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Critical flux investigation in treating o/w emulsion by TiO_2/Al_2O_3-PVDF UF membrane

Xuesong Yi, Yong Wang, Limei Jin and Wenxin Shi

ABSTRACT

A standard transmembrane pressure (TMP) step method has been used in membrane fouling assessment in tube ultrafiltration (UF) membrane system treating oil water (o/w) emulsion operated at constant TMP. Three flux reduction curve with different o/w concentration based on TMP variation were concluded by experiment, then, to describe fouling behavior and identify the occurrence of fouling in the so-called critical flux. Furthermore, sub-critical and super-critical flux experiment with a long time was determined, and zero rate of flux reduction (d*F*/d*t*) was never found during the whole trial period, indicating that critical flux in o/w UF process with its strict definition could not be defined in this paper. However, quasi-critical flux exists, under which the pollution rate was very slow. Moreover, a high-efficiency four steps cleaning method: mechanic scraping, pure water wash, pure water reverse wash, and dosing cleaning, was explored. It concluded that critical flux in real o/w UF system determined by TMP-step method can be used to predict long-term critical behavior with useful data on fouling propensity.

Key words | critical flux, membrane fouling, oil/water emulsion, TiO_2/Al_2O_3-PVDF, ultrafiltration

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INTRODUCTION

Membrane fouling in ultrafiltration (UF) processes can be characterized through critical flux determination, which can be mitigated effectively via sub-critical flux operation. As early as 1995, the concept of membrane fouling with critical flux condition was initially proposed (Field *et al.* 1995), and stated that the membrane fouling is very weak or does not even occur with solvent transfer only. In order to better understand membrane fouling characteristics, numerous researchers make great efforts to prove this standpoint, and it was reviewed in-depth by Bacchin *et al.* (Bacchin *et al.* 2006). However, the critical flux in oil/water (o/w) ultrafiltration process has few reports, means little special efforts have been devoted to this field.

From our previous research results (Yi *et al.* 2011, 2013), polyvinylidene fluoride (PVDF) membrane modified by TiO_2/Al_2O_3 nano-particles has good anti-oil pollution performance due to membrane hydrophilicity enhanced by these nano-particles; moreover, several important parameters had been also got by Millipore stirred cell UF process. However, for the compressible characteristics of oil particles, they enter the pores, causing membrane holes plugging; at the same time, a cake layer formed gradually from gel on the membrane surface, leading to the effective area with surface channel decreases; moreover, although the adsorption capacity is weak, it still exists and plays a positive role in flux attenuation. Thus, membrane pollution becomes serious with time. Numerous reports (Espinasse *et al.* 2008; Melidis *et al.* 2016) have proved that there is a critical flux in the process of ultrafiltration, and access to this parameter is essential to control membrane fouling.

In general, the critical flux of ultrafiltration process can be obtained by continuous flow or transmembrane pressure (TMP) step method, where membrane fouling assessment rely on every step of the filtering resistance increase. Compared with flux-stepping method, TMP step method is considered to be much more efficient in investigating the critical flux for the present study. As a result of fluid turbulence flow through the membrane, always maintained with a certain level, which makes the oil particles deposition and deformation on the membrane surface become more difficult, leading the TMP method seems very reliable

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(Ochando *et al.* 2014). The chief aim of the current work is to gain the behavior of separating unstable and concentrated emulsions by UF system, especially at the phase inversion point.

The present study attempts to find the critical flux of o/w using modified PVDF UF membrane. Firstly, endeavors to minimize the interference of membrane compression with time, affecting critical flux determination, through higher TMP pre-compact. Secondly, through a large number of comparative tests, using multi-compartment UF model specially designed for finding TMP under which a stable flux can be obtained. Thirdly, a long time comparing the experiment between critical or sub-critical flux and non-critical flux was studied. Finally, cleaning methods for TiO_2/Al_2O_3-PVDF ultrafiltration membrane polluted by o/w were achieved. The results obtained would lay the groundwork for understanding the filtration characteristic, especially the critical flux and pollution controlling in treating o/w. The results will provide valuable insights into understanding.

MATERIALS AND METHODS

Membrane and apparatus

A laboratory-scale cross-flow tube ultrafiltration membrane system (Figure 1), was a process designed specifically to evaluate the fouling-related critical flux treating o/w emulsion properly. This UF system consisting of a membrane module made of TiO_2/Al_2O_3-PVDF, a kind of weak hydrophobic membrane with nominal pore size of 0.05 um (100 KD), which has four tubes, 10 mm diameter, 250 mm long, and the total effective area of 0.31 m^2; feed tank; cleaning solution tank; pumps; valves; pressure gauge; flowmeter, etc. This system was operated in a series of fixed TMP mode, and the required TMPs were provided by the submersible pump, through adjusting the valves between the feed and the effluent outlet.

