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Evaluation of antifouling and chemical resistance of flower membrane prepared using thermally induced phase separation (TIPS) process

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ABSTRACT

In this study, we discussed the characterization and water treatment properties of the newly designed flower type membrane which has multi-bore structures prepared by the thermally induced phase separation process. The flower membrane for water treatment purposes was made of hydrophobic polyvinylidene fluoride polymer. The antifouling characteristics during the water treatment were studied using bovine serum albumin as a model compound and the chemical resistance was evaluated after long-term impregnation in hypochlorous acid (NaOCl) solution to understand the long-term stability of the membranes. Water permeability and mechanical strength of the membranes after prolonged chemical exposure was measured to observe the change in mechanical property and long-term performance of the membrane. Zeta potential measurements were used to find how the surface pollution affected the membrane performance and morphologies of the surface and cross-section of the membrane were confirmed by using scanning electron microscopy. To understand the efficiency of chemicals in the actual process, chemically enhanced backwashing was also carried out using citric acid and sodium hypochlorite in the lab-scale water treatment process.

Keywords: Chemical resistance; Flower membrane; Fouling; Polyvinylidene fluoride (PVDF); Thermally induced phase separation (TIPS)

1. Introduction

The rapid growth of industrialization and the release of hazardous waste such as organic dyes, oil, heavy metals, etc. into the environment has seriously damaged the global water quality [1–3]. Clean and safe water is an important and necessary requirement for living life. The United Nations report warns that more than half of the population will suffer from water shortages by 2025 as a result of climate change and water pollution [4–6]. Efforts to mitigate this inevitable global challenge to avail good quality water demand continued research to develop efficient and sustainable technologies for water purification. During the past few decades, various membrane separation techniques have been used extensively for water purification [7,8]. Controlling membrane morphology with respect to the end-use is a key factor in developing successful membranes. Among various methods, phase inversion is currently the mainstream technique used for most membrane applications. Thermally-induced phase separation (TIPS) membranes are inherently more reproducible and less prone to defects and the elevated working temperature in this process allows a wider selection of solvents and polymer [9]. TIPS methods are usually employed for semi-crystalline polymers and exhibit a highly porous and symmetric structure which is suitable for microfiltration. Among the various available polymers, polyvinylidene

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fluoride (PVDF) provides outstanding performances based on its excellent inherent properties such as high thermal stability, great chemical resistance, and good processability [10].

Fouling is a phenomenon in which contaminants adhere to the membrane surface and blocks the porous structure directed to the deterioration of membrane performances. In order to maintain the performance of the membrane, a washing process is necessary. The process of washing includes physical and chemical cleaning [11,12]. The physical washing method is mainly backwashing, in which the solvent such as clean distilled water flows in the opposite direction to the solution permeation. In chemical washing, contaminants are removed by using a base or an acid. These chemicals may affect the life of the membranes. Therefore, it is necessary to maintain the stability of the membranes in both the physical and chemical environment [13,14].

In this work, we studied the pollution and chemical safety of PVDF based hollow fiber membranes prepared using TIPS by Pure Envitech Co. Ltd. The effect of bovine serum albumin (BSA) fouling on to the permeability over time, charging after contamination through Zeta potential, a structure using Fourier-transform infrared spectroscopy (FT-IR), and morphology was analyzed. In addition, chemical resistance and mechanical stability after prolonged exposure in both basic and acidic solutions as well as the efficiency of the chemical solution in antifouling in the water treatment process were also reported.

2. Experimental

2.1. Material

PVDF based flower hollow fiber membrane manufactured by TIPS was collected from Pure Envitech Co., Ltd., and further washed with ethanol (Daejung, Korea). BSA (Bovine Serum Albumin, lyophilized powder) used for membrane fouling resistance test was supplied by Sigma-Aldrich, USA. BSA is a protein containing Albumin and is well known as a material that contaminates the membrane because it causes membrane fouling relatively well. Citric acid collected from Sigma Aldrich, USA and basic hypochlorite (sodium hypochlorite solution 12%) received from Junsei, Japan were used for conducting chemical resistance tests. Distilled water was used as the solution for measuring permeability, and was made using Aqua MAXTM (Younglin Instruments, Korea).

