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Activated Carbon-Loaded Polydimethylsiloxane Membranes for the Pervaporation of 1-Butanol from Aqueous Solutions

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Butanol has shown potential as an alternative biofuel. It can be obtained through ABE fermentation, which produces 1-butanol, ethanol and acetone. Pervaporation is a potential separation process, since it can be successfully applied to remove trace components such as butanol, which is toxic to the cells. The development of an effective membrane is the limiting factor for this technology. Activated carbon-containing polydimethylsiloxane membranes were prepared by varying the filler content up to 2 wt%. The resulting membranes were characterized for the separation of model solutions with 1-butanol, acetone, ethanol and water by pervaporation. The effects of activated carbon load (0, 1, 2 wt%) and temperature (25, 40, 55ºC) on flux and separation factor were evaluated. The addition of 1 wt% activated carbon increased membrane free volume, changed surface morphology and showed flux of 45 g/m^{2}h, with separation factor for 1-butanol of 370, at 55ºC.

Keywords: *Activated carbon, Butanol, Membrane, Pervaporation, Polydimethylsiloxane.*

1. Introduction

Butanol has emerged as a potential alternative biofuel both in the replacement of gasoline and as an intermediate in chemical synthesis, in accordance with the biorefinery concept[1]. The use of biomass to produce butanol is well known as the ABE process[2,3], in which the fermentation of sugars by *Clostridium acetobutylicum* results in acetone, 1-butanol and ethanol (ABE). The major limitation of this route is the toxicity of 1-butanol to the cells, which is responsible for the low yield of the entire process[4]. The toxic content to the cells is reported in the literature to be above 20 g/L of 1-butanol in the fermentation broth[5].

To circumvent this problem, many papers have been published showing different attempts to remove 1-butanol from the medium to allow the fermentation to go further[6,7]. The idea is to maintain the concentration of 1-butanol below the toxic level simultaneously to its production[8]. One of the main promising technologies is pervaporation, a membrane-based process in which a liquid solution is fed to a module, the preferred permeant diffuses and evaporates through the membrane and is condensed in the permeate side. This method is ideal to remove trace components from the feed solution[9]. The advantage of pervaporation over other techniques is the use of mild conditions, especially regarded to temperature and pH, which is very important to prevent cell death in fermentation broths[10].

Since the organics are in low concentration in the medium, hydrophobic membranes are investigated to perform the separation, especially polydimethylsiloxane (PDMS) and poly(ether-block-amide), (PEBA)[5,8,10-13]. Silicone rubber is among the best polymers to perform such separations, as it is known from the literature[8,10-13]. Being a macromolecule in which the main chain is formed by Si-O-Si branched with alkyl side groups, the polymer is highly flexible and no polar, able to reject water from the fermentation broth. However, the high flux obtained through polydimethylsiloxane membranes is usually accompanied of low selectivity, so that water is co-transported along with the organics from the feed to the permeate side[8,10].

To increase the selectivity of elastomeric polymers, there are attempts to produce mixed matrix membranes, defined as a composite material in which a solid phase is dispersed in a continuous one, with the aim to provide an additional transport mechanism through the film[14]. There are many papers in the literature about this subject, but the dispersion of the solid phase in the polymeric matrix remains unsolved in most cases[14]. The most common solid phase dispersed in polydimethylsiloxane membranes for ABE recovery is silicalite[12,15].

Silicalite-filled polydimethylsiloxane commercial membrane (Pervap 1070) was investigated for the separation of butanol/water mixtures, up to 0.5 wt% of the alcohol in feed stream, at 65ºC. The results revealed that the permeate flux was 500 g/m^{2}h and separation factor of 45[12]. In another approach, the improvement in silicalite dispersion over polydimethylsiloxane

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was investigated by means of vinyltrimethoxysilane. The pervaporation of ABE aqueous solution up to 1.6 wt% in feed, at 50ºC, led to a permeate flux of 90 g/m^{2}h, and separation factor butanol/water up to 160. The increase in membrane separation factor over water was attributed to the high load (68 wt%) of the modified silicalite in the membrane, which augmented the tortuous path for water permeation[15].

The investigation of zeolite as the dispersed phase in polydimethylsiloxane was evaluated in the separation of ethanol/water solutions. In the membrane preparation step, they have added zeolites prior and after mixing PDMS pre-polymer and crosslinker. The addition of the inorganic particles after PDMS crosslinking was more effective for the removal of ethanol due to the aggregation of solid particles, with the increase both permeability and selectivity[16].

