Recycle of ceramic substrate of PDMS/ceramic composite membranes towards alcohol-permselective pervaporation

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\textbf{ABSTRACT}

Nowadays, membrane recycling has received increasing attention in water treatment, gas separation and pervaporation. Compared with polymeric substrates, inorganic substrates possess higher mechanical and thermal stability, which can be reused to balance the high cost. In this work, for the first time, we studied the recycle of inorganic substrate that was used for fabricating polymeric composite membranes. A facile approach was proposed to recycle ceramic substrate from PDMS/ceramic composite membranes with thermal degradation followed by ultrasonic cleaning. The thermal degradation compositions of PDMS membrane under air or nitrogen atmosphere were investigated by using TGA-IR, XRD and XPS analysis. Influence factors of the recycle approach including degradation conditions, cleaning approach and multi-recycle process were explored to optimize the transport properties of ceramic substrate and PDMS/ceramic composite membrane. The interfacial morphologies and adhesion of the PDMS membrane coated on the recycled ceramic substrate were characterized by SEM and nano-scratch measurement. The results demonstrated that PDMS composite membrane fabricated on the ceramic substrate with 10 times recycle by thermal degradation in nitrogen at 800 °C for 4 h and ultrasonic cleaning could still achieve >92% separation performance and interfacial adhesive force of the fresh PDMS/ceramic composite membrane. Specifically, the membrane exhibited stable flux of 1.2 kg/m\textsuperscript{2}h and separation factor of 8.1 for 120 h continuous pervaporation separation of 5 wt% ethanol/water at 40 °C. Additionally, ~75% energy saving relative to synthesizing fresh ceramic substrate was estimated for applying the feasible recycle approach.

1. Introduction

With the rapid development of the industrial application of membrane technology, a large amount of waste materials has been produced during the preparation and utilization of membranes. At present, most of the waste membrane materials are disposed of by stacking or landfilling. However, the industry of producing membrane materials involve high energy consumption and pollution, and the resulting ecological and environmental issues have become significant in recent years [1,2]. Therefore, membrane recycling has received increasing attention for various kinds of membrane materials.

To fabricate this kind of composite membrane, polymer solution is coated on a porous substrate to obtain a thin membrane layer that can be used for separation of organic-water or organic-organic via pervaporation [3–7]. Compared with polymeric membranes, inorganic membranes show advantages in mechanical strength and thermal stability [8–10]. Our group developed a kind of inorganic-supported polymeric composite membranes, which were mainly applied for pervaporation application [11–13]. It was demonstrated that the excessive swelling of the polymeric membrane layer under elevated temperature and/or high feed concentration can be restricted by the rigid inorganic substrate, which is favorable for enhancing the separation performance and structural stability of composite membranes [14–17]. Among them, the polydimethylsiloxane (PDMS)/ceramic composite membrane exhibited outstanding pervaporation performance for recovery of alcohols from aqueous solution and in-situ fermentation process [14,16]. Despite the potential of inorganic-supported polymeric composite membranes, they are disadvantageous in that higher cost of inorganic...
substrate compared with polymeric substrate for practical application [18,19]. Nevertheless, this limitation can be overcome by developing membrane recycling and reuse technology.

According to literature, the studies related to membrane recycling and reuse can be classified into membrane cleaning and membrane regeneration [20–22]. Fouling is recognized as a major challenge of the operated membrane process, resulting in the increase of energy consumption, production costs and the decrease of membrane lifespan [23]. Membrane cleaning and membrane regeneration are indispensable post-treatment processes for the sustainable utilization of membranes in industrial applications. Nowadays, most studies focused on physically or chemically cleaning the foulants on filtration membranes [24–26]. These membranes applied for water treatment and distillation are mainly composed of polymers, including poly (vinylidene fluoride) (PVDF), polyethersulfone (PES), polysulfone (PSf), polyamide (PA) and so on. Compared with polymeric membranes, the membrane regeneration under harsh conditions is more suitable for inorganic membranes due to the high thermal stability and chemical stability of inorganic materials. Among the inorganic membranes, the ZSM-5 zeolite membranes deactivated faster at higher test temperature due to carboneous species trapped in the zeolite pores for separation of C4 and C6 isomers system [27]. A calcination process was utilized to regenerate ZSM-5 membrane in the air at 480 °C for 8 h. The xylene isomers separation performance of used MFI zeolite membrane could be also reversed after heating the membrane under vacuum at 150 °C [28] or under O2 atmosphere at 200 °C [29]. Recently, T-type zeolite membrane was applied for bio-oil pervaporation dehydration, in which the membrane surface was repetitive fouled by the complex components in fermentation broth [30]. After calcination at 220 °C, the fouled zeolite membrane was regenerated and possessed a good reusability. For the recycle of the composite membranes, calcination method was also applied to remove the organic polymer layers on the metal support [31]. Different from calcination and thermal degradation, Vane et al. recovered the separation performance of ZSM-5 filled PDMS mixed-matrix membrane whose zeolite pores were adsorbed and blocked by organic acids, esters and other products in fermentation broth by soaking the membrane in n-butanol [32].

