Antifouling Ability of Hydrophilic PVDF-TiO_2 membrane Evaluated by Critical Flux and Threshold Flux

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Abstract. The PVDF flat-membrane was modified by hydrophilic nano-TiO_2, which blending by ultrasonication and mechanical stirring pretreatment in phase inversion method. To evaluate the permeate productivity and anti-fouling capacity of protein solution, both the critical flux (J_{CW}) and threshold flux (J_{TH}) of PVDF and PVDF-TiO_2 membrane were firstly measured by Advanced Constant Pressure-step Method in cross-flow filtration apparatus. Some evaluation indicators were utilized to analyze the results, such as Flux vs. Time and TMP vs. Time Curves, flux decline rate (dFlux/dt) and TMP-$Flux_{ave}$ curve. Two type fluxes were compared, results exhibited that hydrophilic PVDF-TiO_2 modified membrane possessed a higher level of both J_{CW} and J_{TH} and better anti-protein fouling ability after testing by Advanced Constant Pressure-step Method.

1 Introduction

Membrane separation technology was widely used in both water and wastewater treatment, especially for pressure-driven membranes which consisted of four types, porous micro-filtration (MF) or ultra-filtration membranes (UF), or dense nano-filtration (NF) or reverse osmosis (RO) membrane [1]. For porous MF and UF, they were gradually accepted in practical application, due to low-pressure and energy consumption. During practical filtration process, reaction of membrane and contaminants occurred by physical, chemical or biological effects, easily leading to fouling problems limited the application scope. Fouling problem of UF had become one research hotspot. There were three ways to solve the aforementioned problems, treatment of feeds [2], hydrophilic modification of membrane [3], and operation control by critical flux (CF) and threshold flux (TF) [4]. The first route was achieved by extra auxiliary methods, and the latter two routes did not require additional cost investments.

In last decades, various novel hydrophilic additives were attractive for UF membrane fabrication, owing to some advantages, such as rich hydrophilic functional groups and brilliant modification performance [5]. As compared to carbon nanotube [6] and graphene oxide [7], inorganic metal-based oxide was seemingly more available by commercial

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purchased or self-preparation. Except for Al_2O_3 [8], Ag [9], SiO_2 [10] and so forth, nano TiO_2 had attracted lots attention because of high hydrophilicity of less toxicity which commonly used in UF modification [11, 12].

For operation control, CF or TF operation was often realized by no or low fouling rate, to obtain a less cleaning frequency and longer membrane life in practical significance [13]. After the CF concept proposed in 1995 [14], some researchers found that ideal state of CF, no fouling, might be in very low flux level or did not exist, especially the composition of feeds was complicated [15]. Then, a mild concept of low fouling rate operation named TF, was put forward in 2011 [4]. References investigation showed four major research directions of CF/TF operation, the existence [16], new measuring methods [17], the practical significance [18], and the relationship of operation and fouling [19].

Regarding to hydrophilic modified UF membrane, particularly of nano-TiO_2 modification, some research gaps put in an appearance. Did the ideal CF operation of modified membrane exist or not. And did the modified membrane had a higher CF and TF level to promote productivity, when it owned a better anti-fouling ability. The purpose of this study was to give better understanding on the anti-fouling capacity of nano-TiO_2 modified UF membrane, from CF and TF perspective. For this, one modified membrane was fabricated by PVDF polymer and nano-TiO_2 particle with assist of novel promote pre-treatment. The CF and TF values of PVDF and modified PVDF-TiO_2 membranes were firstly measured by Advanced Constant Pressure-step Method. Fouling behavior of two PVDF membranes were analyzed by fouling resistance.

2 Materials and Measurements

2.1 Fabrication of pristine and modified membranes

Both pristine PVDF and PVDF-TiO_2 membrane were fabricated by phase inversion method which clearly described in our previous study [20]. Pristine PVDF membrane was made with weight ratio of PVDF : PVP : DMAc =19:1.3:79.7, and PVDF-TiO_2 membrane with weight ratio of nano-TiO_2 : PVDF : PVP : DMAc=1:19:1.3:78.7. The nano-TiO_2 was added into DMAc solvent with direct ultrasonication pre-treatment for 1 h, the mixture was kept for 25℃ by constant temperature circulating water tank. The direct ultrasonication was realized by Cell disruption instrument which named new model Ultrasonic Processor (FS-450, China).

