Article

Separation of Benzene/Cyclohexane Mixtures by Pervaporation Using Poly (Ethylene-Co-Vinylalcohol) and Carbon Nanotube-Filled Poly (Vinyl Alcohol-Co-Ethylene) Membranes

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Received: 22 October 2020; Accepted: 29 November 2020; Published: 30 November 2020

Abstract: Poly(ethylene-co-vinylalcohol) (E-VOH) and carbon nanotube-filled poly (vinyl alcohol-co-ethylene) (E-VOH/CNT) were used as membranes to separate benzene/cyclohexane mixtures by pervaporation technique. To reach this goal, E-VOH and E-VOH/CNT membranes were prepared by solvent casting method and characterized by differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The swelling tests were used to study the mass transfer of the benzene/cyclohexane mixture and their pure components. The separation by pervaporation process was carried out at 25 °C in which the effect of CNTs incorporated into E-VOH matrix and the initial concentration of benzene in the feed on the permeate flux, j, and separation factor, β, performance was investigated. The results obtained were very promising, in which the integration of CNTs through E-VOH chains increased the absorption area and raised the flux to 740 g/m²·h. The separation factor increased to 9.03 and the pervaporation separation reached an index of 5942.2 g/m²·h for the azeotropic mixture during 3 h of the separation process. In contrast, for the unfilled E-VOH membrane, it was found that these parameters were a rise of 280 g·m⁻²·h⁻¹, separation factor of 12.90 and pervaporation separation index of 3332.0 g/m²·h, under the same conditions. Likewise, the calculation of the performance of the E-VOH/CNT membrane with regard to that of the unfilled membrane indicated 2.64 for the total flux and 0.70 for the separation factor. It was also revealed that the best compromise of the filled membrane in terms of total cumulative flux and separation factor is obtained for the feed containing the azeotropic mixture.

Keywords: benzene/cyclohexane mixture; pervaporation; carbon nanotubes/poly (ethylene-co-vinyl alcohol membrane; mass transfer

1. Introduction

Cyclohexane is used widely in the petrochemical industry, generally required to be highly refined as a raw material, and produced industrially from heavy naphtha by dehydrogenation of benzene. Separating benzene from the reaction medium is practically impossible or very expensive by conventional means because benzene and cyclohexane have similar temperatures of vaporization and form an azeotrope that further complicates their isolation. Indeed, current industrial separation methods for this mixture are principally azeotropic distillation and extractive distillation, which present multiple difficulties because of the need for a secondary distillation to remove the added auxiliary...
agent that prevents formation of the azeotrope. Consequently, the complexity of this separation process increases the cost considerably [1–5].

The pervaporation (PV) technique has proven successful at selective separation of many organic volatiles and homogeneous mixtures and gained considerable interest because of its low cost, eco-friendly process, high selectivity, and ease of integrating into a production chain in petrochemical plants as well as having the unique advantage of possibly enabling separations at low temperatures, which would avoid the risk of degrading heat-sensitive components.

Many studies have investigated selective separation of the benzene and cyclohexane azeotropic mixture by using the PV technique to obtain the best selectivity and permeability. The decisive factor for successful separation by PV is selection of an appropriate polymer enabling development of a membrane that provides the best PV parameters for a particular separation. The affinity for polymers containing hydroxyl groups is higher for benzene than for cyclohexane because of benzene’s π electrons. This is shown by a comparison of the water solubility of benzene (1.8 g/L) with that of cyclohexane (0.0561 g·L⁻¹) at 298K. Therefore, several polar and hydrophilic polymers are usually used in this process, such as polyacrylonitrile [6], polyurethane [7], poly (cellulose acetate) [8], poly (vinyl chloride) [9], and poly (vinyl alcohol) (PVA) [10]. The latter is frequently used because of its high affinity for water, good stability, and ease in preparing flexible polymer membranes at low cost.

Indeed, Yamazaki et al. [11] used PVA membranes to investigate the separation of a benzene/cyclohexane mixture and obtained low total flux (0.002 kg·µm⁻²·h⁻¹) and good selectivity (10.0). These findings revealed that a glassy PVA membrane had low permeability to benzene, so it required modification either by chemical or physical methods. The most popular and simplest modification method was to use fillers, such as carbon molecular sieves (CMSs) [10] or β-cyclodextrin (β-CD) [4]. CMS used to fill PVA effectively increased the permeation flux in compositions of CMS/PVA from 21.87 to 59.25 g·m⁻²·h⁻¹, which was followed by a decrease, whereas the separation factor reached 23.21 and then decreased beyond 59.25 g·m⁻²·h⁻¹. Cross-linked (PVA) membranes filled with β-CD considerably increased the separation factor from 16.7 to 27.0 and permeation flux from 23.1 to 30.9 g·m⁻²·h⁻¹ for a benzene/cyclohexane (50/50, wt %) mixture at 50 °C. Similarly, Park et al. [12] physically modified the pervaporative properties of PVA by blending this polymer with polyallylamine to investigate the benzene/cyclohexane separation by pervaporation and obtained a maximum flux of 2.3 kg·µm⁻²·h⁻¹ and a selectivity of 11.9. The separation of aromatic compounds from aliphatic mixtures is quite challenging. A novel graphite-filled poly(vinylalcohol)- Chitosan (PVA-CS) hybrid membrane for PV of benzene-cyclohexane mixtures has been reported [13,14]. It was found that both of the permeation flux and the separation factor (SF) improved with incorporation of graphite. The presence of specific α- and π-bond interactions between graphite and benzene enhanced the separation performance.

Polyethylene (PE) with different grades was also used as a membrane to separate benzene from benzene/cyclohexane mixtures. Indeed, Rautenbach et al. [15] used PE (type not identified), and obtained a total flux and a selectivity of 30.0 kg·µm⁻²·h⁻¹ and 2.5, respectively, whereas Huang et al. [16] used low-density PE and obtained a total flux of 10.8 kg·µm⁻²·h⁻¹ and a selectivity of 1.6. Based on the comparison of the results obtained by these two research groups, we can conclude that the best flux was obtained when the PE membrane was used, whereas the best selectivity was achieved by using the PVA membrane. The combination of these two polymers could potentially give a membrane that provides a suitable compromise between flux and selectivity. So far, however, no investigations have reported on a benzene/cyclohexane separation using a membrane made by combining PE and PVA. However, mixing PE with PVA leads to an immiscible blend that provides very poor quality materials, and its random mechanical and diffusion properties do not allow it to be used as a pervaporation membrane. On the other hand, poly (ethylene-co-vinyl alcohol) (E-VOH), which comprises units of PE and PVA in its structure, is an alternative that combines the pervaporative properties of the two polymers.
E-VOH (Scheme 1) is a copolymer in which the hydrophilic–hydrophobic properties can be easily controlled by its ethylene vinyl alcohol co-monomeric composition. This copolymer has been widely used as food packing material because of its flexibility and good gas barrier properties. This copolymer is synthesized by polymerization of ethylene with vinyl acetate giving the poly (ethylene-co-vinyl acetate) followed by hydrolysis of the functional groups [17].

Scheme 1. Structure of principal chemical used in this work.

Carbon nanotubes (CNTs) (Scheme 1) have, among other desirable properties, excellent chemical stability, high mechanical strength and thermal stability, and a large surface area [18,19]. These nanostructures can interact with a variety of compounds through different mechanisms such as hydrogen bonding, π–π stacking interactions, electrostatic and van der Waals forces, and hydrophobic interactions [20]. They have been explored as solid phase extraction (SPE) materials due to their chemical and thermal stability characteristics, ordered porosity, and high selective surface area (SSA), which promote high sorption capacity to analytes [21].

These carbonic structures have continued to attract the attention of many researchers in different fields since their (re)discovery by Sumio Lijima in 1991. Among the areas that have interested these researchers is the development of a new generation of composite membranes based on CNTs that enable selective separation of organic–organic mixtures with high fluxes. The high absorbability of CNTs has been employed in different membrane separation techniques involving different solute transport mechanisms [22–25]. According to theoretical studies conducted separately by Hinds et al. [26] and Hummer et al. [27], the rate of permeation of certain volatile liquids through CNTs exceeds the rate predicted by conventional models. This predicted improvement has been attributed to different factors, such as the smooth surface of CNTs, rapid transport without friction, molecular order [28], and high diffusivity [29,30]. Indeed, the van der Waals attractive forces which occur between these tubular nanostructures tend to group them into aggregates. Materials made of CNTs are widely used
as pervaporation membranes, especially to dehydrate alcohols. In fact, the use of PVA membranes incorporated with 1 wt % of multi-walled CNTs allowed to increase the water flux while maintaining the same selectivity [14,31].

