

Antibiofouling polysulfone ultrafiltration membranes via surface grafting of capsaicin derivatives

Qun Wang, Jian Wang, Xueli Gao, Hui Yu, Zhun Ma, Yushan Zhang and Congjie Gao

ABSTRACT

Biofouling is a critical issue in the membrane separation process as it can increase the operational cost by lower down membrane permeability. Covalent binding of an antibacterial agent on the membrane surface to kill microorganisms to hinder biofouling formation process draws great attention. In this study, we used three kinds of capsaicin derivatives, MBHBA, HMBA, and HMOBA, to fabricate antibiofouling membrane via UV-assisted photo grafting method. The influence of these capsaicin derivatives on membrane properties was investigated and compared. The results suggest that HMBA showed the best UV activity, followed by HMOBA and MBHBA successively. Due to the difference of functional groups among capsaicin derivatives, there is an increase in membrane wettability of HMBA and HMOBA-modified membranes, while there is a decrease for MBHBA-modified membrane. MBHBA-modified membrane showed enhanced irreversible fouling, which is in contrast to that of HMBA- and HMOBA-modified membranes. The modified membranes showed similar antibacterial activity against *Escherichia coli*. The practicability of the modified membranes was examined by dipping them into tap water and seawater for 30 days, and the results displayed the modified surfaces have the potential to relieve biofouling for separation membranes.

Key words | antibacterial, antibiofouling, capsaicin derivatives, surface modification, ultrafiltration membrane, UV-assisted grafting

Qun Wang

Jian Wang (corresponding author)

Xueli Gao

Congjie Gao

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China
E-mail: swordking8856@163.com

Jian Wang

Hui Yu

Yushan Zhang

The Institute of Seawater Desalination and Multipurpose Utilization, MNR(Tianjin), Tianjin 300192, China

Zhun Ma

College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Congjie Gao

Ocean College, Zhejiang University of Technology, Hangzhou 310014, China

INTRODUCTION

Membrane biofouling, which would debase the separation performance and may induce secondary pollution, is a critical issue in the membrane separation process. Biofouling refers to the aggregation and metabolism of microorganisms on the solid surface. Traditionally, pretreatment and membrane cleaning is vital methods to control membrane biofouling. Increasing attention has been paid on membrane surface modification to inhibit or hinder the development of biofouling.

Several papers focused on the hydrophilization of membrane surface using superhydrophilic material, such as poly(ethylene oxide) (Roosjen *et al.* 2005) and poly(carboxybetaine methacrylate) (Cheng *et al.* 2009). These could reduce the adhesion of microorganisms by more than 99.99%. However, there are still a few cells attached to the membrane surface (Xu *et al.* 2010) and will form biofilm

according to the development process of biofouling. Thus, construction of the antibacterial surface to kill these cells could be seen as the last resort for membrane biofouling control. Incorporation of inorganic antibacterial materials, such as Ag, Ti, Cu and Zn (Li *et al.* 2008; Kim & Van der Bruggen 2010; Zhu *et al.* 2018), with broad-spectrum antibacterial property, can endow membranes with excellent antibacterial activity. However, they tend to dissolve into the feed solution during the membrane process, which would produce secondary pollution (Chou *et al.* 2005; Zhu *et al.* 2018).

Covalent binding of organic antibacterial agents or functional groups on the membrane surface is another strategy. Presently, increasing attention has been paid to prevent biofilm formation using natural products like plant extracts rather than synthetic chemicals (Dobosz *et al.* 2015). Kim *et al.* (Kim *et al.* 2009) directly immobilized a quorum

quenching enzyme (acylase) onto a nanofiltration membrane. The modified membrane exhibits much better antibiofouling property: water flux of the modified membrane decreased by 10% while that of the pristine membrane decreased by 40% after operation for 38 h. Ponnusamy *et al.* (Ponnusamy *et al.* 2009, 2013) found that vanillin can reduce biofilm formation on reverse osmosis membranes by 46.5%.

Capsaicin is a fat-soluble, odorless, pungent tasting, off-white solid with a melting point of 62–65 °C (Leng *et al.* 2013). It is a naturally occurring alkaloid that exists in a variety of red peppers or chilies (Wang *et al.* 2014). It has been well known to interact at primary sensory neurons exerting the specific actions of excitation, desensitization, and neurotoxicity (Tsuchiya 2001). Many types of research focused on possible antibacterial effects found an inhibitory effect on both Gram-positive (*Streptococcus* and *Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacteria with various degrees (Tsuchiya 2001; Leng *et al.* 2013). To facilitate its processing, Yu *et al.* (Liangmin 2004) developed a variety of capsaicin derivatives.

In our previous works (Gao *et al.* 2013; Wang *et al.* 2014), we were trying to exerting the best effect of one kind of capsaicin derivatives. Herein, we select three kinds of capsaicin derivatives, named MBHBA, HMBA and HMOBA (as

shown in Figure 1(a)), to modify PSf membranes via UV assisted graft polymerization method. Their impact on membrane performance, such as hydrophilicity, surface roughness, antifouling property and antibacterial activity, was investigated and compared with each other. The results demonstrated that HMBA-modified PSf membrane possesses the best antibiofouling property, followed by HMOBA- and MBHBA-modified PSf membranes. The primary purpose is trying to get a better understanding of the influence of different kinds of capsaicin derivatives and provide the necessary data for their practical applications.

