Cement/PVDF hollow-fiber hybrid basement membrane: Preparation, microstructure, and separation application

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(Received March 20, 2022, Revised September 12, 2022, Accepted November 10, 2022)

In this study, cement/PVDF hollow-fiber hybrid membranes were prepared via a mixed process of diffusion-Abstract. induced phase separation and hydration. The presence of X-ray diffraction peaks of Ca(OH)2, an AFt phase, an AFm phase, and C-S-H phase confirmed the hydration reaction. Good hydrophilicity was obtained. The cross-sectional and surface morphologies of the hybrid membranes showed that an asymmetric pore structure was formed. Hydration products comprising parallel plates of Ca(OH)₂, fibrous ettringite AFt, and granulated particles AFm were obtained gradually. For the hybrid membranes cured for different time, the pore-size distribution was similar but the porosity decreased because of blocking of the hydration products. In addition, the water flux decreased with hydration time, and carbon retention was 90% after 5 h of rejection treatment. Almost all the Zn^{2+} ions were adsorbed by the hybrid membrane. The above results proved that the obtained membrane could be alternative as basement membrane for separation application.

adsorption; asymmetric pore structure; basement membrane; cement/PVDF hybrid membrane; rejection Keywords:

1. Introduction

Membrane separation methods include ultrafiltration, nanofiltration, microfiltration, reverse osmosis, as discussed by Drioli and Giorno (2010). There are many advantages to the use of membrane technology. For example, membrane separation is just a physical process that does not require the addition of chemicals. Compared with other treatment methods, it requires less energy, and thus reduces the operating cost. Membranes are also easy to manage and represent a simple process. Membrane separation is regarded as one of the most efficient processes. Owing to these excellent advantages, membrane technology is widely used in industrial separation field. Clay adsorptive microfiltration membranes were synthesized by Fatemeh et al. (2019) and used chromium removal from high polluted water. Ang et al. (2020) introduced application of low dimensional carbon membrane in gas separation. Liu et al. (2018) discussed pervaporation separation of aromatic/ alophatic hydrocarbon mixtures in chemical industry. Superhydrophilic and underwater superoleophobic membrane was prepared via 3D printing technology and was used in oil/water separation by Li et al. (2020).

Membranes can be divided into organic, inorganic, and organic/inorganic hybrid membranes according to Buonomenna and Golemme (2012). Although organic membranes are being produced in various modes, and large quantities of organic membranes are used in different industrial fields, they are known to be less resistant under certain acute conditions. For example, organic solvents in

wastewater may dissolve the polymer membrane, and high temperatures may destroy the organic membrane. High or low pH may corrode the organic membrane and damage the pore structure. However, inorganic membranes can be applied widely. Because they are stable in chemical, thermal, and other corrosive conditions, inorganic membranes can be applied in harsh environments with high or low pH values or high temperatures. For example, Chen et al. (2020) fabricated Ce0.8Sm0.2O2-8-carbonate hollow fiber membranes and separated CO₂ at medium-high temperature. MFI-Zeolite-coated ceramic tubular membranes were used in solution with high acid or alkali concentration, as described by Govindan et al. (2019). Li et al. (2019) fabricated GO-TiO₂ modified PVDF hollow fiber membrane and conducted the filtration experiments on humic acid. The interception rate of the modified membrane increased by 12% approximately.

Inorganic/organic hybrid membranes are being considered promising separation materials. The separation layer is thin and reduces the resistance of the feed solution while the basement membrane with macropores provides large flux. Many inorganic membranes are used as basement membranes. For example, α -Al₂O₃ substrates are common basement membranes that are usually coated with a y-Al₂O₃ sol. Kubo et al. (2020) used a commercially available α -Al₂O₃ tubular support as a basement membrane. The mean pore diameter of the core layer was 700 nm, whereas that of the outer surface layer was 150 nm. Tubular alumina supports with an open porosity of approximately 40% and an average pore size of 2 µm had also been used to prepare microfiltration membranes, as reported by Qin et al. (2015). Chang et al. (2010) coated nano-sized Al₂O₃ on microfiltration membrane. The coating decreased the mean pore size and increased the pure water flux. Bindes et al.

