Polydimethylsiloxane (PDMS) Membrane Filled with Biochar Core-shell Particles for Removing Ethanol from Water

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A new type of biochar-SiO_2 core-shell particles (BCNPs) was successfully prepared *via* the sol-gel-sediment method. The characteristics of BCNPs were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). This novel filler was added to a polydimethylsiloxane (PDMS) matrix to prepare composite membranes to separate ethanol from water *via* pervaporation (PV). The effect of BCNPs on the performance of the membranes was researched. Experimental results showed that the addition of BCNPs led to remarkably improved PV performance of composite membranes. When a BCNPs content was 5 wt.% for a 10 wt.% ethanol solution at 40 °C, the best PV performances gained were the separation factor of 11.9 and the corresponding permeation flux of 227 $g \cdot m^{-2} \cdot h^{-1}$.

Keywords: Pervaporation; Ethanol recovery; Core-shell; PDMS; Membrane

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INTRODUCTION

Ethanol biofuel has become more popular as a renewable biomass resource. Generally, the concentration of ethanol in the feed would be no more than 8 wt.% when produced by a traditional fermentation method. This is because the high ethanol concentration will inhibit the reproduction of yeast cells or even kill them, which means that the fermentation process would be stopped. To improve the efficiency of ethanol production, the continuous removal of ethanol from feed is necessary. Pervaporation (PV) is a membrane separation process for ethanol production by which the components could be segregated in passing through a porous polymeric or inorganic membrane depending on their different molecular diffusion rates. Compared with other separation technologies, such as carbon dioxide extraction (Chhouk *et al.* 2017), solvent extraction (Pasdaran *et al.* 2017), and vacuum distillation (Li *et al.* 2017)), PV is simple, cost-effective, and energy-efficient (Naidu *et al.* 2005; Wee *et al.* 2008).

Polydimethylsiloxane (PDMS) is one of the most common hydrophobic materials used in the PV process. To achieve better PV performances of the PDMS membranes, inorganic particles, such as silicalite-1, carbon black, carbon nanotube, *etc.*, have been added to the PDMS matrix to prepare the composite membranes (Jia *et al.* 1992; Vankelecom *et al.* 1997; Vane *et al.* 2008; Huang *et al.* 2009; Ning *et al.* 2016; Ashraf *et al.* 2017; Athanasekou *et al.* 2017). Biochar is made from biomass by pyrolysis (Lan *et al.* 2016). According to the literature (Luo *et al.* 2016), it can be concluded that the functional

groups, C-O, C=O, carboxyl groups, and an aromatic ring structure are found on the surface of biochar by FTIR, which makes it easy to graft with other groups for improving its ethanol selectivity.

As the name implies, core-shell is a nano-assemble structure that is prepared by a nanomaterial coated on another by chemical bonds or other forces. Because of its unique structural characteristics, a core-shell structure can provide the advantages of inside and outside materials. This approach has broad applications in the areas of catalysis, photocatalysis, batteries, gas storage, and separation (Carolan *et al.* 2017). For the first time, the biochar core-shell particles were prepared and added into membranes.

In this work, the BCNPs were successfully prepared by a sol-gel-sediment process that used biochar and tetraethyl orthosilicate (TEOS) as the raw material. Core-shell particles with hierarchical porous structures are composed of amorphous carbon and amorphous silica. Therefore, the unique structure can significantly improve the compatibility of fillers with PDMS (Posthumus *et al.* 2004).

The BCNPs were added to the PDMS matrix for preparing the PV composite membrane that was used for ethanol separation. The influence of preparation conditions on ethanol PV performance was also investigated.

EXPERIMENTAL

Materials

The PDMS (107#RTV) and sodium hydroxide were purchased from Sigma-Aldrich (St. Louis, USA). Cetyltrimethyl ammonium bromide (CTAB), tetraethylorthosilicate (TEOS), ethanol, n-hexane, and dibutyltin dilaurate (DBTOL) were obtained from Sigma-Aldrich (St. Louis, USA) and used as analytical reagents. The chemically pure silane coupling agent YDH-171 (CH_2=CH-Si(OCH_3)$_3$) was purchased from Sigma-Aldrich (Shanghai, China). Cellulose acetate microfiltration membranes (CA), of which the average pore size was 0.45 μm, were purchased from Fisher (St. Louis, USA). The biochar was made by an experimental pyrolysis system (GSL-1100X, Hefei Kejing Materials Technology Co., Ltd., Hefei, China).

Preparation of BCNPs

Biochar was prepared by tree bark powder at 407 °C under a N_2 atmosphere and then extracted with toluene to remove residual oil. Next, 200 g of H_2O, 0.50 g CTAB, and 0.50 g biochar were then added into a beaker. The solution in the beaker was stirred at room temperature for 24 h. Then, 50 mL was taken out above biochar suspensions and added to a beaker with 250 mL NaOH solution (0.01 M) and 12.5 mL mixture (TEOS: ethanol, v = 1/4). The beaker was exposed to ultrasonic vibrations for 1 min then put into a 60 °C water bath for 20 min. After, 30 seconds of oscillation was allowed the beaker was placed into a 60 °C water bath for 12 h. After the reaction, the sample was centrifuged and cleaned alternately with deionized water and ethanol several times and then dried at 105 °C for 24 h. The BCNPs were modified with YDH-171 in n-hexane.

Preparation of composite membranes

Firstly, the prepared BCNPs (0.01 g, 0.03 g, 0.05 g, and 0.07 g) were mixed with YDH-171 by a 1:1 weight ratio in n-hexane (4.5 g) and then introduced to the PDMS /n-hexane (1/4.5 g) solution, respectively. After the addition of TEOS (0.1 g) and DBTOL

(0.02 g), the prepared mixture was cast onto CA membranes that had been pretreated with deionized water. Finally, composite membranes were placed in the atmospheric environment for 24 h and then moved into an oven to remove the residual solvent.

