Научно-практический электронный журнал
Оригинальные исследования (ОРИС), *ISSN 2222-0402*
www.ores.su
original-research.ru

UDC 621.593

МЕМБРАННАЯ ДИСТИЛЛЯЦИЯ ДЛЯ ОБЕССОЛИВАНИЯ ВОДЫ

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Аннотация

Перед миром стоит растущая необходимость в технологиях повторного использования и энергосберегающего опреснения воды. В статье изложены ключевые принципы функционирования мембранной дистилляции, её преимущества и текущие недостатки, а также практическое применение в промышленности.

Ключевые слова: мембранная дистилляция, давление пара, производительность, пермеат, подаваемый раствор, гидрофобная мембрана, гидрофидбная мембрана, дистиллят, размер пор, отходящее тепло.

MEMBRANE DISTILLATION FOR WATER DESALINATION

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ABSTRACT

The world faces an emerging need for water-reuse and energy efficient desalination technology. The article outlines key principles for the proper function of membrane distillation, it's advantages and current drawbacks, as well as real-world applications in industry.

Key words: membrane distillation, vapor pressure, flux, permeate, feed stream, hydrophobic membrane, hydrophilic membrane, distillate, pore size, waste heat.

"If we could produce fresh water from salt water at a low cost, that would indeed be a great service to humanity, and would dwarf any other scientific accomplishment."

John F. Kennedy

71 % of our planet is water, but over 96 % of that water is inaccessible or highly saline water. Among the freshwater we are producing, the contribution is a mere 1 % [1].

The map shows regions with a growing need to turn to seawater reclamation or wastewater reclamation for water supply (Fig.1). In doing this, greenhouse gas emissions must be decreased. Concerns with water scarcity and greenhouse gas emissions are leading to new technologies.

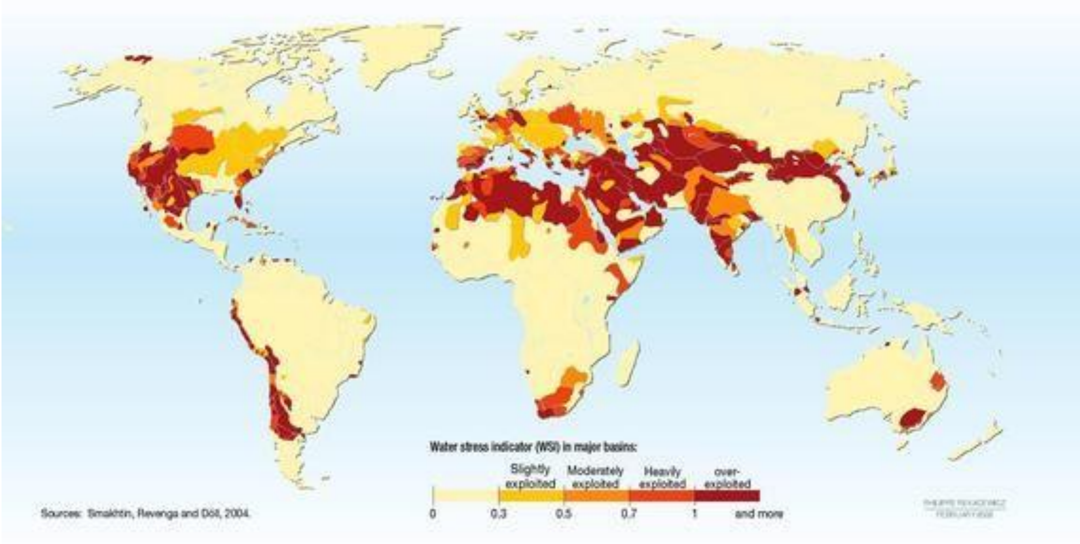

Figure 1. *Global water sustainability*

A primary weak-point in pressure-driven separation processes is the osmotic-pressure limitation. In reverse osmosis (RO), a pressure higher than the osmotic pressure must be applied. The RO membrane works by a solution-diffusion mechanism. The material of the membrane is made in a way that the solution and permeability rate of the water molecule is 10 000 times higher than that of the salt molecule, which means there are chemical interactions between the membrane matrix and the feed [2]. In MD, the membrane is porous, leaving behind problems such as fouling and chemical interactions.

Desalination is classified either by a phase change with evaporation and condensing the recovering or with the use of a membrane. Membrane distillation (MD) is a hybrid of both.