EXPERIMENTAL

Materials

PSf flat sheet ultrafiltration (UF) membrane was purchased from Shanghai MegaVision Membrane Engineering & Technology Co., Ltd (China). MBHBA, HMBA and HMOBA were obtained from Key Laboratory of Marine Chemistry Theory and Technology (Ministry of Education), Ocean University of China. Ethanol was purchased from Fuyu Fine Chemical Reagent Co. (Tianjin, China) and used as received for the preparation of the monomer solution. *E. coli* was

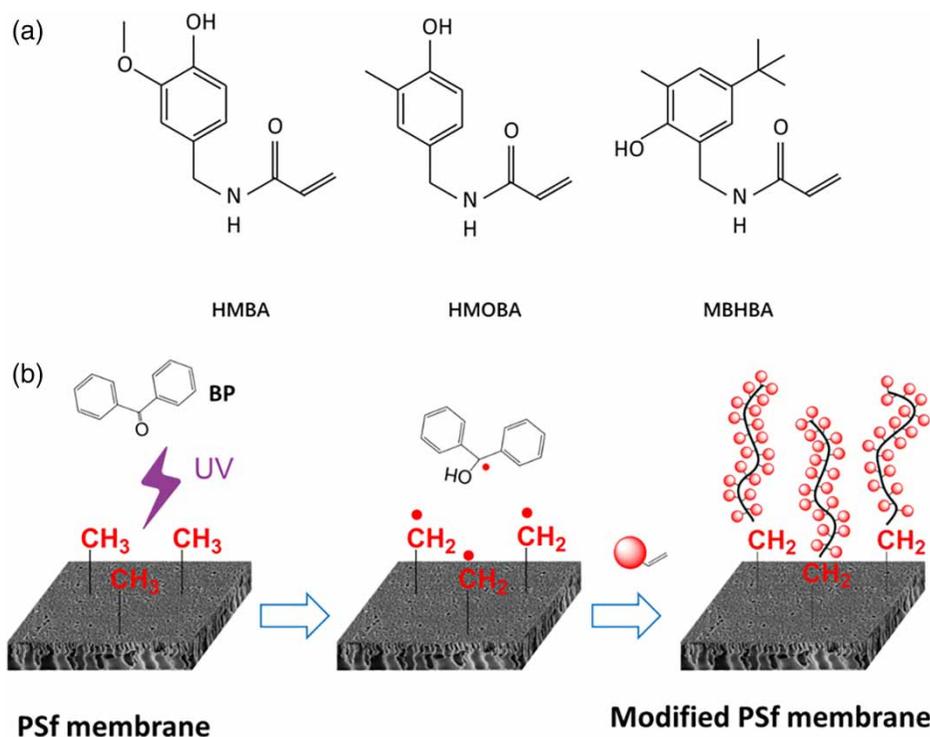


Figure 1 | Molecular structure of capsaicin derivatives used in this study (a) and reaction mechanism of UV assisted graft polymerization (b).

obtained from the School of Medicine and Pharmacy, Ocean University of China. Bovine serum albumin (BSA, MW = 67 kDa, pI = 4.7, Cat. A9647) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China).

Surface modification of PSf membranes

PSf membrane was modified as follows. Firstly, the PSf membrane was rinsed thoroughly with deionized (DI) water, followed by immersing in 90% aqueous ethanol solution for 15 min. Then the membrane was immersed in 40 mL of the deoxidized monomer solution. After that, the membrane was placed in a self-manufactured UV chamber (30 W, ~300 nm) for UV irradiation (Figure 1(b) illustrates the reaction mechanism). Finally, the modified membrane was rinsed with an aqueous ethanol solution thoroughly to remove the monomers and homopolymers on the membrane surface.

Membrane characterizations

The pristine and surface functioned membranes were dried at 30 °C in the hood for 24 h and then horizontal attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker Optics) was used to characterize their chemical composition.

Atomic force microscopy (AFM) measurements were performed on a Multimode AFM with Nanoscope V Multi-Mode controller (Veeco, USA) and the membrane surfaces were imaged in a scan size of 5 μm × 5 μm.

Static water contact angle (SWCA) was used to characterize the hydrophilicity of the membrane, which was measured by a DSA100 video contact angle system (KRÜSS, Germany) at 25 °C and relative humidity was (30 ± 2)%. The deionized water (5 μL) was dropped on the sample surface at 10 different sites, and the average of the measured values was taken as its SWCA.

Evaluation of membrane intrinsic properties

Pure water flux (J_{w0}) and BSA rejection rate (R_{BSA}) of the membranes were measured in a laboratory-scale crossflow UF unit. The effective membrane area available for permeation was 19.63 cm², the crossflow velocity was fixed at ~1.2 m/s, and the temperature was 25 ± 0.5 °C. The loaded membrane was first compacted with DI water at an applied pressure of 0.15 MPa for 40 min. Then, the applied pressure was subsequently decreased to 0.1 MPa to determine the pure water flux (PWF). After that, BSA solution prepared by dissolving 1.0 g of BSA in 1 L of phosphate buffer

saline (PBS, pH = 7.4) was used as feed solution to determine the BSA rejection rate at 0.1 MPa by measuring the absorbance of permeate and feed solution using a UV-VIS spectrophotometer (UV-2450, Shimadzu). PWF and R_{BSA} were calculated according to the following equations:

$$J_{w0} = \frac{m}{\rho \cdot A \cdot t} \quad (1)$$

where J_{w0} is pure water flux, L·m⁻²·h⁻¹; m is the weight of the permeate water of UF membranes, kg; ρ is the density of pure water at 25 °C, kg·L⁻¹; A is the effective membrane area available for permeation, m²; t is the duration of time, h.

$$R_{BSA} = \left(1 - \frac{A_p}{A_0}\right) \times 100\% \quad (2)$$

where R_{BSA} is the rejection of BSA, %; A_p is the absorbance of permeate water at 248 nm; A_0 is the absorbance of feed water at 248 nm.

Membrane fouling experiments

A crossflow membrane filtration unit and the corresponding protocol (as described in our previous work (Gao *et al.* 2013)) were used to determine the fouling reversibility of the membranes. In brief, the pure flux of UF membranes was first measured (0.1 MPa) followed by filtrate of BSA solution for 30 min (0.1 MPa). Then, fouled membranes were flushed with deionized water for 5 min (0 MPa) and pure water flux was measured again (0.1 MPa). Filtration of each membrane was repeated for three times (marked as cycle 1, cycle 2 and cycle 3).