According to these authors, the addition of an appropriate amount of CNTs led to a decrease in the crystallinity of the PVA and to a stimulated micro-orientation, thus reducing the free volume between the PVA chains. The reduction in free volume disadvantages the increase in the degree of swelling of the membrane, but also offers a shorter alternating diffusion path, allowing the molecules to transit rapidly. In order to have a uniform dispersion of the CNTs in the polymer matrix constituting the membrane, Zhao et al. [32] used a polymer matrix based on polyelectrolytes. Although the dispersion of the nanofillers was uniform, however, significant damage of the CNTs was observed through the cross section scanning electron microscopy (SEM) images of the resulted membranes. For the same purpose, multi-walled CNTs (MWCNTs) have been functionalized with poly (3-hydroxybutyrate) (PHB), then aligned in the CS matrix [33]. The presence of PHB in this case improved the compatibility of CNTs with CS, and hence a uniform distribution in the matrix was observed. The use of the resulting membranes showed better fluxes and selectivities for water in the dehydration of 1, 4-dioxane. PVA has also been used to modify MWCNTs to obtain a uniformly distributed membrane involving CS and MWCNTs to dehydrate acetone [34]. We hypothesized that CNTs could be successfully exploited as a non-organic filler because of its performance properties, such as low density, high surface area, and high flexibility. Incorporation of a controllable amount of these CNTs into poly (E-VOH) is expected to improve the resulting membrane’s permeability by increasing the benzene–polymer contact surface.

In this study, E-VOH alone and filled with CNTs (CNT/E-VOH) membranes were prepared by the solvent casting route and characterized by differential scanning calorimetry (DSC), Thermogravimetry analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) methods. Transfer of benzene/cyclohexane mixtures through the prepared membranes was investigated by examining swelling rates.

In addition, a kinetic study of the separation of benzene from the azeotropic benzene/cyclohexane mixture was carried out by the pervaporation technique to study the effect of the CNT/E-VOH composition on the pervaporative parameters (total flux and selectivity).

2. Materials and Methods

2.1. Materials

Poly (vinyl alcohol-co-ethylene) (E-VOH) (ethylene, 32 mol%) and carbon nanotubes (CNTs) (purity ≥95%, nanotubes multiwalled ≥95%, average internal diameter 8–10 nm, external diameter ≥ 14 nm, average length 10–50 µm) were purchased from Chengdu Ornanic Chemicals Ltd. (Chengdu, China). Benzene, cyclohexane and N, N dimethylformamide (DMF) were purchased from Scharlab (Barcelona, Spain). All chemicals were used without further purification.

2.2. E-VOH and E-VOH/CNT Membranes Preparation

E-VOH and E-VOH/CNT membranes were prepared by using the solvent casting method. For the E-VOH membrane, 1.0 g of E-VOH was dissolved in 25 mL of DMF under heating at 85 °C and stirring until complete dissolution (~2 h). For the E-VOH/CNT membrane preparation, 0.01 g of CNTs was immediately added to the E-VOH/DMF solution under moderate stirring until a homogeneous mixture was obtained. The suspension was smoothly sprayed over a Teflon plate surface and then heated in an oven maintained at 80 °C until the resulting film was insoluble in water (hydrogel formation). To extract all residual solvents and reactants from the obtained membranes, the films were dried at 80 °C under a high vacuum for 24 h. The average thickness of the prepared membranes was 80 ± 3 µm. A solubility test was performed by immersion of a small piece of the prepared membrane in DMF. Noting that the choice of the massic composition of CNTs in the E-VOH/CNT nanocomposite (1.0 wt %) was taken from the literature as the best composition leading to obtain a better compromise between
the pervaporative flux and the selectivity of membrane using comparable membranes such as poly
(vinyl alcohol)/chitosan-wrapped carbon nanotubes [35,36] and poly vinyl alcohol/multiwalled carbon
nanotubes membranes. [35,36]

2.3. Membrane Characterization

The surface morphologies of the membranes were examined by S4700 Hitachi SEM (Scientific
Instruments Ltd. Tokyo, Japan) with an acceleration voltage of 20.00 kV. The samples were fractured in
liquid nitrogen and then coated with gold by using a JEOL JFC-1600 Auto Fine Coater operated at
20 mA for 80 s prior to the analysis.

Thermal properties of membranes were measured by DSC (Shimadzu DSC 60A (Kyoto, Japan)
and TGA (Mettler-Toledo International Inc. Columbus, OH, USA). An 8.0-mg sample was pressed
into an aluminum DSC pan, placed in the heating module, and scanned from ~50 °C to 200 °C at
a heating rate of 10 °C/min. The glass transition temperature, \( T_g \), of the sample was taken directly
on the thermogram of the polymer as the midpoint in the heat capacity change with temperature,
and the melting point, \( T_m \), was taken from the top of the corresponding peak. TGA of each sample
was carried out on a Shimadzu TGA 60 under dynamic nitrogen gas. Afterward, 4–10 mg of each
sample was carefully loaded into the TGA aluminum pan and heated from 25 to 600 °C at a heating
rate of 20 °C-min\(^{-1}\).

XRD patterns of pure E-VOH, CNTs, and E-VOH/CNT nanocomposites were recorded using a
BRUKER D8 advance Diffractometer (Bruker, Karlsruhe, Germany) equipped with monochromatic
Cu-Kα radiation at 40 kV and 40 mA with scanning speed in 2θ of 2°-cm\(^{-1}\).

2.4. Benzene/Cyclohexane Mixture Preparation

The separate mixtures containing different compositions of benzene and cyclohexane were
prepared by mixing known amounts of these substances in an Erlenmeyer flask and maintained before
use under magnetic stirring at 25 °C for 15 min. Four mixtures containing different benzene/cyclohexane
compositions were prepared by the same method. The preparation conditions are summarized in Table 1.

| Mixture    | Benzene (mL) | Cyclohexane (mL) | Composition (wt %) |
|------------|--------------|------------------|-------------------|
| Benz/Cycl10| 2.5          | 22.5             | 11.11  88.89      |
| Benz/Cycl30| 7.5          | 17.5             | 32.52  67.48      |
| Benz/Cycl50| 12.5         | 12.5             | 52.92  47.08      |
| Benz/Cycl80| 20.0         | 5.0              | 81.79  18.21      |

2.5. Mass Transfer

The swelling measurements of the membranes in the mixture and in the pure solvents were
performed at 25 °C. Six dried pieces of membrane 3 cm × 3 cm with 233 ± 3 µm thickness were weighed
and then separately immersed in cyclohexane, benzene, and their mixtures with continuous stirring
until saturation (at constant mass). During the swelling process, each film was removed from the
vessel at different intervals, their surfaces dried with tissue to absorb remaining liquid, and weighed.
This experimentation was repeated two times and the results obtained were taken from the arithmetic
average. The degree of swelling (DS) was determined from Equation (1):

\[
DS(\%) = \frac{w_t - w_o}{w_o} \times 100
\]

where \( w_t \) and \( w_o \) are the weight of the swollen membrane at time \( t \) and weight of the membrane before
the swelling process, respectively.
2.5.1. Sorption

For a solvent–polymer system, the sorption equilibrium is rapid relative to diffusion. The activity coefficient of a solvent in a polymeric solution, $\gamma_1$, is related to its solubility parameter by the following equation:

$$RT \log \gamma_1 = V_1 \phi_1^2 (\delta_1 - \delta_p)^2$$

(2)

where $\delta_1$, $V_1$, and $\phi_1$ are the Henssen solubility parameter, molar volume of the solvent, and the volume fraction of solvent, respectively. $T$ is the temperature of the experiment and $R$ is the gas constant.

According to the modified theory of Flory–Huggins by Blanks and Prausnitz [37], the interaction parameter, $\chi_{1,p}$, can be calculated from the difference between the solubility parameter of the solvent, $\delta_1$ and that of the polymer, $\delta_p$, according to the following equation:

$$\chi_{1,p} = \beta' + \frac{V_1}{RT} (\delta_1 - \delta_p)^2$$

(3)

where $\beta'$ is the entropic factor most often eq Blanks et al. and Scott et al. to 0.34 [38,39].

