Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1043651

57 (2016) 10980–10987
May

Taylor & Francis
Taylor & Francis Group

Characterization and antifouling performance of negatively charged PES/mesoporous silica ultrafiltration membrane for raw water filtration

Xue Li, Jian Huang*, Yu Zhang, Yaoping Lv, Ziming Liu, Zengnian Shu

College of Ecology, Lishui University, Zhejiang 323000, Lishui, China, Tel. +86 578 2271308; emails: 1371729002@qq.com (X. Li), huangjianzhy@126.com (J. Huang), 285228267@qq.com (Y. Zhang), Tel. +86 578 2683088; email: yaopinglv@163.com (Y. Lv), Tel. +86 578 2271308; email: 308766533@qq.com (Z. Liu), Tel. +86 578 2271328; email: shuzengnian@126.com (Z. Shu)

Received 20 October 2014; Accepted 15 April 2015

ABSTRACT

Ultrafiltration (UF) has become one of the best technologies in the surface water treatment due to the increasing strict regulations for drinking water quality. However, the low rejection for the natural organic matter (NOM) and the membrane fouling restrict its wider application. In this study, polyethersulfone (PES) UF membranes modified by mesoporous silica (MS) particles were fabricated by phase inversion process and their surfaces were further negatively charged. The separation properties and antifouling performances of the modified membranes were investigated. Results indicated that the negatively charged modification could be an effective way for better removal of NOM and reduction of the membrane fouling. The foulant amount on the pure PES membrane after filtration of the raw water could reach to 0.032 mg/cm^2, however, it decreased to 0.011 mg/cm^2 for nPES/MS membrane. The raw water purification experiments exhibit that the membrane could maintain a relative high flux and the rejection for the NOM over 99% throughout the whole experiment, which indicates that the nPES/MS membranes could be successfully applied in the raw water filtration.

Keywords: Antifouling; Ultrafiltration; Negatively charged; Water treatment

1. Introduction

Ultrafiltration (UF) has been widely used in the water and wastewater treatment due to its wide range of advantages compared to traditional separation methods [1,2]. The membrane material properties play an important role in the membrane process. Polyethersulfone (PES), one of the most popular membrane materials, has been widely used to fabricate UF membrane due to its excellent chemical, thermal, and mechanical stabilities [3,4]. PES membranes exhibit some advantages such as broad operating temperature, wide pH value, and the ability to maintain their mechanical properties in the harsh environment. However, PES membrane is prone to be fouled during the filtration process because of their hydrophobic nature, leading to the gradual decrease of permeation flux and frequent membrane cleaning, which increase the operation cost and shorten the membrane life.

Hydrophilic membrane surface encounters less organic and biological fouling caused by substances such as proteins, natural organic matters (NOM), and bacteria [5,6]. Extensive studies have focused on making hydrophilic, brush, or hydrogel structures on

---

*Corresponding author.

membrane surfaces to alleviate initial fouling [7,8]. In spite of the improvement in both hydrophilicity and fouling resistance of the modified membrane, most of the techniques have their shortage. For example, surface grafting involves high degree of process complexity and cost, improving the membrane surface hydrophilicity as well as the membrane flux is not easy to achieve. Coating may reduce the membrane performance with the unavoidable accumulation of the coated layer on the pore surface and the coated layer may also be removed after a long usage of the membranes [9].

Blending with hydrophilic nanoparticles is a more effective approach to cope with membrane fouling; beneficial effects of nanoparticles-based membranes on the mitigation of membrane fouling have been reported recently from many researchers [10–12]. A variety of inorganic fillers such as titanium dioxide (TiO_2), alumina (Al_2O_3), zirconium (ZrO_2), carbon nanotubes (CNTs), silica (SiO_2), and Fe_3O_4 have been used to fabricate inorganic polymer composite membranes [9,12]. Among them, silica has received significant interest for its high hydrophilicity, chemical stability, and easy preparation. Compared to solid silica, MS materials possess special properties such as higher specific surface area, large pore volume, tunable pore structures, and well-defined surface property for modification; they usually have uniform pore channels with a diameter range of 2–10 nm and can be modified in various ways. Many researchers investigated the effect of MS on the membrane performance and the results indicated that the modified membranes showed improved antifouling property, especially for the protein separation. However, rare study focuses on the study of the antifouling performance of this novel membrane for raw surface water filtration.

