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Preparation of hollow fibre membranes from PVDF/PVP blends and their application in VMD

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ABSTRACT

Microporous hydrophobic poly(vinylidene fluoride) (PVDF) hollow fibres were prepared by the dry–wet spinning technique. N,N-Dimethylformamide (DMF) was used as solvent, while water and poly(vinyl pyrrolidone) (PVP) were used as pore forming additives. Mixtures of DMF or ethanol in water were employed as bore fluids.

The influence of different parameters on the fibres characteristics was explored. Particular attention was focused on the PVP concentration and on the composition of the bore fluid. The obtained fibres exhibit good structure, excellent mechanical properties, high porosity (up to 80%) and an average pore size ranging from 0.12 to 0.27 μm. Fibres were tested in vacuum membrane distillation (VMD) configuration, using distilled water as feed. The effect of membrane properties on the water vapor fluxes was investigated. For the prepared membranes, the measured fluxes ranged between 3.5 and 18 kg/m^2 h at 50 °C and 20 mbar vacuum pressure. Some selected fibres were assessed for long term stability. Constant performances were observed up to 2 months. Furthermore, preliminary VMD tests on salty water were also performed, in order to verify fibres suitability for seawater desalination.

1. Introduction

Nowadays, it is widely recognized that, besides the global warming, water shortage is becoming a major emergency. In last years, membrane distillation (MD) was proposed as a valid alternative to traditional desalination techniques, such as multi-stage flash vaporization (MSFV), or coupled to reverse osmosis (RO) (integrated membrane systems), for its lower energy consumption and lower influence of osmotic pressure, respectively. Membrane distillation is a separation method in which a hydrophobic and microporous membrane is used with a liquid feed phase on one side of the membrane and a condensing, permeate phase on the other side. The driving force for transport is the partial pressure difference across the membrane. The principles of MD have been reviewed by many authors [1–4]. The possibility of using alternative energy sources, such as geothermal and solar energy, as well as to exploit low grade or waste energy, has been highlighted [5–7].

Although based on the same principle, MD processes can be divided in different categories, depending on the method applied for establishing the required driving force. Among the different MD configurations, vacuum membrane distillation (VMD) has attracted increasing interest for various applications beside seawater desalination, i.e.: removal of volatile organic compounds (VOCs) from water, concentration of aqueous solutions, and separation of non-volatile components form water such as ions, colloids and macromolecules. The application areas range from environmental waste clean-up to food processing [8–18]. In VMD, the liquid feed is brought in contact with one side of a hydrophobic membrane, while vacuum is applied at the permeate side. Vapor condensation takes place outside of the module.

VMD results in many advantages, with respect to conventional separation techniques, and, from an economic point of view, is comparable to alternative membrane processes, such as pervaporation [19]. With respect to other MD configurations, VMD allows to reach higher partial pressure gradients and, hence, higher fluxes and plant productivity. It performs better than DCMD in terms of transmembrane fluxes, energy consumption/permeate flow ratios and evaporation efficiency [20].

Recently, MD potentialities, in terms of productivity, costs and efficiency, have been examined in details [21]. Authors investigated the effect of different parameters on the MD performance. Membrane critical features resulted to be the thermal conductivity and the porosity.

The heat lost by conduction through the membrane reduces the thermal gradient, which is the driving force of the process, thereby negatively affecting the transport.

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Table 1
Separation performance of PVDF flat sheet (FS) and hollow fibre (HF) membranes for VMD reported in the literature.

MD process	Membrane	Membrane properties	Dope composition	J/°C	Ref
VMD/pure H_2O	FS	Pore size 0.22 μm Porosity 70.5%	DMAC, H_2O	1.39 kg/m^2 h (feed 25 °C)	[44]
VMD/pure H_2O	HF	Avg. Pore size 0.031 μm Effective porosity 1516 m^{-1}	DMAC, LiCl/H_2O	0.5 kg/m^2 h (feed 50 °C)	[46]

Abbreviations: DMAc: dimethylacetamide; FS: flat sheet; HF: hollow fibre; VMD: vacuum membrane distillation.

