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Sulfonated chitosan/polyvinyl alcohol/SiO_2 hybrid membrane for alkali recovery with diffusion dialysis

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ABSTRACT

Herein, chitosan (CS) is modified into sulfonated CS by reaction with 1, 3 propanesultone (PS) for obtaining ion exchange group. Then, to enhance their mechanical properties, polyvinyl alcohol (PVA) is blended, and tetraethyl orthosilicate (TEOS) is introduced into matrix to cross-link with sulfonated CS by sol-gel method. Eventually, a serial of novel sulfonated CS/PVA/SiO_2 hybrid membrane with varied sulfonated CS content are prepared. On this basis, the effect of sulfonated CS content on physical and chemical properties is extensively investigated by ATR-FTIR, SEM, TGA and DMA studies. Those membranes have good homogeneity, thermal stability and flexibility. In addition, ion exchange capacity, water uptake and linear expansion in water also are tested. The results demonstrate that IEC augments from 0.10 mmol/g to 0.65 mmol/g with the increasing content of sulfonated CS content and the range of water uptake and linear expansion in water is 10–25%, 15–20%, respectively. Diffusion dialysis (DD) for alkali recovery is evaluated with $NaOH/Na_2WO_4$ mixture. Compared to the previously reported hybrid membranes, the developed membranes reveal excellent OH^- ion transport performance (U_{OH}: 0.0135–0.0160 m/h) and acceptable selectivity (S: 15.6–26.9). Therefore, the developed membranes have potential application in alkali recovery with DD.

Keywords: Sulfonated chitosan (CS); Polyvinyl alcohol (PVA); Hybrid membrane; Diffusion dialysis; Alkali recovery

1. Introduction

Alkali waste is widely distributed in paper, leather, printing, dying, tungsten, and aluminum ore smelting industries [1]. The conventional methods for treating alkali waste, such as neutralization with acids, concentration and burning (in paper industry), require large amount of acids, consume high quantity of energy, or produce waste gas [2,3]. Compared to these treatment methods, diffusion dialysis (DD) is a membrane separation technology based on concentration gradient, in which alkali can spontaneously diffuse from waste water side to reception side. Hence, DD is regarded as a green method for recovering alkali, which has the characteristics of environment-friendly and low-energy consumption [4–6].

Ion exchange membrane is a critical component of DD process. In recent years, owing to the synergistic effect of both organic and inorganic materials, hybrid ion exchange membranes have aroused growing interest in varieties of membrane separation processes [7–11], such as electro-dialysis, DD, donnan dialysis, bipolar membrane electro-dialysis, fuel cell and electrical batteries [12–18].

Chitosan (CS) is an abundant and inexpensive polysaccharide with low toxicity [19]. Because of the presence of hydroxyl and amino groups that can be transferred to ion exchange groups, CS has been considered as a promising

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membrane material [20]. In addition, hydroxyl and amino groups may enhance the diffusion of OH^- ion, due to the presence of hydrogen bond between hydroxyl or amino groups and OH^- ions [21–23]. However, chitosan membranes have poor mechanical properties, which restrict the application in membrane process [24]. In order to be availably utilized as membrane material, it is indispensable to enhance their mechanical properties. Blending with other polymer is already proved to be a preferable solution, especially PVA with favorable mechanical properties and excellent film-forming properties [25]. What is more, CS and PVA are highly hydrophilic polymers, which is in favor of compatibility during blending process.

Herein, firstly, CS with sulfonic acid group is synthesized by reacting with propane sultone. Secondly, blending with PVA is employed to enhance the mechanical properties of CS membrane. The last but not the least, tetraethyl orthosilicate (TEOS) is introduced for crosslinking sulfated CS and PVA, and sulfated chitosan/polyvinyl alcohol/SiO_2 hybrid membranes are prepared. Ultimately, diffusion dialysis (DD) is investigated to evaluate the alkali recovery performance of prepared membranes.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA), Chitosan (CS), isopropyl alcohol, 1,3-propane sultone (PS) and tetraethyl orthosilicate (TEOS) were supplied from Shanghai Sinopham Chemical Reagent Co., Ltd (Shanghai, China). The polymerization degree of PVA was 1750±50. The deacetylation degree of CS was 90%. All chemicals were analytical pure. Deionized water was used in the experiment.