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(2020) extracted green tea using asymmetric alumina hollow fiber membrane and obtained high turbidity reduction. He et al. (2011) discussed the protein interaction behavior with modified Al₂O₃ membrane using bovine serum albumin as model protein. Ortega-lugo et al. (2020) used mixed-conducting ceramic-carbonate membrane to separate CO₂/O₂ and obtained high permeation flux. α -Al₂O₃ hollow fiber microfiltration membrane was modified by Fu et al. (2018) and membrane exhibited high retention rate for multivalent ions and low retention rate for monovalent ions, respectively. Bukhari et al. (2018) prepared oxidation-bonded SiC membrane for microfiltration. Das et al. (2021) prepared mullite bonded porous SiC ceramic membrane and studied its permeability and removal of turbidity. Li et al. (2019) coated ZrO₂ sol on SiC substrate membrane to enhance the chemical corrosion resistance. Pd and Pd alloy membranes are usually used to enhance gas permeability, as reported by Liu et al. (2020). A glass fiber membrane was chosen by Siyal et al. (2018), who coated it with fluorographite particles to enhance the evaluated amphiphobicity. The fabrication of inorganic membranes requires complex procedures including powder preparation, shape formation, drying, and calcination. The complex process is difficult to reproduce on a large scale and the Cost Per Unit is high. Calcination alone usually takes a long time and consumes significant amounts of energy.

Cement is known to be different from ceramic, glass, and other inorganic materials. The strength of cement developed as a result of hydration reactions at room temperature in a few hours as reported by Aïtcin and Flatt (2015), whereas Al₂O₃, SiC, or glass must be calcined at temperatures above 1000 °C to obtain high strength. Furthermore, cement-based materials are composed of hierarchical pores with a wide size range. According to Hewlett and Liska (2017), the macropores have widths of several micrometers, and some gel pores exist between hydration products with widths of approximately 1-10 nm. The various pore sizes could provide cement adsorption and rejection abilities for pollutants. Zhang et al. (2014) prepared microporous cementitious slices with a thickness of at least 5 mm. Shafie et al. (2012) prepared Zeolite/ cement composite membranes with thickness of 1.8-2.2 mm via a mixed procedure of grinding, dry pressing, and curing. Wang et al. (2022) fabricated a Al₂O₃/CaAl₁₂O₁₉ membrane using calcium aluminate cement as raw materials. The obtained membrane featured a porous structure and showed great gas permeability. Abdullayev et al. (2020) studied cement-based membrane supports from ultrafine Portland cement using freeze- casting route. The water flux in the range between 79 and 180 L/($h \cdot m^2$) was obtained.

Thin, flat inorganic membranes generally have larger wastewater permeation rates. Zhang *et al.* (2014) prepared porous flat glass membrane with the thickness of 200 μ m. However, the thin membrane was so brittle that separation performance could not be tested. To address this issue, thick flat membrane was prepared in order to obtain mechanical strength. Flat membranes with the thickness of 20 mm were fabricated, as reported by Xu *et al.* (2019). Ge *et al.* (2015) prepared inorganic membrane with a diameter of 40 mm

and height of 10 mm. Hollow fiber membrane with high surface area/volume ratios has also been proposed. The compactness of a membrane module made from hollow fiber membranes could exceed that of other membrane systems. Compared to thick, flat membranes, these hollowfiber membranes are several hundred micrometers thick. Because the operating pressure is usually below 1 MPa, the thin membrane wall could still avoid rupture. The unique pore structure and excellent advantages of cement hollow-fiber membranes make them applicable as substrates for composite membranes.

The objective of this study was to take advantage of the good properties of cement/PVDF hollow-fiber hybrid membranes, including low cost, easy preparation, and the lack of a need for calcination. Hybrid membranes were prepared using a simple combined procedure of diffusion-induced phase separation and hydration. X-ray diffraction was used to analyze the phase composition of hybrid membranes cured for different hydration times. The hydrophilicity of the hybrid membrane was studied by measuring the contact angle. The cross-sectional and surface morphologies of the hybrid membranes after hydration were observed. The pore size and porosity of the hybrid membranes were also tested. Experiments were also carried out to evaluate the water flux, carbon rejection, and Zn^{2+} ion adsorption.