The use of carbonaceous fillers in PDMS is gaining attention of the researchers. Shi and coworkers investigated the dispersion of carbon black in polydimethylsiloxane for the pervaporation of water/ethanol mixture, by means of the surface modification of the solid phase. By using ethanol feed content of 13.73 wt% and 30ºC, the permeate flux was increased to 234 g/m^{2}h, while the separation factor remained around 9[17].

Activated carbon is a well-known material, largely used as adsorbent, due to the micro porosity, which causes an increased specific area. The adsorption/desorption cycles of 1-butanol, toluene and butyl acetate in activated carbon was reported in the literature[18]. The results showed heat of desorption of butanol from activated carbon higher than the heat of vaporization. Differential scanning calorimetry and temperature-programmed desorption revealed that butanol strongly interacted with activated carbon, so that the it could be desorbed only in higher temperatures[18].

Azimi and coworkers[19] investigated the use of activated carbon-loaded PDMS membranes for the separation of model binary solution of butanol in water (5 g/L). The results showed that the addition of activated carbon content from 2 to 8 wt% caused an increase in membrane selectivity, while the flux showed a maximum value at 6 wt% of the filler. Regarding the temperature, both flux and selectivity were increased from 37 to 57ºC.

These results lead to the investigation of activated carbon as the dispersed phase in silicone membranes in this work. From the previous state-of-art, it was seen that its use as filler in PDMS can act both decreasing the free volume fraction for permeation, such as a typical mixed matrix membrane, but also as an adsorbent of butanol, so that we could have a facilitated transport due to the specific interaction butanol/activated carbon. Our goal was the preparation and characterization of activated carbon dispersed in polydimethylsiloxane membranes aiming the separation of 1-butanol from model quaternary solutions by means of pervaporation. The effects of activated carbon content and temperature were addressed to evaluate the potential of this system for the removal of the organics from synthetic solutions mimicking the fermentation broth.

2. Experimental

2.1 Materials

Polystic commercial silicone glue with acetic cure (Pulvitec), which is a mixture of methyltriacetoxysilane (up to 5 wt%) and ethyltriacetoxysilane (up to 5 wt%) as stated by the manufacturer, toluene (Nuclear) and activated carbon (Merck) were used in membrane preparation. 1-butanol, acetone and ethanol were obtained by Synth, with purity higher than 99.5 wt%.

2.2 Activated Carbon Characterization

Activated carbon was previously milled so that it passed through a 400 mesh screen, 38 µm (Tyler). The resulting powder was dried at 120ºC for 1 hour and stored in a desiccator. The granulometry of activated carbon was analyzed by laser diffraction (Horiba LA-950). A small amount of the sample was added to the equipment cell, where it was mixed with water. The suspension was then degassed and inserted into the equipment for laser diffraction measuring. The mean size registered was of 23.4 µm.

The surface area was determined by nitrogen adsorption (Quantachrome, Nova 1000), using the BET isotherm model. The sample was degassed in a vacuum oven at 200ºC for 4 hours, followed by cooling the sample down to 25ºC, when the sample weight was determined. After that, the activated carbon was cooled to -195.7ºC and small amounts of N_2 were admitted into the chamber so that a plot of the volume of N_2 as a function of the pressure could be obtained and the surface area was calculated. The surface area of activated carbon used was 855 m^2/g.

2.3 Membrane Preparation

In order to prepare dense integral membranes, the desired amount of Polystic glue and toluene were transferred to a plastic flask. The system was closed and magnetically stirred at 25ºC, for 40 minutes. The amount of activated carbon was added to the solution in order to prepare membranes with 0, 0.5, 1 or 2 wt% of solid phase related to the polymer (Polystic glue). The suspension was cast in a flat Teflon plate and allowed to dry in a fume hood for 24 h, at 25ºC. Membranes were then transferred to an oven at 120ºC, for 1 hour. After that, membranes were stored in a desiccator until use.

2.4 Membrane Characterization

Membrane characterization comprised measurement of thickness, scanning electron microscopy, SEM, attenuated total reflectance Fourier transform infrared spectroscopy, ATR-FTIR, thermogravimetric analysis, TGA, and free volume by positron annihilation lifetime spectroscopy, PALS.

Membrane thickness was determined by means of a digital micrometer (Mitutoyo® Absolute). The results were reported as the average and standard deviation of at least 5 different points of the films.