Methods

Characterization of BCNPs and membrane

X-ray photoelectron spectroscopy (XPS) was conducted using an EscaLab Xi+ (Thermo Fisher Scientific, Waltham, USA) at 1252 eV. The XRD samples BCNPs was treated at 900 °C for 10 min. X-ray powder diffraction (XRD) patterns were acquired by a Rigaku D/MAX2200PC (Japan Rigaku Corporation, Shimadzu, Japan) with Cu-Kα radiation (40 kV, 20 mA). A contact angle apparatus (Mitutoyo519-109, Mitutoyo Corporation, Tokyo, Japan) was used to define the surface hydrophobicity properties for the prepared PDMS nanocomposite membranes. The morphology of BCNPs, and the surface and cross-sectional morphology of BCNPs modified PDMS nanocomposite membranes were conducted by scanning electron microscopy (SEM, XL30, FEI, Bethlehem, USA). It was noted that all specimens were gold-coated before the measurements (Leica EM ACE200, New York, USA).

The samples were immersed in ethanol for 48 h to test the ethanol solubility degree and diffusion coefficient. The average solubility degree of the PDMS separation layer was obtained according to the weight change from the dry sample (W_d) to the saturated wet sample (W_s), as shown in Eq. 1,

$$SD(\%) = \frac{W_s - W_d}{W_d} \quad (1)$$

The diffusion rates of ethanol in the PDMS active layer were measured following the method reported by Marais *et al.* (2000). The diffusion coefficient *D* can be measured as Eq. 2,

$$\ln\left(1 - \frac{\Delta M}{\Delta M_{eq}}\right) = -\ln\frac{\pi^2}{8} + \frac{\pi^2 Dt}{L^2} \quad (2)$$

where, *L* is the initial thickness of the membrane (cm), ΔM is the ethanol mass (g) at experiment time *t* (s), and ΔM_{eq} is the ethanol weight absorbed in the sample when the adsorption equilibrium is reached (g); *D* can be calculated according to the received slope.

The permeation flux and separation factor are two critical parameters in evaluating the PV performance of membranes. The definition of flux (*J*) is conformed to the following Eq. 3,

$$J = \frac{Q}{At} \quad (3)$$

where, *Q*, *A*, and *t* are the permeation weight (g), effective membrane area (cm^2), and operating time (h), respectively.

The selectivity (α) of the composite membrane can be expressed as Eq. 4,

$$\alpha = \frac{Y_A X_B}{X_A Y_B} \quad (4)$$

where X_A and Y_A are the ethanol mass fractions in the feed and PV liquid, respectively. Similarly, X_B and Y_B are the water mass fractions. The feed concentration and experiment time were 10 wt.% and 40 min, respectively.

RESULTS and DISCUSSION

XPS Characterization of BCNPs

Compared with biochar, the surface properties of the BCNPs were transformed. As shown in Fig. 1, XPS was performed to determine and analyze the content of carbon, oxygen, and silicon. Characteristic peaks arose at binding energies of 284.5 eV (C_{1s}), 532.7 eV (O_{1s}), and 103.4 eV (Si_{2p}) (Fig. 1). The figure shows C, O, and Si atomic compositions of 43%, 41%, and 15%, respectively. The SiO_2 may have been introduced through the deposition process. The surface of BCNPs may not only be changed into a hydrophobic state, but also may enable BCNPs to be more compatible with PDMS for PV applications.

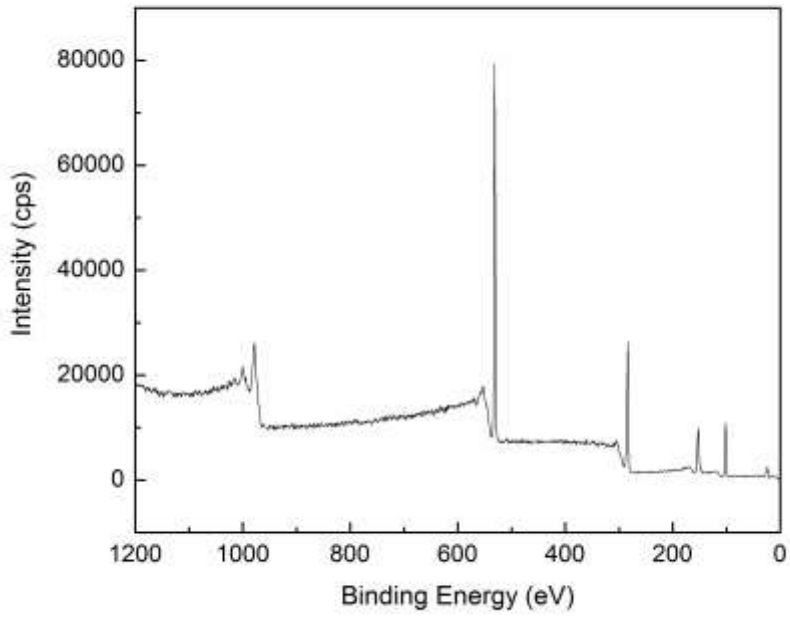


Fig. 1. XPS spectra of BCNPs

XRD Test

The XRD patterns were analyzed in biochar, BCNPs, and 900 °C BCNPs. For biochar and BCNPs, the same characteristic peaks were obtained, which showed that the grafted biochar contained no crystalline structure of SiO_2 (Fig. 2). For BCNPs at 900 °C, the diffraction peaks at 22.3°, 28.5°, and 32.2° can be observed in Fig. 2. After a certain high-temperature treatment, the clear characteristic diffraction peak of the cristobalite appeared in the XRD pattern.

