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Evaluating the anti-fouling property of the hydrophilically modified porous PTFE membrane

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ABSTRACT

The flat sheet PTFE membrane was modified into hydrophilicity via deposition of fluorinated cationic surfactant. The anti-fouling property of the membranes was investigated using lysozyme (LYS) and humic acid (HA) as typical foulants and further evaluated by Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory. The results indicated that the wettability of the PTFE membrane can be manipulated by concentration of surfactant solution, and the super hydrophilic membrane with water contact angle of 2.1° was obtained with 0.8 wt% of surfactant solution. The super hydrophilic PTFE membrane showed highest cleaning efficiency of 62.5% and better anti-fouling property. XDLVO analysis further suggested that the super hydrophilic PTFE membrane had the strong repulsion force to HA and LYS and displayed better anti-fouling property due to the highest positive total interaction energy (ΔG^{TOT}) value. Linearly fitting on membrane practical fouling process and XDLVO results proved the consistency of the XDLVO theory with the practical anti-fouling process.

Keywords: PTFE membrane; Wettability; Anti-fouling; XDLVO theory

1. Introduction

Membrane filtration has become an important separation technology for water reclamation and reuse due to that it works without addition of chemicals, with a relatively low energy use and easy and well-arranged process conductions [1–3]. However, when the semipermeable membrane was incorporated in filtration systems, the filtration performance would gradually deteriorate caused by membrane fouling, which can shorten its service life and increase costs of hydraulic/chemical cleaning and membrane module replacement, etc. [4–7]. Membrane fouling has largely impeded the widespread application of membrane process. Thus, numerous researches concentrated on developing a membrane with high anti-fouling properties, including manipulating or improving membrane surface charge, roughness, hydrophilicity and so on [8–11]. Hydrophilization of membrane surface has been regards as an efficient way to improve membrane's anti-fouling property. Our previous works indicated that when the aqueous water solutions were separated, the super hydrophilic membrane showed higher anti-fouling performance than hydrophilic or hydrophobic membrane [15,16].

Polytetrafluoroethylene (PTFE) is widely utilized as separation and filtration membrane due to its mechanical properties and perfect chemical stability. However PTFE membrane has low surface tension and poor hydrophilicity, easily causing membrane fouling, which limits the applications of PTFE membrane in water treatment [17–20]. Various surface modification methods have been used to improve the hydrophilicity of PTFE membranes. For instance, the hydrophobic PTFE flat membrane has been endowed with excellent hydrophilicity, high water permeation flux and superior anti-fouling property via co-deposition of catechol (CA) and PEI followed by surface mineralization of γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560). The

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water contact angle of the PTFE membrane dropped from 135 ± 1.4° of the pristine membrane to 18.26 ± 2.2°, and the permeate flux increased from 4000.0 L/m^2·h to 9750.3 L/m^2·h, due to hydrophilization effect and the opened smallest pores for water. The obtained hydrophilized PTFE membrane showed an excellent anti-fouling performance to oils [11]. Also, the polymerized dopamine (PDA) and PEI deposited onto PTFE hollow fiber membrane via co-deposition endowed the membrane greatly improved hydrophilicity and water permeate fluxes [21]. In addition, the porous PTFE flat membrane has been modified into super hydrophilicity by deposition of cationic fluorocarbon surfactant in our previous work [22]. The water contact angle dropped from 156.8°of the nascent PTFE membrane to 4.3°. However, the relationship between wettability of the hydrophilized PTFE membrane and its filtration performance as well as the anti-fouling property is still unknown.

Herein, the flat sheet PTFE membrane was modified into hydrophilicity via deposition of the fluorinated cationic surfactant, and the anti-fouling property of the as-prepared PTFE membrane with different wettability was investigated using lysozyme (LYS) and humic acid (HA) as typical foulants. The variation of permeation fluxes and fouling performance of the PTFE membranes with different wettability was researched. And the interaction forces and free energy between the membrane surfaces with different wettability and the two foulants were analyzed by the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory, and the effect of the wettability of the membranes on the anti-fouling behavior was discussed.