Membrane distillation is a thermal separation process (Fig. 2). The hot feed stream and cold permeate stream are separated by a hydrophobic porous membrane, forbidding liquid water from passing the membrane. By applying a temperature gradient, the water vapor will migrate from the hot to the cold side. Due to the temperature difference between both streams, vapor passes through the membrane into the permeate. MD runs at atmospheric pressure and requires a minimum temperature difference from 25 – 30°. As long as there is a difference in temperature between the feed and permeate, water may evaporate even at low temperatures.

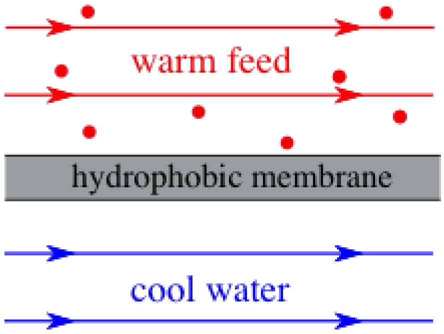

Figure 2. *Direct contact membrane distillation*
Tilton, De Caluwe, 2018 [3]

The process occurs on porous membranes. If the material of the membrane is hydrophilic, then liquid solutions, from the effect of capillary forces, will instantly fill the pores. If T1 > T2, the vapor's partial pressure of the evaporated component will create a gradient force enabling the movement from one phase to another. Clausius- Clapeyron's equation (1) shows the relationship between the vapor's pressure and temperature [4].

$$\ln\frac{P1}{P2} = \frac{\Delta H}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \quad \Delta H - evaporation\ heat \qquad (1)$$

Although the membrane must be hydrophobic, it is known that the entrance of water through pores depends on the pore size : the greater the radius, the easier for water to enter. Laplace's equation distinctively proves the relationship (2) [4].

$$\Delta P = -\frac{2\sigma}{R}\cdot\cos\theta \quad \sigma - surface\ tension\ of\ water \qquad (2)$$
$$\theta - contact\ angle\ of\ the\ membrane's\ material$$

There are different possibilities of how MD can configurate (Fig. 3). In direct contact membrane distillation (DCMD), a generally used and widespread configuration, the hot feed and cold permeate stream is separated by a hydrophobic microporous membrane. Although water itself does not pass, water vapor evaporates through the pores, resulting in a clean distillate stream.

In the air gap MD (AGMD), a stagnant air-gap on the permeate side is interposed between the membrane and a condensing plate. Sweeping gas MD (SGMD) takes the permeate and condensate outside the module. Stripping cold inert gas or air is used as a carrier for the produced vapor molecules on the permeate side. SGMD is useful for concentrating of non-volatile compounds. Condensation happens outside the module [5]. In certain applications, for example, to remove volatile compounds, a vacuum may be applied on the permeate side (VMD).

