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Membrane Distillation - Examples of Applications in Technology and Environmental Protection

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Abstract

This paper presents membrane distillation (MD), a separation process based on evaporation through pores of a hydrophobic membrane. Different configurations of the process were considered. Membrane properties, transport phenomena through the membranes, and module designs have been discussed. Applications of MD in water and wastewater treatment as well as in the food industry have been presented. The concentration of sulfuric acid solution obtained after extraction of apatite phosphogypsum by MD, in order to recover lanthane compounds has been presented. The possibility of recovery of HO from metal pickling solutions by MD has been shown.

Keywords: membrane distillation, vapour permeation, water purification, fruit juice concentration, concentration of acid solution, wastewater treatment

Introduction

The driving force for membrane processes may have quite a different character. Very often it is a pressure difference that affects the mass transport through a membrane. In other cases it is a concentration gradient or an electrical potential gradient.

Membrane distillation is a thermally driven process. Although thermally driven processes have been known for many years, the membrane distillation process is still considered a new, promising membrane operation. This process has been studied since the 1960's [1, 2]. Development in membrane manufacturing in the 1980's allowed us to obtain commercial membranes with desired properties. Improvements in module design and better understanding of phenomena occurring in a layer adjacent to a membrane also contributed to renewed interest in MD [3-6]. In comparison with other separation operations, MD has very important advantages: practically a complete rejection of dissolved, non-volatile species, lower operating pressure than pressure-driven membrane processes, reduced vapour space (practically to membrane thickness) compared to conventional distillation. Low operating temperature (considerably below boiling point) of a feed enables the utilization of waste heat as a preferable energy source. The possibility of utilizing of alternative energy sources such as solar, wave or geothermal energy is particularly attractive [7, 8].

The Principle of MD

MD is a process in which a microporous, hydrophobic membrane separates aqueous solutions at different temperatures and compositions [9-13]. The temperature difference existing across the membrane results in a vapour pressure difference. Thus, vapour molecules will be transported from the high vapour pressure side to the low vapour pressure side through the pores of the membrane. According to Terminology for Membrane Distillation [14], the name membrane distillation should be applied for membrane operation having the following characteristics:

- the membrane should be porous,
- the membrane should not be wetted by process liquids,
- no capillary condensation should take place inside the pores of the membranes,
- only vapour should be transported through the pores of the membrane,

- the membrane must not alter vapour equilibrium of the different components in the process liquids,
- for each component the driving force of the membrane operation is a partial pressure gradient in the vapour phase.

The principle of direct contact membrane distillation is presented in Fig 1. The process essentially involves the following steps:

- evaporation of volatile compounds of a feed at the warm feed/membrane interface,
- transfer of vapour through the membrane pores,
- condensation of the permeate at the membrane/cold distillate interface.

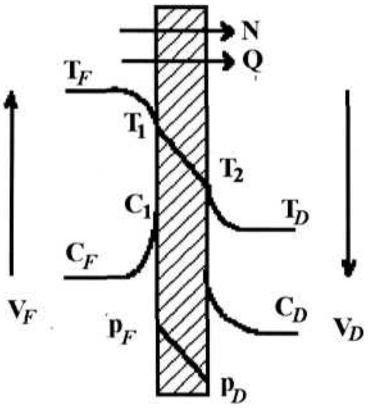

Fig. 1. The principle of direct contact membrane distillation.

Fig. 2 illustrates different MD configurations commonly used to obtain the required driving force. In all solutions the membrane is directly exposed to the warm solution, but the method of permeate condensation is different. In direct contact MD (Fig. 2A) the cold distillate is in direct contact with the membrane and vapour transported through the membrane condenses directly in a stream of cold distillate. In the gas-gap MD system (Fig. 2B), the permeate is condensed on a cooling surface. In this case, the total length of vapour diffusion is the sum of membrane thickness and air gap. The condensed distillate does not have to be in contact with the membrane. In a low pressure MD system (Fig. 2C), the pressure is applied on the distillate side and the condensation of the permeate takes place outside the module. In the last MD system, a sweeping gas is applied and permeate condensation occurs outside the module (Fig. 2D).