2.2. Dissolution of PVA

The dissolution process of PVA was as follows. The quantified PVA particle was dipped in deionized water for 24 h, and then slowly heated up to 100ºC and maintained for 2.5 h. In this way, 5.0 wt% PVA solutions were prepared for later using.

2.3. Sulfonating of CS

Sulfonating of CS was prepared by adding 3 g chitosan powder to 30 mL isopropyl alcohol, stirring for 60 min, and then adding 2.44 g 1,3-propanesultone to the solution at 95ºC. The mixture was continued to react under refluxing for 24 h. The product was filtered and washed with deionized water. By this mean, sulfonated CS was obtained for next experiment.

2.4. Preparation of sulfonated CS/ PVA /SiO_2 hybrid membranes

The pre-measured sulfonated CS was dropped into PVA (1 g) solution (5.0 wt%). Then the mixed solution was added with 0.25 mL TEOS and was stirred at 60ºC for 24 h. Subsequently, the prepared solution was cast onto glassplates and dried at room temperature for 48 h. Finally, before kept at 130ºC for 4 h,the films were peeled off from the glass plate, and heated from 60ºC to 130ºC with the rate of 10ºC/h. The dosage of sulfonated CS with respect to PVA was changed from 5%, 10%, 33%, 66% to 100%. Hence, five sulfonated CS/PVA/SiO_2 hybrid membranes were prepared and named as P-C/1, P-C/2,P-C/3, P-C/4 and P-C/5, respectively. The synthesis process is shown in Fig. 1.

2.5. Membrane characterizations

The spectra of two hybrid membranes were analyzed by the Bruker FTIR spectrometer, in the range of 4000–400 cm^{-1}. The thermal stability of three hybrid membranes was determined by the Shimadzu TGA-50H analyzer. The surface morphologies of two hybrid membranes were characterized by using scanning electron microscopy (SEM, FEI, Sirion200).

Dynamic mechanical analyzer (Model Q800) with increasing rate of 0.2500 N/min was adopted to collect the mechanical properties of five hybrid membranes.

Ion exchange capacity (IEC) values of five hybrid membranes were evaluated by detecting the content of $–SO_3H$ groups via acid base titration method. The dry weighted hybrid membranes were changed into Na^+ form in 1.0 M

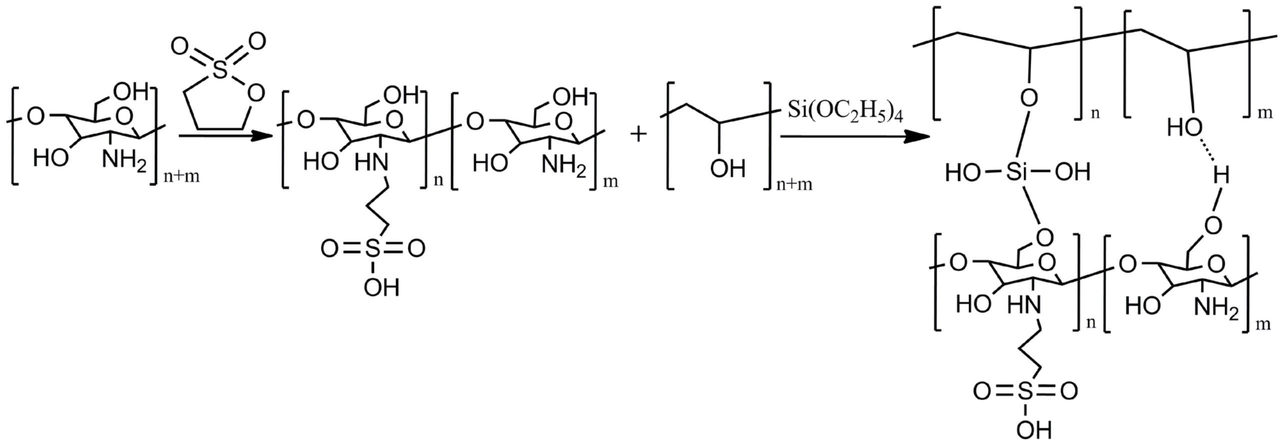

Fig. 1. Synthesis process of sulfonated CS/PVA/SiO_2 hybrid membranes.