2. Experimental section

2.1. Chemicals and materials

PTFE porous membrane with 0.2 µm pore size was supplied by Haining Jin Zhenglv Technology Co., Ltd (Jiaxing, China). The fluorinated cationic surfactants was provided by Shanghai Jianbang Industrial Co. Ltd. (Shanghai, China). Humic acid (HA) was obtained from Sigma-Aldrich Chem. Co. (USA). Lysozyme (LYS) was obtained from Nokasn Life Science and Technology Co., Ltd. (Beijing, China). Unless otherwise specified, all reagents and chemicals were of analytical grade.

2.2. Filtration and anti-fouling performance of the modified PTFE membranes

The porous PTFE membranes were modified using the similar method as our previous work [22] with concentration of the fluorinated surfactant varying within 0, 0.2 wt%, 0.4 wt%, 0.6 wt% and 0.8 wt%. The obtained membrane were labeled correspondingly as 1$^\#$, 2$^\#$, 3$^\#$, 4$^\#$, and 5$^\#$ respectively. Then, the filtration performance of the membranes was evaluated using a home-made cross-flow with system similar to our previous work [16,22]. The effective area of the membrane was 22.9 cm^2. Prior to measurement, the system was pressurized to 0.1 MPa with a diaphragm pump for about 20 min to reach a stable state. 50.0 mg/L of HA and LYS water aqueous solution was used as feed solution. The permeate flux, J, was calculated by

$$J = \frac{V}{A \times T \times P} \tag{1}$$

where V is the volume of the permeate liquid passed across the membrane of area A (m^2) in the time period T (h) at operative pressure P (MPa).

And the normalized flux (NF) was calculated by

$$NF = \frac{J}{J_0} \tag{2}$$

where J is the instant flux and J_0 is initial flux. After the filtration was performed for 8 h, the PTFE membranes were rinsed by deionized water, and the pure water flux J_w was measured again.

Then, the flux recovery ratio (FRR) can be calculated by

$$\text{FRR} = \left(\frac{J_w}{J_0}\right) \times 100\% \tag{3}$$

And the cleaning efficiency (η), which was denoted as removal rate of foulants and flux recovery rate, was calculated by

$$\eta = \frac{J_0\left(J_W - J\right)}{J_W\left(J_0 - J\right)} \tag{4}$$

2.3. XDLVO theory analysis

The XDLVO theory has widely been used to illustrate the interaction of aqueous foulants with surfaces of polymeric membranes [15,23–25]. According to XDLVO theory, in an aquatic environmental system, the inter facial energy between a membrane and foulant is the sum of the Liftshiz-van der Waals, Lewis acid-base, and electrostatic double layer interactions, which was calculated according to reference [15]. The water contact angle (WCA) of the dried membrane surface was measured using DSA-100 static contact angle instrument of the German Cruise (Kruss) company to give the surface tension of the membrane and foulants, respectively, determined from the extended Young equation [26]. The instant WCA was obtained within 3 s, and the volume of the liquid drop was 3 µL. The WCA of each sample was measured at least ten times. To measure WCA of foulants surface, HA and LYS solution were deposited onto glass slides and dried for 24 h in an oven at 30° to form a flat solid surface. And the fouled membranes used for XDLVO theory evolution were obtained by filtering HA and LYS water solutions for 8 h to form a cake layer on the membrane surface. The free energy per unit area was calculated according to the value of the surface tension [27].

3. Results and discussions

3.1. Wettability of the modified PTFE membranes

The wettability of the PTFE membranes before and after modification manifested by water contact angle (WCA) is shown in Fig. 1. It was noted that the WCA of the modified membrane decreased with concentration of the fluorinated surfactant solution. The WCA of the PTFE pristine membrane in Fig. 1a was 144.1°, exhibiting a higher hydrophobic surface due to its internal chemical structure. After modified with 0.2 wt% of solution for 30 min, the WCA of the

