A novel method of surface modification to polysulfone ultrafiltration membrane by preadsorption of citric acid or sodium bisulfite

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Abstract. In membrane processes, various agents are used to enhance, protect, and recover membrane performance. Applying these agents in membrane modification could potentially be considered as a simple method to improve membrane performance without additional process. Citric acid (CI) and sodium bisulfite (SB) are two chemicals that are widely used in membrane feed water pretreatment and cleaning processes. In this work, preadsorptions of CI and SB were developed as simple methods for polysulfone ultrafiltration membrane modification. It was found that hydrogen bonding and Van Der Waals attraction could be responsible for the adsorptions of CI and SB onto membranes, respectively. After modification with CI or SB, the membrane surfaces became more hydrophilic. Membrane permeability improved when modified by SB while decreased a little when modified by CI. The modified membranes had an increase in PEG and BSA rejections and better antifouling properties with higher flux recovery ratios during filtration of a complex pharmaceutical wastewater. Moreover, membrane chlorine tolerance was elevated after modification with either agent, as shown by the mechanical property measurements.

Keywords: ultrafiltration; modification; citric acid; sodium bisulfite; membrane property

1. Introduction

Ultrafiltration (UF) has become a very important technology for concentration, purification, and fractionation in diverse fields such as food, textile, pharmacy, chemical, paper, and leather industries (Cheryan 1998). However, successful application of UF technology is greatly limited by membrane fouling. To mitigate this problem and promote UF technology applications, surface modification has been considered as a potential route to prepare membranes with better antifouling properties by improving the hydrophilicity, roughness, and/or charge properties of membrane surface. Various modification methods including physical adsorption and chemical bond formation were used by researchers (Basri 2011, Boributh 2009, Brink 1993, Chinpa 2010, Hosseini 2010, Kang 2008, Kavitskaya 2005, Ma 2007, Morel 1997, Pal 2008, Reddy 2003, Yu 2009). Considered a long-term

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effect, covalent grafting by chemical coupling (Chinpa 2010, Ma 2007), UV-induced (Kang 2008, Yu 2009) or plasma-initiated methods (Hosseini 2010, Pal 2008) were desirable to increase antifouling properties. However, most of these approaches need special instruments or modification conditions that restrict their applications. In comparison, adsorption of modification agents through Van Der Waals attraction and/or hydrogen bonding is a simple method to improve membrane properties (Brink 1993, Boributh 2009, Guo 2010, Kavitskaya 2005, Morel 1997, Reddy 2003). It has been reported by Reddy (Reddy 2003) that the polyethersulfone UF membrane, modified by physical adsorption of poly (sodium 4-styrenesulfonate), showed improved antifouling properties. In Fan's work (Fan 2008), the preadsorption of polyaniline nanofiber to polysulfone (PS) UF membrane through hydrogen bonding also dramatically improved membrane permeability. Although adsorption methods suffer from the loss of modification agents as filtration time increases, the modification process can simply be repeated.

In membrane feed water pretreatment and cleaning processes, there are various agents applied to control membrane fouling. The impacts of the applied agents on membrane properties have been discussed in section 1.1. Citric acid (CI) and sodium bisulfite (SB) are widely used in membrane feed water pretreatment and cleaning processes (see section 1.2). From our experiment results, it is interesting to point out that the adsorption of CI or SB to PS UF membrane can improve membrane rejection, achieve better antifouling property, and prevent degradation of PS membrane by bleach solution.

Hence, prefiltrations of CI and SB solutions were developed as novel and easy methods for PS UF membrane surface modification in this work. The changes in membrane chemical composition were evaluated by attenuated total reflectance spectra-Fourier transform infrared spectrometry (ATR-FTIR). Membrane surface Hydrophilicity was characterized by contact angle measurements. Membrane permeability and rejection were tested, and antifouling properties were evaluated using UF experiments with a complex pharmaceutical wastewater as the feed. In addition, an accelerated ageing of the membrane was simulated by soaking it in the sodium hypochlorite solution with concentration of 400 ppm at pH 8. Membrane mechanical properties including tensile strength at break point (Ts) and elongation at break point (El) were measured to characterize membrane chlorine tolerance, as Ts and El showed high sensitivities to PS membrane degradation (Causserand 2008, Gaudichet-Maurin 2006, Rouaix 2006).

1.1 Impact of applied agent on membrane properties in membrane process

In membrane processes, there are two prevalent methods used to control membrane fouling. The one is feed water pretreatment by chlorination, coagulation/flocculation, dechlorination, acidification, and antiscalant dosing, etc. (Al-Amoudi 2007, Liikanen 2002, Maartens 2002, Zhao 2006). The other is membrane cleaning after fouling with chemicals such as acids alkalis, surfactants, oxidants, metal chelating agents, and enzymes, etc. (Al-Amoudi 2007, Liikanen 2002, Maartens 2002). Pretreatment and/or cleaning with proper agents under optimized conditions will maximize efficiency and membrane lifetime by minimizing fouling, scaling, and membrane degradation. A large number of agents are available for feed water pretreatment and chemical cleaning. It is inevitable that these applied agents directly contact polymer-based membrane. Some agent-membrane combinations are incompatible and result in irreversible loss of membrane performance, and/or even reduce membrane lifetime (Maartens 2002). However, there are other agents that are compatible with membrane and improve membrane properties such as permeability (Nyström 1997, Zhu 1998) and

rejection (Wilbert 1998).