2.2. Manufacturing of membrane module

SEM images of the inner as well as the outer surface and cross section of the membrane are presented in Fig. 1. The membrane was cut to 17 cm in size and washed with ethanol. The membrane module was prepared by attaching a 6 mm urethane tube on one end of the membrane. Since the diameter of the membrane was large, a module was prepared using a single strand of membrane. First, both ends of the

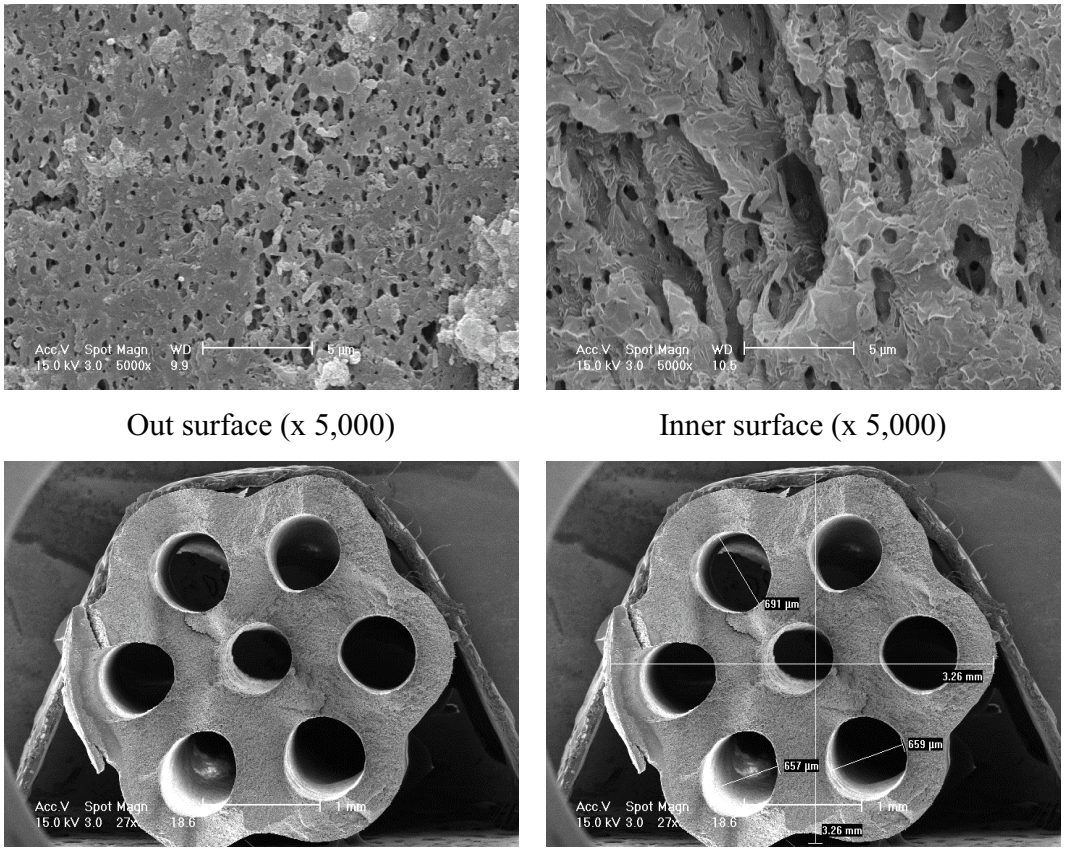


Fig. 1. Morphology of membranes.

membrane were cut by using a knife so that no pores were damaged. Then, one end of the membrane (1 cm length) was fixed inside the urethane tube, using super glue. Care should be taken not to create any block inside the urethane tube so that the solution flows well. Dead-end filtration method was used to produce purified water in which the other end of the membrane module was fixed using epoxy so as to completely prevent the leakage of solution through the pores (Fig. 2). The effective membrane area of the prepared module was 2.37 cm^2.

2.3. Characterization

2.3.1. Pollution resistance test

In the pollution resistance test, the BSA solution was pumped through the membrane using a rotary pump to create fouling inside the membrane and then its effect on the permeation rate of distilled water coming out through the membrane was analyzed. As shown in Fig. 3, a return valve was installed between the line flowing from the BSA solution to the membrane and the pressure gauge installed in front of the membrane to maintain a constant permeation pressure of the solution applied to the membrane. The experiment was carried out by minimizing the error in permeation rate during test using a pressure gauge. 1, 3, 5, 10, and 15 ppm of BSA in distilled water was used as a fouling agent for pollution resistance test. The BSA solution was thoroughly stirred for 24 h at 100 rpm at 25°C to ensure the feed solution was well mixed inside the cell during the experiment. Clean distilled water was streamed into the membrane for about 10 min, and the BSA solution was permeated at a pressure of 2 bar after stabilizing the permeability. Water flux was measured until the endpoint of 1 cc/min.

2.3.2. Measurement of zeta potential

To identify the surface pollution of the membranes, zeta potential measurements were conducted. The measurement was performed using SurPASS (Antor Paar GmbH, Graz, Austria) electrokinetic analyzer, and the streaming potential according to the pH change was measured. The Zeta potential refers to the potential difference through the fluidized bed of the electrical double layer generated by the electrodynamic phenomenon. In this test, the pollution of the membrane was predicted by measuring potential difference according to pH change [15]. The effect of cleaning with ethanol (chemical cleaning), hot water and contamination with 1, 5, 10, and 15 ppm BSA solution on Zeta potential was measured separately. During sample preparation, a thin surface layer of the membrane was fixed on to a ceramic mount (20 mm × 10 mm) as shown in Fig. 4. 0.001 M KOH electrolyte solution was made to circulate over the membrane surface in an adjustable gap cell. To study the stability of the contaminated membrane, Zeta potentials of the membranes were measured over a pH range by adjusting pH using either 0.01 M HCl or 0.01 M NaOH aqueous solution.