Filtration resistance was calculated according to the data of cycle 1. According to the standard Darcy's law filtration model, water permeation rate can be described Equation (3), which can be used to calculate total resistance ($R_m + R_r + R_{ir}$) by using flux of the fouled membrane (J_{fouled}).

$$J = \frac{\Delta P}{\mu(R_m + R_r + R_{ir})} \quad (3)$$

where J is water flux, L·m⁻²·h⁻¹; ΔP is operational pressure, Pa; μ is the viscosity of water at 25 °C; R_m is the resistance of the membrane, m⁻¹; R_r is the resistance of reversible fouling, m⁻¹; R_{ir} is the resistance of irreversible fouling, m⁻¹.

Total filtration resistance ($R_{total} = R_m + R_r + R_{ir}$) were obtained from the water flux of the fouled membrane (J_{fouled}) by Equation (4):

$$R_{total} = \frac{\Delta P}{\mu \cdot J_{fouled}} \quad (4)$$

R_m was calculated out by J_{w0} because of the absence of membrane fouling. Thus, Equation (3) was simplified as Equation (5):

$$R_m = \frac{\Delta P}{\mu \cdot J_{w0}} \quad (5)$$

After cleaning, reversible fouling of the membrane was eliminated. We use the recovered pure water flux (J_{rec}) to calculate ($R_m + R_{ir}$) according to the following equation:

$$(R_m + R_{ir}) = \frac{\Delta P}{\mu \cdot J_{rec}} \quad (6)$$

Finally, R_{ir} and R_r were obtained by the operations of the equations mentioned above.

Antibacterial properties

Plate count colony-forming units (CFU) method

The antibacterial activity of the pristine and surface functionalized PSf membranes were tested as follows. Firstly, a test inoculum (*E. coli*) with a concentration of 6×10^5 cells/mL was prepared. Then, prepare six specimens, (50 ± 2) mm \times (50 ± 2) mm, for each kind of membranes and disinfected with 70% (v/v) alcohol and then placed in sterile Petri dishes. Followed by transfer 0.1 mL of testing inoculum on one membrane surface and covered with another membrane and make sure that the test inoculum does not leak beyond the edges of the membranes. After that, incubate the samples at a temperature of 308.15 K and relative humidity of not less than 95% for 24 h. Thereafter, the bacteria were recovered, followed by performing 10-fold serial dilutions, from 1 to 10,000 folds. Pour plate culture method of viable bacteria was conducted by inoculating 1 mL of the dilutions. After incubation, count the number of colonies in the Petri dishes containing 30 to 300 colonies to calculate antibacterial activity (E_b) of the corresponding membranes.

$$E_b = \frac{N_b - N_m}{N_b} \times 100\% \quad (7)$$

where N_b and N_m are the numbers of colonies corresponding to the control test and the membrane, respectively.

Morphological study of the impact of capsaicin derivatives on *E. coli*

Morphological study of *E. coli* affected by capsaicin derivatives was investigated as follows. All the membranes

(20 mm \times 20 mm) were dipped in 50 mL of *E. coli* suspension (with 6×10^5 colonies forming units per milliliter) and cultured in an incubation shaker ($r = 200$ rpm) at 37 °C for 4 h. Then the membranes were taken out and rinsed gently with PBS for three times to remove the cells that reversibly adhered to the membrane surface. Thereafter, the adhered cells were fixed with a glutaraldehyde solution (3% in volume). Following by dehydrated with sequential exposure to different concentrations of ethanol (ranging from 25% to 100%) and dried in air, the samples were gold sprayed and sent to scanning electron microscope (SEM) (HITACHI S-4800) inspection.

Antibiofouling behaviors against seawater and tap water

In order to investigate the antibiofouling properties of the membranes against seawater and tap water, we tested the membranes according to literature (Zhang *et al.* 2012). Firstly, the pristine and modified PSf membranes were dipped into tap water and raw seawater (Shilaoren Beach of Qingdao) for 30 days. The tap water and seawater were first filtrated with microfiltration membrane (0.45 μ m) before use. The pure water flux of the fouled membranes was measured with the method as described earlier. Surface morphology of fouled membranes was observed with SEM.

RESULTS AND DISCUSSION

FTIR-ATR analysis

The antibacterial activity of capsaicin derivatives could ascribe to the capsaicin derivative moieties, and FTIR is an effective way to characterize functional groups. Herein, FTIR-ATR was used to investigate the chemical composition of the pristine and modified membranes. All of the modified membranes were UV-irradiated for 6 min.

As shown in Figure 2, the absorbance peaks at $1,654 \text{ cm}^{-1}$ and $\sim 1,540 \text{ cm}^{-1}$ is corresponding to C=O stretching vibration and N-H bending vibration of secondary acid amide, separately. The enhancement of the absorbance peak at $1,290 \text{ cm}^{-1}$ and $1,270 \text{ cm}^{-1}$ represents C-N stretching vibration of secondary acid amide and C-O stretching vibration of the phenolic hydroxyl group, separately. The results mentioned above confirmed the successful graft polymerization of capsaicin derivatives on the PSf membrane surface. To distinguish membranes modified with different capsaicin derivative, the absorbance peak at $1,032 \text{ cm}^{-1}$,

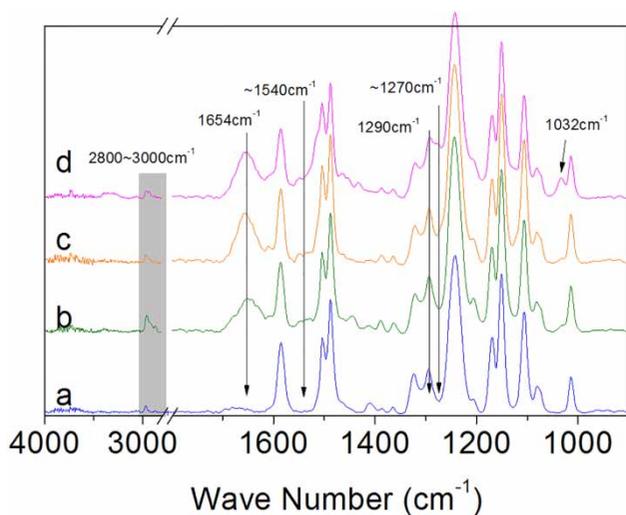


Figure 2 | ATR-FTIR spectra of the membranes: (a) PSf membrane, (b) PSf-g-pMBHBA membrane, (c) PSf-g-pHMOBA membrane, (d) PSf-g-pHMBA membrane.

which represents C-O-C stretching vibration of methyl-phenoxide (Ph-O-R), is only present in PSf-g-pHMBA membrane. MBHBA molecule contains more methyl groups and as a result, the absorbance peaks between $2,800\text{ cm}^{-1}$ and $3,000\text{ cm}^{-1}$, which corresponding to the C-H stretching vibration of methyl ($-\text{CH}_3$), of PSf-g-pMBHBA membrane are relatively stronger than that of PSf-g-pHMOBA membrane. As a conclusion, capsaicin derivatives are efficiently grafted onto the PSf membrane surface.