Oxidants such as sodium hypochlorite, chlorine dioxide, hydrogen peroxide, and chloramines, which are effective in reducing membrane biofouling, are frequently used in feed water pretreatment and membrane cleaning processes. When oxidants are contacted with polymer-based membranes, oxidation and hydrolysis of the polymers can cause the changes in membrane properties (Causserand 2008, Gaudichet-Maurin 2006, Gitis 2006, Rouaix 2006). Exposure of PS membranes to chlorine at a fairly high concentration leads to degradation of the PS membranes with obvious declines in membrane mechanical properties (Ts and El), which is believed to be caused by the chain scission in PS molecules (Causserand 2008, Gaudichet-Maurin 2006, Rouaix 2006). The most probable locations of the scission are at the sites of sulfone and isopropylidene bridges (Gaudichet-Maurin 2006).

Nonionic and ionic surfactants are widely used in membrane cleaning process to remove organic/ inorganic foulants (Al-Amoudi 2007, Liikanen 2002). They are also applied in feed water pretreatment process to enhance membrane inorganic ion rejections (Christian 1998, Morel 1997). Impacts of surfactants on membrane properties were studied in references (Doulia 1997, Field 1994, Jönsson 1991, Mietton-peuchot 1996, Wilbert 1998). It was found that even at a very low concentration (below critical micelle concentration), surfactant might interact with membrane. For example, when surfactant was in monomer form, the hydrophobic part of surfactant was adsorbed to membrane while the hydrophilic part was directed towards aqueous solution, resulting in an increase in membrane surface hydrophilicity. On the other hand, as the surfactant was adsorbed to membrane, the membrane pore sizes decreased, which reinforcing membrane steric hindrance (Field 1994, Mietton-peuchot 1996). Wilbert *et al.*(1998) studied the effects of elevated hydrophilicity and reinforced steric hindrance after adsorption of surfactant to membrane. Their results indicate that a cost saving was possible due to the flux and salt rejection improvements exhibited after modification with surfactant.

As discussed above, the agents applied in membrane processes may cause the changes in membrane properties. This point is worthy of attention, since a better understanding of the impacts of the applied agents on membrane properties in membrane process could be helpful to better application of the agents in fouling control. Moreover, the favorable interactions between the applied agents and membrane could potentially be developed as a simple membrane modification method, i. e., the membrane can be modified by prefiltration of the agent solution without additional process.

1.2 Properties of CI and SB

The molecular structural formulas of CI, SB, and PS were shown in Table 1.

CI is a common organic acid which is widely present in citrus fruits and pineapples. It is frequently used as an antioxidant in bleach solution and as a cleaning agent in membrane process (Gabelich 2005, The Dow Chemical Company 2011). Antioxidants are electron donors, which preferentially react with free radicals. Their activity depends mainly on the number and positions of hydroxyl groups within the molecule. As a multi-carboxylic molecule, CI has high activity in reaction with free radicals by chain transfer or termination, to prevent propagation reactions in an oxidation process (see Eqs. (1)-(4)) (Causserand 2008).

$$C_3H_4(OH)(COOH)_3 + HO\bullet \rightarrow H_2O + C_3H_4(O\bullet)(COOH)_3 \quad\quad (1)$$

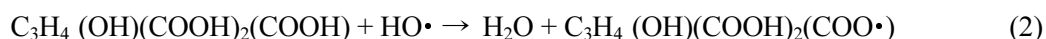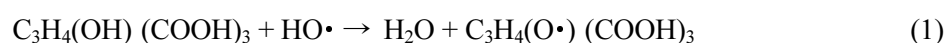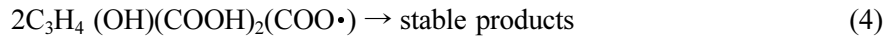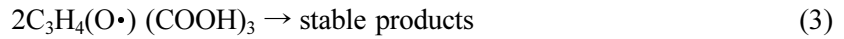$$C_3H_4(OH)(COOH)_2(COOH) + HO\bullet \rightarrow H_2O + C_3H_4(OH)(COOH)_2(COO\bullet) \quad\quad (2)$$

Table 1 Structure formulas of citric acid, sodium bisulfite, and polysulfone

Matter	Abbreviation	Structural formula
Citric acid	CI	HO, OH, OH, O, O, OH (citric acid structure)
Sodium bisulfite	SB	HO–S(=O)–ONa
Polysulfone	PS	polysulfone repeating unit with SO_2, ether, $C(CH_3)_2$ groups, subscript n

$$2C_3H_4(O\bullet)(COOH)_3 \rightarrow \text{stable products} \qquad (3)$$

$$2C_3H_4(OH)(COOH)_2(COO\bullet) \rightarrow \text{stable products} \qquad (4)$$

CI is used alone as a cleaning agent in membrane process due to its acidity. For example, with concentration of 0.5~3.0 wt.% is thought to be effective in removing metal oxides and calcium carbonate scale from membrane surface (The Dow Chemical Company 2011).