2.3.3. Fourier-transform infrared spectroscopy

FT-IR (FT-IR, Nicolet Impact 400, Thermo Scientific) in the wavenumber range of 3,500–650 cm^{-1} was used to check the effect of ethanol, hot water and BSA solutions on both inner and outer surface structures of the membranes.

2.3.4. Morphology

A field emission scanning electron microscope (Philips XL30 S FEG, Netherlands, FE-SEM) was used to confirm the surface and cross-sectional morphologies of the membrane contaminated with BSA solution. The cross-sectional morphology of the hollow fiber membranes was measured using

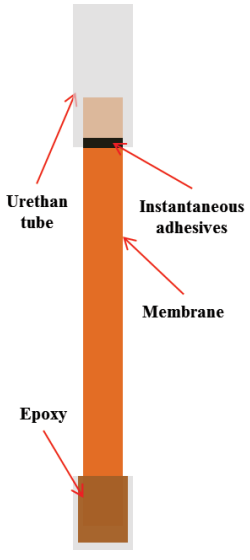


Fig. 2. Schematic diagram of the membrane module.

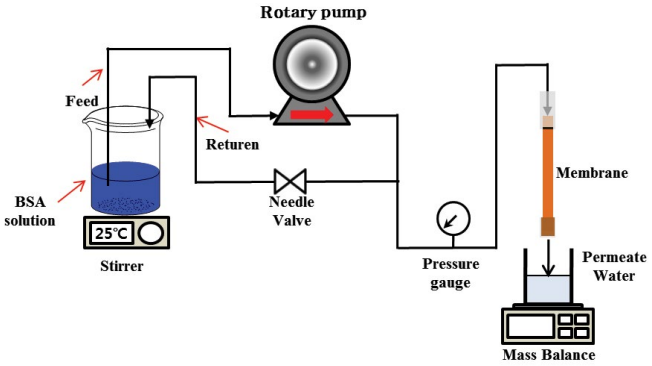
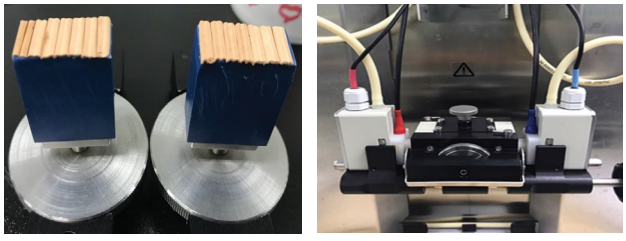


Fig. 3. Schematic diagram of pollution resistance test apparatus.



(a) Ceramic mounts with samples (b) Equipped adjust gap cell

Fig. 4. Photograph of Zeta potential apparatus.

a cryogenically fractured surface. The samples were sputtered with a thin layer of gold coating using an ion coating machine (JEOL JFC-1100E) at 5 mA for 300 s under vacuum.

2.3.5. Chemical resistance

Chemical resistance tests were conducted using both acidic and basic solutions. The membranes were impregnated in aqueous citric acid solution (1 and 2 molar concentrations) and a basic sodium hypochlorite solution (3% and 6%) separately for a long time. Tensile strength using a universal test machine (UTM, LLOYD-LR 10K, UK) and water flux were measured after 6 d. The effective measuring length was 10 cm and the speed was 5 mm/min. Morphology of the membranes after chemical resistance testing was also studied using FE-SEM.

2.3.6. Anti-fouling property

To study the antifouling behavior of the membrane, lab-scale experimental set up as shown in Fig. 5 was used. The effective length of the hollow fiber membrane used in the experiment was 10 cm and the effective membrane area was 0.019872 m^2. The procedure used was as follows: Firstly pure water flux was tested at 1 bar pressure (Jw1, L/m^2h) to determine the permeability of the membrane, and the value obtained was 484 LMH. Then, 10 ppm BSA solution in water was fed into the filtration system for 10 min to foul the membrane. Then the pure water flux of the membranes was tested (permeability after pollution). After that, the membrane was flushed with a chemical solution (chemically enhanced backwashing) for 1, 2, 3, 4 and 5 min separately and allowed sedimentation for 20 min and their pure water flux of the membrane was measured (Jw2, L/m^2h). The flux recovery ratio was calculated using the following equation to evaluate the membrane antifouling property. The unit used for water permeation is LMH (L/m^2h), where L is permeation, M is unit area, and H is unit time.