NaCl solution for 24 h. Afterwards, the solutions were titrated with 0.05 M NaOH solution and IEC values were gated by the equation:

$$IEC = \frac{V_{NaOH} \times N_{NaOH}}{W_{dry}} \tag{1}$$

where V_{NaOH} and N_{NaOH} (0.05 M) were the titrated volume and concentration of the NaOH solution, W_{dry} is the weight of dry membrane, respectively.

The water uptake (W_R) of hybrid membrane was investigated by measuring the change in weight between the dried membrane and wet membrane. Firstly, the pre-weighted hybrid membrane was dried for 12 h at 60°C and then was immersed in deionized water for 48 h at 25°C. Afterward, the hybrid membranes were taken from deionized water after removing the surface water. Eventually, the wet hybrid membranes were re-weighed. W_R value was calculated with the following equation:

$$W_R = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{2}$$

where W_{wet} and W_{dry} were the weights of wet and dry hybrid membranes, respectively.

The linear expansion ratio (LER) in 25°C water for 48 h was employed to evaluated imensional stability of hybrid membranes in water, based on the following equation:

$$LER = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \tag{3}$$

where L_{wet} and L_{dry} were the lengths of wet and dry hybrid membranes, respectively.

2.6. Diffusion dialysis experiments

The performance of prepared hybrid membranes was evaluated via an alkali recovery by diffusion dialysis (DD) process. The test equipment had two compartments. The feed side was poured into the mixture solution of 1.0 mol/L NaOH and 0.10 mol/L Na_2WO_4, and the diffusate side was filled with deionized water. The membrane was fixed among two sides at 25°C.

The diffusion time was fixed as 1 h. The concentrations of NaOH in two sides were analyzed by titration with HCl, and the concentrations of Na_2WO_4 in diffusate side were analyzed by ultraviolet spectrophotometry, respectively. The separation factor (*S*) was defined as the ratio of dialysis coefficients (*U*) of NaOH and Na_2WO_4 in the diffusate side. While *U* was calculated as below [21]:

$$U = \frac{M}{At\Delta C} \tag{4}$$

where *M* was the amount of constituent diffused in moles, *A* was the effective membrane area in square meters, *t* was the diffusion time in h, and ΔC was the logarithm average concentration between the two sides in moles per cubic meters and calculated by the following equation:

$$\Delta C = \frac{C_f^0 - \left(C_d^t - C_f^t\right)}{\ln\left[C_f^0 / \left(C_d^t - C_f^t\right)\right]} \tag{5}$$

where C_f^0 and C_f^t were the concentrations of constituent in feed side at time 0 and *t*, respectively, and C_d^t was the concentrations of constituent in diffusate side at time *t*.

3. Results and discussion

3.1. ATR–FTIR spectra

Fig. 2 exhibits the ATR–FTIR spectra of hybrid membranes P-C/1 and P-C/5. The broad peak around 3200–3600 cm^{-1}, is from the stretching vibrations of –OH groups. The peaks appear at 2925 cm^{-1} and 1644 cm^{-1} can be attributed to the stretching of $–CH_2–$ and CH-groups, respectively [21]. The peak at 1100 cm^{-1} is due to formation of Si-O-Si bonds from the condensation reaction between Si-OH groups, while the characteristic peak at 1045 cm^{-1} is attributed to Si-O-C bonds from the condensation reaction between Si-OH groups and C-OH groups [22,23]. The Si-OH groups are from hydrolysis of TEOS, and the C–OH groups are from PVA and CS. Therefore, it can be confirmed that the crosslink network between TEOS and polymer (PVA or CS) is developed during the preparation process. In addition, the peaks at 1034 cm^{-1} and 1148 cm^{-1} are ascribed to the S=O stretching vibration of sulfonic acid group from sulfonated CS, which are in good accordance with report on sulfonated CS membranes [20,26].

