



## Bentonite – Polyurethane Mixed Matrix Membranes for Pervaporation

A.V. Ramos<sup>a\*</sup> and A. C. Habert<sup>a,b</sup>

<sup>a</sup> Programa de Engenharia da Nanotecnologia, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

<sup>b</sup> Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

\*andresa@pent.coppe.ufrj.br

### Abstract

Pervaporation is characterized by the separation of liquid mixtures due mainly to the affinity of one of the compounds with the membrane material. The separation occurs as a sweeping gas or vacuum is kept in the downstream side of the membrane, creating a concentration difference across the membrane that promotes the mass flow [1]. The liquid on the feed is adsorbed by the membrane, diffuses through the material, and is desorbed on the permeate side, where it evaporates; the permeate is then condensed. Isopropanol is a secondary alcohol produced by microorganisms that can be used to esterify fats. Its production is of great interest to the biorefinery industry as a “green” substitute of methanol used for producing biodiesel [2]. Water/Isopropanol is frequently used as feed mixture to test hydrophilic membranes in pervaporation processes because isopropanol is frequently used as substitute for ethanol by the industry. While hydrophilic membranes present great permeability to water and can separate water/isopropanol mixtures, the swelling due to the affinity to water is so that it can hinder its industrial applications. Hydrophobic membranes, on the other hand, might perform poorly in comparison[3]. Thus, this study aimed to assess how incorporating a hydrophilic nanoparticle into an organophilic polymer affected the membrane separation of water/isopropanol mixtures in pervaporation.

Bentonite-Polyurethane mixed matrix membranes were prepared as follows. Firstly, the membrane casting solution was prepared by dispersing the hydrophilic Bentonite (Sigma Aldrich, Germany) in tetrahydrofuran (Neon Comercial, Brazil) with the aid of an ultrasound (Eco-sonics, Brazil) for 30 minutes, followed by the addition of 10% of polyurethane (BASF, Germany) under stirring for 24 hours. The membrane-forming solution was verted into Teflon petri dishes and the membranes carefully casting-dried. Bentonite was used in 0, 10, 20, 30 and 40% wt. proportions.

Pervaporation was carried out at 30°C using different water-isopropanol ratios as feed. Permeation flux and the S separation factor are measurement of how well the membrane separates water from isopropanol. Each membrane was weighted before and after the pervaporation to determine the amount of liquid retained due to the pervaporation. The degree of swelling was determined by soaking dry membranes in feed stock with different compositions of water–isopropanol mixtures at 30 °C for 24 h to attain equilibrium swelling. The membranes were then wiped with tissue paper carefully to remove the surface adhered solvent and weighed as quickly as possible on a digital microbalance. Samples were taken at least in triplicates.

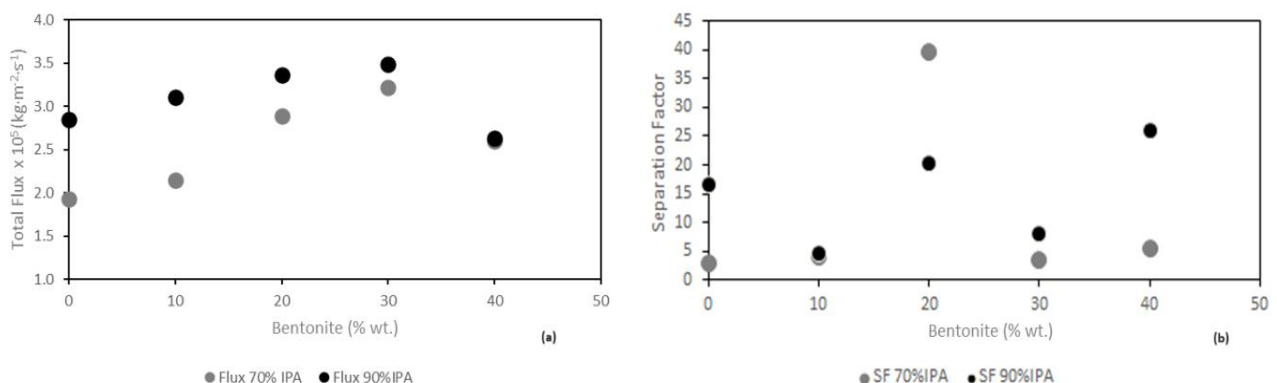


Fig. 1 – Total Flux (a) and Separation Factor (b) of water-isopropanol mixtures containing 70% isopropanol (●) or 90% isopropanol (●)

The results in Fig. 1(a) indicate that the increase in bentonite concentration up to 30% wt. resulted in higher permeation flux, while the greatest separation factor was observed for bentonite-polyurethane membranes containing 20% of bentonite. Although a feed richer in isopropanol (90%) achieved its greatest separation factor when the membranes contained 40% wt. of bentonite, the total flux was the lowest, which is not desirable. One can hint the competition between sorption and diffusion in the transport mechanism is reversed at higher bentonite concentrations, i.e. the



increased diffusional limitations due to a barrier effect overcome preferential sorption, leading to lower flux. Hence, on this investigation, the best separation performance was reached with 20% wt. bentonite-polyurethane mixed matrix membranes.