This suggested that the amorphous SiO_2 on the surface was transformed into cristobalite after treatment at 900 °C. It can be concluded that the surface of BCNPs was amorphous silica, which was suitable for the PV membrane because of its high surface area and polyporous structure.

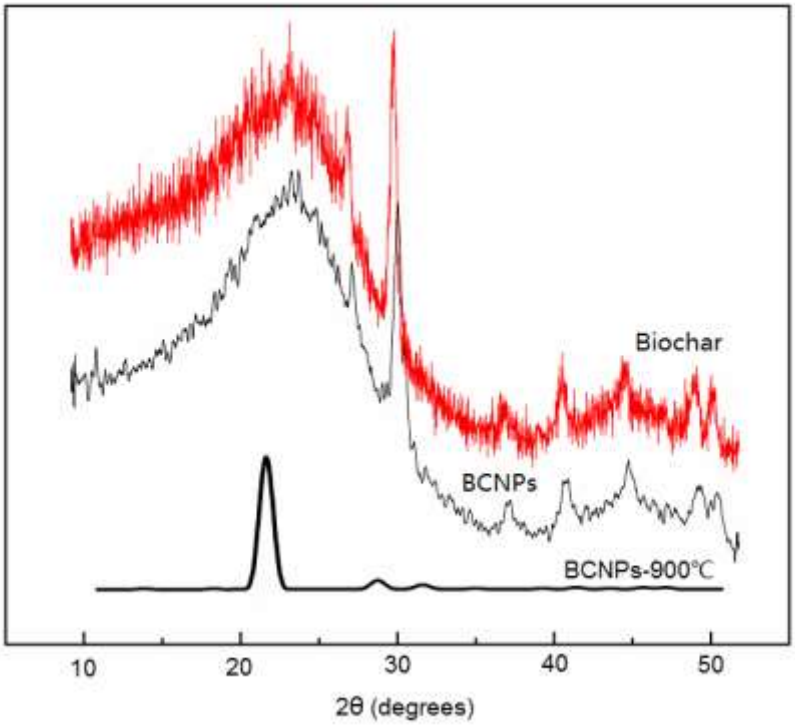


Fig. 2. XRD patterns of BCNPs

Contact Angle Test

Figure 3(a) shows the water contact angles on the surface of the PDMS composite membrane with the 1 wt.%, 3 wt.%, 5 wt.%, and 7 wt.% content of YDH-171 modified BCNPs. Compared with the unfilled membrane, the contact angle of water at the composite membranes with BCNPs was improved (Fig. 3(a)).

It was found that the contact angle of water rose as the content of modified BCNPs was increased. This indicated that the surface of the composite membrane represented higher hydrophobicity as a result of the addition of BCNPs. An enhanced hydrophobicity of the surface of composite membranes was obtained with the coated SiO_2 and the hydrophobic groups of the silane coupling agent.

The contact angles of ethanol at the composite membrane's surface are shown in Fig. 3(b). Usually, the ethanol contact angle considerably decreases with the increase in the modified BCNPs content. This means that the addition of grafted BCNPs enhanced the compatibility between the composite membranes and ethanol. However, in the present study, the contact angles of ethanol presented almost no difference among the membranes with different contents of BCNPs.

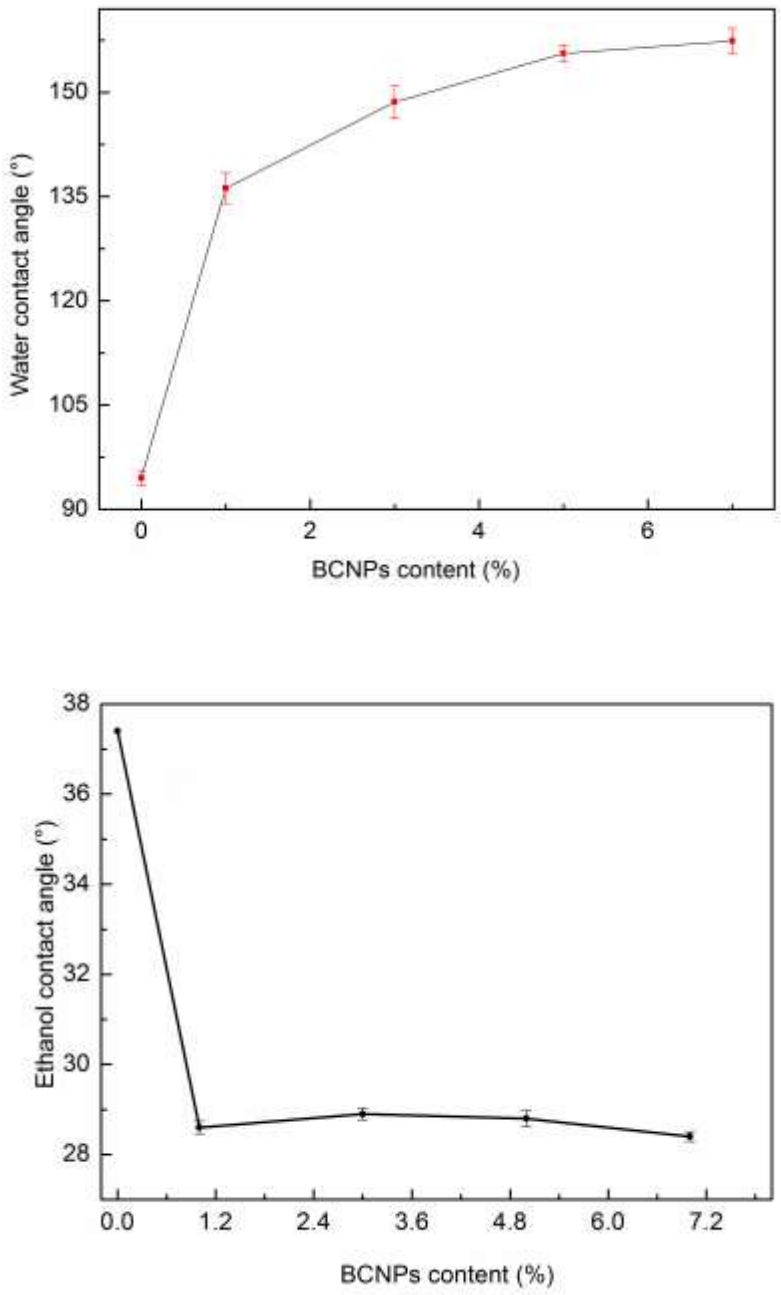


Fig. 3. Contact angles of water (a) and ethanol (b) on the composite membranes surfaces