2.5.2. Diffusion

According to Comyn [39], the kinetic that governs the swelling dynamic in a material, such as a polymer, is generally given by Equation (4).

$$\frac{w_t}{w_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[ \frac{-D(2n+1)^2 \pi^2 t}{l^2} \right]$$

(4)

where $w_t$ and $w_{\infty}$ are the masses of the sorbed molecules at time $t$ and at maximum absorption, respectively, $l$ is the polymer film thickness, $D$ is the diffusion coefficient, and $n$ is the diffusion exponent (also called the kinetic order) indicating solvent transport mechanism in the membrane. Equation (5) can be rearranged and then linearized as follows:

$$\ln \left(1 - \frac{w_t}{w_{\infty}}\right) = \ln \left( \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \right) - \frac{D(2n+1)^2 \pi^2 t}{l^2}$$

(5)

For a first kinetic order ($n = 1$), Equation (5) takes the following simplified expression:

$$\ln \left(1 - \frac{w_t}{w_{\infty}}\right) = 0.721 - \frac{88.73Dt}{l^2}$$

(6)

The diffusion coefficient, $D$, can be obtained from the slope of the linear portion of the curve corresponding to the variation of $\ln \left(1 - \frac{w_t}{w_{\infty}}\right)$ versus time.

Desorption of the benzene/cyclohexane mixtures from the membrane was performed by using the apparatus of Scheme 2. The membrane that swelled in the mixture until saturation was placed into a bottom flask (C) connected to a cooled trap (B). The vapor of the mixture, created by the dramatic diminution of the pressure caused by the liquid nitrogen (A), was then driven to the cold trap. The compositions of the absorbed mixture collected in the cold trap were analyzed by gas chromatography (Agilent 6850, Santa Clara, CA, USA). Helium was used as carrier gas with a flow rate of 10 mL/min. Samples taken were injected using a 10 µL-syringe. The capillary column used had a length of 30 m and an internal diameter of 0.25 mm. The stationary phase used was non polar made of 5% phenyl poly silpenylene-silicone impregnating the internal face of the column with a thin layer of 0.25 µm. The oven temperature was maintained at 200 °C for all analyses. To minimize errors due to the different experimental processes that may have affected the swelling results (sorption, diffusion, and desorption), the values were taken from the arithmetic mean of two measurements and the error bar was taken into account in calculations.
2.6. Pervaporation Experiments

Separation of the cyclohexane/benzene mixture was performed by using the pervaporation apparatus of Scheme 3 described by Ping et al. [42]. The effective area of the membranes was 28 cm², the initial feed was 25 mL, and the downstream and the upstream (in the feed) pressures were approximately 10 mmHg and 760 mmHg, respectively. The temperature of the pervaporation process was 30 °C. The compositions of the feed mixture and permeate were analyzed by gas chromatography (Agilent 6850, USA).

The total cumulative permeate flux (J) was calculated according to the equation:

\[
J = \frac{w(kg)}{A(m^2) \times Time(h)}
\]  
(8)

where \( w \) is the mass of the permeate, \( A \) is the effective area of the membrane in contact with the feed, and \( Time \) is the permeation time.

The separation factor (\( \beta \)) is expressed as follows:

\[
\beta_{benz/cyclohx} = \frac{P_{benz}}{P_{cyclohx}} / \frac{F_{benz}}{F_{cyclohx}}
\]  
(9)
where $P_{\text{benz}}$ and $P_{\text{cyclohx}}$ are the weight fractions of benzene and cyclohexane in the permeate, respectively, and $F_{\text{benz}}$ and $F_{\text{cyclohx}}$ are the weight fractions of benzene and cyclohexane in the feed mixture, respectively.

Membrane efficiency was estimated by the pervaporation separation index ($PSI$) calculated from Equation (10) [43]:

$$PSI = J\left(\frac{F_{\text{benz}}}{F_{\text{cyclohx}}} - 1\right)$$

![Scheme 3. The pervaporation apparatus used in this investigation.](image)

3. Results and Discussion

3.1. Membrane Characterization

In polymer nanocomposites, the most important subject to consider is the dispersion of nanofillers in the polymer matrix. A uniform and homogeneous distribution of nanofillers leads to improve properties of the starting polymeric materials and leads to obtain reproducible membranes. On the other hand, the tendency of nanomaterials to agglomerate caused by excessive van der Waals forces between nanoparticles leads to deterioration of the properties of polymer nanocomposites, leading to a nonreproducible membrane.

3.1.1. SEM Analysis

SEM images of CNTs and the surface morphology of virgin E-VOH and E-VOH/CNT nanocomposite membranes before and after use in the pervaporation process are shown in Figure 1. The CNTs image clearly shows the typical shapes characterizing these nanoparticles that resemble strands of boiled spaghetti. These particles are practically uniform and homogeneous with an external diameter size varying between 16.7 and 19.2 nm, thus reflecting the dimensions indicated on the product data sheet. The micrograph of the E-VOH membrane shows a smooth and uniform surface morphology devoid of any aggregated particles or holes or grooves, indicating that the membrane has withstood the conditions of its preparation, especially when it is subjected to a high vacuum during
the drying step. However, the micrograph of the dried E-VOH/CNT-membrane shows a well-packed surface of polymer-coated CNTs uniformly dispersed and randomly oriented in the polymer matrix. The diameter size of the CNTs covered with E-VOH was uniform and varied between 20.2 and 26.6 nm, allowing a polymer layer thickness varying between 3.5 and 7.4 nm, which was estimated by simple subtraction of the diameter of the CNTs measured. As can be seen, although the image of this same membrane had swollen in the benzene/cyclohexane mixture (50:50 v/v%), the covered CNTs, some of which appear on the surface, had diameters varying between 26.6 and 39.5 nm. The diameter is an important indicator of the DS of the E-VOH/CNT hybrid membrane in the mixture to be separated. On the other hand, after repeating the pervaporation process three times under the same conditions, we found that the results were reproducible with few experimental errors while the properties of the membranes used were well preserved. So, the E-VOH/CNT membrane remained stable for all the remaining experiments.

![Figure 1. Scanning electron microscopy (SEM) images of Poly(ethylene-co-vinylalcohol) (E-VOH) and poly (vinyl alcohol-co-ethylene)(E-VOH/CNT) membranes before and after use in the pervaporation process.](image)

3.1.2. DSC Analysis

DSC was performed to show the uniform distribution of the CNTs in the polymer matrix. Figure 2 shows the DSC thermograms of the pure E-VOH and E-VOH/CNT nanocomposite. The $T_g$ and $T_m$ for the pure copolymer were 63 °C and 176 °C, respectively, and an important shift of 9 °C in the $T_g$ value was observed when only 1.0 wt % of CNTs was incorporated into this copolymer matrix, whereas the $T_m$ value remained unchanged. According to Qui et al. [44], the appearance of a shift in the $T_g$ value for a nanocomposite indicates full homogeneity at the 20–40 nm scale. The positive shift in the $T_g$ value when passing from the pure E-VOH to E-VOH/CNT nanocomposite is probably caused by adhesion of the CNTs to the polymer chains, thus limiting sliding of the chains and/or by a succession of CNT
barriers reducing the heat transfer within the polymer matrix because the heat conductivity of carbon is lower than that of the polymer.

![Differential scanning calorimetry (DSC) thermograms of E-VOH and E-VOH/CNT membranes.](image)

**Figure 2.** Differential scanning calorimetry (DSC) thermograms of E-VOH and E-VOH/CNT membranes.

### 3.1.3. TGA

The effect of the CNTs on the thermal stability of E-VOH was investigated by TGA in nitrogen gas atmosphere. Figure 3 shows a comparison between the diagram of virgin copolymer and that loaded with CNT nanoparticles. CNTs are endowed with excellent thermal stability [45], and their mass loss of MWCNTs begins above 500 °C [46]. As can be observed from these curve profiles, pure E-VOH have excellent thermal stability in which the first decomposition process begins at about 350 °C, which agree with that of the literature [47]. For both samples, a second step of decomposition less marked is observed, which started at about 450 °C. According to Alvarez et al. [47], based on the comparison between the thermal decomposition of pure poly(vinylalcohol)(PVA) and that of pure poly(ethylene)(PE), it was found that the decomposition thermogram of (E-VOH) exactly overlapped those of PVA and PE together in the same conditions. This finding revealed that the thermal degradation of (E-VOH) at temperature ranged between 350 and 450 °C is due principally to the decomposition of the PVA fraction in this copolymer. According to Holland et al. [48], the decomposition of PVA in the same range of temperature leads to water elimination and chain scission through a six-membered transition state leading to volatile products formation, such as aldehydes and ketones. While, during the second stage (after 450 °C) the decomposition of ethylene sequences occurs causing the departure of ethylene and other volatile hydrocarbons. The addition of CNT nanoparticles in the E-VOH matrix practically did not affect its thermal stability, but resulted in a modification of the decomposition mechanism by reducing the amount of products eliminated during the first step and increasing those eliminated during the second step. To close this part of this work, we can report that membranes made of E-VOH and incorporated with CNT nanoparticles can easily be used as pervaporation membranes in a wide temperature range.
Figure 3. Thermogravimetry analysis (TGA) thermograms of E-VOH and E-VOH/CNT nanocomposite.