Current studies have concentrated on the removal of membrane fouling through physical or chemical approaches to restore membrane properties, reutilize and prolong the membrane lifespan. However, very few attentions were paid to reuse the substrate of a composite membrane, which is actually possible and meaningful to reduce the membrane cost especially for highly stable inorganic substrate. Thermal degradation is related to the chemical bond energy of the polymer. The lower the chemical bond energy, the more prone to degradation. Hence, when the ambient temperature exceeds the complete decomposition temperature of the polymer, the polymeric membrane layer could be decomposed by thermal degradation process. In this work, we aim to explore the feasibility of recycling inorganic substrate from spent inorganic-supported polymeric composite membrane. On the one hand, the recycle of substrate from spent composite membrane faces more challenges in completely removing the coated materials on the surface and penetrated into the pores of substrate. On the other hand, compared with polymeric substrate, inorganic substrate withstanding very high temperature can maintain its chemical and structural properties during the degradation process of polymeric membrane layer [33]. More importantly, it is critical to preserve the intrinsic pore structure, surface properties and mechanical strength of the substrate during the recycle process. The effects of recycled substrate on the formation, transport properties and stability of the composite membrane should be systematically studied.

Here, we proposed a facile approach combing thermal degradation with ultrasonic cleaning to recycle the ceramic substrate from PDMS/ceramic composite membrane. As shown in Fig.1, PDMS solution is coated on the surface of fresh ceramic substrate to form the fresh PDMS/ceramic composite membrane. To recycle the ceramic substrate, the composite membrane is calcined in air or nitrogen atmosphere to degrade the PDMS coating. After calcination, the degradation residues of PDMS mainly including silica particles are removed from surface and pores of the ceramic substrate by water rising or ultrasonic cleaning. The
Recycled ceramic substrate is employed to fabricate new batch of PDMS composite membrane that is applied for pervaporation separation of ethanol/water mixtures to evaluate the performance of the recycle approach. The degradation mechanism was investigated by characterizing the chemical structures of effusions and residues, and the recycle process was optimized by studying the effects of calcination conditions (atmosphere, temperature and time), cleaning method and recycling number on the transport resistance of the ceramic substrate as well as morphology, separation performance and stability of the PDMS/ceramic composite membrane. To further evaluate the feasibility of the proposed approach, we explored the recycling of ceramic substrate from spent PDMS/ceramic composite membranes applied in real-world distillery plants.

Fig. 2. (a-b) TG/DTG curves; (c-d) 3D TGA-FTIR spectra and (e-f) IR spectra of PDMS dense film thermally degraded under air or N$_2$ atmosphere with a heating rate of 5 °C/min from room temperature to 800 °C.
2. Experimental

2.1. Materials

Hydroxyl-terminated polydimethylsiloxane (PDMS), Shanghai Resin Factory, China. Tetraethyl orthosilicate (TEOS, 98%), dibutyltin dilaurate (DBTOL, 95%), n-butanol (AR) and n-heptane (AR), Shanghai Lingfeng Chemical Reagent Co., Ltd, China. Tubular ceramic (ZrO$_2$/Al$_2$O$_3$) substrates were homemade with average pore size of 200 nm and o.d./i.d. of 12/8 mm. Air and nitrogen with high purity of 99.999%, Nanjing Special Gas Factory Co., Ltd.