NOM is commonly found in surface and ground waters and considered as the most important foulant due to the interaction between membrane surface and NOM [13,14]. Recent studies have shown that charged UF membranes had a higher NOM rejection and less fouling tendency than the neutral membrane. Wei et al. modified the PES membrane by electrophoresis-UV grafting treatment, and the modified membrane surfaces exhibited more hydrophilic and negatively charged features, which can improve NOM retention and present lower fouling tendency than the unmodified membrane [15].

In this study, the PES/MS silica UF membranes were fabricated according to our previous method [16], and the PES/MS membrane surface was further negatively charged modified. The separation and antifouling properties of the modified membranes in the raw water filtration were investigated systematically.

2. Materials and methods

2.1. Materials

Pure PES membrane and PES/MS nanocomposite membrane with 2% of MS were fabricated according to our previous report [16]. Bovine serum albumin (BSA 67,000 g/mol), 3-bromopropanesulfonic acid sodium salt, NaOH, and NaCl were purchased from Sigma–Aldrich Co. All other chemicals used in the experiments were commercially analytical grade. Raw water used in this study was obtained in Oujiang River, Lishui, Zhejiang Province, China. Quality of raw water and treated water in this study was shown in Table 1. The source water was pretreated using a 0.45-μm microfiltration membrane to remove colloid, particles, and other suspended substance before all the UF tests. Water quality was analyzed according to the methods reported in GB/T5750.3-2006, China.

2.2. Modification of PES membranes

To obtain a negatively charged PES/MS membrane, the original membrane was first equilibrated with 0.1 M NaOH and then immersed in a 2 M solution of 3-bromopropanesulfonic acid sodium salt in 0.1 M NaOH for 48 h. The membranes were then washed with 0.1 M NaOH and deionized water [17].

2.3. Characterization of membranes

Surface hydrophilicity of the unmodified and modified membranes was investigated by contact angle value using a contact angle goniometer (CAM200, KSV Instruments Ltd). The membrane porosity ε (%) and surface mean pore radius r_m (μm) were calculated by the following equations, respectively [18].

$$\varepsilon\ (\%) = \frac{(W_w - W_d)/D_w}{(W_w - W_d)/D_w + (W_d/D_p)} \times 100\% \tag{1}$$

where, P is the porosity of membrane (%), W_w is the wet sample weight (g), W_d is the dry sample weight (g), D_w (0.998 g/cm^{-3}), and D_p (0.37 g/cm^{-3}) is the density of the water and polymer, respectively. Three samples for each membrane were calculated and the average value was reported.

Table 1
Water quality of raw water and treated water

Items	Raw water	Treated water	Water standard
Colority	11.00	7.00	15
Turbidity	3.20	0.06	1
pH	7.8	7.7	6.5–8.5
COD (mgL^{-1})	12.21	5.31	50
NH_3-N (mgL^{-1})	1.32	1.01	–
Total bacterial count (mL^{-1})	109	0	–

$$r_m = \sqrt{\frac{(2.9–1.75\varepsilon) \times 8\eta lQ}{\varepsilon \times A \times \Delta P}} \tag{2}$$

where, η is the water viscosity (8.9×10^{-4} Pa s), l is the membrane thickness (m), Q is the volume of the permeate water per unit time ($m^3 \ s^{-1}$), A is the effective area of the membrane (m^2), and ΔP is the transmembrane pressure (Pa).

The surface charge property of the unmodified and modified UF membrane was examined using a device constructed from two Plexiglas chambers with Ag/AgCl electrodes inserted at each end. Data were obtained using 10 mM KCl at pH 7, with the fluid flow directed through the membrane pores. All results in this study are reported in terms of apparent zeta potential data as calculated by the equation reported in the literatures [19].