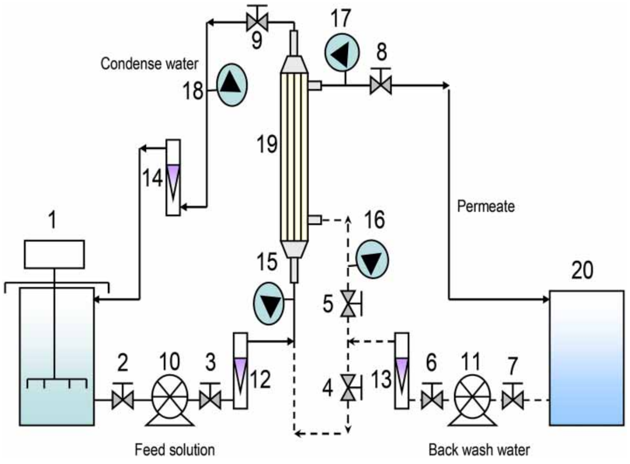

Figure 1 | Schematic diagram of cross-flow UF experimental set-up. 1. feed tank; 2–9 valves; 10 feed pump; 11 back wash pump; 12–14 flowmeters; 15–18 pressure gauges; 19 membrane module; 20 permeate (cleaning solution) tank.

The decrease in permeate flux (*J*) was continuously monitored at predetermined intervals using a graduated cylinder at each TMP step. In order to eliminate the influence of temperature (*t*) on critical flux determination, effluent values need to correct to 20 °C with the following equation (Howe & Clark 2002):

$$J_{20} = J_t \times 1.024^{20-t} \tag{1}$$

Emulsion characteristics and analysis

The o/w emulsion mother liquor configuration was as follows: 200 mg of crude oil from the Daqing oil field was added as base oil, and 400 mg of anionic surfactant (sodium dodecyl sulfate (SDS), 98%, Tianjin) as co-solvent to 500 mL of deionized water. To ensure the emulsifying and dispersing properties of oil particles, mother liquor should be mixed by high-speed shearing instrument for 30 min, then dilute the mother liquor with initial pH value of 7.2 into the concentration required for the experiments.

In the first 3 days, the volume diameter of the oil droplets measured by a Malvern Mastersizer Particle Size Analyzer, with a range of 0.1–0.6 μm, and the average size was about 0.3 μm; even after 7 days, this parameter of particles was maintained at 0.2–0.8 μm, indicating this oil emulsion was very stable, and the detailed analysis about particle size was reported by Yi *et al.* (Yi *et al.* 2011).

Zeta potential characteristics were determined by continuous titration method using Malvern Non0-Z, which are provided in Figure 2. It can be seen from this figure that Zeta potential increased slowly with pH increasing below pH 11, then this value decreased rapidly. The main reason of this trend can be analyzed as: at low pH value, H^+ was involved in neutralization reaction with oil particles caused oil/emulsion water lost stability, then oil particles gathered and turned bigger and bigger, which led to a relatively lower potential; at high pH value (above 11), excessive OH^- made the emulsion had already stable lose stability again, then the potential decreased again. After careful consideration of range tolerance to acid and alkali which means pH of 6–11, beyond which the o/w particles

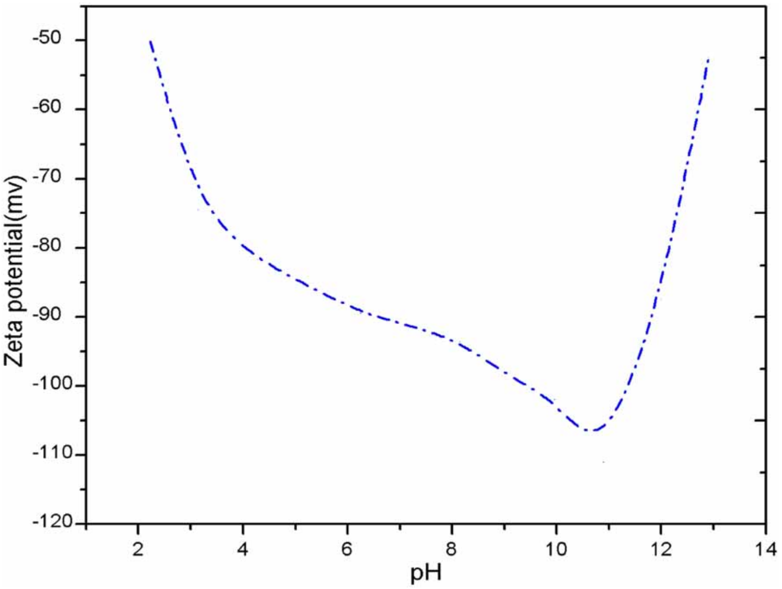

Figure 2 | Zeta potential characteristics of o/w.