2.2. Preparation of PDMS/ceramic composite membrane

The PDMS/ceramic composite membrane was prepared by dip-coating the PDMS solution on the outer surface of fresh tubular...
ceramic substrate (S0), which was recorded as the fresh PDMS membrane (M0). The detailed membrane fabrication procedure was described in our previous work [34]. Briefly, PDMS prepolymer was dissolved in n-heptane and crosslinker TEOS and catalyst DBTOL were added to form the PDMS coating solution (catalyst/crosslinker/polymer/solvent = 1:10:100:1000 in weight ratio). Following the same recipe and procedure, the recycled ceramic substrate (experimental about the recycle is described in the next section) was dip-coated with PDMS solution to fabricate new batch of PDMS/ceramic composite membrane, which is recorded as Mn (M1-M10) according to the recycle time (n) of the ceramic substrate Sn (S1–S10).

Fig. 6. Effect of degradation time on (a) water permeance of recycled ceramic substrate from calcination in air or N₂ atmosphere at 800 °C and (b) separation performance of PDMS membrane coated on the recycled ceramic substrate.

Fig. 7. Effect of water rising on (a) water permeance of recycled ceramic substrate from calcination in air or N₂ atmosphere at 800 °C for 4 h and (b) separation performance of PDMS membrane coated on the recycled ceramic substrate. S0: fresh substrate, S1: 1st round recycled substrate, S2: 2nd round recycled substrate; M0: PDMS membrane coated on fresh substrate, M1: PDMS membrane coated on 1st round recycled substrate, M2: PDMS membrane coated on 2nd round recycled substrate.

Fig. 8. Effect of ultrasonic cleaning on (a) water permeance of recycled ceramic substrate from calcination in air or N₂ atmosphere at 800 °C for 4 h and (b) separation performance of PDMS membrane coated on the recycled ceramic substrate. S0: fresh substrate, S1: 1st round recycled substrate, S2: 2nd round recycled substrate, S3: 3rd round recycled substrate; M0: PDMS membrane coated on fresh substrate, M1: PDMS membrane coated on 1st round recycled substrate, M2: PDMS membrane coated on 2nd round recycled substrate, M3: PDMS membrane coated on 3rd round recycled substrate.
Fig. 9. SEM cross-section (left), surface (middle) with EDX mapping of Si element (right) images of (a) fresh ceramic substrate; (b) recycled ceramic substrate after thermal degradation under air atmosphere; (c) recycled ceramic substrate after thermal degradation under air atmosphere and then treated by water rising; (d) recycled ceramic substrate after thermal degradation under air atmosphere and then treated by ultrasonic cleaning; (e) recycled ceramic substrate after thermal degradation under N₂ atmosphere; (f) recycled ceramic substrate after thermal degradation under N₂ atmosphere and then treated by water rising; (g) recycled ceramic substrate after thermal degradation under N₂ atmosphere and then treated by ultrasonic cleaning.
2.3. Recycle of ceramic substrate

The PDMS/ceramic composite membrane was calcined in a muffle furnace (700–900 °C) under an atmosphere of high-purity air or nitrogen with a flow rate of 50 mL/min. The heating rate and cooling rate were 2 °C/min, and the holding time varied from 1 h to 4 h. The calcined composite membrane was cleaned by deionized water washing or ultrasonication for 30 min to remove the residue of degraded PDMS membrane, and dried in an oven at 100 °C overnight to obtain the recycled ceramic substrate. The fresh ceramic substrate that was not coated with PDMS was recorded as fresh substrate (S0). After being coated with PDMS layer to form PDMS/ceramic composite membrane, and then calcined, cleaned and dried, the obtained ceramic substrate was recorded as S1. In the next cycle, the recycled ceramic substrate (S1) was coated with PDMS layer and then calcined, cleaned and dried to obtain a new batch of ceramic substrate that was recorded as S2. By analogy, the ceramic substrate recycled by n times was recorded as Sn.