SEM (FEG Quanta 200 FEI) tests were performed in order to evaluate membrane morphology. Samples were coated by a thin layer of gold, typically 2-3 nm, by means of sputtering (Baltec, MD20).

ATR-FTIR analysis was conducted in the Bruker Alpha equipment, with software opus 7.2, to evaluate the chemical bonding of the resulting samples, specially related to the polymer crosslinking.

TGA analysis was done in the TA Instruments Q5000 TGA model equipment. 8 mg of the sample were transferred to a platinum pan and heated from 30 to 800ºC, at 10ºC/min, under nitrogen atmosphere, 25 mL/min.

PALS measurements were made as described elsewhere[20]. Briefly, tests were conducted in a conventional fast-fast coincidence system (ORTEC) with temporal resolution of 240 ps, given by ^{60}Co prompt curve. The ^{22}Na positron source was sandwiched between two membrane samples with constant temperature of 25ºC. Three components were used in the fitting.

2.5 Pervaporation Experiments

Pervaporation experiments were performed to evaluate the transport properties of the samples for a model quaternary solution of 1-butanol, acetone, ethanol and water (solvent). Tests were done in a standard experimental setup shown schematically in Figure 1.

One liter of the model solution was pumped from the jacket feed tank to the 9 cm^2 membrane module. The solution temperature was controlled during the entire experiment. The permeate stream was maintained under vacuum so that the permeating species could evaporate as they permeated the membrane. A sensor was used to monitor the pressure in the permeate stream. Once the species permeated the membrane, they were trapped in a U-tube, which was immersed in liquid nitrogen. Permeate stream was removed with 4 and 8 hours of experiment. The non-permeating species were returned back to the feed tank.

The effects of activated carbon content (0-2 wt%) and temperature (25-55ºC) were evaluated. It is worth noting that the range of each variable was determined by experimental reasons. The use of 2 wt% of carbon activated as the maximum value was due to the fact that higher loads caused the brittleness of the films, which did not allow their use in permeation tests. Regarding the temperature, the central point was set at 40°C by considering the optimal temperature of the *C. acetobutylicum* fermentation broth[5]. 1-butanol concentration was fixed in 12 g/L, which is about half of the toxic content to the cells. The proportion between 1-butanol, acetone and ethanol was fixed in 6:3:1 in weight, since this is the expected resulting production of *C. acetobutylicum* fermentation broth.

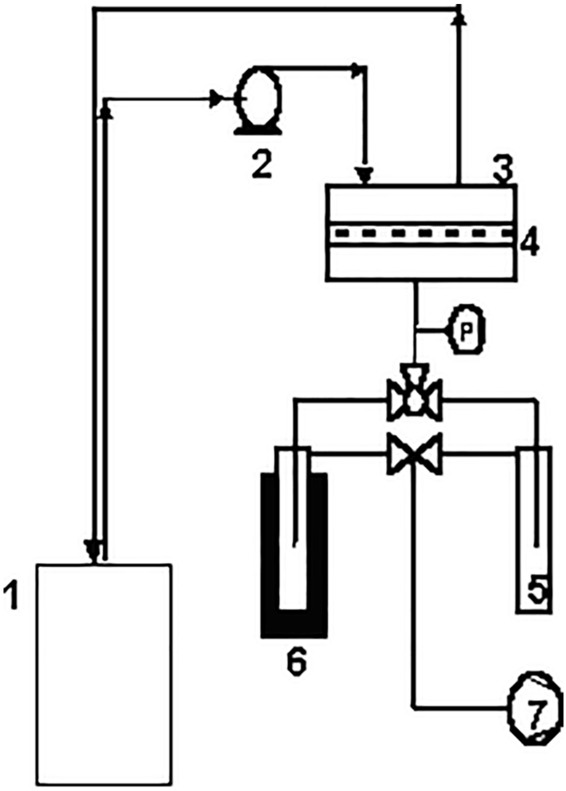

Figure 1. Pervaporation set up. 1- Feed tank, 2 - drive pump, 3 - pervaporation cell, 4 - membrane, 5 - condenser, 6 - liquid nitrogen.