2.4. Filtration and separation experiments

A cross flow filtration apparatus was used to measure pure water flux, raw water and BSA separation of pure PES, and modified PES UF membranes. The raw water was prefiltered by 0.45-μm microfiltration membrane to remove the inorganic particles. Each membrane was initially compacted for 1 h at 400 kPa to get a steady flux, and then the flux was recorded at 100 kPa. All the experiments were performed at room temperature (25 ± 1℃). At least five samples were measured for each type of membrane, and the average data were reported. The protein solutions were prepared by dissolving it in phosphate (1 g/L, pH 7.0). The flux recovery ratio (FRR) was calculated using the following equation:

$$\mathrm{FRR} = \frac{J_{w1}}{J_{w0}} \times 100\% \tag{3}$$

where J_{w1} is water flux of the polluted membrane after cleaning, J_{w0} is water flux of initial membrane.

Solute rejection was measured at 100 kPa in the same apparatus with aqueous solutions of BSA prepared by dissolving it in phosphate (1 g/L, pH 7.0). The BSA concentration in the feed and permeate samples were determined by a UV–vis spectrophotometer (Spectra Max M2, Molecular) at 280 nm, and the rejection of proteins (R) was calculated by the following equation:

$$R = 1 - \left(\frac{C_p}{C_f}\right) \times 100 \tag{4}$$

where, C_p and C_f is the permeate concentration and the feed concentration, respectively.

To evaluate the fouling performance of the membranes, foulants amount on the membrane surface was measured after the filtration of raw water. The fouled membranes were soaked in NaOH solution and stirred periodically for one day to dissolve the foulants from the membranes. Then, the dissolved organic carbon was measured by a TOC analyzer (TOCVCPH, Shimadzu) to calculate the mass of foulant [20].

3. Results and discussion

3.1. Membrane characterization

The morphologies of the membrane surface and cross section were examined using a scanning electron microscope (SEM, JSM-6300F, JEOL). The membrane samples were frozen and fractured in liquid nitrogen, and both the surface and cross section of the samples were gold sputtered for observation. Fig. 1 shows the surface and cross section morphologies of the pure PES membrane and the PES/MS membrane. Compared to pure PES membrane, some nanoparticles could be observed on the surface of PES/MS hybrid membrane. To reduce the interfacial energy between the casting solution and the water bath, the hydrophilic MS particles would migrate from PES matrix toward water bath during the exchange of the solvent