As the penetration depth ($\sim 1\text{ }\mu\text{m}$) of the IR wave is much higher than the grafted polymers, we considered sulfone group does not have to change in its absorbance upon grafting. Therefore, the peak height of the sulfone group at $1,151\text{ cm}^{-1}$ served as the reference. According to reference (Pieracci *et al.* 1999; Kaeselev *et al.* 2001), the degree of grafting (DG) was calculated by the peak height ratio of the carbonyl band (H_{1665}) to the reference (H_{1151}):

$$DG = \frac{H_{1665}}{H_{1151}} \quad (8)$$

The DG results of the modified membranes were listed in Table 1. The pristine PSf membrane has a very small DG value (~ 0.03) might be caused by the additives used by the supplier to produce the PSf membrane. The DG value of the modified membranes is 0.21, 0.29 and 0.30 for PSf-g-pMBHBA membrane, PSf-g-pHMOBA membrane and PSf-g-pHMBA membrane, separately. That means the UV reactivity of the capsaicin derivatives shows the order as follows: HMBA > HMOBA > MBHBA. Additionally, as reported in our previous works (Gao *et al.* 2013; Wang

Table 1 | Chemical and morphological parameters of the membranes

Membrane type	DG	WSCA (°)	Surface roughness	
			Rq/nm	Ra/nm
PSf	0.03 ± 0.01	76.7 ± 1.8	9.5 ± 0.8	7.6 ± 0.5
PSf-g-pMBHBA	0.21 ± 0.01	89.1 ± 4.8	5.9 ± 0.4	4.5 ± 0.2
PSf-g-pHMOBA	0.29 ± 0.02	64.2 ± 4.5	5.8 ± 0.4	4.6 ± 0.3
PSf-g-pHMBA	0.30 ± 0.02	57.9 ± 4.2	5.6 ± 0.3	4.4 ± 0.2

et al. 2014), the DG can be controlled by varying the UV-irradiated duration.

Membrane morphology

Surface roughness is one of the parameters for comparing different membranes, which can be correlated with membrane fouling behavior and membrane hydrophilicity (Homayoonfal *et al.* 2010). AFM images of the pristine and modified PSf membranes are illustrated in Figure 3 and the corresponding surface roughness values were listed in Table 1. Surface chemical modification of the PSf membrane resulted in the decrease of membrane surface roughness, from $R_q = 9.5\text{ nm}$ and $R_a = 7.6\text{ nm}$ of PSf membrane to $R_q = 5.6\text{--}5.8\text{ nm}$ and $R_a = 4.4\text{--}4.6\text{ nm}$ of the modified membranes. These results were contrary to other literature (Homayoonfal *et al.* 2010; Qiu *et al.* 2010), which might be caused by the grafting density of the monomers being much lower. However, SEM images indicated that due to the grafting of polymers on pore wall or membrane surface, the pore size of the membranes was decreased, which would be responsible for the decrease of the membrane surface roughness.

Membrane hydrophilicity

The average SWCA of ultrapure water on the surface of pristine and modified membranes was listed in Table 1. The pristine PSf membrane has an SWCA of 76.7° , while that of the modified membranes is 89.1° , 64.2° and 57.9° for PSf-g-pMBHBA membrane, PSf-g-pHMOBA membrane and PSf-g-pHMBA membrane, respectively. The results indicate that MBHBA endows PSf membrane a more hydrophobic surface while HMOBA and HMBA endow PSf membrane a more hydrophilic surface. As in literature (Lu *et al.* 2013), the microstructure and the chemical composition of the membrane surface are mainly responsible for membrane hydrophilicity. For modified membranes in this work, as their surface roughness are similar to each other,