3.2. Membrane morphologies

The morphologies of hybrid membranes P-C/1 and P-C/4 are probed by using their SEM images of cross-section, which are shown in Fig. 3. From Fig. 3 it can be observed that the ratio of sulfonated CS in hybrid membranes remarkably influences the morphology. Only few small agglomerations distribute in P-C/1 hybrid membrane, and the cross-section is nearly smooth. With the increasing sulfonated CS, hybrid membranes tend to be rough and show phase separation. It

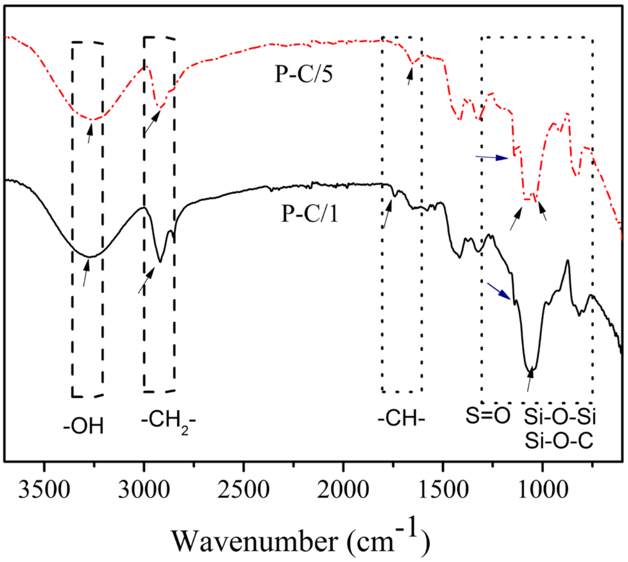

Fig. 2. ATR–FTIR spectra of sulfonated CS/PVA/SiO_2 hybrid-membranes P-C/1 and P-C/5.

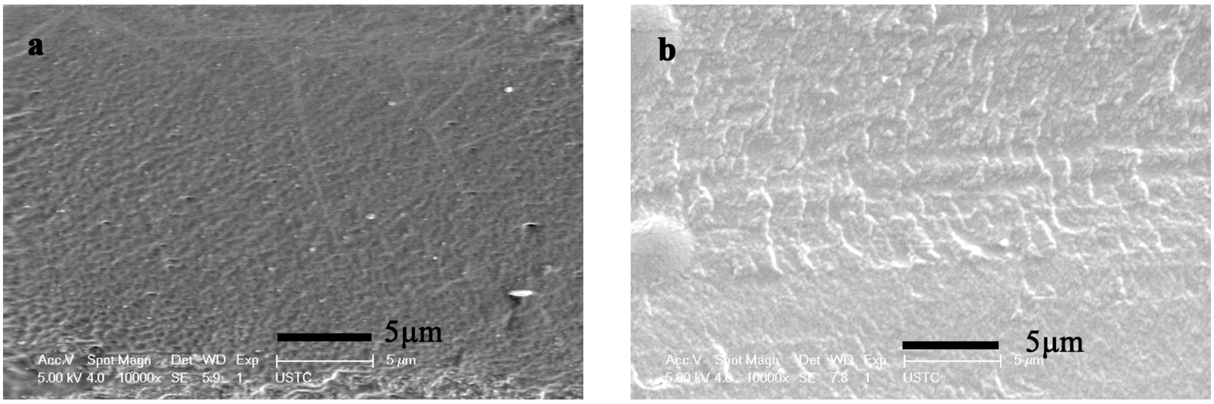

Fig. 3. Cross-section morphologies of sulfonated CS/PVA/SiO_2 hybrid membranes P-C/1 (a) and P-C/4 (b).

maybe ascribed to that the hydrogen bonds between sulfonated CS molecules are growing stronger with the increasing of sulfonated CS, which leads to the aggregation of sulfonated CS. Hence, it is proved that the excessive sulfonated CS is unfavorable for membrane uniformity and may cause phase separation.

