RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Polyelectrolyte complexes nanofiltration membranes: performance modulation via casting solution pH

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qiang Zhao[a], Yan-Li Ji[a], Jia-Kai Wu[a], Ling-Ling Shao[a], Quan-Fu An*[a], Cong-Jie Gao[b,c]

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China.*
[b] *Department of Chemical Engineering and Bioengineering, Zhejiang University, Hangzhou 310027, China*
[3] *The Development Center of Water Treatment Technology, Hangzhou 310012, China*

Nanofiltration (NF) membranes were prepared from a solution processable polyelectrolyte complex (PEC) between sodium carboxymethyl cellulose (CMCNa) and poly (2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC). Electrostatic complexation structures of the PEC were studied by light transmittance and field emission electron scanning microscopy (FESEM). It is found that that the electrostatic complexation structure of the PEC membranes determines their NF performance, which is conveniently tailored via the pH values of casting solutions. For membranes prepared at the optimum solution pH 2.1, their water flux and salt rejection to K_2SO_4 (1 g L^{-1}) are 18 g $m^{-2}h^{-1}$ and 97 %, respectively, when the operation pressure and temperature are 0.6 MPa and 25 ^oC. Both the water permeability and the salts selectivity are substantially improved compared to the pristine CMCNa NF membrane. In addition, antifouling performance of the PEC membrane is improved, coupled with an exceptional stability versus the operation time.

1. Introduction

Nanofiltration (NF) is a pressure-driven separation technology with membrane pore sizes (ca. 1 nm) and operation pressure (0.5 ~ 1.5 MPa) falling between those of reverse osmosis and ultrafiltration.[1] NF is playing an active role in addressing today's challenges encompassing clean water, sustainable environment, and molecular separation.[2-6] NF membranes reject solutes through a combination of size sieving effect and charge exclusion effect (Donnan exclusion). In this regard, thin membranes with narrowly distributed nanopores and tailored surface charges are sought after, as exemplified by phase inversion asymmetric membranes[7-9] and interfacial polymerized thin film composite membranes.[10-11] More recently, other complementary membranes such as surface grafting,[12] solution coating,[13] biomimetic fabrication,[14] and spun fibrous membranes[15-16] are also being pursued for NF applications.

Electrostatic layer-by-layer (LbL) assembly between oppositely charged polyelectrolytes represents a versatile means to multilayered polyelectrolyte complex (PEC) membranes with tailored thicknesses and structures.[17] LbL PEC films are playing pivotal roles in molecular separation, surface engineering, and energy conversion.[18-19] In particular, recently they are also proven well suited for NF.[20] For example they have been applied in both the water-borne[21-24] and solvent resistant NF processes[25] including ion separation, brackish water desalination, and organics removal. However, despite the wealth of successes already achieved, the preparation of LbL PEC membranes is time consuming and laborious, representing a hurdle to both the research and practical ends.[26] As such, new materials that are structurally analogous to LbL PEC membranes but more easily accessible are earnestly demanded. Therefore we are interested in solution-mixed PECs, not only because they possess electrostatic complexation structures equivalent to that of LbL PEC membranes,[27-28] but also for the synthetic ease as they are accessible *via* a single step of solution mixing. Very recently we exploited solution-mixed PECs as NF membranes, giving rise to PEC NF membranes (PECNFMs) with reasonable flux and salts rejection.[29] The successful application of solution-mixed PEC as NF membranes alleviated the burden arising from the laborious preparation of LbL films. Yet, there are much unknown with respect to the general availability of this strategy, the separation mechanism, and the

performance tailoring, to name just a few. Furthermore, the correlation between the electrostatic complexation structures of as-prepared PECNFMs and their NF performances is still lacking, along with the need to further improve separation performances.

The aim of this study is to investigate the effect of the electrostatic complexation structures of PECNFMs on their NF performances, and ultimately to improve the separation performances and antifouling properties. We choose sodium carboxymethyl cellulose (CMCNa) and poly (2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC) as starting materials for preparing solution processable PECs. This is because CMCNa possesses both the carboxylic acid groups (COOH) and the hydroxyl groups (OH) that render the PECs soluble and covalently crosslinkable. Meanwhile, PDMC's hydrophilicity is beneficial for higher separation performance.

2. Experimental

2.1. Materials

CMCNa (degree of substitution: 0.85) was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. The intrinsic viscosity of CMCNa in 0.01M NaCl at 30 ^{o}C is 1198.3 mL g^{-1}. PDMC (*M*w=300 000 g/mol) was purchased from HenYi chemical plant, Shanghai, China. Glutaraldehyde (25.0 wt%), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4, 95.0 ~ 98.0 wt%), sodium chloride (NaCl) and potassium sulfate (K_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Bovine serum album (BSA, biological regent) was purchased from Aladdin-reagent Co., Ltd. Polysulfone ultrafiltration supporting membranes (MWCO = 35,000 Da) were kindly provided by the Development Centre of Water Treatment Technology, Hangzhou, China. Deionized water with a resistance of 18MΩ cm was used in all experiments.

