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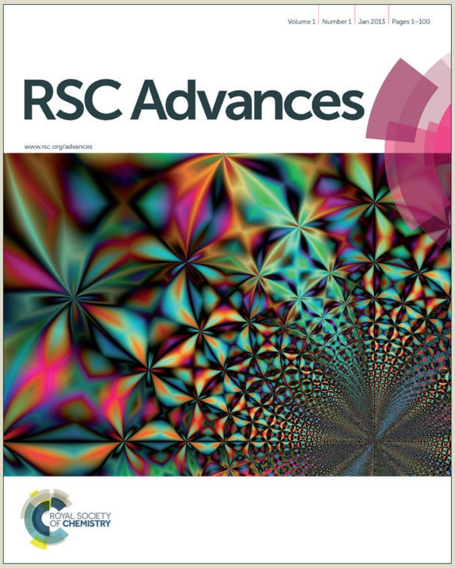

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Recovery of chemically degraded polyethyleneimine by a re-modification method: prolong the lifetime of cation exchange membranes

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Selectivity for monovalent cations is an important property of cation exchange membranes (CEMs). The cation exchange membranes of the type of CSO modified with polyethyleneimine have a higher selectivity for monovalent cations than the multivalent cations. Unfortunately, the loss of selectivity for these kinds of CSO seems to be unavoidable due to fouling and degradation of polyethyleneimine groups. In this situation, a “re-modification” technique was developed for recovery of fouled CSO, activating the fouled CSO by methanol and a sulfuric acid solution with ultrasonic vibration, followed by a layered surfacial electro-deposition method to prolong the lifetime of cation exchange membranes. A series of electrodialysis experiments for Na^+/Ca^{2+} separation was performed for evaluating and comparing the monovalent cation selectivity of the samples. The restoration of the surface and cross section morphology after “re-modification” was demonstrated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). As a result of the re-modification method the membranes with chemically degraded polyethyleneimine were again made functional. The ion exchange groups of the CSO modified with polyethyleneimine was successfully recovered, giving the membrane again a high permselectivity.

1. Introduction

The application of ion exchange membranes in separation of ions is an important recurrent problem in industrial applications especially in water treatment.[1] One of the most important features is the monovalent selectivity in CEMs for it can improve the selectivity of cations.[2,3] As a result of extensive studies, the ionic radius, hydrated ionic radius and charge density were found to be involved in the monovalent selectivity of cation or anion exchange membranes.[4-6] CEMs modified with polyethyleneimine (PEI) have been widely used in desalination and concentration of salt solutions in today’s industry.[7] Polyethyleneimine also has been used in many other applications,[8,9] increasing the pore density and as an additive in preparation of enhanced UF membranes,[10] decreasing membrane fouling.[11] Due to its relevant characteristics, high content of amine groups, high reaction activity and good film-forming characteristics, polyethyleneimine has been employed to improve the performance of CEMs.[12-14] Generally, CEMs are prepared by sulphonation of a polymer, so that the surface is covered with anionic groups.[15,16] In order to improve the monovalent cation selectivity of these membranes, surface modification is an effective method.[4,7,18] To this end, the positively charged polymers of polyethyleneimine can be attached to the surface of a CEM.[19]

Membrane fouling is one of the major problems for cation exchange membranes, which not only weakens the monovalent selectivity, but also reduces the flux and increases the membrane resistance.[20] Generally, membrane fouling is the accumulation of undesired inorganic compounds, macromolecules, or solid materials at the membrane–solution interface or inside the membranes.[21] The precipitate on the surface or in the interior of the membrane contributes to fouling of the CEMs, which will cause a poorer monovalent selectivity.[22-24] Furthermore, in the process of using CEMs modified with polyethyleneimine, polyethyleneimine groups may degrade. This may be another main reason for which these kinds of membranes lose the monovalent selectivity.[25] The above two reasons cause a loss of monovalent selectivity. At that stage, membranes are typically replaced. On the one hand, this increases the cost, while it also causes secondary environmental pollution, a waste of resources and economic losses.

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The monovalent selectivity of cation exchange membranes determine by the affinity in equilibrium conditions between the positive charges of the membranes and the solution counterions. Polyethyleneimine is a prominent monovalent selective modification material for cation exchange membrane because of its positive charge groups;[26] methods to modify on the CEMs surface have been repacked;[27-28] new methods for modification materials.[29-33] In recent years, many studies have been carried out to clean fouled membranes. However, there is a lack of studies to restore the loss of functional groups in ion exchange membranes.