2.4. Characterizations

Thermal degradation of PDMS dense films was characterized by online TGA-FTIR technique coupling Thermogravimetric Analysis (TGA 8000) and Fourier-transform Infrared Spectroscopy (PerkinElmer Inc.). The released volatiles during degradation reaction were in-situ analyzed. These membrane samples were degraded under air or nitrogen with a flow rate of 35 mL/min at temperature ranging from room temperature to 800 °C with a rate of 5 °C/min 32 scans were accumulated with a resolution of 4 cm⁻¹ for each spectrum. The membrane morphologies were imaged by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi), and element mapping was carried out by energy dispersive X-ray spectrometer (EDX). The chemical structure of the recycled ceramic substrate was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) and IR recorded by Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Nicolet) in the range of 4000-400 cm⁻¹. The residues of PDMS dense film degraded under air or nitrogen atmosphere were detected by X-ray diffractometer (XRD, D8-advance, Bruker) in the range of 10–60 ° with a Cu Kα radiation. Nano-scratch measurement was conducted to test interfacial adhesion of PDMS/ceramic composite membranes by Nano-Test (NanoTest™, Micro Materials) system.

2.5. Pure water permeation test

Through the change of pure water permeance, the difference in transport resistance between the fresh and recycled ceramic substrate can be compared. Cross-flow filtration device was applied for testing the water permeance of ceramic substrate at 20 °C and 2.0 bar. The pure water permeance was calculated as follows:

\[ P = \frac{M}{\rho \times \Delta p \times A \times t} \]  

where \( P \) is pure water permeance, \( M \) is the mass of permeate water, \( \rho \) is the density of water at a certain temperature, \( \Delta p \) is the transmembrane pressure difference, \( A \) is the effective membrane area, \( m^2 \); \( t \) is the effective time, h.

2.6. Pervaporation measurement

The details of the pervaporation experiment were described in our previous work [35]. Briefly, 5 wt% ethanol/water mixtures were used as the feed solution, which was fed into a membrane module (effective membrane area: 18.84 cm²) with a flow rate of 15 L/h at 40 °C. The membrane permeate under vacuum of 200 Pa was collected in liquid nitrogen traps. The compositions in the feed and permeate side were analyzed by gas chromatography (GC-2014, Shimadzu, Japan). The evaluation of the membrane separation performance is based on total flux \( (J, g/m^2h) \) and separation factor \((\beta)\), which are obtained from Equations (2) and (3), respectively:

\[ J = \frac{M}{At} \]  
\[ \beta = \frac{y_i / x_i}{y_f / x_f} \]

where \( M \) is the weight of the permeate side product, \( A \) is the effective
membrane area, and \( t \) is the permeation time; \( y \) and \( x \) are the weight percentages of component in permeate and feed side, respectively. \( i \) and \( j \) is the symbol of the component \( i \) and \( j \) in the separation system.

3. Results and discussion

3.1. Characterizations of PDMS membrane degradation

The thermal degradation behavior of PDMS dense film was studied by TGA. Air and \( N_2 \) were selected as the thermal treatment atmosphere due to the easily available and inexpensive source. Under air atmosphere (Fig. 2a), an initial gradual mass loss was only 8.2% before 386.8 °C. The weight loss of 33.5% was occurred between 386.8 and 455.7 °C, corresponding to the oxidation of methyl groups on PDMS chains [36]. The PDMS backbone was significantly degraded between 455.7 and 700.3 °C with weight loss of 43.9%, which is attributed the high energy of Si–O bonds in the cross-linked PDMS networks [37]. Additionally, under \( N_2 \) atmosphere (Fig. 2b), the PDMS membrane started to decompose at 330 °C, leading to a weight loss of 20.7% from 30 to 383.4 °C. The weight loss is above 73% between 383.4 and 568.5 °C owing to the occurrence of a large amount of cyclic oligomers [38]. Compared with air atmosphere, the residue content of PDMS degraded under \( N_2 \) was much lower (0.4% vs 14.5%).

To further understand the degradation mechanism of PDMS membrane, a real-time TGA/FT-IR was employed to in-situ analyze the composition of effusion during the thermal degradation under air or \( N_2 \) atmosphere. As shown in Fig. 2c–f, the IR absorbance corresponding to the vibrational modes of different chemical bonds and functional groups was on-line collected from gas products in the furnace of TGA at each temperature interval versus the wavenumber [39]. Characteristic peaks of Si–O–Si and Si–CH\(_3\) were found in both air and \( N_2 \) atmosphere, corresponding to production of liner or cyclic siloxane [40,41]. Additionally, for PDMS degraded under air atmosphere (Fig. 2c), characteristic peaks of H\(_2\)O (3750-3500 cm\(^{-1}\)) and CO\(_2\) (2400-2250 cm\(^{-1}\)) were found when the temperature was increased to 421.3 °C. They are attributed to thermo-oxidation process of methyl groups of PDMS [42].