SB is generally used to remove free chlorine from feed water, and can also be used as a biocide in membrane process (Gabelich 2005, The Dow Chemical Company 2011). It reduces hypochlorous acid according to Eq. (5).

$$NaHSO_3 + HOCl \rightarrow HCl + NaHSO_4 \qquad (5)$$

The shock treatment, which is the addition of a biocide into the feed stream during normal plant operation for a limited time period, is considered as an effective way to control biofouling. In a typical application, SB solution with concentration of 0.05~0.1 wt.% is dosed into the feed stream for 30 min (The Dow Chemical Company 2011). When the system must be shut down for a long time, SB solution with concentration of 0.5~1.0 wt.% has been proven effective to control biological fouling for membrane module. Colloidal fouling has also been reduced by this method. As a side benefit, no acid is required for calcium carbonate control because of the acidic reaction of bisulfite (see Eq. (6)).

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \qquad (6)$$

Both CI and SB contain hydroxyls in the molecular structures. Hydrogen bonds could form between the hydroxyls of CI or SB and the strong electronegative groups such as oxygen in the ether bond and sulfone group in the main chain of PS (Schuster 1976, Yoon 2006). Such hydrogen binding could reinforce the adsorption of CI or SB to PS UF membrane, and thus causes changes in membrane properties. Thus, it is expected that PS UF membrane modified by CI or SB might have relatively stable structure.

2. Experimental

2.1 Materials

Flat-sheet asymmetric PS UF membranes with nominal molecular weight cut off (MWCO) of 30,000 were purchased from Hangzhou Development Center of Water Treatment Technology (China). Analytical grade CI and SB were purchased from Tianjin Kewei Co. (China) and used without further purification. Bovine serum albumin (BSA, molecular weight 67,000) was electrophoretically pure and purchased from Tianjin Zhengjiang High-technology Company. Polyethylene glycol (PEG, molecular weight 35,000) was purchased from Sigma-Aldrich. Pharmaceutical wastewater was supplied by a pharmaceutical company in Shijiazhuang (China). The wastewater, whose water quality are shown in Table 2, contained large amounts of organics (sugar, proteins, starches, fats, amino acids, nucleic acids, and antibiotic residuals) and inorganic materials (inorganic particles, monovalent and divalent ions). Pure water with conductivity less than 10 μs/cm was produced by a two stage reverse osmosis system.

2.2 Membrane modification procedures

The new membrane surfaces may contain monomer residues, additives and other contaminants. In order to remove these substances, the membranes were cleaned using the following sequence: (1) the membranes were immerged into 0.2 wt.% sodium carbonate solution for 2 h; (2) after being rinsed with pure water, the membranes were soaking in 2.0 wt.% isopropyl alcohol solution for 2 h; and (3) the membranes were rinsed and immerged in pure water overnight before use.

After the above cleaning, the membrane pieces with effective filtration area of 66.47 cm^2 were pre-compacted under transmembrane pressure (TMP) of 0.3 MPa with a laboratory-scale crossflow test unit (Fan 2008). Then, the membrane pure water fluxes were measured under TMP of 0.15 MPa, crossflow velocity of 0.22 m·s^{-1}, and temperature of 25°C. Those membranes with pure water flux measurement fluctuations lower than 5% (relative to average) were denoted as "unmodified membranes" and chosen to do the following modification experiments.

The membranes were modified by filtration of the aqueous solutions of CI or SB under TMP of

Table 2 Composition of a pharmaceutical wastewater

Item	Value[a]	Item	Value[a]
pH	7.8	Temperature/^{o}C	25
Turbidity/NTU	7.28	Chroma/Pt-Co	682
Conductivity/μs·cm^{-1}	3910	COD/mg L^{-1}	399.2
K$^+$/mg L^{-1}	110.8	BOD$_5$/mg L^{-1}	37.3
Ca^{2+}/mg L^{-1}	170.9	NH$_3$-N/mg L^{-1}	13.5
Na$^+$/mg L^{-1}	469.1	P/mg L^{-1}	13.8
Mg^{2+}/mg L^{-1}	17.2	SO$_4^{2-}$/mg L^{-1}	998.4
Fe^{2+}/Fe^{3+}/mg L^{-1}	1.56	HCO$_3^-$/mg L^{-1}	506.5
Ba^{2+}/mg L^{-1}	0.009	Cl$^-$/mg L^{-1}	167.5
SiO$_2$/mg L^{-1}	7.18	Br$^-$/mg L^{-1}	27.3

[a]The test temperature applied is 25°C

0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, and temperature of 25°C. The concentration of CI or SB solution was maintain at 1.0 wt.% by adding fresh solution every 30 min. After 240 min filtration, the membranes were cleaning with pure water and denoted as "modified membranes".