2.2. Preparation of PECNFMs

First, the CMCNa-PDMC PECs were synthesized in the same method reported in our previous study;[30] the molar ratio of PDMC monomer to CMCNa monomer of this PEC material is 0.31 (calculated from elemental analysis). In detail, aqueous solutions of CMCNa (300 mL, monomer mole concentration: 0.01 M) and PDMC (200 mL, monomer mole concentration: 0.01 M) were prepared respectively, with HCl concentration in both solutions kept at 0.009 M. The PDMC solution was added into the CMCNa solution (600 rpm stirring) at a speed of 10 ±1 mL min^{-1}, yielding PEC precipitates (CMCNa-PDMC PEC) when CMCNa was fully neutralized by PDMC. The precipitates were collected by filtration and washed three times with deionized water to remove impurities. Noteworthy, the as-prepared PEC possesses carboxylic acid groups (COOH) and hydroxyl groups (OH) that are crucial for the subsequent membrane preparation (Fig. 1).

Second, PECNFMs were prepared via solution casting followed by a glutaraldehyde chemical cross-linking (Fig. 1). In detail, CMCNa-PDMC PEC (0.16 g) and glutaraldehyde (36 mg) were dissolved in 20 mL of 0.02 M NaOH to form PEC dispersions. The mechanism that renders the PEC soluble in aqueous NaOH has been exhaustively proved in our previous studies.[30] In general, the COOH groups in PECs are deprotonated into carboxylate groups (COO^{-}) by aqueous NaOH, thus endowing water solubility to the PECs. Next, pH of the PEC dispersion was tailored to adjust PECs aggregate particles structures. Finally, the PEC dispersion was cast on a polysulfone supporting membrane and kept for 3 mins, then the superfluous liquids on the membrane were drained off by a glass rod and the composite PECNFMs were dried at 50 ^{o}C for 3 h (Fig. 1a). During the drying, the covalent crosslinking reaction between hydroxyl groups (on PEC) and aldehyde groups (on glutaraldehyde) took place to stabilize the membrane structure (Fig. 1b). Noteworthy, PECNMF prepared from PEC dispersion with a pH value of X is denoted as PECNMFX.

For the preparation of CMCNa NF membranes, CMCNa (0.16 g) and glutaraldehyde (36 mg) were dissolved in 20 mL water. The pH of CMCNa solution was tailored to the designed value. Then CMCNa NF membranes were prepared following the same procedure for PECNFMs described above.

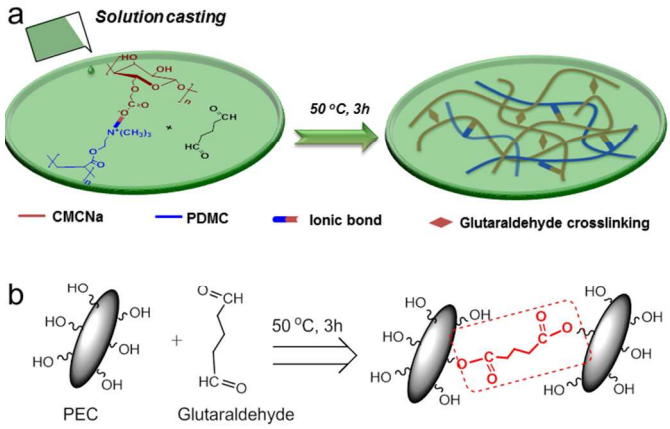

Fig. 1. (a) Schematic preparation of CMCNa-PDMC PEC nanofiltration membranes via solution casting followed by drying and glutaraldehyde crosslinking, (b) chemical crosslinking reaction between hydroxyl groups on PEC and glutaraldehyde crosslinker during the drying step.

2.3. Nanofiltration tests

NF performances of PECNFMs were performed on the same apparatus in our previous study.[29] Feed solution was cycled at a high speed (0.55 L/min); the operation pressure was kept ≤ 0.6 MPa to minimize the concentration polarization effect. Flux (*J*) and rejection (*R*) of NF processes were calculated in equations below.

$$J = V/(A \times t) \quad (1)$$

$$R = 1 - C_p/C_f \quad (2)$$

Above, V is the volume of permeate water through NF membranes, A is the effective membrane area (22.4 cm^2), t is the operation time. C_p and C_f are the salt concentrations in the permeation and feed, respectively, which were determined with electrical conductivity (DDS-11A, Shanghai Leici Instrument Works, China).

Antifouling performances of PECNFMs were examined with 1 g L^{-1} K_2SO_4 and 0.1 g L^{-1} model organic foulant BSA. After being pre-pressurized (0.7 MPa, 1 h), all the permeation tests were conducted at 25 °C under 0.6 MPa. First, an aqueous 1 g L^{-1} K_2SO_4 solution was filtrated through the membrane for 6 h, and then an aqueous 1 g L^{-1} K_2SO_4 with 0.1 g L^{-1} BSA was subsequently filtrated for the next 6 h. Then the membrane was washed thoroughly with deionized water for 2 h (the washing time was not counted in the filtration plots. Finally, the membrane was retested with 1 g L^{-1} K_2SO_4 solution. The water flux of PECNFMs was determined every hour in the filtration process.