2. Experimental procedure

2.1 Materials

A commercial 52.5R Portland cement was chosen as the raw material because it has been widely used in industry. The cement was sieved through a 400-mesh screen, and cement powders with a certain particle size were obtained. Poly(vinylidene fluoride) (PVDF, W#1300; Kureha Chemical Industry Co., Ltd., Tokyo, Japan) was used as the binder. N, N-Dimethylacetamide (DMAc, Reagent-grade; Tianjin Fuchen Chemical Reagent Plant, Tianjin, China) was used as the solvent to dissolve the PVDF binder. Deionized water was used during the procedure. The carbon ink (S636) was purchased from Deli group and diluted in the water to obtain carbon black solution with a certain concentration. Zinc chloride (ZnCl₂, analytical grade) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. A ZnCl₂ aqueous solution with a concentration of 30 mg/L was prepared in advance.

2.2 Preparation of cement/PVDF hollow-fiber hybrid membrane

A well-known diffusion-induced phase separation procedure was used to prepare the cement/PVDF hollowfiber hybrid membrane. The fabrication of the cement/ PVDF hollow-fiber hybrid membrane was like that of a glass hollow-fiber membrane previously prepared by Zhang *et al.* (2022). According to our former study from Zhang *et al.* (2019), the particle size of cement was important, and it had effect on dosage of cement and viscosity of casting

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Parameters	Values							
Compositions of hybrid membrane, wt.%								
PVDF	8							
DMAc	43							
Cement powder	49							
Hybrid membrane preparation								
Temperature and time for PVDF dissolved in DMAc	60 °C, 2 h							
Temperature and time for cement mixed in PVDF solution	60 °C, 12 h							
Standing time of casting solution before spinning procedure	12 h							
Temperature of casting solution for spinning	40 °C							
Nitrogen pressure	0.2 MPa							
Distance between spinneret and coagulation bath	5 cm							
Rate of core layer flow	40 mL/min							
Inner and outer coagulant, temperature D	Deionized water, 45 °C							
Diameter of inner tube of core layer liquid and outlet of casting solution	0.8 mm, 2.5 mm							
Standing time of precursor membrane in water	24 h							
Curing procedure								
Temperature	40 °C							
Relative humidity	50%							
Hydration time (days)	1, 7, 14, 21, 28							

Table 1 Preparation conditions of cement/PVDF hollowfiber hybrid membranes

solution. So, PVDF, DMAc, and cement powder were used at a weight ratio of 8:43:49, which consulted reference from Zhang *et al.* (2019) and (2022).

After spinning, the cement/PVDF hollow-fiber precursor membranes were obtained. The precursor membranes were then kept in water for 24 h. DMAc was then thoroughly dissolved in deionized water, resulting in complete solidification of the precursor membrane. Finally, the precursor membranes were stored in a box for different numbers of days for cement hydration. The temperature and relative humidity were 40 °C and 50%, respectively. Ultimately, cement/PVDF hollow-fiber hybrid membranes were obtained.

The preparation conditions are summarized in Table 1.

2.3 Characterization

Deionized water and carbon black were used to evaluate the flux and separation performance of the hybrid membranes, and the transmembrane pressure was 0.1MPa. An ultraviolet spectrophotometer (UV TU-1810, General Analysis, Beijing, China) was used to measure the absorbance of the carbon black solution. Standard carbon black solutions with certain concentrations were prepared in advance, and the absorbance data for the standard solutions were also obtained. The standard curves of absorbance were fitted using a linear regression method. The corresponding equations were defined by the fitting straight line, and the relationship between absorbance and concentration was obtained from the equation.

The water flux F_w and rejection R were calculated using Eqs. (1) and (2), respectively.

$$F_{w} = \frac{Q}{At}$$
(1)

where Q, A, and t represent the volume of permeated water, effective membrane area, and permeation time, respectively.

$$R = \frac{C - C_1}{C}$$
(2)

where C and C_1 are the carbon black concentrations in the feed and permeation solutions, respectively.