2.3 Characterizations of CI/SB modified membranes

2.3.1 Membrane chemical composition tests

Unmodified and modified membrane samples were rinsed three times by pure water and dried at 40°C in vacuum. Then, the changes in chemical bonds on membrane surfaces were analyzed by FTIR (MAGNA-560, Thermo Nicolet Corp., USA) with an ATR unit (ZnSe crystal, 45°). The infrared spectra were recorded in wave number range of 400-4000 cm^{-1}.

2.3.2 Surface static contact angle measurements

The hydrophilicity of membrane surface was characterized based on water contact angle measurement with sessile drop method. Contact angles were measured at room temperature by a contact angle goniometer (OCA15EC, Dataphysics, Germany) equipped with a video camera. A total of 2 μL pure water droplet was placed on a dry membrane surface using a motor-driven microsyringe. SCA 202 software was used to calculate the static contact angle (Duan 2010). The sample preparation for contact angle measurement was as follows. The membrane samples were washed with pure water for three times. Then, the contact angles of all the membrane samples were measured immediately after they were conditioned overnight at 40°C with relative humidity of 50% and cooled to room temperature. In order to minimize the inaccuracy of measurement, at least eight contact angles on different locations of the membrane samples were averaged to get a reliable result.

2.3.3 Surface pore size and porosity measurements

Membrane pore sizes were determined by the frozen temperature of water in membrane pores using Differential Scanning Calorimetry (DSC, PerkinElmer, USA) (Fan 2008). 10-20 mg membrane sample was put in a sealable aluminum pan before one drop of pure water was added to keep excess water in the pan. Then, the pan was cooled down to 258 K at a rate of 0.5 K/min. The pore radius distribution curves were obtained using the following expressions (Iza 2005)

$$R_P = -\frac{64.67}{\Delta T} + 0.57 \tag{7}$$

$$W_a = -5.56 \times 10^{-2} \Delta T^2 - 7.43 \Delta T - 332 \tag{8}$$

$$\frac{dV}{dR_P} = \frac{m}{64.67k} \frac{\Delta T^2}{W_a} \gamma \tag{9}$$

where R_P, ΔT, W_a, m, k, V, and γ are pore radius, temperature shift, apparent energy of water solidification, sample weight, cooling rate, pore volume, and heat flow, respectively.

For the test of membrane porosity (ε), wet membrane samples were weighed before being dried in vacuum until a constant mass was obtained. The ε was determined by the mass loss of wet membrane after drying, as described in Eq. (10) (Fan 2008, Xu 2002).

$$\varepsilon = \frac{(m_w - m_d)/\rho}{AL} \tag{10}$$

where m_w is the weight of wet membrane sample, and m_d is the weight of dry membrane sample. A, L, and ρ are membrane sample area, membrane sample thickness, and pure water density, respectively.

2.3.4 Filtration studies

Pure water, BSA aqueous solution (pH 7), and PEG aqueous solution (pH 7) were used as feed to test membrane permeability and rejection under TMP of 0.15 MPa, crossflow velocity of 0.22 m·s^{-1}, and temperature of 25°C. An UV-vis spectrometer (8453E, HP) was used to determine BSA and PEG concentrations.

Membrane fouling behaviors were studied through ultrafiltration experiments with a pharmaceutical wastewater (see Table 2) for three cycles. In every cycle, the pure water flux was first measured under the test conditions described above and denoted as J_{iw}, then treatment of pharmaceutical wastewater was conducted under TMP of 0.15 MPa, crossflow velocity of 0.22 m·s^{-1}, and temperature of 25°C. After 2 h operation, the membrane was cleaned by pure water for 30 min under TMP of 0.1 MPa, crossflow velocity of 0.34 m·s^{-1}, and temperature of 25°C. The pure water flux was measured in the final step and denoted as J_w. In order to evaluate membrane antifouling property, flux recovery ratio (FRR) was calculated using the following expression

$$FRR(\%) = \frac{J_w}{J_{iw}} \times 100\% \tag{7}$$

2.3.5 Degradation studies

Sodium hypochlorite (NaClO) solution with concentration of 400 ppm at pH range of 8-10 was confirmed to accelerate the degradation of PS membrane (Causserand 2008, Gaudichet-Maurin 2006, Rouaix 2006). In the present study, NaClO with concentration of 400 ppm at pH 8 was prepared to test the membrane chlorine tolerance. The unmodified and modified membrane samples were exposed to NaClO solution under light-proof conditions for 0, 2, 4, 6, 8 10, and 15 days. The NaClO solution was replaced by new solution every 2 days. Membrane mechanical properties (Ts and El at break) were measured using a DMA Q800 (TA Instruments, USA) at 25°C, after being rinsed by pure water and dried in the air. In order to minimize the inaccuracy of measurement, at least four Ts (or El) measurements on the same type of membrane sample were averaged to get a reliable result.

3. Results and discussion

3.1 ATR-FTIR analysis

As shown in Fig. 1, in general, unmodified and modified membranes have very similar infrared absorption bands at the wave number range of 650-2000 cm^{-1}. The similarity of the infrared spectra over this range confirmed that the membranes had the same basic structure of PS after modification with CI or SB.