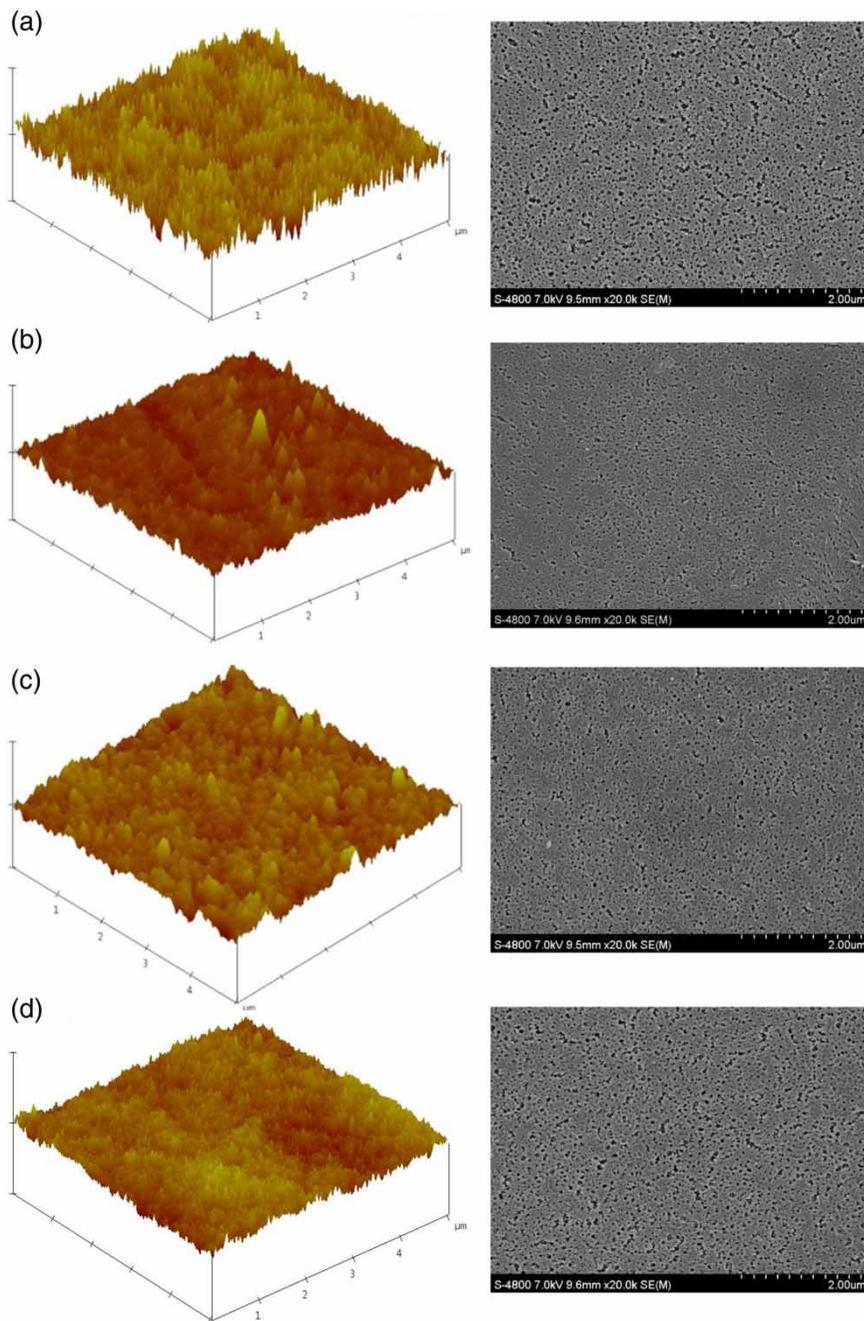


Figure 3 | AFM images (a1-d1) and SEM images (a2-d2) of the pristine and modified membranes: (a) PSf membrane, (b) PSf-g-pMBHBA membrane, (c) PSf-g-pHMOBA membrane, (d) PSf-g-pHMBA membrane.

the change of hydrophilicity is dependent on the surface chemical composition.

Membrane permeability

Figure 4 illustrated the pure water flux and BSA rejection rate of the pristine and modified PSf UF membranes. There is a

significant change in membrane permeability. After surface modification, pure water flux is decreased from $1,457 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $1,000\text{--}1,160 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ while the BSA rejection rate is increased from 76% to 80–83%. These results are induced by the change of pore size and membrane hydrophilicity. Among modified membranes, PSf-g-pMBHBA membrane has the biggest pore size but the smallest pure

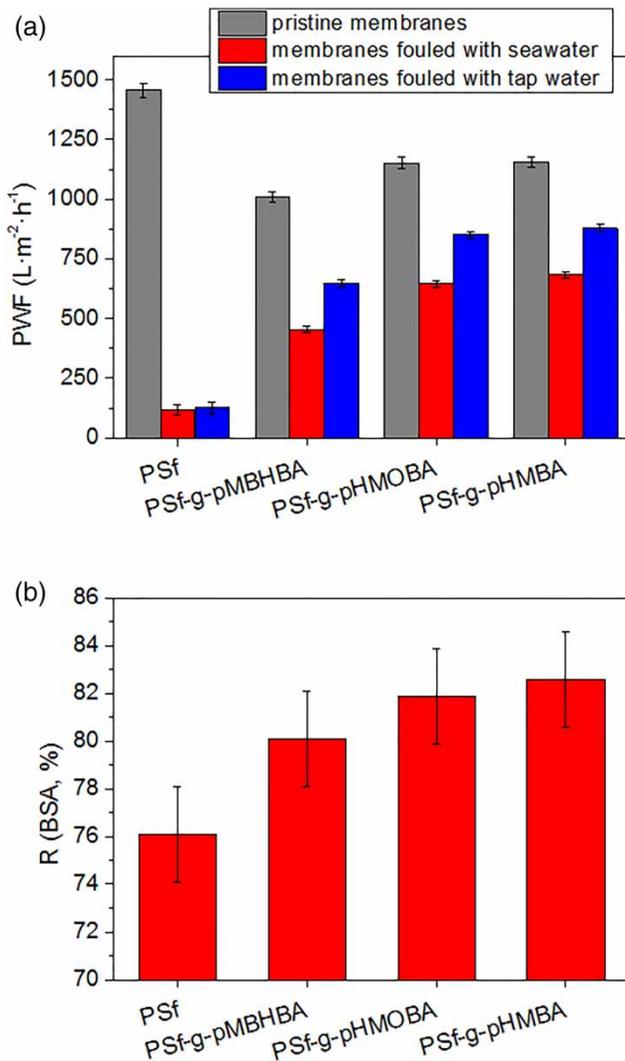


Figure 4 | Pure water flux (PWF) of the neat and fouled membranes (a) and BSA rejection rate of the neat membranes (b).

water flux, which might be caused by the hydrophobicity of the membrane surface. The observations mentioned above imply that UV modification is nondestructive.