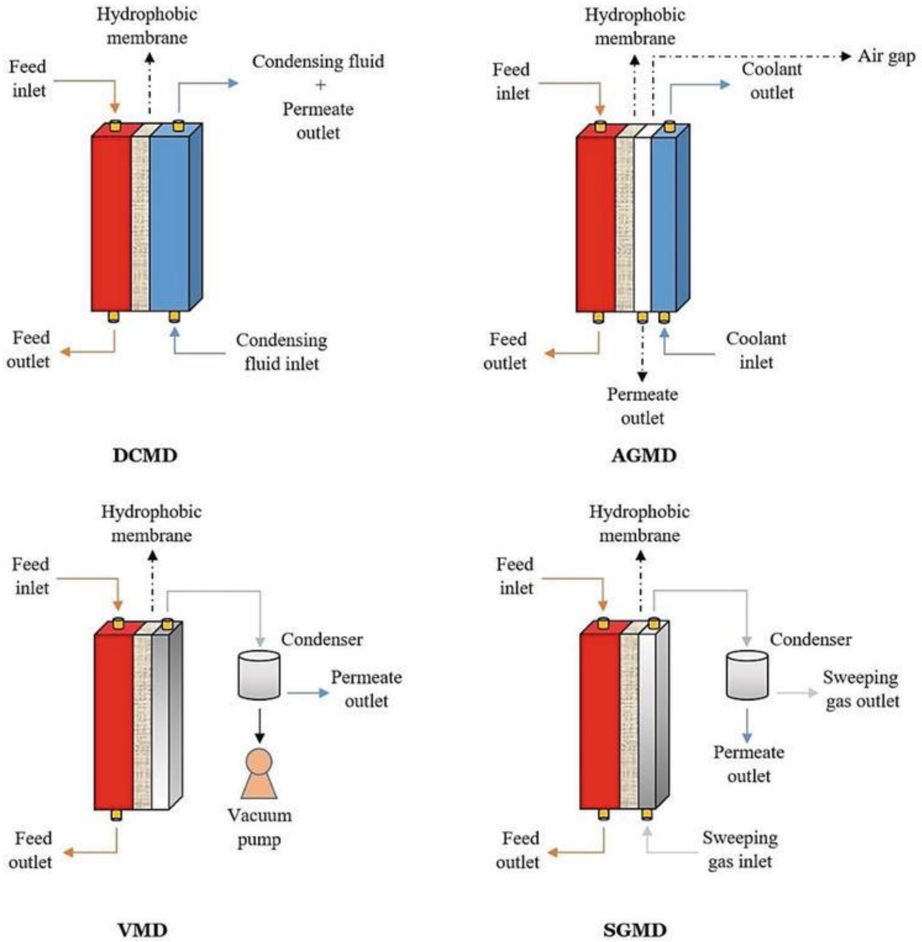

Figure 3. *Membrane distillation configurations*

Kebria, Rahimpour, 2020 [6]

Key advantages on MD :

- *Produces a pure distillate*
- *Operates at atmospheric pressure*
- *Evaporation at low temperatures*
- *Operation is possible with waste heat (industry) and solar thermal energy*
- *Reduced electrical costs → no need to pump feed stream into the membrane*
- *Operates at high concentrations → crystallization*
- *Less fouling and cleaning expenditure*
- *Applicable in low temperature applications (temperature sensitive liquids)*

One of the key advantages of membrane distillation is the presence of a vapor pressure driving force. The graph, illustrating vapor pressure as a function of temperature, shows a significantly smaller flux for MD operation. Treating highly concentrated solutions using pressure driven processes requires an abundance of energy. With MD, even with high concentrations, the driving force decreases slightly. This advantage has led to research for the treatment of high fouling and scaling feed waters, including produced waters in the oil and gas industry, valuable metal recovery in mineral harvesting. In the work of Tzahi Cath [1] (Fig. 4), the initial solution of 150 $\frac{g}{l}$ was concentrated to 300 $\frac{g}{l}$, leading to an expeditated evaporation process in evaporation beds.

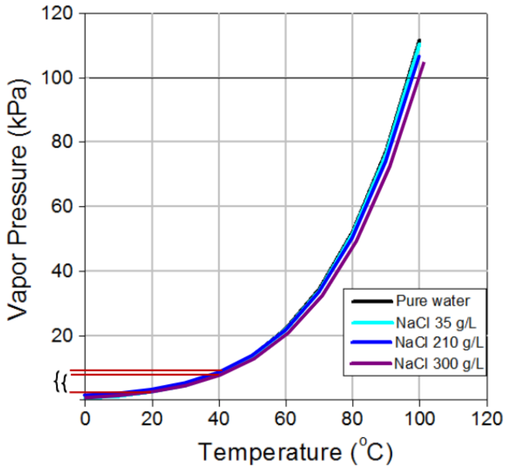

***Figure 4.** Vapor pressure driving force*
Tzahi Cath [1]

The second advantage is the production of a distillate-quality product. Through reverse osmosis or osmotic type membranes, there is passage of the contaminants. The graphs for membrane distillation for estrone and estradial (Fig. 5), however, show a 100 % rejection. There is a direct benefit for the high removal of emerging and traditional contaminants.