Table 3 provides probable assignments of infrared absorption bands for unmodified and modified
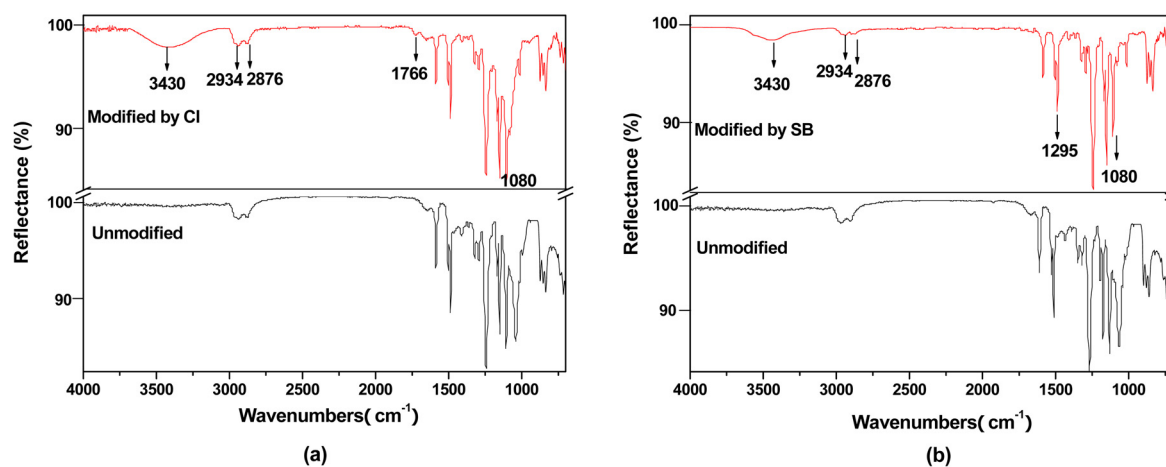
Fig. 1 ATR-FTIR analyses comparing modified with unmodified PS membranes: (a) membrane modified by CI vs. unmodified one; and (b) membrane modified by SB vs. unmodified one. Modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, the agent solution concentration of 1.0 wt.%, temperature of 25ºC, and time of 240 min

Table 3 Possible assignments of the IR spectra of unmodified and modified PS membranes

Band frequency (cm^{-1}) for PS membrane			Spectra assignments
Unmodified	Modified by CI[a]	Modified by SB[a]	
	3430	3430	O-H stretching
2870~2950	2870~2950	2870~2950	aliphatic C-H stretching
	1766		C=O stretching (acid)
1411~1580	1411~1580	1411~1580	C=C stretching in the aromatic rings
1323	1323	1323	C-SO$_2$-C asymmetric stretching
1295	1295	1295	S=O stretching
1240	1240	1240	C-O-C symmetric stretching
1157	1157	1157	C-SO$_2$-C symmetric stretching
1080, 1014,	1080, 1014,	1080, 1014,	aliphatic C-C / aromatic C-H
873	873	873	bending, rocking
635~855	635~855	635~855	C–H rocking vibrations

[a]The modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, the agent solution concentration of 1.0 wt.%, temperature of 25 ºC, and time of 240 min

membranes (Pouchert 1981). After modification with CI, the infrared adsorption bands at 3430 cm^{-1} and 1766 cm^{-1} appeared. These two bands are attributed to the stretching vibrations of O-H and C=O groups, respectively, which could be caused by the adsorption of CI (see Table 1) to membrane. One of the adsorption mechanisms could be Van Der Waals attraction. In addition, the H-donating groups including -COOH and -OH from CI may react with the strong electronegative groups such as oxygen in the ether bond and sulfone group in the main chain of PS (see Table 1) to form hydrogen bonds (Schuster 1976). The hydrogen bonding reinforced the adsorption of CI and thus intensified infrared absorption bands for O-H and C=O on the modified PS membrane surface.

The coverage of CI on membrane surface was further confirmed by the fact that the infrared absorption bands at 2870~2950 cm^{-1} and 1080 cm^{-1}, which were assigned to aliphatic C-H and C-C stretching vibrations respectively, increased on the modified PS membrane surface.

For PS membrane modified by SB, it can be seen that the O-H stretching vibration frequency at 3430 cm^{-1} appeared, and the S=O stretching vibration frequency at 1295 cm^{-1} was intensified. These results should be caused by the adsorption of SB via Van Der Waals attraction. Similar to CI, hydrogen bonding might also contribute to the adsorption of SB, which has the H-donating group –OH (see Table 1). However, the hydrogen bonding may be weakened by the electrostatic repulsion between HSO_3^- and electronegative groups of PS (Schuster 1976). This suggested that the interaction between SB and PS membrane was mainly through Van Der Waals attractions, which were weaker than those between CI and PS membrane as discussed above. In the infrared spectrum of the membrane modified by SB, the bands for C-H and C-C at 2870~2950 cm^{-1} and 1080 cm^{-1} respectively, decreased. This may be attributed to the coverage of inorganic substance SB onto PS membrane surface, resulting in the weakening of the characteristic bands for organic species.

