

Carbon nanotube enhanced PVA-mimic enzyme membrane for post-combustion CO₂ capture

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ABSTRACT

A carbon nanotube (CNT) enhanced polyvinyl alcohol (PVA)-mimic enzyme nanocomposite membrane was developed for CO₂ separation from flue gas under humidified conditions. A thin layer of PVA membrane containing mimic enzyme with uniformly dispersed CNTs on a porous support was prepared by dip coating. The thicknesses of the membranes was controlled by adjusting the polymer concentrations in the casting solutions. The membranes with the optimal concentration of the mimic enzyme (Zn-cyclen, 0.005 mmol/g) and different loadings of CNTs (0, 0.5, 1.0 and 1.5 wt%) in PVA at pH 5, 9 and 12 were prepared and tested for CO₂/N₂ separation. The addition of the CNTs as nano-fillers increased the degree of water swelling in the membrane, thus also significantly improved the CO₂/N₂ separation performance. A membrane containing 1.0 wt% CNTs at pH 12 showed the highest CO₂ permeance of 0.98 m³ (STP)/m² h bar and a CO₂/N₂ selectivity of 120, which is 30% higher in CO₂ permeance and 15% higher in CO₂/N₂ selectivity compared with that of the counterpart membranes without CNT addition.

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1. Introduction

Global warming is one of the most investigated environmental issues of the current era. Unchecked greenhouse gas (GHG) emissions over the last few decades, especially CO₂, are the main culprits in this scenario. The combustion of fossil fuels for energy production is the largest point source of CO₂ emissions. Moreover, this emission usually has a large volume, at near ambient pressure and with a low CO₂ concentration. Highly efficient separation technologies must be used to capture CO₂ from these sources as the separation driving force is relative low.

Membrane technology has been widely recognized as a promising technology for CO₂ capture and emission regulation. Compared to other technologies, the characteristic features of membranes, such as simple process design, low production and operational costs, environment friendliness, and easy maintenance, have proven to be advantageous (Ghoniem, 2011; Mulder, 2003; Olajire, 2010; Zhang et al., 2014). During membrane development, to reach both high CO₂ permeance and CO₂/N₂ selectivity are of great interest, as this is the key for efficient CO₂ separation (Scholes et al., 2008). Facilitated transport membranes with a thin, dense selective layer on a porous support have shown high separation perfor-

mances (Ansaloni et al., 2015; Bao and Trachtenberg, 2006; Dai et al., 2016a,b; Deng and Hägg, 2015; Deng et al., 2006; He et al., 2015; Liao et al., 2014; Qiao et al., 2015; Rafiq et al., 2016; Sandru et al., 2010; Zhao et al., 2012). Most of the recently reported facilitated transport membranes contain amino groups that function as “carriers” to enhance CO₂ transport.

Enzymatic membranes containing natural occurring enzymes (e.g., carbonic anhydrase) is a special type of facilitated transport membrane that achieves efficient CO₂ separation by mimicking the mechanism of the mammalian respiratory system, but is not yet considered feasible for up-scaling or industrial applications (Floyd et al., 2013). The main drawbacks of natural enzymes include a limited lifetime, a very high cost, and the enzyme activity being lost due to fluctuations in temperature and pH as well as the presence of impurities (Bao and Trachtenberg, 2006; Cheng et al., 2008; Figueroa et al., 2008; Floyd et al., 2013; Hägg and Deng, 2015; Singer et al., 2014). Enzymatic membranes containing a synthetic metal organic complex that resembles the enzyme's activities (mimic enzyme) were reported to overcome these problems (Saeed and Deng, 2015; Yao et al., 2012). In our earlier work, a polyvinyl alcohol (PVA)-based composite membrane containing Zn-cyclen as the mimic enzyme was reported to have a high CO₂/N₂ separation performance; a CO₂ permeance of 0.69 m³ (STP)/m² h bar and a CO₂/N₂ selectivity of 107 were documented (Saeed and Deng, 2015). This PVA-mimic enzyme membrane performs best in highly water swollen conditions and functions even at very low CO₂ partial

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pressures, which are particularly suitable for CO₂ separation from flue gas; these conditions fit the post-combustion CO₂ emissions features, e.g., low CO₂ concentration and high moisture content (Ghoniem, 2011; Mulder, 2003; Olajire, 2010).

In the presence of an enzyme, CO₂ hydration to produce HCO₃[−] ions is catalyzed and hence separation performance is greatly increased. A mimic enzyme has similar functions and a smaller molecule with a higher thermal stability compared with a natural enzyme, and it is resilient towards high pH and impurities in the gas phase. Even a small quantity of mimic enzyme can significantly enhance the CO₂ hydration rate (Davy et al., 2011; Floyd et al., 2013; Satcher et al., 2011).

The catalytic mechanism of CO₂ hydration promoted by Zn-cyclen can be explained in two main steps (Kulik et al., 2014): first, a carbon dioxide molecule is attached to the Zn²⁺ active site to form a meta-stable complex, and second, the complex is then attacked by a Lewis base (OH[−]) to produce bicarbonate (HCO₃[−]). In this two-step process, CO₂ is converted to HCO₃[−] and the active sites in the mimic enzyme are left unreacted (Floyd et al., 2013; Zhang and Van Eldik, 1995). The water ligand attached to the mimic enzyme needs to be deprotonated (activate) to catalyze the CO₂ hydration reaction, and the pH of this membrane needs to be maintained higher than the pK_a of the mimic enzyme (Hartono et al., 2014). A PVA solution in water has a pH of around 5. To maintain the pH higher than the pK_a of the mimic enzyme (pK_a = 7.9), sodium hydroxide (NaOH) solution was added. In addition, adjusting the pH to be basic makes the PVA-based membrane more water swollen.

One approach to tailoring a facilitated transport membrane to further improve the separation performance is by adding nano-fillers to the selective layer. These nano-fillers can open up the polymer chains in the membrane to improve the facilitated transport effect and gas diffusion, therefore increasing the CO₂ permeation. Nano-fillers such as CNTs, TiO₂, silica, and Zeolite matrix have been reported to improve the CO₂ facilitated transport and separation performance of various polymeric membranes (Ahmad and Hägg, 2013; Saeed et al., 2012).