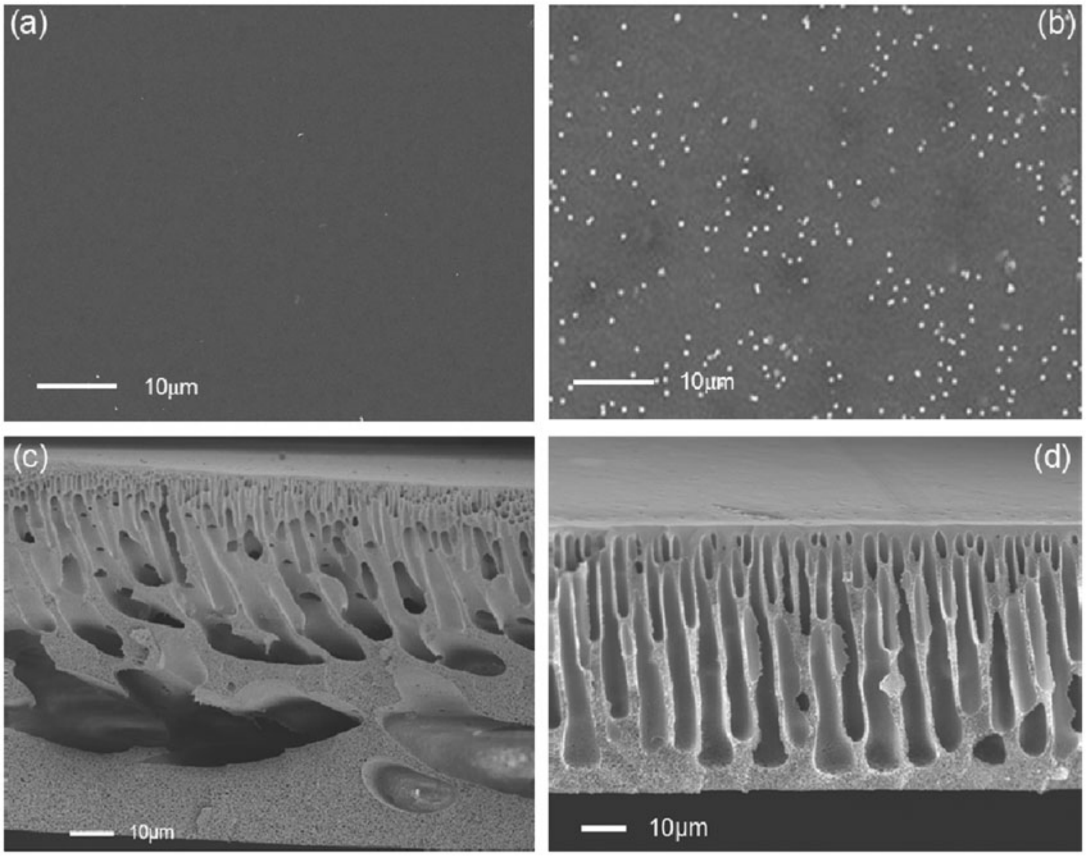

Fig. 1. The SEM pictures of the surface and cross section of pure PES membrane (a,c) and PES/MS (b,d) membrane.

and nonsolvent, which lead to the aggregation of the MS particles on the membrane surface. The MS particles on the membrane surface would improve the hydrophilicity of the PES membrane, which was confirmed by the contact angle data. As shown in Table 2, the contact angle of the PES membrane decreased from 68° to 56°, when the MS loading increased from 0 to 2%, the nPES/MS exhibited similar hydrophilicity as that of PES/MS membrane. As can be seen in Fig. 1, an evident boundary between sub-layer and bottom layer can be observed in the pure PES membrane. However, the finger-like microvoids of the PES/MS membrane enlarged across the membrane thickness, and become wider close to the back side of the membrane. The improved pore connectivity could reduce the filtration resistance and further decrease the membrane fouling.

The modified membranes also show higher porosity than that of the pure PES membrane as can be seen in Table 2. The reason could be the increase in the pore size and the pore number due to the addition of the MS particles, as observed from the cross section images of the membranes. The addition of the MS particles does not have any significant effect on the surface pore size of the membrane and all the membranes have a similar pore radius.

Table 2
Performances of unmodified and modified membranes

Membrane	Contact angle (°)	Pure water flux (L/m^{2}h)	Mean pore radius (nm)	Porosity (ε)	BSA rejection (%)	Zeta potential (mv)
PES	68 ± 1.2	88 ± 2.2	12.9 ± 0.9	69.2 ± 0.9	97	−6.24 ± 0.9
PES/MS	56 ± 1.3	110 ± 2.6	14.6 ± 1.1	75.9 ± 1.1	98	−6.31 ± 0.8
nPES/MS	57 ± 1.8	106 ± 4.7	12.8 ± 1.2	75.2 ± 1.3	99	−13.25 ± 1.2

Stable flux of the modified membranes is 110 and 106 L/m^2 h, respectively, which is much higher than that of the pure PES membrane, 88 L/m^2 h. The reason maybe that the hydrophilicity of the membranes increased as the MS particles was incorporated and the interconnectivity throughout the membrane thickness improved, which, decreased the membrane hydraulic resistance and increased water flux.