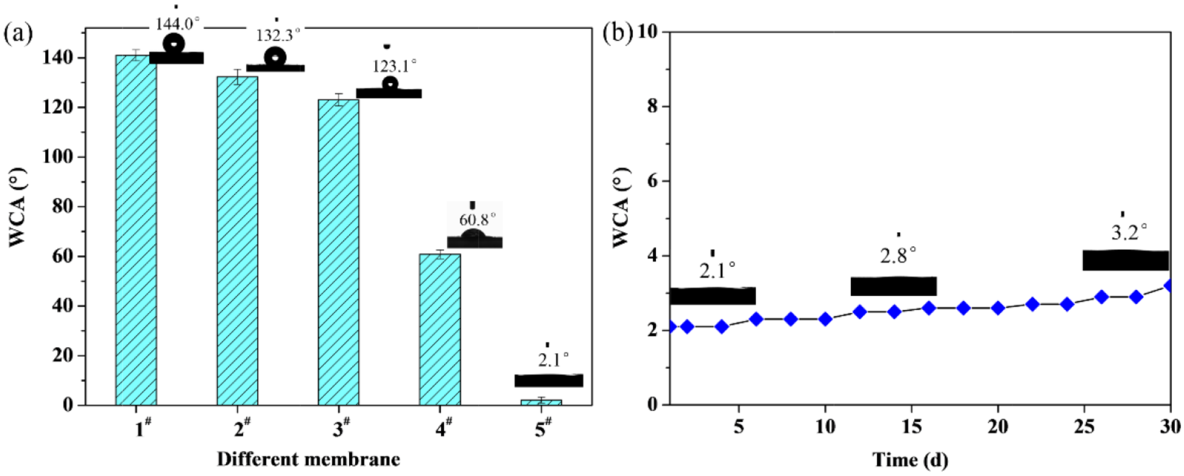

Fig. 1. (a) The effects of concentrations of the fluorocarbon surfactant solution on water contact angle of PTFE membrane (b) the wettability persistence of the modified membrane (5#).

membrane decreased to 132.3°. Then, the WCA gradually reduced to 2.1° exhibiting a super hydrophilic surface when the concentration of fluorocarbon surfactant was increased to 0.8 wt%. This indicated that the wettability of the PTFE membrane can be well manipulated by the concentration of fluorocarbon surfactant solution. The reason was attributed to that the fluorocarbon chains of the surfactant have a good compatibility with that of PTFE, and such bridging effect would change surface chemistry and make the hydrophilic groups of the fluorocarbon surfactant expose outside and induce in a super hydrophilic surface [28]. The higher concentration of the surfactant solution would lead to more hydrophilic groups exposed on the membrane surface. Thus, the PTFE membrane was modified into super hydrophilicity with 0.8 wt% of solution. Furthermore, the wettability durability of such super hydrophilic membrane ($5^{\#}$) was investigated as shown in Fig. 1b. It can be seen that the WCA of the membrane surface displayed a little increase from 2.1° to 3.2° within 30 d in ambient environment. This indicated that the super hydrophilic wettability of the modified PTFE membrane showed higher stability.

Such wettability stability was further investigated by variation of pure water flux of the membranes with running time. As shown in Fig. 2 that the pristine hydrophobic PTFE membrane $1^{\#}$ wetted by ethanol showed an initial flux of 63963.2 L/(m^2·h·MPa), and the flux sharply decreased with running time. After 3 h, the flux decreased to 6390.3 L/(m^2·h·MPa). In contrast, the super hydrophilic membrane $5^{\#}$, which need not to be wetted by ethanol showed a relatively stable pure water flux. After 8 h, the water flux decreased from initial 69870.9 L/(m^2·h·MPa) to 60620.4 L/(m^2·h·MPa). This really indicated that the modified super hydrophilic membrane showed a much stable wettability.

3.2. Filtration and anti-fouling performance of the modified PTFE membranes

The permeate flux of different membranes for filtration of 50.0 mg/L of HA and LYS water aqueous solution are shown in Fig. 3, respectively. Noted that both fluxes for filtration of HA and LYS solution decreased with increasing the hydrophilicity of PTFE membrane surface. Also, it can be seen from Fig. 3 that two distinctive stages regard to the flux decline in filtration process during the whole filtration while fouling process. At the initial stage, both HA and LYS foulants were rapidly adsorbed or deposited onto membrane surface during filtration, so the membrane was promptly fouled and the flux declined drastically. During the second stage, flux decline gradually slowed down to reach a steady state. Comparing with Fig. 3a, the flux of the PTFE membrane fouled by LYS displayed a faster and more severe diminishing rate in Fig. 3b. Obviously, the super hydrophilic membrane surface displayed a lowest flux decline, indicating a good anti-fouling property. Noted from Fig. 3, when the effluent volume was 5000.0 mL, the normalized flux of PTFE original membrane dropped to 0.072 and 0.096 for HA and LYS foulants, respectively, while that of the super hydrophilic PTFE membranes just dropped to 0.279 and 0.193, respectively. This indicated that the highly hydrophilic surface could really improve the membrane's anti-fouling performance. Such result was in consistence