The adsorption of Zn^{2+} was measured using a laboratory-scale membrane module apparatus. A $ZnCl_2$ aqueous solution of a certain concentration was added to the tank. The hybrid membranes cured for 7 d, 14 d, and 21 d were placed in the tanks separately and the adsorption took place. After adsorption, the hybrid membranes were removed from $ZnCl_2$ solution. Inductively coupled plasma atomic emission spectrometry (ICP-OES; Varian 700-ES, Agilent, USA) was used to measure the concentrations of the initial and adsorbed solutions.

3. Results and discussion

Fig. 1(a) shows the particle-size distribution of cement powder sieved through a 400-mesh screen. The D50 median particle size of the cement powder was 13.41 µm according to the results of the particle-size distribution measurement. The particle size has an important effect on the spinning procedure and solidification of precursor membranes in coagulation baths. The solidification procedure could be considered as a quenching process. In this process, the polymer-rich solid-phase PVDF and cement powder formed the precursor membrane. Then, the solvent DMAc was diffused into the coagulation bath deionized water. The pore channels originated from the accumulation of PVDF and cement particles. Cement powder with large particle sizes offered fewer channels, whereas that with small particle sizes supplied more channels and reduced the flow resistance of solvent DMAc. However, small particle sizes also mean high surface area and surface energy, preventing easy mixing of the cement into the casting solution. As a result, a suitable particle size should be selected. Abdullah et al. (2018) chose Al₂O₃ powders with particle sizes of 1 μm, 0.5 μm, and 0.01 μm as raw materials. Lee et al. (2019) synthesized ceramic hollow fiber membrane using commercial α -Al₂O₃ powder with the particle size of 0.5 um. In this study, after being sieved using a 400-mesh screen, the cement powder with a D50 of 13.41 µm met the requirement and was used in our experiment.

Fig. 1(b) shows a photograph of cement/PVDF hybrid hollow-fiber precursor membrane. The precursor membrane



Fig. 1 (a) Particle-size distribution of cement powder, (b) photograph of PVDF/cement hollow-fiber membrane



Fig. 2 XRD results of cement powder and PVDF/cement hollow-fiber membranes under different hydration times

was kept in deionized water to remove the solvent DMAc. The membrane sample with uniform diameter showed flexibility by its ability to stretch tens of meters. This implied that the ratio of raw materials and the process were appropriate in our experiment.

Crystallinity has been considered as one of the most important features that influences the mechanical strength



Fig. 3 Water contact angle of hybrid membranes cured for different numbers of days

of inorganic membranes, as reported by Liu *et al* (2021). Fig. 2 shows the phase compositions of the cement powder and hybrid membranes under different hydration times. Even in the cement powder alone, many diffraction peaks were observed in the XRD results. Crystalline peaks of $3\text{CaO}\cdot\text{SiO}_2$ (C₃S), $2\text{CaO}\cdot\text{SiO}_2$ (C₂S), and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C₃A) were observed in the XRD results of the hydrated PVDF/cement hollow-fiber membranes. The broad peak in the range of 10° - 20° was attributed to the amorphous phase. The crystalline phases and amorphous phase originated from the starting cement material and formed during the preparation of the cement powder.

The peaks of the cement/PVDF hollow-fiber hybrid membranes appear to be higher than those of the cement powder. Except for the partial presence of PVDF binder, the amorphous peaks could be ascribed to the formation of the hydration product C-S-H. The peak intensities of C₃S and C₂S clearly decrease as a function of the hydration time. This result could be explained by the fact that C₃S and C₂S were dissolved in the liquid phase during the hydration procedure. In addition, many new diffraction peaks were observed compared with the cement powder. The new phases in the cured hybrid membranes corresponded to Ca(OH)₂ and AFt ettringite respectively, which could be attributed to the well-known hydration procedure. The Ca²⁺ dissolved into the deionized water quickly, and crystalline calcium hydroxide precipitated as the content of Ca²⁺ saturated in the liquid phase. At the same time, C₃A also dissolved in the deionized water and reacted with Ca²⁺ and SO₄²⁻ ions in the liquid phase as the hybrid membrane was cured, yielding the AFt ettringite phase.