In this paper, the loss of functional groups of a used CSO was reversed by a re-modification method in view of recovering fouled and chemically degraded polyethyleneimine groups. Firstly, the fouled membranes were cleaned, because the precipitates of calcium and magnesium salts on the surface or in the inner structure of membranes are thought to be part of CEM fouling. Then the fouled CSO were re-modified by adding new polyethyleneimine groups on the surface of the CEM by a specific, newly developed method.

This study is aimed at improving the monovalent cation selectivity of commercial CSO under electrodialysis (ED) conditions, and creating a highly negative charge on the membrane surface. To the best of our knowledge, the re-modification of CSO using polyethyleneimine deposition in the ED process, and the simultaneous recovery of the monovalent cation selectivity of ion exchange membranes have not been reported yet.

2. Experimental

2.1. Materials

Cation exchange membranes of the type of CSO (SELEMION^{TM}, Japan) were used. These contain polyethyleneimine groups, after their industrial use for separating Na^+/Ca^{2+} ions many times, this kind of membranes have no selectivity function for monovalent cations but the ions separated were normal. The characteristic properties of this kind of membrane are shown in Table 1. The anion exchange membrane membrane (FUJIFLM Corp. Japan) was used to prevent leakage of cations. The characteristic properties of AEMs are also show in Table 1. Other chemicals, including NaCl, $CaCl_2$, $CaSO_4$, H_2SO_4, methyl alcohol were used in this research and all chemicals were used as received. Milli-Q water (Millipore, Bedford, MA, USA) was used in all experiments.

2.2. The preparation of the fouled CSO

The fouled CSO was the membrane with chemically degraded polyethyleneimine. It was rinsed using distilled water. In order to clean the fouling materials, the membrane was immersed in 10% methanol or ethanol solution for 2 h with the frequency of the ultrasonic vibration waves at 40 kHz and then rinsed using distilled water three times. In this study, we preferred over other alcohols for the polarity of methanol higher than the ethanol. After that, the membrane was immersed in 0.05 M sulfuric acid for 2 h with ultrasonic vibrating and rinsed with distilled water three times to remove the chemically degraded polyethyleneimine groups. Finally, the CSO was immersed in Milli-Q water. This obtained membrane is named pre-treated membrane.

2.3. Surface modification and characterization

The polyethyleneimine solutions were prepared by dissolving 10 g/L of polyethyleneimine with 0.5 M NaCl (as a supporting electrolyte) in Milli-Q water. No other materials in the solution. The CEM was clamped in the middle of four cells and the other two auxiliary membranes were both anion exchange membranes to prevent leakage of cations. Furthermore, 0.2 M Na_2SO_4 solutions were used as electrode solution for both cathode and anode. The surface modification of the CSO was conducted on a lab-made ED apparatus, as shown in Figure 1. The polyethyleneimine with 0.5 M NaCl solutions were placed in one compartment of the two middle cells, and a 0.5 M NaCl solution was placed in the other compartment. One surface of the CSO was then modified via an ED experiment with the polyethyleneimine solutions. In this work, the ED experiment was tested at a current density of 10 mA/cm^2. To improve the stability of the re-modified membrane, the membrane was immersed in Epichlorohydrin solution as crosslinking agent for 2 h. After the above process, the membrane was rinsed using Milli-Q water.

Table 1. Characteristics of the commercialized CEMs and AEMs used in this study

Membrane type	Thickness (μm)	IEC (mmol g^{-1})	Area resistance (Ωcm^2)	Transport number (%)	pH stability
CSO (CEM)	100	1.04	2.9	97	2-12
Homogeneous (AEM)	125	1.06	1.3	98	2-13

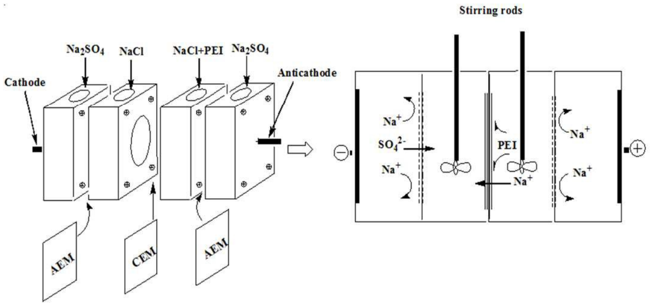

Fig. 1 The surface modification of the CSO on a lab-made ED apparatus.