lose stability easily leading to o/w particles becoming bigger. Then, along with zeta potential decreasing, electrostatic repulsion between membrane surface and o/w particles turn smaller, which may result in membrane fouling more serious. Thus, neutral or alkalescent conditions may be a good choice for the UF process.

Cleaning process

The membrane module must be cleaned systematically before each critical flux trial. The cleaning procedure was as follows. (1) Remove membrane module from system, mechanical scraping with sponge ball by manual operation, then installed again. (2) Forward rinse with water. Start the backwash constant flow pump 11 (left to run), open the valves 4, 6, 7, 9, close the valves 2, 3, 5, 8, lotion efflux. (3) Reverse flush with water. Start the backwash constant flow pump 11 to open the valves 5, 6, 7, 9 regulating valve 8, close the valves 2, 3, 4 lotion efflux. (4) Extra *in situ* chemical cleaning was performed by successive soaking in 0.1 wt % NaOH solution, 1 wt % NaClO, and 1 wt % SDS at 30 °C for 20 min. Then the membrane pure water flux can recover to the initial flux.

Data process disposal

Fluxes were continuously recorded in each TMP-step: the initial flux (F_i) and the final flux (F_f), can be defined as flux obtained before a sudden increase in filtration resistance within initial stage of TMP step, and flux at the end of the TMP cycle, respectively. Actually, in the first 30 s after the start of the TMP step, the flux value was converted to F_i, arbitrarily. It is possible to define parameters related to fouling, which are the instantaneous change in flux, from these two flux values: ($\Delta F = F_i^n - F_f^{(n-1)}$), the rate of flux decrease ($dF/dt = (F_f^n - F_i^n)/(t_f^n - t_i^n)$) and the average flux ($F_{ave} = (F_f^n + F_i^n)/2$).

TMP remains constant in each TMP step, thus, the flux reduction means an increase in filtration resistance, which is monitored in a fixed duration to evaluate the membrane fouling. Once, the flux decreases more than 10% of its initial value (i.e. the first 30 s), which is considered to be significant (Qu *et al.* 2015). It should be noted that in activated sludge system, high concentration organic wastewater, and other complex mixed liquors, strict 'zero fouling' is non-existent, even when operating below the critical flux (Guglielmi *et al.* 2007), indicating that the transition from 'rapid unbearable fouling' to 'slow sustainable fouling' rather than non-fouling occurring in such UF process.

RESULTS AND DISCUSSION

Membrane compaction

PVDF is a kind of organic polymer; it can be compacted under certain pressure. The variation of pure water flux F_P

($L/h{\cdot}m^2{\cdot}kPa$) for increasing and decreasing TMP cycles has been determined. Moreover, in order to avoid flux reduction caused by mechanical deformation of the solid polymer, F_P of membrane compacted by nitrogen with even higher pressure than that of operation was also studied.

Figure 3 shows the variation of F_P with a TMP increasing (line 1) and decreasing cycle (line 2) using new membrane, while F_P of a compacted membrane (line 3) with TMP increasing was also carried out. In the two consecutive cycles, it is clearly visible of the F_P decreasing for membrane compaction, especially in the first TMP increasing cycle shown as line 1; moreover, upon increasing TMP from 0.02 MPa to 0.2 MPa, *Fp* decreased from 3.75 to 2.50 $L/h{\cdot}m^2{\cdot}kPa$, which was almost 33.3%. While, in the relaxation sequence, *Fp* decreased sharply until 26.8% of its initial value at 0.02 MPa. At the same time, *Fp* has scarcely changed throughout the process of about 2.55 $L/h{\cdot}m^2{\cdot}kPa$. Thus, it was considered that compaction has serious implications in the UF process. Asymmetric porous structure of the tube membrane skin had mechanical deformation, leading to increase of the skin layer. Consequently, permeability decreasing gradually along with resistance increasing was observed in two independent cycles due to the twisted channels. A similar result has been reported by Profio *et al.* (Profio *et al.* 2011) and it is necessary to have membrane compacted before using.