2.4. Characterizations

The light transmittance of PEC dispersions was measured with a spectrophotometer (Spectrophotometer-722, Shanghai Third Analytical Instruments Factory, China) at a wavelength of 680 nm. Please note: light transmission is a well-documented method to study the colloid dispersions of complex aggregates.[31] Morphologies of PECNFMs were studied with field emission electron scanning microscopy (FESEM) (FEI SIRION-100, USA). To investigate the morphologies of PEC particles, dilute PEC dispersions (0.05 wt%) was deposited on silicon wafer, dried at 20 °C, coated with gold, and observed with FESEM.

3. Results and discussion

3.1. Effect of pH value on structures of PEC aggregate particles

First we set out to investigate the structure of PEC casting solution, which is normally comprised of PEC aggregate (PECA) colloidal particles formed through the electrostatic complexation between CMCNa and PDMC chains.[27] In addition to this feature, it is noteworthy that there are residual carboxylate groups (COO^-) on CMCNa-PDMC PECA particles. The protonation of these carboxylate groups, which depends on solution pH, is a key factor that determines the particle stability. As seen from Fig. 2, the plot of light transmittance of PEC dispersion versus pH value can be divided into three regions. The light transmittance decreases slowly in the pH 8.8 – 5.0 (region I), then drops prominently from pH 5.0 to pH 2.5 (region II), and followed a sharp increase thereafter (region III). In the region I, the PECA particles appear stable because of the negative charges from COO^- groups.[32] In the region II, the protonation degree of COO^- groups gradually increases with decreasing pH value below 5, correlating well with its pKa value. Consequently the electrostatic repulsion between negatively charged PECA particles gradually decreases, leading to the inter-particles micro-coalescence accompanied by an increase in turbidity.[33] In the region III (pH < 2.5), interestingly the light transmittance increases rapidly and the dispersion becomes transparent again, implying that the electrostatic complexation is considerably weakened at this stage, with weakly complexed PECA particles being the main building blocks.[33]

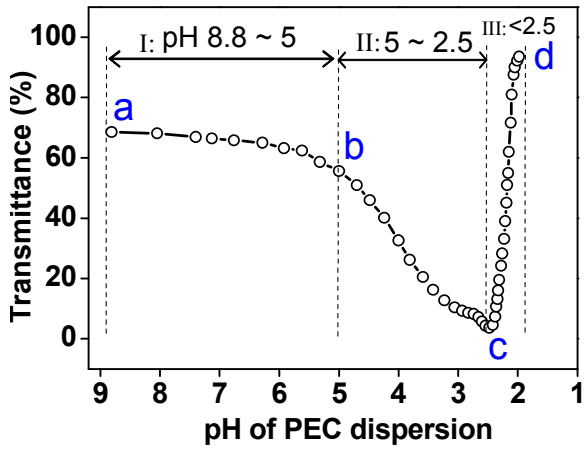

Fig. 2. Effect of pH values of PEC dispersion (0.1 wt%) on its optical transmittance at 680 nm.

To support the observation, morphologies of PECA particles at different pH values were examined by FESEM (Fig. 3). Indeed, submicron sized PECA particles are visualized at pH 8.8 (Fig. 3a), whereas the particulate morphology is retained till pH 5.0 (Fig. 3b), in good agreement with the stable light transmittance in the region I in Fig. 2. With decreasing pH to 2.5 (region II in Fig. 2), large aggregates with sizes around tens of microns reveal (Fig. 3c), likely owing to the inter-particle coalescence due to the lack of electrostatic repulsion forces caused by the protonation of COO- groups. With further decreasing pH below 2.5, these large aggregates decompose into smaller ones with weakened inter-chain electrostatic complexation (Fig. 3d). Noteworthy, the original particle morphology in Fig. 3a and Fig. 3b are not seen in Fig. 3c and Fig. 3d, because PECA particles adopt loosen architectures that prone to merge when the repulsion force between particles is weakened with decreasing pH.[34] Furthermore, the effect of pH on PECA particles is reasonably reflected in the morphologies of their corresponding membranes made from these casting solutions (Fig. 4). While the CMCNa membrane and PECNFM2.1 feature smooth and dense surfaces (Fig. 4a and Fig. 4d), the rough surfaces of PECNFM5.0 (Fig. 4b) and PECNFM2.5 (Fig. 4c) correlate well with the macroscopic aggregation of PECA particles in their casting solutions. In addition, the thickness of CMCNa and PECNFM2.1 are 261 nm and 362 nm according to the crossectional SEM pictures (Fig. 4e, Fig. 4f).