As the responses, membrane flux and separation factor were calculated according to Equations 1 and 2[21].

$$J = \frac{m}{At} \tag{1}$$

$$a_{ij} = \frac{y_i / y_j}{x_i / x_j} \tag{2}$$

In Equation 1, J is the permeate flux, in g/(m^2.h), m is the mass of permeate, in g; A is membrane area, in m^2 and t is the time of permeation, in hour. In Equation 2, α_{ij}, the separation factor, is the ratio between the mass fraction of components i and j in permeate side and feed side of the membrane. The "y" is related to the permeate side, and "x" to the feed side. The subscripts i and j define butanol and water, respectively, since the permeation of ethanol and acetone were not of our interest in this work, but their effect in butanol permeation was considered instead.

The quantification of butanol both in feed and permeate was performed by gas chromatography (CG 17A, Shimadzu), equipped with a Carbowax 20M column. The detector was

FID-type (flame ionization detector). N_2 was used as sweep gas. The conditions of the analysis were temperature of injector of 220ºC, temperature of detector of 260ºC, operating pressure of 14 kPa, column flow of 0.31 mL/min, linear velocity of 9.7 cm/s, total flow of 31 mL/min. The program in the column was constant temperature of 35ºC for 7 minutes, heating from 35 to 60ºC, at 5ºC/min., constant temperature of 60ºC for 5 minutes, followed by a heating step from 60 to 90ºC, at 10ºC/min. Samples were injected in triplicate.

Karl Fischer tests were conducted in order to quantify the water in permeate stream in an automatic titrator (Schott, Titroline KF). The analysis comprised the titration of a known weight of the sample against the Karl Fischer reagent up to the potentiometric end of titration.

3. Results and Discussion

3.1 Membrane Characterization

By following the procedure described before, homogeneous and defect-free films were obtained. The results of membrane thickness are presented in Table 1.

Samples showed high thickness, ranging from 88 to 220 µm. This can be ascribed to the high viscosity of casting solution, causing variation in the amount transferred to the plate on each test. However, it was noticed a low standard deviation in membrane thickness. It was also not direct dependent on the activated carbon content, although the activated carbon-free membrane was the thinnest one. It is worth noting that the thickest membrane was the one with 1 wt% of activated carbon. The investigation of asymmetric membranes can be conducted in a future step, aiming the decrease in skin layer to increase membrane flux.

SEM images of different activated carbon-load membranes are presented in Figure 2. Membrane aspect was typical of silicone films, with high smooth surface, which can probably indicate good dispersion of activated carbon. No phase separation could be observed. Upon comparing the membranes, it was noticed that the smoothness surface of PDMS (Figure 2a) is different from the others. Membranes with 0.5 and 2 wt% of activated carbon showed the same aspect, with apparent higher roughness surface compared to pure PDMS. On the other hand, 1 wt% activated carbon membrane showed a different aspect, more likely to the PDMS membrane than the other activated carbon-containing ones.

Table 1. Results of membrane thickness as a function of activated carbon load.

Activated carbon (wt%)	Membrane thickness (µm)
0	88 ± 4
0.5	170 ± 20
1	220 ± 40
2	129 ± 4

ATR-FTIR results of membranes with different activated carbon content are presented in Figure 3. No significant differences were noticed in the spectra as a function of activated carbon content. In fact, some interesting findings were the absence of absorption bands around 3300 cm^{-1} and 1700 cm^{-1}, which are typical of hydroxyl and carbonyl groups, respectively, as would be expected for silicone with acetic cure. This result suggested that both hydroxyl terminal group and carboxylated structures were completely reacted in the final product, leading to a high crosslinking degree. Another hypothesis to the absence of such peaks are the interaction of the filler and the polymeric matrix. As the silicone used was commercial glue, FTIR was conducted in order to determine the presence of additives or impurities in the polymeric matrix, but the typical pattern of polydimethylsiloxane was obtained. No clue about differences in the polymeric structure could be addressed.

On the other hand, bands from 2852 to 2962 cm^{-1} related to C-H stretching of the sp^3 carbon and also bands at 1412 and 1258 cm^{-1}, usually related to the stretching of C-H of $-Si(CH_3)_2-$ groups were identified. Two overlapping bands at 1007 and 1074 cm^{-1} were noticed and are usually caused by the stretching of Si-O-Si from the main chain of silicone. Bands at 865, 795 and 699 cm^{-1} were ascribed to the stretching of the $Si-(CH_3)_2$ bonding.

The results of TGA are presented in Figure 4. In general, it was noticed a weight loss of about 10% in the early heating process, i. e., for temperatures lower than 200ºC, which was regarded to the presence of volatile components, such as toluene (membrane solvent) and adsorbed gases. It was noticed that the addition of activated carbon slightly increased membrane thermal stability, probably due to the interaction between the filler and the polymeric matrix.