As water plays an important role in the facilitated transport of the mimic enzyme membranes, in this work CNTs were introduced into the PVA-mimic enzyme membrane matrix to improve the water uptake in the PVA matrix and hence the membrane's CO₂ separation performance. CNTs were selected based on a preliminary study, in which the addition of the hydrophilic CNTs, TiO₂ nanoparticles and cellulose fibrils (CFs) in a PVA membrane matrix were investigated, and CNTs was found the best suitable nano-filler for the CO₂ separation under humidified conditions. In addition, the CNT dispersion and CNT aggregation in polymers, especially in PVA, have been well documented in literature and our early work (Deng and Hägg, 2014). The high cost of CNTs as nano-fillers in membranes were usually considered as a disadvantage, but the influence of the cost in this membrane is negligible: only a very small amount of nano-fillers were added into the PVA matrix (e.g., approx. 1% CNTs in PVA) in the selective layer of the composite membrane, where the thickness is usually less than 1 μm. Moreover, the CNTs used in this membrane (VGCF-XTM) is commercially available with a large scale production by Showa Denko (Denko, 2016). Nevertheless, a new project to replace CNTs with more hydrophilic and cheaper alternative materials (e.g., nanocellulose fibrils) is currently ongoing.

Many CNT-PVA membranes with excellent mechanical properties and enhanced performance have been reported in the literature (Bin et al., 2006; Chen et al., 2005; Coleman et al., 2006; Hu et al., 2012; Liu et al., 2007; Peng et al., 2007; Shirazi et al., 2011). Miaudet et al. (2005) studied the interaction between PVA and CNTs and showed that in PVA, fibers can be aligned, and the crystallinity of PVA can be altered above the glass transition temperature. CNTs acted as nano-spacers to improve the separation performance while

maintaining a higher mechanical strength of the membranes. Bin et al. (2006) reported a significant improvement in PVA mechanical properties by the addition of multi-wall CNTs. The addition of CNTs to a PVA membrane has also been reported to show a higher water flux in a study of dehydration by evaporation (Hu et al., 2012; Peng et al., 2007; Shirazi et al., 2011). A PVAm/PVA membrane containing CNTs has been reported to have both high CO₂ permeance and CO₂/CH₄ selectivity, especially for elevated and high pressure operations (Deng and Hägg, 2014). The uniformly dispersed CNTs in the membrane reduced the compaction of the selective layer resulted from pressurization at high pressures. Ansaloni et al. (2015) and Zhao et al. (2014) investigated the performance of PVA membranes containing functionalized CNTs at elevated temperatures and pressures for the separation of CO₂ from N₂, CH₄, and H₂. They investigated the effects of parameters in membrane preparation (e.g., CNT loading and membrane thickness) and separation processes (e.g., pressure, temperature, and humidity) for the optimization of the separation performance.

In this work, multi-walled CNTs were used as nano-fillers and well-dispersed into the selective layer of a PVA-mimic enzyme membrane to increase the volume of the water swollen in the polymer matrix in order to enhance the CO₂ transport through the membrane, and hence to improve the CO₂/N₂ separation performance, especially the CO₂ permeance. The PVA-mimic enzyme membranes containing different loadings of CNTs at various pH levels were prepared and tested with a simulated flue gas containing 10% CO₂ in N₂ at various feed pressures and feed gas humidity levels (50–100%). The effect of CNT loading in the membrane on the water swelling capacity was investigated. The preparation conditions were optimized to reach the highest CO₂ permeance and CO₂/N₂ selectivity.

2. Experimental

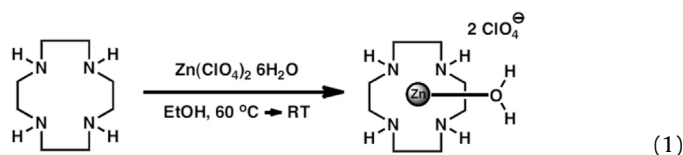
2.1. Materials

Analytical grade Zinc perchlorate hexahydrate (in crystalline form), 1,4,7,10-Tetraazacyclododecane (97% purity), absolute ethanol and polyvinyl alcohol (PVA) (MW 89,000–99,000, 89% hydrolyzed) were purchased from Sigma Aldrich. NaOH was purchased from VWR. The Polysulfone (PSf) ultrafiltration membrane (MWCO 50,000) was provided by Alfa Laval. All the chemicals and materials were used without further purification.

The multi-walled CNTs (VGCF-XTM, diameter 15 nm, length 1–3 μm) were kindly supplied by Showa Denko K.K. (SDK, Japan). A SEM and TEM images of the VGCF-XTM CNT can be found in Fig. 1 (Takahiro and Toshiya, 2015). Fig. 1(a) shows many kinks and bends in the CNTs, probably caused by the defects and broken wall structures, which is more clearly in the TEM image in Fig. 1(b). The good dispersion of the VGCF-XTM CNTs in the PVA/PVAm membranes was reported in our early work (Deng and Hägg, 2014). These CNTs can be readily distributed in water and aqueous polymer solutions.

2.2. Synthesis and characterization of the mimic enzyme (Zn-cyclen)

The reaction involved in the synthesis of the mimic enzyme Zn-cyclen is presented in Eq. (1) (Satcher et al., 2011).



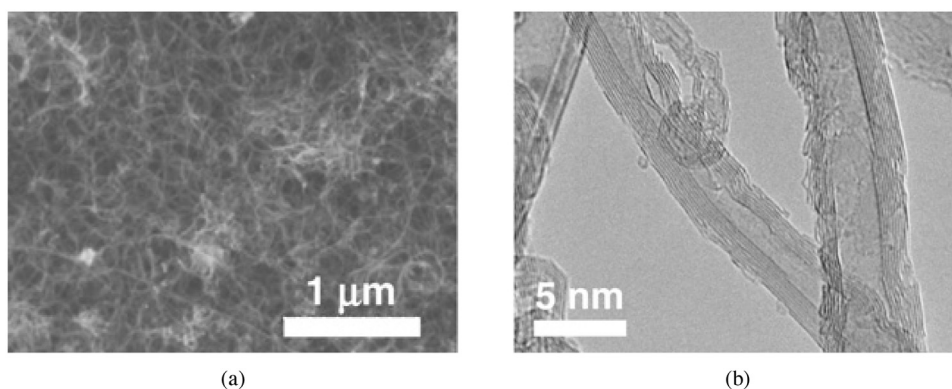


Fig. 1. SEM (a) and TEM (b) images of VGCF-XTM CNTs, reprinted from (Takahiro and Toshiya, 2015).