3.3. Mechanical properties study

In order to evaluate mechanical properties of hybrid membranes, the tensile strength (TS) and elongation at break (E_b) are summarized in Table 1. The TS values are from 11.1 to 30.5 MPa, and the E_b values are from 187 to 407%. The TS results are approximate to the results of other CS/PVA membranes cross-linked with glutaraldehyde (TS: 12.2–25.3 MPa), while the E_b results are higher than the results of above-mentioned membrane (TS: 6–48%) [27]. It is indicated that the strength of prepared membranes is acceptable and the flexibility is superior. The difference in flexibility is attributed to the different cross-linking agent. During the present work, TEOS is used as cross-linking agent, which contains four cross-linking groups, whereas glutaraldehyde adopted as cross-linking agent in above-mentioned work contains two cross-linking groups. The enhanced cross-linking degree may be beneficial to the flexibility of membrane. Hence, the higher flexibility of present membranes should be mainly attributed to the using of TEOS.

In addition, the TS and E_b values of present membranes irregularly vary with the sulfonated CS content, which indicates that the mechanical properties of prepared membrane are complicatedly influenced by sulfonated CS. Also, the sulfonated CS content can affect cross-linking degree and phase segregation between PVA and sulfonated CS. It may have synergetic influence on membrane mechanical properties.

Table 1
TS and E_b values of sulfonated CS/PVA/SiO_2 hybrid membranes

Membrane	TS (MPa)	E_b (%)
P-C/1	15.5	244
P-C/2	13.1	327
P-C/3	30.5	187
P-C/4	11.8	196
P-C/5	14.7	407

3.4. Thermal stability study

Figs. 4 and 5 represent the TGA and DrTGA diagrams of sulfonated CS/PVA/SiO_2 hybrid membrane P-C/3, P-C/4 and P-C/5, respectively. Apparently, there are three principal weight loss regions in the TGA and DrTGA diagrams. The first weight loss in 70–130°C regions is mainly assigned to the loss of absorbed water in membrane, because the hybrid membranes have plenty of hydrophilic groups, comprised of –OH group and –SO_3H group. Beyond 200°C, the decomposition of hybrid membranes is rapid, which arises from the degradation of side groups in sulfonated CS [28]. The total weight loss of membranes P-C/3 and P-C/4 is about 35%, while membrane P-C/5 loses 60% weight in second region. The sulfonated CS content is higher in membrane P-C/5, and hence the degradation rate is faster. In addition, it is also observed from Fig. 5 that the second weight loss stage of P-C/5 starts at temperature much higher than that of P-C/3 or P-C/4. This may be attributed to the increasing hydrogen bond between sulfonic acid and amino groups with rising sulfonated CS content in membrane P-C/5 [29]. In the third region up to 410°C, the weight loss may be ascribed to the cleavage of the polymer backbone of hybrid membranes [29]. The membranes P-C/3 and P-C/4 retain 55% and 50% of the initial weight, while membrane P-C/5 retains 35%, respectively. In this stage, the hybrid membranes exhibit steep decomposition. The total weight loss of three hybrid membranes is about 70%, 68% and 90%, respectively. Based on these observations, it is concluded that the sulfonated CS content in hybrid membranes has a very profound effect on thermal stability.

3.5. Ion exchange capacity (IEC) study

Ion exchange capacity (IEC), shows the content of ion exchangeable groups existing in hybrid membrane, which is indicated in Fig. 6. Based on Eq. (1), the values are calculated and ranges from 0.10 to 0.65 mmol/g. The maximum IEC value is 0.65 mmol/g for membrane P-C/5. It proves that the IEC values increase with the growing content of

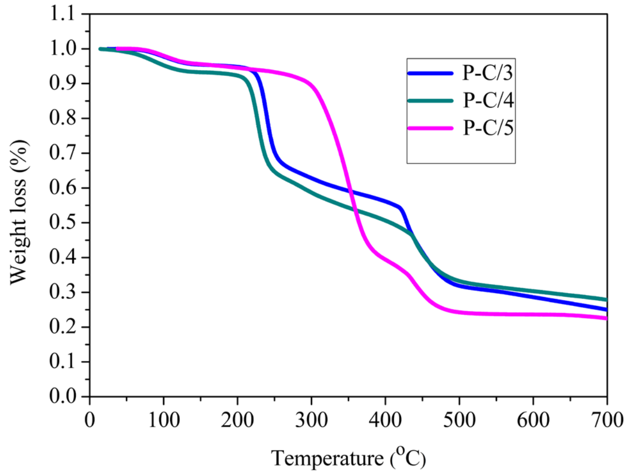

Fig. 4. TGA diagrams of sulfonated CS/PVA/SiO_2 hybrid membranes P-C/3, P-C/4 and P-C/5.

