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Dual mode antifouling ability of PVDF membrane with surface anchored amphiphilic polymer

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Abstract

Polydimethylsiloxane-graft-polyethylene glycol (PDMS-graft-PEG), an amphiphilic polymer with four hydrophilic arms, were prepared and used to improve the antifouling property of PVDF membranes by dip-coating method. The interface properties of modified PVDF membranes were investigated and the increased molecular weight of PEG segment exhibited a negative effect on the anchoring ability of PDMS-graft-PEG on membrane surface. The antifouling properties of modified membranes were significantly improved due to the dual mode antifouling ability of fouling repulsion (PEG) and fouling release (PDMS). BSA adsorption mass on modified membrane surface decreased to a low level, and the enhanced water flux recovery ratio after washing (FRR-W) of modified membranes were obtained for the two typical pollutants of bovine serum albumin and sodium alginate. It was demonstrated that surface anchoring was an effective way to improve the interface characteristics of membrane material with functional polymers.

1. Introduction

As one of the most important technologies used in water treatment, membrane technology has attracted a lot of attention.[1] However, membrane fouling problem exists in almost all the membrane process due to the adsorption and accumulation of various pollutants on the membrane surface and pore surface, especially the ultrafiltration and microfiltration process, leading to the reduced separation efficiency and increased cost of membrane application.[2-5] Therefore, the preparation and modification of non-fouling or low fouling membrane are imperative and urgent.

In general, hydrophilic modification of membrane materials is an effective way to improve the antifouling property. Water molecules can be preferentially adsorbed on the membrane interface due to the hydrogen bonds and ionic bonds of hydrophilic components, the formed interface hydration layer is able to effectively inhibit the non-specific adsorption between pollutants and membrane materials, reducing the irreversible membrane fouling.[6-9] PEG based and zwitterion based materials[10-11]are considered to be the best fouling-resistant materials due to their superior hydration ability. As the most widely used antifouling material, PEG based polymers with linear C-O-C segments, can exhibit strong hydrogen bonds with water molecules and superior segment athletic ability as steric barrier for pollutant molecules.[12-15] On the other hand, some kinds of strong hydrophobic material with lowest surface energy such as PDMS and fluorinated copolymer, are also able to exhibit strong antifouling capacity. According to the fouling release ability of PDMS resulting from the shear resistance property,[16] even the adsorbed pollutants can be converted to reversible fouling as purgeable pollutants.

Nowadays, PEG based and PDMS based polymer used for the improvement of antifouling properties of membrane materials are mainly through surface grafting and blending methods,[17-20] but there are some high technical requirements for surface grafting and blended copolymer due to the harsh reaction conditions and circumscribed fouling resistance of introduced materials. In recent years, there is a simple modification method for hydrophobic membrane, the functional amphiphilic copolymer can be fixed onto hydrophobic membrane surface by hydrophobic interaction[21-22], and the modified membranes are able to show the improved antifouling property. Nishigochi[23] reported that poly (MPC-co-BMA) anchored onto PVDF membrane surface with hydrophobic interaction significantly reduces the adsorption of BSA on the PVDF membrane surface. PPO-b-PSBMA copolymers was used to enhance the surface hydrophilicity and protein resistance of PVDF membrane by hydrophobic interaction,[24] the modified membrane showed excellent anti-adsorption property to single-protein solution and complex plasma feed.

In this paper, the functional polymers with dual-mode antifouling property were used to construct the fouling resistance surface. PDMS-g-PEG with four-arm were prepared though directional reaction of terminal functional groups and used to modify PVDF membrane by dip-coating method, surface properties of modified PVDF membranes were characterized by ATR-FTIR, CA, SEM and AFM, and the antifouling properties were investigated though adsorption fouling and filtration fouling. This paper aims to provide a simple modification method for constructing functional surface to improve the antifouling property of separation membrane using multifunctional polymer.