Cyclen in ethanol solution (5 ml) was added with an equimolar Zn (ClO₄)₂ ethanol solution over a period of 1.5 h. Unlike the reactants, the produced Zn-cyclen is not soluble in ethanol, thus it was separated from the solution by using vacuum filtration and then being washed several times with absolute ethanol. Mass spectroscopy and HNMR were used to determine the molecular composition of the produced Zn-cyclen and to confirm its existence.

2.3. Membrane preparation

PVA nanocomposite membranes containing mimic enzyme and well-dispersed CNTs in a thin, dense selective layer over a PSf porous support were prepared by dip coating. The thicknesses of the selective layers were determined by adjusting the concentrations of the PVA in the casting solutions. A concentrated PVA solution (10 wt%) was first prepared. This PVA solution was diluted with CNT dispersed water and sonicated for 4 h at an intensity level of 40, and then for 1 h at an intensity level of 20 by using a sonication device (Sonics Vibra-CellTM). PVA is a hydrophilic material with a pH value in the casting solution at 5 (acidic). As it is necessary to maintain a pH value higher than the pK_a of the chosen mimic enzyme to catalyze the hydration reaction, the pH value of the PVA-based casting solution was adjusted to be basic by adding 0.1 M NaOH solution. The weight of the bottle containing this PVA-CNT solution was measured before and after sonication to determine the loss of water by evaporation. The deionized water was added to this solution to maintain the concentration of PVA at 2.0% by weight. The loadings of the CNTs were calculated with respect to the PVA in the solution. The casting solution containing 2.0 wt% PVA and different loadings of CNTs (0.5, 1 and 1.5 wt%) with respect to the PVA was filtered by using a 5 μm PTFE porous filter to remove large CNT clusters and to ensure the continuous dispersion of the nanofillers. PVA films containing CNTs (0.5, 1 and 1.5 wt%) were casted. The degree of darkness in the color of the sample films increases with respect to CNT concentrations.

Defect free membranes containing different concentrations of CNTs were casted by dip coating on porous polysulfone (PSf) support. A flat sheet PSf support membrane washed with deionized water was masked on a glass slab and dipped into the casting solution for 30 s. The coated membrane was withdrawn and held nearly vertically to allow any extra solution to flow off evenly and form a homogeneous and continuous film. This procedure was repeated twice to ensure a defect-free and consistent coating. The twice-coated membrane was dried overnight at room temperature in a dust-free environment and then heat treated at 110 °C for 1 h to produce a physically cross-linked membrane.

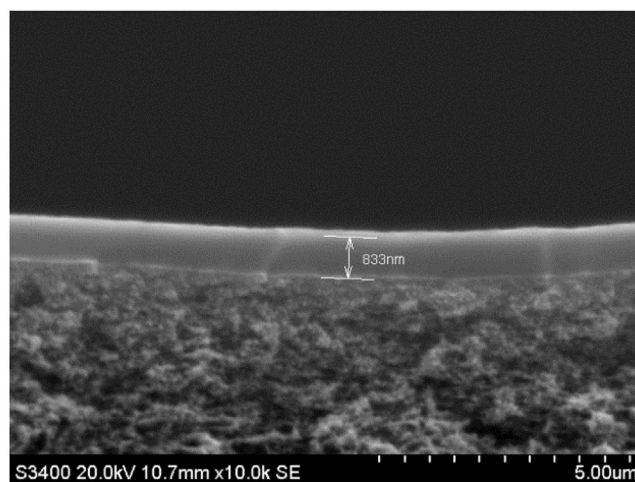


Fig. 2. Cross-section SEM picture of a PVA-CNT membrane on a PSf support.

2.4. Membrane morphology

The membrane morphology (cross-section and surface) was examined by field emission scanning electron microscopy (FESEM, Zeiss Ultra 55 Limited Edition). The cross-section samples were prepared by fracturing the membrane in liquid nitrogen and being coated with gold. The SEM images of the CNT/PVA-mimic enzyme membrane surface indicates a uniform and defect-free membrane. The thickness of the membrane can be determined from the cross-section SEM image, as seen in Fig. 2: a casting solution containing 2 wt% PVA was used to cast the membrane and a coating layer was obtained with a thickness of approximately 0.83 μm. The thicknesses of all the membranes were controlled by adjusting the concentration of the PVA in the casting solution at 2.0 wt%. Multiple samples were casted at this concentration and the selective layer thicknesses were measured varying between 0.81 and 0.85 μm.

2.5. Swelling test

The swelling behavior of the PVA films containing CNTs in a humidified environment was studied at room temperature. The experiments in a preliminary study showed that the dispersion of more than 2.0 wt% CNTs in a PVA solution was not stable, and hence the CNT loadings in the PVA polymer solution were set to be less than 2.0 wt% in this study. The low ratio of stable CNT dispersion could be due to the long and entangled chains of PVA and the high viscosity of the PVA solutions. Similar observations have been reported in the literature. The CNT loading was thus varied at 0.5,

1.0, and 1.5 wt% in PVA, and the effect of the CNT loadings was evaluated to find the optimal loading. PVA membranes with various CNTs loading and with and without pH adjustments were cast in a Teflon dish to produce self-supported films. The casting solution (5 ml) was poured onto a Teflon dish and dried at 45 °C overnight to produce samples of similar thickness. The sample films were peeled off from the Teflon dish and heated at 110 °C for 1 h, then cooled down to room temperature and dried in vacuum chamber at 25 °C for at least 3 h to remove the absorbed moisture. Vacuum dried samples were quickly weighed and then placed in a well-sealed humidification chamber with saturated water vapor (100% relative humidity at room temperature). These samples were tested periodically to measure the degree of water swelling by gravimetric analysis. Two parallel samples of each type were tested to take the average value. The degree of swelling was calculated based on a gravimetric analysis of the samples. Eq. (3) was used for the calculation of the degree of swelling (Deng and Hägg, 2010).

$$\% \text{swell} = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

Where W_s and W_d are the masses of the swollen and dry membranes, respectively.