The curves followed the typical pattern of polydimethylsiloxane: an initial weight loss at about 400ºC related to the exit of the lateral groups from the main chain, followed by a slight change on weight loss rate at about 500ºC, usually ascribed to the degradation of the main chain of siloxane.

The results of τ_3 and I_3, the longest component of the positron lifetime spectrum and the free volume concentration, respectively, for the membranes with varying content of activated carbon are presented in Figure 5. Both τ_3 and I_3 showed the same behavior: an increase with the addition of activated carbon content up to 1 wt%, in which both the free volume and the concentration of cavities reached a maximum, followed by a decrease for 2 wt% activated carbon membrane. This result indicated that the addition of 1 wt% activated carbon changed the polymer chain arrangement significantly, increasing both the free volume and the concentration of voids of the material. It can be reasoned in terms of the low affinity between activated carbon and PDMS, which may cause micro-voids in this interface, increasing free volume fraction and distribution over the film up to 1 wt% carbon load[17]. However, with the increase to 2 wt%, the nucleation

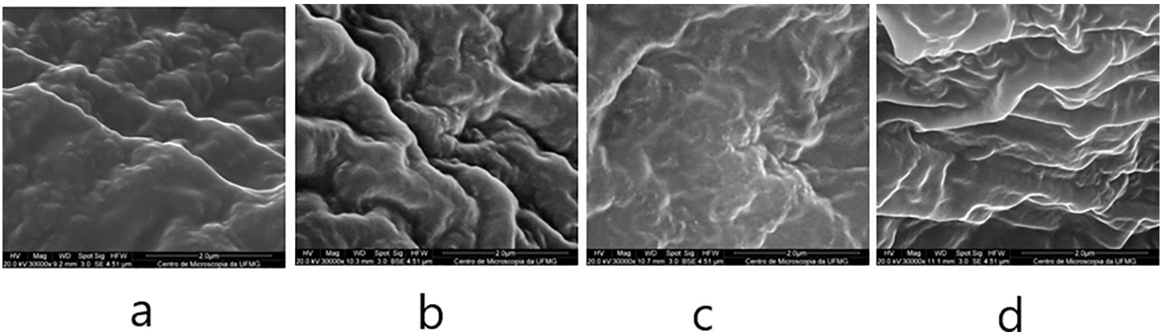

Figure 2. SEM images of membranes with different activated carbon load: (a) no activated carbon, (b) 0.5 wt%, (c) 1 wt%, (d) 2 wt%.

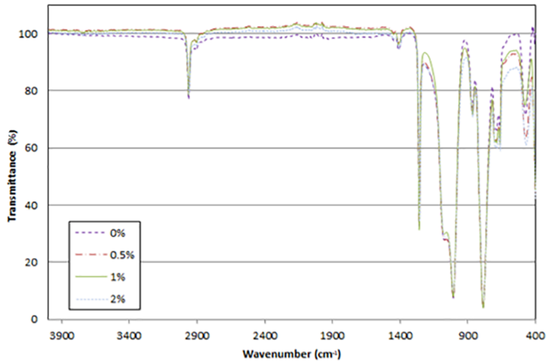

Figure 3. ATR-FTIR spectra of membranes with different activated carbon load.

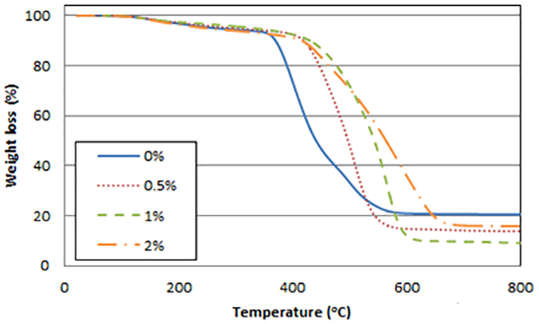

Figure 4. Thermogravimetric analysis of membranes with different activated carbon load.

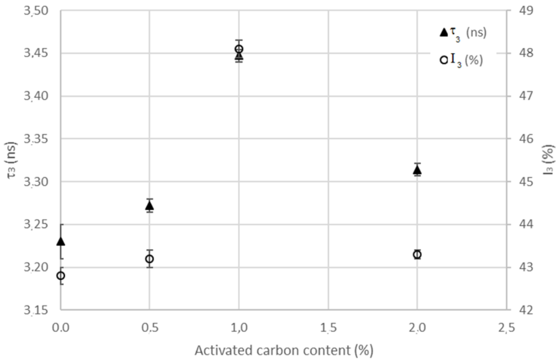

Figure 5. PALS measurements (τ_3 and I_3) of membranes with different activated carbon load.

of the particles was favored instead of dispersion, decreasing both τ_3 and I_3.