Morphologic Analysis of Composite Membranes

The morphology of BCNPs is shown in Fig. 4(a), where the particle size of the BCNPs was around 60 nm. Figures 4(b) and 4(c) show the surface and cross-section morphologic characteristics of the PDMS/CA composite membrane with 5 wt.% content of modified BCNPs. The interface of the CA support layer and the active layer was also observed with SEM as shown in Fig. 4(d). It was clear that the active layer adhered to the surface of the CA layer tightly and that the modified BCNPs dispersed well within the PDMS matrix.

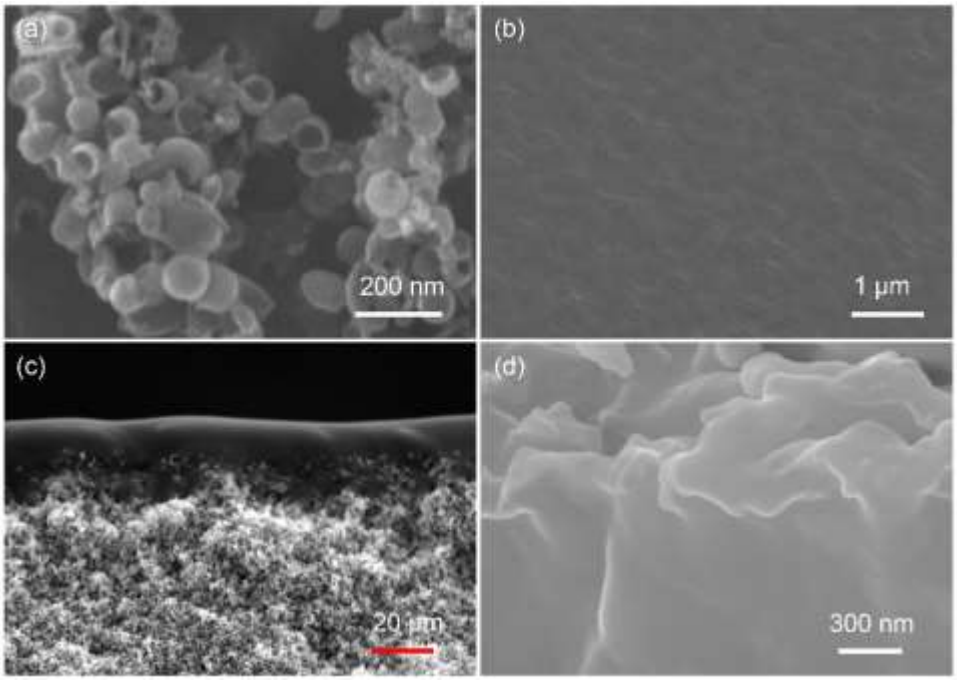


Fig. 4. SEM images of BCNPs and PDMS/CA composite membranes with 5 wt.% BCNPs; (a) BCNPs; (b) Surface; (c) Cross-sectional; and (d) Interface of CA and PDMS

Effect of BCNPs on Ability for Membranes to Absorb Ethanol

The solubility degrees were tested, with three replications for each sample. First, the separation layers of the composite membranes were soaked in 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.% ethanol solutions, respectively. The solubility degrees of the composite membranes all increased with an increment in the BCNP content (Fig. 5).