2.4. Permselectivity Measurement

The permselectivity measurement of the membrane was conducted on the same lab-made ED apparatus, as shown in Figure 2. The CSO re-modified with polyethyleneimine sample was clamped in the middle of the four chambers. In our studies, membrane area adopted in the permselectivity measurements was 19.625 cm^2. Solutions with NaCl and $CaCl_2$ were in the middle of two cells and a NaCl solution was used as electrode solution. All the anions were chloride ions in order to avoid the influence of anions on the selectivity. In addition, 0.2 M NaCl solutions were used as electrode solution for both cathode and anode. The ED experiment was carried out at a current density of 7.65 mA/cm^2. The concentration of Na^+ and Ca^{2+} in the dilute chamber was measured by cation chromatography every 10 min.[34,35] At the same time, the conductivity in the diluted compartment was also measured.

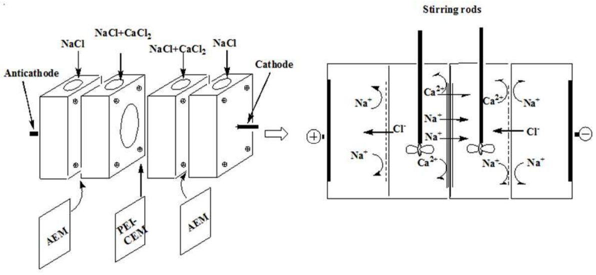

Fig. 2 Permselectivity measurements of the membrane.

2.5. Characterization

The changes of the foundational groups on the membrane surface were monitored by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Nicolet 6700) at room temperature to provide information about the chemical structure of the fouled and re-modified membranes. The changes in the fouled, pre-treated and re-modified CSO surface morphology were observed by scanning electron microscopy (S-4700 Hitachi, Tokyo, Japan). SEM images of membranes were taken after being dried in a vacuum oven, and then coated with gold. To quantify the membrane surface elemental composition of the fouled membrane, pre-treated membrane and re-modified membrane, all the membranes were analyzed by X-ray photo-electron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan) the anode was mono (Al (Mono)) (45 W). The step was 1000.0 meW and dwell time was 100 ms. The charge neutralizer was on current 1.8 A, balance 3.3 V and bias 1.0 V.

3. Results and discussion

3.1. Characterization of the re-modified membrane

The ATR-FTIR spectra of the fouled CSO, pre-treated CSO and CSO after re-modification are presented in Fig. 3. In the spectra of re-modified membrane, the band at 1480 cm^{-1} was assigned to the bending vibration of C–N indicating the existence of PEI on the CEM.[36] The peak intensity of the ATR-FTIR spectrum changes significantly. Due to the stretching vibration of the polyethyleneimine groups and the deformation vibration of N-H, the bands at 3430 cm^{-1} increase substantially.[12] The differences of the fouled membrane surface, pre-treated membrane surface and the membrane surface after re-modification can be identified. Compared to the change of the fouled membrane surface and pre-treated membrane surface, due to the presence of fouling and shedding polyethyleneimine groups, the peak intensity of fouled membrane surfaces of ATR-FTIR spectra is smaller than that of the of pre-treated membrane surface. After re-modification of polyethyleneimine groups on the membrane surface, the peak intensity of ATR-FTIR spectra change significantly.

Fig.4 (A) shows the images of the commercial CSO, the CEM with the colour of dark brown. However, the fouled CSO with chemically degraded as shown in Fig.4 (B), the fade of dark brown and fouling materials on its surface. After pre-treated membrane and re-modification of polyethyleneimine, the surface of membrane change cleaner and the colour of membrane change, as shown in Fig.4 (C). To further verify the differences between the fouled, pre-treated membrane and re-modified membrane, the membrane surface morphology was observed by SEM. Figure 5. An obvious difference was detected between the three images. These surface morphology differences might be due to the different materials present on the CSO surface. For the fouled membrane, due to the presence of fouling and shedding polyethyleneimine groups stick-like materials occurred and no obvious tiny flake shaped bulge on the surface was observed. For pre-treated membranes there are some tiny flake shaped bulges on the surface without fouling material. For the re-modified surface membrane, the tiny flake shaped bulge on surface is more concentrated.