Furthermore, the residues of thermally degraded PDMS under air or \( N_2 \) atmosphere were analyzed by XRD and IR. As shown in Fig. 3a, a broad peak at around 12.2° was observed in XRD pattern of PDMS dense film, corresponding to the characteristic peak of crosslinked PDMS network. After thermal degradation, the residues of PDMS are mainly consisted of amorphous SiO\(_2\), as indicated by the consistent XRD peak at 23.4 °C for SiO\(_2\) powder. Generally, the strong broad hump of amorphous SiO\(_2\) is detected at ~23° in XRD pattern [43,44]. It was found that the characteristic broad peak of amorphous SiO\(_2\) was related with the heating temperature [45,46]. With an increase of heating temperature, this peak was shifted to lower 2θ values. The XRD results of our samples are consistent with the above reports. The IR spectra in Fig. 3b indicate the distinct change of chemical structure of PDMS membrane before and after thermal degradation [47]. The characteristic peaks attributed to SiO\(_2\) (1103 cm\(^{-1}\), Si–O–Si; 956 cm\(^{-1}\), Si–OH; 794 cm\(^{-1}\), Si–O) are both found in the IR spectra of residues obtained in the air and \( N_2 \) atmosphere. It further confirms that the final product of thermally degraded PDMS is SiO\(_2\), despite of different weight percent obtained in the air and \( N_2 \) atmosphere.

According to the above results, thermal degradation reaction of PDMS membrane was speculated in Fig. 4. When being calcined in muffle furnace under air atmosphere, the PDMS membrane mainly undergoes thermal oxidation reaction. Linear siloxane substrates are released and meanwhile SiO\(_2\) is formed. As the reaction continues, the fluffy aggregate SiO\(_2\) nanoparticles are layered on the surface of ceramic substrate like snowflakes [36,47]. By contrast, under \( N_2 \) atmosphere, the PDMS membrane mainly undergoes hydroxyl-terminated unbuttoning degradation reaction to generate volatile cyclic siloxane (e.g., boiling point of hexamethylocyclotrisiloxane: 134 °C [48–50]), which can be easily exited into the gas at elevated temperature. As a result, a very limited amount of SiO\(_2\) (0.4 wt%) was left as residues of the \( N_2 \) atmosphere.

![Fig. 12. Interfacial adhesion test by applying nano-scratch technique on PDMS/ceramic composite membrane using fresh ceramic substrate (M0) or recycled ceramic substrate from each cycle (M1-M10): (a) interfacial adhesion between PDMS membrane and ceramic substrate, (b) nano-scratch profile and (c) SEM image of surface nano-scratch morphology.](image-url)
Fig. 13. Photo and SEM images of cross-section and surface of PDMS/ceramic composite membrane using fresh ceramic substrate (M0) or recycled ceramic substrate from each cycle (M1-M10).
3.2. Optimization of recycle approach

3.2.1. Effect of degradation conditions

To optimize the recycle conditions, the PDMS/ceramic composite membranes were calcined at various temperatures and time under air or N₂ atmosphere. We studied the effect of degradation conditions on the transport resistance (pure water permeance) of ceramic substrate and the pervaporation performance (total flux and separation factor) of PDMS/ceramic composite membrane. As shown in Fig. 5, under N₂ atmosphere, the water permeance of the recycled ceramic substrate and total flux of the prepared PDMS/ceramic composite membrane tend to increase and then keep stable by increasing the degradation temperature from 700 °C to 900 °C. The main reason is the degradation temperature of PDMS layer in the N₂ is higher than 700 °C (Fig. 2b). Considering the energy consumption, degradation temperature of 800 °C is more favorable for recycling the ceramic substrate in the N₂ atmosphere calcination. In comparison, the water permeance of the recycled ceramic substrate and separation performance of the PDMS composite membrane is constant by varying the degradation temperature from 700 °C to 900 °C in the air. Because the final degradation temperature of PDMS dense film in the air is lower than 700 °C, the PDMS membrane layer can be completely decomposed by varying the temperature from 700 °C to 900 °C (Fig. 2a). Furthermore, compared with air, the N₂ atmosphere calcination afforded lower transport resistance to the recycled ceramic substrate as indicated by the higher water permeance, and thus higher total flux to the as prepared PDMS/ceramic composite membrane. This can be attributed to the much lower content of residues (SiO₂) after degradation of PDMS dense film. Apparently, compared with air atmosphere, this degradation feature under N₂ atmosphere is more beneficial for completely removing the PDMS from the ceramic substrate.