Upon comparing the results of PALS, thickness and SEM, it was possible to distinguish the membrane with 1 wt% activated carbon, which could be an evidence of different polymer chain arrangements with the addition of the filler.

3.2 Pervaporation

Pervaporation tests were conducted to evaluate the separation of 1-butanol from water in the presence of ethanol and acetone using activated carbon-loaded membranes. The selectivity of the membrane for acetone and ethanol were not presented since our main interest was butanol. As the membrane with 0.5 wt% of activated carbon did not show significant difference in behavior of characterization tests (SEM, ATR-FTIR, TGA and PALS), transport properties were analyzed for membranes with 0, 1 and 2 wt% of the filler. The effects of temperature and activated carbon content on membrane flux and separation factor were investigated. Membrane flux and separation factor were determined according to Equations 1 and 2. The results are presented in Table 2, in which the high separation factor (α) for butanol/water of the tests can be noticed. All measurements presented deviations lower than 10%.

3.2.1 Activated carbon load effect

According to Table 2, the addition of 1 and 2 wt% of activated carbon in PDMS decreased membrane flux, compared to pure PDMS. However, as the membranes showed a markedly difference in thickness, the result was normalized (product between the flux and membrane thickness). This property is related to membrane permeability, an intrinsic property of the material, since the driven force was kept the same for all tests. It was shown that, for 25ºC, the highest permeability was found for the membrane with 1 wt% of the filler, followed by the 2 wt% and no filler-added, with values of 4, 3 and 2 x 10^{-3} g/m.h, respectively. This result can be explained in terms of PALS measurements. The increase in permeability was directly related to the increase in free fraction volume of membranes. Membrane with the highest

Table 2. Membrane transport properties in pervaporation tests. 1-butanol feed content of 12 g/L.

Test	Temperature (ºC)	Activated carbon load (wt%)	Flux (g/m^{2}h)	Flux x thickness (g/mh)	$\alpha_{1\text{-butanol/water}}$ (dimensionless)
1	25	0	26 ± 2	2.31 x 10^{-3}	154
2	25	1	18.1 ± 0.5	3.98 x 10^{-3}	278
3	25	2	24 ± 2	3.15 x 10^{-3}	349
4	40	1	29.4 ± 0.8	6.47 x 10^{-3}	212
5	55	1	45 ± 3	9.86 x 10^{-3}	370

τ_3 also showed the highest concentration of I_3, as shown in Figure 5, which caused a major effect in permeability.

PDMS membrane showed a high separation factor, 154, which is one magnitude higher than similar works in the literature, varying from 9-40[4,19,22,23]. Probably this high selectivity is regarded to the use of a commercial glue instead of the usual PDMS kit. However, the use of additives in such material was not revealed in FTIR spectra. Another possible explanation for the differences in selectivity was the free volume of the membranes, but this characterization was not performed in the cited works.

Amongst the activated carbon loaded membranes, the increased separation factor of 1-butanol through the 2 wt% membrane can be related to the affinity and adsorption of this less polar species, compared to water. In such membrane, the lower values for I_3 and τ_3 should favor smaller particles transport like water. This indicated that the effect of the activated carbon load in membrane affinity (thermodynamic parameter) was more important than the kinetic one. In another words, the addition of more activated carbon increased the additional mechanism for butanol permeation, indicating a facilitation way caused by such filler in the final product.

3.2.2 Temperature effect

The increase in temperature caused an increase on 1 wt% activated carbon membrane flux. This could be reasoned in terms of the energy supply for the polymeric chain motion, which favored the diffusion of the penetrants through the membrane. The apparent activation energy for water and butanol, estimated by an Arrhenius plot, were 35.6 and 29.8 kJ/mol respectively.