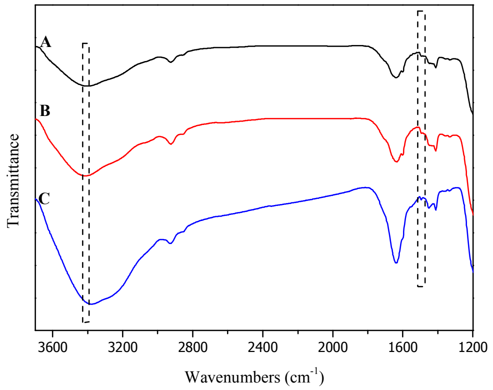

Fig. 3 FT-IR spectra of the CSO fouled (A), pre-treatment (B) and re-modification (C).

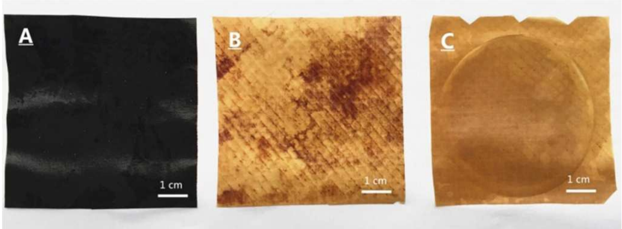

Fig. 4 Images of CSO (A), chemically degraded membrane (B) and re-modified membrane(C).

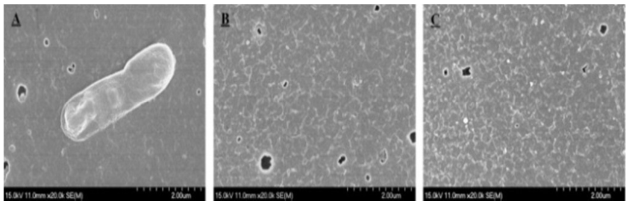

Fig.5 SEM images of the surface of the fouled membrane (A), the pre-treated membrane (B) and the re-modified membrane (C).

The SEM images of cross-section of fouled membrane, pre-treated membrane and re-modified membrane are shown in Fig. 6 (A), (B), and (C), respectively. According to SEM images, the average thickness of substrates is about 0.090 mm and the thickness of modified layer is about 3 μm. In the case of the re-modified membrane the modified layer can be distinguished from the membrane substrate while this layer cannot be found out in Fig. 6 (A), (B). The SEM cross-section image of the fouled membrane (A) and pre-treated membrane (B) does not show the functionalized layer clearly. However, the re-modified cross sectional membrane (C) clearly shows the polyethyleneimine layer.

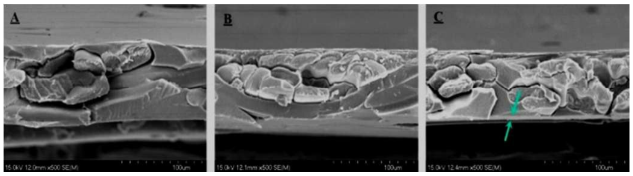

Fig. 6 SEM images of the cross section of the fouled membrane (A), of the pre-treated membrane (B) and of the re-modified membrane(C)

The chemical composition of the surface of the fouled membrane, pre-treated membrane and re-modified membrane was further analyzed by XPS, as shown in Fig 7. For comparison, the main corresponding elements C, O, N and S in the chemical structure of the membrane were measured under the same conditions. Fig. 7 (A), (B) and (C) show the wide spectra of membrane. The peaks of four elements at 529.7eV, 397.2eV, 282.2 eV, and 165.8eV can be assigned to O 1s, N 1s, C 1s and S 2p, respectively. Fig. 7 (A) was the fouled membrane spectra. In comparison with the spectra of the fouled membranes, the peak intensity of O 1s obviously decreased (Fig. 7 (B)). However, the peak intensity of O 1s in the re-modified membrane surface obviously increased compared to Fig. 7 (B). This is because the re-modified polyethyleneimine and the epichlorohydrin as crosslinking enhanced the O 1s elements. The corresponding element ratios of these membrane surfaces are shown in Table 2. It can be seen that the C 1s atomic ratio of the pre-treated membrane is the highest, followed by the fouled membrane and the re-modified membrane. For the re-modified membrane, the N 1s atomic ratio is the lowest, because the polyethyleneimine groups were crosslinked to the membrane surface accurately, and the N 1s of polyethyleneimine atomic ratio is very low. It can also be seen that the S 2p atomic ratio does not change, which illustrates that the sulfuric acid groups of the CSO were not changed, and the base films were not changed.