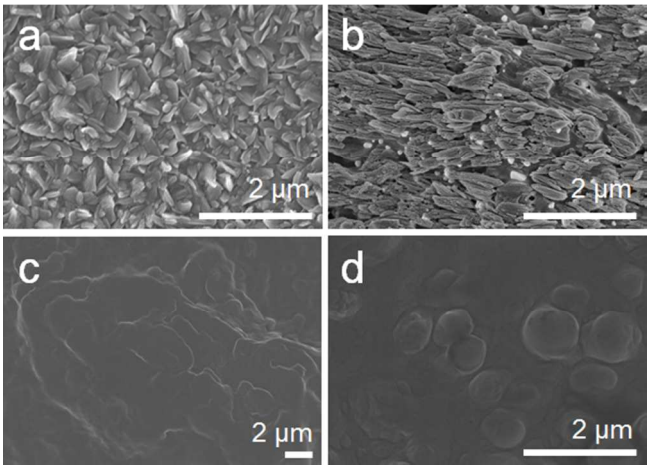

Fig. 3. FESEM morphologies of PECA particles at pH values of (a) 8.8, (b) 5.0, (c) 2.5, and (d) 2.1, respectively.

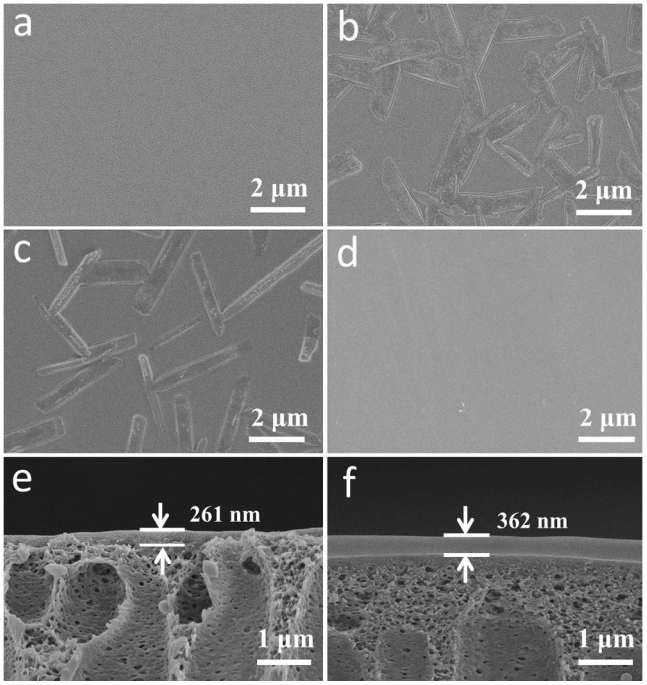

Fig. 4. (a-d) FESEM surface morphologies of CMCNa membrane, PECNFM5.0, PECNFM2.5, and PECNFM2.1, respectively; (e,f) cross-sectional morphologies of the CMCNa membrane and PECNFM2.1, respectively.

3.2. Effect of pH values on NF performances of PECNFMs

While the pH of PEC casting solution heavily affect the structures of PECA particles (Fig. 2 ~ Fig. 4), the next curiosity is to understand its influence on the membranes' NF performance (Fig. 5). For membranes made from casting solution with decreasing pH from 7 to 2.1, the water flux first increases and then decreases and *vice versa* for the K_2SO_4 rejection. The inflexion point appears at pH 2.5. Not surprisingly, the NF performances dependence on pH values of PEC casting solution is in agreement with the PECA structure dependence on pH. For example, within experimental error, even the turning pH points in both cases (Fig. 2 and Fig. 5) agree well with each other. Before the inflexion (pH 7 ~ 2.5), the coagulation of PECA particles (Fig. 2a and Fig. 2b) increase with decreasing pH, leading to inhomogeneous membranes coupled with ineffective crosslinking; thus the flux increases and rejection decreases. At the turning point of pH 2.5, a high permeation flux (ca. 45 L $m^{-2}h^{-1}$) and a low K_2SO_4 rejection (50 %) are obtained, indicative of an inhomogeneous membrane under this condition (the coalescence morphology shown in Fig. 4c is consistent with the observation from Fig. 3c). With further decreasing the pH value of PEC dispersion to pH 2.1, the K_2SO_4 rejection increases sharply from 50 % to 97 %; meanwhile, the flux decreases to a reasonable value of 18 $m^{-2}h^{-1}$. As discussed in Fig. 2, at the pH 2.1 PECA particles adopted a weakly complexation configuration that is beneficial for homogeneous dispersion, thus leading to a membrane with uniform and dense structures (Fig. 4d and Fig. 4f) that allow for higher salt rejection. More significantly, both the water flux and salt rejection of PECNFM2.1 are much higher than those of previous PEC membranes under the similar operation condition,[29] primarily due to the improved hydrophilicity of PDMC component and the optimized configuration of PECA particles. In the following section, we choose PECNFM2.1 to study the effects of operation conditions on NF performances, if not otherwise specified.