3.2 Membrane surface contact angle

Table 4 shows changes in membrane surface contact angles after modifications with CI and SB. It was observed that the contact angles decreased after modification with both agents. This is attributed to an increase in polar groups like O-H, C=O, and S=O on membrane surface after the agent adsorption. It was also observed that the surface contact angles of the membranes modified by CI decreased more obviously than that of the membranes modified by SB, which could be explained by the more polar groups in CI molecular and the stronger adsorption of CI to PS membrane via hydrogen bonding.

3.3 Membrane surface porosity and pore size distribution

Porosity measurement results are also shown in Table 4. Compared with the unmodified membranes, membrane porosities decreased a little when modified by CI, while no obvious changes were observed when modified by SB. These were probably because the stronger adsorption of CI might

Table 4 Changes of membrane properties after modification with CI and SB

	Unmodified membrane	Membrane modified by[a]	
		CI	SB
Contact angle (°)	69.2±2.4	54.0±2.0	59.7±2.0
Porosity (%)	39.1±0.4	38.1±0.5	39.0±0.7
Pure water flux (L/m²h)	218.5±10.8	206.4±10.0	260.8±8.8
PEG rejection (%)	65.2±0.6	67.9±0.7	66.7±1.0
BSA rejection (%)	98.7±0.5	99.1±0.6	99.2±0.5
FRR(1st cycle) (%)	54.7±0.7	71.5±1.2	62.5±1.0
FRR(2nd cycle) (%)	69.1±0.8	79.1±1.4	72.2±1.8
FRR(3rd cycle) (%)	85.1±1.1	86.4±1.2	79.2±1.4

[a]The modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, the agent solution concentration of 1.0 wt.%, temperature of 25°C, and time of 240 min
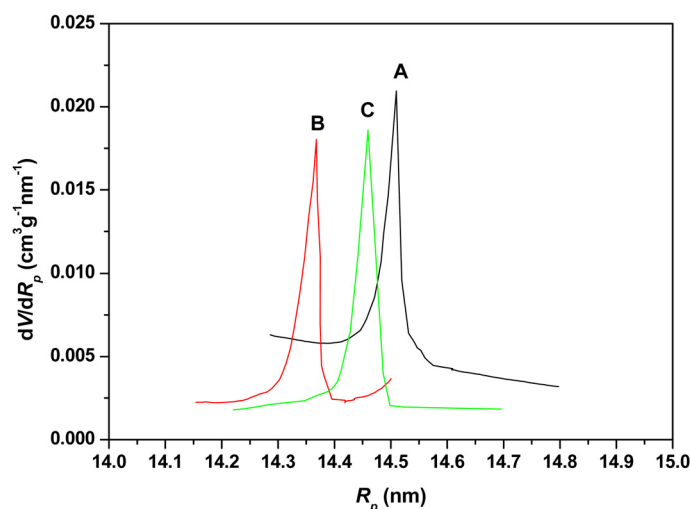
Fig. 2 Pore size distribution of the membranes. Membrane samples A, B, and C are unmodified membrane, membrane modified by CI, and membrane modified by SB, respectively. Modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, the agent solution concentration of 1.0 wt.%, temperature of 25°C, and time of 240 min

cause the pore blocking and the decrease of membrane porosity, while the weaker adsorption of SB had no obvious effect on membrane porosity.

Fig. 2 presents the pore size distributions of membranes obtained form DSC measurements. The pore sizes of unmodified membranes ranged from 14.4 to 14.6 nm, while, the membranes modified by CI had pore sizes ranged from 14.2 to14.4 nm, and the membranes modified by SB had pore sizes ranged from 14.3 to 14.5 nm. The reasons why modified membranes had lower pore sizes than unmodified ones were the same as discussed above.

3.4 Membrane permeability and rejection properties

The pure water fluxes of unmodified and modified membranes are shown in Table 4. Compared with unmodified membranes, membrane fluxes decreased a little when modified by CI. However, membrane fluxes increased when they were subjected to SB modification. The differences in flux changes when modified by CI and SB could be explained by the balance between the pore-covering effect and the increase of hydrophilicity of membrane surface after the agent adsorption (Su 2008). As discussed in section 3.2, hydrophilicity increased for both the membranes modified by CI and the membranes modified by SB. As confirmed in section 3.3, the porosity and pore sizes decreased for the membranes modified by CI, and had no obvious changes for the membranes modified by SB. Thus, for the membranes modified by CA, the greater pore-covering effect caused a decrease in pure water fluxes, while the elevated hydrophilicity dominated the permeability of the membranes modified by SBS and caused an increase in pure water fluxes.

Table 4 also presents membrane rejections. Compared with unmodified membranes, there was an increase in rejections of modified membranes. The reasons should be that the membrane pore sizes decreased by the agent adsorption, which made the organic macromolecules difficultly pass through, and caused higher PEG and BSA rejections. The change in membrane surface charge property after

adsorption of CI or SB could be another reason for the increase in BSA rejection. That is, after adsorption of CI or SB, the membrane surface is negatively charged. The solution pH value is 7, which is higher than BSA isoelectric point (pH 4.8), so the BSA molecules are negatively charged, which can be rejected by membrane surface through electrostatic repulsion.