3.1.4. XRD Analysis

XRD analysis was used in this work to indirectly know the extent of the adhesion of CNT particles to the E-VOH polymer through the evolution of the crystalline structure of each component, thus confirming the results obtained previously by DSC analysis. Therefore, E-VOH/CNT nanocomposite and its pure components were recorded in 10–70 ° range and their spectra are grouped in Figure 4. As can be observed from these patterns, the E-VOH exhibits its two principal characteristic peaks centered at 19.35° (intense) and 40.0° (less intense) attributed to the (101) crystal plane and the compound peak of crystalline planes of (111), (1̅1̅1), (210) and (21̅0), attributed to the PVA units, respectively [49,50]. The CNTs spectrum exhibits its principal peak centered at 26.5° assigned to (002) of its graphite plane [34]. On the other hand, the nanocomposite involving E-VOH and CNTs shows a sharp peak at 26.5° assigned to the (002) of the graphite plane, confirming the presence of CNTs in the E-VOH matrix. The disappearance of the peak at 29.2° and the small shifting of 20 to the higher value of the signal of attributed to E-VOH component in E-VOH/CNT nanocomposite and its narrowing indicates a slight modification of the crystalline structure of the copolymer. This fact reveals that the CNTs are well exfoliated and homogenously distributed in the E-VOH matrix. Similar results were also observed by Tang et al. [51,52] on the investigation of rhodamine B-decorated grapheme as a reinforcement in polyvinyl alcohol composites (RhB-G/PVA). This result confirms that of the DSC analysis and indicates a perfect adhesion between CNT nanoparticles and E-VOH matrix. It is worth noting that the interfacial adhesion between the filler and the polymer is considered as a key factor leading to achieving satisfied composites. When such a material is used as a pervaporation membrane, the results obtained will be reproducible, and the properties of the components involved will be reflected in the hybrid material obtained. Indeed, the uniform dispersion of the CNT nanoparticles in the polymer...
matrix leads to an increase in the spacing between chains or groups of chains favoring the passage of a large amount of molecules improving the flux rate, which is lacking in most selective membranes.

![Figure 4. X-ray diffraction (XRD) patterns of pure E-VOH, pure carbon nanotubes (CNTs), and E-VOH/CNT nanocomposite containing 1.0 wt % of CNTs.](image)

3.2. Mass Transfer

3.2.1. Swelling Degree

The results of the swelling degree of the E-VOH and E-VOH/CNT membranes in benzene, cyclohexane, and their mixture with equal ratios are presented in Figures 5 and 6, respectively, and the maximum swelling of these membranes (at equilibrium) are summarized in Table 2. Comparison of these data show that the E-VOH membrane swells very little in cyclohexane, in which only about 0.18 wt % of its mass was absorbed during a period of 169 h, whereas this same membrane absorbed approximately five times more benzene under the same conditions (0.92 wt %). This phenomenon is principally due to the difference in the polarity between benzene and cyclohexane. Although the polarity of benzene, which is due to the resonance of the 6 $\pi$ electrons, is low, that of cyclohexane is practically zero. Under these conditions, the E-VOH membrane, which is predominately hydrophilic, has a greater affinity for benzene (slightly polar), although it is weak.
A comparison of the variations in the swelling degree versus time of the virgin membrane E-VOH and that containing CNTs with respect to the benzene/cyclohexane mixtures with equal compositions is presented in Figure 5. As can be seen from these curve profiles, incorporation of CNTs in E-VOH matrix considerably increased the swelling capacity of the resulting membrane in this mixture. Indeed, a maximum increase in the swelling degree of 3.67 times was obtained for the CNT/E-VOH membrane relative to the degree for the virgin E-VOH. In this case, the effect of CNTs on absorbability was clearly noticeable by the extent of the absorbed amount of mixture. The reason for the phenomenon appeared to be the same as that in the case of the two separate components. As can also be seen from the data of Table 2, the mixture was better absorbed than either of the pure components regardless of the membrane type used.

Figure 5. Variations in the swelling degrees of pure E-VOH and CNT/E-VOH nanocomposite membranes vs. time in benzene and cyclohexane at 25 °C.

Figure 6. Comparison of the swelling degrees between E-VOH and E-VOH/CNT membranes in benzene/cyclohexane mixtures with equal compositions versus time measured at 25 °C.
Table 2. Comparison of the swelling degrees between E-VAL and E-VAL/CNT membranes in benzene/cyclohexane mixtures with different compositions.

| Membrane      | Benzene | Benzene/Cyclohexane (50:50 wt %) | Cyclohexane |
|---------------|---------|---------------------------------|-------------|
| E-VOH         | 0.92    | 4.20                            | 0.18        |
| E-VOH/CNT     | 2.05    | 16.50                           | 1.25        |

On the other hand, the addition of CNTs to E-VOH as a nanocomposite considerably improved the swelling rate of the resulting membrane. Indeed, the swelling capacity for each component significantly increased for both benzene (from 0.92 to 2.05 wt %, 2.22 fold) and cyclohexane (from 0.18 to 1.25 wt %, 6.94 fold). The increase in the swelling capacity of the CNTs-containing membrane is due to the increase in the polymer-component contact area of the resulting material. The more significant increase in the swelling degree of cyclohexane relative to that of benzene observed when CNTs was incorporated in the E-VOH membrane appeared to be due to the non-polar character of the CNTs [53], which has greater affinity for this alicyclic compound than for benzene. Although the extent of the swelling capacity of the E-VOH/CNT membrane towards cyclohexane appeared to evolve relatively faster than that of its co-component benzene, its absorbed amount always remained low, which hampered its absorption selectivity in the mixture with benzene.

A comparison of the variations in the swelling degree versus time of the virgin membrane E-VOH and that containing CNTs with respect to the benzene/cyclohexane mixtures with equal compositions is presented in Figure 5. As can be seen from these curve profiles, incorporation of CNTs in E-VOH matrix considerably increased the swelling capacity of the resulting membrane in this mixture. Indeed, a maximum increase in the swelling degree of 3.67 times was obtained for the CNT/E-VOH membrane relative to the degree for the virgin E-VOH. In this case, the effect of CNTs on absorbability was clearly noticeable by the extent of the absorbed amount of mixture. The reason for the phenomenon appeared to be the same as that in the case of the two separate components. As can also be seen from the data of Table 2, the mixture was better absorbed than either of the pure components regardless of the membrane type used.

3.2.2. Sorption

The activity coefficient and the Flory interaction parameter of the polymer with regard to each solvent have been used to estimate the sorption dynamic of this solvent/polymer system. In this way, $\gamma_1$, and $\chi_{1,p}$ of benzene and cyclohexane in the E-VOH membrane have been estimated from Equation (2) and Equation (3), respectively, using the data of Table 3 taken from the literature [54,55]. The results are presented in Table 4.