The transport of 1-butanol showed apparent activation energy lower than water. This result is not in accordance with the literature. For instance, Rozicka and coauthors[22], which investigated the apparent activation energy of the binary system (butanol/water) in Pervap 4060 membranes, noticed values of 58 and 38 kJ/mol for butanol and water, respectively. They concluded that the addition of activated carbon caused a decrease in 50% on the energetic barrier for the alcohol transport. On the other hand, Azimi and coworkers[19] found activation energy of 66.4 and 43.9 kJ/mol for butanol and water, respectively, in the permeation of binary solutions to activated carbon-loaded PDMS, leading to the conclusion that butanol permeation is more susceptible to temperature changes. However, although water has the highest apparent activation energy in this work and the lower affinity to PDMS, it showed the highest flux since it is the smaller specie and its concentration in feed is the highest one (higher driven force for transport)[22,23]. The decrease in butanol apparent energy can be related to the facilitation that the addition of activated carbon caused in its transport, which is confirmed by the result of selectivity observed for the 2 wt% membrane, as aforementioned.

Regarding separation factor, 1-butanol showed a minimum value at 40ºC. This could be explained due to the favored interaction of activated carbon with 1-butanol, which caused its stripping from the membrane only at 55ºC, increasing the transport rate. Similar result was reported in the literature[18], indicating that the adsorption is governed by chemical character.

It is worth to note that the separation factor for 1-butanol reported in this work for the membrane of 1wt% of activated carbon and 55ºC, was higher than similar systems[5,19,24,25], but literature shows various works presenting values as high as 200 for pervaporation systems[2,7,26]. Upon comparing our results with Azimi and coworkers[19], in which activated carbon nanoparticles (20-40 nm and 1400 m^2/g) was dispersed in PDMS kit by means of toluene, it should be considered that our filler has different particle size and specific area (23400 nm and 855 m^2/g), together with a more selective PDMS, which could explain the increase on separation factor in 18-fold. In another words, the presence of higher pores could favor the permeation of a higher permeant, favoring the transport of butanol in such particle, instead of through highly constrained pathways, even with higher porosity. Regarding the flux, our values were lower, probably due to the high thickness of this membrane (220 µm). For instance, Zhou coworkers reported 90 g/m^{2}h of flux in similar conditions[15].

4. Conclusion

The results revealed the potential of the system activated carbon/polydimethylsiloxane as membranes for the separation of ABE solutions by pervaporation. The addition of activated carbon caused a different arrangement of silicone chains, as shown by TGA, SEM and PALS. Pervaporation tests showed that 1-butanol permeation was favored for the filler content of 2 wt%, probably due to the role of sorption in the lower free volume membrane. The high separation factor observed for 1-butanol at 55ºC indicated that the interaction of this alcohol with activated carbon was high and suggests a facilitated transport through the membrane, since the energy for desorption is supplied.