Hydrophilicity has been studied by many researchers and is considered as an important standard when a membrane is used in the separation field. Fig. 3 shows the water contact angles and photographs of the hybrid membranes cured for different numbers of days. It should be mentioned that the water penetrated the hybrid membrane easily and quickly owing to the abundance of pores on the membrane surface. As a result, the photographs and contact angle data were captured once the water contacted the membrane surface. The contact angle



Fig. 4 Cross-sectional morphologies of hybrid membranes cured for (a, a1, and a2) 1 d, (b, b1, and b2) 7 d, (c, c1, and c2) 14 d, (d, d1, and d2) 21 d, and (e, e1, and e2) 28 d

was 94.7°, and hydrophobicity was observed when the hybrid membrane was cured for 1 d. However, with additional curing, the contact angles decreased below 90°. In other words, the hybrid membrane exhibited good hydrophilicity. This change can be attributed to the surface composition of the hybrid membranes. During the first period of the hydration reaction, the hydrophobicity of the hybrid membrane was determined by the polymer PVDF covering the surface of the hybrid membrane. However, hydration products such as Ca(OH)₂ and the C-S-H, AFt, and AFm phases formed on the surfaces of the hybrid membranes and improved the hydrophilicity. Good hydrophilicity was achieved when the membrane was cured for 14 d. It is known that a low contact angle indicates easier passage of the feed solution through the pores of the membrane. This implied that the hybrid membrane obtained in our study could be used in many fields as a basement membrane because of its good hydrophilicity.

Fig. 4 shows the cross-sectional morphologies of the cement/PVDF hollow-fiber hybrid membranes cured for



Fig. 5 Surface morphologies of the hybrid membranes cured for (a) 1 d, (b) 7 d, (c) 14 d, (d) 21 d, and (e) 28 d

different numbers of days. As shown in Figs. 4(a)-(e), the hollow-fiber hybrid membranes were prepared successfully. The thickness of hybrid membrane was about 500 μ m. The wall was thin, but it could endure the transmembrane pressure due to the round structure. It can be seen from the Fig. 4(a1) that the asymmetric pore structure remained when the hybrid membrane was cured for 1 d. Some macropores were found in the inner layer and outer layers, whereas some sponge-like pores were also seen within the hybrid membrane. The asymmetric pore structure was not

as obvious as in a common polymer membrane. The reason could be the fact that 49 wt.% cement particles were added into the casting solution. The phase exchange between solvent DMAc and non-solvent deionized water was impeded by the cement powder, and the regular asymmetric structure was not easy to form. However, because the hybrid membrane was kept in deionized water and cured for several days, the hydration products, such as the C-S-H and AFT phases and Ca(OH)₂, blocked the pores and the asymmetric pore structure became more and more obscure, as shown in Figs. 4(a1)-(e1).

Figs. 4(a2) - (e2) exhibit the magnified microstructure of the hybrid membranes and show the different kinds of hydration products. During the first stage of 1 d, many parallel plates were observed in the hybrid membranes, which was considered to be Ca(OH)₂. Naturally, the amorphous C-S-H phase should cover the surfaces of the cement particles. The presence of Ca(OH)₂ and the C-S-H phase was ascribed to the hydration reaction of C₃S and C₂S. During the pre-induction period, Ca²⁺, K⁺, Na⁺, and SO₄²⁻ ions dissolved rapidly into the liquid phase. Especially C₃S and C₂S, high ratios of which existed in the cement, released Ca2+ into the deionized water. As the liquid phase became saturated with respect to Ca(OH)₂, crystalline calcium hydroxide precipitated from the liquid phase onto the C₃S and C₂S surface. At the same time, a layer of the C-S-H phase formed on the cement particle surface.