2.6. Permeation test

A mixed gas permeation rig specially designed for humidified operations was used to analyze the performance of the membrane, the same as was used in Deng et al. (2009). The feed gases were supplied from a premixed gas cylinder. The temperature of the flat sheet membrane cell was maintained in a thermostatic cabinet. A flat sheet module with a circular membrane (diameter of 50 mm) was used in this work. Water saturated feed gas (10 vol.% of CO₂ in CO₂/N₂ gas mixture) and sweep gas (Helium) streams were regulated by mass flow meters and supplied to the membrane module. A dry feed gas bypass line was used to adjust the relative humidity. The feed side relative humidity was measured online by using a humidity analyzer, placed on the retentate gas stream immediately after the permeation cell. The permeate gas was analyzed by an online GC (MicroGC3000) to determine the gas stream composition. The feed and permeate gas flowrates were measured by the soap bubble method, whereas the operating pressures of all the gas streams were recorded by pressure transmitters (MKS) and logged directly into a computer (by Labview). The permeation experiments were carried out at 25 °C with a feed pressure varying from 1 to 3 bar. The separation performance was recorded when the system had been stabilized.

The selectivity (α) was calculated from the permeance of the CO₂ (P_{CO_2}) and (P_{N₂}), as expressed in Eq. (4) (Wijmans, 2003).

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (4)$$

The permeance of the gas was reported in units of [m³(STP)/(m² h bar)]. For a convenient comparison of the results, the unit conversion table of some commonly used gas permeance units is given in Table 1.

3. Results and discussion

PVA membranes containing 0–1.5 wt% CNTs were prepared with the pH value in the casting solution adjusted to be 5, 9 and 12 to study their effect on the performance of the membrane. The concentration of the mimic enzyme in the membrane casting solutions was 0.005 mmol/g PVA; this has already been optimized in our previous work (Saeed and Deng, 2015).

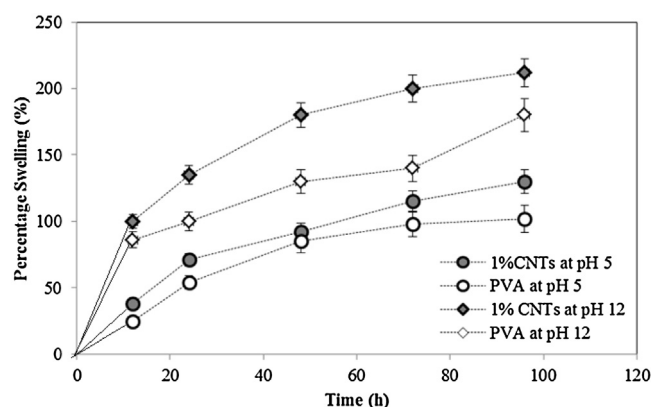


Fig. 3. Swelling behavior of PVA membranes with and without CNT loadings, at pH 5 and pH 12 under fully humid conditions at 25 °C.

3.1. Effect of CNT loadings on the degree of water swelling

The effect of CNT loadings on the swelling degree (water uptake) of membrane was first studied and optimized. Four sets of sample films with and without CNTs at pH 5 and 12 were placed in a humidified environment at room temperature for several days to investigate their swelling conditions during the process. A gravimetric analysis of these samples was conducted periodically to determine their degree of swelling based on the weight gain. The degree of swelling was calculated based on Eq. (4). The percentage of water swelling in the four samples is plotted with time in Fig. 3.

As presented in Fig. 3, it can be seen that the degrees of water swelling of all sample films increase with time. The PVA sample without pH adjustment seems reached its equilibrium state at the end of the test, i.e. 96 h, while the other three samples tend to approach their respective equilibrium degrees of swelling, but at different rates. The PVA sample shows the lowest water swelling capacity, while the sample of PVA with the addition of CNTs shows a much quicker increase in the degree of swelling with time, and a higher degree of swelling at the end of the test, suggesting a higher equilibrium water uptake. By the addition of 1.0 wt% CNTs with respect to PVA, the degree of swelling increases by approximately 30% after 96 h. By adjusting the pH from 5 to 12, the degree of swelling of the CNTs/PVA sample increases dramatically from 130% to 210%. These results clearly show that the addition of CNTs can significantly improve the water swelling capacity of PVA, and the effect of CNT addition on the degree of swelling is more prominent in the PVA samples made at pH 12 as compared to the samples made at pH 5. The increases in the degree of swelling implies that the addition of the CNTs may have positive effect to water solubility in the PVA matrix, which results in an increase in water uptake of the membrane.

The kinetic of the swelling in the PVA and PVA/CNT samples at pH 5 and 12 was studied by using a simple analysis based on the second order equation: the equilibrium swelling degrees of the samples with the swelling–time curve can be evaluated, as expressed in Eq. (5) (Mohan et al., 2005). The integration of Eq. (5) over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$ gives Eq. (6):

$$\frac{dS}{dt} = k_s(S_{eq} - S)^2 \quad (5)$$

$$\frac{t}{S} = \frac{1}{k_s S_{eq}^2} + \left(\frac{1}{S_{eq}}\right)t \quad (6)$$

where S is the swelling degree at time t , k_s is the swelling rate constant and S_{eq} denotes the theoretical equilibrium swelling degree.

The t/S versus t graphs for the PVA and PVA/CNT samples were plotted in Fig. 4 based on the swelling–time curve in Fig. 3, and then

Table 1
Permeance unit conversion table.

	GPU	m ³ (STP)/m ² bar h	mol/m ² Pa s	m ³ (STP)/m ² Pa s
GPU	1	0.00274	3.38E–10	7.60E–12
m ³ (STP)/m ² bar h	365.5	1	1.24E–07	2.78E–09
mol/m ² Pa s	2.96E+09	8.09E+06	1	0.0225
m ³ (STP)/m ² Pa s	1.32E+11	3.60E+08	44.5	1

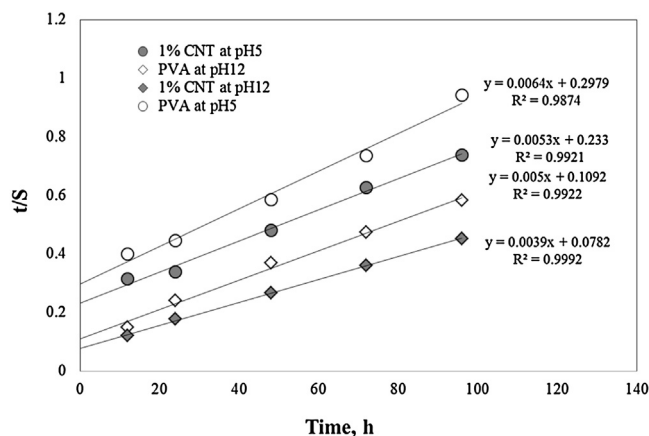


Fig. 4. Time/swelling degree (t/S) as a function of time (t) for PVA and PVA/CNT at pH 5 and 12.