3.5 Membrane antifouling property and stability

Synthetic BSA solutions are frequently used to investigate UF membrane antifouling properties (Brink 1993, Chinpa 2010, Hosseini 2010, Kang 2008, Ma 2007, Pal 2008, Yu 2009). But they are quite different from an industrial wastewater stream, which usually contains large quantities of both organic and inorganic substances. In this work, a complex pharmaceutical wastewater whose composition was shown in Table 2 was collected to study membrane antifouling property.

Fig. 3 presents the fluxes for the three cycles of ultrafiltration operation. It was observed that after three cycle wastewater ultrafiltrations, the pure water fluxes of membranes modified by CI and SB retained at 97.8 L/(m^{2}h) and 84.5 L/(m^{2}h), respectively, while the pure water flux of unmodified membrane decreased to 73.5 L/(m^{2}h). That is to say, during the wastewater ultrafiltrations, membranes modified by CI and SB maintained higher permeate fluxes than unmodified membrane. These differences were attributed to the better antifouling properties for modified membranes, as discussed in the following.

From Table 4, it was observed that in the first two ultrafiltration cycles, the modified membranes, especially ones modified by CI, had higher FRR values than the unmodified ones. This suggested that the adsorption between feed foulants and membrane was weakened after modification with CI or SB, and thus, the membrane could get higher flux recovery after simple water flush. The better antifouling property of modified membrane could be due to that the adsorbed agent CI or SB on the
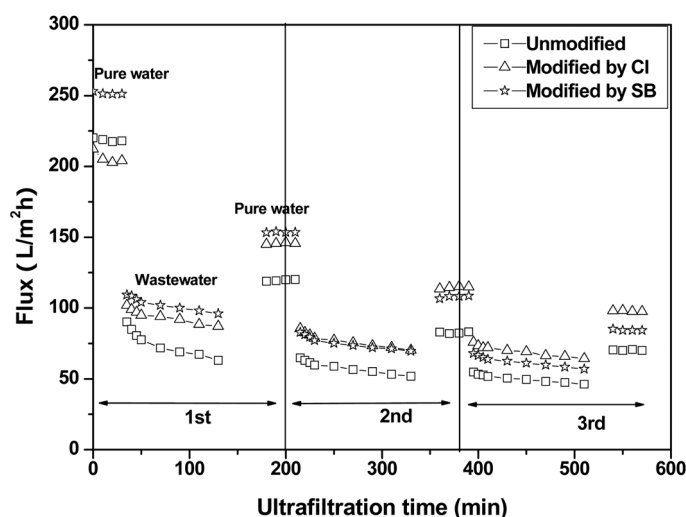

Fig. 3 The time-dependent flux in the three cycles of ultrafiltration operation for the unmodified and modified PS membranes. Modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, the agent solution concentration of 1.0 wt.%, temperature of 25°C, and time of 240 min. The wastewater composition is shown in Table 2. Ultrafiltration conditions applied are TMP of 0.15 MPa, crossflow velocity of 0.22 m·s^{-1}, and temperature of 25°C

outer surface of the membrane could reduce the direct contact between membrane surface and foulants in the solution, and protect membrane from severe fouling. On the other hand, increased hydrophilicity of modified membrane surface was also responsible to higher resistance to membrane fouling (Crozes 1993, Maartens 2002). As compared with the membranes modified by SB, the better antifouling property for the membranes modified by CI could be resulted from the fully covering by CI and the higher hydrophilicity after modification.

As shown in Table 4, in the third ultrafiltration cycle, membranes modified by CI had similar FRR values to unmodified ones, and membranes modified by SB had lower FRR values than unmodified ones. These results suggested that after three ultrafiltration cycles (about 600 min), the modified membranes had similar or even lower antifouling properties compared to the unmodified ones, which may be caused by the desorptions of CI and SB with increasing ultrafiltration time. Hence, remodification by CI and SB solutions may be necessary after three ultrafiltration cycles (about 600 min) to retain good performance.

In addition, the filtrations under different transmembrane pressures (TMPs) including 0.06 MPa, 0.1 MPa, and 0.15 MPa with the same volume of wastewater were carried for the membranes modified by CI. The results show that after 600 minutes filtration of waste water, the membrane FRR values are 87.6±1.5%, 86.4±1.2%, and 85.5±1.2%, respectively. The FRR values are all similar to that for the unmodified membrane. That is to say, after 600 min filtration under different TMPs, all the membranes need to be remodified. This suggests that the TMP has no effect on agent desorption.

In an industry filtration process, the remodification by CI or SB can be performed in the following two ways: (1) when the membrane system is working in continual operating mode, the filtration of CI or SB solution can be performed intermittently, so that the lost CI or SB on the membrane surface can be compensated; (2) when the membrane system needs to be shut down for maintenance, the membrane can be immerged into CI or SB solution, the desorption of the agent on the membrane surface can be suppressed, and the static adsorption of the agent could help membrane partly recovery its antifouling property. These two aspects could help to construct an antifouling and stable membrane system. Higher quality of water products and longer life of membranes will be obtained in such a system.