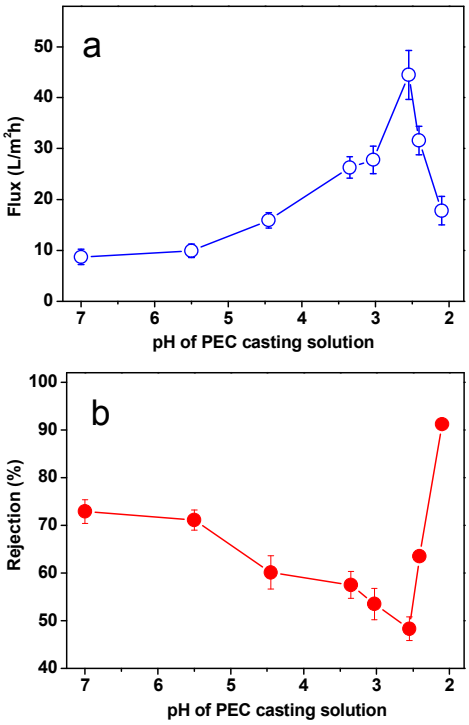

Fig. 5. Effects of pH values of PEC casting solution on NF performances tested with 1g L^{-1} K_2SO_4 aqueous solution at 25 °C and 0.6 MPa, (a) water flux, (b) salt rejection.

3.3. Effects of operation conditions on PECNFMs' NF performances

Fig. 6 shows the effect of operating pressure on NF performances of PECNFM2.1 at 25 °C. The water flux increases from 4.5 L $m^{-2}h^{-1}$ to 18 L $m^{-2}h^{-1}$ with increasing the operating pressure (0.2 ~ 0.6 MPa); meanwhile the salt rejection increases from 89.0 % to 97.0 %. In line with the Spiegler–Kedem model,[35] the water flux of NF membranes is in direct proportion to the trans-membrane pressure (the difference between operating pressure and osmotic pressure). The osmotic pressure can be neglected when the K_2SO_4 feed concentration is as low as 1 g L^{-1}, thus the water flux of PECNFM2.1 increases linearly with increasing the operating pressure, as observed in Fig. 6. In addition, the rejection of PECNFM2.1 to K_2SO_4 increases with increasing the water flux; it is envisioned that the salt concentration of permeation decreases owing to the obvious increase of water flux, thus the salt rejection of PECNFM2.1 increases. A similar phenomenon has been documented in Speigler and Kedern's work,[36] where the salt rejection of NF membranes also showed a linear increase with the water flux.

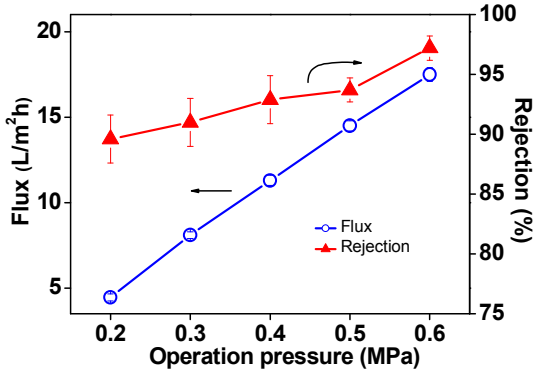

Fig. 6. Effect of operating pressure on NF performances of PECNFM2.1 tested with 1 g L^{-1} K_2SO_4 aqueous solution at 25 °C.

Fig. 7 shows the effect of feed temperature on NF performances of PECNFM2.1 tested with 1 g L^{-1} K_2SO_4 aqueous solution at 0.6 MPa. With increasing feed temperature (25 °C ~ 40 °C), the water flux of PECNFM2.1 increases from 18.0 L $m^{-2}h^{-1}$ to 30.0 L $m^{-2}h^{-1}$, accompanied by the stable K_2SO_4 rejection (96.0 % ~ 98.0%). While the increasing of water flux is commonly due to the higher mobility of water molecules at higher feed temperatures,[36] the stable rejection to K_2SO_4 salt represents a distinctive attribute of the current membrane system, particularly given that most of NF membranes fail to retain a stable salt rejection owing to the excessive swelling at elevated feed temperatures.[37-38] Put another way, the PECNFM is capable of breaking the normal trade-off between the water flux and the salt rejection. This beneficial feature stems primarily from the double crosslinked network structure of PECNFM. The membrane was crosslinked by both the inter-chain electrostatic complexation bonding and the chemical crosslinking between glutaraldehyde and CMCNa, both of which resist the excessive swelling at even a high temperature.[38-39] As such, the PECNFM2.1 features a good separation performance in a wide range of feed temperatures.

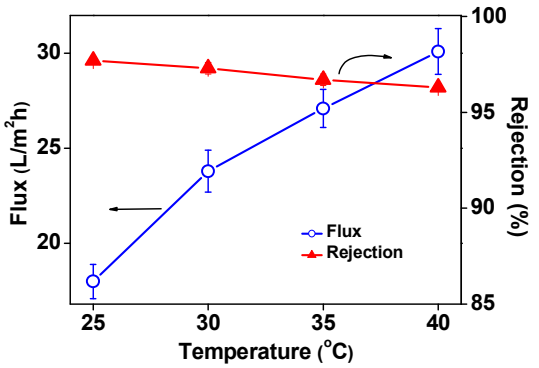

Fig. 7. Effect of feed temperature on NF performances of PECNFM2.1 tested with 1 g L^{-1} K_2SO_4 aqueous solution at 0.6 MPa.