3.2. Flux decline in UF experiments

Fig. 2 shows the normalized filtrate flux ratio (J/J_0) during the constant pressure (100 kPa) filtration of the raw water by unmodified and modified PES membranes. J/J_0 is the ratio of flux during the filtration process over the flux at the beginning of the filtration for each individual membrane. It can be seen that flux of the pure PES membrane declined rapidly during the first 40 min filtration and the flux declined by 55% after 120 min of filtration. However, the flux decline ratio is only 30% for PES/MS membrane, and the negatively charged nPES/MS membrane had the lowest decline ratio of 23%, implying the good antifouling performance of the modified membrane. Surface water is known to contain three potential membrane fouling categories, namely microbial content (bacterial, viruses, etc.), organic content, NOM, and inorganic content. As the inorganic particles and bacterial could be removed easily during the prefiltration process, the main mechanisms responsible for the fouling in the UF filtration are the interactions between the NOM and the membrane surfaces. A major fraction of NOM present in surface or ground waters is composed of humic acid [21], which is strongly negatively charged at a pH greater than 4.7 [22]. Due to the electrostatic repulsion between the negatively charged humic acid and the negatively charged membrane, nPES/MS membrane with zeta potential of −13.25 mV would reject more HA compared to pure PES and PES/MS membranes. It should be noted that the pure PES membrane has the similar negative charge as that of PES/MS membrane, but has the most serious fouling among three kinds of membranes. This is due to that the pure PES membrane is more hydrophobic compared to the modified PES membranes, and HA is prone to depositing on the membrane surface, pure PES membrane experienced the worst flux decline. These results indicated that negative charge and hydrophilicity of the membrane surface both play important roles in the fouling control; nPES/MS has excellent hydrophilicity and most negative charge on the membrane surface, which makes it have the best antifouling performance.

3.3. Antifouling performance

In order to further verify the better performance for the modified membrane, the water (FRR) after cleaning was analyzed for pure PES membrane and modified PES membrane. Fig. 3 shows that the modified PES membranes have higher water FRR than that of the pure PES membrane, and nPES/MS membrane has the highest FRR value. The reason may be that higher membrane hydrophilicity and more negative charge on the membrane surface would alleviate the interaction between membrane surface and the pollutants, thus, the pollutants sorption content on the membrane surface and membrane pore decreases.

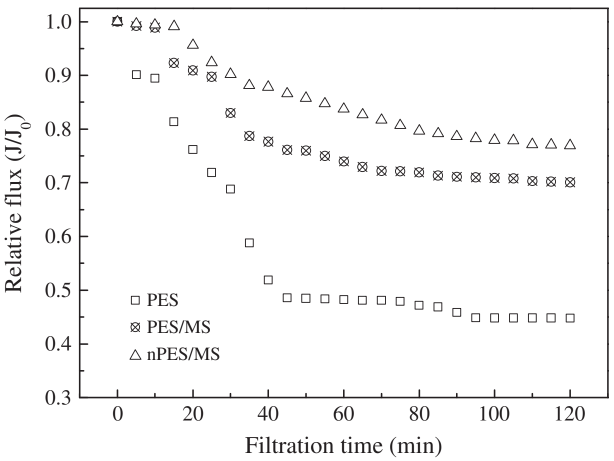

Fig. 2. Normalized filtrate flux during filtration of raw water with modified and unmodified membranes.

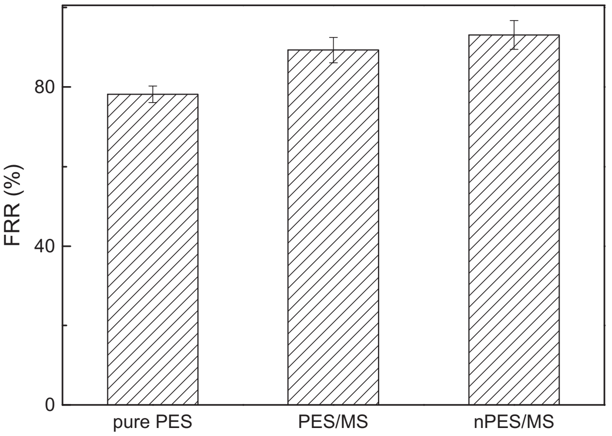

Fig. 3. FRR value for modified and unmodified PES membranes.

The flux decline observed during the raw water filtration is due to the combined effects of NOM adsorption on or within the membrane pores, and NOM concentration polarization. To further investigate the performance of the modified PES membranes during the raw water filtration, a resistance-in-series model was applied to evaluate the various hydraulic resistances involved in UF, consisting of total hydraulic resistance.

$$J = \frac{\Delta P}{\eta R_t} \tag{5}$$

where J is the permeation flux (L/m^2 h), ΔP is the operation pressure (Pa), η is the viscosity of permeate (Pa s), and R_t is the total hydraulic resistance (m^{-1}).