Antifouling performances

The antifouling behavior of the pristine and modified PSf membranes was measured with a laboratory-scale device as the method in our previous work. The operation process can be divided into three phases: the first 5 min in the curve is referred to pure water filtration; the following 30 min ultrafiltration of BSA solution; the third phase is membrane cleaning by pure water flushing for 5 min. Time-dependent water flux and normalized water flux of membranes to filtrate BSA solution (1 g/L in PBS solution) are illustrated

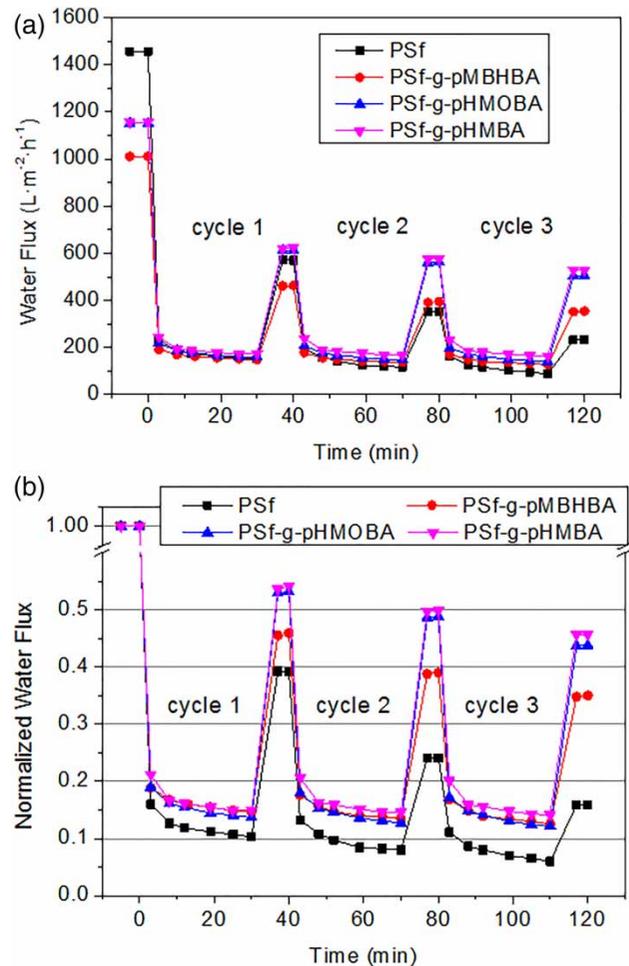


Figure 5 | Time-dependent water flux of the pristine and modified membranes when filtrate BSA solution (1 g/L in PBS solution): (a) water flux and (b) normalized water flux. Test protocol: in each cycle, the first 5 min is referred to pure water filtration, followed by ultrafiltration of BSA solution for 30 min. At last, the membrane is cleaned by pure water for 5 min.

in Figure 5. As can be seen, there is an accentuated flux decline when BSA solution was introduced. This is due to the deposition of BSA on the membrane surface, which lead to an increase in water transport resistances. It is clear that membranes modified with capsaicin derivatives show enhanced antifouling property. Even the initial water flux of the membranes was somewhat changeable, and they became comparable only after 2 min of filtration. Therefore, these data can serve as evidence that the modified membranes have better antifouling performance.

To further evaluate membrane fouling behavior, pure water flux (J_{wo}), the flux of the fouled membrane (J_{fouled}) and cleaned membrane (J_{rec}) in cycle 1 (Figure 5(a)) is used to calculate membrane resistance according to Equations (4)–(6). Values of total membrane resistance (R_{total}), pristine membrane resistance (R_m), reversible

Table 2 | Membrane fouling behavior of pristine and modified membranes

Membrane type	R_{total}		R_m		R_r		R_{ir}	
	$\times 10^{11} m^{-1}$	%	$\times 10^{11} m^{-1}$	%	$\times 10^{11} m^{-1}$	%	$\times 10^{11} m^{-1}$	%
PSf	26.82	100.00	2.76	10.29	19.75	73.64	4.31	16.07
PSf-g-pMBHBA	26.70	100.00	3.98	14.91	18.31	68.58	4.71	17.64
PSf-g-pHMOBA	25.46	100.00	3.49	13.71	18.88	74.16	3.08	12.10
PSf-g-pHMBA	23.52	100.00	3.48	14.80	17.11	72.75	2.94	12.50

Note: The data in this table were calculated according to cycle 1 (in Figure 5(a)). R_{total} , R_m , R_r and R_{ir} means total filtration resistance, the resistance of the membrane, the resistance of reversible fouling and the resistance of irreversible fouling.

membrane fouling resistance (R_r) and irreversible membrane fouling resistance (R_{ir}) are listed in Table 2. R_m of modified membranes is increased from $2.76 \times 10^{11} m^{-1}$ of the PES membrane to $3.98 \times 10^{11} m^{-1}$, $3.49 \times 10^{11} m^{-1}$ and $3.48 \times 10^{11} m^{-1}$ of PSf-g-pMBHBA membrane, PSf-g-pHMOBA membrane and PSf-g-pHMBA membrane, respectively. These would be contributed to by the minimization of the membrane pore size and variation of membrane hydrophilicity derived from surface grafting. After being fouled by BSA, membrane filtration resistance of the modified membranes decreased. However, PSf-g-pMBHBA membrane showed an increased R_{ir} and a decreased R_r compared to the PSf membrane, indicating its worse antifouling property. PSf-g-pHMOBA membrane and PSf-g-pHMBA membrane showed a decrease in R_{ir} , indicating their better antifouling property. These results were highly dependent on the membrane wettability induced by grafting of capsaicin derivatives, of which the MBHBA-modified membrane showed a significant decrease in wettability, while HMOBA and HMBA modified membranes showed an increase in wettability. As the hydrophobic surface tends to adsorb pollutants, which would act as an interlayer between microorganisms and antibacterial agents and, at last, result in a less antibacterial surface. Therefore, to endow the membrane surface with enhanced antibiofouling performance, HMBA and HMOBA are the best choices.