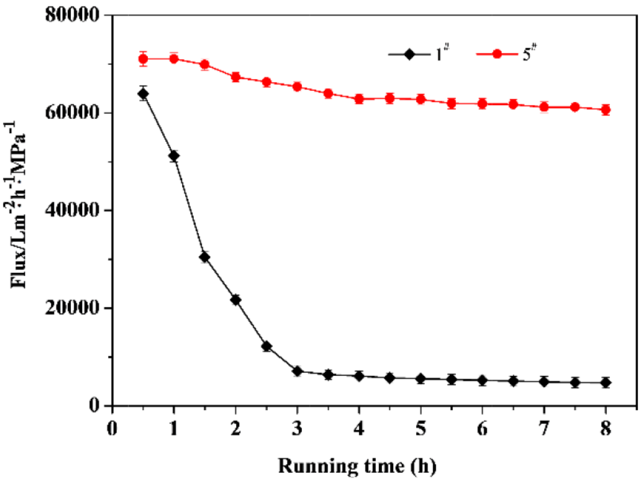

Fig. 2. The variation of pure water flux of the membranes with running time.

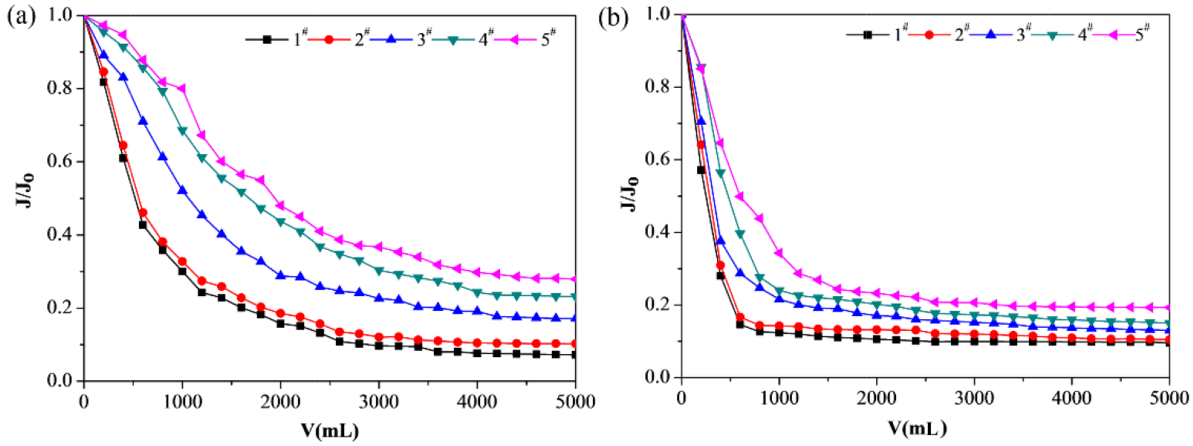

Fig. 3. Flux variations of different wettability membranes, the foulant was (a) HA (b) LYS (Conditions: 50.0 mg/L concentration of solution; 0.1 MPa; temperature: 25).

