate).
The expression of solute flux, J2, for such mixed system gives:

$$J2 = \underbrace{[D/L \times \Delta\pi/RT]}_{\text{Diffusive term}} + \underbrace{[(1-\sigma')\,J1 \times C2]}_{\text{Convective term}}$$

Where, σ' is a transport coefficient, C2: solute concentration, and J2: solute flux

3.4 FLUX EQUATION FOR AN AQUEOUS SYSTEM

The standard equation for water flux in a pressure driven system (UF, NF, RO) gives
$Jw = A\ (\Delta P - \Delta\pi)$, where A is the water permeability coefficient (A is a combination of two convective and diffusive terms).
Modeling of the solute flux can be expressed by three terms that are convection, diffusion and electrical repulsion (Donnan exclusion). And the Nernst-Planck equation is typically used to describe the transport of an electrolyte in water as reported below:
$J2 = [(D_s\ dC_s/dx) - (z_i\,C_s\,D_s\,F/R_gT\ d\Phi/dx) + (J_w \times C_s)]$, where: C_s: solute concentration;
J_w: water flux; z_i: value of the solute charge; F: Faraday constant; D_s: solute diffusivity, Φ: Donnan potential of the membrane; and R_g: gas constant.

The three terms in this equation represents flow due to diffusion, electrical repulsion and convection, respectively. Moreover, for a negatively charged membrane, the transport of ionic species is mainly influenced by the charge of the negative co-ion. For instance, the rejection of NaCl, Na_2SO_4 and Na_3PO_4 raises, respectively – due to electrical repulsion increase with (-1), (-2) and (-3) co-ion charge. Such phenomena is known as Donnan exclusion.

IV) Applications: Production of Drinking Water via Membrane Technology

This paragraph presents two concrete examples where membrane technology is used for water desalination and the production of drinking water. It is found that systems relying mainly on reverse osmosis offer a satisfactory solution to treat water at reasonable cost and meet high quality standards. A summary of findings reported by two research groups from Cyprus (S. Kalogirou) [3] and Jordan (O. Al-Jayyousi et al.) [4] are presented below :

1st topic: Research by S. Kalogirou from ' Higher Technical Institute' in Cyprus

Cyprus suffers from severe droughts that can last a long time and create serious water shortage problems. Past governmental efforts have initially focused on the erections of dams but these did not suppress the weather dependence and had a negative ecological impact. More recently, the government decided to install RO desalination plants as a means to eliminate water shortage. As Cyprus does not possess fossil fuel resources, it entirely relies on fuel imports for its energy needs. The high grade energy (electricity) used to operate these plants is produced from imported fuels and costs 25% of the price of the desalinated water. Given the high level of solar radiation in this region, it is now envisioned to develop RO plants that are partially powered from solar energy. The author's study considers solar energy systems that combine photovoltaics with RO units. It demonstrates that photovoltaic cells producing 20,000 kW of electricity can provide a third of the needs in desalinated water by functioning at an average rate of 8 hours per day. It is also shown that substantial energy savings are generated by combining photovoltaics with RO membranes; and that the investment in such technologies will pay back after nearly 18 years of service.

2nd topic: Research by O. Al-Jayyousi et al., from 'Civil Eng. Dpt, Applied Science University'-Amman

Objective is to evaluate the water quality from RO units used in Jordan against bottled and tap water. Analyses on the quality and cost of the water sources are being conducted. The research strategy relies on both laboratory experimental analysis as well as field survey of several RO units. The study shows that all three water sources comply with Jordanian water standards. More specifically, it appears that tap water –unlike RO and bottled water - does not meet the allowable limits in terms of its chemical properties (hardness, total dissolved solids). When water quality and cost are simultaneously taken into account, RO-produced water constitutes the most attractive approach.

Conclusion

This tutorial provides some information on pressure-driven filtration processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Transport mechanisms describing these systems are reviewed based on the phenomenological descriptions of solute and solvent displacement through UF/NF and RO membranes. The course ends with two research studies that highlight the benefit of RO-based technology for the treatment of raw water and production of drinking water.

References:

[1]: E.L Cussler, "Diffusion – Mass Transfer in Fluid Systems", Chap. 17, pp 427-466, 2nd Edition, Cambridge University Press, 1997.

[2]: J.A. Hestekin, C.N. Smothers et al., in "Membrane Technology in the Chemical Industry", pp 173-190 - Editors: S.P Nunes and K.V. Peinemann; publ: Wiley-VCH, 2001.

[3]:S.A Kalogirou, *Desalination*, (138), pp137-144, 2001.

[4]: O. R. Al-Jayyousi and M. Mosen, *Desalination*, (139), pp237-247, 2001.