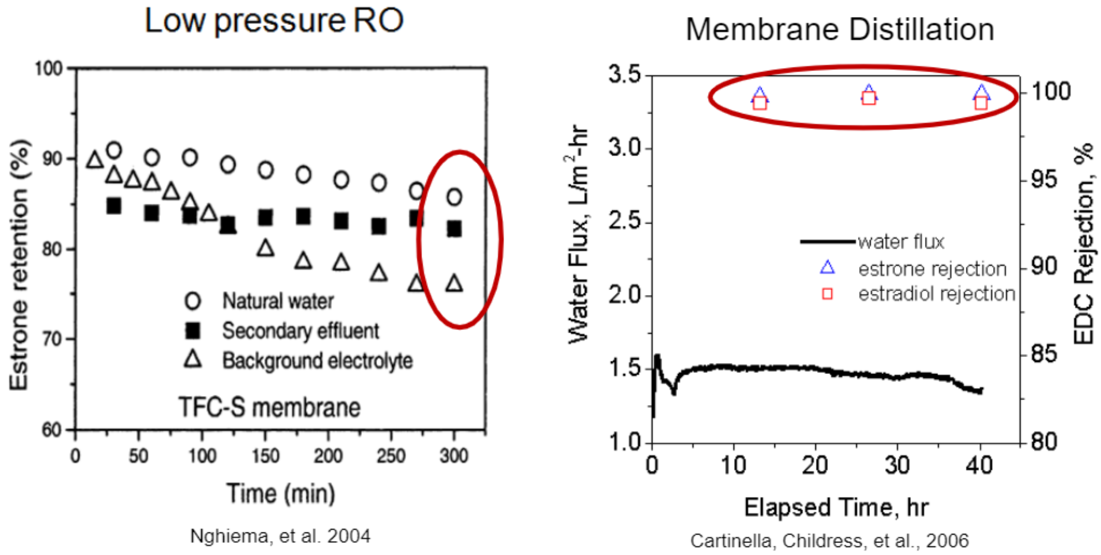

***Figure 5.** Distillate quality product [1]*

The third advantage, although other technologies share this relationship, is the compatibility with thermal energy. This allows energy, for example, in a salinity gradient solar pond, to be both collected and stored for further use in membrane distillation. Also not excluded is the use of solar thermal, geothermal or waste heat. Waste heat may be from machines (electrical and diesel generators) or heat exchangers (condensers, power plant cooling towers).

These three advantages have led to newer applications of membrane distillation - treatment of low fouling and scaling feed waters. While low molecular weight organics, urea, boron and arsenic can pass through RO membranes, MD allows for contaminant removal for small water systems. Also, in the work of Dr. Childress, reconcentration of forward osmosis draw solution using waste heat has led to a fully integrated membrane bioreactor system for wastewater treatment in remote applications.

A commonly used MD application is the separation of water. Several possibilities are known for separating water in MD. Water from a wastewater stream may be separated by desalination or, similarly to the galvanic industry, through the recovery of rinsing water. The concentrate may also be the product for reuse. Examples include metal recovery from rinsing water, juice concentration, COD concentration or in the pulp & paper industry to increase the concentration of the black liquor. MD allows for the recovery of liquid containing metals (Au, Pd, Cr, Co, Fe, Zn,..).

MD is also applied for the separation of volatiles. The volatile component may serve as a product in the permeate, while the waste/ by-product would be the feed stream, giving way for applications, such as the recovery of ammonia for fertilizer production or further use in the fuel cell, recovery of aroma compounds, separation of alcohols. In the case the waste / by-product is the permeate, volatile ingredients may be reduced in the feed. This is applied in wastewater treatment to separate ammonia from plants, biogas residues to bring them into the field without restrictions.

Dr. Childress' objective was to characterise the range of contaminants/ contaminant classes MD can remove, develop a small-scale pilot MD system with an adaptable heat exchanger and operate a system implementing on-site waste heat. The work hypothesized that volatiles would evaporate faster than water at a rate proportional to their inverse Henry's constant. While chloride and fluoride rejections were high, the lower sulfate rejection was predicted to be an artifact of low sulfate concentration in the DDW. In a study with arsenic, boron and chromium, boron passage was present, which showed to increase with higher concentrations (Fig. 6).