2. Experimental

2.1 Chemicals and reagents.

Polyvinylidene fluoride (PVDF, MG15) was purchased from Arkema. Polydimethylsiloxane with terminal hydroxyl (HO-PDMS-OH, Mw~4000) was purchased from Fangzhou chemical (China). Trimesoyl chloride (TMC) and sodium alginate (SA) were purchased from Aladdin chemical Co. (China). Bovine serum albumin (BSA，67000Da) and polyethylene glycol (PEG, Mw~ 400, 1000, 4000, 10000) were purchased from Sinopharm Chemical Reagent Co.(China). Dimethylacetamide (DMAC) and dichloromethane (CH_2Cl_2) were analytical grade, and all the reagents were used as received without further purification.

2.2 Synthesis of PDMS-g-PEG.

The four-arm copolymers of PDMS-g-PEG were prepared by the way of quantitative and progressive reaction. HO-PDMS-OH and TMC were dissolved in CH_2Cl_2 and kept to react for 1 hour with molar ratio of 1: 2 under magnetic stirring, PEG with different molecular weights (Mw~400, 1000, 4000 and 10000) were respectively added to the above solution for another 2h reaction under magnetic stirring to generate the final reaction products. the molar ratio of PEG and PDMS was 8:1, which was greater than the theoretical value (4:1) to increase the reaction chance of end groups.

2.3 Modification of PVDF membrane.

Neat PVDF membranes were prepared though non-solvent induced phase separation (NIPS) method, PVDF/PEG20000/DMAC (5g/3g/25g) was selected to prepare the casting solution. The freeze-dried PVDF membrane was immersed in the above PDMS-g-PEG solution to absorb for 2 hour in a water bath oscillator, and a crosslinking process was introduced by immersing membrane in TMC (0.1%) solution for 10 minutes. At last, the membrane was put in distilled water to oscillatory rinse for another 5h. The PVDF membranes immersed in PEG reaction solution with different molecular weight (Mw~ 400, 1000, 4000, 10000) for modification were labeled M400, M1000, M4000, M10000

2.4 Characterization.

The prepared amphiphilic PDMS-g-PEG were examined with infrared spectroscopy (IR, Nicolet 8700, USA). The surface composition of membranes was investigated with attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 8700, USA) and X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS UltraDLD, Japan) with the take-off angle at 90°. The stability of anchored PDMS-g-PEG polymers were investigated according to the peak intensity of Si-O bond in ATR-FTIR spectra before and after immersing in alkaline solution (pH10 and pH12) prepared by NaClO for 1 hour. Water contact angles (CA) on the membranes surface were measured by OCA40Micro (Dataphysics Co., Germany) at room temperature to evaluate the surface wetting ability, and the results were obtained using the drop shape image analysis system. Surface morphology of PVDF and modified membranes were viewed with field emitting scanning electron microscope (SEM, Hitachi SU8010, Japan), all the samples were coated with gold before observation. The surface roughness (Rms) of membranes were characterized with Rq value using a Agilent5500 atomic force microscope (AFM, Agilent Technologies Inc., USA) in the tapping mode,

2.5 Permeation experiments.

The separation properties of membranes were measured by a dead end filtration unit with effective filtration area of 12.5 cm^2, the pressure of filtration cell was supplied by a water pump and all the filtration experiments were carried out at the pressure of 0.1MPa. The volume of the water permeation was collected and stable flux was calculated by the following equation (1).The rejection ratio (R) of model pollutant (BSA, pH 7.4, 1g/L) was calculated from the feed and the permeate concentrations via UV spectrophotometer (UV-1800, Shimadzu) according to the following equation (2).

$$J = \frac{V}{A \times t} \qquad (1)$$

$$R = (1 - \frac{C_P}{C}) \times 100\% \qquad (2)$$

Where J (L/m^2h) is the volume of permeated water, t (h) is the permeation time and A (m^2) is effective area for filtration, C and C_p are the concentrations of BSA in the feed and permeate, respectively.