It is assumed that total hydraulic resistance is the sum of intrinsic membrane resistance (R_m), internal fouling resistance (R_c), and fouling resistance (R_f), which can be calculated based on the experimental data [23]. Table 3 shows that the total hydraulic resistance of pure PES membrane was 0.721×10^{13} m^{-1}. However, the total hydraulic resistance of the modified membrane was dramatically improved, which is only 0.225×10^{13} and 0.208×10^{13} m^{-1}, respectively. Furthermore, the fouling resistance accounted for 22.2% of the total resistance for pure PES membrane. The contribution from the deposit or adsorption of NOM for PES/MS and nPES/MS membrane is much lower than that of the unmodified membrane. This attributed to the electrostatic repulsion between the same charged HA and nPES/MS membrane and the improvement of membrane hydrophilicity. This result indicated that the hydrophilicity and negatively charge property of the membrane have significant effect on the membrane fouling control.

Fig. 4 shows the mass of the foulant on the membrane surface after the filtration of raw water. The amount of the organic foulant on the pure PES membranes surface is largest, which could reach to 0.032 mg/cm^2. It decreased dramatically to 0.016 mg/cm^2 for the PES/MS membrane, revealing that the increase in membrane hydrophilicity could lead to less NOM adsorption. Similar phenomenon had also been reported by Violleau et al. [24]. It should be noted that when the PES/MS was further negatively charged, the foulant amount on the membrane further decreased to 0.011 mg/cm^2, implying that the membrane surface charge could aleve the fouling of the membrane. These results verified that antifouling capability of the modified membranes was better than that of the pure PES membrane.

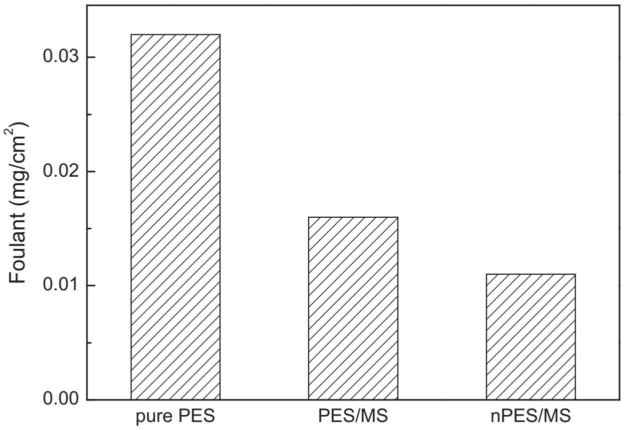

Fig. 4. Mass of the foulant on per unit of the membrane surface.

3.4. Membrane separation performance for raw water

The filtration performance of modified and unmodified membranes was studied with Oujiang river surface water at 0.1 MPa at room temperature. The membrane was washed with pure water after every 3 h operation. Fig. 5 shows the variation of the permeate flux and organic matter rejection for raw water for four rounds during 12 h operation. The results show that the flux of all the membrane decreased as the experiment went on in each round of experiment. This is due to the adsorption of the NOM on the membrane surface over time, forming a cake layer, increasing the resistance to permeate. At last, for the nPES/MS membrane, the end flux of the last round was 65.9 L/m^2 h, which decreased 26.1% comparing to the initial flux of the first round. However,

Table 3
Resistance analysis on PES, PES/MS, and nPES/MS membranes (R: $\times 10^{11}$ m^{-1})

Membranes	R_t ($\times 10^{13}$ m^{-1})	R_m ($\times 10^{13}$ m^{-1})	R_c ($\times 10^{13}$ m^{-1})	R_f ($\times 10^{13}$ m^{-1})	R_f/R_t (%)
PES	0.721	0.489	0.072	0.16	22.2
PES/MS	0.225	0.181	0.015	0.029	12.9
nPES/MS	0.208	0.179	0.012	0.017	8.2