Membranes having higher porosity ensure better molecular diffusion and, therefore, higher flux. The effect of membrane thickness is more complex. Thinner membranes offer lower resistance to the transport, but, membranes of reduced thickness leads to higher heat losses by conduction.

Different papers have pointed out that the search for new materials and the development of suitable membranes are of primary importance for the future commercialization of MD, in order to improve the process productivity and reduce its costs.

The production of membranes suitable for MD has been discussed in different works. They can be divided in two main categories: (a) surface modification to turn hydrophilic flat sheet or hollow fibre membranes into hydrophobic ones and (b) preparation of flat membranes or fibres, from binary or ternary dopes, starting from a hydrophobic polymer, and using a suitable solvent and pore forming or other additives.

Surface modifications of hydrophobic membranes, like coating, grafting or incorporation of macromolecules usually aim at the production of a membrane having reduced transport resistances. In fact, the hydrophilic part provides mechanical support with low resistance to transport, leading to high fluxes, while the modified surface ensures the required hydrophobicity [22–34].

In recent years, polyvinylidene fluoride (PVDF) became a popular membrane material due not only to its good hydrophobicity and excellent chemical stability, but also to the feasibility of forming hollow fibres and membranes via a phase inversion method; several examples of PVDF membrane preparation for various applications are already reported in literature [35–38].

There are different studies that have examined the possibility of producing PVDF flat sheet and hollow fibre membranes for application in MD [39–55]. Table 1 shows the VMD transmembrane fluxes reported in literature, with both PVDF flat sheet and hollow fibre membranes.

In the recent papers [52–55], different approaches to improve PVDF membranes morphology and performances were proposed.

Teoh and Chung [52] prepared hydrophobic polyvinylidene fluoride–polytetrafluoroethylene (PVDF–PTFE) hollow fibres showing improved hydrophobicity and macrovoid-free structure.

Wang et al. [53] produced mixed matrix PVDF hollow fibre membranes by adding hydrophobic cloisite clay particles to the polymeric dope. These fibres have high porosity but a layer of nanoscale pores thus ensuring high fluxes, good thermal insulation and reduced risk of membrane pore wetting because of the high LEPw (water liquid entry pressure).

Table 3
Hollow fibre spinning base conditions.

Spinning conditions	
Bore fluid	EtOH:H_2O 30:70; DMF:H_2O 15–35:85–65
Bore fluid injection rate (ml/min)	7–20
Bore fluid temperature (°C)	50
Coagulation bath	H_2O 100%
Coagulation bath temperature (°C)	20
Polymeric dope temperature (°C)	85
Polymeric dope flow rate (g/min)	12
Air gap (cm)	25
Room temperature (°C)	25

Bonyadi and Chung [54] obtained highly porous and macrovoid-free PVDF hollow fibre membranes co-extruding the polymeric dope and the solvent by means of a triple spinneret. The solvent flow at the fibres outer surface prevented the formation of a dense skin, increased the outer surface porosity of the PVDF fibres and eliminated the formation of macrovoids.

Finally, Hou et al. [55] proposed the synergic use of two pore forming agents (LiCl and PEG 1500) which led to fibres with high porosity and good hydrophobicity.

The aim of this research work was the production of microporous hydrophobic PVDF hollow fibres suitable for VMD, by using water and poly(vinylpyrrolidone) as pore forming additives.

Different works already reported about the use of water as pore forming additive for preparing both flat sheet and hollow fibre membranes for MD [44], sometimes in combination with other additives, such as LiCl [46].

PVP is widely used in preparing membranes and fibres to adjust pore size and pore size distribution, increase membrane permeability, produce hydrophilic membranes and prevent fouling. It is mainly combined in blends with polysulfone (PSU), polyethersulfone (PES) and polyvinylidene fluoride (PVDF) to prepare membranes for ultra- (UF) and microfiltration (MF) to be used in: biomedical applications (e.g. dialysis), water purification, waste

Table 2
PVDF dopes composition.

Membrane dope	1	2	3	4	5	6
Polymer						
PVDF Solef 6020 (%)	20	20	20	20	20	20
Solvent						
DMF (%)	68	65	63	59	74	65
Additives						
PVP (K-17) (%)	6	9	11	15	0	15
H_2O (%)	6	6	6	6	6	0