2.6 Fouling test.

The adsorption fouling and filtration fouling were employed to investigate the antifouling properties of modified PVDF membranes. For the adsorption fouling, protein adsorbed on the membrane surface under static and dynamic conditions (with or without stirring) were executed though quantitative analysis with BSA as model pollutant. All the tested membranes were cut into regular shape and immersed into BSA (0.5g/L, pH 7.4) phosphate buffer solution. After the adsorption process with or without stirring for 12 h at room temperature to reach adsorption equilibrium, the concentrations of BSA solution before and after adsorption were measured with UV–vis spectrophotometer and adsorption mass on membrane surface were calculated with the following equation (3).

$$M = \frac{10^3 (C_0 - C_d) V}{2S} \qquad (3)$$

Where M is the adsorption mass (ug/cm^2), C_0 and C_d are the concentrations (g/L) of BSA before and after adsorption test. V (L) is the BSA solution volume and S (cm^2) is membrane area,

For the filtration fouling, BSA and SA were used as two kinds of model pollutants. The fouled flux recovery ratio (FRR), and the fouled flux recovery ratio after washing (FRR-W) were employed to evaluate the antifouling ability, it should be notice that the membrane with the higher values of FRR and FRR-W indicated the better antifouling properties. The executed loop filtration process consisted of three steps, first of all, stable flux (J) was obtained by pure water filtration, secondly, the feed solution was changed to pollutants solution (BSA or SA) and another stable flux (J_P) was obtained, followed, pollutants solution was changed to pure water again and stable flux (J_2) was obtained, then a washing process was introduced and the membrane was taken out from the filter system to immerse in the phosphate butter for 30min and rinsed with pure water for 10 min, and reinstalled back into filtration unit, the second water flux (J_{2w}) of pure water was recorded at the end. Another model pollutants SA (1g/L) solution were used to test the antifouling ability of prepared membranes with the same mode, all the FRR, FRR-W were calculated by the equation (4) (5), respectively.

$$\mathrm{FRR} = \frac{J_2}{J} \times 100\% \qquad (4)$$

$$\mathrm{FRR-W} = \frac{J_{2w}}{J} \times 100\% \qquad (5)$$

3. Results and discussion

As shown in Fig.1, based on the directed reaction of end groups and feeding order, the esterification reaction could occur between the PDMS-OH and TMC, followed by the reaction between PEG and remained functional groups of TMC, and the final reaction product should be an amphiphilic polymer with four-arm structure. The IR spectra of PDMS-g-PEG1000 and PDMS-g-PEG4000 were shown in Fig. 2. Obviously, the two polymer spectrum exhibited same characteristic peaks and different peak intensity. The peaks of 2962cm^{-1} and 1260 cm^{-1} were assigned to the absorption peak of methyl, and the 1093 cm^{-1} and 1024cm^{-1} were stretching vibration peak of Si-O bond, which were all assigned to PDMS, The strong peak at 1730 cm^{-1} indicated that the esterification reaction of chloride and hydroxyl occurred and TMC was a composition of synthetic polymer. In addition, broad peak of 3100 cm^{-1}~3400cm^{-1} was characteristic absorption peak of OH and 2876 cm^{-1} belonged to the stretching vibration of CH_2, which were attributed to the characteristic absorption peak of PEG, all these results demonstrated that PDMS, TMC and PEG were exist in the synthesized copolymer of PDMS-g-PEG1000 and PDMS-g-PEG4000, so hydrophilic PEG component and hydrophobic PDMS component constituted the amphiphilic polymer PDMS-g-PEG.

The amphiphilic polymer could be assembled onto hydrophobic membrane surface by hydrophobic interaction,[24] the composition of the modified membrane surface were measured by ATR and XPS. Fig. 3a showed the ATR spectra of PVDF membranes before and after modification with the wave number range from 700 cm^{-1} to 1800cm^{-1}. Both the 1093 cm^{-1} and 1024cm^{-1} peaks assigned to Si-O bond characteristic peak were observed on all the spectra of modified membranes, furthermore, the peak intensity of Si-O bond varied with the molecular weight of PEG, M400 and M10000 showed the strongest and weakest peak intensity of Si-O bind, respectively, indicating that low molecular weight PEG was conducive to anchor the copolymer on membrane surface. PEG hydrophilic component was able to affect the hydrophobic interaction between amphiphilic polymer and PVDF membrane. The XPS analysis of membrane surface composition was shown in Table 1. According to the composition of PVDF membrane and PDMS-g-PEG, Si element and F element belonged to

PDMS and PVDF, respectively, and O element belonged to PEG and TMC. The Si/F ratio and Si/O ratio of PVDF membrane were 0, suggesting that there was no Si element in PVDF membrane. For M400, M1000, M4000 and M10000, Si/F ratio decreased from 0.95 to 0.04, indicating PDMS-g-PEG covered the PVDF membrane surface and the adsorbed amount decreased with the increasing molecular weights of PEG. Furthermore, Si/O ratio also decreased with the increasing molecular weight of PEG, which proved that the incremental PEG component in the PDMS-g-PEG copolymer.