Determination of critical flux conditions by TMP step method

In order to study the appropriate operating conditions to avoid membrane fouling (or not very obvious, e.g. reduced less than 10%), the critical flux (J_c) with different o/w concentration has been estimated. In fact, the critical flux is defined as a flux decline does not occur or declines at relatively low rates with time, below a certain flux; meanwhile, particles accumulation on membrane surface is not appeared when the permeate flux is below J_c (Ochando-Pulido & Stoller 2015).

It is an effective way to observe the flux permeability transition between constant and intermittent condition with initial fouling by plotting permeate flux (J) versus TMP. A common practice to estimate J_c, using a constant increase in TMP with a fixed duration for each increment, which can give a steady permeate flux at low TMP in general; however, the flux decrease rate increased obviously, once J_c is exceeded (Defrance & Jaffrin 1999). This method is superior to the flux-step method, for it is convenient and stable to TMP control than that of flux, especially, when permeate was little which cannot be controlled easily. Figure 4 shows the permeate flux and TMP as a function of the time for increasing TMP operating mode. For each flux reduction curve with different o/w concentration, 5 mg/L (red), 20 mg/L (green), 100 mg/L (blue), which

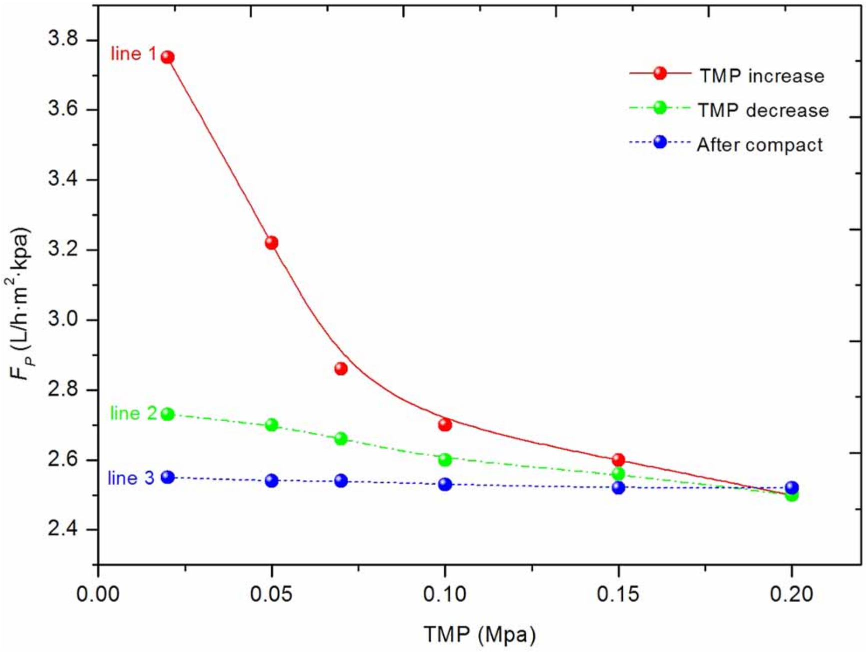

Figure 3 | Variation of *Fp* with a TMP increasing and decreasing cycle.

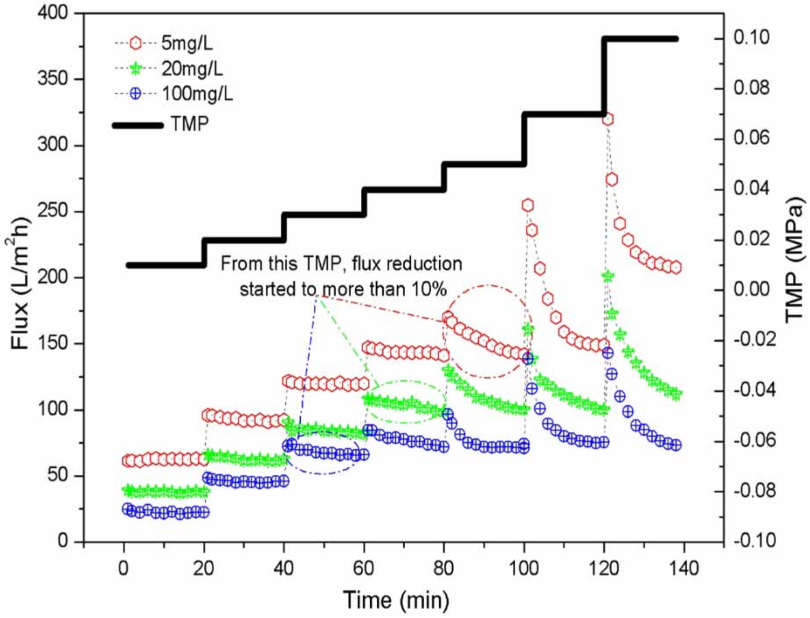

Figure 4 | Permeate flux (J) and trans-membrane pressure (TMP) as a function of the time (t) for o/w emulsion of 5 mg/L, 20 mg/L and 100 mg/L UF tests, at increasing TMP steps. The circle evidences the range of values where fouling started to become obvious. Please refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/wst.2017.445.