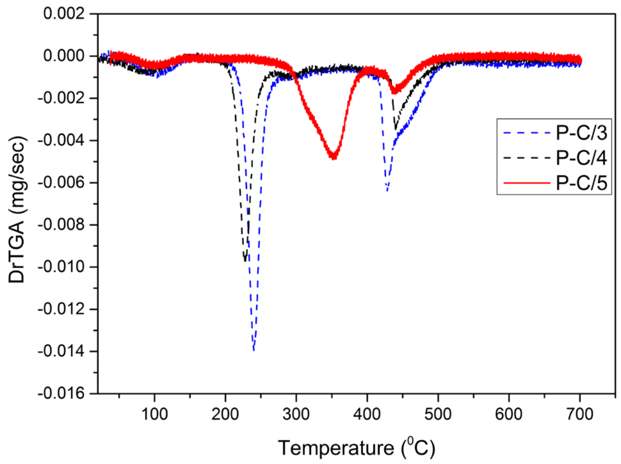

Fig. 5. DrTGA diagrams of sulfonated CS/PVA/SiO_2 hybrid membranes P-C/3, P-C/4 and P-C/5.

sulfonated CS in hybrid membrane, due to the available –SO_3H groups from sulfonated CS.

3.6. Water uptake and linear expansion ratio (LER) in water study

Fig. 7 indicates the Water uptake (W_R) values of hybrid membrane. It is revealed that the values increase from 62% for membrane P-C/1 to 85% for membrane P-C/3 and then decrease to 67%–68% from membrane P-C/4 to membranes P-C/5. There are plenty of hydrophilic groups in sulfonated CS chain, such as –SO_3H groups, –NH groups and –OH groups. Thus, the hybrid hydrophilicity of membrane is enhanced with the increasing sulfonated CS content, and the increasing trend of water uptake is observed from membrane P-C/1 to membrane P-C/3. Nevertheless, as the sulfonated CS content further increases, the water uptake values decrease to 67–68%. This may be due to hydrogen bond readily forming between PVA and sulfonated CS chain with the incremental sulfonated CS content. The hydrogen bond results in physical crosslinking in membrane matrix and restricts the expanding of membrane. As a consequence, the water uptake values are reduced [30].

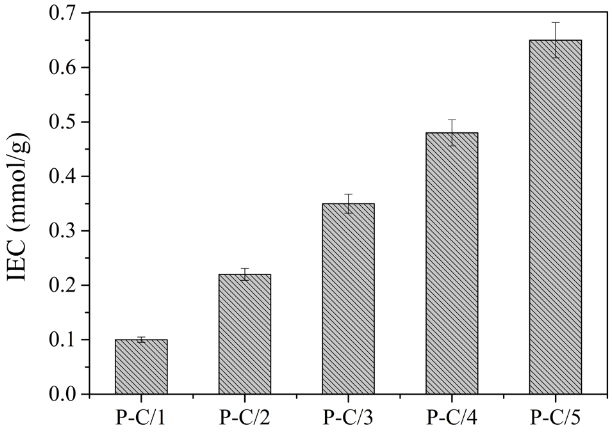

Fig. 6. Ion exchange capacity (IEC) values of sulfonated CS/PVA/SiO_2 hybrid membranes.

The linear expansion ratio (LER) of hybrid membrane in water are investigated and also depicted in Fig. 7. The LER values range from 15% to 20%, which are approximately equal to those of the reported PVA-based hybrid membranes for alkali recovery by diffusion dialysis (LER: 13.3%–20.8%) [22]. It illustrates that the prepared membranes have good dimensional stability in water, which is favorable to the running of diffusion dialysis [22]. As for the variation tendency of LER values for membrane P-C/1-P-C/5, it is similar to that of Water uptake values, and also can be explained by the same reason. Also, the hydrophilicity and crosslinking synergistically affect the swell property of hybrid membrane.