Table 3. Molar volume and Hansen solubility parameter of E-VOH, benzene, and cyclohexane determined at 30 °C.

| Component     | $V_1$ (ml·mol$^{-1}$) | $\delta_1$ (MPa)$^{0.5}$ |
|---------------|------------------------|----------------------------|
| E-VOH         | 44.02                  | 23.1 [54]                  |
| Benzene       | 80.16                  | 18.6 [55]                  |
| Cyclohexane   | 147.4                  | 16.8 [55]                  |

Table 4. Values of the activity coefficients of the solvents and Flory interaction parameters of the E-VOH/benzene and E-VOH/cyclohexane systems.

| E-VOH/Solvent System | $\gamma_1$ | $\delta_1 - \delta_p$ (MPa)$^{0.5}$ | $\chi_{1,p}$ |
|----------------------|------------|--------------------------------------|--------------|
| E-VOH/Benzene        | 1.40       | $–4.47$                              | 0.689        |
| E-VOH/Cyclohexane    | 1.04       | $–6.27$                              | 2.636        |
As can be seen from these values, neither benzene nor cyclohexane are ready to form a solution with E-VOH ($\chi_{1,p} > 0.5$). Indeed, the incompatibility of the two-polymer–solvent systems was expected because of the differences in polarity between the components in each system. Indeed, the polarity of benzene due to the resonance of the three $\pi$-bonds, although very weak, makes its affinity for E-VOH higher than that of cyclohexane which has a completely non-polar character ($\chi_{\text{benz,E-VOH}} \approx 3.83 \cdot \chi_{\text{cyclohx,E-VOH}}$). This result shows that benzene had much better affinity for the E-VOH-membrane than that of its saturated homologue. On the other hand, the $\gamma_1$ value of cyclohexane near the unit indicates formation of a much diluted solution in which the role of this pairing of polymer–solvent was inverted (E-VOH becomes the solvent and cyclohexane the solute). Indeed, this trend is similar to that of the swelling results regarding this compound.

Indeed, the concentration of each component in four benzene/cyclohexane mixtures (10, 30, 50, and 80 v%) absorbed by each membrane during the swelling process was evaluated and the selective absorption of the E-VOH and E-VOH/CNT membrane factors $\beta_{\text{benz/cyclohx}}^{ab}$ were determined according to Equation (7) and are summarized in Table 5. As can be seen from these data, whatever the membrane used, the concentration of benzene increased as its initial concentration in the feed increased leading to a significant increase in the $\beta_{\text{benz/cyclohx}}^{ab}$. This observation does not seem to be surprising in the liquid separation by pervaporation process; on the other hand, the fall in the selective absorption of the membrane factor when the CNT/E-VOH composition was 1.0 wt % seems to be new and deserves to be explained. Indeed, this phenomenon can be attributed to a decrease in the density of E-VOH due to the spacing between the polymer chains produced by inserting CNT particles in the polymer matrix. This fact allows the easier diffusion of a greater number of cyclohexane molecules accompanied by those of benzene through this hybrid membrane.

**Table 5.** Compositions of the benzene/cyclohexane mixture absorbed and the selective absorption factor of the E-VOH and E-VOH/CNT membrane factors.

| Membrane | Initial Feed Composition (wt %) | Mixture Absorbed Composition (wt %) | $\beta_{\text{benz/cyclohx}}^{ab}$ |
|----------|---------------------------------|-------------------------------------|----------------------------------|
|          | Benzene  | Cyclohexane  | Benzene  | Cyclohexane  |                        |
| E-VOH    | 10       | 90          | 72.12    | 27.88       | 06.69                 |
|          | 30       | 70          | 80.55    | 19.45       | 17.15                 |
|          | 50       | 50          | 88.32    | 11.68       | 57.18                 |
|          | 80       | 20          | 95.02    | 04.98       | 361.0                 |
| E-VOH/CNT| 10       | 90          | 67.56    | 32.44       | 04.34                 |
|          | 30       | 70          | 73.07    | 26.93       | 07.35                 |
|          | 50       | 50          | 83.13    | 16.87       | 24.28                 |
|          | 80       | 20          | 92.22    | 7.78        | 140.51                |

Based on the quantitative and qualitative results obtained of the mixture absorbed by E-VOH and E-VOH/CNT membranes, the results of the separation of benzene/cyclohexane mixture are now predicted. Indeed, these data revealed that the best performance in the selectivity is obtained by the virgin E-VOH membrane, while the better total flux is given by the nanocomposite membrane.

### 3.2.3. Diffusion

The diffusion coefficient, $D$, of benzene, cyclohexane, and their mixtures with equal composition in E-VAL and E-VAL/CNT membranes is derived from the slope of the linear portion of each curve corresponding to the variation of $-\ln\left(1 - \frac{w}{w_\infty}\right)$ versus time of Figures 7 and 8, respectively, and Equation (6). The values of $D$ obtained are gathered for comparison in Table 6.
Figure 7. Variation in $-\ln\left[1 - \frac{W_t}{W_\infty}\right]$ of the E-VOH membrane in benzene, cyclohexane, and their mixtures with equal composition vs. time.

Figure 8. Variation in $-\ln\left[1 - \frac{W_t}{W_\infty}\right]$ of E-VOH/CNT in benzene, cyclohexane, and their mixtures with equal composition vs. time.
Table 6. Diffusivity parameters of benzene and cyclohexane in E-VOH membrane measured at 25 °C.

| Membrane          | Benz/Cyclohx Mixture (wt/wt) | n  | $D \, (\mu m^2 \cdot s^{-1}) \cdot 10^2$ |
|-------------------|-------------------------------|----|----------------------------------------|
| E-VOH             | 100:0                         | 1.0| 2.83                                   |
| E-VOH/CNT         | 1.0                           |    | 0.18                                   |
| E-VOH             | 50:50                         | 1.0| 2.60                                   |
| E-VOH/CNT         | 1.0                           |    | 2.94                                   |
| E-VOH             | 0:100                         | 1.0| 4.43                                   |
| E-VOH/CNT         | 1.0                           |    | 0.10                                   |

All curve profiles in the variation of $-Ln[1 - \frac{w_t}{w_{\infty}}]$ versus time show straight lines for all membranes, indicating that the diffusion mechanism for both benzene and cyclohexane as well as their mixtures with equal ratios are characterized by first-order kinetics, thus confirming the proposed hypothesis ($n = 1$) in Equation (5). This indicates that neither the composition mixture nor the nature of the component nor the addition of CNTs affected the mechanism of their transport in the membrane.

3.3. Separation of Benzene/Cyclohexane Mixture

Given the encouraging results in the study of transfer of benzene, cyclohexane, and their mixtures through the E-VOH and E-VOH/CNT membranes, we then investigated their separation by using the pervaporation technique.

3.3.1. Separation of Benzene/Cyclohexane by E-VOH Membrane

Pervaporative parameters for benzene/cyclohexane mixtures with different compositions were calculated from the total mass of permeate and benzene/cyclohexane compositions according to Equations (8) and (9). To examine the effect of the change in the feed composition on the pervaporative parameters during time and testing the stability of the physicochemical and mechanical properties of the membrane used during the separation process, the variation of the cumulative total flux and the separation factor as a function of time were plotted, and the curves obtained are grouped in Figures 9 and 10, respectively. As can be seen from the curve profiles of Figure 9, the cumulative total flux decreased with time for any mixture composition, but more markedly for those containing 10 wt % and 30 wt % of benzene during the first hour of the pervaporation process. During this period, the large amount of the mixture absorbed during the swelling step (before the start of the separation process) is immediately released. This result seems to be obvious considering the previous mass transfer results in which the flux through the E-VOH membrane was higher for benzene than for cyclohexane. In this situation, benzene in relatively small amounts in the feed decreased more quickly, causing a rapid decrease in the flux. On the other hand, the smooth curve profiles showing no signs of abnormality due to a possible change in membrane properties are observed.

On the other hand, the variation in the separation factor versus time in Figure 10 reveals the highest values for the benzene/cyclohexane mixture contained the highest benzene content (80 v%). The curve corresponding to this mixture reached a maximum of 30 at about 1.4 h of the pervaporation process and then decreased while retaining its best performance, reaching 26.2 during 10 h. For the azeotropic mixture (50 v% benzene), the profile of the corresponding curve also shows a maximum during the same period, but less remarkable, with a separation factor $\beta_{benz/cyclohx}$ that decreased by approximately half (12.90) and then quickly stabilized at 12.60 during the remaining separation period. In the mixtures containing less benzene, $\alpha$ was relatively lower for both mixtures (30 v% and 10 v% benzene), which stabilized at 11.10 and 10.20, respectively, after approximately 1.4 h of the separation process. For the mixture rich in benzene, the increase in the separation factor during about the first hour of the separation process is probably due to the selective absorption of benzene that occurred during the swelling period (before starting the separation process). This can be confirmed by their high $\beta_{benz/cyclohx}$ values of Table 4.
During this period, the large amount of the mixture absorbed during the swelling step (before the start of the separation process) is immediately released. This result seems to be obvious considering the previous mass transfer results in which the flux through the E-VOH membrane was higher for benzene than for cyclohexane. In this situation, benzene in relatively small amounts in the feed decreased more quickly, causing a rapid decrease in the flux. On the other hand, the smooth curve profiles showing no signs of abnormality due to a possible change in membrane properties are observed.