Table 2. Average chemical compositions of the different membranes (limited to C, O, N, S)

Membrane types	Elements (at. %)			
	C 1s	O 1s	N 1s	S 2p
Fouled	70.34	22.37	5.80	1.49
Pretreatment	72.30	24.25	1.89	1.56
Re-modified	68.64	19.05	10.79	1.52

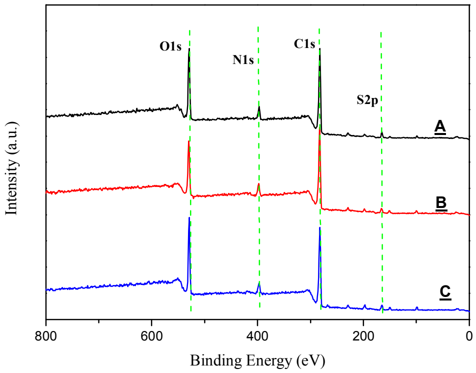

Fig. 7 XPS images of fouled CSO（A）, pre-treatment CSO (B) and re-modified CSO (C).

3.2. Performance of re-modified membranes: monovalent cations selectivity

The selectivity of monovalent cations is a key performance parameter to be restored after re-modification. To investigate the perm-selectivity of the re-modified CSO membranes, the equivalent concentration of Ca^{2+} relative to Na^{+} was measured in the diluted compartment. The concentration of each cation was measured in the diluted compartment by cation chromatography every 10 min and the total time was 80 min. In the diluted compartment as well as in the concentrated compartment, the concentration in the feed section of Ca^{2+}

and Na^+ was both 2.50 g/L. The number of cations passing through the CSO from the diluted compartment to the concentrated compartment is needed to calculate the ion flux. Thus, the Fig. 8, shows the Na^+ and Ca^{2+} concentrations in the diluted compartment was plotted as a function of time in ED process. Fig. 8 (A) shows the commercial CSO separate the Ca^{2+} and Na^+ ions change in diluted compartment equivalent and the concentration of Ca^{2+} ions higher than Na^+ ions in the ED process. Thus, the commercial CSO has the effect of perm-selectivity of cations. However, the Fig. 8 (B) shows the fouled CSO, the concentration of Na^+ ions higher than Ca^{2+} ions. When after re-modification of the CSO, as shows in Fig. 8 (C) the re-modified CSO show the same phenomenon as the commercial CSO in diluted compartment equivalent.