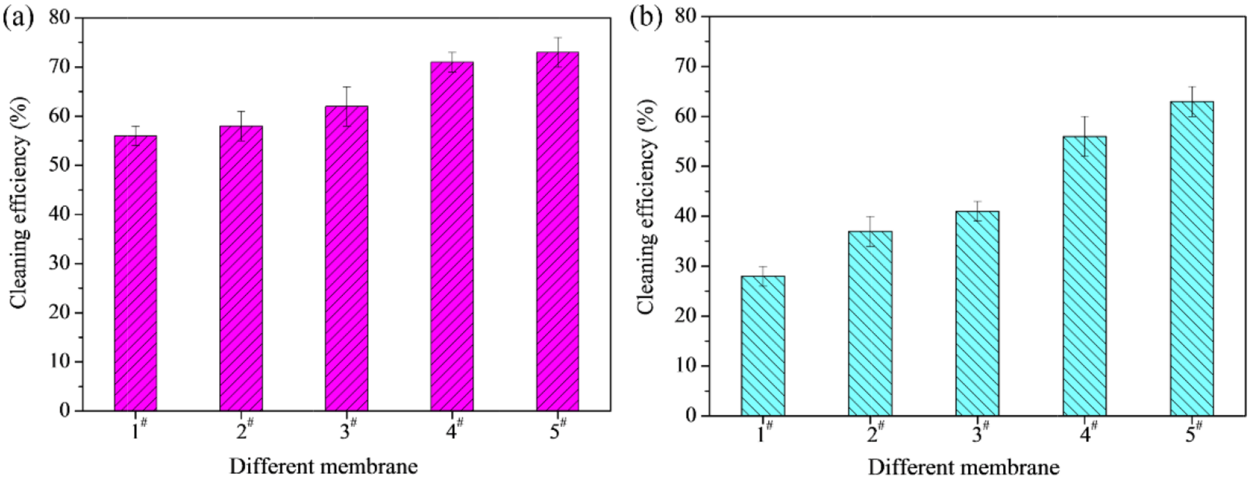

Fig. 4. Cleaning efficiency of different membrane fouled by (a) HA (b) LYS.

with our previous work [15,16,22]. This was due to that water molecule layers were preferentially formed on the membrane surface during the filtration, which hindered the contact of foulant with the membrane surface, and induced in an improved anti-fouling property [29].

In order to investigate the anti-fouling performance of the membranes, the fouled PTFE membranes was rinsed by water and the corresponding cleaning efficiency is shown in Fig. 4. It can be seen that after the fouled membranes were rinsed, the cleaning efficiency of the membranes obviously increased with enhancing membrane hydrophilicity. For the membrane fouled by HA which showed a higher cleaning efficiency than that fouled by LYS, it indicated that the membrane was easier to be fouled by LYS than HA. This was probably ascribed to that HA molecule showed higher polarity than LYS, and it was easily washed out from the hydrophilic surface during rinsing. It was interesting to observe that the super hydrophilic membrane ($5^{\#}$) displayed a highest cleaning efficiency, which were 73.1% and 62.5% for HA and LYS fouled membrane, respectively. This further demonstrated that the super hydrophilic surface displayed good anti-fouling property.

Therefore, the cycle cleaning effect of the super hydrophilic membrane ($5^{\#}$) was further investigated in comparison with pristine PTFE membrane using 50.0 mg/L HA aqueous solution as feed solution. As shown in Fig. 5, after the first cycle of fouling and cleaning, the flux recovery ratio (FRR) of the membrane $5^{\#}$ was 69.6%, while that of the pristine membrane $1^{\#}$ just was 49.4%. At the end of the tenth cycle, the FRR of the super hydrophilic membrane $5^{\#}$ and the pristine membrane $1^{\#}$ were 65.4% and 34.6%, respectively. The super hydrophilic PTFE membrane showed much higher FRR than the hydrodrophobic pristine PTFE membrane and displayed an effective fouling resistance to HA foulant.

3.3. XDLVO theory analysis on anti-fouling property of the membrane

The interfacial energy between the foulants and the membranes (including clean and fouled membrane) were assessed by XDLVO theory. The surface tension components, adhesion free energy, and cohesion free energy of the membranes and foulants were determined by WCA measurement as shown in Table S1. The Lifshitzevander Waals (LW), Lewis acid-base (AB) and electrostatic double-layer (EL) components of the adhesion/cohesion free energy were calculated using Eqs. (2)–(7) of [15]. The total interaction energy (ΔG^{TOT}) was determined by the sum of the LW, AB and EL free-energy components. According to previous analysis [15], since the value of EL free energy was much smaller than the other two components, it was considered that EL free-energy has almost no effect on the total free energy, therefore, the effect of EL free-energy on the total free energy was ignored herein.