$$\text{Flux recovery ratio} = \frac{(\text{Jw2} \times 100)}{\text{Jw1}}$$

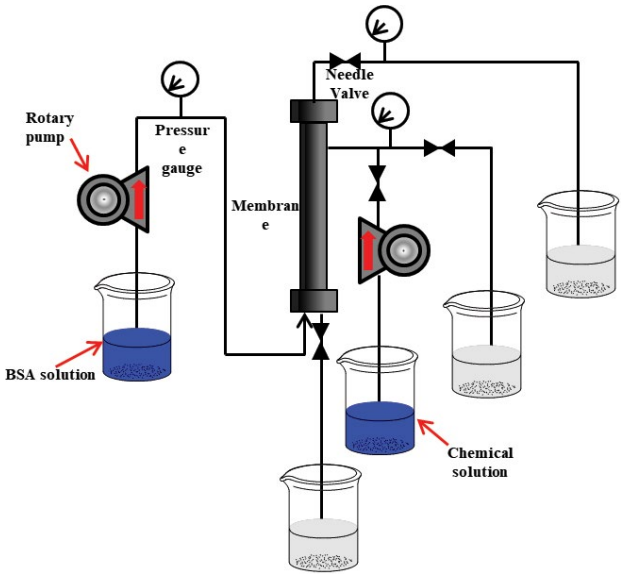


Fig. 5. Schematic diagram of the lab-scale water treatment process.

3. Results and discussion

3.1. Pollution resistance

Fig. 6 shows the water flux variations of the PVDF hollow fiber membranes due to the BSA concentration. Only a small reduction in water flux occurs in the case of membranes without BSA fouling and, the permeability remains constant after 30 min. A sharp reduction in the percentage of relative water flux up to the range of about 10%–40% during the first 30 min followed by a slow reduction is noticed in all the polluted membranes. Moreover, a decrease in relative water flux with an increase in BSA concentration also observed, which helps to get an idea about how fouling affects the water permeation of the membranes.

3.1.1. Measurement of zeta potential

Zeta potential investigation was conducted to study the surface charges of the polluted membranes and the results are presented in Fig. 7. It can confirm the level of pollution by checking whether any functional group has been introduced on to the membrane surface. The absorption of BSA solution on the membrane causes change in Zeta potential, which will give an idea about the contamination [16]. The membranes washed with ethanol and hot water shows almost stable potential change. However, the membranes contaminated with BSA shows very high zeta potential. Membranes after chemical cleaning shows negative potential in the pH range of 3.0–7.75. As expected BSA fouled membranes are positively charged below a pH of 5, while negatively charged at higher pH conditions. Most of the membrane fouling substances has negative charges,

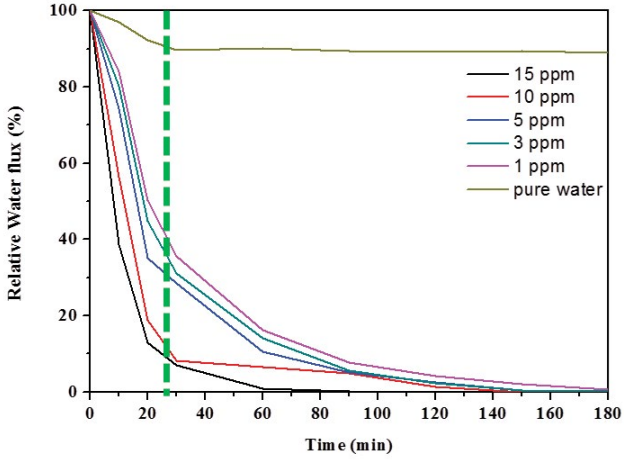


Fig. 6. Effect of BSA concentration on water flux.

and the membrane after fouling become slightly more negative with increasing pH probably due to anion absorption. Hence exhibits change in Zeta potential with change in BSA concentration as well as pH.

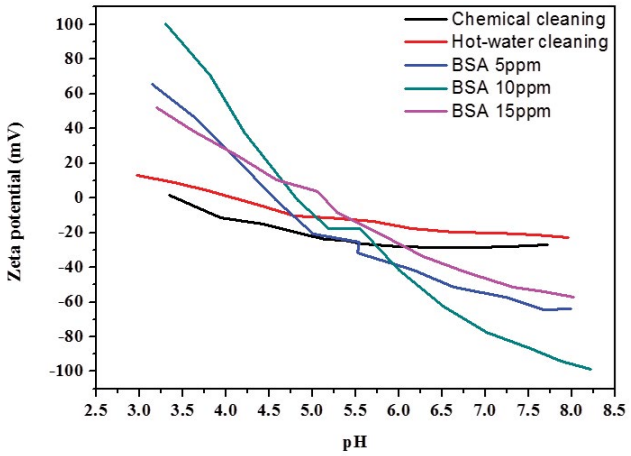


Fig. 7. Effect of BSA concentration on zeta potential.