3.7. Performance of diffusion dialysis (DD) for alkali recovery

NaOH and Na_2WO_4 are intermediate product in tungsten ore smelting industry, and are main ingredients of wastewater from tungsten ore smelting industry [1]. Hence, to evaluating the performance of diffusion dialysis for alkali recovery, NaOH/Na_2WO_4 mixed solution is used as a testing object. DD performances, comprised of dialysis coefficient of alkali (U_{OH}) and separation factor (S), are calculated and presented in Fig. 8. The U_{OH} values ranges between 0.0135 and 0.0160 m/h, and the S values range between 15.6 and 26.9.

As shown in Fig. 8, the U_{OH} values firstly increase from 0.0135 to 0.0160 m/h when adding sulfonated CS content, while the U_{OH} values decrease and remain almost constant with further increasing sulfonated CS content. Ion exchange capacity and crosslinking degree can be obligated to the variation trend of U_{OH} values. With increasing the content of sulfonated CS, ion exchange capacity is enhanced due to the growing content of –SO_3H group. Thus, Na^+ ions readily transport through membrane and hence more OH^- ions diffuse from feed side to water side due to static draw force. When the sulfonated CS further increases, the crosslinking between sulfonated CS and PVA may be strengthened. It is disadvantageous to the transport of OH⁻ ions and lead to the decreasing of U_{OH} values. In addition, it is also found that the S values decrease with increasing sulfonated CS content. The phase separation is enhanced with the increased sulfonated CS in hybrid membranes, which is proved by SEM. This leads to the decreasing of membrane selectivity. The phase separation is detrimental to the membrane selectivity, which is similar to other reported work [21].

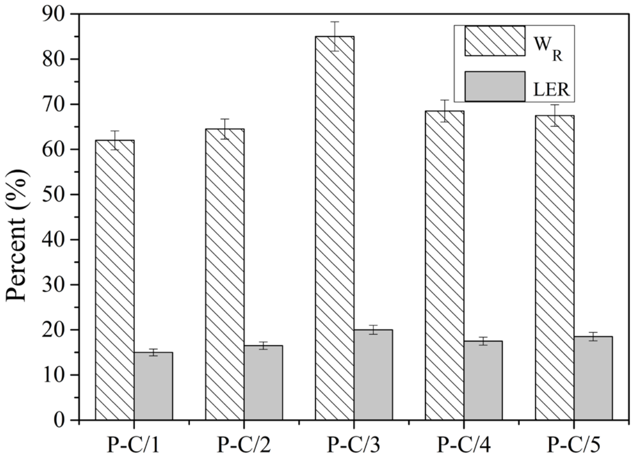

Fig. 7. Linear expansion ratio (LER) and water uptake (W_R) values of sulfonated CS/PVA/SiO$_2$ hybrid membranes.

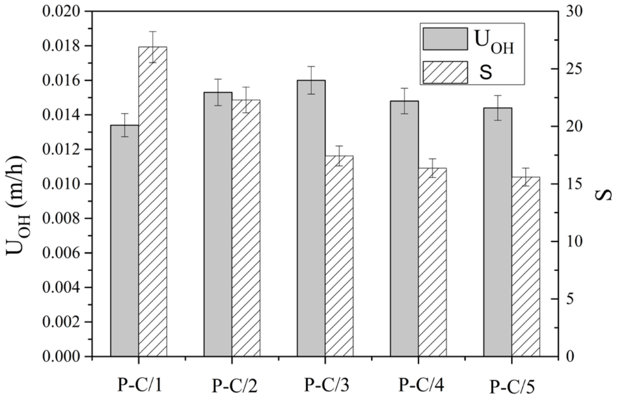

Fig. 8. Dialysis coefficients of OH⁻ ion (U_{OH}) and separation factor (S) of sulfonated CS/PVA/SiO$_2$ hybrid membranes in NaOH/Na$_2$WO$_4$ system.

A comparison of between the reported two-component or three-component hybrid cation exchange membranes containing –SO$_3$Na groups is used to evaluate DD performances. Table 2 lists the U_{OH} and S values from some reported literatures.