Then, PVDF polymer and PVP were added into mixture for mechanical stirring (24 h) and statically placed in water bath at 55℃ (24 h) to finish degassing stage. Certain amounts of casting solution was poured onto clear glass and then casted by thin-film casting doctor blade (~200 μm). Certain volume of deionized water was put as coagulation bath to complete the phase inversion process. The pristine membrane was marked as PVDF, and the modified membrane was marked as PVDF-TiO_2(MSU2).

2.2 Filtration set-up and determination procedures

One cross-flow filtration set up was used, three sensors were put near influent and effluent position to measure real-time pressure. The feeds was protein solution with bovine serum albumin concentration of 30mg/L, and cross-flow velocity was 15 cm/s. The bovine serum albumin was measured by ultraviolet radiation spectrophotometry at a λ of 280 nm. The effective area of membrane cell was 42 cm^2, and membrane was compacted at 2 bar for 20 min before CF and TF testing.

Based on the strict concept of CF, Field [14] proposed two types, one was the strong form (J_{SW}) corresponding to feed solution were pure water, another one was the weak form (J_{CW}) corresponding to feeds consisted of water and foulants. For the concern of anti-fouling ability evaluation, only J_{CW} was measured in our study, which tested by the Advanced Constant Pressure-step Method. This method [21] applied the TMP up to a maximum TMP and back analogous to the initial TMP step (Fig. 1(a)). The upping TMP step named as X, and the initial TMP step named as 1-X. The operating order was step 1 → step 2 → step 1-2 → step 3 → step 1-3→⋯. For instance, fouling occurred at step 4 and permeate flux decline was observed here, revealing that the critical flux was situated between step 3 and step 4. At same time, the permeated flux wouldn't be same at step 1-3 and step 1-4. It meant the critical TMP should be below step 4, and the critical flux should be measured at the corresponding critical TMP. If no fouling occurred between step 3 and step 4, the permeated flux of those two steps shouldn't be decreased with filtration time and it also should be same at step 1-3 and step 1-4.

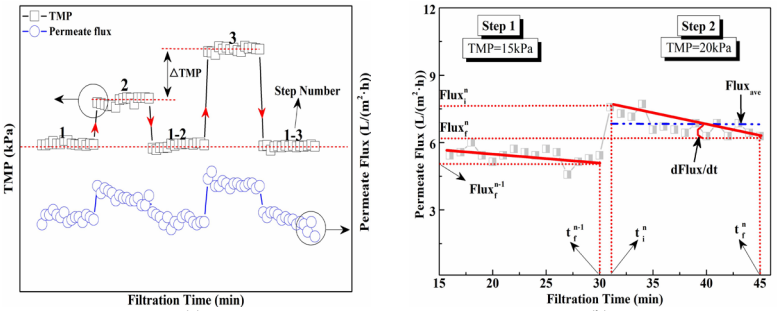

Fig. 1. The (a) Measurement Procedures and (b) Evaluation Indicators of the Advanced Constant Pressure-step Method in Our Study.

The evaluation indicators of the Advanced Constant Pressure-step Method was shown in Fig. 1(b). The ideal CF was corresponding to no fouling, thus the permeate flux should keep same with no decline and dFlux/dt should be zero. The dFlux/dt was permeate flux decline rate in one pressure step, which equaled to the slope (k) of permeate flux curve (Equation (1)). The $Flux_{ave}$ meant the average flux level in one pressure step, which was calculated by average value collected one time per minute in Equation (2). The TF could be estimated by dFlux/dt kept for low value.

$$Flux(t)=k\times t+b \quad (1)$$

Where, Flux(t) was the real-time permeate flux collected by electronic balance ($L/(m^2\cdot h)$), and t was the filtration time (min), k was the slope of fitting linear, b was one constant.

$$Flux_{ave}=\sum (Flux_i^n+\cdots+Flux_f^n)/15 \quad (2)$$

Where, $Flux_i^n$ was the initial flux at pressure step n, and $Flux_f^n$ was the final flux at pressure step n, 15 was the collected times at one pressure step.