can be divided into two distinct regions. In the first zone, for TMP up to around 0.04 MPa, 0.03 MPa, 0.02 MPa for red curve, green curve, and blue curve, respectively, flux decreased slowly, along with fouling that occurred just for low values to some extent, and even can be depicted as negligible. When TMP reach 0.05 MPa, 0.04 MPa, and 0.03 MPa, accordingly, the decrease of flux was steeper, though still not very obvious, which was beyond 10%, compared with the initial flux, resulting in a more serious membrane fouling under these permeation conditions. And this can be seen as the critical condition (Huang *et al.* 2014). Therefore, J_c has been considered to lie around 120 L/m^2 h, 70 L/m^2 h, 40 L/m^2 h, with the critical TMP of 0.04 MPa, 0.03 MPa, 0.02 MPa for 5 mg/L, 20 mg/L, and 100 mg/L, accordingly.

In fact, there are two easily distinguishable ways of defining the critical flux. Since the fouling caused by adsorption between solute and membrane is negligible, flux obtained during sub-critical flux state is essentially the same as pure water flux acquired under the same conditions; however, the diversity is TMP flux curve begins to deviate from the curve of pure water flux after critical flux has been reached, while this definition cannot be used widely for the polarization and the other problems in real water UF process. However, in the other form, assuming that membrane fouling occurs on start-up and the velocity is also very fast, then the flux-TMP curve is significantly lower than that of pure water. In general, the critical flux appears at the inflection point where the straight line becomes the curve (Stoller & Chianese 2006). In this study, o/w emulsion with higher concentration as the UF substance, leading to serious polarization, thus, the second critical flux form was suitable.

It can be seen from Figure 4, which shows the J-TMP relation experiments of o/w emulsion with different concentration under constant pressure operating conditions, that the o/w emulsion curves diverge from a straight line beyond certain values of TMP, for the adsorption of foulants. This is consistent with the definition of the second form of critical flux, demonstrating that a fairly low but non-zero fouling rate can be detected even under critical flux or sub-critical flux conditions, due to the interaction of the o/w emulsion and membrane.

Thus, the J-TMP curve of oil/emulsion with 5 mg/L, 20 mg/L, and 100 mg/L starts not to be linear in according to data reported in Figure 4, for TMP = 0.05 MPa, 0.04 MPa, and 0.03 MPa, with a flux of about 120 L/m^2 h, 75 L/m^2 h, and 50 L/m^2 h, successively.

Long term operation

Considering the previous experimental results, here, 5 mg/L o/w emulsion was used to do the subsequent filtration test. The filtration system was run for as long as 24 h to simulate continuous operation (Singh 2008) with a constant TMP of 0.03 MPa (sub-critical) and 0.05 MPa (super-critical) periodic filtration (585 s) and back washing with the permeate (15 s) (Yigit *et al.* 2009); the result was shown in Figure 5.

In the case of the sub-critical condition (TMP = 0.03 MPa), flux decreased only very slowly for the first 6 h (from 86.4 to 80.3 L/m^2 h, corresponding to $dF/dt =$ 1.0 L/m^2 h) and then decreased even slower to 76.2 L/m^2 h at around 24 h. The flux variation indicated that the test compared to previous runs may indicate a poor definition of membrane rejection characteristics, and variability tendencies by organic contaminations, as well as cleaning efficiency with slight differences. Meanwhile, no apparent lag time has been observed for the trial operating at the super-critical condition (TMP = 0.05 MPa), flux decreased from 131.3 to 82.1 L/m^2 h in the first 6 h, corresponding to $dF/dt = 8.2$ L/m^2 h, and to 64.7 L/m^2 h by hour 24. Clearly, there has a noticeable fouling propensity even at the initial stage of experiment. Finally, it can be noted that dF/dt obtained in this process is much lower during the sub-critical condition than that in super-critical condition.