Fig. 8 shows the NF performances of PECNFM2.1 and CMCNa membranes in separating divalent (K_2SO_4) and monovalent (NaCl) salts. When tested with K_2SO_4 and NaCl feed solutions, the water flux of PECNFM2.1 in both cases is around 18.0 $m^{-2}h^{-1}$ (Fig. 8a), more than one time higher than that of the CMCNa membrane (8.5 L/m^2h). Given that the thickness of PECNFM2.1 (ca. 350 nm, Fig. 4f) is even larger than that of CMCNa membrane (ca. 260 nm, Fig. 4e), PECNFM2.1 outperforms CMCNa in terms of both the apparent flux and the permeability. This higher permeability is probably attributed to their unique microstructures, i.e., water channels may form between PECA particles in PECNFM2.1 and allow for highway transfer of water molecules through PECNFMs (Fig. 4a). Furthermore, the two membranes displace a significant difference in rejecting NaCl salt, i.e., 2% for PECNFM2.1 and 40% for CMCNa (Fig. 8b), though the rejection of both membranes to K_2SO_4 is similar (above 97.0%). Donnan exclusion theory tells that the repulsive interaction between negatively charged NF membranes and multivalent ions is stronger than that to monovalent ions, thus justifying the higher rejection to K_2SO_4 than to NaCl.[24] More interestingly, compared to CMCNa membranes, the PECNFM2.1 features a high efficiency in separating divalent and monovalent salts. As shown in Fig. 8b, the membrane rejects most of K_2SO_4 salts (rejection > 97%) while allowing the majority of NaCl salts to pass (rejection = 2%). Noteworthy, the separation performance of PECNFM prevails not only the pristine CMCNa membrane, but also some other cellulose acetate membranes in literatures.[40] In this regard we note that the PECNFM2.1 possess both the cationic and anionic groups which resemble an analogous bipolar structure promoting a higher divalent/monovalent salts separation, in stark contrast to the pristine CMCNa membrane which possesses only anionic carboxylate groups.[29] Collectively, the PECNFM is underscored by a combination of high water flux and exceptional efficiency in separating salts mixtures, both of which are of critical importance in practical desalination applications.

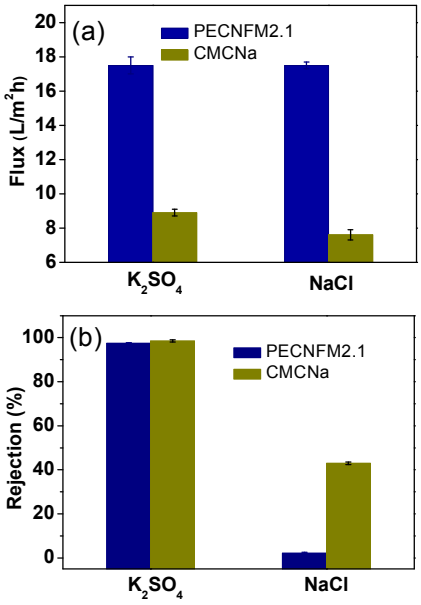

Fig. 8. NF performances of PECNFM2.1 and CMCNa membranes tested with K_2SO_4 (1 g L^{-1}) and NaCl (1 g L^{-1}) aqueous solution at 25 °C and 0.6 MPa, (a) water flux, (b) salt rejection.

3.4. Antifouling property and stability of PECNFMs

Antifouling properties and long-term stability of porous membranes are crucial for their practical applications;[5, 41] cross-flow filtration experiments were conducted to address this issue. The antifouling properties of PECNFM2.1, PECNFM2.5, and PECNFM3.5 were investigated with K_2SO_4 (1 g L^{-1}) and model foulant BSA (0. 1 g L^{-1}) aqueous solution (pH = 6.5) at 25 °C under 0.6 MPa. As shown in Fig. 9, while there is no appreciable change in the water flux of PECNFM2.1 in 18 h of filtration test, the water flux of both PECNFM2.5 and PECNFM3.5 presents a noticeable variation. Fouling is a notorious but ubiquitous problem for NF membranes, e.g., the commercial NF membranes of both NTR-7450 and NF-270 suffer a severe water flux decline in a continuous test.[42] Yet in this study, the PECNFM2.1 exhibits a good antifouling performance. Moreover, in a 18 h continuous filtration test, the rejection of PECNFM2.1 to K_2SO_4 maintains in the range of 97 % – 95 %, along with a stable water flux around 17.5 $m^{-2}h^{-1}$ (Fig. 10). SEM examinations show that both the surface and cross-section morphologies of the PECNFM2.1 membrane after the continuous filtration test are not much affected (supporting information Fig. S1) compared to the membrane before the test (Fig. 4d and 4f). As such, aside from the antifouling property, the membrane structure is stable to afford a steady NF performance. From the above discussion, it could be concluded that PECNFMs represent novel NF membranes embedded with good separation performance, stability, and antifouling property.