2.3 Fouling resistance

After measuring J_{CW} and J_{TH}, the fouling resistance was calculated by resistance-in-series model put in Equation (3) [22]. Where, the J was permeate flux, the ΔP was the

pressure average value in one step, the μ was permeate viscosity of water at 25 ℃, and R_t was the total fouling resistance. R_t was also the sum of R_m, R_c and R_f. The R_m was intrinsic resistance related to membrane structure and characterization. The R_c was the gel or cake layer resistance formed by foulants concentration polarization and precipitation, belonged to reversible resistance removed by physical cleaning that fouled membrane was flushed with tap water for 5 min of each side. The R_f was the adsorption or blockage resistance formed by foulants adsorption into membrane surface or inside pores, which belonged to the irreversible fouling.

$$J=\triangle P/(\mu\times R_t)=\triangle P/(\mu\times(R_m+R_c+R_f)) \quad (3)$$

3 Results and discussion

3.1 Critical flux estimation

3.1.1 The Flux vs. Time and TMP vs. Time Curves

The PVDF and PVDF-TiO_2(MSU2) had similar protein rejection of nearly 60% (BSA=500mg/L) but different pure water flux level of 50.96±8.53 and 117.95±8.96 (L/(m^2·h), respectively. During Advanced Constant Pressure-step Method, the pressure-step was alternatively increased and then decreased to initial level, which was easily to observe flux decline behavior especially when J was exceeded than J_{CW}. The Flux vs. Time and TMP vs. Time Curves (FT-TT curves) was shown in Fig. 2. The flux began to decrease at step 2 of PVDF and at step 3 of PVDF-TiO_2(MSU2) membrane. Protein fouling happened from 15 kPa to 20 kPa for PVDF and from 20 kPa to 25 kPa for PVDF-TiO_2(MSU2) membrane. It meant critical TMP of PVDF and PVDF-TiO_2(MSU2) was less than 15 kPa and 20 kPa, respectively, which same with the estimation by the dFlux/dt discussed in Fig. 3. However, because of the instrument limitation we couldn't measure a lower TMP value less than 15 kPa, thus the ideal J_{CW} of PVDF was not exist and J_{CW} of PVDF-TiO_2(MSU2) was exist based on the direct observation. The J_{CW} of PVDF and PVDF-TiO_2(MSU2) were ＜5.43 and 16.92 (L/(m^2·h), respectively.

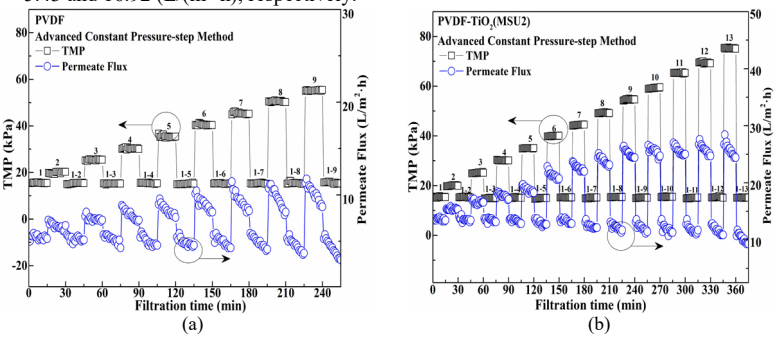

Fig. 2. The Flux vs. Time and TMP vs. Time Curves of (a) PVDF and (b) PVDF-TiO_2(MSU2) Membrane, Testing by Alternating Constant Pressure-step Method

3.1.2 The dFlux/dt

Additionally, the J_{CW} could be estimated by dFluxt/dt equalled to zero, which was demonstrated in Fig. 3. It was clearly that no zero dFlux/dt of both TMP ascending phase and relaxation phase was found, which might related to instrument precision and high accuracy required for operation. Depending on the dFlux/dt≈0 reflected no fouling occurred, the J_{CW} was estimated as following. For PVDF membrane, when TMP step raised from step 1 to step 2, the dFlux/dt decreased to less than -0.05, which showed the irreversible fouling occurred. And for PVDF-TiO_2(MSU2), when step 1 raised TMP to step 2, the dFlux/dt seemed remained near zero. When step 2 decreased to step 1-2, the dFlux/dt decreased to near -0.05, which illustrated that fouling occurred between step 1 and 2, then showed at step 1-2 due to fouling hysteresis effect. Therefore, based on the result obtained by dFlux/dt, the critical TMP of PVDF and PVDF-TiO_2(MSU2) was less than and equal to 15 kPa, their J_{CW} were ＜5.43 and 13.88 L/(m^2·h), respectively.