**Figure 9.** Change in permeate total flux for benzene/cyclohexane mixtures with different compositions versus time using the E-VOH-membrane.

**Figure 10.** Change in the separation factor of benzene/cyclohexane mixtures with different compositions versus time using the E-VOH-membrane.
To better describe the dependence between the two pervaporative parameters ($\beta_{\text{benz/cyclohx}}$ and $J$), the variation in the separation factor as a function of cumulative total flux is plotted for all mixtures in Figure 11. For a benzene/cyclohexane mixture containing 80 v% of benzene, the selectivity significantly increased, with the total flux reaching a maximum of $30.0 \times 10^{-2}$ kg·m$^{-2}$·h$^{-1}$ and then slowly decreased with increasing total flux beyond that value. The decrease in $\beta_{\text{benz/cyclohx}}$ value in the second portion of this curve appears to be completely normal when using the static pervaporation technique and is caused by the continuous decrease of benzene in the feed, whereas in the first part it appears abnormal, probably because of possible reorganization of polymeric chains constituting the membrane. In this situation, the chain deployment promotes an increasing affinity for benzene with regard to the E-VOH membrane enabling selective absorption of a large amount of this component. This anomaly of the significant increase in selectivity during the first part of the curve can also be caused by a rapid desorption of a large amount of benzene—in particular in the case of the mixture rich in component, absorbed during the step of swelling, because the separation process was started only after leaving for a while the swelling of the membrane by the mixture to be separated.

![Figure 11](image-url)

**Figure 11.** Change in the separation factor for benzene/cyclohexane mixture with different compositions versus total flux rate in the E-VOH–membrane.

3.3.2. Separation of Benzene from Benzene/Cyclohexane Mixtures through an E-VOH/CNT-Membrane

The effect of the CNTs incorporated into the E-VOH membrane was investigated under the same conditions as that of the virgin membrane, and the results for flux and selectivity are illustrated in Figures 12 and 13, respectively. As shown in the curves in Figure 12, the order of the total flux performance obtained by varying the benzene concentration in the feed observed in the previous results using the virgin E-VOH membrane was well preserved in this study. In fact, the total flux decreased continuously over time more slowly for mixtures rich in benzene (80 v% and 50 v%) for the same reasons mentioned for a virgin membrane. As in the case of the virgin membrane, the behavior of the total flux for these two mixtures behaves differently from those containing 10 and 30 v% of benzene. Indeed, the total flux of the mixtures rich in benzene decreased slowly throughout the duration of
the separation process; meanwhile, those containing less benzene decreased significantly. This can be interpreted as in the case of using the virgin membrane.

![Figure 12](image1.png)

**Figure 12.** Change in the permeate total flux for benzene/cyclohexane mixtures with different compositions versus time using the E-VOH/CNT-membrane.

![Figure 13](image2.png)

**Figure 13.** Change in the separation factor for benzene/cyclohexane mixture with different compositions versus time in the E-VOH/CNT-membrane.
It is also very important to note that the incorporation of CNTs into the E-VAL-membrane considerably enhanced the total flux relative to that obtained with the virgin membrane.

The effect of integration of CNTs into the E-VOH membrane on the separation factor for the different feed compositions is illustrated in Figure 13. As can be seen from these curve profiles, the separation factor of the EV-OH/CNT membrane relative to the two benzene-rich mixtures slowly increased during about the first 1.4 h of the separation process to stabilize beyond. On the other hand, for the two other mixtures containing less benzene, the selectivity stabilized or slightly decreased during the first 2.30 h to stabilize beyond. This phenomenon has already been observed and explained in the case of the virgin E-VOH membrane in the previous section.

It is useful to compare the results of Table 7 obtained with these two membranes under the same conditions during 3 h of the separation process. Indeed, the change from the virgin E-VOH membrane to the E-VOH/CNT-membrane multiplied the total flux by 2.11–3.63 depending on the benzene/cyclohexane composition of the feed. This result shows that the main study objective of increasing the total flux was achieved principally because of the increase in the specific surface of the membrane provided by incorporation of adequate amounts of CNTs in the E-VOH membrane. This effect is shown in Scheme 4.

Table 7. Total flux and separation factors obtained with the E-VAL and E-VOH-CNT membranes during 3 h of the separation process.

| Benz/Cyhx Mixture (v/v) | Flux (kg m⁻² h⁻¹) | Flux Performance | Separation Factor \( \beta_{\text{Benz/cyclohx}} \) | Separation Factor Performance |
|------------------------|-------------------|------------------|---------------------------------|-----------------------------|
|                        | E-VOH             | E-VOH/CNT       | \( J_{\text{E-VOH/CNT}}/J_{\text{E-VOH}} \)* | \( \beta_{\text{E-VOH/CNT}}/\beta_{\text{E-VOH}} \)** |
| 10:90                  | 0.06              | 0.18            | 3.00                            | 10.20                       | 0.49                        |
| 30:70                  | 0.08              | 0.29            | 3.63                            | 11.10                       | 0.54                        |
| 50:50                  | 0.28              | 0.74            | 2.64                            | 12.90                       | 0.70                        |
| 80:20                  | 0.44              | 0.93            | 2.11                            | 12.22                       | 0.41                        |

* \( J_{\text{E-VOH/CNT}}/J_{\text{E-VOH}} \): Cumulative total flux obtained with E-VOH/CNT membrane/Cumulative total flux obtained with E-VOH membrane.** \( \beta_{\text{E-VOH/CNT}}/\beta_{\text{E-VOH}} \): Separation factor of E-VOH/CNT membrane toward benzene/Separation factor of E-VOH membrane toward benzene.

Scheme 4. Absorption areas of E-VOH and E-VOH/CNT membranes.
The separation factor increased slightly over time for mixtures rich in benzene and reached a pseudoequilibrium at 12.22 achieved during the first 3 h of the process for the mixture containing 80 v% of this component and was 9.03 for the azeotropic mixture (50 v%). The separation factors for the mixtures containing less benzene were lower and stabilized during the same period at 6.0 for 30 v% benzene and 5.0 for 10% benzene by volume. The comparison of the results with those obtained from the virgin membrane shown in Table 7 reveals that the addition of CNTs caused a depression in the separation factor by about half.

The variation in the separation factor as a function of total flux is shown in Figure 14. As can be observed from these traces, the $\beta_{\text{benz/cyclohx}}$ value varies with the composition of the mixture in the feed. Indeed, for the two mixtures rich in benzene, $\alpha$ significantly decreased with an increase in the total flux at the limit of 0.4 kg·m$^{-2}$·h$^{-1}$, then tended to stabilize beyond that point.

![Figure 14](image-url)

**Figure 14.** Change in the separation factor for benzene/cyclohexane mixture with different compositions versus total flux rate in the E-VOH/CNT-membrane.

The decrease in $\beta_{\text{benz/cyclohx}}$ with increasing total flux was evident in the separation of volatile organic mixtures when using the pervaporation process and is due to the depletion of benzene in the feed. The value of $\beta_{\text{benz/cyclohx}}$ tended to stabilize when the benzene in the initial feed was 30 v% and increased from 5.50 to 6.33 when benzene was 10 v% and the total flux increased from 0.88 to 9.52 kg·m$^{-2}$·h$^{-1}$. The pseudo-stability and increase in the separation factor, previously observed with the virgin E-VOH membrane, appears to be due to rearrangement of the polymer chains that increased passage of benzene through the E-VOH/CNT-membrane. Despite the decrease in the selectivity by incorporation of CNTs into the E-VOH membrane, the compromise between the selectivity (5 and 12.22) and flux (0.18 and 0.93 kg·m$^{-2}$·h$^{-1}$) shows the E-VAL/CNT-membrane to be one of the most efficient for benzene/cyclohexane separation using the pervaporation technique when compared with the results using other types of membranes reported in the literature (Table 8).
Table 8. Comparative values of the total flux and separation factor for equal-ratio benzene/cyclohexane mixture separation by pervaporation techniques using different membranes.