Antibacterial activities

Antibacterial activity of PSf membranes modified with capsaicin derivatives was investigated and compared. As described in Table 3, the three membranes show similar antibacterial activity, where PSf-g-pHMOBA membrane exhibits the best antibacterial efficiency, followed by PSf-g-pMBHBA membrane and PSf-g-pHMBA membrane. This order is not corresponding to the DG of the corresponding membranes, which showed an order of

Table 3 | Antibacterial efficiency of the membranes against *E. coli*

Membrane type	Loading CFU	CFU after incubating for 24 h	Antibacterial efficiency/%
PSf	$\sim 6 \times 10^4$	$(4.85 \pm 0.27) \times 10^4$	-
PSf-g-pHMBA	$\sim 6 \times 10^4$	43 ± 13	99.911 ± 0.034
PSf-g-pHMOBA	$\sim 6 \times 10^4$	32 ± 12	99.934 ± 0.030
PSf-g-pMBHBA	$\sim 6 \times 10^4$	35 ± 15	99.928 ± 0.037

DG(HMBA) > DG(HMOBA) > DG(MBHBA). We considered that the different structure of the three kinds of capsaicin derivatives is responsible for it. Yu suggested (Liangmin 2004) that the phenolic hydroxyl group is the key point that capsaicin derivatives can exhibit antibacterial activity. Sun *et al.* (Junshe & Decong 1996) investigated the structure dependence of phenols on their antibacterial activity via the computational approach of quantum chemistry. They found that weaker electron-donating groups will lead to a larger partial moment of the dipole, which will increase the antibacterial activity of phenols. We considered that alkyl groups are much weaker electron-donating groups compared to alkoxy groups. Capsaicin derivatives with alkyl groups, therefore, may be having much better antibacterial activity. As a result, the three membranes show similar antibacterial activity even with different DG values.

Capsaicin could change the cytomembrane fluidity to exert antibacterial activity and led to the disruption of the cell cytomembranes (Cowan 1999; Tsuchiya 2001), which would change the morphology of bacteria cells. We selected *E. coli* as test strains to investigate cell morphology changes on the pristine and modified membrane (as shown in Figure 6). As in our previous work (Wang *et al.* 2014), cells on the pristine membrane surface showed a smooth and regular surface, while cells on the surface of modified membranes showed disruption or deformation of the cells. The penetration of capsaicin derivatives into the cells that lead

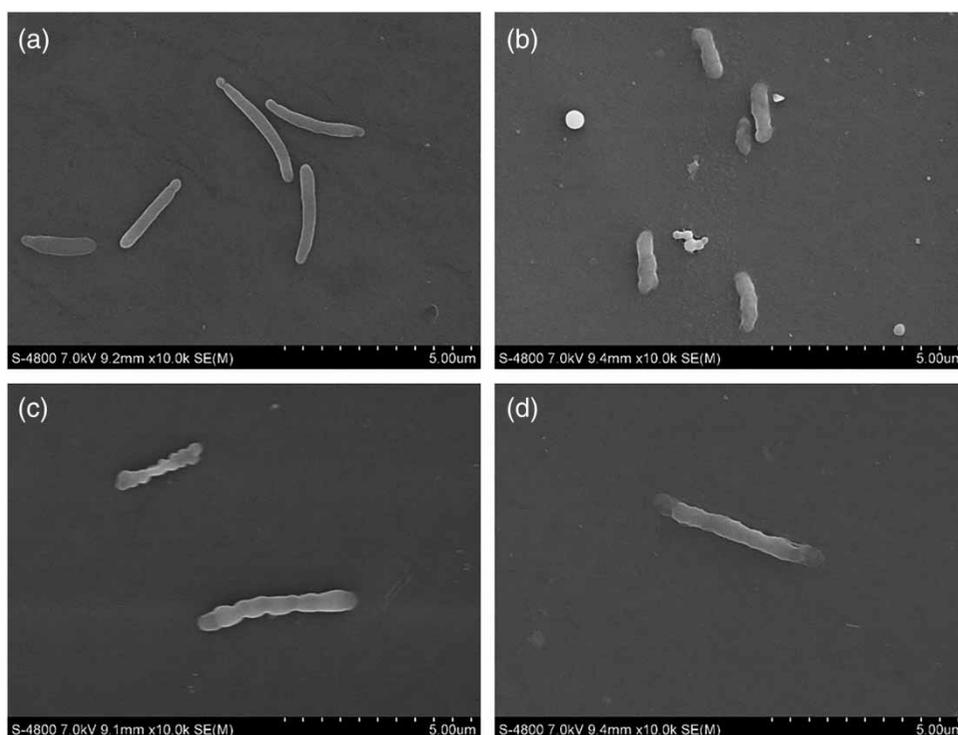


Figure 6 | Morphological inspection of *E. coli* on the membrane surface: (a) PSf membrane, (b) PSf-g-pMBHBA membrane, (c) PSf-g-pHMOBA membrane, (d) PSf-g-pHMBA membrane.

to the release of cellular content is responsible for their antibacterial activity. This observation is in accordance with other literature (Bajpai *et al.* 2009; Perreault *et al.* 2013) and provides sufficient evidence for membranes' antibiofouling potential.

Antifouling behaviors against seawater and tap water

The practicability of membranes modified with capsaicin derivatives was further investigated by dipping into tap water and seawater for 30 days. As illustrated in Figure 7, the pristine membrane was covered with a thick layer of foulant, while that on the modified membranes was much thinner, indicating the capsaicin derivatives endow PSf membranes with better antifouling properties by changing their surface properties, such as antibacterial activity, wettability (Chapman Wilbert *et al.* 1998; Al-Juboori & Yusaf 2012) and roughness (Al-Juboori & Yusaf 2012). Increase in the hydrophilicity and decrease in the roughness of the membrane surface can lead to a decline in the attachment of foulants and microorganisms (Chapman Wilbert *et al.* 1998; Al-Juboori & Yusaf 2012) while enhancing the antibacterial activity can lead to the death of adhered cells. The antibacterial activities of the membranes, as shown in Table 1, were almost the same, thus the hydrophilicity and

roughness of the membrane surface would give a significant impact on membrane biofouling formation. In this study, the hydrophilicity of the membrane is changed remarkably, which is the main reason that the membrane with the best antibacterial properties is not the one showing the best antifouling properties. Therefore, as shown in Figure 7, HMBA-modified membrane showed the best antifouling performance, followed by HMOBA- and MBHBA-modified membranes, successively. This will reduce chemical cleaning frequency of the membrane process by enhancing its operational stability and reliability, which are also benefits to environmental protection by reducing pollutant discharge. It should be noted that the thick foulant layer in Figure 7(a-1) is very complicated because it contains not only microorganisms but also other pollutants.

We also measured the pure water flux of membranes fouled with seawater and tap water and the results were shown in Figure 4(a). The pure water flux of the PSf membrane decreased by 92% (from $1,457 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to less than $150 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) after one-month exposure to seawater and tap water, while that of the modified membranes decreased only by around 50%. The above result provides additional evidence that membranes modified with capsaicin derivatives endow much better antifouling properties.