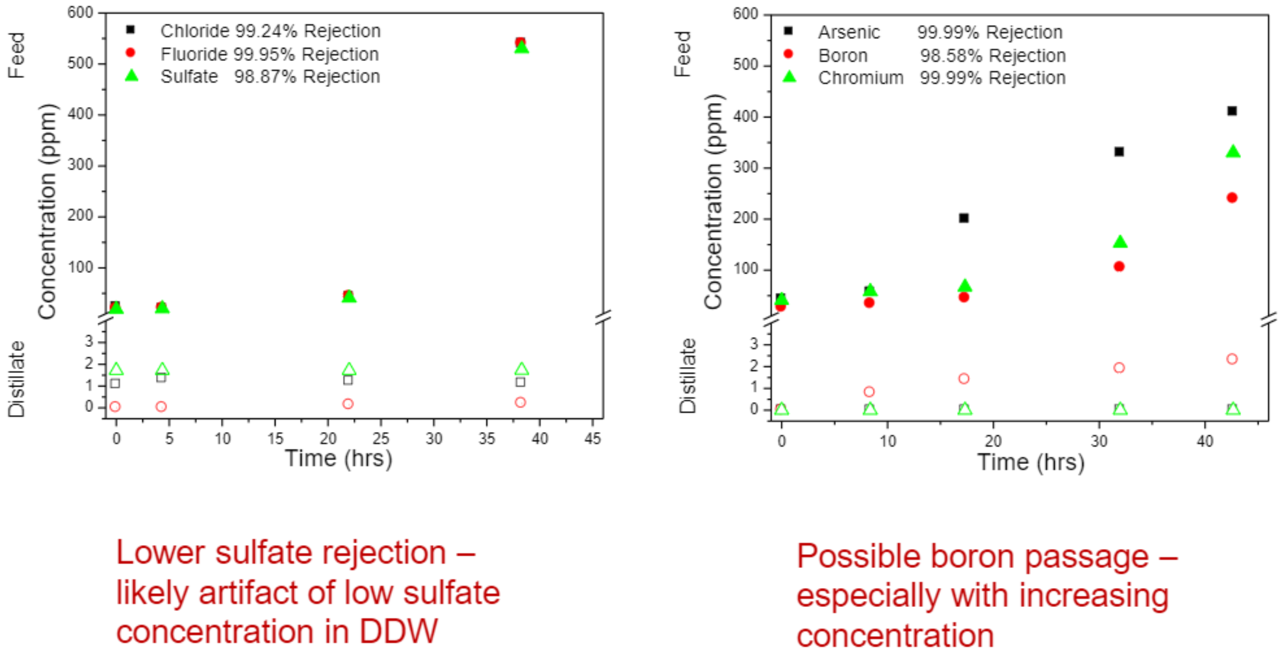

Figure 6. *Bench scale results : Ions and metals rejection [1]*

MD does have particular requirements or drawbacks, which, in essence, is the reason for the absence of commercialisation :

- membrane must be thin
- necessary high porosity
- low adsorbidity of moisture
- membrane pores must always be dry

the thicker the membrane → the higher the resistance → the lower the flux

- membrane pore size must be small (in the range of 0.1 - 0.5μm)
- the membrane should have a high resistance to heat and flow
- high cost of membranes for MD
- a fair amount of conductivity

According to AEE INTEC, benchmarks for MD showed a necessary 280 – 700 kWh/ m^3 [7]. The required energy for MD depends on the operating temperature (more energy is required at a lower temperature), internal heat recovery and the properties of liquid used as a feed stream (viscosity, concentration). The use of waste heat substantially lowers the cost.

One of the key factors determining the efficiency of MD is, not coincidently, the membrane itself. The requirements for the membrane in MD are mutually contradictive. The membrane must be highly hydrophobic to reject all water and pore size must be as small as possible. On the other hand, the pore size must be larger to reduce the mass transfer difference for the water flux. The membrane should be as thin as possible to reduce the barrier resistance to mass transfer and as thick as possible to reduce the resistance to heat transfer.

The solution, according to Dr. Mohammed Rasool Qtaishat [2], was to design a membrane made of a very thin hydrophobic and thick hydrophilic layer. The top hydrophobic layer would prevent penetration of the liquid water, with the resistance to mass transfer being at its minimum. Since both hydrophilic and hydrophobic layers contribute to the heat transfer and only the hydrophobic layer adds to the mass transfer, the heat conductivity may be reduced by the hydrophilic layer.

In industry, the membrane must be casted in one single step. A hydrophobic polymer must be mixed with a hydrophilic polymer in one solution. During casting, the hydrophobic polymer, with a lower surface energy, by the thermodynamic forces migrates to the top surface, leaving the bunk of the membrane hydrophilic. The hydrophilic layer has a significant effect on the membrane performance.

Dr. Mohammed Rasool Qtaishats' research exemplifies that the membrane with the highest hydrophilic conductivity and thinnest hydrophobic layer produced the highest performance. The module design is as important as the membrane in membrane distillation.

Thanks to three primary advantages, MD is ideal for removing contaminants in small water systems, especially in complex regulatory environments :

- simple treatment equipment (membrane module, couple of low-pressure pumps)
- broad spectrum of contaminant removal
- operation with low-grade ("waste") heat

From the mining, galvanic, pulp & paper, chemical, textile, bio-based, food and beverage industries to processes such as desalination, wastewater treatment, hybrid systems, MD has benefited a multitude of industries.

Water reuse and energy consumption are the key factors determining the efficiency of desalination technology. Compared to conventional desalination methods, MD processes are both energy and resource efficient. Despite challenges emerging technologies face before commercialisation, the growth of MD on the market may substantially reduce the environmental impacts from desalination.

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