Since each TMP-step lasted only for 20 min, which was employed to determine the critical flux in previous section, can hardly predict accurately for the absolute value of the fouling rate over a long period of time. It has been clearly shown that continuous flux decrease-free operation with continuity system cannot exist more than 1 day even under TMP of 0.03 MPa. The fouling rate, expressed by dF/dt, usually decreases with time, which may be 10–100 times lower than that measured in the short-term TMP step test, if the entire operating cycle is long enough. Thus, it can be speculated that irreversible contaminants contribute little to flux decrease in short-term, low TMP operating conditions. While it is claimed that membrane cleaning is not required for a long time when the UF system is operated at a sufficiently low flux (Yuan *et al.* 2010), the critical flux behavior observed during the long-running experiments indicating that no such sustained operation is a real existence. This finding is similar to the conclusion drawn by Navaratna and Jegatheesan (Navaratna & Jegatheesan 2011). However, if we only arbitrarily define the critical time, which can be considered at the point of flux decreasing trend line of about 95% initial value just for the purpose of the present study, then the critical time may even exceed 24 h.

Membrane cleaning process

From the analysis above, oil particles are in the presence of emulsification or dissolution in o/w solution, which is easy to adsorb on the surface of hydrophobic organic membrane surface according to 'The Like Attracts Like Theory' that any substance has the same characteristic attract each other (Wawrzkiewicz 2012), and then collide and coagulate on the membrane surface. Therefore, o/w impurities trapped in the membrane surface in the filtration process, then form gel and cake layer gradually; moreover, when some

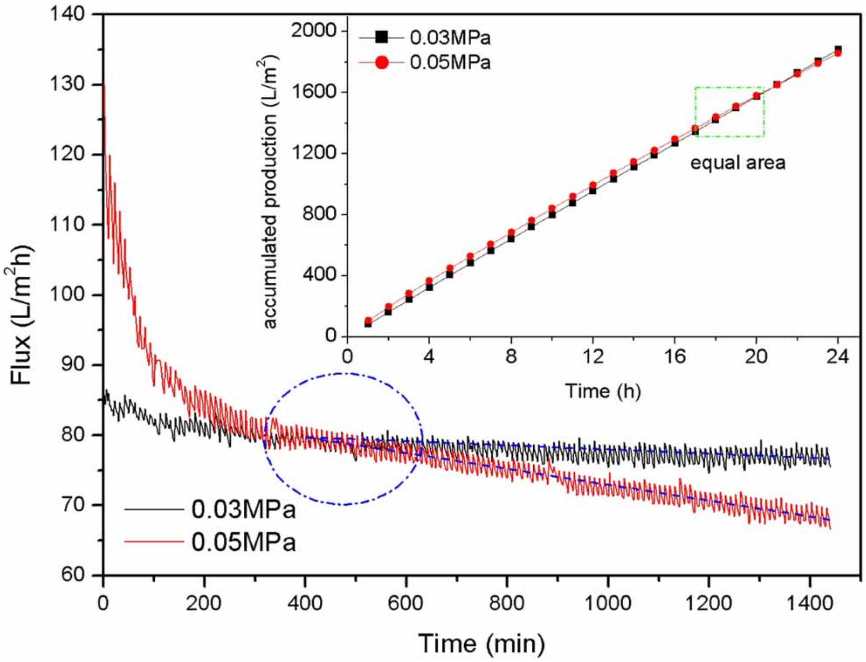

Figure 5 | Permeate flux (J) comparison between subcritical TMP (0.03 MPa) and supcritical TMP (0.05 MPa) as a function of the time (t).

dissolved oil particles enter and coalescence in pores, which leading to pore blocking. What is more serious is that hydrogen bonding force between particles and membrane is more powerful, which is impossible to clean just by simple hydraulic flushing. Therefore, a variety of UF membrane cleaning methods were studied to determine the best cleaning methods, which was shown in Figure 6.