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6. References

1. Harvey BG, Meylemans HA. The role of butanol in the development of sustainable fuel technologies. *Chemical Technology and Biotechnology*. 2011;86(1):2-9.
2. Díaz VHG, Willis MJ. Kinetic modelling and simulation of batch, continuous and cell-recycling fermentations for acetone-butanol-ethanol production using Clostridium saccharoperbutylacetonicum N1-4. *Biochemical Engineering Journal*. 2018;137:30-39.
3. van der Merwe AB, Cheng H, Görgens JF, Knoetze JH. Comparison of energy efficiency and economics of process designs for biobutanol production from sugarcane molasses. *Fuel*. 2013;105:451-458.
4. Xue C, Zhao J, Chen L, Yang ST, Bai F. Recent advances and state-of-art strategies in strain and process engineering for biobutanol production by Clostridium acetobutylicum. *Biotechnology Advances*. 2017;35(2):310-322.
5. Yen HW, Chen ZH, Yang IK. Use of the composite membrane of poly(ether-block-amide) and carbon nanotubes (CNTs) in a pervaporation system incorporated with fermentation for butanol production by Clostridium acetobutylicum. *Bioresource Technology*. 2012;109:105-109.
6. Huang J, Meagher MM. Pervaporative recovery of n-butanol from aqueous solutions and ABE fermentation broth using thin-film silicalite-filled silicone composite membranes. *Journal of Membrane Science*. 2001;192(1-2):231-242.
7. Abdehagh N, Tezel FH, Thibault J. Separation techniques in butanol production: Challenges and developments. *Biomass and Bioenergy*. 2014;60:222-246.
8. Liu G, Wei W, Wu H, Dong X, Jiang M, Jin W. Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol ethanol (ABE) fermentation-PV coupled process. *Journal of Membrane Science*. 2011;373(1-2):121-129.
9. Jiang LY, Wang Y, Chung TS, Qiao XY, Lai JY. Polyimides membranes for pervaporation and biofuels separation. *Progress in Polymer Science*. 2009;34(11):1135-1160.
10. Liu G, Hou D, Wei W, Xiangli F, Jin W. Pervaporation Separation of Butanol-Water Mixtures Using Polydimethylsiloxane/Ceramic Composite Membrane. *Chinese Journal of Chemical Engineering*. 2011;19(1):40-44.
11. Chen C, Xiao Z, Tang X, Cui H, Zhang J, Li W, et al. Acetone-butanol-ethanol fermentation in a continuous and closed-circulating fermentation system with PDMS membrane bioreactor. *Bioresource Technology*. 2013;128:246-251.
12. Fouad EA, Feng X. Pervaporative separation of n-butanol from dilute aqueous solutions using silicalite-filled poly(dimethyl siloxane) membranes. *Journal of Membrane Science*. 2009;339(1-2):120-125.
13. Yi S, Wan Y. Separation performance of novel vinyltriethoxysilane (VTES)-g-silicalite-1/PDMS/PAN thin-film composite membrane in the recovery of bioethanol from fermentation broths by pervaporation. *Journal of Membrane Science*. 2017;524:132-140.
14. Noble RD. Perspectives on mixed matrix membranes. Journal of Membrane Science. 2011;378(1-2):393-397.
15. Zhou H, Su Y, Chen X, Yi S, Wan Y. Modification of silicalite-1 by vinyltrimethoxysilane (VTMS) and preparation of silicalite-1 filled polydimethylsiloxane (PDMS) hybrid pervaporation membranes. *Separation and Purification Technology*. 2010;75(3):286-294.
16. Lue SJ, Chien CF, Mahesh KPO. Pervaporative concentration of ethanol-water mixtures using heterogeneous polydimethylsiloxane (PDMS) mixed matrix membranes. *Journal of Membrane Science*. 2011;384(1-2):17-26.
17. Shi S, Du Z, Ye H, Zhang C, Li H. A Novel Carbon Black/Polydimethylsiloxane Composite Membrane with High Flux for the Separation of Ethanol from Water by Pervaporation. *Polymer Journal*. 2006;38(9):949-955.
18. Popescu M, Joly JP, Carré J, Danatoiu C. Dynamical adsorption and temperature-programmed desorption of VOCs (toluene, butyl acetate and butanol) on activated carbons. *Carbon*. 2003;41(4):739-748.
19. Azimi H, Tezel FH, Thibault J. Effect of embedded activated carbon nanoparticles on the performance of polydimethylsiloxane (PDMS) membrane for pervaporation separation of butanol. *Journal of Chemical Technology and Biotechnology*. 2017;92(12):2901-2911.
20. de Sales JA, Patrício PSO, Machado JC, Silva GG, Windmöller D. Systematic investigation of the effects of temperature and pressure on gas transport through polyurethane/poly(methylmethacrylate) phase-separated blends. *Journal of Membrane Science*. 2008;310(1-2):129-140.
21. Li SY, Srivastava R, Parnas RS. Separation of 1-butanol by pervaporation using a novel tri-layer PDMS composite membrane. *Journal of Membrane Science*. 2010;363(1-2):287-294.
22. Rozicka A, Niemistö J, Keiski RL, Kujawski W. Apparent and intrinsic properties of commercial PDMS based membranes in pervaporative removal of acetone, butanol and ethanol from binary aqueous mixtures. *Journal of Membrane Science*. 2014;453:108-118.

23. Kujawski J, Rozicka A, Bryjak M, Kujawski W. Pervaporative removal of acetone, butanol and ethanol from binary and multicomponent aqueous mixtures. *Separation and Purification Technology*. 2014;132:422-429.

24. Liu S, Liu G, Zhao X, Jin W. Hydrophobic-ZIF-71 filled PEBA mixed matrix membranes for recovery of biobutanol via pervaporation. *Journal of Membrane Science*. 2013;446:181-188.

25. Liu S, Liu G, Shen J, Jin W. Fabrication of MOFs/PEBA mixed matrix membranes and their application in bio-butanol production. *Separation and Purification Technology*. 2014;133:40-47.

26. Oudshoorn A, van der Wielen LAM, Straathof AJJ. Assessment of Options for Selective 1-Butanol Recovery from Aqueous Solution. *Industrial and Engineering Chemistry Research*. 2009;48(15):7325-7336.