According to XDLVO theory, the ΔG^{TOT} value provides a quantitative insight on fouling tendency between foulant and membrane surface. Positive value of ΔG^{TOT} indicates repulsive interaction, whereas a negative one implies attractive [15]. The adhesion free energy between membranes and foulants is shown in Table 1. It can be seen that the value of ΔG^{TOT} gradually increased with enhancing the hydrophilicity of the membrane surface, indicating that the modified hydrophilic PTFE membranes showed obvious repulsion to the foulants. Remarkably, ΔG^{TOT} of the super hydrophilic PTFE membrane $5^{\#}$ respectively fouled by HA and LYS showed positive value of 82.328 $mJ\cdot m^{-2}$ and 51.004 $mJ\cdot m^{-2}$. Whereas for the hydrophobic PTFE pristine membrane $1^{\#}$, the value of ΔG^{TOT} was negative value of –34.764 $mJ\cdot m^{-2}$ and –70.505 $mJ\cdot m^{-2}$, respectively. This indicated that the hydrophobic PTFE membrane was more susceptible to be fouled than the hydrophilic membrane. Moreover, the modified super hydrophilic PTFE membrane $5^{\#}$ showed a highest ΔG^{TOT} value, indicating that the super hydrophilic membrane displayed better anti-fouling property in the early stage of filtration. This analysis result was in consistence with that of Fig. 4. In addition, it can be noted form Table 1 that similar to variation of ΔG^{TOT}, the ΔG^{AB} value gradually increased with increasing hydrophilicity of the PTFE membrane, indicating the AB repulsion between the clean membrane and foulants increased. Therefore, the effect of the wettability of the PTFE membrane on the interaction between membrane and foulants was mainly attributed to AB force.

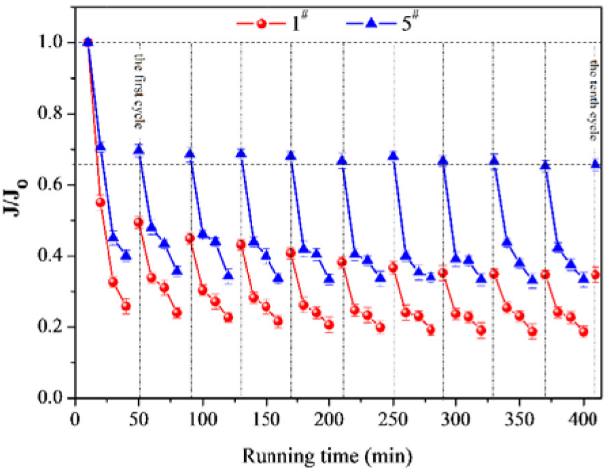

Fig. 5. The fouling and cleaning cycling test of the super hydrophilic membrane $5^{\#}$ and the pristine membrane $1^{\#}$ using 50.0 mg/L HA as feed solution.

During the practical filtration process, the initial attachment of foulants onto clean membrane surface is mainly controlled by the adhesion energy. When the membrane surface was covered by foulants, the fouling tendency would be governed by the cohesion energy between the approaching foulants and the deposited foulants on the membrane surface [15,30]. Table 2 presents the cohesion free energies between foulants and the membranes fouled by HA and LYS, respectively. Notably, the cohesion free energy value of the super hydrophilic membrane $5^{\#}$ still was largest, which was 34.15 $mJ\cdot m^{-2}$ and 6.863 $mJ\cdot m^{-2}$, respectively. Whereas for the hydrophobic PTFE original membrane 1# the value was decreased to 21.953 $mJ\cdot m^{-2}$ and –40.582 $mJ\cdot m^{-2}$. This indicated that the super hydrophilic membrane 5# displayed a largest repulsive force against the approaching foulants in the late stage of filtration. Therefore, form the analysis by XDLVO theory, the super hydrophilic PTFE membrane $5^{\#}$ really showed good anti-fouling property on HA and LYS no matter in the early or late stage of filtration. And the increased hydrophilicity of the membrane greatly facilitated to improve its anti-fouling property. This was much in accordance with the results of part of 3.2.

3..4 Fitting analysis on membrane fouling trends and free energy of interface

To evaluate the effectiveness of the XDLVO analysis on the effect of hydrophilicity of PTFE membrane on anti-fouling property, the result difference between membrane practical fouling process and XDLVO analysis was carried out by linearly fitting. The trend of membrane fouling (*K*) was calculated by:

Table 1
Adhesion free energy between membranes and foulants

Membranes	Adhesion free energy (HA) ($mJ\cdot m^{-2}$)			Adhesion free energy (LYS) ($mJ\cdot m^{-2}$)		
	ΔG^{LW}	ΔG^{AB}	ΔG^{TOT}	ΔG^{LW}	ΔG^{AB}	ΔG^{TOT}
1#	4.852	–39.616	–34.764	3.516	–74.021	–70.505
2#	4.875	–28.446	–23.571	3.532	–63.609	–60.077
3#	4.978	–15.300	–10.322	3.606	–51.122	–47.516
4#	–1.196	54.361	53.165	–0.867	18.135	17.268
5#	–1.771	84.099	82.328	–1.283	52.287	51.004