With a hydration time of 7 d, parallel plates of Ca(OH)₂ were also found, as shown in Fig. 4(b2), which were accompanied by the presence of fibrous hydration products. The fibrous products were regarded as AFt ettringite, which can be explained by the hydration reaction of C₃A. C₃A dissolved in the liquid phase and reacted with Ca2+ and SO₄²⁻ ions, resulting in the formation of the AFt phase. The fibrous AFt phase nucleated first on the surface of the particles and grew toward the pore spaces. This analysis was supported by the XRD results. When the membranes were cured for 14 d and 21 d, an increasing number of fibrous AFt phases were observed, implying further hydration. However, the fibrous phases were gradually replaced by granulated particles in the hybrid membrane cured for 28 d. The granulated particles were the AFm phase. This phenomenon can be explained by the intensive hydration reaction, which is a well-known transformation of the AFt phase to the AFm phase during the hydration process.

Fig. 5 shows the surface morphologies of hybrid membranes cured for different numbers of days. As seen in the Figs. 5(a)-(c), the surfaces of the hybrid membranes cured for 1 d, 7 d, and 14 d were dense and almost uniform, and they were different from the rough surface of traditional cement. This dense surface could be attributed to the presence of the PVDF binder in the casting solution. When the casting solution was added to the coagulation bath, the PVDF solidified on the membrane surface, resulting in the formation of a dense and uniform surface. The obtained hybrid surface could therefore be used as basement membrane for both inorganic and organic coatings. However, after curing for 21 d and 28 d, many particles



Fig. 6 Roughness of hybrid membranes cured for (a) 1 d, (b) 14 d, and (c) 28 d

were attached to the surfaces of the membranes as shown in Figs. 5(d)-(e). We considered these particles to be Ca(OH)₂ in view of Ca²⁺ precipitation on the cement surface from the liquid phase. The precipitated Ca(OH)₂ should be removed if the hybrid membrane is to be used as a basement membrane.

Fig. 6 shows the surface roughness of membrane samples cured for 1 d, 14 d, and 28 d. As shown in Figs. 6(a) and (b), for hybrid membranes cured for 1 d and 14 d, the roughness was small and the surfaces were smooth, which could be attributed to the presence of PVDF on the membrane surface, as mentioned in Fig. 5. However, the roughness was 1.239 for the hybrid membrane cured for 28 d in Fig. 6(c), and many bulges were observed on the membrane surface. This could be explained by the presence of Ca(OH)₂ particles that resulted from Ca²⁺ precipitation.

The porosity of the hybrid membrane as a function of number of hydration days and pore-size distribution are shown in Fig. 7. The porosity decreased when the hybrid membranes were cured for several days as shown in Fig. 7(a). The porosity would likely decrease further after curing for 28 d. The porosity had effect on the water flux and separation performance. So, the effects of the cement ratio, viscosity of the casting solution, temperature of the coagulation bath, and phase exchange between DMAc and deionized water on the pore structure should be researched



Fig. 7 (a) The porosity as a function of hydration time. Pore-size distribution of hybrid membranes hydrated for (b) 1 d, (c) 7 d, and (d) 28 d

in more detail in the future. However, according to the N_2 adsorption/desorption measurements, the pore-size distribution showed a bimodal structure, with pore diameters of



Fig. 8 (a) Pure water flux of cement/PVDF hybrid membranes as function of hydration and treatment time. (b) Carbon retention versus treatment time

approximately 200 nm and 3 µm in the hybrid membrane as seen in Figs. 7(b)-(d). Macropores with diameters of approximately 200 µm are seen easily in Fig. 4, especially for the hybrid membrane cured for 1 d. These macropores were retained even when the membrane was cured for 21 d and 28 d, as shown in Figs. 4(d1) and (e1), respectively. Thus, the pores in the hybrid membrane could be separated into three types. Macropores that could be seen through the naked eye resulted from the phase exchange between solvent DMAc and non-solvent deionized water during the spinning procedure. Other macropores with diameters of approximately 3 µm and 200 nm existed in the cured cement owing to incomplete water utilization by the hydration reaction. Although they could not be detected by N₂ adsorption/desorption measurements, the these micropores were also found in the cured hybrid membrane owing to the presence of the C-S-H gel phase. With continued hydration, hydration products such as Ca(OH)₂, a fibrous AFt phase, and a granulated AFm phase formed. These hydrates grew homogeneously on the particle surfaces and partially filled the macropores. As a result, the porosity decreased with increasing hydration time. The similar pore-size distribution of the hybrid membranes cured for different numbers of days indicated that the hydration products had less of an effect on the pore microstructure, despite the fact that the hydrates occupied the macropore channels, as shown in Figs. 4(a1)-(e1).