| Membrane                               | Temperature (°C) | Total Flux (g·m⁻²·h⁻¹) | Separation Factor | PSI (g·m⁻²·h⁻¹) | Reference |
|----------------------------------------|------------------|--------------------------|-------------------|------------------|------------|
| β-CD/PVA/GA                             | 20               | 30.9                     | 27.0              | 803.4            | [4]        |
| Tosylcellulose                         | 30               | 6.0                      | 28.8              | 168.0            | [56]       |
| Chitosan/Ag⁺/CNT                        | 20               | 358.0                    | 7.9               | 2466.3           | [57]       |
| NBR/hydrin/PMMA                        | 60               | 160.0                    | 7.3               | 1008.0           | [58]       |
| P(AN-b-MA)                             | 30               | 70.0                     | 10.5              | 665.0            | [59]       |
| Boltorn W3000/ceramic                  | 40               | 278.0                    | 4.1               | 861.8            | [60]       |
| CMS/PVA                                | 50               | 72.0                     | 20.8              | 1424.7           | [10]       |
| AAOM,[C₈mim]PF₆/PU                     | 45               | 12.2                     | 34.2              | 405.0            | [40]       |
| [emim][PF₆]WPU                         | 50               | 190.0                    | 8.4               | 1406.0           | [41]       |
| PEA I                                  | 50               | 320.0                    | 6.9               | 1888.0           | [61]       |
| PEA II                                 | 50               | 520.0                    | 6.5               | 2860.0           | [61]       |
| PEA III                                | 50               | 570.0                    | 5.9               | 2793.0           | [61]       |
| PEA IV                                 | 50               | 550.0                    | 7.6               | 3630.0           | [61]       |
| PVA + 5:1 poly (ANco-AA) coated (1:1) NaMMT clay 8 wt % | 30               | 168.6                    | 137.2             | -                | [62]       |
| E-VOH                                  | 25               | 280.0                    | 12.9              | 3332.0           | This work  |
| E-VOH/CNT                              | 25               | 740.0                    | 9.0               | 5942.2           | This work  |

(a) β-CD/PVA/GA: β-cyclodextrin filled cross-linked poly(vinyl alcohol); (b) Chitosan/Ag⁺/CNT: Chitosan/Ag⁺ ion/carbon nanotube; (c) NBR/hydrin/PMMA: nitrile butadiene rubber/tercopolymers of ethylene oxide/epichlorohydrin/allyl glycidyl ether/poly(methyl methacrylate); (d) P(AN-b-MA): Polyacrylonitrile-block-poly(methyl acrylate); (e) CMS/PVA: carbon molecular sieve/poly(vinyl alcohol); (f) AAOM,[C₈mim]PF₆/PU: Anodic aluminum oxide membrane [1-Octyl-3-methylimidazolium] hexafluorophosphate/polyurethane; (g) [emim][PF₆] WPU: 1-ethyl-3-methylimidazolium hexafluorophosphate/waterborne polyurethane; (h) PEA: Poly(ether amide) I; (i) PEA: Poly(ether amide) II; (j) PEA: Poly(ether amide) III; (k) PEA: Poly(ether amide) IV; (l) PVA + 5:1 poly (ANco-AA) coated (1:1) NaMMT clay 8 wt %.

Comparison of the results in terms of separation factor, which is obtained by pervaporation process with the absorption selectivity factor, which is obtained by the swelling process using both virgin E-VOH and E-VOH/CNT membranes, reveals that these two parameters vary in the same direction, with both increasing as the initial concentration of benzene in the feed increased. On the other hand, benz/cyclohex was increased much faster than the benz/cyclohex. This is probably due, among other things, to the effect of the high vacuum exerted by the pump which goes in the direction of increasing the total flow and decreasing the separation factor, notably when the membrane thickness used in the pervaporation process was much less thick than that used in the sorption experiment. Knowing that in the pervaporation process the more the total flux increases, the more the separation factor decreases. Figure 15 shows the variation of benz/cyclohex as function of benz/cyclohex for the virgin E-VOH and E-VOH/CNT membranes. The curve profile for E-VOH shows a straight line with a slope of 0.0524, while that for the hybrid membrane shows a logarithmic trend. The first case in which the E-VOH membrane is used indicates that the parameter that affects the separation factor acts with the same behavior regardless of the initial mixture composition. On the other hand, in the second case in which the E-VOH/CNT membrane is employed, this effect behaves differently, notably when the initial concentration of benzene in the feed was 80 v%.
In order to examine the performance of the CNT-containing membrane over time in terms of flux and selectivity compared to that of the virgin membrane, the variation of $J_{E-VOH/CNT}/J_{E-VOH}$ ratio and $\beta_{E-VOH/CNT}/\beta_{E-VOH}$ ratio was plotted as a function of time, and the curves obtained for all composition mixtures are gathered in Figures 16 and 17, respectively. As can be seen from the curve profiles of Figure 15, the cumulative total flux performance of the CNT-containing membrane, with regard to that of the unloaded, changes linearly with time for virtually all of the compositions. All values of the $J_{E-VOH/CNT}/J_{E-VOH}$ ratio are well above the unit, revealing that the incorporation of CNTs into the E-VOH matrix increased the performance of the cumulative total flux for all feed compositions. The slight increase of the $J_{E-VOH/CNT}/J_{E-VOH}$ ratio observed for the feed containing 80% by volume of benzene is probably due to the slower depletion of the large quantity of benzene in the feed during the separation process. For the azeotropic mixture, the performance increased faster and stabilized during the two last hours at 4.12. However, for the two feeds containing less benzene, the cumulative total fluxes ratios significantly decreased following practically the same trend and converge with that of 80 v% of the aromatic component towards the same value ($2.40 \pm 0.15$) reached at the end of the separation process. The decrease in the flux performance for the feed containing 10 and 30 v% benzene seems to be mainly due to its rapid exhaustion over time until the two compositions are equal, which reflects the convergence of the two corresponding curves at the end of the separation period. For all mixtures investigated, the values of the $\beta_{ab}$ ratio were plotted as a function of time, and the curves obtained for all composition mixtures are well above the unit, revealing that the incorporation of CNTs into the E-VOH matrix increased the performance of the cumulative total flux for all feed compositions. The decrease in the flux performance for the feed containing 10 and 30 v% benzene seems to be mainly due to its rapid exhaustion over time until the two compositions converge with that of 80 v% of the aromatic component towards the same value (2.40 ± 0.15) reached at the end of the separation process. For all mixtures investigated, the values of the $\beta_{ab}$ ratio were plotted as a function of time, and the curves obtained for all composition mixtures are well above the unit, revealing that the incorporation of CNTs into the E-VOH matrix increased the performance of the cumulative total flux for all feed compositions. The slight increase of the $J_{E-VOH/CNT}/J_{E-VOH}$ ratio observed for the feed containing 80% by volume of benzene is probably due to the slower depletion of the large quantity of benzene in the feed during the separation process. For the azeotropic mixture, the performance increased faster and stabilized during the two last hours at 4.12. However, for the two feeds containing less benzene, the cumulative total fluxes ratios significantly decreased following practically the same trend and converge with that of 80 v% of the aromatic component towards the same value ($2.40 \pm 0.15$) reached at the end of the separation process. The decrease in the flux performance for the feed containing 10 and 30 v% benzene seems to be mainly due to its rapid exhaustion over time until the two compositions are equal, which reflects the convergence of the two corresponding curves at the end of the separation process. For all mixtures investigated, the values of the $\beta_{ab}$ ratio were plotted as a function of time, and the curves obtained for all composition mixtures are well above the unit, revealing that the incorporation of CNTs into the E-VOH matrix increased the performance of the cumulative total flux for all feed compositions. The slight increase of the $J_{E-VOH/CNT}/J_{E-VOH}$ ratio observed for the feed containing 80% by volume of benzene is probably due to the slower depletion of the large quantity of benzene in the feed during the separation process. For the azeotropic mixture, the performance increased faster and stabilized during the two last hours at 4.12. However, for the two feeds containing less benzene, the cumulative total fluxes ratios significantly decreased following practically the same trend and converge with that of 80 v% of the aromatic component towards the same value ($2.40 \pm 0.15$) reached at the end of the separation process. The decrease in the flux performance for the feed containing 10 and 30 v% benzene seems to be mainly due to its rapid exhaustion over time until the two compositions are equal, which reflects the convergence of the two corresponding curves at the end of the separation process.
process. On the other hand, the pseudo linearity in $J_{E-VOH/CNT}/J_{E-VOH}$ curves versus time for the mixtures containing 10, 30, and 50 v% benzene intersect at about 4 h from the separation process at a value of $3.10 \pm 0.13$, indicating that whatever the composition of the mixture to be separated at this time retains the same efficiency.