Since the stability of hydrophobic interaction is not as good as covalent bond, and PVDF membranes were typically used in the harsh environment, the stability of anchored PDMS-g-PEG was investigated by treatment with alkaline environment, and evaluated by the detected peak intensity variation of the Si-O bond in ATR-FTIR spectra. As shown in Fig. 3b, the peak intensity decreased slightly after the treatment by NaClO solution with pH value at 10, and the peak intensity sharply dropped due to the harsh environment with pH at 12, indicating anchored polymers on membrane surface by hydrophobic interaction could stably exist in a weak alkaline environment.

Fig. 4 showed the surface wetting ability of neat and modified PVDF membranes. There is no regular for the initial contact angle (CA) of membrane surface in Fig. 4a, but the CA of the modified membranes showed the decreasing tendency as the time increase and M4000 exhibited the minimum CA at 49°, indicating the anchored PDMS-g-PEG were able to carry out phase separation process and the opposite migration of hydrophilic and hydrophobic segments changed the wetting ability of modified membrane surface. In addition, Fig. 4b exhibited the advancing angles and receding angles of all the membranes. The increased advancing angles of modified membrane were attributed to the low surface energy segments of PDMS, the decreased advancing angles of modified membrane were attributed to the high surface energy segments of PEG. It could be inferred that the anchored PDMS-g-PEG changed the microenvironment of the membrane surface by surface reconstruction.

Surface morphologies of PVDF membranes before and after modification were shown in Fig. 5, a lot of membrane pores were observed on the uniform PVDF membrane surface, and there was no difference between M10000 and neat PVDF membrane. The surface morphologies of modified M1000 and M4000 membrane were changed significantly with the dimension of membrane pore diminishing apparently, indicating the distinct adsorbed mass of PDMS-g-PEG1000 and PDMS-g-PEG4000 on the membrane surface, and the adsorption amount of PDMS-g-PEG10000 was less than others. These results indicated that the amphiphilic polymer with appropriate molecular weight cold be adsorbed onto the membrane surface, and affected the microstructure of membrane surface. Table 2 listed the Rms of neat and modified PVDF membranes, for the range of 5um ×5um and 1um ×1um, the similar variations of Rms were observed for all the membranes. M4000 exhibited the changed Rms value at 30.231nm, indicating the PDMS-g-PEG was absorbed on PVDF surface, and the larger roughness, the more amount of adsorbed polymer. M10000 showed approximate Rms with PVDF membrane, indicating a little adsorbed amount of PDMS-g-PEG10000 on membrane surface. All these AFM results were consistent with the SEM results, and the increased molecular weight of PEG showed a negative effect on the anchoring effect of PDMS-g-PEG copolymers on membrane surface.

Separation performances of modified PVDF membrane were investigated and the flux and rejection results were shown in Fig. 6. There are no significant differences on the flux for all the membranes, but the rejection showed an increasing trend for PVDF, M400, M1000 and M4000 membrane and M4000 membrane exhibited the highest R value of 81%. Considering with the above XPS and SEM results, it could be concluded that the increased R values were resulted from the reduced membrane pores and hydrophilic PEG component due to the adsorbed PDMS-g-PEG. Hydrophilic and hydrophobic segments could play different effect for water flux, so that the water fluxes of modified membranes were messy. The changed separation efficiency proved that physical structure and chemical properties on the membrane surface were altered due to the fixed four-arm PDMS-g-PEG polymer onto membrane surface by dip-coating method.