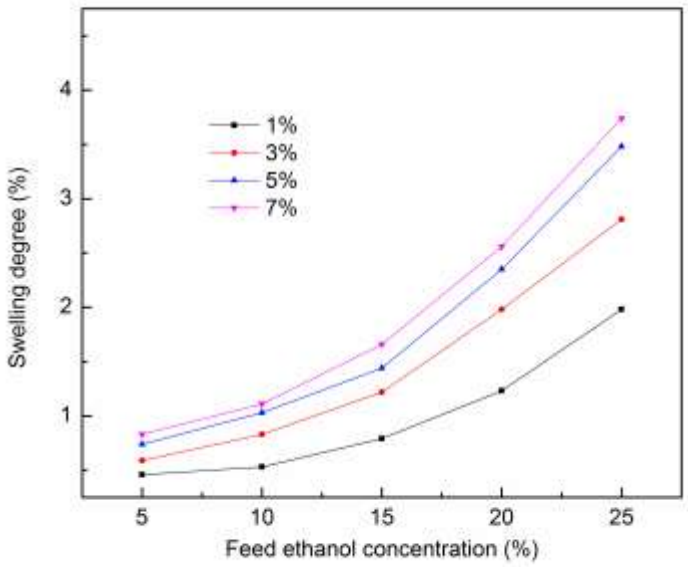
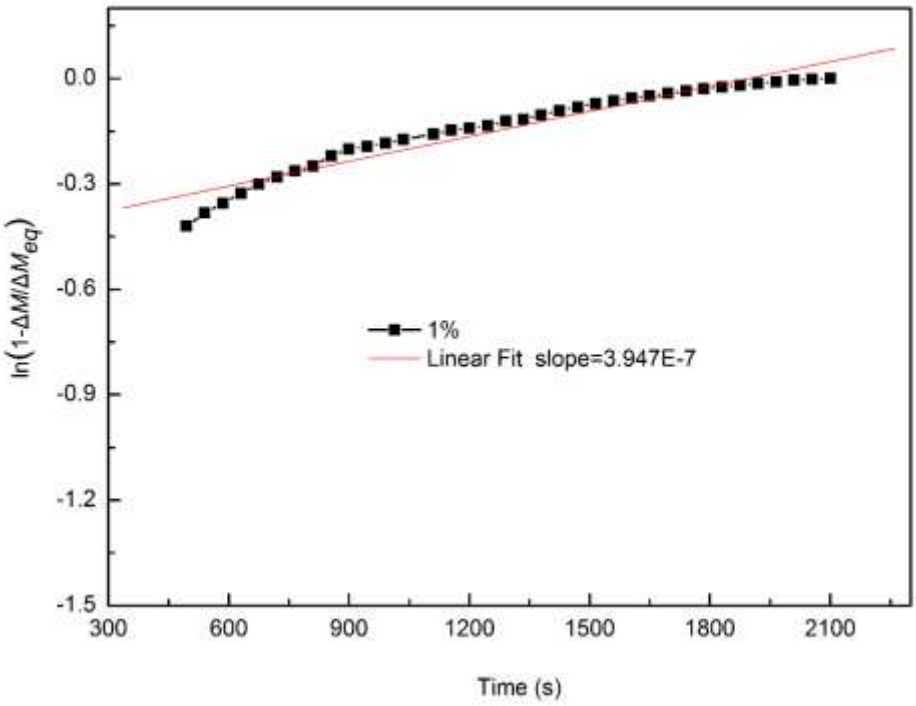
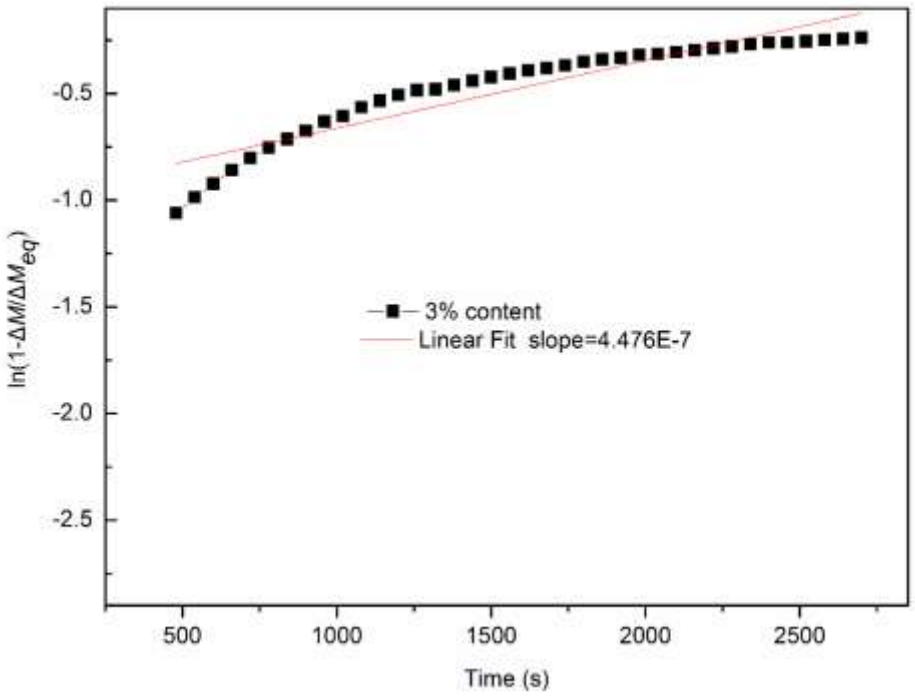


Fig. 5. The swelling degree of the composite membrane with different contents of BCNPs

This was because the increment of BCNPs enhanced the compatibility of the membranes. The solubility of the composite membrane grew with the increase of the concentration of ethanol in the feed (Fig. 5). The composite membranes had more of a chance to come into contact with ethanol because the BCNPs content and the concentration of ethanol in the feed were higher; therefore, the solubility of the membranes increased.