If the term "membrane distillation" is used without any specification, this term applies to the direct contact membrane distillation.

The separation mechanism is based on the vapour/liquid equilibrium [13, 15, 16]. This means that the component with the highest partial pressure will exhibit the highest permeation rate. MD is a highly selective operation for non-volatile species, such as ions, colloids, macromolecules, which are unable to evaporate and diffuse across the membrane. The solutes are completely rejected and the permeate is then pure water. When volatile species are present in the feed they will be also transported through the membrane. According to the vapour/liquid equilibrium, permeate composition depends on the composition and temperature of a feed.

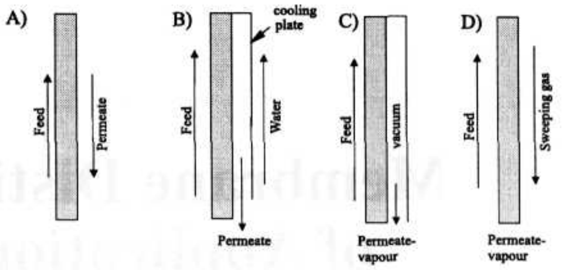

Fig. 2. Membrane distillation configuration: A) direct contact MD, B) air-gap MD, C) low pressure MD, D) sweeping gas MD.

Membrane Characteristics

The membranes used in MD rather act as a physical support for a liquid/vapour interface, but their choice for the process is very important. The membranes have to meet several requirements simultaneously. The presence of only the vapour phase in the membrane pores is a necessary condition for MD. Therefore, hydrophobicity of the membrane (i. e. its non-wettability which prevents the bulk liquid transport across the membrane) plays an essential role in this process. The MD membranes are prepared from hydrophobic polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP), or poly(vinylidene fluoride) (PVDF), which have a low surface energy. Moreover, these polymers exhibit excellent chemical resistance and good thermal stability.

A contact angle measured on a hydrophobic surface should be greater than 90°. For example, the parameter measured on PTFE or PVDF membrane surface was 108° or 107°, respectively [13, 17].

Membranes prepared from hydrophobic polymers do not permit for the flow of liquid through the membrane until a critical penetration pressure is exceeded. In this case the liquid may penetrate the membrane pores and non selective flow is observed. Liquid entry pressure of water (LEP_W) is a very important parameter which determines the magnitude of pressure which should not be exceeded. LEP_W can be calculated using the Laplace equation [18]. The presence of surfactants or organic solvents may significantly reduce the liquid surface tension, causing membrane wetting. The wetted membrane must be completely dried and cleaned before subsequent use.

Membrane porosity is the parameter which affects permeate flux (Fig. 3). Higher membrane porosity corresponds to a larger diffusion area inside the membrane, taking part in the vapour transport. Higher porosity also reduces the amount of heat lost by conduction. Thus, a porosity higher than 70% is required [19]. Higher porosity often corresponds to a larger pore size. Drioli [20] and Schneider with co-workers [19] recommended a maximum pore radius of 0.5-0.6 µm. This value ensures that temperature, process pressure and salt concentration fluctuations do not result in membrane wetting. The

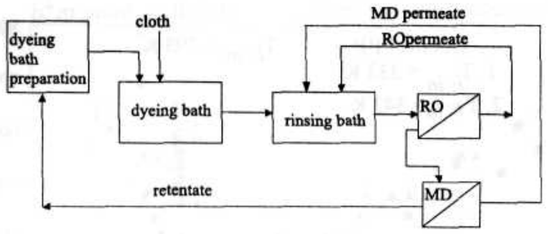

Fig. 12. Scheme of dye recovery and recycle by using integrated RO/MD techniques [37].

on a certain level. In this case there is a danger of growing the crystals inside pores of the membrane and wetting the membrane. In this case, when the solutes are not easily crystallized, their concentration will increase, causing a rise in solution viscosity. Then the permeate flux will decrease to zero. The MD-crystallization technique was investigated to recover taurine from the wastewater of their production [38].