Table 2
Swelling kinetic study data.

	Slope	Intercept	S_{eq}	$K_s \times 10^4$ (g gel/g water)/h
PVA at pH5	0.0064	0.298	156	1.37
1% CNT in PVA pH5	0.0053	0.233	189	1.20
PVA at pH12	0.005	0.109	200	2.29
1% CNT in PVA pH12	0.0039	0.078	256	1.95

the theoretical equilibrium swelling (S_{eq}) values and the swelling rate constant (k_s) of the samples were calculated from the constants of the linear equations shown in Fig. 4. The data from the analysis can be found in Table 2.

The theoretical equilibrium swelling degrees of the PVA/CNT samples with 1% CNT prepared at pH 5 and pH 12 were 189% and 256%, respectively, which are approx. 20–30% higher than those for the PVA samples prepared at the same conditions (around 156% and 200%, respectively). The swelling rate constants (k_s) for the PVA/CNT samples are slightly lower than that of the PVA samples, implying that it is faster for PVA samples to reach the swelling equilibrium. The addition of CNTs can increase the equilibrium swelling degree to a certain extent, but its influence to the swelling rate is not significant. These results suggest that the addition of CNTs cannot accelerate the membrane swelling process, but it is believed can provide extra nano-spaces for water condensation inside the polymer matrix and hence the PVA/CNT samples reach a higher equilibrium swelling degree.

3.2. Effect of CNT loadings on the CO₂/N₂ separation performance

The separation performance of a PVA membrane containing CNTs (0.5–1.5%) was studied to determine the optimal CNT loading. Fig. 5 shows the effect of CNTs on the separation performance of a membrane without pH adjustment (i.e., pH = 5). As can be seen, the CO₂ permeance increases with the increase of the CNT loading, and reaches the highest CO₂ permeance of 0.34 m³(STP)/(m² bar h) at the CNT loading of 1.0 wt%, which is nearly doubled of that of the PVA membrane without CNTs. A further increase in the CNT load-

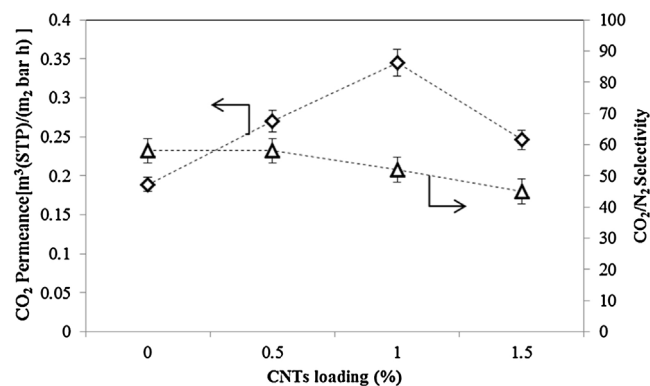


Fig. 5. Effect of CNT loading in a PVA membrane (at pH 5) on the CO₂ permeance and CO₂/N₂ selectivity. Fully humidified feed gas containing 10% CO₂ in N₂ at 1.2 bara and 25 °C.

ing from 1.0 wt% to 1.5 wt%, however, results in a notable drop in the CO₂ permeance. Meanwhile, the CO₂/N₂ selectivity decreases monotonically with an increase in CNT loading, but the effect is not significant: only an approximately 10% decrease was recorded from a CNT loading of 0–1.0 wt%. The increase in CO₂ permeance with the CNT loading suggests that the addition of the VGCF-XTM CNTs has positive influence to the CO₂ transport in this membrane. This may be due to the enhancement of water uptake capacity in the CNT-PVA matrix. Nevertheless, the presence of CNTs and the enhanced water swelling capacity did not lead to the facilitated transport of CO₂, as the CO₂/N₂ selectivity did not increase.

When the CNT loading is increased from 1.0% to 1.5 wt% with respect to PVA, an obvious decline in separation performance can be observed. The CO₂ permeance for the PVA membrane containing 1.5 wt% CNTs was found to be appreciably lower than that of membrane containing 1.0 wt% CNTs. The CO₂/N₂ selectivity of the PVA membrane containing 1.5 wt% CNTs is also slightly lower than all other tested membranes. This is believed to be due to the more occupied gas diffusion path by the dispersed CNTs in the PVA matrix at a higher CNT loading. The CNTs used in this work has a very low density (0.08 g/cm³), which is 15 times lower as compared to the density of the PVA film (1.2–1.3 g/cm³). An increase in CNT loading from 1.0 to 1.5 in weight percentage with respect to PVA would result in a very large increase in terms of the volume percentage. The benefit again by the enhanced water swelling from the increased CNTs is thus counterweighed.

Experiments confirm that the addition of well-dispersed CNTs in the PVA membrane is an effective method to enhance water uptake and hence the separation performance in this membrane, especially the CO₂ permeance. The mass transfer resistance in a CO₂-selective membrane is generally presented with the CO₂ permeance: a membrane with a higher CO₂ permeance contributes a lower CO₂ mass transfer resistance to the separation system. As the CO₂ permeance in the CNT enhanced mimic enzyme membrane significantly increases by adding the nano fillers and mimic enzymes, the mass transfer resistance of the membrane largely decreases, which can effectively reduce the total energy consumption in the CO₂ separation process: Energy consumption and the cost have been the main obstacles in using CO₂ capture membrane processes.