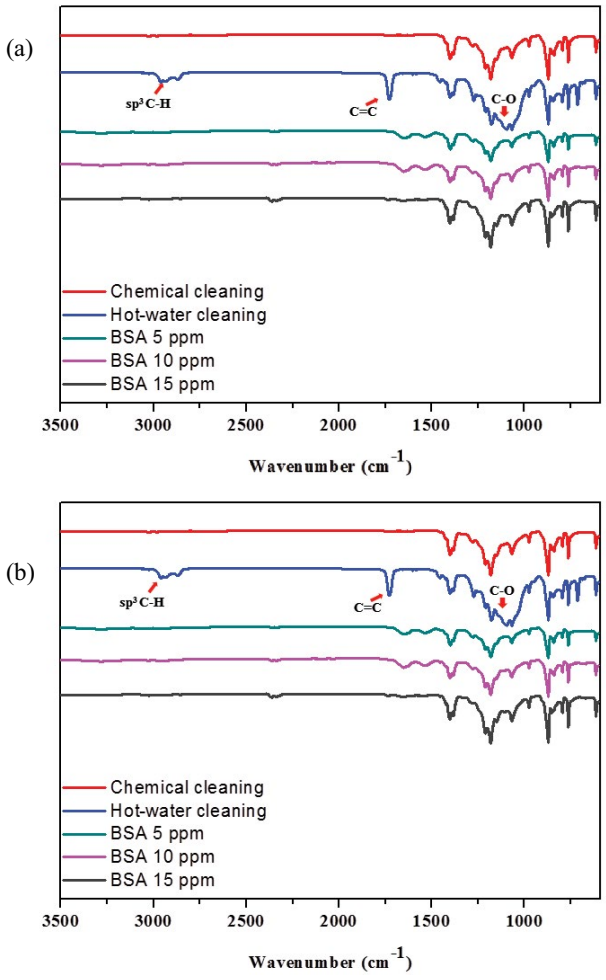


Fig. 8. Effect of BSA concentration on (a) outer and (b) inner surface structures of the membrane using FT-IR.

3.1.2. Observation of FT-IR

FT-IR was measured for the qualitative analysis of the contaminated membrane. The analysis was done on the outer and the inner surface of the membranes (Fig. 8). The peak corresponding to C=C and C=H of PVDF has been disappeared and the band corresponding to C–O vibration has been shifted towards higher wavenumber after chemical cleaning and BSA fouling which means the inner surface becomes dense after treated with the pollutant. More effects of fouling with an increase in BSA concentration onto the inner surface were expected, but no difference in FT-IR spectra among the inner and outer surfaces was noticed.

3.1.3. Observation of morphology

The pollution level of the membrane was also onfirmed using FE-SEM (Figs. 9 and 10). For comparison, membrane

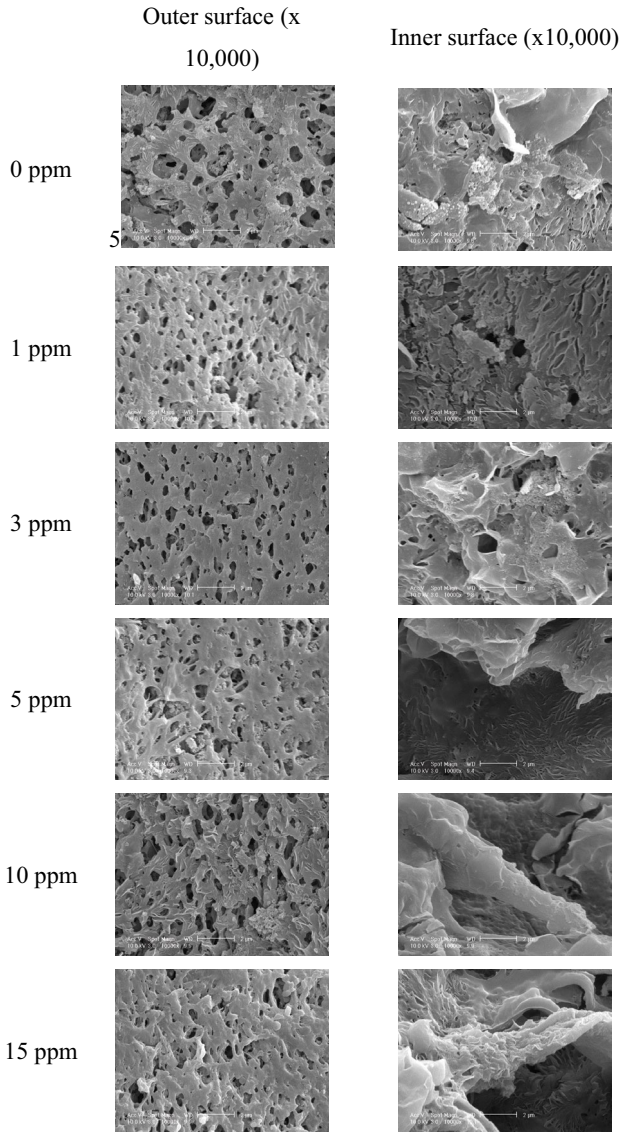


Fig. 9. Outer and inner surface morphologies of BSA polluted membranes.