The Concentration of Non-Volatile Acids

Investigations have shown the possibility of MD aplication for concentration of diluted non-volatile acids such as sulfuric or phosphoric [13]. Fig. 13 shows MD of sulfuric acid solutions. The obtained data indicate that the permeate flux decreased with an increase of acid concentration in the feed. The separation coefficient was above 98% for all the experiments. The temperature and the concentration polarization phenomena decreased the achievable acid concentration due to a high viscosity of concentrated solutions [13, 39]. The raw phosphoric acid can be concentrated to about 32% P2O5. The permeate flux then decreased to 100 dm^3/dm^2d (at the feed temperature equal to 333 K).

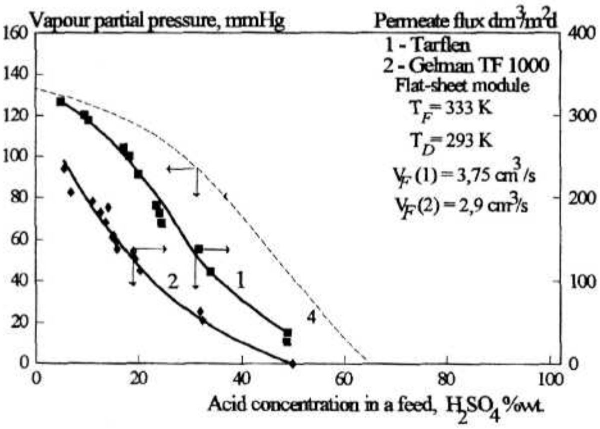

Fig. 13. MD of sulfuric acid solution. Relationship between permeate flux and initial concentration in the feed [13, 39].

Phosphogypsum from apatite Kola, waste by-product from the manufacture of phosphoric acid by the wet-process route, canbe a source of rare earth elements [40].

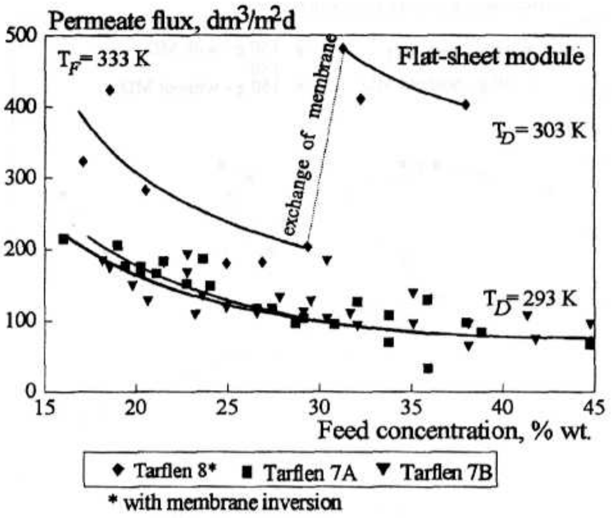

Fig. 14. The concentration of acid solution after extraction of apatite phosphogypsum. Dependence of permeate flux on the feed concentration [13, 41].

Experimental results show that the membrane distillation process can be applied for concentration of sulfuric acid solution obtained after apatite phosphogypsum extraction used to recover lanthane compounds [41]. The initial solution was 16% H_2SO_4, saturated by apatite phosphogypsum and contains, among other substances, 1.6 g La2O3. The concentration process was carried out till the concentration of sulfuric acid in the solution reached about 40%. Fig.14 presents results of the MD concentration [13, 41]. After cooling of the concentrated solution,