Antifouling properties of modified membranes were investigated by adsorption fouling and filtration fouling. The results of static and dynamic adsorption fouling were shown in Fig. 7 with BSA as the adsorption pollutant. According to the comparison of the static adsorption capacity of each membrane, the BSA adsorption amount of modified membranes decreased significantly, the adsorption mass of M4000 membrane decreased to 22ug/cm^2. As for the dynamic adsorption, adsorption capacity of M400, M1000 and M4000 membranes decreased more significantly with the minimum value of adsorption mass at 10ug/cm^2. Ultra low adsorption capacity for BSA indicated modified membrane obtained the ability to suppress nonspecific adsorption between pollutant and hydrophobic membrane surface due to the anchored four-arm PDMS-g-PEG. During the static adsorption fouling process, the reconstruction of the amphiphilic PDMS-g-PEG provided the basis for improving the anti-adsorption ability. PEG molecules with extended state were capable of decreasing the probability of BSA molecules closing to membrane surface and aggregating due to the hydrophilicity and locomotor activity of PEG chains. For the dynamic adsorption fouling, even adsorbed BSA molecules on the membrane surface could be released by shear flow resulting from the shear resistance of PDMS segments, with dual mode antifouling property of PEG and PDMS, the adsorption capacity for pollutant of PVDF membrane were further weakened. Adsorption mass of M10000 was similar to PVDF membrane, indicating the minimum amount of PDMS-g-PEG polymer was anchored on M10000 membrane surface, which was consistent with the above characterization data.

The test results of filtration fouling were shown in Fig. 8a using BSA as pollutant feed. Due to the strong hydrophobic interaction between PVDF and hydrophobic part of BSA, BSA was able to induce serious irreversible fouling to PVDF membrane. Fig. 8b showed the FRR values of PVDF, M400, M1000 and M4000 membranes without washing were 57%, 61%, 66% and 71%, respectively. The increased FRR values of modified membranes indicated the introduced PDMS-g-PEG could exhibit repulsive ability for pollutant during filtration process. Furthermore, the FRR-W values after washing were 62%, 75%, 86% and 90%, and the enhanced FRR values showed preferable ability to release pollution during flushing process. The reversible fouling composition of membrane fouling increased due to the anchored PDMS-g-PEG, leading to the reduction of irreversible fouling ratio to reduce the effects of pollution on the separation efficiency and prolong the service time of PVDF membrane. Surface phase separation of anchored PDMS-g-PEG in water enhanced the functional performance of the amphiphilic polymer, fouling repulsion ability of PEG segments and fouling release ability of PDMS segments provided these characteristic dual mode antifouling properties for PVDF membrane.

Fig. 9a showed the filtration fouling results with SA as pollutant feed. The hydrophilic SA with the characteristic of cake layer formation during filtration, could quickly decrease the separation effect of separation membrane. However, FRR values and FRR-W values were significantly increased after surface modification with anchored PDMS-g-PEG on PVDF membrane surface, and FRR-W value of M4000 was as high as 95%. Obviously, due to the phase separation behavior and dual mode antifouling function of PDMS-g-PEG amphiphilic polymer, the adsorption and deposition of pollutants on the membrane surface were suppressed, leading to remit irreversible fouling significantly.

4. Conclusions

The amphiphilic polymer of PDMS-graft-PEG with four arms were fabricated and anchored to alter the interface properties of membrane surface by hydrophobic interaction for improving the antifouling property of PVDF membrane. The modified PVDF membranes exhibited dual mode antifouling ability of fouling repulsion and fouling release, exhibiting improved anti-adsorption ability and enhanced FRR-W values for the two typical pollutants feed BSA and SA, and the irreversible fouling had been effectively reduced. It was demonstrated that surface anchoring was an effective way to improve the interface characteristics of hydrophobic material for antifouling modification.