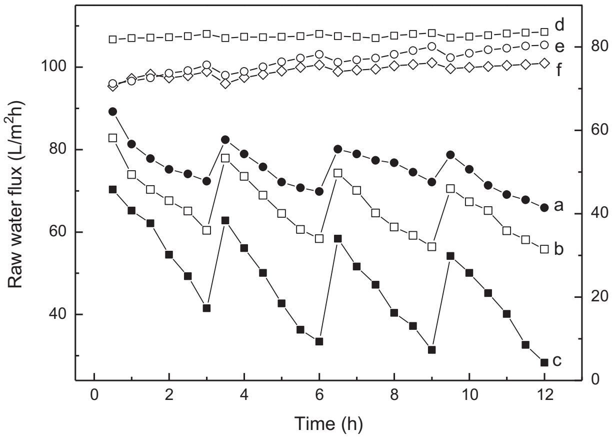

Fig. 5. The long term operation performance for raw water filtration. a, b, c is the raw water flux for nPES/MS, PES/MS, and pure PES membrane, respectively; d, e, f is the TOC removal for nPES/MS, pure PES, and PES/MS membrane, respectively.

for the PES/MS and pure PES membranes, the end flux of the last round was 55.8 and 28.3 L/m^2 h, which decreased to 32.6 and 59.7%, respectively. Pure PES membrane encountered most serious fouling due to its hydrophobic surface and less negative charge. It is evident from Fig. 5 that nPES/MS membrane has the highest rejection for the organic matter and kept stable above 82% during the 12 h operation. On the contrary, PES/MS and pure PES exhibit lower organic matter removal. It is interesting that the organic matter rejection for pure PES membrane slightly increased during the filtration. The reason maybe that the pure PES membrane is prone to be fouled, and the pollutant on the membrane surface preventing the passage of organic matter molecular, which increase the rejection coefficient. The relative stability of the flux and rejection during the experiment could partly indicate the stability of the nPES/MS membrane for raw water purification.

4. Conclusion

The flux evolution and rejection performance of modified PES UF membranes for surface water was systematically investigated to understand the effect of hydrophilicity and charge on the membrane surface on the permeate quality and flux. The following conclusions can be drawn from this study.

(1) The presence of nanoparticles in the composite membrane increased the surface hydrophilicity of the membrane, and further enhanced the antifouling capability of PES/MS membrane.
(2) Surface charge modification could be an effective way to achieve higher NOM removal and lower membrane fouling simultaneously. The nPES/MS membrane exhibited higher FRR value than that of the pure PES membrane, while the foulants amount on the membrane surface is only 0.011 mg/cm^2 after the raw water filtration.
(3) The raw water flux did not decrease too much and the rejection for the organic matter could be kept stable above 82% during the 12 h operation. The nPES/MS membrane could be successfully applied in the surface water treatment.

Acknowledgments

This research was supported by Zhejiang Provincial Natural Science Foundation of China under Grant No. LQ14B060001, the Foundation of Zhejiang Educational Committee under Grant No. Y201328359 and Foundation of Science and Technology Department of Zhejiang Province of China under Grant No. 2013C33019.

References

[1] S.J. Xia, Y.M. Zhou, R. Ma, Y.J. Xie, J.W. Chen, Ultrafiltration of humic acid and surface water with tubular ceramic membrane, Desalin. Water Treat. 51 (2013) 5319–5326.
[2] Z.L. Kiss, S. Kertész, S. Beszédes, C. Hodúr, Z. László, Investigation of parameters affecting the ultrafiltration of oil-in-water emulsion wastewater, Desalin. Water Treat. 51 (2013) 4914–4920.
[3] V. Vatanpour, M. Esmaeili, M.H.D. Farahani, Fouling reduction and retention increment of polyethersulfone nanofiltration membranes embedded by amine-functionalized multi-walled carbon nanotubes, J. Membr. Sci. 466 (2014) 70–81.
[4] J. Zhu, N.N. Guo, Y.T. Zhang, L. Yu, J.D. Liu, Preparation and characterization of negatively charged PES nanofiltration membrane by blending with halloysite nanotubes grafted with poly (sodium 4-styrenesulfonate) via surface-initiated ATRP, J. Membr. Sci. 465 (2014) 91–99.
[5] M. Campinas, M.J. Rosa, Assessing PAC contribution to the NOM fouling control in PAC/UF systems, Water Res. 44 (2010) 1636–1644.
[6] M. Elimelech, X. Xiaohua Zhu, A.E. Childress, Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes, J. Membr. Sci. 127 (1997) 101–109.
[7] W.Z. Lang, X. Zhang, J.P. Shen, H.P. Xu, Z.L. Xu, Y.J. Guo, The contrastive study of chemical treatment on the properties of PVDF/PFSA and PVDF/PVP ultrafiltration membranes, Desalination 341 (2014) 72–82.