Fig. 14. Separation performance of PDMS membrane coated on the 10th round recycled substrate (M10) during continuous pervaporation process for 5 wt% ethanol-water mixtures at 40 °C.

Fig. 15. (a) Schematic of recycling ceramic substrate from spent PDMS/ceramic composite membrane; (b) photos of spent PDMS/ceramic composite membrane and PDMS membrane coated on the recycled ceramic substrate (N₂ atmosphere, 800 °C, 4 h) with a length of 80 cm; (b) Separation performance of PDMS composite membranes (M0 and M1) for 5 wt% ethanol-water mixtures at 40 °C. M0: PDMS membrane coated on the fresh ceramic substrate; Spent M0: the membrane taken out of the spent pervaporation membrane module; M1: PDMS membrane coated on 1st round recycled substrate.
calcination of PDMS under N₂ than air (Fig. 2a and b).

By setting the optimal degradation temperature as 800 °C, the degradation time was varied from 1 to 4 h to recycle the ceramic substrate under air or N₂ atmosphere. As shown in Fig. 6, with the increase of degradation time, both the water permeance of the recycled ceramic substrate and the total flux of the corresponding PDMS/ceramic composite membrane were gradually enhanced. It suggests that sufficient time (4 h in the studied case) was required to fully degrade the PDMS coated on the surface and in the pores of ceramic substrate. It is speculated that the required time would also be dependent on the temperature, flow rate and feed mode of the atmosphere, which deserves further studies in future work. Overall, the ethanol/water separation factor of all the PDMS membrane coated on the recycled ceramic substrate is kept at around 7.7, which is very close to that of the fresh PDMS/ceramic composite membrane (8.1). This result highlights the feasibility of fabricating a defect-free PDMS membrane layer on the recycled ceramic substrate derived from thermal degradation of PDMS/ceramic composite membrane.

3.2.2. Effect of cleaning method

As indicated by the TGA, IR and XRD characterizations (Figs. 2 and 3), the main residues of thermal degradation of PDMS dense film in air or N₂ atmosphere are SiO₂. After thermal degradation of PDMS/ceramic composite membrane, it was expected that SiO₂ would be left in the ceramic substrate, leading to the increase of transport resistance. Firstly, we tried water rising method to remove the SiO₂ from the ceramic substrate. The results for two times of thermal degradation (at optimal condition: 800 °C, 4 h) water rising recycle process are shown in Fig. 7.

Compared with the fresh substrate (S0), the water permeance of the 1st round recycled ceramic substrate (S1) from air degradation was decreased by 25.8%. As a result, compared with the fresh PDMS/ceramic composite membrane (M0), the total flux of the PDMS membrane using 1st round recycled ceramic substrate (M1) was decreased by 32.7%. By contrast, there is only minor declines in water permeance of the 1st round recycled ceramic substrate (6.45%) and total flux of the corresponding PDMS composite membrane (8.7%) by using N₂ degradation. This is because the PDMS homogenous membranes underwent a two-stage thermal oxidation reaction in the air, thereby the final mass weight of the residue is much higher than that of the degraded PDMS membrane in the N₂. The above comparison in 1st round recycle again illustrates that N₂ atmosphere is more favorable for degrading the PDMS membrane coated on the ceramic substrate.

In 2nd round recycle, however, significant decreases (44.0-56.7%) were observed for water performance of the ceramic substrate (S2) and total flux of the PDMS composite membrane (M2), despite of the degradation atmosphere. Meanwhile, as increasing the recycled times, a gradual decline of separation factor was found in the PDMS membrane coated on the recycled ceramic substrate. It was inferred that the water rising could not fully remove the residual (SiO₂ particles) accumulated in the nanopores of the ceramic substrate. The hydrophilic SiO₂ particles would increase the transport resistance and decrease the hydrophobicity of the composite membrane. To fully remove the residual in ceramic substrate, we introduced water-bath ultrasonication to clean the substrate after the thermal degradation process. As can be seen in Fig. 8, the gradual declines in water permeance of the substrate and separation performance of the membrane were effectively inhibited by replacing the water rising with the ultrasonic cleaning, especially for the N₂ degraded samples. This result indicates that integrating the low-content residue of thermal degradation in N₂ with efficient residue removal of ultrasonic cleaning could almost fully recover the performance of the ceramic substrate and the prepared PDMS/ceramic composite membrane. The performance of the N₂ thermal degradation/ultrasonic cleaning approach will be further examined in the next section.