Tables

Table 1. XPS analysis results of neat and modified PVDF membranes

Samples	Si/F Atomic ratio	Si/O Atomic ratio
PVDF	0	0
M400	0.95	0.62
M1000	0.65	0.37
M4000	0.19	0.12
M10000	0.04	0.05

Table 2. AFM analysis results of neat and modified PVDF membranes

Samples	Rms (5um ×5um)	Rms (1um ×1um)
PVDF	12.534 nm	5.324 nm
M400	15.657 nm	7.767 nm
M1000	25.165 nm	9.141 nm
M4000	30.231 nm	10.977 nm
M10000	13.461 nm	6.322 nm

Figures

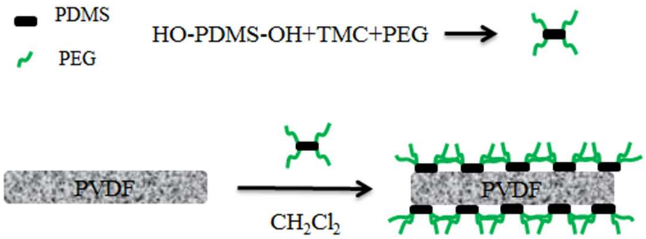

Fig.1. Schematic diagram of amphiphilic polymer synthesis and membrane modification

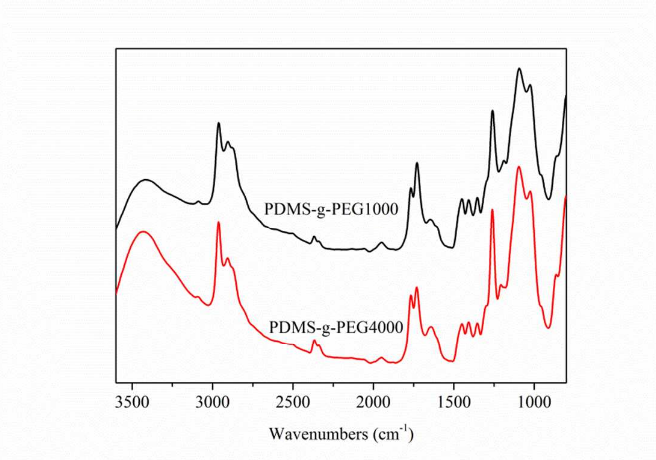

Fig. 2. IR spectra of PDMS-g-PEG1000 and PDMS-g-PEG4000 copolymer.

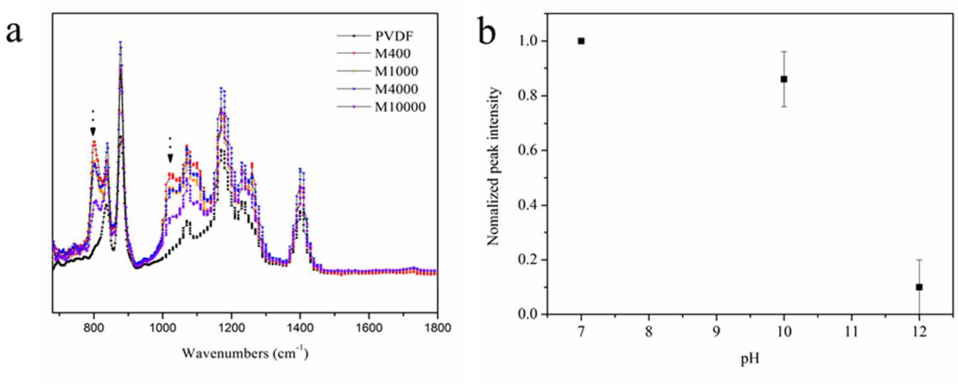

Fig. 3. a, ATR spectra of PVDF membranes before and after modification. b, normalized peak intensity of Si-O bond before and after alkali treatment.