Figure 6 shows the recovery of water flux of membrane polluted by o/w with four step continuous cleaning methods. It is obvious that mechanical scraping with a sponge ball by manual operation is remarkably ineffective, for the membrane flux not only restores, but also reduces to some extent. The reasons may be: although the sponge ball rolling can reduce cake layer thickness, this operation may cause the inner layer of the viscous oil layer covering on the surface of the membrane more tightly and uniformly. At the same time, oil substances may be pressed into the membrane pores, resulting in pore blockage. All in all, both of the reasons greatly enhance the filtration resistance, leading to flux reduction obviously (Liu *et al.* 2014). The next step is hydraulic flushing by permeate water, with the extension of the hydraulic flushing time, the flux recovery rate of flux was improved to a certain extent. It can be restored to 0.65 in the first 5 min; after the next 10 min rinsing, the flux can be increased to 0.81; a 10 min rinsing once more, the flux even up to 0.92; and then remained stable, no longer with the extension of time to increase. It is mainly because of the strong disturbance of water flow that the oil on the surface of the membrane is dissolved. The third stage adopts hydraulic backwashing, but found that the flux declined, especially in the first 10 min, the flux declined to 0.77 from 0.92. After that, continuous backwash did not promote the increase of membrane flux, indicating that hydraulic backwashing is not suitable for o/w UF. The reason can be analyzed as: in the process of backwashing, the oil material which is assembled in the membrane pores is not able to be put into the interception liquid, but the oil material is further collided and gathered to form larger particles, and the pore is blocked. From the earlier work of our research group (Yi *et al.* 2011), PVDF is easy to turn color (from white to brown), aging and even becoming brittle in alkaline solution. Thus, the last step was soaking in NaClO (1%) and 12 SDS (0.5%) solution, the results showed that after 30 min immersion, pollutant can be effectively removed, for its flux reached a recovery of about 0.90 and 0.95, respectively. The effect of SDS is slightly better than NaClO; the main reason is SDS has a hydrophilic tail and a hydrophobic head, increasing solubility of oil particles in water, and the oil was eluted from the membrane easily.

CONCLUSIONS

From the results expressed here, it is noticeable that membrane fouling in treating o/w emulsion takes place at

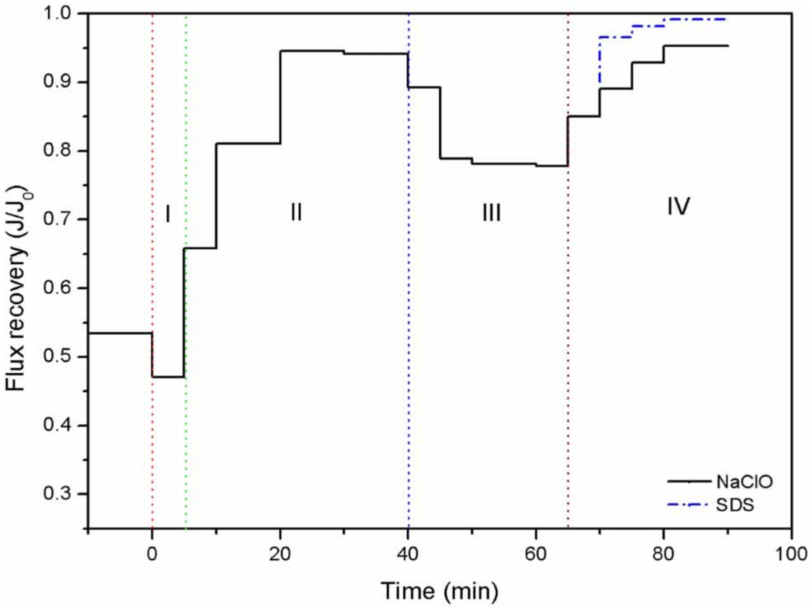

Figure 6 | Flux recovery of membrane with different cleaning method (I: Mechanic scraping; II: Pure water wash; III: Pure water reverse wash; IV: Dosing cleaning).

certain TMP, then becomes dramatic when TMP reaches or exceeds the so-called critical flux (or in its weak form) pressure, when the appearance of the flux decreases significantly. The critical flux determined by the TMP method can satisfy the membrane system to maintain stability, and alleviate membrane fouling rate.

The critical flux decreases very slowly, and the cumulant of flux determined by long-term experiments are higher than that of non-critical flux value after a certain time. Meanwhile, there was no absolute '0' fouling, though the fouling rate is slight in this o/w UF system.

Finally, after evaluating the advantages and disadvantages of four step cleaning methods and giving reasons analysis, water flushing, NaClO (1%) and (SDS) (0.5%) solution soaking used in turn may be the best way to clean membrane polluted by o/w.

REFERENCES

Bacchin, P., Aimar, P. & Field, R. W. 2006 Critical and sustainable fluxes: theory, experiments and applications. *Journal of Membrane Science* **281** (1-2), 42–69.

Defrance, L. & Jaffrin, M. Y. 1999 Comparison between filtrations at fixed transmembrane pressure and fixed permeate flux: application to a membrane bioreactor used for wastewater treatment. *Journal of Membrane Science* **152** (2), 203–210.