The influence of recycle conditions on the substrate morphology is illustrated in Fig. 9. The residual SiO₂ particles on the surface of ceramic substrates were observed after the thermal decomposed of PDMS
membrane layer in the air or N₂ atmosphere. For the air thermal degradation, a large amount of residues was covered on the surface of ceramic substrate even after water rising or ultrasonic cleaning. Some of the substrate pores were filled with the residues, leading to the additional transport resistance and lowered permeation rate of the substrate and PDMS composite membrane. Compared with air atmosphere, N₂ thermal degradation provided the substrate less residues that can be nearly completely removed using the subsequent ultrasonic cleaning. Indeed, the ceramic substrate recycled by N₂ thermal degradation/ultrasonic cleaning approach exhibited very similar pore structures and EDX Si element distribution on the surface.

3.3. Membrane performance of multi-recycle process

3.3.1. Membrane separation performance

In order to further explore the feasibility of the substrate recycle approach (N₂ thermal degradation/ultrasonic cleaning), we carried out 10 cycles of the recycle process. Namely, repeating “recycling ceramic substrate from PDMS/ceramic composite membrane and then coating PDMS on the recycled ceramic substrate to form a new batch of PDMS/ceramic composite membrane” on a fresh ceramic substrate by 10 times. As shown in Fig. 10, compared with the fresh ceramic substrate (S0), water permeance of the recycled ceramic substrate from each cycle (S1–S10) is all above ~2000 L/m²/h/bar, showing a recovery rate of more than 90%. Furthermore, the PDMS composite membrane (M1–M10) fabricated by using the recycled ceramic substrate from each cycle was maintained separation performance as high as (~92.6% in terms of total flux) the fresh PDMS/ceramic composite membrane (M0). These results demonstrated that the proposed recycle approach is effective and controllable, realizing almost fully recovery of the separation performance of fresh PDMS/ceramic composite membrane even after 10 times of recycle.

Furthermore, X-ray photoelectron spectroscopy (XPS) was utilized to analyze the chemical composition of the recycled ceramic substrate from each cycle. The content of Si element in the fresh ceramic substrate (S0) and the recycled ceramic substrates from N₂ thermal degradation/ultrasonic cleaning (S1–S10) are summarized in Fig. 11. The low Si content (%) in the fresh ceramic substrate is due to the impurity of the Al₂O₃ and ZrO₂ raw materials as well as the background of the XPS analysis. Clearly, this low Si content was kept constant in the recycled ceramic substrate from each cycle. This result further confirms the excellent efficiency of the proposed recycle approach for removing the PDMS coating from the ceramic substrate.

3.3.2. Membrane stability

The interfacial adhesion between the PDMS membrane and ceramic substrate is another critical parameter to evaluate the feasibility of using recycled ceramic substrate to fabricate PDMS/ceramic composite membrane. We employed nano-scratch technique to probe the interfacial behavior of the PDMS membrane fabricated on the recycled ceramic substrate from each cycle. According to the on-load depth and residue depth curves, the interfacial adhesion force can be determined [51]. As shown in Fig. 12a, the interfacial adhesion of PDMS composite membrane using the recycled ceramic substrate from each cycle is nearly the same to the fresh PDMS/ceramic composite membrane (29.2 mN). Fig. 12b and c displays the nano-scratch behavior of the PDMS membrane on the surface of ceramic substrate. The cracking of the PDMS/ceramic interface is unclear owing to the occurrence of elastic recovery on the PDMS layer.

In addition, we characterized the morphology of PDMS composite membrane (M1–M10) fabricated on the recycled ceramic substrate from each cycle (S1–S10). As shown in Fig. 13, each PDMS membrane layer is homogenous and defect-free, showing identical thickness (~6 μm) and without interfacial defect with the ceramic substrate even after 10 times of recycle.