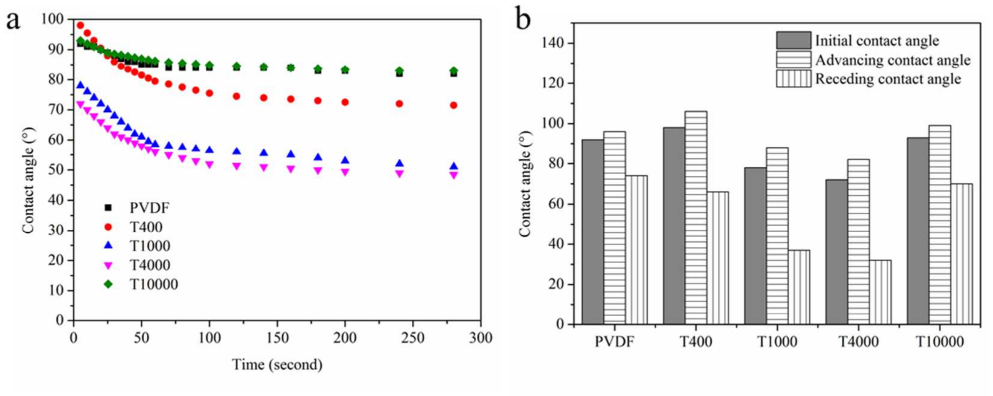

Fig. 4. Water contact angle of neat and modified PVDF membranes (a: time dependent contact angle variation. b, advancing and receding contact angles).

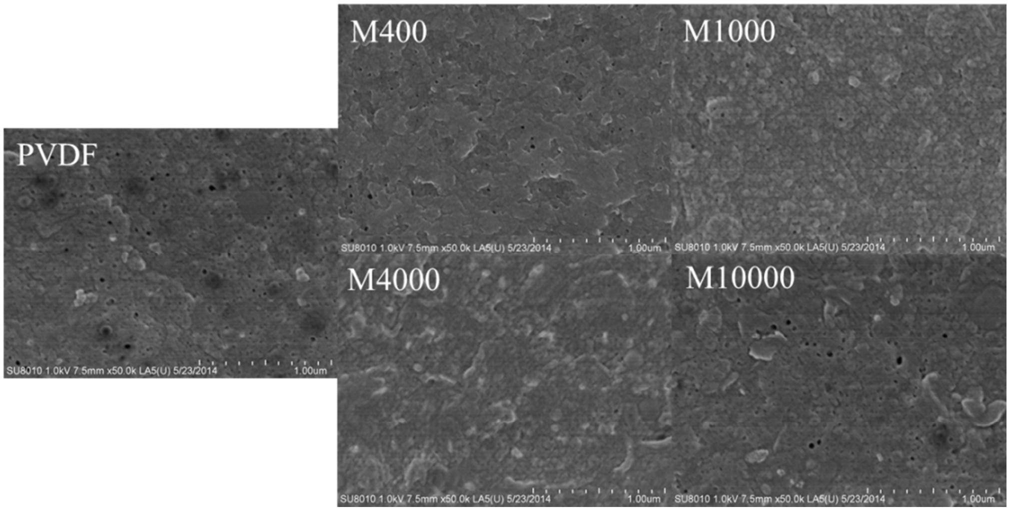

Fig. 5. SEM images of neat and modified PVDF membranes.

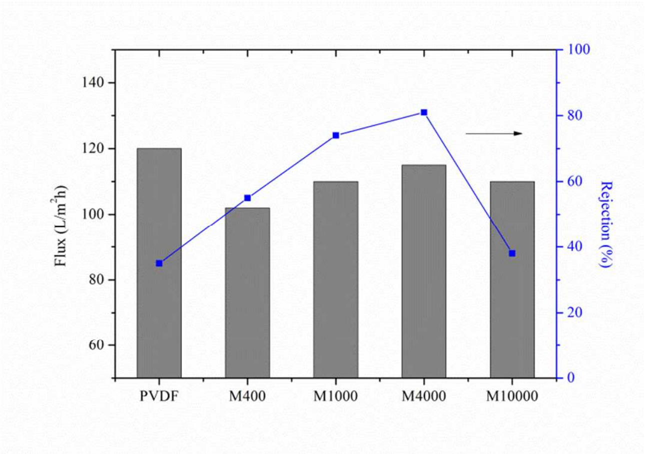

Fig. 6. Separation performances of neat and modified PVDF membranes (0.1MPa).