The pure water flux of the cement/PVDF hybrid membrane cured for different numbers of days was studied.



Fig. 9 Adsorption of Zn^{2+} and ICP measurement results for hybrid membranes cured for (a) 7 d, (b) 14 d, and (c) 21 d

As shown in Fig. 8(a), the water flux decreased as a function of the hydration time. It has already been shown that hydration products, including the C-S-H phase, Ca(OH)₂, and AFt and AFm phases, filled the pores in the hybrid membrane. This effect could have been responsible for the decreased porosity, as shown in Fig. 7(a). The effect of treatment time on the water flux was also studied. As shown in Fig. 8(a), for the hybrid membrane cured for 1 d, the water flux decreased to 69 L·m⁻²·h⁻¹ from 153.5 $L \cdot m^{-2} \cdot h^{-1}$ as the treatment time was prolonged to 7 h. This decrease was similar to that of the other polymer membranes and could be explained by the blocking of pores owing to foulant adsorption on the membrane. For other hybrid membranes cured for 7 d, 14 d, 21 d, and 28 d, the same tendency was observed, and the water flux started to stabilize after the feed solution was treated for 5 h. After

Based	Shape	Temperature	Pore size	Porosity	Contact	Thickness of	Flux	Reference
membrane	-	(K)	(µm)	(%)	angle (*)	support layer	$1.2-3*10^{-6} \text{ mol}/(\text{m}^2.\text{s}.\text{Pa})$	Kubo et al
Al ₂ O ₃	tubular		0.15, 0.7	40		1 mm	for He, H ₂ , and N ₂	(2020)
Al ₂ O ₃	tubular		2.1	44.1		2.4 mm	, ,	Qin <i>et al.</i> (2015)
Al_2O_3	tubular		0.16	40	33		505 L/($m^2 \cdot h$) for water	Chang <i>et al.</i> (2010)
Al_2O_3	hollow fiber	1623	0.2, 13	62	20°	0.9 mm	2.56x10 ⁻⁹ m ³ /(s·m ² ·Pa) for water	Bindes <i>et al.</i> (2020)
Al ₂ O ₃	plate/tube		0.1/0.2		60°	2.2 mm/2 mm	342 L/(m ² ·h) for BSA solution	He et al. (2011)
SiC	flat-tubular	1673	1.8	47		1 mm	210 L($/m^2 \cdot h \cdot bar$) for water	Bukhari <i>et al.</i> (2018)
SiC	flat	2473	5.2			6 mm	355-273 L/(m ² ·h·bar) for water	Li et al. (2019)
Cement	slice	RT	0.1	28.1		5, 10, 20 mm		Zhang <i>et al.</i> (2014)
geopolyme r	disk	333	75			20 mm	245 kg/(m ² ·h) for water	Xu et al. (2019)
Glass	hollow fiber	1018	0.003-90			500 µm		Zhang <i>et al.</i> (2022)
Glass	hollow fiber	1003	0.003-100			300 µm	125.3-129.5 L/(m ² · h) for water	Wang <i>et al.</i> (2021)
Glass	hollow fiber	983	0.008-100			300 µm		Zhang <i>et al.</i> (2019)
Cement/ PVDF	hollow fiber	RT	0.2/3	17	27°	500 µm	17.5-65.7 L/(m ² ·h) for water	Current study

Table 2 Comparison of properties for various inorganic membrane

curing for 28 d, the stable water flux was 17.5 $L \cdot m^{-2} \cdot h^{-1}$. The water flux could be explained by the dense surface and low porosity of hybrid membrane. The solidification of PVDF led to the dense surface and prevented water from permeating through the membrane. When the hybrid membrane was cured for 28 d, hydration products, Ca(OH)₂, fibrous AFt phase, and granulated AFm phase filled the pore, yielding the low porosity. The mixed effect of dense surface and low porosity result in low water flux. Further research should be conducted to improve the flux. How to adjust the solidification of PVDF and control the formation of hydration products should be studied as important issues.