The 20% wt. bentonite-polyurethane membrane was used for pervaporation of water-isopropanol feed with different composition ratios from 5 to 100% isopropanol and the results are presented in Fig. 2(a). The permeate flux raises linearly with the increase in isopropanol content up to 90%, with a correlation factor of 0.97. However, when the feed was 100% isopropanol, the permeate flux dropped drastically, reaching  $5.6 \cdot 10^{-8} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ . These results suggest that the transport through the membrane is enhanced by the coupling effect between water and isopropanol, which was also observed by Das et al. [4] studying polyvinyl alcohol membranes. The membrane performance achieved in this work was similar to the crosslinked hydrophilic membranes developed by Das et al. [4] and greater than other hydrophobic membranes in literature [3].

Fig. 2(b) brings the amount of liquid absorbed by the membrane when small pieces were dipped into water-isopropanol solutions and due to the pervaporation (PV). It can be observed that when the membranes were stored in the solution for 24 hours, they retained more liquid than during the pervaporation. Also, the membrane retained much less isopropanol after pervaporation of a pure isopropanol feed than it does when stored dipped in isopropanol. These results indicate that although the swelling test is a good indicator of membrane integrity after immersed in the feed solution, the amount of liquid absorbed might not reflect the real conditions of PV.

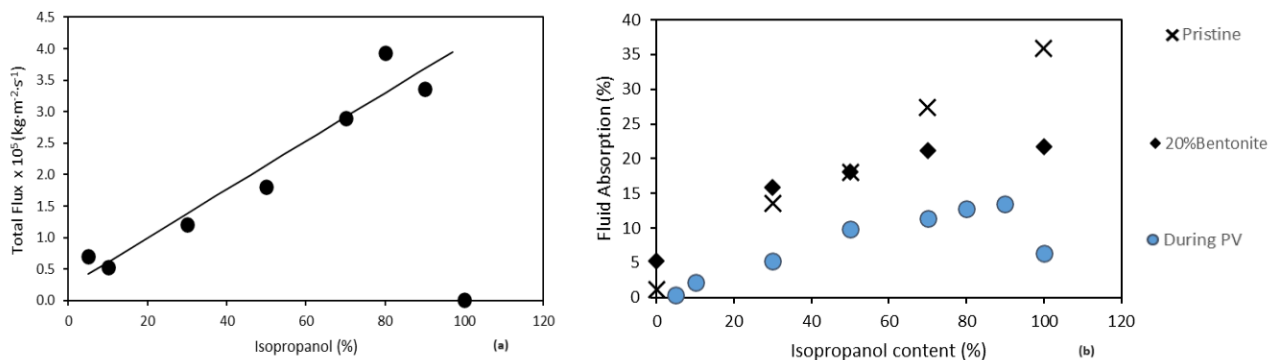


Fig. 2 – Permeate flux for different feed compositions (a) and swelling of pristine (x) and 20% wt. bentonite (◆) membranes in controlled environment and 20% wt. bentonite after pervaporation (●)

The results observed in this work indicate that the presence of bentonite enhanced the separation of water-isopropanol mixtures and suggest that the water-alcohol affinity favored the pervaporation. Furthermore, the mass gain of the membranes after the pervaporation should be followed to better describe the separation process. Bentonite-polyurethane mixed matrix membranes seem to have good potential for water-alcohol separation via pervaporation and should be considered for further studies.

## References

- [1] P. Shao, R.Y.M. Huang, Polymeric membrane pervaporation, 2007. <https://doi.org/10.1016/j.memsci.2006.10.043>.
- [2] L. Liang, R. Liu, A.D. Garst, T. Lee, V.S. i. Nogué, G.T. Beckham, R.T. Gill, CRISPR Enabled Trackable genome Engineering for isopropanol production in Escherichia coli, *Metabolic Engineering* 41 (2017) 1–10. <https://doi.org/10.1016/j.ymben.2017.02.009>.
- [3] W.Z.A.W. Jusoh, S.A. Rahman, A.L. Ahmad, N.M. Mokhtar, Modifications on Polymeric Membranes for Isopropanol Dehydration Using Pervaporation: A Review, in: Inamuddin, A.M. Asiri (Eds.), *Applications of Nanotechnology for Green Synthesis*, Springer International Publishing, Cham, 2020: pp. 97–124. [https://doi.org/10.1007/978-3-030-44176-0\\_5](https://doi.org/10.1007/978-3-030-44176-0_5).
- [4] P. Das, S.K. Ray, S.B. Kuila, H.S. Samanta, N.R. Singha, Systematic choice of crosslinker and filler for pervaporation membrane: A case study with dehydration of isopropyl alcohol–water mixtures by polyvinyl alcohol membranes, *Separation and Purification Technology* 81 (2011) 159–173. <https://doi.org/10.1016/j.seppur.2011.07.020>.