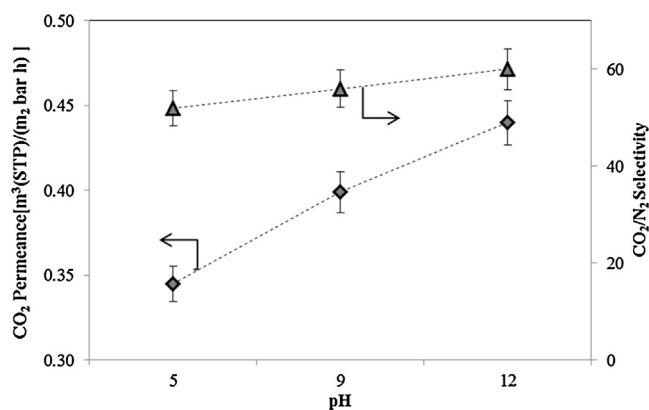


Fig. 6. Effect of pH on the CO₂ permeance and CO₂/N₂ selectivity of a PVA membrane containing 1.0 wt% CNTs. Fully humidified feed gas containing 10% CO₂ in N₂ at 1.2 bara and 25 °C.

As a significant drop in membrane separation performance was obtained by increasing the CNT loading to over 1.0 wt%, the optimal CNT loading with respect to PVA was determined to be 1.0 wt% CNTs in this membrane.

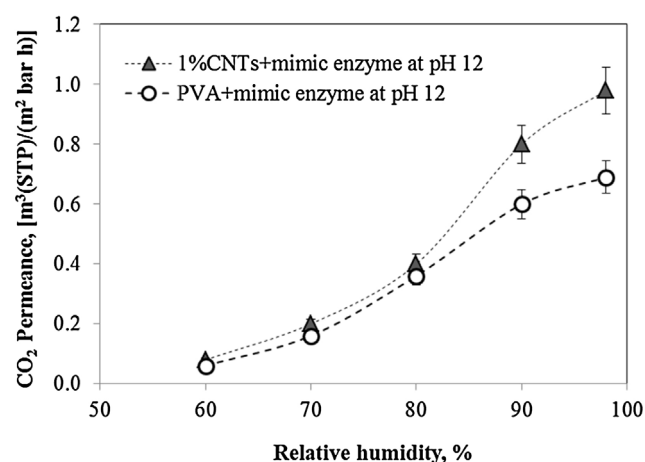
3.3. Effect of pH on the CO₂/N₂ separation performance

The effect of pH on the separation performance of a PVA membrane containing the optimal loading of CNT (1.0 wt%) is presented in Fig. 6. It can be seen that both the CO₂ permeance and the CO₂/N₂ selectivity increase with the increase of the pH value. By adjusting the casting solution from pH 5 to 12, the CO₂ permeance of this membrane increased from 0.34 to 0.44 m³(STP)/(m² bar h) (25% increase) and the selectivity increased from 52 to 60 (13% increase).

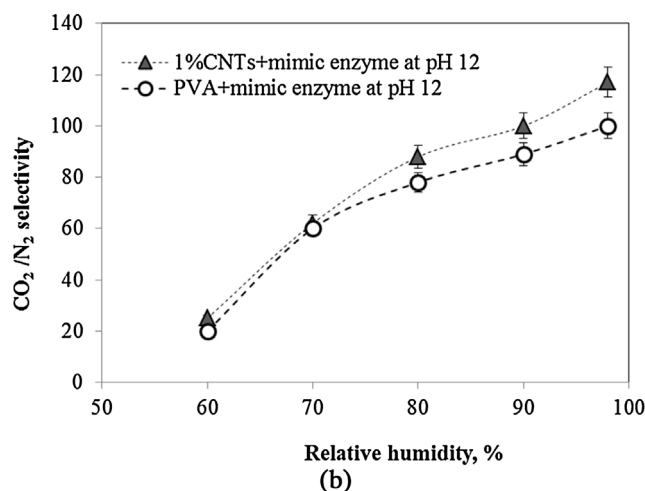
The above results suggest that the separation performance of the water swollen CNT/PVA membrane can be improved by adding CNTs and increasing the pH value to be basic (by the addition of the NaOH solution). The improvements can be attributed to the increase of water swelling capacity in the membrane, which may increase the chain flexibility and the free volume in the PVA matrix and eventually results in an increase in the CO₂ permeance. The results also show that the addition of CNTs and adjustment of the pH can only contribute to the increase in CO₂ permeance without fundamental impact on CO₂/N₂ selectivity, suggesting that the CO₂ transport mechanism through water swollen PVA is still solution-diffusion: the CO₂/N₂ selectivity is not above the theoretic selectivity (approx. 60) calculated from the solubility and diffusivity values of CO₂ and N₂ in water at the operating conditions. It also suggests that although the membrane is prepared at pH 12, the performance cannot be maintained in a CO₂ rich gas stream over time, as the CO₂ will react with the basic moieties and tend to drop the pH value in the system. With the presence of mimic enzyme, however, the CO₂ hydration occurs selectively with H₂O according to the mimic enzyme catalytic mechanism (Davy, 2009; Saeed and Deng, 2015; Satcher et al., 2011). The reversible CO₂ hydration is quick and without consuming the basic moieties, thus the pH value can be maintained, and the selectivity can be increased.

3.4. Effect of relative humidity on the CO₂/N₂ separation performance

The water swollen in this membrane not only opens up the PVA polymer network and increases the gas/ion diffusivity, but most importantly, it also attaches to the mimic enzyme as a temporary ligand to complete the catalytic hydration cycle. By adding CNTs to the membrane, the water swelling capacity of the PVA selective layer increases (see Fig. 3). The excess water favors the



(a)



(b)

Fig. 7. Effect of relative humidity on the CO₂ permeance (a) and CO₂/N₂ selectivity (b) of a PVA-mimic enzyme membrane with and without 1.0 wt% CNTs at pH 12. Feed gas containing 10% CO₂ in N₂ at 1.2 bara and 25 °C.

activation of the mimic enzyme to promote the CO₂ facilitated transport. Relative humidity in the feed side of the membrane was found strongly influence the water swelling degree of the membrane (Deng and Hägg, 2010). The effect of relative humidity in the feed gas (50–100%) on the CO₂ permeance and CO₂/N₂ selectivity of the PVA-mimic enzyme membranes with and without CNTs was studied, which confirms the influence of CNT addition, as presented in Fig. 7.