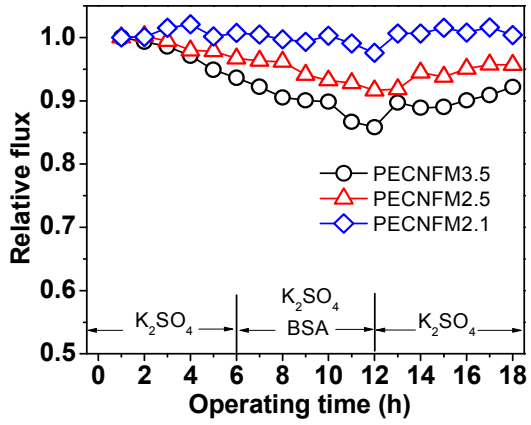

Fig. 9. NF performances of PECNFMs tested with 1 g L^{-1} K_2SO_4 and 1 g L^{-1} K_2SO_4 +0. 1 g L^{-1} BSA aqueous solution at 25 °C and 0.6 MPa.

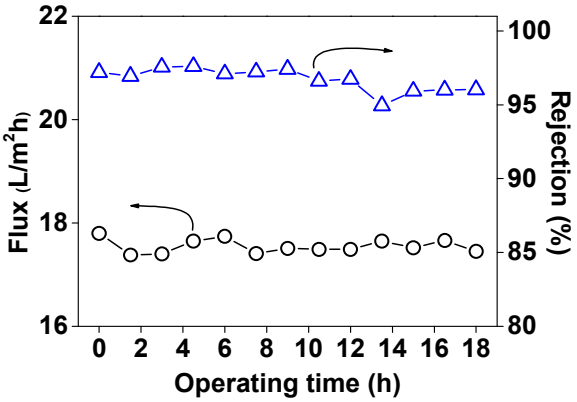

Fig. 10. PECNFM2.1's NF performance versus operating time tested with 1 g L^{-1} K_2SO_4 aqueous solution at 25 °C and 0.6 MPa.

4. Conclusions

A solution processable PECs between sodium carboxymethyl cellulose and poly (2-methacryloyloxy ethyl trimethylammonium chloride) was prepared and dissolved in aqueous NaOH to form dispersions composed of PEC aggregate (PECA) nanoparticles. With decreasing the pH value of PEC dispersion from 8.8 to 2.5, PECA particles first shrink due to the deprotonation of carboxylate groups and then undergo a secondary agglomeration. With further decreasing from pH 2.5 to pH 2.1, a phase transition from agglomerated PECA particles to weakly complexed PECA particles takes place. Accordingly, NF performance of PECNFMs correlates well with the casting solution pH, with the PECNFM2.1 giving the optimum separation performance. In detail, the water flux and rejection to K_2SO_4 aqueous feed (1 g L^{-1}, 25 °C, 0.6 MPa) are 18 g/m^2h and 97 %, respectively. Moreover, not only the permeation flux of PECNFMs is two times as large as that of pristine CMCNa membranes (8.5 $m^{-2}h^{-1}$), they also show higher efficiency in separating salts mixtures (K_2SO_4 and NaCl). Last, PECNFMs feature improved antifouling performance against foulant BSA combined

with a stable performance versus operation time. This study strengthens the understanding on PECNFMs made from solution-mixed PECs, thus pointing to new strategies for engineering high performance polyelectrolyte NF membranes.

Acknowledgements

This research was financially supported by the NNSFC (21106126, 51173160), the National High Technology Research and Development Program of China (2012AA03A602) and the National Basic Research Program of China (2015CB655300).