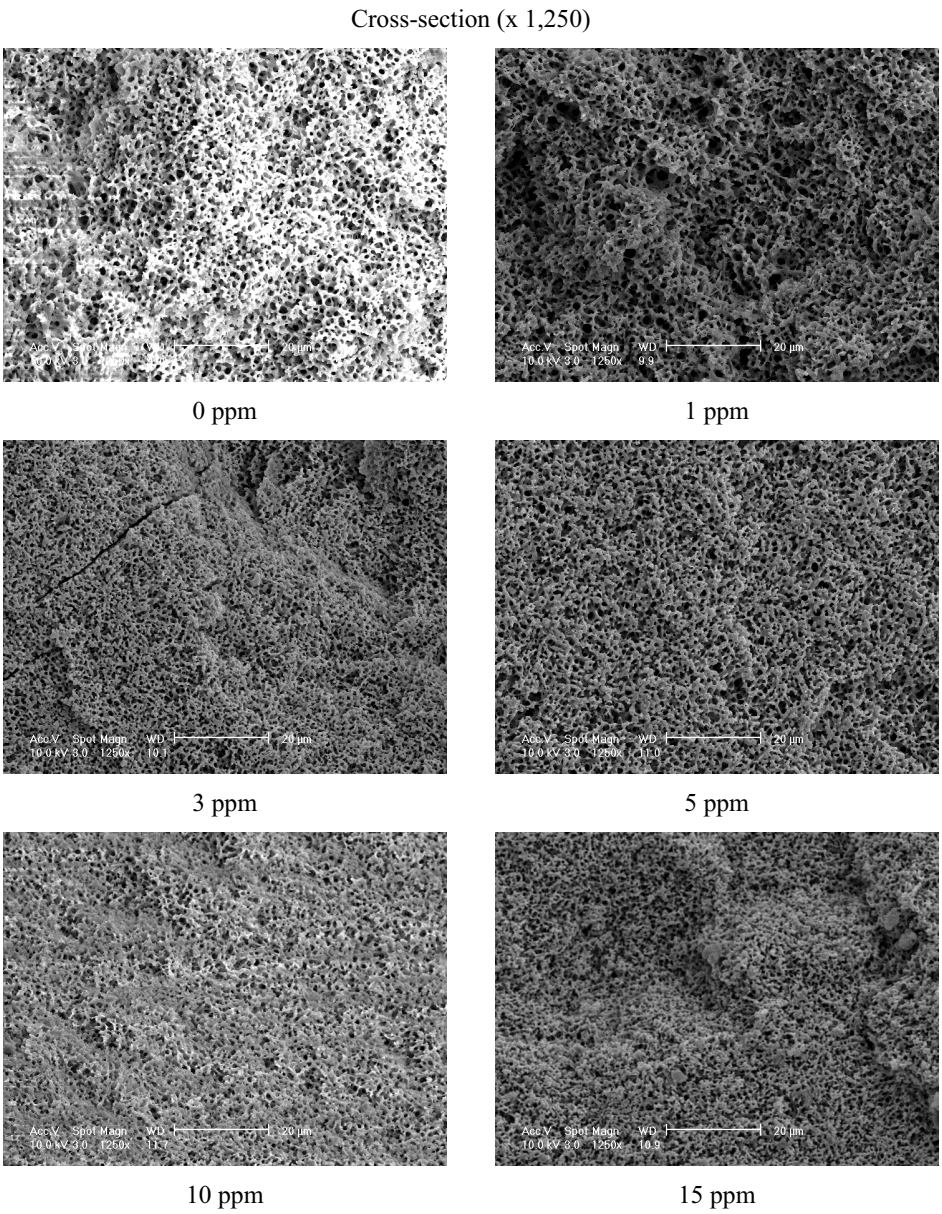


Fig. 10. Cross-sectional morphologies of BSA polluted membranes.

sample without any fouling (0 ppm) is also analysed. As can be seen from Fig. 9, no significant changes observed among the outer and inner surfaces, but the blockage of pores according to the concentration of BSA in the cross section was noticed (Fig. 10). At low concentrations, pores were slightly blocked by BSA, and at 10 ppm and 15 ppm, many pores were blocked. These observations are consistent with the results of the permeability experiment and zeta potential measurement.

3.2. Chemical resistance

Fig. 11 shows the change in permeability and tensile strength of the membranes after impregnated in acidic and basic solutions over time. No significant change in water permeability, as well as tensile strength even after prolonged exposure of about 90 d, are observed. This suggests that the PVDF membranes prepared by TIPS are having enough chemical and mechanical stabilities.