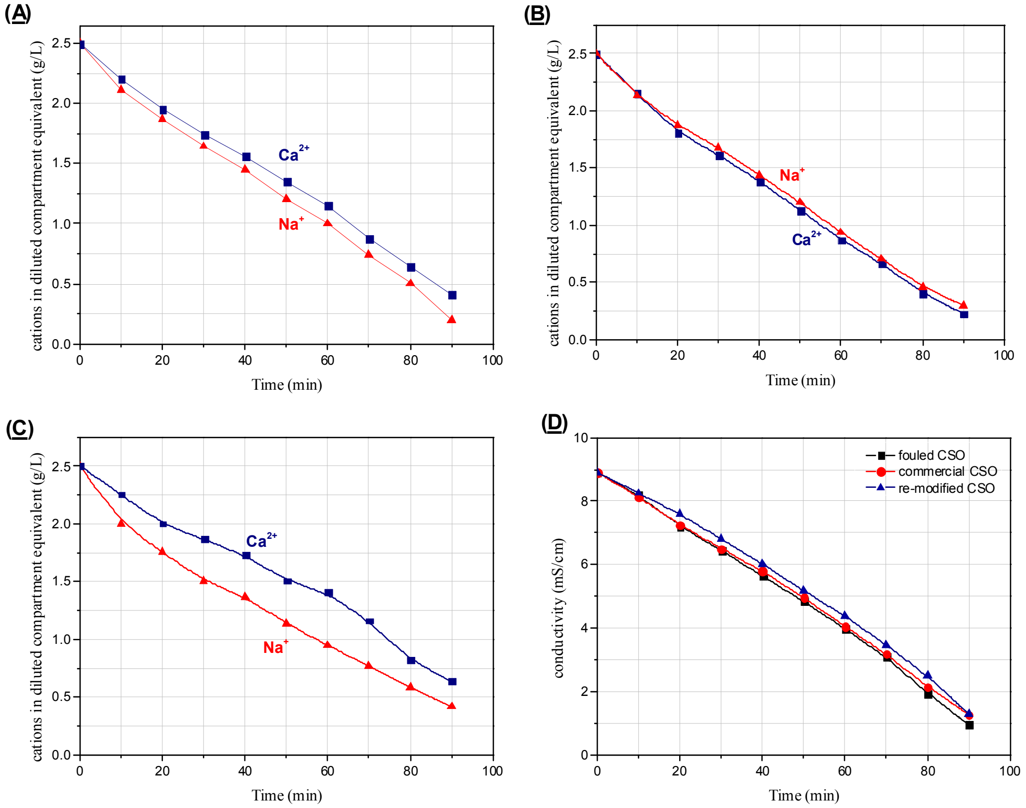

Fig. 8 Time-dependent amounts of Na^+/Ca^{2+} and conductivity in the diluted compartment during ED process.

Fig. 8 (D) shows the time-dependent reduction of the conductivity in the diluted compartment during ED. No obvious difference was observed between the diluted compartment of the fouled CEM modified with polyethyleneimine and the re-modified CEM for the conductivity. This indicates that the membrane before and after re-modification are both excellent for separating ions i.e., the failed membrane still has its ion exchange functionality even though the selectivity has disappeared, as demonstrated. A slight difference can be suspected, which is probably related to the additional polyethyleneimine layer that was added to the re-modified membrane, which causes an additional resistance.

However, the equivalent concentration of Ca^{2+} relative to Na^+ value which was measured in the diluted compartment cannot be accurately used to characterize the separation in the commercial CSO, fouled CSO and re-modified CSO. Thus, the separation efficiency, a new parameter, was constructed here as an alternative for this parameter. What's more, the separation efficiency allows making an objective comparison of concentration of Ca2+ relative to Na+ value and calculated from the gradient of the smoothed lines in Fig. 8. The separation efficiency is relatively constant as a function of time, it reflects the relative difference in transport rate and ranges from -1 (no separation) to 1 (complete separation). The separation efficiency S of component Na^+ and Ca^{2+} was evaluated as

$$S(t) = \frac{(c_D(t)/c_D(0)) - (c_M(t)/c_M(0))}{(1 - c_D(t)/c_D(0)) + (1 - c_M(t)/c_M(0))} \times 100\%,$$

where c_D and c_M are the concentrations of divalent ions and monovalent ions in the diluted compartment. In this evaluation, $c_D(t)$ and $c_M(t)$ are the concentrations of the Ca^{2+} ions and Na^+ ions in diluted compartment after t min. $c_D(0)$ and $c_M(0)$ are the concentrations of the Ca^{2+} ions and Na^+ ions in diluted compartment at the start of the experiment. To evaluate the monovalent selectivity after re-modification, it is assumed that Ca^{2+} is the slowest permeating component. If the separation efficiency S is a positive number, the membrane has a monovalent selectivity. This reflects the relative difference in transport rate. It can be seen from Fig. 9 the separation the efficiency of fouled membrane is a negative number, indicating no monovalent selectivity. The separation efficiency of re-modified membrane is positive, reflecting monovalent selectivity between Na^+ and Ca^{2+} ions. After 80 min, the separation efficiency naturally falls back to zero, due to the depletion or both Na^+ and Ca^{2+} ions, for normal operating conditions, a lower residence time is realistic. At t=30 min, the re-modified membrane show a significant monovalent selectivity apposite to the fouled membrane.

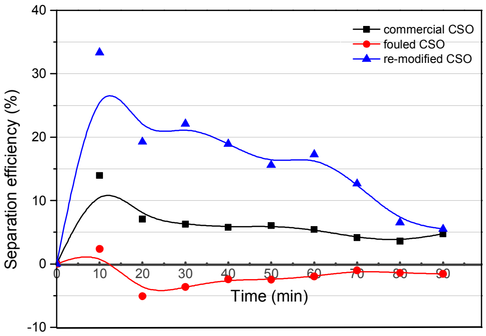

Fig. 9 Separation efficiencies (%) as a function of time

Conclusions

Surface re-modification with polyethyleneimine was used to improve the monovalent cation selectivity of fouled CSO in the ED process. In this study a method was developed for simultaneous restoration of the fouled membrane in terms of the fouling and chemically degraded polyethyleneimine groups, to improve of the monovalent cation selectivity of a commercial standard cation exchange membrane. By immersing the fouled CSO in a methanol solution, followed by immersion in sulfuric acid with ultrasonic vibration, it is possible to remove the chemically degraded polyethyleneimine groups. After treatment of the fouled membrane, the CSO had no residual fouling and chemically degraded polyethyleneimine groups. After that, using surface modification with ED was applied by using deposition and chemical crosslinking with a polyethyleneimine solution. Epichlorohydrin as crosslinking agent was used in order to improve the stability of polyethyleneimine groups. After re-modification, the monovalent cation selectivity of the membrane was improved.