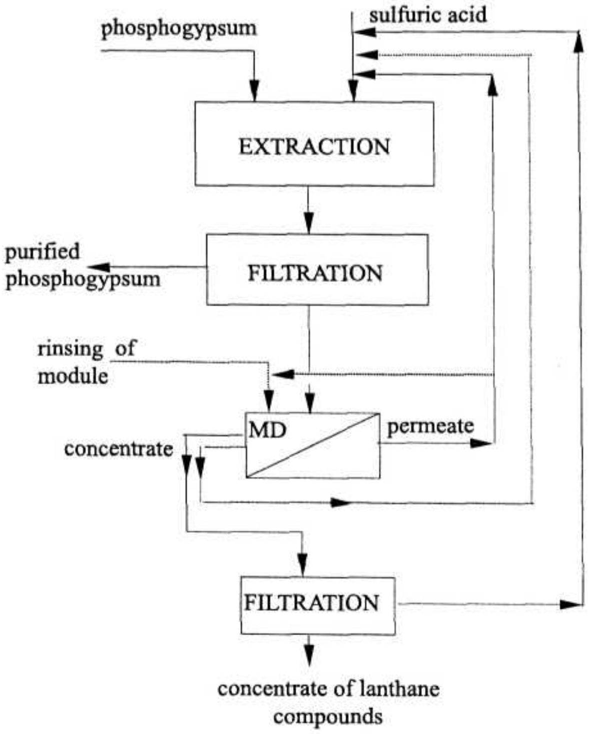

Fig. 15. The block diagram of system for preparation of lanthane compounds concentrate from phosphogypsum by MD.

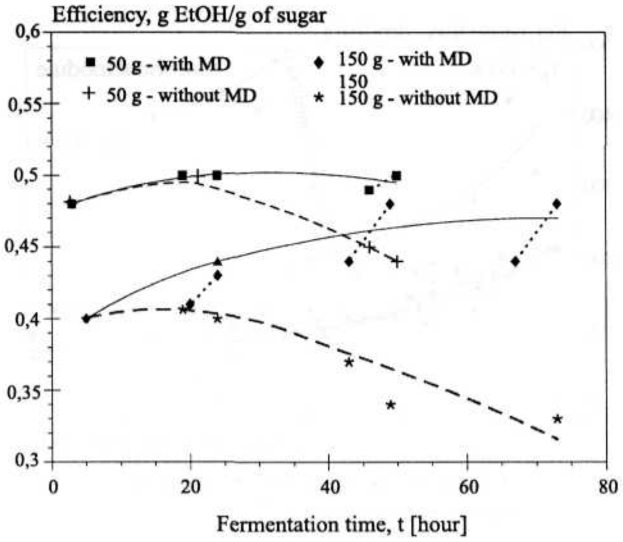

Fig. 16. Ethanol production. The comparison of results obtained by the conventional bioconversion and integrated bioconversion/MD system.

lanthanides precipitated. The content of lanthane compounds in the precipitate amounted to 25%. The block diagram for this novel technology is presented in Fig. 15.

MD Application for Recovery of Volatile Compounds from Aqueous Solutions

Substances more volatile than water pass easier across a hydrophobic microporous membrane; therefore, the permeate is enriched in these substances.

Fermentation/MD - Integrated System

Ethanol is an example of such substances that preferentially vaporize from aqueous solutions. Traditionally, ethanol is produced by fermentation of biomass in the batch fermenter. The solution after fermentation contains 7-19% of alcohol. Unfortunately, the fermentation products are also inhibitants of the process. Together with the increase of ethanol concentration the rate of bioconversion falls to zero, the cell density in the fermenter remains low and a concentrated sugar solution cannot be completely fermented. This problem may be solved by integration of fermenter with a suitable separation technique. MD may by applied to continue the separation of ethanol from the fermenting broth [42]. Fig. 16 shows results of both the conventional bioconversion and integrated with MD. It is clear that the process integrated with MD is more profitable. The performance of fermentation in the membrane bioreactor allows for a considerable acceleration of its course and increases its efficiency through the selective removal of fermentation products.

HCL Recovery from Industrial Effluents

Before electroplating, the metal surface has to be clean. Different acids such as HCl, HNO_3 or H_2SO_4 are used for these purposes as a pickling liquor to remove surface oxides. The spent pickling liquors contain residual acid and suitable salts. Their composition depends on metal objects. Frequently they contain very harmful heavy metals. The components must be removed, recovered or recycled for environmental reasons. A neutralization procedure is used traditionally.