Measurement of Ethanol Diffusivity





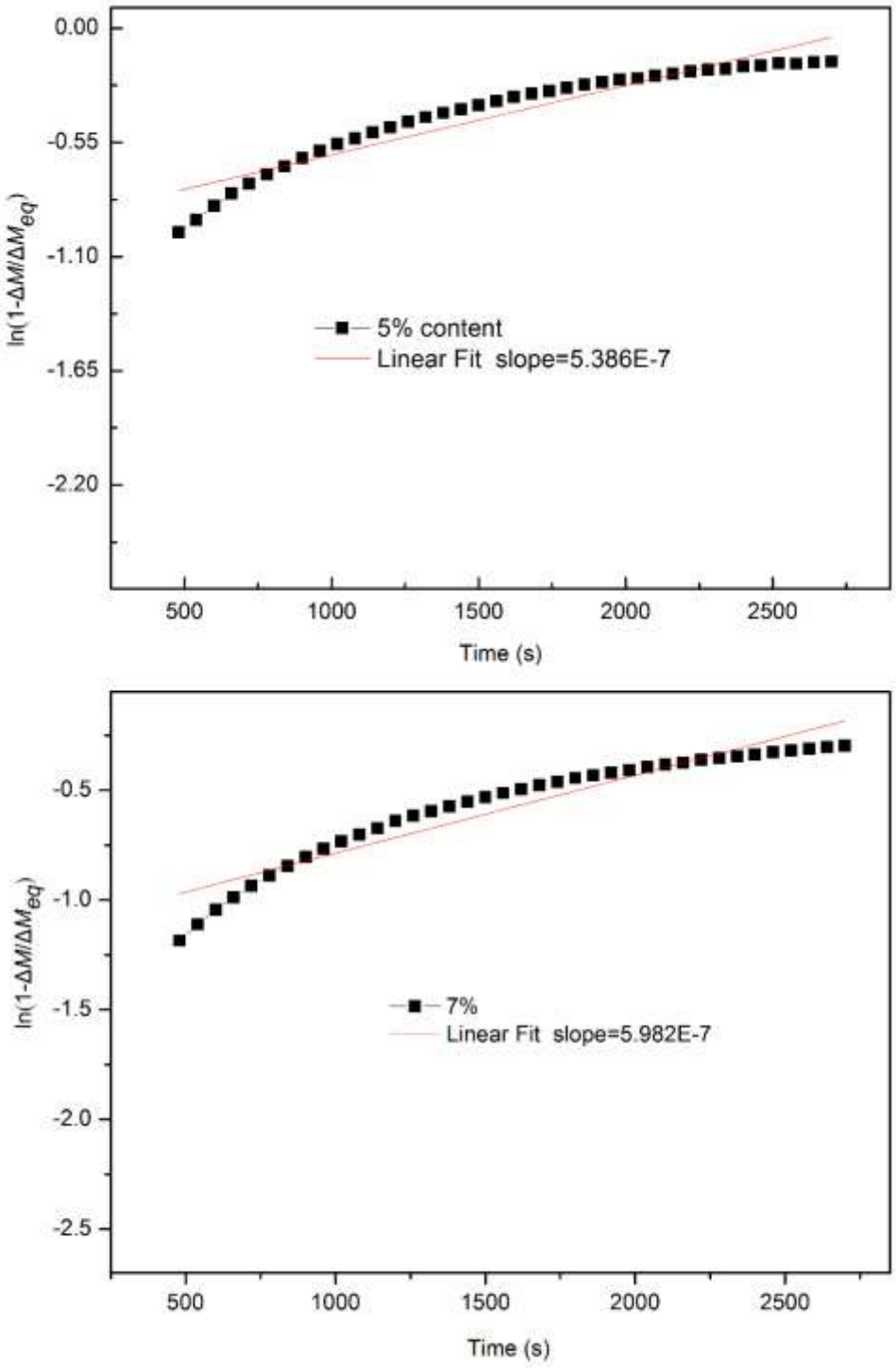


Fig. 6. The diffusivity of the composite membranes with modified BCNPs

According to Eq. 2 and Fig. 6, ln(1−Δ*M*/ΔMeq) as a function of *t* was linearly dependent. Thus, the diffusivity was calculated by the slope of the semi-log plot for different grafted BCNPs. In terms of the slope numbers of the ethanol diffusivity in the composite membranes containing BCNPs (1 wt.%, 3 wt.%, 5 wt.%, and 7 wt.%), the

diffusivities were 3.95 $cm^2 \cdot s^{-1}$, 4.48 $cm^2 \cdot s^{-1}$, 5.39 $cm^2 \cdot s^{-1}$, and 5.98 $cm^2 \cdot s^{-1}$, respectively. Each sample was tested three times. According to the increment of the separation factor, it was concluded that the application of novel filler successfully improved the performance of composite membranes.

PV Performances

As shown in Fig. 7, the permeation fluxes of the membranes increased with the amplified addition of BCNPs, where three test times were taken for each sample. The addition of BCNPs improved the fluxes of the composite membranes. This was mainly due to the enhancement of the ethanol adsorption ability. It has been reported that the diffusivity of ethanol increased as the free volume of the membranes increased (Merkel *et. al* 2002; Gomes *et. al* 2005). The free volume of composite membranes increased because the chain packing was disrupted by the addition of BCNPs, which resulted in an improved flux.

The curve of the separation factor of composite membranes with BCNPs is shown in Fig. 7. The separation factor for the membranes with BCNPs was much higher than the unfilled membrane; each membrane sample was measured three times. This result was caused by hydrophobic property and dispensability. According to the contact angle data, the hydrophobicity of membranes with BCNPs was higher than the unfilled membrane so the composite membranes with BCNPs were more compatible with ethanol. Therefore, the membranes with BCNPs had a higher separation factor.

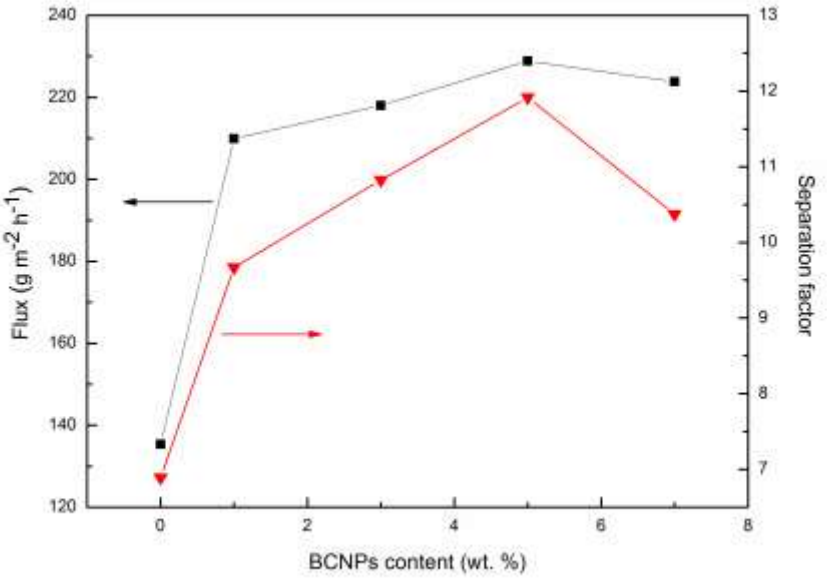


Fig. 7. The influence of BCNPs content on the PV performance

With an increment of the addition of BCNPs in the active layers, the separation factors initially increased and then decreased. The chain packing was disrupted and the free volume increased with the addition of BCNPs. However, the free volume in the active layers was also inhabited with more BCNPs. Consequently, there was a balance between the two mechanisms. More ethanol was dissolved into the active layers in the PV process if the free volume increased. Accordingly, the swelling of the active layer improved; hence, the diffusion efficiency of the molecules was higher, which led to a larger flux. The size of

the water molecule was smaller and the separation factor declined due to the higher increment of water diffusivity than the increment of ethanol diffusivity.