Fig. 7 shows the effect of relative humidity on the CO₂ permeance and CO₂/N₂ selectivity of a mimic enzyme promoted PVA membrane with and without the addition of 1.0 wt% CNTs. As can be seen in Fig. 7, the relative humidity in the feed gas has a very strong influence on the CO₂ separation performance. Both PVA-mimic enzyme membranes with and without CNT loading show clear increase in CO₂ permeance as well as CO₂/N₂ selectivity with increasing relative humidity, which suggests that the mimic enzyme-based PVA membrane should operate under fully humidified conditions to take advantage of the mimic enzyme catalytic function in the CO₂ hydration reaction to improve the CO₂/N₂ separation performance.

The plots in Fig. 7 also show that the effect of the relative humidity on the performance in the membranes with and without CNT loading is different. The CO₂ permeances of both membranes in Fig. 7(a) are quite similar in the low relative humidity range, i.e., when relative humidity is lower than 80%, where the CO₂/N₂ selec-

tivities of both membranes are also similar. When the relative humidity increases to be 80% and above, the difference in CO_2 permeance becomes significant in the membranes with and without CNT loading. As mimic enzyme requires a water ligand to function, the separation performance qualitatively reflects the water uptake in the mimic enzyme membranes. Based on the separation performance, it is reasonable to assume that the rate of water swelling in both membranes was similar in the range of low humidity (<80%), but at higher humidity level, more water was retained in the membrane containing CNTs, most likely due to the nano-spacer effect resulted from the nano-size structure of the CNTs. The Free volume increase mechanism and Solubility increase mechanism in nanocomposite membranes can explain the nano-spacer effect (Cong et al., 2007).

A CO_2 permeance of $0.98 \text{ m}^3 (\text{STP})/(\text{m}^2 \text{ bar h})$ is obtained at the maximum relative humidity in the PVA-mimic enzyme membrane with 1.0 wt% CNT loading, whereas that of the counterpart membrane without CNT loading is only $0.65 \text{ m}^3 (\text{STP})/(\text{m}^2 \text{ bar h})$, which is more than 30% lower. Both membranes have similar CO_2/N_2 selectivity at the same relative humidity when relative humidity is lower than 80%, but the selectivity increases more in the PVA-mimic enzyme membrane with CNT loading, maybe due to the increased water uptake from nano-spacer effect and that more accessible water favors the function of water for the catalytic effect for CO_2 facilitated transport.

3.5. Effect of feed gas pressure on the CO_2/N_2 separation performance

The CO_2/N_2 separation performances of the PVA and the PVA-mimic enzyme membranes with and without CNTs were tested at various feed pressures (1–4 bara) to study the effect of pressure on CO_2 permeance and CO_2/N_2 selectivity. The results are plotted with operating pressures as x-axis in Fig. 8. Fig. 8(a) shows the CO_2 permeances of the four membranes. It can be seen that the influence of the feed pressure on the CO_2 permeance is different in the membranes with and without mimic enzyme. Both PVA-mimic enzyme membranes exhibit a dramatic decline in CO_2 permeance with increasing feed pressures, while the PVA membranes without mimic enzyme show a relatively stable CO_2 permeance. The CO_2/N_2 selectivity of these membranes have a similar trend, as shown in Fig. 8(b), where the CO_2/N_2 selectivity of two PVA membranes with and without CNT loading are nearly the same at various pressures.

From Fig. 8(a) it can be also seen that the effect of the addition of CNTs in PVA membranes with and without mimic enzyme is different. In the PVA membrane without mimic enzyme, the CO_2 permeance decreases slightly with an increase in feed pressure, which may be attributed to the compaction of the membrane under pressure. Polymeric membranes are usually subjected to compaction due to the pressure difference between feed and permeate gas streams. This effect becomes intensified in highly water swollen membranes. The addition of CNTs may reduce the compaction and thus maintain a higher water uptake in the membrane. The PVA membrane with CNT loading can therefore maintain a better separation performance even at higher feed gas pressures. As expected, the addition of CNTs increases the CO_2 permeance of the PVA membrane, which becomes more significant at higher pressures. Nevertheless, in these two membranes, the influence of neither CNT addition nor pressure change on the membrane separation performances is significant. This indicates that CO_2 separation in these two membranes is mainly based on the solution-diffusion mechanism, in which gas permeance is determined by the solubility and diffusivity of the gas in the membrane that theoretically do not change with the change of feed gas concentration or partial pressure.

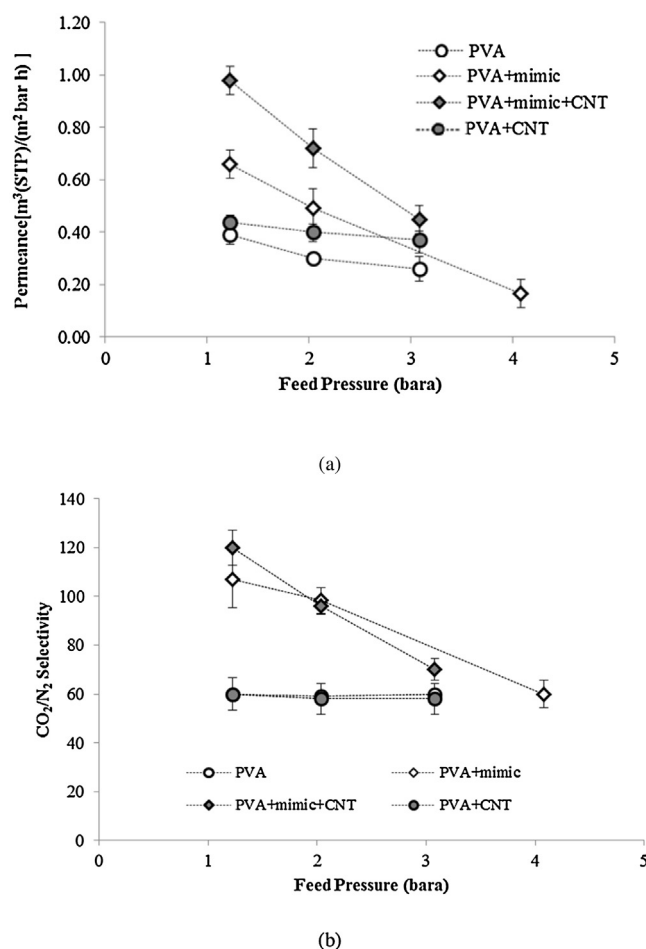


Fig. 8. Effect of pressure on the CO_2 permeance (a) and CO_2/N_2 selectivity (b) of a PVA membrane with and without CNTs and mimic enzyme at pH 12. The humidified feed gas contains 10% CO_2 in N_2 , at 25 °C.