Acknowledgements

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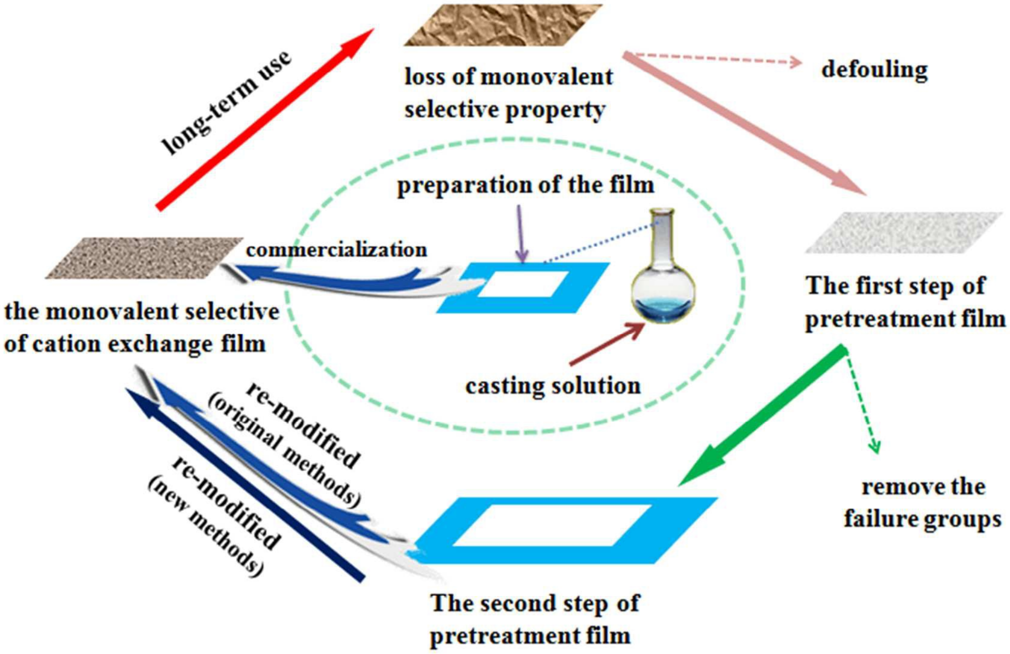
References