From Table 2 it can be commented as follows:

For two-component hybrid cation exchange membranes, The U_{OH} values of SPPO/SiO$_2$ hybrid membranes and SPPO/nano-silica are 0.0014–0.0022 m/h and 0.015 m/h [5,31], while those of PVA/SiO$_2$ hybrid membranes are 0.0102–0.0111 m/h [32]. It is exhibited that PVA-based hybrid membranes have preferable OH⁻ ion transport performance. Compared with SPPO-based hybrid membranes, the advantage of OH⁻ ion transport in PVA-based hybrid membranes can be attributed to the hydrogen bonding between –OH groups and abundant –OH groups throughout the PVA-based hybrid membrane matrix [5,21–23]. This is also proved by the U_{OH} values of SPPO/PVA/SiO$_2$ hybrid cation exchange membranes (0.0070–0.0130 m/h) [33]. It is higher than those of SPPO/SiO$_2$ hybrid membranes and lower than those of PVA/SiO$_2$ hybrid membranes. Similarly, for three-component hybrid cation exchange membranes, the U_{OH} values of prepared sulfonated CS/PVA/SiO$_2$ hybrid membranes are higher than that of SPPO/PVA/SiO$_2$ hybrid cation exchange membranes, which is ascribed to the hydrophilic of difference between SPPO and sulfonated CS. Moreover, compared to other PVA-based hybrid membranes, the results are acceptable [34,35].

Consequently, in present work, the prepared sulfonated CS/PVA/SiO$_2$ hybrid membranes also indicate excellent OH⁻ ion transport performance and acceptable selectivity in DD for alkali recovery.

4. Conclusions

In summary, CS is sulfonated by reaction with 1, 3 propanesultone (PS) and blended with PVA. On this basis, a serial of novel sulfonated CS/PVA/SiO$_2$ hybrid membrane with varied sulfonated CS content are reported by sol-

Table 2
Dialysis coefficients (U_{OH}) and separation factors (S) of the prepared sulfonated CS/PVA/SiO$_2$ hybrid membranes and previously reported membranes in NaOH/Na$_2$WO$_4$ system

Membranes	IEC (mmol/g)	U_{OH} (m/h)	S	Ref
Sulfonated poly(phenylene oxide) (SPPO)	2.26	0.0014	36	[5]
SPPO/SiO$_2$	1.44–2.28	0.0014–0.0022	63–301	[5]
SPPO/nano-silica	1.87–2.00	0.015	34	[31]
PVA/SiO$_2$ (containing –SO$_3$Na groups)	0.72–1.05	0.0102–0.0111	16.9–18.5	[32]
SPPO/PVA/SiO$_2$	0.44–1.34	0.0070–0.0130	12.5–181	[33]
PVA/PSSS/SiO$_2$ (containing –SO$_3$Na groups)	1.03–1.64	0.0072–0.0208	16.8–25.7	[34]
PVA/MIDA/SiO$_2$ (containing –SO$_3$Na groups)	1.14–2.13	0.0090–0.0120	16.0–19.9	[35]
Sulfonated CS/PVA/SiO$_2$	0.10–0. 65	0.0135–0.0160	15.6–26.9	This work

gel method. The effect of sulfonated CS content on physical and chemical properties is investigated by ATR-FTIR, SEM, TGA, DMA studies, which shows that the prepared membranes have good homogeneity, thermal stability and flexibility. Ion exchange capacity, water uptake and linear expansion are also tested. The ion exchange capacity augments from 0.10 mmol/g to 0.65 mmol/g with the increasing content of sulfonated CS content in membrane matrix. The range of water uptake and linear expansion in water is 10–25%, 15–20%, respectively.

Diffusion dialysis (DD) for alkali recovery is tested with $NaOH/Na_2WO_4$ mixture. By comparing the other reported works, the developed membranes possess excellent OH^-ion transport performance (U_{OH}: 0.0135–0.0160 m/h) and acceptable selectivity (S: 15.6–26.9). Therefore, the developed membranes can be adopted in alkali recovery with DD.

Acknowledgments

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