Table 2
Cohesive free energy between foulants and the fouled membranes membranes

	Cohesive free energy (HA and HA fouled membrane) ($mJ·m^{-2}$)			Cohesive free energy (LYS and LYS fouled membrane) ($mJ·m^{-2}$)		
	ΔG^{LW}	ΔG^{AB}	ΔG^{TOT}	ΔG^{LW}	ΔG^{AB}	ΔG^{TOT}
1#	5.057	16.896	21.953	1.138	–41.720	–40.582
2#	5.222	17.601	22.823	1.211	–38.534	–37.323
3#	4.217	20.830	25.047	0.938	–33.254	–32.316
4#	5.385	24.568	29.953	1.065	–25.148	–24.083
5#	5.670	28.481	34.151	1.388	5.475	6.863

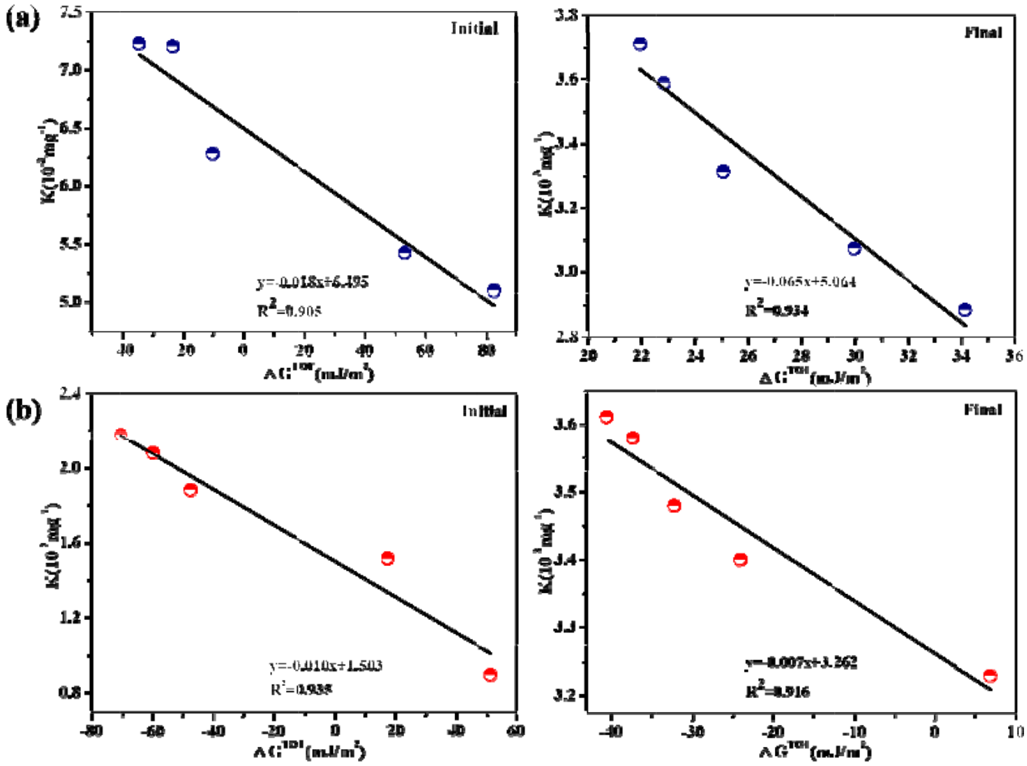

Fig. 6. Correlations between *K* and inter facial free energy of adhesion and cohesion for (a) HA (b) LYS foulants and the corresponding fouled membrane during the initial and final stage.

$$K = \frac{\Delta J}{J_0 \times \Delta V \times C_0} \tag{5}$$

where C_o is the concentration of foulants in aqueous solution.