3.6 Membrane chlorine tolerance

Contact with chlorine is a major cause of polysulfone membrane degradation (Causserand 2008). In this study, accelerated ageing of membranes was simulated by soaking the membranes in NaClO solution with a concentration of 400 ppm at pH 8. Membrane mechanical properties (Ts and El) were monitored versus soaking time, and the results were shown in Fig. 4. It was observed that both Ts and El at break for PS membranes decreased continuously with soaking time, which is attributed to oxidation and hydrolysis of membrane polymer by NaClO solution (Causserand 2008, Gabelich 2005, Gaudichet-Maurin 2006, Gitis 2006, Rouaix 2006).

For membranes modified by CI or SB, decreases in Ts and El were not as obvious as unmodified ones, indicating that the membrane chlorine tolerances increased after modification with CI or SB. It was probably due to that both CI and SB are antioxidants. CI and SB adsorbed to membranes could react with chlorine in the water first, thus weakened the interaction between PS and chlorine, and in turn slowed down the membrane degradation rate.

Fig. 4 also shows that with increasing concentration of the agent solution, the higher chlorine
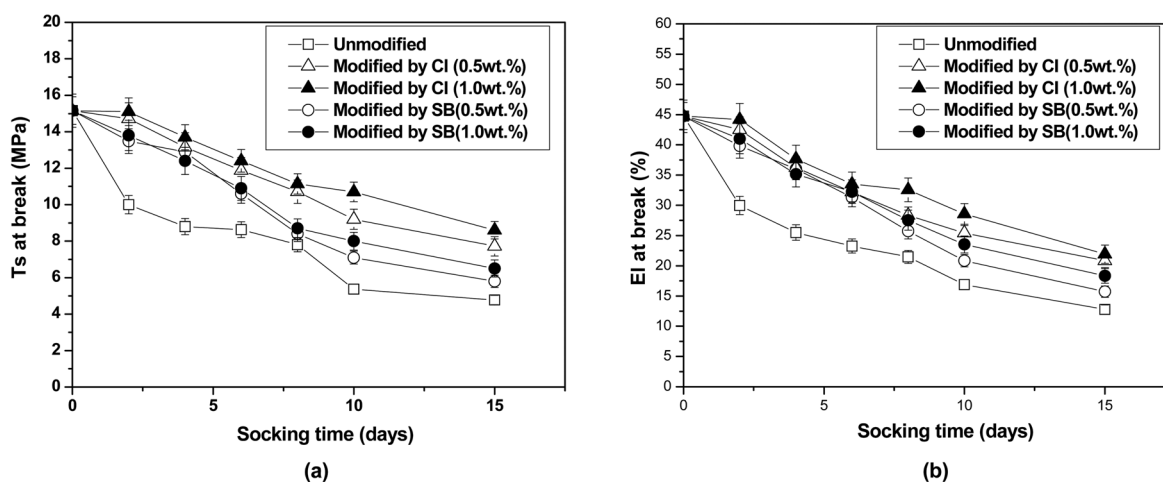
Fig. 4 Variation with time of mechanical properties of PS membranes soaked in 400 ppm NaClO at pH 8: (a) variation of Ts at break, and (b) variation of El at break. Modification conditions applied are TMP of 0.1 MPa, crossflow velocity of 0.11 m·s^{-1}, temperature of 25°C, and time of 240 min

tolerance was observed for the modified membranes. These results suggest that the more agent molecules adsorbed onto membrane surface, the higher chlorine tolerance was obtained, which also confirm that the agent CI or SB adsorbed on membrane surface could react with chlorine first, and protect membrane from degradation.

4. Conclusions

Performance improvements of PS UF membrane modified by preadsorption of CI and SB were investigated. IR spectra analysis supported that the hydrogen bonding and the Van Der Waals attraction were the main causes for the adsorptions of CI and SB to membrane, respectively. After modification with CI or SB, the membrane hydrophilicity increased due to the introduction of large amounts of polar covalent bonds such as O-H, C=O, and S=O to membrane surface. Membrane pure water flux increased when modified by SB, but decreased a little when modified by CI, which can be explained by the balance between the pore-covering effect and the increase in hydrophilicity. For membranes modified by CI or SB, an increase in PEG and BSA rejections was observed, which could be due to a decrease in membrane pore sizes after agent adsorption. Membrane antifouling property was improved after the agent adsorption, which was attributed partly to the elevated hydrophilicity, and partly to the adsorbed agent on the outer surface of membrane (the reduction of direct contact between feed foulants and membrane). It is worthy to note that membranes modified by CI and SB had better chlorine tolerances. This result was expected because both CI and SB are antioxidants and adsorption of either can inhibit the degradation of PS membrane by chlorine. Generally, this work showed that prefiltration of CI or SB solution could be considered as a novel and easy method for PS UF membrane modification to improve membrane rejection, antifouling property, and chlorine tolerance.

Acknowledgements

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