Influence of Feed Concentration on PV Performances

This showed the influence of the feed concentration on the PV performances for a composite membrane with 5 wt. % BCNPs at 40 °C (Fig. 8). The flux of the composite membranes increased with the increment of feed concentration, but the trend of the separation factor was the converse (Fig. 8). Ethanol got more of a chance to be dissolved into the membrane with the increment of feed concentration during the PV process. Consequently, there was a rise in the swelling degree of the separation layer, which resulted in an improvement of the free volume of the separation layer. Therefore, the diffusion rates of the components in the membrane increased and resulted in an increment of the flux. The increment of the water diffusion rates was larger than the increment of the diffusion rates of ethanol due to the difference in molecular size. Therefore, the separation factors of the composite membrane reduced.

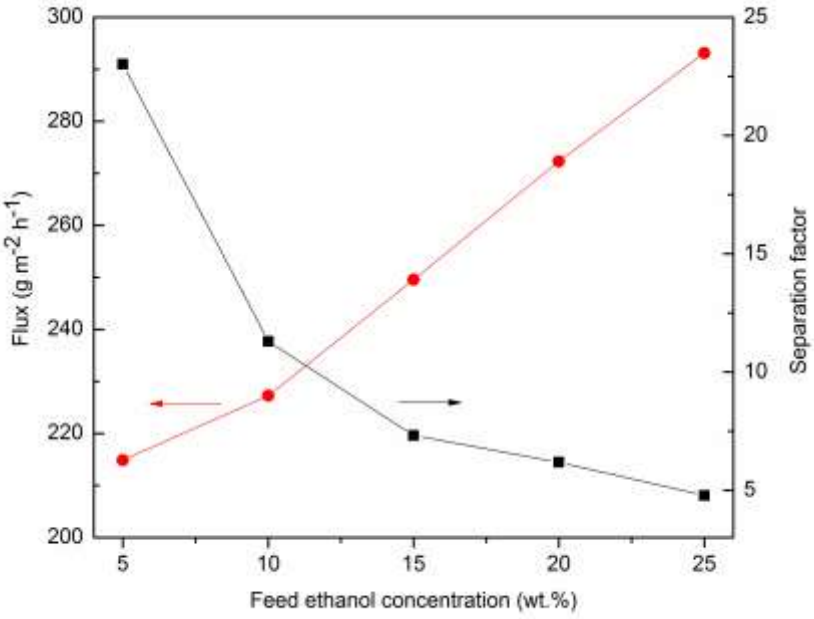


Fig. 8. Influence of ethanol concentration on PV performances for the composite membrane

Influence of Feed Temperature on PV Performances

The effect of feed temperature on the separation factor and flux was calculated and is shown in Fig. 9. An increment of the feed temperature caused clear increment of the flux for the composite membrane with 5 wt. % BCNPs. This showed that the feed temperature influenced the PV performances on the molecular solubility, the activity of PDMS, and the free volume of the active layer (Adnadjević *et. al* 1997). The experiment result was due to the fact that as the feed temperature rose up, the thermal motion of polymer chains heightened. Thus, the free volume was enlarged. Therefore, the diffusivity of molecular increased due to the increment in temperature, which led to permeation improved flux. In addition, the separation factor of ethanol decreased gradually with an increment in the temperature, as shown by Mohammadi *et. al* (2005).

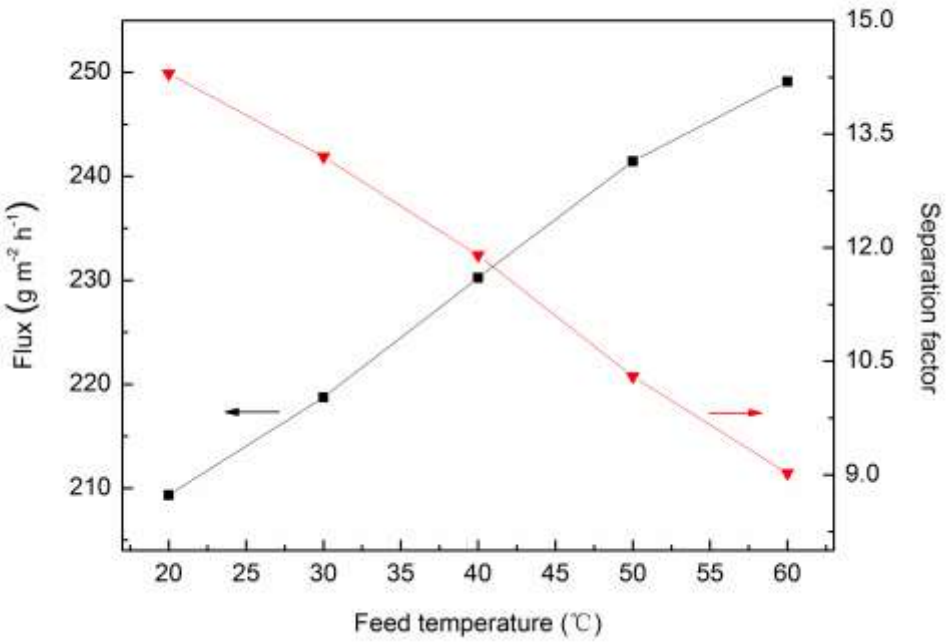


Fig. 9. Influence of feed temperature on PV performances of a composite membrane with 5 wt.% modified BCNPs