The structural stability of the PDMS composite membrane fabricated on the recycled ceramic substrate was further verified in continuous pervaporation separation process during over 120 h. As shown in Fig. 14, the PDMS/ceramic composite membrane using the 10th round recycled substrate (M10) still exhibited stable and high separation performance: total flux of ~1200 g/m²·h and separation factor of ~8.0 for 5 wt% ethanol/water at 40 °C. The ceramic substrate recycled by N₂ thermal degradation/ultrasonic cleaning approach, having fully recovered pore structures and surface properties, contributed to the nearly 100% preserved structural stability of PDMS/ceramic composite membrane.

3.3.3. Recycle utilization

We further studied the recycle of ceramic substrate from spent PDMS/ceramic composite membranes (length of 80 cm) applied in real-world distillery plants. Before calcination under N₂ atmosphere at 800 °C for 4 h, we simply wiped the foulants on the surface of the used membrane (Fig. 15a and b). These foulants remarkably reduced separation performance of PDMS/ceramic composite membrane, especially the total flux decreasing from 1200 to 572 g/m²·h. Through N₂ thermal degradation and ultrasonic cleaning, PDMS membrane was coated on the recycled ceramic substrate with 80 cm in length. As shown in Fig. 15c, separation performance of PDMS membrane using 1st round recycled ceramic substrate (M1) is ~1200 g/m²·h of total flux and 7.8 of separation factor, which is as high as the PDMS membrane coated on the fresh ceramic substrate (M0). This result confirms that the potential of the proposed thermal degradation/ultrasonic cleaning approach in practical application.

3.3.4. Energy saving estimation

The ceramic substrate used in this work is composed of α-Al₂O₃ layer and ZrO₂ layer, as shown in Fig. 16a. To synthesize a fresh ceramic substrate, the α-Al₂O₃ layer is sintered at 1300 °C for 2 h with heating and cooling rate of 2 °C/min (Fig. 16b); then the ZrO₂ layer is coated on the α-Al₂O₃ layer and sintered with heating rate of 2 °C/min to 800 °C and heating rate of 1 °C/min to 1200 °C and holding at 1200 °C for 2 h followed with a cooling rate of 2 °C/min (Fig. 16c). In comparison, to obtain a recycled ceramic substrate, the membrane is degraded at 800 °C for 4 h with heating and cooling rate of 2 °C/min. According to the empirical formula for power of muffle furnace [52], the energy consumption of sintering the ceramic substrate is calculated as follows:

$$P = C \times T \times F^{0.9} \times t^{1.55}$$

$$W = P \Delta t$$

where $P$ is electric power (W); $T$ is the time for the empty furnace to heat up to the working temperature (°C); $F$ is the effective area of the inner wall of the furnace, including the sum of all areas of the furnace bottom, side walls and furnace roof (m²); $t$ is the working temperature of the furnace (°C); $C$ is factor, the value of 30–35 for furnaces with large heat dissipation, and the value of 20–25 for furnaces with small heat dissipation. $W$ is electric work (J). $\Delta t$ is working time (s). Compared with sintering temperature procedure of a fresh ceramic substrate, the energy consumption of the recycled ceramic substrate is saved by ~75% via degradation of polymer coating on the ceramic substrate from each recycle.

4. Conclusions

In this work, we proposed a thermal degradation/ultrasonic cleaning approach to recycle ceramic substrate from PDMS/ceramic composite membrane. With the optimal recycle conditions (N₂ thermal degradation at 800 °C for 4 h followed by ultrasonic cleaning), the transport resistance of the ceramic substrate, indicated by pure water permeance, are recovered by 90.2% compared with the fresh one. The PDMS composite membrane fabricated on the recycled ceramic substrate
maintained reproducible pervaporation separation performance and interfacial adhesion as high as those of fresh PDMS/ceramic composite membrane during 10 times of recycle processes. The PDMS membrane using 10th round recycled ceramic substrate exhibited stable flux of 1.2 kg/m²h and separation factor of 8.1 for 5 wt% ethanol/water mixtures during 120 h continuous operation at 40 °C. The feasible and energy efficient recycle approach is promising to develop cost-effective and high-performing ceramic supported polymeric composite membrane towards practical application.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


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Y. Wang, Z. Zhang, P. Zhao, Z. Yuan, Design and power analysis of electric furnace heating system for diamond products, Ind. Furn. 38 (2016) 40–43.