Desalination and Water Treatment
www.deswater.com

51 (2013) 606–608
January

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doi: 10.1080/19443994.2012.705505

Gas separation process: analysis of composite membranes based on alumina/PVDF at lower power consumption energy

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Received 29 February 2012; Accepted 15 June 2012

ABSTRACT

Human activity have been emitting greenhouse gases into the atmosphere for a long time. To separate these gases, especially CO_2 and CH_4, polymeric membranes have been used in the chemical industry as this technology has a lower power consumption when compared to other separation processes. In this work, α-alumina ceramic tubes (support) were internally impregnated with poly(fluoride vinylidene) (PVDF), and the permeability and selectivity of the membrane to CO_2, CH_4, and O_2 was studied. All membranes (MT1 and MT2), when tested at low pressures, presented higher selectivity to CH_4 gas, and with increasing pressure the selectivity for CO_2 increased as well. The MT2 membrane was more efficient in the separation of CO_2/CH_4 gases, which is an important result because both of them are the most impacting gases to the greenhouse effect and the most difficult to separate using membrane process.

Keywords: Composite membranes; Alumina/PVDF; Gás separation; GHG

1. Introduction

Ceramic membranes have high thermal and chemical resistance, easy cleaning, and longer life, but high costs and little flexibility in comparison to polymeric membranes. Polymer films have the function to promote high selectivity, while the inorganic porous support promotes high flow [1,2]. Polymeric membranes have been used for the separation of gases, mainly in the chemical industry, since it has lower power consumption energy, is compact, modular, and reduces greenhouse effect gases, especially the oil area, separating CO_2/CH_4, H_2/O_2, O_2/N_2, and natural gas, among others [3].

Polyvinylidene fluoride (PVDF), a widely used polymer, is used in the preparation of membranes. It is a hydrophobic and nontoxic polymer having high thermal and chemical resistance [4]. The solubility of PVDF is restricted. The most used solvents to dissolve this polymer are strongly polar solvents such as: dimethylformamide (DMF), dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), tetrahydrofuran, and 1-methyl-2-pirrolydone (NMP) [5].

The ideal gas separation process occurs when a high flux and high selectivity are obtained, but both do not usually occur at the same time [6].

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

Table 1
Membrane permeability and selectivity for MT1 and MT2 CO_2, CH_4, N_2, and O_2 at different pressures

Membrane	Pressure (bar)	Permeability (MBarrer)				Selectivity		
		CO_2	N_2	CH_4	O_2	α CO_2/N_2	α CO_2/CH_4	α CO_2/O_2
MT1	0.5	355	412	604	389	0.86	0.59	0.91
	1	240	261	503	261	0.92	0.48	0.92
	1.5	307	312	503	298	0.98	0.61	1.03
	2	313	309	431	306	1.01	0.73	1.02
MT2	0.5	137	158	223	155	0.87	0.61	0.88
	1	144	177	172	151	0.81	0.84	0.95
	1.5	161	160	160	144	1.01	1.01	1.12
	2	130	130	131	120	1.00	0.99	1.08

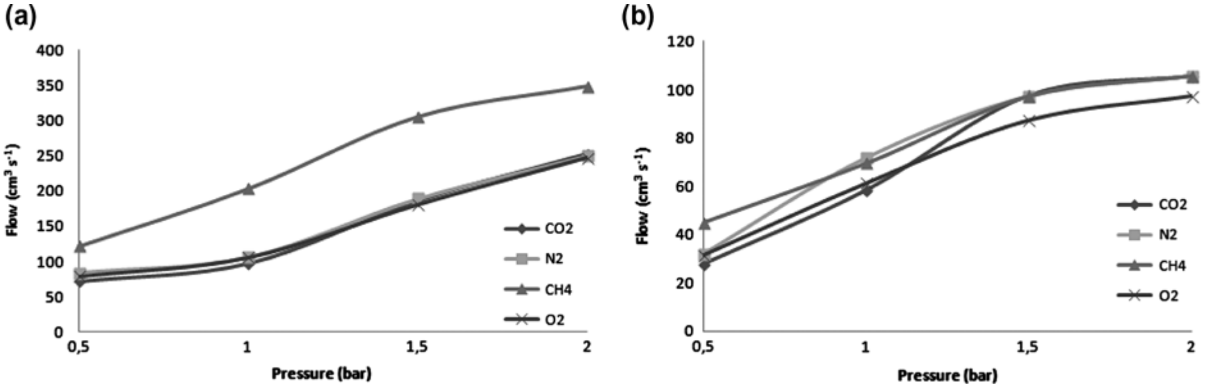

Fig. 1. Fluxes of CO_2, CH_4, N_2, and O_2 at different pressures (0.5, 1.0, 1.5, and 2.0 bar) for MT1 (A) and MT2 (B).