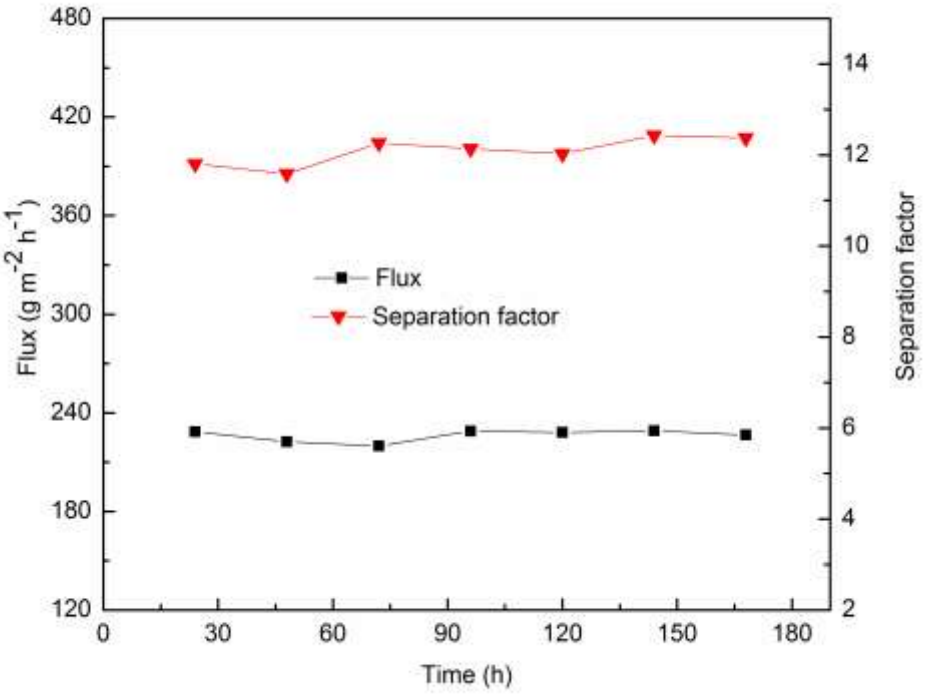


Fig. 10. The influence of test period on PV performance of composite membrane

A 168-h test was taken in the composite membrane filled with 5 wt.% BCNPs in 10 wt.% ethanol aqueous solution at 40 °C (Fig. 10). The PV performance of the composite membrane almost remained constant. For the low ethanol concentration fermentation, the PV performance of composite membranes with BCNPs was stable. This implied that the PV property of the composite membranes would not reduce, although there was an appearance of swelling of the composite membranes.

Table 1 compares pervaporation performances of the PDMS composite membranes filled with BCNPs prepared in this study with some published data on PDMS composite membranes filled with other types of fillers for the separation of ethanol from water. Compared to nano-Silicalite, Silicalite, Zerolite, fumed silica, carbon black, and BCNP-filled membranes had very promising performance.

Table 1. Influence of Different Fillers in the Composite Membranes on Ethanol Separation Performance

Fillers	Filler Content (wt %)	Ethanol Feed Conc. (wt %)	Temp. (°C)	Separation Factor	Flux ($g \cdot m^{-2} \cdot h^{-1}$)	Reference
Nano-silicalite-1	30	6	35	15.7	–	(Moermans *et. al* 2000)
Silicalite-1	60	5	22.5	16.5	51	(Moermans *et al.* 2000)
Silicalite-1	77	5	22	37	150	(Jia *et. al* 1992)
Silicalite-1	50	5	50	29.3	–	(Jia *et al.* 1992)
Silicalite-1	15	3	41	4.8	170	(Dobrak *et. al* 2010)
Fumed silica	20	5	40	7.0	–	(Tang *et. al* 2007)
USY	50	–	30	16.1	–	(Adnadjević *et. al* 1997)
ZSM-5	30	–	35	5	250	(Adnadjević *et al.* 1997)
ALPO-5	50	–	30	5.2	–	(Adnadjević *et al.* 1997)
$[Cu^{II}_2(bza)_4(pyz)]_n$	3	5	25	2.3	23	(Takamizawa *et. al* 2007)
Carbon black	4.5	13.7	20	10.1	127.32	(Shi *et. al* 2006)
Carbon black	10	6	35	9	49.8	(Vankelecom *et. al* 1997)
Carbon black	10	–	35	9	–	(Shi *et al.* 2006)
Carbon black	1.5	13.73	30	9	189	(Vankelecom *et al.* 1997)
SiO_2@Biochar	5	10	40	11.9	226	This work

CONCLUSIONS

A novel composite membrane was prepared for the removal of ethanol from water, with the separation layer made of biochar core-shell particles mixed with PDMS and the CA support layer.

1. The results illustrated that the core-shell particles homogeneously dispersed in the PDMS matrix with no obvious defects and that the separation layer adhered to the CA layer tightly.
2. The swelling of the composite membranes was improved with the increment of filler content in the ethanol/water solution.
3. The diffusivity and the solubility of ethanol increased as the modified BCNPs content increased.
4. The PV performances of the composite membranes were enhanced significantly with the addition of core-shell particles.
5. The membranes that had the best PV properties contained 5 wt.% of BCNPs. When used with a 10 wt.% ethanol/water solution at 40 °C, the membrane achieved a separation factor of 11.9 and a constant permeation flux of 227 $g \cdot m^{-2} \cdot h^{-1}$. This showed that the Biochar@SiO_2 core-shell particles were a better type of filler for filling in ethanol/water PV separation membranes.

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