References

1 M. G. Buonomenna, *RSC Adv.* **2013**, *3*, 5694-5740.
2 Q. Zhao, Q. F. An, Y. L. Ji, J. W. Qian and C. J. Gao, *J. Membr. Sci.* **2011**, *379*, 19-45.
3 P. Vandezande, L. E. M. Gevers and I. F. J. Vankelecom, *Chem. Soc. Rev.* **2008**, *37*, 365-405.
4 J. Radjenovic, M. Petrovic, F. Ventura and D. Barcelo, *Water Res.* **2008**, *42*, 3601-3610.
5 B. Van der Bruggen, M. Manttari and M. Nystrom, *Sep. Purif. Technol.* **2008**, *63*, 251-263.
6 S. Cheng, D. L. Oatley, P. M. Williams and C. J. Wright, *Adv. Colloid Interface Sci.* **2011**, *164*, 12-20.
7 H. Y. Hwang, D. J. Kim, W. J. Yim and S. Y. Nam, *Desalination* **2012**, *289*, 72-80.
8 S. Darvishmanesh, J. C. Jansen, F. Tasselli, E. Tocci, P. Luis, J. Degreve, E. Drioli and B. Van der Bruggen, *J. Membr. Sci.* **2011**, *379*, 60-68.
9 N. Ghaemi, S. S. Madaeni, A. Alizadeh, P. Daraei, M. M. S. Badieh, M. Falsafi and V. Vatanpour, *Sep. Purif. Technol.* **2012**, *96*, 214-228.
10 Q. An, F. Li, Y. Ji and H. Chen, *J. Membr. Sci.* **2011**, *367*, 158-165.
11 R. L. Han, S. H. Zhang, L. J. Hu, S. S. Guan and X. G. Jian, *J. Membr. Sci.* **2011**, *370*, 91-96.
12 R. Bernstein, E. Anton and M. Ulbricht, *Acs Appl Mater Inter* **2012**, *4*, 3438-3446.
13 Y. Ji, Q. An, Q. Zhao, H. Chen and C. Gao, *J. Membr. Sci.* **2011**, *376*, 254-265.
14 G. F. Sun, T. S. Chung, N. P. Chen, X. M. Lu and Q. P. Zhao, *RSC Adv.* **2013**, *3*, 9178-9184.
15 S. Kaur, S. Sundarrajan, D. Rana, T. Matsuura and S. Ramakrishna, *J. Membr. Sci.* **2012**, *392*, 101-111.
16 H. Y. Ma, C. Burger, B. S. Hsiao and B. Chu, *Acs Macro Lett* **2012**, *1*, 723-726.
17 G. Decher, *Science* **1997**, *277*, 1232-1237.
18 Y. H. Yang, L. Bolling, M. Haile and J. C. Grunlan, *RSC Adv.* **2012**, *2*, 12355-12363.
19 R. Chollakup, W. Smitthipong and A. Chworos, *RSC Adv.* **2013**, *3*, 4745-4749.
20 N. Joseph, P. Ahmadiannamini, R. Hoogenboom and I. F. J. Vankelecom, *Polym. Chem.* **2014**, *5*, 1817-1831.
21 S. Wenqian, P. Bacchin, P. Aimar, M. L. Bruening and V. V. Tarabara, *J. Membr. Sci.* **2010**, *349*, 268-278.
22 H. Q. Tang, S. L. Ji, L. L. Gong, H. X. Guo and G. J. Zhang, *Polym. Chem.* **2013**, *4*, 5621-5628.
23 G. F. Sun, T. S. Chung, K. Jeyaseelan and A. Armugam, *RSC Adv.* **2013**, *3*, 473-481.
24 C. Cheng, A. Yaroshchuk and M. L. Bruening, *Langmuir* **2013**, *29*, 1885-1892.
25 X. F. Li, S. De Feyter, D. J. Chen, S. Aldea, P. Vandezande, F. Du Prez and I. F. J. Vankelecom, *Chem. Mater.* **2008**, *20*, 3876-3883.
26 H. Q. Wang, X. H. Yan, G. L. Li, C. Pilz-Allen, H. Mohwald and D. Shchukin, *Adv. Healthc. Mater.* **2014**, *3*, 825-831.
27 S. A. Sukhishvili, E. Kharlampieva and V. Izumrudov, *Macromolecules* **2006**, *39*, 8873-8881.
28 Q. Zhao, M. J. Yin, A. P. Zhang, S. Prescher, M. Antonietti and J. Y. Yuan, *J. Am. Chem. Soc.* **2013**, *135*, 5549-5552.
29 Y. L. Ji, Q. F. An, Q. Zhao, H. L. Chen, J. W. Qian and C. J. Gao, *J. Membr. Sci.* **2010**, *357*, 80-89.
30 Q. Zhao, Q. An, Z. Sun, J. Qian, K. R. Lee, C. J. Gao and J. Y. Lai, *J. Phys. Chem. B* **2010**, *114*, 8100-8106.
31 W. Wei, Y. P. Tan, N. R. M. Rodriguez, J. Yu, J. N. Israelachvili and J. H. Waite, *Acta Biomaterialia* **2014**, *10*, 1663-1670.
32 S. S. Shiratori and M. F. Rubner, *Macromolecules* **2000**, *33*, 4213-4219.
33 Q. F. Wang and J. B. Schlenoff, *Macromolecules* **2014**, *47*, 3108-3116.
34 J. van der Gucht, E. Spruijt, M. Lemmers and M. A. C. Stuart, *J. Colloid Interface Sci.* **2011**, *361*, 407-422.
35 Y. Z. Xu and R. E. Lebrun, *Desalination* **1999**, *122*, 95-105.
36 J. Gilron, N. Gara and O. Kedem, *J. Membr. Sci.* **2001**, *185*, 223-236.
37 M. Manttari, A. Pihlajamaki, E. Kaipainen and M. Nystrom, *Desalination* **2002**, *145*, 81-86.
38 M. T. Uddin, M. S. I. Mozumder, M. A. Islam, S. A. Deowan and J. Hoinkis, *Chem. Eng. Technol.* **2007**, *30*, 1248-1254.
39 Q. Zhao, J. W. C. Dunlop, X. Qiu, F. Huang, Z. Zhang, J. Heyda, J. Dzubiella, M. Antonietti and J. Yuan, *Nat Commun* **2014**, *5*.
40 J. Miao, G. H. Chen, L. L. Li and S. X. Dong, *Sep. Sci. Technol.* **2007**, *42*, 3085-3099.
41 R. J. Gohari, E. Halakoo, W. J. Lau, M. A. Kassim, T. Matsuura and A. F. Ismail, *RSC Adv.* **2014**, *4*, 17587-17596.
42 R. Liikanen, I. Miettinen and R. Laukkanen, *Water Res.* **2003**, *37*, 864-872.