Espinasse, B., Bacchin, P. & Aimar, P. 2008 Filtration method characterizing the reversibility of colloidal fouling layers at a membrane surface: analysis through critical flux and osmotic pressure. *Journal of Colloid & Interface Science* **320** (2), 483–490.

Field, R. W., Wu, D., Howell, J. A. & Gupta, B. B. 1995 Critical flux concept for microfiltration fouling. *Journal of Membrane Science* **100** (3), 259–272.

Guglielmi, G., Saroj, D. P., Chiarani, D. & Andreottola, G. 2007 Sub-critical fouling in a membrane bioreactor for municipal wastewater treatment: experimental investigation and mathematical modelling. *Water Research* **41** (17), 3903–3914.

Howe, K. J. & Clark, M. M. 2002 Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environmental Science & Technology* **36** (16), 3571–3576.

Huang, J., Liu, L., Zeng, G., Li, X. & Peng, L. 2014 Influence of feed concentration and transmembrane pressure on membrane fouling and effect of hydraulic flushing on the performance of ultrafiltration. *Desalination* **335** (1), 1–8.

Liu, Y., Li, X., Yang, Y., Ye, W. & Ji, S. 2014 Analysis of the major particle-size based foulants responsible for ultrafiltration membrane fouling in polluted raw water. *Desalination* **347** (17), 191–198.

Melidis, P., Ntougias, S., Vasilatou, V., Skouteris, G. & Azis, K. 2016 Biofouling aspects and critical flux evaluation in an intermittently aerated and fed submerged membrane bioreactor. *Environmental Processes* **3** (1), 1–11.

Navaratna, D. & Jegatheesan, V. 2011 Implications of short and long term critical flux experiments for laboratory-scale MBR operations. *Bioresource Technology* **102** (102), 5361–5369.

Ochando, J. M., Hodaifa, G. & Martinez-Ferez, A. 2014 Threshold flux measurement of an ultrafiltration membrane module in the treatment of two-phase olive mill wastewater. *Chemical Engineering Research & Design* **92** (4), 769–777.

Ochando-Pulido, J. M. & Stoller, M. 2015 Kinetics and boundary flux optimization of integrated photocatalysis and ultrafiltration process for two-phase vegetation and olive washing wastewaters treatment. *Chemical Engineering Journal* **279**, 387–395.

Profio, G. D., Ji, X., Curcio, E. & Drioli, E. 2011 Submerged hollow fiber ultrafiltration as seawater pretreatment in the logic of integrated membrane desalination systems. *Desalination* **269** (1-3), 128–135.

Qu, F., Du, X., Liu, B., He, J. & Ren, N. 2015 Control of ultrafiltration membrane fouling caused by *Microcystis* cells with permanganate preoxidation: significance of in situ formed manganese dioxide. *Chemical Engineering Journal* **279**, 56–65.

Singh, R. 2008 Sustainable fuel cell integrated membrane desalination systems. *Desalination* **227** (1), 14–33.

Stoller, M. & Chianese, A. 2006 Optimization of membrane batch processes by means of the critical flux theory. *Desalination* **191** (1), 62–70.

Wawrzkiewicz, M. 2012 Comparison of the efficiency of amberlite IRA 478RF for acid, reactive, and direct dyes removal from aqueous media and wastewaters. *Industrial & Engineering Chemistry Research* **51** (23), 8069–8078.

Yi, X. S., Shi, W. X., Yu, S. L., Ma, C., Sun, N., Wang, S., Jin, L. M. & Sun, L. P. 2011 Optimization of complex conditions by response surface methodology for APAM–oil/water emulsion removal from aqua solutions using nano-sized TiO_2/Al_2O_3 PVDF ultrafiltration membrane. *Journal of Hazardous Materials* **193** (2), 37–44.

Yi, X. S., Yu, S. L., Shi, W. X., Wang, S., Sun, N., Jin, L. M. & Sun, L. P. 2013 Estimation of fouling stages in separation of oil/water emulsion using nano-particles Al_2O_3/TiO_2 modified PVDF UF membranes. *Desalination* **319** (10), 38–46.

Yigit, N. O., Civelekoglu, G., Harman, I., Koseoglu, H. & Kitis, M. 2009 Effects of various backwash scenarios on membrane fouling in a membrane bioreactor. *Desalination* **237** (1–3), 346–356.

Yuan, D., Fan, Y., Guoliang, X. U., Yang, W. & Yan, Y. U. 2010 Research in critical flux theories of membrane bioreactor. *Membrane Science & Technology* **30** (2), 97–103.

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