The morphology of the membranes after chemical exposure was also studied. From Figs. 12 and 13, the defect-free outer and inner surface morphology and the cross-sectional image shows that there is no noticeable change and the membrane is stable in chemical environment.

3.3. Membrane fouling test

It is well understood that the membrane fouling could result in a reduction of permeability and shorten membrane life. Water backwashing and chemical enhanced backwashing (CEB) verification in the water treatment process shows little efficiency after water backwashing, and it is confirmed

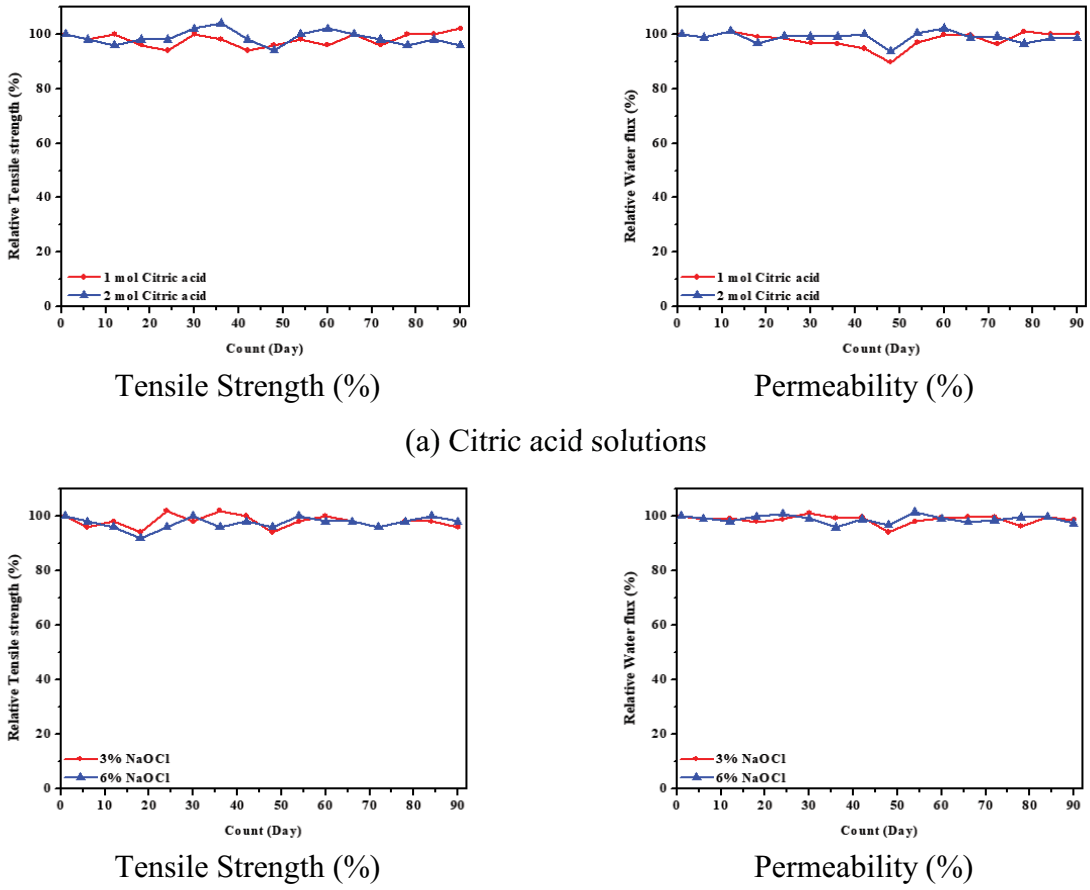


Fig. 11. Effect of chemical treatment on water flux and tensile strength of membranes.

Table 1
Antifouling property of the membranes

	Water back washing	Citric acid 0.5%	Citric acid 0.9%	H_2SO_4 0.5%	H_2SO_4 0.9%	NaClO 0.5%	NaClO 0.9%
Permeability after pollution	91.51	92.54	92.84	92.43	93.63	62.42	63.85
Jw2, 1 min	92.78	119.85	123.82	120.11	124.26	158.23	172.49
Jw2, 2 min	93.63	128.45	132.44	128.82	131.88	164.42	180.56
Jw2, 3 min	93.69	136.62	137.88	135.64	138.54	175.55	187.53
Jw2, 4 min	93.84	141.82	146.82	139.76	144.22	178.64	194.15
Jw2, 5 min	93.96	146.88	152.53	146.28	149.77	183.46	208.82
Recovery ratio after 5 min (%)	19.41	30.35	31.51	30.22	30.94	37.90	43.14

that the efficiency of sodium hypochlorite is higher than that of citric acid in CEB (Table 1). A maximum recovery ratio of about 43.14 % after 5 min chemical enhanced backwashing using sodium hypochlorite observed reveals their best performance.