1. B. Van der Bruggen, A. Koninckx and C. Vandecasteele, *Water Research*, 2004, **38**, 1347-1353.
2. X. T. Le, P. Viel, P. Jégou, A. Garcia, T. Berthelot, T. H. Bui and S. Palacin, Journal of Materials Chemistry, 2010, 20, 3750.
3. R. Guinamard, A. Chatelier, M. Demion, D. Potreau, S. Patri, M. Rahmati and P. Bois, *The Journal of Physiology*, 2004, **558**, 75-83.
4. L. Ge, L. Wu, B. Wu, G. Wang and T. Xu, *Journal of Membrane Science*, 2014, **459**, 217-222.
5. G. S. Gohil, R. K. Nagarale, V. V. Binsu and V. K. Shahi, *Journal of Colloid and Interface Science*, 2006, **298**, 845-853.
6. J. Li, M. l. Zhou, J.y. Lin, W.y. Ye, Y.q. Xu, J.n. Shen, C.j. Gao and B. Van der Bruggen, *Journal of Membrane Science*, 2015, **486**, 89-96.
7. H. K. Mourad Amara, *Desalination*, 2003, **155**, 79-87.
8. D. Y. a. J. B. L. Ann R. Klemm, *Biochemical Pharmacology*, 1998, **56**, 41-46.
9. L. Q. a. X. Gao, *ACS NANO,* 2008, **2**, 1403-1410.
10. X. Fang, J. Li, X. Li, X. Sun, J. Shen, W. Han and L. Wang, *Journal of Membrane Science*, 2015, **476**, 216-223.
11. J. Xu, Z. Wang, J. Wang and S. Wang, *Desalination*, 2015, **365**, 398-406.
12. M. Wang, X. Liu, Y.x. Jia and X.l. Wang, *Separation and Purification Technology*, 2015, **140**, 69-76.
13. D. Zhu, Z. Xiao and X. Liu, *International Journal of Hydrogen Energy*, 2015, **40**, 5081-5091.
14. M. R. S. Kebria, M. Jahanshahi and A. Rahimpour, *Desalination*, 2015, **367**, 255-264.
15. J. H. Park, M. J. Han, D. S. Song and J. Y. Jho, *ACS Applied Materials & Interfaces*, 2014, **6**, 22847-22854.
16. A. R. Moghadassi, P. Koranian, S. M. Hosseini, M. Askari and S. S. Madaeni, *Journal of Industrial and Engineering Chemistry*, 2014, **20**, 2710-2718.
17. S. M. Hosseini, A. Gholami, P. Koranian, M. Nemati, S. S. Madaeni and A. R. Moghadassi, *Journal of the Taiwan Institute of Chemical Engineers*, 2014, **45**, 1241-1248.
18. S. M. Hosseini, P. Koranian, A. Gholami, S. S. Madaeni, A. R. Moghadassi, P. Sakinejad and A. R. Khodabakhshi, *Desalination*, 2013, **329**, 62-67.
19. Z. W. Huining Deng, Wei Zhang, Baisong Hu, Shaofeng Zhang, *Journal of Applied Polymer Science*, 2015, 41488.

20. Q. Wang, P. Yang and W. Cong, *Separation and Purification Technology*, 2011, **79**, 103-113.
21. Y. Yang, X. Gao, A. Fan, L. Fu and C. Gao, *Journal of Membrane Science*, 2014, **449**, 119-126.
22. N. Cifuentes-Araya, G. Pourcelly and L. Bazinet, *Journal of Colloid and Interface Science*, 2012, **372**, 217-230.
23. J. Xu, G. P. Sheng, H. W. Luo, W. W. Li, L. F. Wang and H. Q. Yu, *Water Research*, 2012, **46**, 1817-1824.
24. Q. Ping, B. Cohen, C. Dosoretz and Z. He, *Desalination*, 2013, **325**, 48-55.
25. S. M. Dockheer, L. Gubler, A. Wokaun and W. H. Koppenol, *Physical Chemistry Chemical Physics*, 2011, **13**, 12429-12434.
26. T. P. N. N. Byung-Moon Jun, Soo-Hyun Ahn, In-Chul Kim, Young-Nam Kwon1, *Journal of Applied Polymer Science*, 2015, 42198.
27. Z. Chen, M. Deng, Y. Chen, G. He, M. Wu and J. Wang, *Journal of Membrane Science*, **2004**, 235, 73-86.
28. Y. Liu, R. Luo, F. Shen, L. Tang, J. Wang and N. Huang, *Applied Surface Science*, 2015, **328**, 163-169.
29. P. Xu, M. Capito and T. Y. Cath, *Journal of hazardous materials*, 2013, **260**, 885-891.
30. M. Wang, K.-k. Wang, Y.-x. Jia and Q.-c. Ren, *Journal of Membrane Science*, 2014, **452**, 54-61.
31. Y. Zheng, Z. Li, X. Wang, X. Gao and C. Gao, *Electrochimica Acta*, 2015, **169**, 150-158.
32. A. H. Galama, G. Daubaras, O. S. Burheim, H. H. M. Rijnaarts and J. W. Post, *Electrochimica Acta*, 2014, **136**, 257-265.
33. M. Amara and H. Kerdjoudj, *Desalination*, 2003, **155**, 79-87.
34. S. Abdu, M. Martí-Calatayud, J. E. Wong, M. García-Gabaldón and M.Wessling, *ACS Applied Materials &Interfaces* ， 2014, **6**, 1843-1854.
35. M. Wang, X. Liu, Y. X. Jia and X. L. Wang, *Separation and Purification Technology*, 2015, **140**, 69-76.
36. N. White, M.Misovich, A. Yaroshchuk and M. L. Bruening, *ACS Applied Materials &Interfaces*, 2015, **4**, 6620-6628.



Graphical abstract Recovery of chemically degraded cation exchange membranes in a cyclic process