However, both the CO_2 permeance and CO_2/N_2 selectivity in the two PVA membranes containing mimic enzyme clearly decrease with the increase in feed pressure: this trend is considered a characteristic feature of facilitated transport membranes resulted from the saturation of the CO_2 carriers at high CO_2 partial pressures, which has been reported by many researchers working with facilitated transport membranes (Deng and Hägg, 2014; Saeed and Deng, 2015; Sandru et al., 2010; Yao et al., 2012). This suggests that the transport mechanisms of the membranes with and without mimic enzyme are different. In the mimic enzyme membranes it is believed that the transport of CO_2 through the water swollen PVA film is facilitated by the mimic enzyme catalyzed CO_2 hydration reaction, as the CO_2 molecules absorbed the membrane are hydrolysed in the presence of mimic enzyme and transport through water swollen domains as bicarbonate ions. At a higher feed pressure, the equilibrium concentration of CO_2 or HCO_3^- in the membrane is higher, which may have caused the deactivation of some catalytic sites in the mimic enzyme and a reduction in CO_2 separation performance, as mimic enzyme is a catalyst that is deactivated in a bicarbonate rich environment (Floyd et al., 2013). The decreasing trend in CO_2 permeance with an increase in feed pressure indicates that the CNT enhanced PVA-mimic enzyme membrane is most suitable for the removal of CO_2 from gas streams with a low CO_2 partial pressure, as in the case of post-combustion CO_2 capture.

The results show that the addition of 1.0 wt% of CNTs in both PVA and PVA-mimic enzyme membranes can improve the CO_2 separation performance. The improvement is more significant

Table 3
Comparison with the literature data.

Membrane	Feed gas		Selectivity α	Permeance $\text{m}^3 \text{ (STP)}/\text{m}^2 \text{ bar h}$	Reference
	Composition	Pressure, kPa			
PVAm/PVA-CNTs	10% CO ₂ in CH ₄	200–1000	45	0.35–0.15	Deng and Hägg (2014)
PVAm/PVA	10% CO ₂ in N ₂	200–1000	174–66	0.58–0.13	Deng et al. (2009)
PVAm/PPO	10% CO ₂ in N ₂	200–1000	120k60	0.998–0.10	Sandru et al. (2010)
DNMDAM-TMC/PS	20% CO ₂ in N ₂	200–1000	70–56	0.47–0.27	Yu et al. (2010)
PVI-Zn complex 1	15% CO ₂ in N ₂	200–1600	75–50	1.23–0.82	Yao et al. (2012)
PVI-Zn complex 2	15% CO ₂ in N ₂	200–1600	65–40	0.95–0.41	Yao et al. (2012)
PVA/mimic enzyme	10% CO ₂ in N ₂	100–300	107–79	0.69–0.49	Saeed and Deng (2015)
CNTs + PVA	10% CO ₂ in N ₂	100–300	60–55	0.44–0.26	This work
CNTs + PVA/mimic enzyme	10% CO ₂ in N ₂	100–300	120–70	0.98–0.49	This work

in PVA membranes containing mimic enzyme. An approximately 30% increase occurs at 1.2 bara. The increase in CO₂ permeance at a higher pressure is lower (e.g., an increase of 0.23 [m³ (STP)]/(m² bar h)] at 2 bara, and approximately 0.14 [m³ (STP)]/(m² bar h)] at 3 bara); however, the ratio of the increase due to the addition of CNTs is quite similar, at around 30%. This suggests that in the mimic enzyme membrane the decrease in CO₂ permeance with the increasing pressure is not resulted from compaction, but mainly due to the reduced facilitated effect at higher feed pressures. The CO₂ permeance of a PVA-mimic enzyme membrane containing CNTs at 1.2 bara was determined to be 0.98 [m³ (STP)]/(m² bar h)] with a CO₂/N₂ selectivity of around 120. By adding CNTs to a mimic enzyme membrane the separation performance of the PVA membrane increased appreciably.

The CNT-enhanced PVA-mimic enzyme membrane shows a CO₂/N₂ separation performance comparable to some high performance membranes reported in recent years, as presented in Table 3 from the comparison of the separation performance of this membrane with some state-of-the-art CO₂ facilitated transport membranes and nanocomposite membranes.

4. Conclusions

A CNT-enhanced water swollen PVA-mimic enzyme nanocomposite membrane was developed and optimized. The addition of CNTs to a PVA-mimic enzyme membrane results in a higher degree of swelling, which improves the separation performance in this facilitated transport membrane. Membranes with CNTs loading showed a higher degree of water swelling, CO₂ permeance and CO₂/N₂ selectivity. The mimic enzyme catalyzes the CO₂ hydration to facilitate CO₂ transport in the membrane. Water is an important component of the CO₂ hydration cycle, which plays a vital role in the facilitated transport. By the addition of only 1.0 wt% CNTs to a PVA-mimic enzyme membrane, the separation performance significantly improved; a CO₂ permeance of up to 0.98 m³ (STP)/m² bar h and CO₂/N₂ selectivity of up to 120 were documented.

The results indicate that this mimic enzyme-based nanocomposite membrane has the potential to become a highly efficient and practical solution for post-combustion CO₂ capture. Moreover, this membrane is simple to prepare. The amount of mimic enzyme in this membrane is very low, and other two main raw materials, such as PVA and NaOH, are easily accessible at a very low cost. However, as the separation performance of the current membrane is still not being competitive compared to a commercial amine absorption process, more effort will be put to optimize nanofillers to promote the facilitated transport and/or maintain the pH conditions, for instance to employ more hydrophilic nano fibers or nanofillers with surface modified functional groups; these are now the main task in an on-going project in our group. Techno-economic analysis, including the cost estimation of the membrane fabrication and the operation of the membrane separation process using the CNT enhance mimic enzyme membrane, gives important information

for the feasibility of the industrial scale application, which will also be conducted in the future work.

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