4. Conclusions

In this study, pollution and chemical resistance tests were conducted to check the applicability of PVDF flower hollow fiber membrane manufactured by Pure Envitech Co., Ltd. for water purification purposes. Membrane pollution test carried out using BSA shows a sharp drop in relative water flux during the first 30 min which confirms the quick formation of contamination within a short span of time. In addition, the variation in water flux with BSA concentration is also supported by the zeta potential and FE-SEM analysis. Stability in water permeability and tensile properties reveals the long term chemical and mechanical stability of the PVDF membranes prepared using the TIPS process. In the water

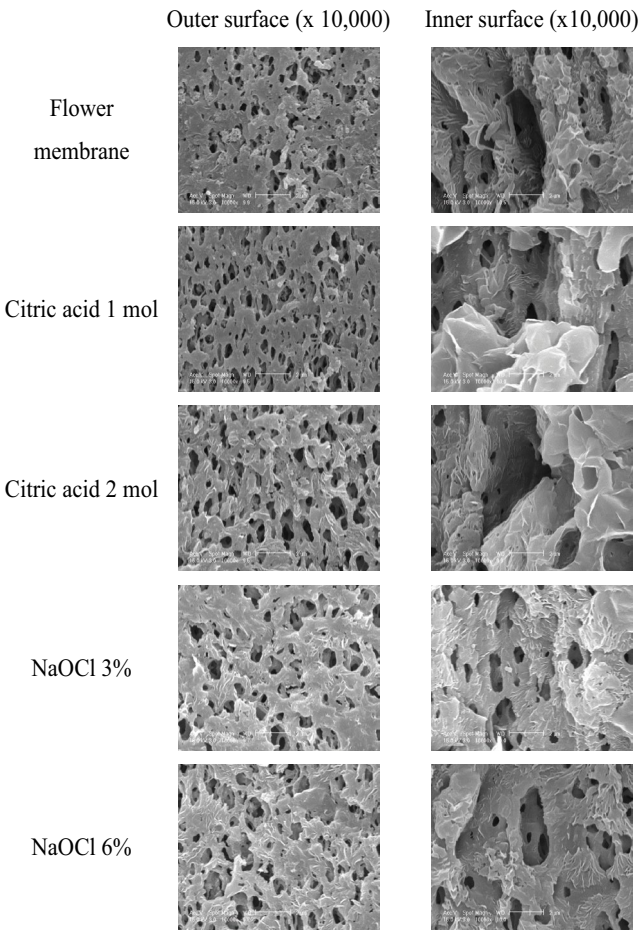


Fig. 12. The outer surface and inner surface morphologies of the membranes after the chemical resistance test.

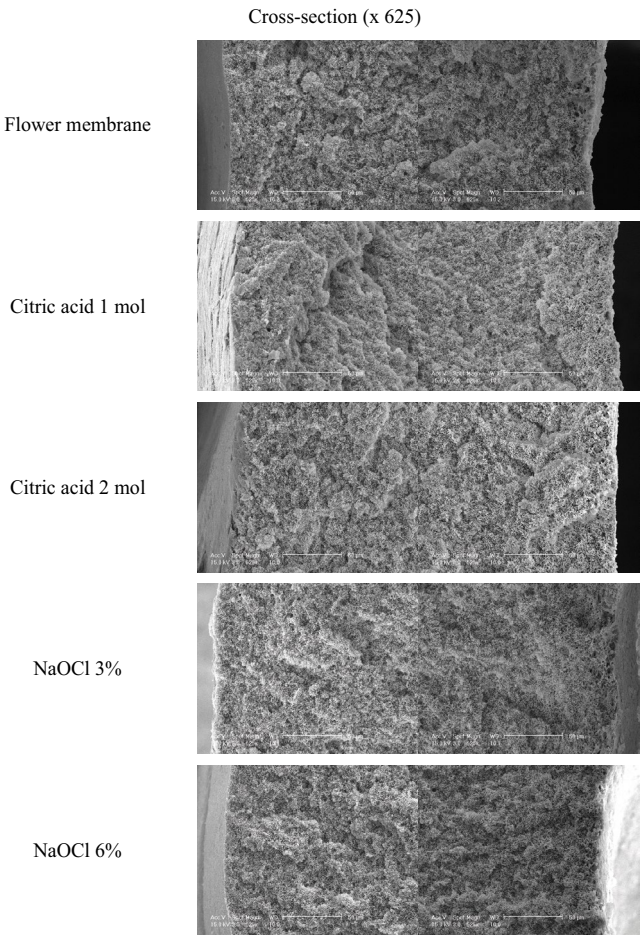


Fig. 13. Cross-sectional morphologies of the membranes after the chemical resistance test.

treatment process, CEB using sodium hypochlorite is more efficient than citric acid and water backwashing.

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