The entire filtration stage was divided into initial and late stages according to the filter cake filtration model. The *K* value in the initial and later phases were fitted with the free energy of adhesion between membrane and foulants and the free energy of cohesion between HA or LYS foulant and the corresponding fouled membrane, respectively. As can be seen from Fig. 6, at either initial or late stage, the linear correlation coefficient between K and the free energy of the interface was in the range of 0.905–0.935, indicating that *K* showed a good linear relationship for both adhesion and cohesion free energy in all stages. This good linear fitting results proved the consistency of the XDLVO theory with the practical anti-fouling performance. And it also showed good applicability to predict the anti-fouling performance of PTFE membrane with different wettability.

4. Conclusions

The polytetrafluoroethylene (PTFE) membrane with different hydrophilicity was obtained using different concentrations of the cationic fluorocarbon surfactant solution. The water contact angle of the modified PTFE membrane can reach 2.1° with 0.8 wt% of solution, achieving super hydrophilicity. The anti-fouling property and cleaning efficiency of the membrane increased with hydrophilicity of the membrane, and the super hydrophilic PTFE membrane showed highest cleaning efficiency of 62.5% and better anti-fouling property. XDLVO analysis further suggested that the super hydrophilic PTFE membrane had the strong repulsion force to HA and LYS and displayed better anti-fouling property due to the highest positive total interaction energy (ΔG^{TOT}) value. Linearly fitting on membrane practical fouling process and XDLVO results proved the consistency of the XDLVO theory with the practical anti-fouling performance. This work showed good applicability to predict the anti-fouling performance of PTFE membrane with different wettability.

Acknowledgments

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Supporting Information

Table S1
Surface properties of the clean membranes as well as the foulants of HA and LYS

Membranes/ foulants	Contact angle			γ_{LW}	γ^{+}	γ^{-}	γ^{AB}	γ^{TOT}
	θ_{wat}	θ_{gly}	θ_{dii}					
1#	141.0 ± 1.12	123.1 ± 1.09	95.8 ± 0.76	10.263	0.070	1.192	0.576	10.839
2#	132.3 ± 0.32	122.9 ± 1.63	95.9 ± 0.61	10.223	0.257	0.008	0.093	10.317
3#	123.1 ± 0.76	122.3 ± 0.25	96.4 ± 0.29	10.026	0.574	1.213	–1.668	8.358
4#	60.8 ± 1.05	89.0 ± 0.96	65.7 ± 1.21	25.303	2.450	58.356	–23.914	1.389
5#	2.1 ± 0.73	70.1 ± 0.64	62.6 ± 1.03	27.079	1.313	115.587	–24.641	2.438
HA	36.4	53.7	39.2	40.010	0.001	51.499	–0.209	39.801
LYS	72.3	75.2	49.7	34.441	0.114	18.589	–2.914	31.527

Table S2
Properties of the HA-fouled membranes

Membranes	Contact angle			γ^{LW}	γ^{+}	γ^{-}	γ^{AB}	γ^{TOT}
	θ_{wat}	θ_{gly}	θ_{dii}					
1#	99.2 ± 1.21	96.8 ± 1.09	114.3 ± 1.05	9.871	1.039	17.392	–8.503	1.368
2#	98.6 ± 0.78	97.6 ± 0.65	114.0 ± 0.91	9.563	0.967	18.099	–8.365	1.198
3#	94.6 ± 1.06	92.7 ± 1.17	110.5 ± 1.29	11.532	1.110	20.646	–9.573	1.959
4#	91.2 ± 1.20	98.4 ± 1.01	108.7 ± 1.28	9.261	0.613	25.264	–7.868	1.392
5#	86.6 ± 0.98	99.8 ± 0.71	105.2 ± 0.45	8.745	0.350	30.173	–6.497	2.2473

Table S3
Properties of the LYS-fouled membranes

Membranes	Contact angle			γ_{LW}	γ^{+}	γ	γ^{AB}	γ^{TOT}
	θ_{wat}	θ_{gly}	θ_{dii}					
1#	101.1±1.42	79.8±1.71	95.8±1.34	17.596	0.007	3.451	0.313	17.909
2#	99.8±1.04	80.3±1.21	96.7±1.30	17.340	0.002	4.713	–0.173	17.167
3#	96.3±0.92	78.4±0.78	96.2±0.69	18.321	0.052	7.218	–1.220	17.101
4#	90.5±1.28	79.3±2.01	93.7±1.79	17.853	0.038	11.797	–1.347	16.506
5#	72.7±0.53	81.5±0.47	92.8±0.52	16.732	0.621	40.421	–10.020	6.712