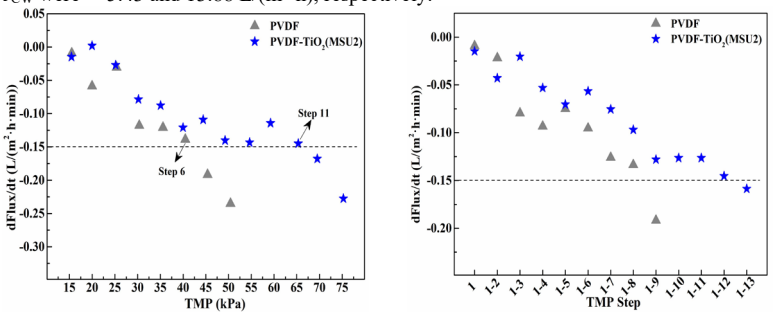

Fig. 3. The dFlux/dt of PVDF and PVDF-TiO_2(MSU2) Membrane at (a) TMP ascending phase and (b) TMP relaxation phase by Advanced Constant Pressure-step Method

3.1.3 The TMP-$Flux_{ave}$ Curves

The J_{CW} also could been evaluated by the TMP-$Flux_{ave}$ curve, according to the Espinasse's studied on the J_{CW} measured by Alternating Constant Pressure-step Method [23]. Set as an example, the first three TMP step of PVDF membrane was step 1→ step 2→ step 1-2, i) if the reversible fouling formed between step 1 and step 2 which could be removed by hydraulic scour of cross flow, the $Flux_{ave}$ of step 1-2 should be close enough to it at step 1, the $Flux_{ave}$ of first three TMP steps should be fitted in linear; ii) or if irreversible fouling formed between step 1 and step 2 which couldn't been removed by cross flow, the $Flux_{ave}$ of step 1-2 would be less than it of step 1, and this would not continue to be linear relationship. For PVDF, from step 1 to step 1-2, the $Flux_{ave}$ was 5.43, 6.66 and 5.26 L/(m^2·h), and the R^2 of fitting linear was 0.9915 which displayed that only reversible fouling formed between 15 and 20 kPa. When TMP raised to step 3 then back to step 1-3, the first five points of the TMP-$Flux_{ave}$ curve would not maintain in linear, because the R^2 decreased to 0.9681 which was less than 0.99. For PVDF-TiO_2(MSU2), first three points from step 1 to step 1-2 could be in linear due to the R^2 was 1. And it same to PVDF, the linear could not keep until step 3, owning to the R^2 decreased to 0.9867. Herein, the critical TMP of PVDF and PVDF-TiO_2(MSU2) were same of 20 kPa at step 2, and the J_{CW} were 6.66 and 15.39 L/(m^2·h), respectively.

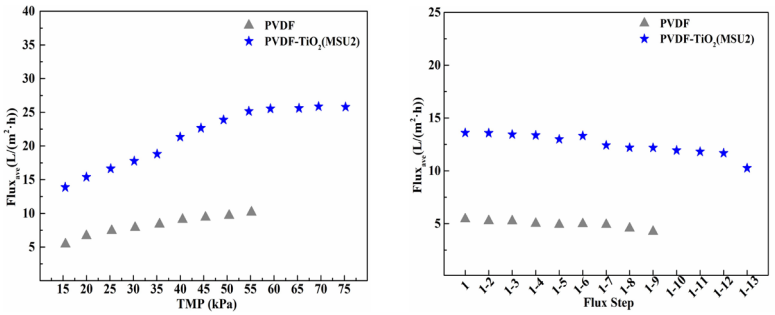

Fig. 4. The TMP-$Flux_{ave}$ curve of PVDF and PVDF-TiO_2(MSU2) Membrane at (a) TMP ascending phase and (b) TMP relaxation phase by Advanced Constant Pressure-step Method

3.2 Threshold flux estimation

Relying on the TF concept put by Field [4], the fouling rate between low and high fouling region was the key-point. According to the dFlux/dt (Fig. 3), we found that dFlux/dt of two membranes were decreased with TMP increased, then it seemly kept for one pseudo-steady state in few steps and dropped dramatically. It looked like dFlux/dt=-0.15 was one demarcation, when dFlux/dt was less than -0.15, the dFlux/dt jump appeared and started to drop dramatically. We used this dFlux/dt jump to differentiate low and high fouling region. Therefore, the threshold TMP of PVDF and PVDF-TiO_2(MSU2) was 40 and 65 kPa, and the J_{TH} were 9.08 and 25.60 L/(m^2·h).