In this work, ceramic tubes of α-alumina (support) were impregnated on the internal surface in the tubular ceramic membrane with PVDF. The ceramic provides mechanical strength to the polymer film and the polymer fills the pores of the micropores support, forming a monolayer that acts as selective material which increases retention of the membrane [7].

2. Materials and methods

The membranes were prepared after the impregnation of PVDF (Solvay Solexis) solution inside the tubular ceramic support. The support (Technical Cetebra Brazil) had an average pore size of 0.64 μm. The 5% PVDF solution (w/v) was prepared using DMF (Vetec) as solvent. The 5% PVDF impregnation solution was performed by *dip coating*, and after the ceramic tubes were immersed in different nonsolvents to obtain a nonselective layer of PVDF by inversion phase process. Pure water was used as a nonsolvent to obtain the tubular membrane (MT1) and sodium dodecyl sulfate (SDS) was used as the clotting agent followed by pure water to the membrane (MT2). The composite membranes remained for six hours at 30 ℃ in the vacuum oven to remove excess solvent.

The CO_2, CH_4, N_2, and O_2 permeability and selectivity with effective area of 107.56 cm^2 and thickness 0.2 cm was measured at different pressures (0.5, 1.0, 1.5, and 2.0 bar). The CO_2, CH_4, N_2, and O_2 permeability were determined in accordance with Eq. (1).

$$P = \frac{q\ell}{A(p_1 - p_2)} \tag{1}$$

where P is permeability expressed in Barrer (1Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg), q is the flow rate of the permeate gas passing through the membrane ($cm^3 s^{-1}$), ℓ is membrane thickness (cm), p_1 and p_2 are the absolute pressures of the feed side and the permeate side respectively (cmHg), and A is the effective membrane area (cm^2). The ideal selectivity

($\alpha_{A/B}$) of the membranes was calculated from pure gas permeation experiments, Eq. (2) [8].

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

3. Results and discussion

Table 1 shows the permeability of pure gases (CO_2, CH_4, N_2, and O_2) and selectivity values for the prepared membranes. The MT1 and MT2 membranes permeability were expressed in MBarrer (Mega Barrer). Without impregnation, the membranes permeability was in the order of 3.500 MBarrer. For the both membranes, an increase in CO_2 selectivity over other gases with increasing pressure was observed, especially for the tests performed with MT2 membranes.

The selectivity of CO_2/CH_4 increased from 0.59 to 0.73 (pressure of 0.5–2.0 bar) in the membrane MT1 and reached 1.01 (pressure 1.5 bar) in the MT2 membrane.

Fig. 1 shows the gas flow using the MT1 and MT2 membranes at different pressures (0.5, 1.0, 1.5, and 2.0 bar). It was observed that with increasing pressure, there was an increase in the gas flow with higher values to CH_4 to the both membranes. The PVDF membranes showed increased flows, up to 1652 $cm^3 s^{-1}$ for CH_4 with 2 bar of gas pressure, while for the MT1 and MT2 membranes were 348 and 105 $cm^3 s^{-1}$, respectively. For CO_2, the gas flow was 1.661 $cm^3 s^{-1}$ for the membranes without impregnation at 2 bar pressure, while for the MT1 and MT2 membranes were 252 and 105 $cm^3 s^{-1}$, respectively.

4. Conclusion

It was observed that in the MT1 membrane higher permeability for all the gases was studied, but exhibited a lower selectivity to CO_2/CH_4 in comparison to the MT2 membrane at any pressure. In conclusion, the MT2 membrane was more efficient in the separation of CO_2/CH_4 gases, which is an important result because both of them are the most impacting gases to the greenhouse effect and the most difficult to separate using a membrane process.

Acknowledgment

The authors would like to thank the UNIVILLE, UCS and CNPq.

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