Fig. 8(b) shows the carbon rejection as a function of treatment time. The cement/PVDF hollow-fiber hybrid membrane cured for 7 d was selected to test the rejection. The highest carbon retention was approximately 90% and was stable after 5 h of rejection treatment. The sieving effect was regarded as the main reason for this. However, the adsorption of pore channels and hydration products cannot be ignored. Macropores with diameters of approximately 2 μ m and 300 nm and capillary pores in the C-S-H phase exhibited strong adsorption. The abundant pores improved and ultimately increased carbon rejection.

Fig. 9 shows the Zn^{2+} adsorption results of the hybrid membranes cured for 7 d, 14 d, and 21 d. After adsorption for 1 d using the membrane cured for 7 d, the concentration of the obtained $ZnCl_2$ solution was close to zero, and the ICP-OES results also showed that there were only trace amounts of Zn^{2+} . The same results were found for the hybrid membranes cured for 14 d and 21 d. These results implied that the cement/PVDF hybrid membrane showed good adsorption ability for Zn^{2+} ions. The Zn^{2+} adsorption mechanism was complicated. The reason that the membrane showed good adsorption ability for Zn^{2+} should be explained by the abundant pore structure and replacement of Zn ions with Ca ions in the cement. The pore system in the hybrid membrane included macropores with diameters of approximately 200 µm, as seen in Fig. 4. Pores with smaller radii were believed to be an integral part of the hydrated products and were called gel pores, whereas pores with greater radii were called capillary pores. A rich pore structure implied that the hybrid membrane provided space for Zn^{2+} adsorption. In addition, the reaction of Zn ions with calcium silicates resulted in the replacement of Ca^{2+} and precipitation reaction took place, as ascribed by Kawai *et al.* (2013).

Table 2 shows a comparison of properties for various basement membranes. The porosity and pore size in this study were similar to those of an Al₂O₃ basement membrane. The water flux of hybrid membrane was low compared to other samples. However, the hollow-fiber membranes showed higher surface areas and a more compact module than typical tubular supports. The cement/PVDF hollow-fiber hybrid membranes did not require calcination, and thus the energy consumption and cost of the preparation procedure were low. The hybrid membrane also showed good hydrophilicity and a thin separation layer, implying that it may exhibit good permeation flux as a basement membrane. As a result, cement/PVDF hollow-fiber hybrid membranes with a simple preparation procedure could be used as basement membranes and expand the application of inorganic or organic membranes.

4. Conclusions

A cement/PVDF hollow-fiber hybrid membrane was successfully prepared. A cement power with a D50 median particle size of 13.41 µm was suitable for the spinning procedure in this study. The XRD results showed that the hydration reaction took place and that hydration products comprising an amorphous C-S-H phase, Ca(OH)₂, and AFt, and AFm phases formed as the hydration reaction progressed. SEM images of the cross-sectional and surface morphologies of the hybrid membranes also showed the formation of hydration products. Parallel plates comprising Ca(OH)₂, as well as fibrous ettringite AFt, and granulated AFm particles were also observed in the hybrid membranes. An asymmetric pore structure was obtained. Good hydrophilicity was observed owing to the formation of hydration products on the surfaces of the hybrid membranes. Owing to blocking of the hydration products, the porosity decreased with prolonged hydration time. In addition, the carbon retention and Zn²⁺ adsorption were tested. The carbon rejection was 90% after 5 h of treatment, and almost all the Zn2+ was adsorbed by the hybrid membrane. The above results suggested that the obtained hybrid membranes could be used as a basement membrane for inorganic or organic coatings.

Acknowledgments

The research described in this paper was financially supported by the National Natural Science Foundation of China [grant number 51402212].

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