3.3 Comparison of J_{CW} and J_{TH} of PVDF and PVDF-TiO_2(MSU2)

On the basis of previous results, the summary of PVDF and PVDF-TiO_2(MSU2) were listed in Table 1. When feeds was protein solution, the J_{CW} and J_{TH} of PVDF and PVDF-TiO_2(MSU2) did exist. The critical pressure of PVDF was ＜15~20 kPa, the J_{CW} was ＜ 5.43~6.66 L/(m^2·h). And for PVDF-TiO_2(MSU2), the critical pressure was 15~20 kPa, but J_{CW} was improved to 13.88~16.92 L/(m^2·h). The threshold pressure of PVDF and PVDF-TiO_2(MSU2) was 40 and 65 kPa, respectively, and their J_{TH} were 9.08 and 25.6 L/(m^2·h). The hydrophilic modified membrane had 2 or 3 times of both J_{CW} and J_{TH} than PVDF membrane, no matter it was evaluated by which indicators. It was inferred that adding nano-TiO_2 was benefit for enhancing productivity of PVDF membrane, when operating at J_{CW} condition. At same time, hydrophilic modified membrane was surmised brilliant anti-protein fouling ability, when operating at threshold pressure condition it had higher J_{TH}.

Table 1. The summary of J_{CW} and J_{TH} evaluated by different indicators

Membrane	Critical Pressure (kPa)	J_{CW} (L/(m^2h))	Evaluation indicator	Threshold Pressure (kPa)	J_{TH} (L/(m^2h))	Evaluation indicator
PVDF	＜15	＜5.43	FT-TT curve	40	9.08	dFlux/dt＜ -0.15
	＜15	＜5.43	dFlux/dt≈0			
	20	6.66	TMP-$Flux_{ave}$			
PVDF-TiO_2 (MSU2)	20	16.92	FT-TT curve	65	25.6	dFlux/dt＜ -0.15
	15	13.88	dFlux/dt≈0			
	20	15.39	TMP-$Flux_{ave}$			

3.4 Fouling mechanism

The fouling resistance of R_t, R_c and R_f was shown in Fig. 5. For PVDF-TiO_2(MSU2) at J_{CW}, the reversible fouling R_e close to 1% of the R_t, which could be neglected. However for PVDF membrane, the irreversible fouling J_f could not been ignored at J_{CW}, and it was increased at J_{TH} level. It was indicated that ideal status of critical flux condition was not found, but the operating results of PVDF-TiO_2(MSU2) was close to it. It was probably due to the irreversible protein contamination occurred easily of hydrophobic PVDF, the ideal J_{CW} was rather small and not detected in our study because instrument limitation. The anti-protein fouling ability of PVDF-TiO_2(MSU2) was enhanced effectively when nano-TiO_2 was added, the J_{CW} level was improved and could be detected.

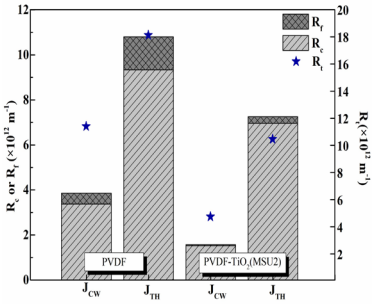

Fig. 5. The fouling resistance of PVDF and PVDF-TiO_2(MSU2) Membrane at J_{CW} and J_{TH}.

When flux increased to J_{TH}, the R_t, R_c and R_f of two membranes were increased with different degree, especially for PVDF. It attributed to the driven force was higher than that at J_{CW}, the shear force provided by cross-flow was weaker than protein sedimentation effect, so that concentration polarization layer or pore blockage might formed quickly at threshold TMP. For modified PVDF-TiO_2(MSU2) membrane, the increased degree of Rc was higher than that of PVDF, due to the threshold TMP was 65 kPa which higher than 30 kPa of PVDF. At same time, no matter at flux level of J_{CW} or J_{TH}, R_t of PVDF-TiO_2(MSU2) was smaller than that of PVDF membrane, which illustrated that fouling degree was severer of PVDF. In brief, it was evidently that hydrophilic modification by nano-TiO_2 was profit to alleviate protein fouling at permeate flux level of both J_{CW} and J_{TH}.

4 Conclusion

When feed solution was protein, the critical flux and threshold flux of PVDF and hydrophilic modified PVDF-TiO_2(MSU2) were successfully evaluated by the Advanced Constant Pressure-step Method depending on some indicators. As compared to PVDF, the PVDF-TiO_2(MSU2) owned greater value at both J_{CW} and J_{TH} which easily guaranteed the productivity at operating optimization. Additionally, the nano-TiO_2 was helpful to alleviate the irreversible fouling degree of PVDF membrane at J_{CW} and J_{TH}, especially decreasing the R_f of PVDF-TiO_2(MSU2) at J_{CW} level which leading the operation close to ideal status of critical flux.

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