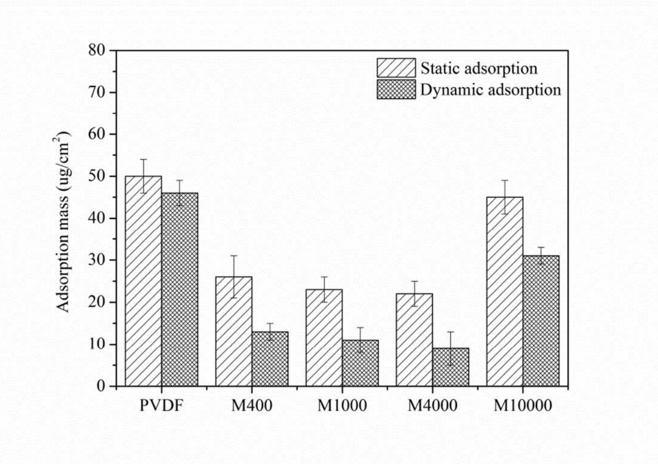

Fig. 7. Adsorption fouling results of neat and modified PVDF membranes

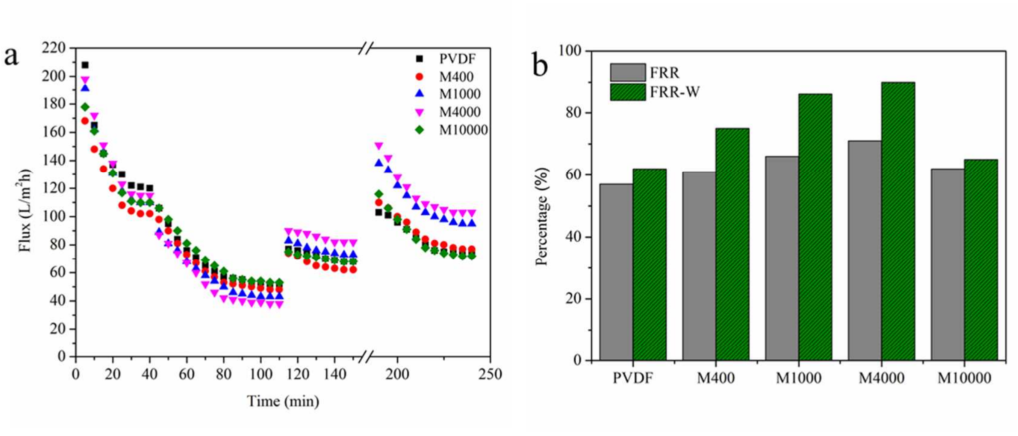

Fig. 8. Fouling test of neat and modified PVDF membranes with BSA as pollutant.(a, time dependent permeate flux variation. 0-50 min, water. 55-110 min, BSA solution. 115-150min, water flux. 155-190min, washing process. 195-240min, water. b, FRR and FRR-W values).

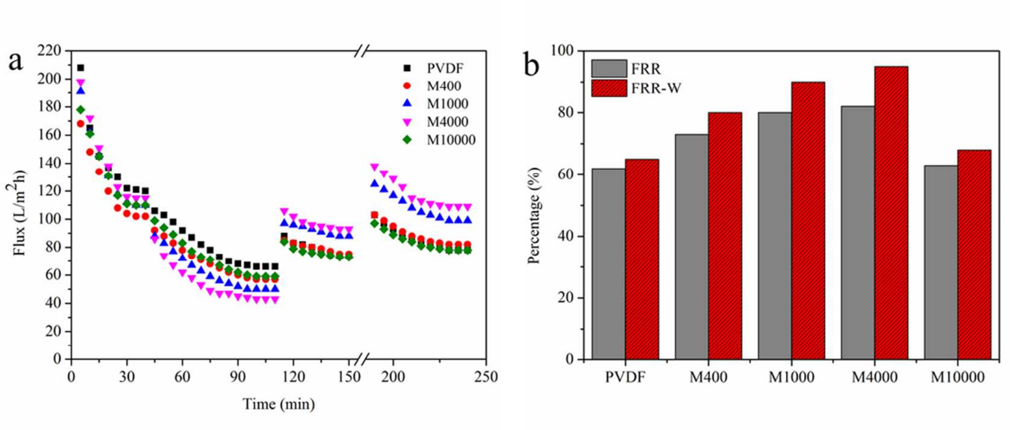

Fig. 9. Fouling test of neat and modified PVDF membranes with SA as pollutant.(a, time dependent permeate flux variation. 0-50 min, water. 55-110 min, SA solution. 115-150min, water flux. 155-190min, washing process. 195-240min, water. b, FRR and FRR-W values).

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