![Figure 16](image)

**Figure 16.** Variation of the $J_{E-VOH/CNT}/J_{E-VOH}$ ratio versus time for the different feed compositions.

Regarding the performance of the E-VOH membrane after addition of CNTs in terms of selectivity, Figure 17 shows practically pseudo stability for all the mixtures investigated. This indicates that the hybrid membrane conserved the same performance in the selectivity during the entire separation period. For all mixtures investigated, the values of the $\beta_{E-VOH/CNT}/\beta_{E-VOH}$ ratio are less than unity indicating that the involvement of CNTs in the E-VOH membrane has resulted in severe loss of its selectivity. This loss varied between 30 and 60% depending on the feed composition. These traces also reveal that the best performance in the selectivity compared to the other mixtures is observed for the azeotropic mixture. However, the performance for the feed rich in benzene was found to be the lowest. This phenomenon can be explained by the significant reduction in the membrane thickness in certain places due to the presence of CNT particles, which reduced the transit path of the two different solvent molecules, causing a decrease in the separation factor. This is not surprising because it is well known in the literature that reducing the membrane thickness leads to an increase in flux at the expense of selectivity [63–65] (59–61). According to Choi et al. [31], using a poly (vinyl alcohol)
membrane to separate ethanol/water mixture, the incorporation of an appropriate amount of CNT into this polymer matrix reduces its crystallinity, and at a stimulated micro-orientation, reduces the free volume between PVA channels. The reduction in the free volume disadvantages the increase in the degree of swelling of the membrane, but also provides a shorter alternating diffusion path allowing the molecules to transit rapidly. This goes in the direction of an increase in the total flow at the expense of selectivity. In contrast, the dramatic drop in selectivity for the mixture containing the most benzene with the increase in that rich in cyclohexane are probably due to a change in the hydrophilic behavior of the original membrane. On the other hand, the dramatic drop in selectivity for the mixture rich in benzene and the increase in that containing the most amount of cyclohexane are probably due to a reduction of the hydrophylic character of the original membrane due to the insertion of the hydrophobic carbon nanotubes [5(509,536),(559,580),66] between the polymer chains. This reduces the intensity of the intermolecular hydrogen bonds, increasing the space between the E-VOH chains, therefore allowing the passage of more cyclohexane molecules by reducing the cumulative flux of benzene, which was favored by its slight affinity with the polar bonds of the virgin copolymer.

![Graph](image-url)

**Figure 17.** Variation of the $\beta_{E-VOH/CNT}/\beta_{E-VOH}$ ratio versus time for the different feed compositions.

Finally, it can be said that the best performance of the filled membrane in terms of total cumulative flux and selectivity are obtained for the feed containing the azeotrophic mixture.
3.3.3. Vapor Liquid Pseudo-Equilibrium (VLPE) Diagrams

The VLPE diagrams of the benzene/cyclohexane mixture separation by pervaporation involving the E-VOH and E-VOH / CNT membranes were inspired from the Sarkhel et al. approach [67]. These authors compare the equilibrium of intraspecific mass transfers which occurs between the vapor and liquid phases of a mixture containing several components placed in real physical contact, often called “equilibrium-vapor equilibrium (VLE),” and that which occurs inside and in the two sides of the membrane in the separation by pervaporation named “pseudo equilibrium-vapor equilibrium (VLPE).” Indeed, the pseudo-equilibrium state was observed to be reached at about 1.5 h of the pervaporation process as shown by the profiles of flux and selectivity curves in Figure 9; Figure 12 for the E-VOH membrane and in Figure 10; Figure 13 for the E-VOH / CNT membrane. After this zone, the permanent regime of the separation process is reached. In this state, aliquots of samples were taken from both the retentate and permeate and then analyzed in order to obtain the pseudo-equilibrium compositions characterized by the molar fraction of benzene in the retentate, $X$, and the molar fraction of benzene in the permeate, $Y$. VLPE data were obtained at 25 °C, the molar fraction of benzene in the feed, $X_F$, varied between 0.1 and 0.8. For all experiments, carried out in the same pervaporation conditions and the results obtained for E-VOH et E-VOH/CNT, membranes are graphically presented in Figures 18 and 19, respectively.

![VLPE diagram for pervaporation of benzene/cyclohexane mixtures using E-VOH membrane at 25 °C.](image-url)
For a given value of $X_F$, the pseudo-equilibrium values exhibiting “X” and “Y” can be read directly from the diagram. Such diagrams are comparable with those of VLE.

4. Conclusions

Our study results of the mass transfer of benzene/cyclohexane mixture through E-VOH and E-VOH/CNT membranes predicted that the best performance in the selectivity is obtained by the virgin E-VOH membrane, while the better total flux is given by the nanocomposite membrane. Indeed, the results obtained in term of the pervaporative parameters showed that E-VOH as a pervaporation membrane was effective for selective separation of benzene from benzene/cyclohexane mixtures, particularly for breaking down the azeotropic mixture. Incorporation of an adequate amount of CNTs into the E-VOH matrix as nanocomposites increased the total flux and decreased the separation factor by approximately half because of an increase in the absorption area and reduction in the membrane thickness in certain places. Indeed, for the two mixtures rich in benzene, $\beta_{\text{benz/cyclohex}}$ significantly decreased with increasing total flux to a limit of 0.4 kg·m$^{-2}$·h$^{-1}$ and then tended to stabilize beyond that point. When the initial concentration of benzene in the feed was 30 v%, $\beta_{\text{benz/cyclohex}}$ tended to stabilize with increasing total flux, but increased when benzene was 10 wt %. Finally, it was also revealed that the best compromise of the filled membrane in terms of total cumulative flux and separation factor is obtained for the feed containing the azeotropic mixture.

Author Contributions: Conceptualization, S.A.; methodology, H.Z.; software, H.Z. and W.S.S.; validation, T.A., H.Z. and S.A.; formal analysis, W.S.S. and H.Z.; investigation, H.Z.; resources, W.S.S.; data curation, T.A.; writing—original draft preparation, H.Z. and T.A.; writing—review and editing, T.A. and W.S.S.; visualization, H.Z.; supervision, T.A.; project administration, T.A.; funding acquisition, S.A. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through Research Group No. RGP-VPP-029.

Conflicts of Interest: The authors declare no conflict of interest.
Abbreviations and Nomenclature

γ  Activity coefficient
Benz  Benzene
β_{Benz/cyclohx}  Benzene/cyclohexane separation factor
CMSs  Carbon molecular sieves
CNTs  Carbon nanotubes
MWCNTs  Multi-walled carbon nanotubes
CS  Chitosan
J  Cumulative total flux
J_{E-VOH}  Cumulative total flux obtained by E-VOH membrane
J_{E-VOH/CNT}  Cumulative total flux obtained by E-VOH/CNT membrane
β-CD  β-cyclodextrin
Cyclohx  Cyclohexane
DS  Degree of swelling
DMF  Dimethylformamid
DSC  Differential scanning calorimetry
D  Diffusion coefficient
β'  Entropic factor most often eq Blanks et al. and Scott
χ_{1,p}  Flory-Huggins interaction parameter between solvent and polymer
GC  Gas chromatography
T_g  Glass transition temperature
w_t  Masses of the sorbed molecules at time t
w_{t,\infty}  Masses of the sorbed molecules at maximum absorption
l  Membrane thickness
V_1  Molar volume of solvent
T_m  Melting temperature
PV  Pervaporation
PSI  Pervaporation separation index
PE  Polyethylene
EV-OH  Poly (ethylene-co-vinyl alcohol)
PHB  Poly (3-hydroxybutyrate)
PVA  Poly(vinylalcohol)
RhB-G  Rhodamine B-decorated graphene
SEM  Scanning electronic microscopy
β_{Benz/cyclohx}^\text{ab}  Selective absorption of the membrane factor
β_{E-VOH}  Separation factor obtained by E-VOH membrane
β_{E-VOH/CNT}  Separation factor obtained by E-VOH/CNT membrane
δ_p  Solubility parameter of the polymer
δ_1  Solubility parameter of the solvent
ϕ_1  Volume fraction of solvent
X  The molar fraction of benzene in the retentate
X_F  The molar fraction of benzene in the feed
XRD  X-Ray diffraction
Y  The molar fraction of benzene in the permeate

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