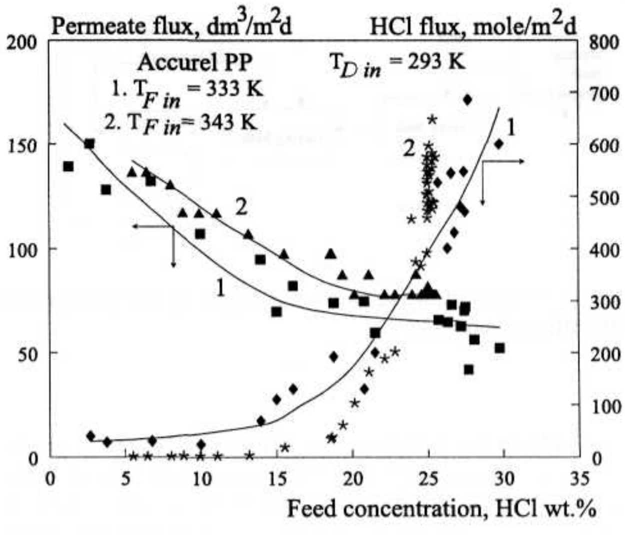

Fig. 17. Dependence of volume permeate flux and HCl molar flux through the membrane on the feed concentration and temperature.

Our experiments with membrane distillation show that it is possible to recover hydochloric acid used for pickling. Moreover, salt can be separated from the spent solution after its concentration to the supersaturated state.

During the MD process both water vapour and gaseous HC1 are transported through pores of the membrane from the warm feed to cold distillate, whereas salt was retained in the feed. The vapour was condensed directly in a cold distillate and gaseous HCl was then dissolved. Vapour composition is mainly affected by a hydrochloric acid concentration in the feed and its temperature (Fig. 17). At low acid concentration in the feed the permeate was pure water. The rise of acid concentration in the feed

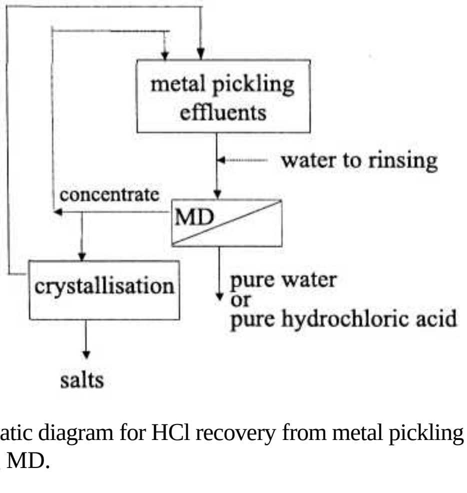

Fig. 18. Schematic diagram for HCl recovery from metal pickling effluents using MD.

above 19% caused a substantial increase in HC1 molar flux through the membrane. The presence of salt in the feed containing HC1 changes the results of MD due to a change of vapour composition. Accumulated salt in the feed decrease HC1 solubility (desalting out effect), thus the molar HC1 flux was then higher than in the case of hydrochloric acid solution without salt [43]. The retention coefficient of the salt was 99.8%, thus permeate was pure hydrochloric acid with a concentration which can be significantly higher than in the feed. The results of the experiments show that MD may be a promising method of HC1 recovery from industrial effluents, Fig. 18 [13]. A part of a concentrated solution may be recycled to favour the HC1 desorption. The useful products will be pure water, pure hydrochloric acid, and metal salts after crystallization from the supersaturated feed. The acid could be used for eatching of the fresh elements.

Summary

More and more examples of MD applications may be given and much research has been devoted to new applications, particularly in the area where advantages of MD make the process very promising. Taking into account the advantages of membrane distillation (especially the possibility of utilization of different energy sources - waste, solar, geothermal, etc.), the method may be very attractive, particularly in small and medium size plants.

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