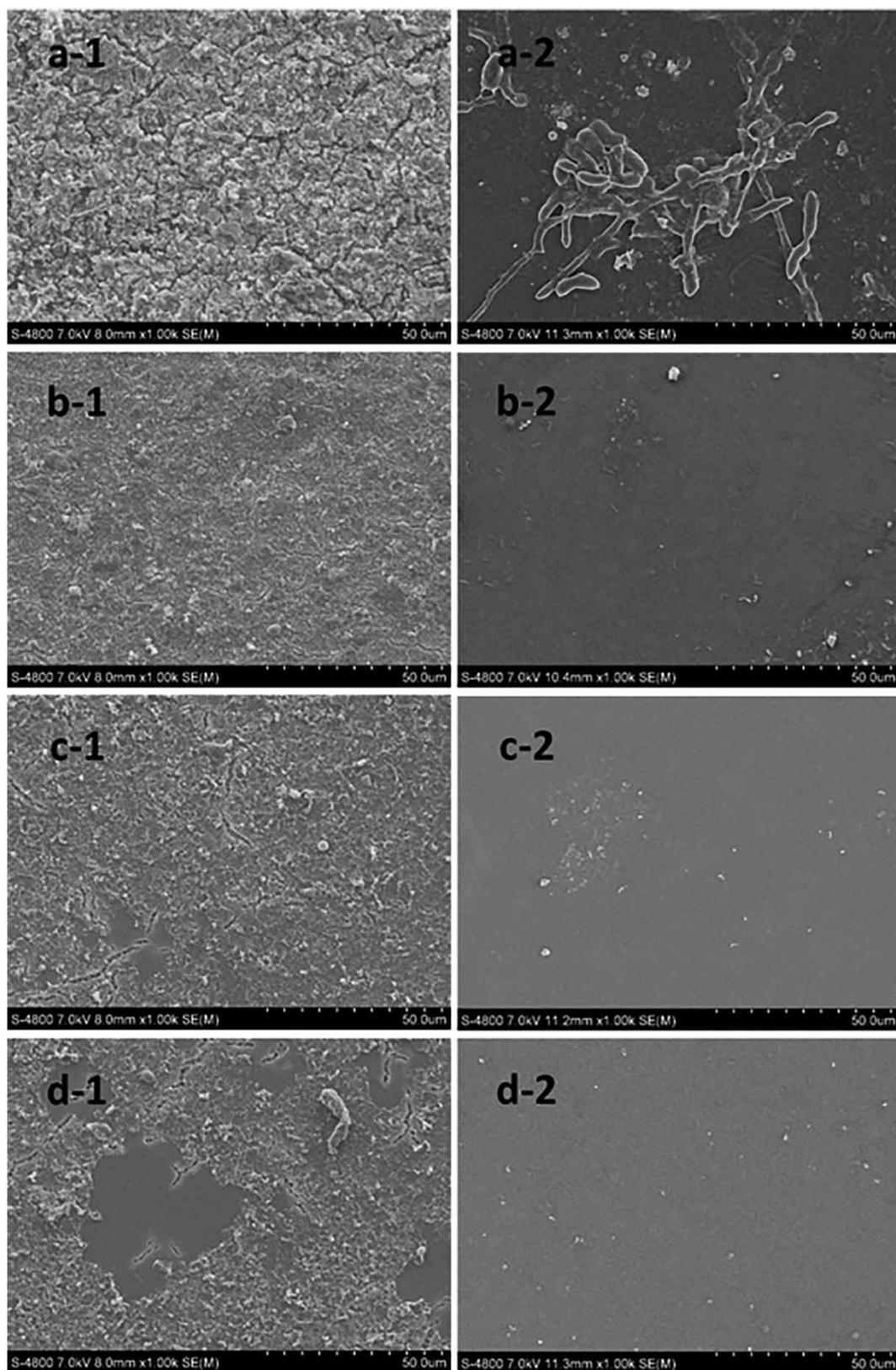


Figure 7 | SEM images of membranes immersed in seawater (a-1–d-1) and tap water (a-2–d-2) for 30 days: PSf membrane, (b) PSf-g-pMBHBA membrane, (c) PSf-g-pHMOBA membrane, (d) PSf-g-pHMBA membrane.

CONCLUSIONS

This paper demonstrated the fabrication of PSf antibiofouling membranes via surface grafting of capsaicin derivatives. Three kinds of capsaicin derivatives were used and their influences on membrane properties were compared. The main conclusions are as follows:

- (1) Capsaicin derivatives are successfully grafted on the membrane surface. This resulted in a decrease in membrane water flux and increase in BSA rejection rate.
- (2) The MBHBA-modified membrane has a more hydrophobic surface, while the HMBA- and HMOBA-modified membranes show more hydrophilic surfaces. As a result, the proportion of irreversible fouling of MBHBA-modified membrane is increased.
- (3) Modified PSf membranes show the efficient antibacterial activity against *E. coli* (more than 99.9% of the cells were killed). The practicability of the modified membranes was investigated by dipping them into tap water and seawater for 30 days, and the results are indicating that the HMBA-modified PSf membrane shows the best antibiofouling property, followed by HMOBA-modified membrane and MBHBA-modified membrane, successively.

The results of this research demonstrated that surfaces modified with capsaicin derivatives have great potential to relieve membrane biofouling. Meanwhile, they can also be used to prepare antibiofouling nanofiltration membranes, reverse osmosis membranes and forward osmosis membranes, etc.

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China (no. 21576250), the financial support from the Public Science and Technology Research Funds Projects of Ocean (201505021), the Yantai '13th Five-Year Plan' Marine Economy Innovation Demonstration Project (YHCX-HS-L-201707), the Young Taishan Scholars Program of Shandong Province and Special Fund for Basic Scientific Research Business of Central Public Research Institutes (K-JBYWF-2016-T14).

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First received 27 September 2018; accepted in revised form 18 May 2019. Available online 25 May 2019