[8] B. Pellegrin, R. Prulho, A. Rivaton, S. Thérias, J. Gardette, E. Gaudichet-Maurin, Multi-scale analysis of hypochlorite induced PES/PVP ultrafiltration membranes degradation, J. Membr. Sci. 447 (2013) 287–296.

[9] Y. Wei, H.Q. Chu, B.Z. Dong, X. Li, S.J. Xia, Z.M. Qiang, Effect of TiO_2 nanowire addition on PVDF ultrafiltration membrane performance, Desalination 272 (2011) 90–97.

[10] N. Bolong, A.F. Ismail, M.R. Salim, D. Rana, T. Matsuura, Development and characterization of novel charged surface modification macromolecule to polyethersulfone hollow fiber membrane with polyvinylpyrrolidone and water, J. Membr. Sci. 331 (2009) 40–49.

[11] Y.F. Zhao, L.P. Zhu, Z. Yi, B.K. Zhu, Y.Y. Xu, Improving the hydrophilicity and fouling-resistance of polysulfone ultrafiltration membranes via surface zwitterionicalization mediated by polysulfone-based triblock copolymer additive, J. Membr. Sci. 440 (2013) 40–47.

[12] C.S. Zhao, J.M. Xue, F. Ran, S.D. Sun, Modification of polyethersulfone membranes—A review of methods, Prog. Mater. Sci. 58 (2013) 76–150.

[13] M. Hashino, K. Hirami, T. Katagiri, N. Kubota, Y. Ohmukai, T. Ishigami, T. Maruyama, H. Matsuyama, Effects of three natural organic matter types on cellulose acetate butyrate microfiltration membrane fouling, J. Membr. Sci. 379 (2011) 233–238.

[14] S. Lee, J. Cho, M. Elimelech, Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling, J. Membr. Sci. 262 (2005) 27–41.

[15] X. Wei, R. Wang, Z. Li, A.G. Fane, Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal, J. Membr. Sci. 273 (2006) 47–57.

[16] J. Huang, K.S. Zhang, K. Wang, Z.L. Xie, B. Ladewig, H.T. Wang, Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties, J. Membr. Sci. 423–424 (2012) 362–370.

[17] R. Van Reis, Charged filtration membranes and uses therefore, USA patent. WO 01/08792 A2 (2001).

[18] J.J. Qin, Y.M. Cao, Y.Q. Li, Y. Li, M. Oo, Hollow fiber ultrafiltration membranes made from blends of PAN and PVP, Sep. Purif. Technol. 36 (2004) 149–155.

[19] M. Nyström, A. Pihlajamäki, N. Ehsani, Characterization of ultrafiltration membranes by simultaneous streaming potential and flux measurements, J. Membr. Sci. 87 (1994) 245–256.

[20] H.K. Shon, S. Vigneswaran, I.S. Kim, Fouling of ultrafiltration membrane by effluent organic matter: A detailed characterization using different organic fractions in wastewater, J. Membr. Sci. 278 (2006) 232–238.

[21] A.W. Zularisam, A.F. Ismail, R. Salim, Behaviors of natural organic matter in membrane filtration for surface water treatment—A review, Desalination 194 (2006) 211–231.

[22] Q. Wang, B.Y. Gao, Y. Wang, Effect of pH on humic acid removal performance in coagulation ultrafiltration process and the subsequent effects on chlorine decay, Sep. Purif. Technol. 80 (2011) 549–555.

[23] T.H. Bae, T.M. Tak, Effect of TiO_2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration, J. Membr. Sci. 249 (2005) 1–8.

[24] D. Violleau, H. Essis-Tome, H. Habarou, J.P. Croué, M. Pontié, Fouling studies of a polyamide nanofiltration membrane by selected natural organic matter: an analytical approach, Desalination 173 (2005) 223–238.